BASIC RESEARCH NEEDS FOR GEOSCIENCES: FACILITATING 21ST CENTURY ENERGY SYSTEMS

From the workshop sponsored by the
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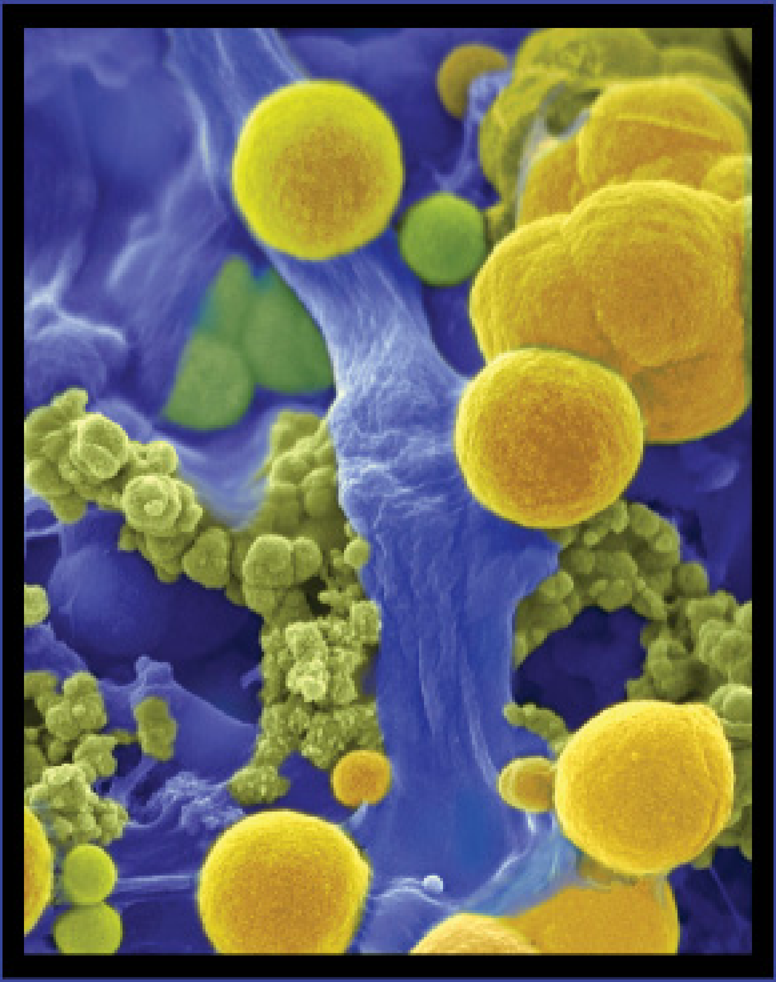
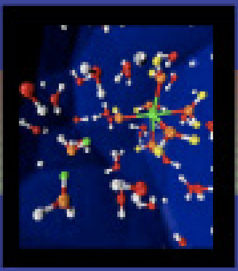
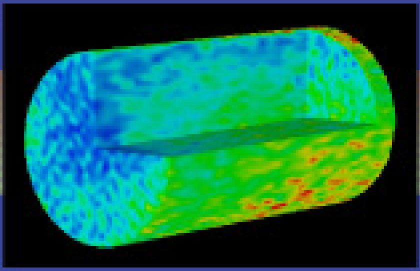
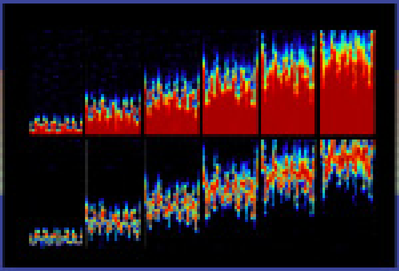
Bethesda MD • February 21–23, 2007









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Report from the Workshop Held February 21-23, 2007

Sponsored by the U.S. Department of Energy, Office of Basic Energy Sciences

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About the cover ➤

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About the cover

Front page:

Center—A scanning electron microscope image of biofilms of sulfate-reducing bacteria (blue) growing in dilute groundwater (~1 part per million dissolved zinc), associated with an abandoned lead-zinc deposit, produce sphalerite (ZnS) particles that aggregate (light green) and form micrometer-diameter spheres (gold). Such biomineralization may assist in groundwater remediation, and may play a role in genesis of some ore deposits. Reprinted by permission of the American Association for the Advancement of Science and author Jill Banfield, University of California Berkeley; image was used on the cover of *Science* **290**(5497), 2000. ***Bottom left***—Hydrolysis dynamics of the Al^{3+} ion at supercritical conditions (T=750K). More results from similar simulations were published in E.J. Bylaska, M. Valiev, J.R. Rustad, and J.H. Weare (2007) Structure and Dynamics of the Hydration Shells of the Al^{3+} Ion, *Journal of Chemical Physics* **126**(10): Art. No. 104505. Courtesy of J. Weare (University of California, San Diego) and E. Bylaska (Pacific Northwest National Laboratory). ***Bottom middle***—Simulation of CO_2 injected into Berea sandstone core under steady-state conditions. Courtesy of Ljuba Miljkovic, Lawrence Berkeley National Laboratory. ***Bottom right***—Optical measurements of the presence of a conservative tracer (top panels; red color) and a reactive tracer (bottom panels; red color) for different times. Fluid propagates from the bottom to the top of the figures through a porous medium consisting of glass spheres. Courtesy of Peter Oates; from his thesis, "Upscaling Reactive Transport in Porous Media: Laboratory Visualization and Stochastic Models," Massachusetts Institute of Technology, 2007.

Back page:

Bottom left—Simulation of dissolved CO_2 migration at Sleipner after 75 years of injection. Courtesy of Erik Lindeberg, SINTEF Petroleum Research. ***Bottom middle***—Simulation of CO_2 migration during a Frio field test of CO_2 injection into a saline aquifer. Courtesy of Christine Doughty, Lawrence Berkeley National Laboratory. ***Bottom right***—Geo-cellular model of rock fracture density in the subsurface. The model is based on the fracture distributions predicted from a combination of: (a) layers with different mechanical properties, (b) the curvature of layers, and (c) the impact of localized faulting. Courtesy of Rock Deformation Research (email • rdr@leeds.ac.uk).

BASIC RESEARCH NEEDS FOR GEOSCIENCES: FACILITATING 21ST CENTURY ENERGY SYSTEMS

TABLE OF CONTENTS

EXECUTIVE SUMMARY ix

INTRODUCTION 1

Sidebar: Scenarios for greenhouse gas emissions 1

Subsurface Geologic Storage Science 2

Workshop Structure and Report Preparation 3

PANEL REPORTS 5

Multiphase Fluid Transport in Geologic Media 7

Current Status 7

Sidebar: Carbon capture and storage 8

Basic Science Challenges, Opportunities and Research Needs 10

Emergent behavior in multiphase systems due to physical and chemical heterogeneity from the pore scale to basin scale 10

Sidebar: Current CO_2 storage projects: The Sleipner and In Salah projects 11

Sidebar: Buoyancy, capillarity, and heterogeneity: Buoyancy-driven flow at all scales 13

Multicomponent, multiphase properties and interactions of mineral-fluid-microbial systems 14

Shallow crustal deformation and fluid flow driven by large anthropogenic perturbations 16

Flow and transport properties of seals, faults, and fractures 18

Dynamic imaging for complex multiphase systems 20

Conclusion 22

Chemical Migration Processes in Geologic Media 23

Current Status 23

Basic Science Challenges, Opportunities and Research Needs 24

Colloids as a critical mode of radionuclide mobility 24

Coupled physical-chemical processes from the mineral surface to the pore scale 24

Sidebar: Unique chemistry in intragranular microfractures and surface microstructures 26

Mineral-water interface complexity and dynamics 27

Biogeochemistry in extreme subsurface environments 28

Equilibrium and reaction rates in perturbed geochemical environments 29

Sidebar: The hypothetical perturbed environment near emplaced nuclear waste in a geologic repository 30

Conclusion 31

Subsurface Characterization 33

Current Status 33

Overview 33

Integrated characterization and modeling of complex geologic systems with large and diverse data sets 34

Sidebar: Hydrologic forcings and climate change 35

In situ characterization of fluid trapping, isolation and immobilization 37

Imaging flow, transport and chemical attributes 39

Monitoring dynamic subsurface processes 43

Basic Science Challenges, Opportunities and Research Needs 44
  Integrated characterization and modeling of complex geologic systems with large and diverse data sets 44
  Scaling laws for flow, transport, reactions, and coupled processes 45
  Data fusion, instrumentation, tracers and uncertainty 45
  Improved geophysical imaging techniques 46
Conclusion 47
  Impacts in the geosciences 47
  Impacts for other fields 48

Modeling and Simulation of Geologic Systems 49
Current Status 49
Basic Science Challenges, Opportunities and Research Needs 50
  Modeling multiple processes at interacting scales 51
  Sidebar: CO_2 leakage 56
  Modeling complex systems with diverse data sets 57
  Quantifying and reducing predictive uncertainty 57
  Computational chemical thermodynamics—Equilibria and reactions 58
  Developing coupled *in silico* biogeochemical models 61
Conclusion 63

GRAND CHALLENGES 65

Computational Thermodynamics of Complex Fluids and Solids 67
Abstract 67
Executive Summary 67
Scientific Challenges 69
Research Approaches 70
  Dynamical methods at the atomic time scale and upscaling 70
  Equations of State for complex systems 73
  Sidebar: Essential data collection for Equation of State (EOS) development 74

Integrated Characterization, Modeling, and Monitoring of Geologic Systems 79
Abstract 79
Executive Summary 79
Scientific Challenges 80
  Optimal detail in geological modeling 80
  Geologic process models of subsurface structure and heterogeneity 81
  Incorporating large and diverse datasets into models 83
  Relating geophysical measurements to *in situ* properties/processes 84
  Developing integrated monitoring approaches 85
  Coupled monitoring and modeling approaches 87
  Quantifying and reducing predictive uncertainty 89
  Early identification and quantification of anomalous behavior 89
Research Approaches 90
Scientific Impacts 91
Technology Impacts 92

Simulation of Multiscale Systems for Ultra-Long Times 95
Abstract 95
Executive Summary 95

Scientific Challenges ... 96
Research Approaches ... 100
Coupling methods used for different scales ... 101
Scientific Impacts ... 102
Technology Impacts ... 103

PRIORITY RESEARCH DIRECTIONS ... 105

Mineral-Water Interface Complexity and Dynamics ... 107
Abstract ... 107
Executive Summary ... 107
Sidebar: Intrinsic structural complexity at mineral-water interfaces ... 108
Summary of Research Direction ... 109
Sidebar: Solid-state charge transport at mineral-water interfaces ... 110
Scientific Challenges ... 111
Scientific Impacts ... 112
Technology Impacts ... 112

Nanoparticulate and Colloid Chemistry and Physics ... 113
Abstract ... 113
Executive Summary ... 113
Sidebar: What is a colloid? ... 114
Summary of Research Direction ... 115
Scientific Challenges ... 115
Sampling ... 116
Atomic-scale characterization of colloid structure ... 116
Theory, modeling and simulation ... 117
Scientific Impacts ... 119
Technology Impacts ... 119

Dynamic Imaging of Flow and Transport ... 121
Abstract ... 121
Executive Summary ... 121
Summary of Research Direction ... 122
Scientific Challenges ... 124
Spatially and temporally continuous measurement of state variables ... 125
Smart tracers ... 125
Groundwater age distribution ... 127
The interaction of physical fields with fluid-filled rocks ... 128
Scientific Impacts ... 129
Technology Impacts ... 129

Transport Properties and *In Situ* Characterization of Fluid Trapping, Isolation, and Immobilization ... 131
Abstract ... 131
Executive Summary ... 131
Scientific Challenges ... 132
Interfacial and surface properties of fluids in fine-grained and fractured media ... 133
Conductivity of faults and fractures ... 133
In situ measurement of fluid-rock interactions in fine-grained media ... 133
Identification and characterization of local flaws in sealing structures ... 134

Prediction of the distribution and efficiency of *in situ* trapping processes 135
Research Approaches 135
Scientific Impacts 136
Technology Impacts 137

Fluid-Induced Rock Deformation 139
Abstract 139
Executive Summary 139
Scientific Challenges 140
Understanding geomechanical processes and properties at all scales 140
Understanding coupled stress, strain, and flow response to pressure and hydrological perturbations in multiphase-fluid saturated systems 141
Understanding permeability evolution due to concomitant geomechanical and geochemical processes 141
Research Approaches 142
Scientific Impacts 142
Technology Impacts 143

Biogeochemistry in Extreme Subsurface Environments 145
Abstract 145
Executive Summary 145
Summary of Research Direction 146
Scientific Challenges 146
Research Approaches 148
Mechanisms of biogeochemical reactions 149
Cellular level models 149
Biofilm dynamics 151
Scientific Impacts 152
Technology Impacts 152

CROSSCUTTING ISSUES 153

The Microscopic Basis of Macroscopic Complexity 155
Summary 155
Scientific Challenges 155
Research Approaches 156
Scientific Impacts 157
Technology Impacts 157

Highly Reactive Subsurface Materials and Environments 159
Summary 159
Scientific Challenges 159
Research Approaches 161
Scientific Impacts 162
Technology Impacts 163

Thermodynamics of the Solute-to-Solid Continuum 165
Summary 165
Scientific Challenges 165
Research Approaches 166
Scientific Impacts 168

Technology Impacts 168
REFERENCES 169
APPENDIX 1: TECHNICAL PERSPECTIVES RESOURCE DOCUMENT Appendix 1 • 1
APPENDIX 2: WORKSHOP PROGRAM Appendix 2 • 1
APPENDIX 3: ALL ATTENDEES AT WORKSHOP Appendix 3 • 1
APPENDIX 4: ACRONYMS Appendix 4 • 1

EXECUTIVE SUMMARY

Serious challenges must be faced in this century as the world seeks to meet global energy needs and at the same time reduce emissions of greenhouse gases to the atmosphere. Even with a growing energy supply from alternative sources, fossil carbon resources will remain in heavy use and will generate large volumes of carbon dioxide (CO_2). To reduce the atmospheric impact of this fossil energy use, it is necessary to capture and sequester a substantial fraction of the produced CO_2. Subsurface geologic formations offer a potential location for long-term storage of the requisite large volumes of CO_2. Nuclear energy resources could also reduce use of carbon-based fuels and CO_2 generation, especially if nuclear energy capacity is greatly increased. Nuclear power generation results in spent nuclear fuel and other radioactive materials that also must be sequestered underground. Hence, regardless of technology choices, there will be major increases in the demand to store materials underground in large quantities, for long times, and with increasing efficiency and safety margins.

Rock formations are composed of complex natural materials and were not designed by nature as storage vaults. If new energy technologies are to be developed in a timely fashion while ensuring public safety, fundamental improvements are needed in our understanding of how these rock formations will perform as storage systems.

This report describes the scientific challenges associated with geologic sequestration of large volumes of carbon dioxide for hundreds of years, and also addresses the geoscientific aspects of safely storing nuclear waste materials for thousands to hundreds of thousands of years. The fundamental crosscutting challenge is to understand the properties and processes associated with complex and heterogeneous subsurface mineral assemblages comprising porous rock formations, and the equally complex fluids that may reside within and flow through those formations. The relevant physical and chemical interactions occur on spatial scales that range from those of atoms, molecules, and mineral surfaces, up to tens of kilometers, and time scales that range from picoseconds to millennia and longer. To predict with confidence the transport and fate of either CO_2 or the various components of stored nuclear materials, we need to learn to better describe fundamental atomic, molecular, and biological processes, and to translate those microscale descriptions into macroscopic properties of materials and fluids. We also need fundamental advances in the ability to simulate multiscale systems as they are perturbed during sequestration activities and for very long times afterward, and to monitor those systems in real time with increasing spatial and temporal resolution. The ultimate objective is to predict accurately the performance of the subsurface fluid-rock storage systems, and to verify enough of the predicted performance with direct observations to build confidence that the systems will meet their design targets as well as environmental protection goals.

The report summarizes the results and conclusions of a Workshop on Basic Research Needs for Geosciences held in February 2007. Five panels met, resulting in four Panel Reports, three Grand Challenges, six Priority Research Directions, and three Crosscutting Research Issues. The Grand Challenges differ from the Priority Research Directions in that the former describe broader, long-term objectives while the latter are more focused.

GRAND CHALLENGES

Computational thermodynamics of complex fluids and solids. Predictions of geochemical transport in natural materials must start with detailed knowledge of the chemical properties of multicomponent fluids and solids. New modeling strategies for geochemical systems based on first-principles methods are required, as well as reliable tools for translating atomic- and molecular-scale descriptions to the many orders of magnitude larger scales of subsurface geologic systems. Specific challenges include calculation of equilibrium constants and kinetics of heterogeneous reactions, descriptions of adsorption and other mineral surface processes, properties of transuranic elements and compounds, and mixing and transport properties for multicomponent liquid, solid and supercritical solutions. Significant advances are required in calculations based on the electronic Schrödinger equation, scaling of solution methods, and representation in terms of Equations of State. Calibration of models with a new generation of experiments will be critical.

Integrated characterization, modeling, and monitoring of geologic systems. Characterization of the subsurface is inextricably linked to the modeling and monitoring of processes occurring there. More accurate descriptions of the behavior of subsurface storage systems will require that the diverse, independent approaches currently used for characterizing, modeling and monitoring be linked in a revolutionary and comprehensive way and carried out simultaneously. The challenges arise from the inaccessibility and complexity of the subsurface, the wide range of scales of variability, and the potential role of coupled nonlinear processes. Progress in subsurface simulation requires advances in the application of geological process knowledge for determining model structure and the effective integration of geochemical and high-resolution geophysical measurements into model development and parameterization. To fully integrate characterization and modeling will require advances in methods for joint inversion of coupled process models that effectively represent nonlinearities, scale effects, and uncertainties.

Simulation of multiscale geologic systems for ultra-long times. Anthropogenic perturbations of subsurface storage systems will occur over decades, but predictions of storage performance will be needed that span hundreds to many thousands of years, time scales that reach far beyond standard engineering practice. Achieving this simulation capability requires a major advance in modeling capability that will accurately couple information across scales, i.e., account for the effects of small-scale processes on larger scales, and the effects of fast processes as well as the ultra-slow evolution on long time scales. Cross-scale modeling of complex dynamic subsurface systems requires the development of new computational and numerical methods of stochastic systems, new multiscale formulations, data integration, improvements in inverse theory, and new methods for optimization.

PRIORITY RESEARCH DIRECTIONS

Mineral-water interface complexity and dynamics. Natural materials are structurally complex, with variable composition, roughness, defect content, and organic and mineral coatings. There is an overarching need to interrogate the complex structure and dynamics at mineral-water interfaces with increasing spatial and temporal resolution using existing and emerging experimental and computational approaches. The fundamental objectives are to translate a molecular-scale description of complex mineral surfaces to thermodynamic quantities for the purpose of linking with macroscopic models, to follow interfacial reactions in real time, and to understand how minerals grow and dissolve and how the mechanisms couple dynamically to changes at the interface.

Nanoparticulate and colloid chemistry and physics. Colloidal particles play critical roles in dispersion of contaminants from energy production, use, or waste isolation sites. New advances are needed in characterization of colloids, sampling technologies, and conceptual models for reactivity, fate, and transport of colloidal particles in aqueous environments. Specific advances will be needed in experimental techniques to characterize colloids at the atomic level and to build quantitative models of their properties and reactivity.

Dynamic imaging of flow and transport. Improved imaging in the subsurface is needed to allow *in situ* multiscale measurement of state variables as well as flow, transport, fluid age, and reaction rates. Specific research needs include development of smart tracers, identification of environmental tracers that would allow age dating fluids in the 50–3000 year range, methods for measuring state variables such as pressure and temperature continuously in space and time, and better models for the interactions of physical fields, elastic waves, or electromagnetic perturbations with fluid-filled porous media.

Transport properties and in situ characterization of fluid trapping, isolation, and immobilization. Mechanisms of immobilization of injected CO_2 include buoyancy trapping of fluids by geologic seals, capillary trapping of fluid phases as isolated bubbles within rock pores, and sorption of CO_2 or radionuclides on solid surfaces. Specific advances will be needed in our ability to understand and represent the interplay of interfacial tension, surface properties, buoyancy, the state of stress, and rock heterogeneity in the subsurface.

Fluid-induced rock deformation. CO_2 injection affects the thermal, mechanical, hydrological, and chemical state of large volumes of the subsurface. Accurate forecasting of the effects requires improved understanding of the coupled stress-strain and flow response to injection-induced pressure and hydrologic perturbations in multiphase-fluid saturated systems. Such effects manifest themselves as changes in rock properties at the centimeter scale, mechanical deformation at meter-to-kilometer scales, and modified regional fluid flow at scales up to 100 km. Predicting the hydromechanical properties of rocks over this scale range requires improved models for the coupling of chemical, mechanical, and hydrological effects. Such models could revolutionize our ability to understand shallow crustal deformation related to many other natural processes and engineering applications.

Biogeochemistry in extreme subsurface environments. Microorganisms strongly influence the mineralogy and chemistry of geologic systems. CO_2 and nuclear material isolation will perturb the environments for these microorganisms significantly. Major advances are needed to describe how populations of microbes will respond to the extreme environments of temperature, pH, radiation, and chemistry that will be created, so that a much clearer picture of biogenic products, potential for corrosion, and transport or immobilization of contaminants can be assembled.

CROSSCUTTING RESEARCH ISSUES

The microscopic basis of macroscopic complexity. Classical continuum mechanics relies on the assumption of a separation between the length scales of microscopic fluctuations and macroscopic motions. However, in geologic problems this scale separation often does not exist. There are instead fluctuations at all scales, and the resulting macroscopic behavior can then be quite complex. The essential need is to develop a scientific basis of “emergent” phenomena based on the microscopic phenomena.

Highly reactive subsurface materials and environments. The emplacement of energy system byproducts into geological repositories perturbs temperature and pressure, imposes chemical gradients, creates intense radiation fields, and can cause reactions that alter the minerals, pore fluids, and emplaced materials. Strong interactions between the geochemical environment and emplaced materials are expected. New insight is needed on equilibria in compositionally complex systems, reaction kinetics in concentrated aqueous and other solutions, reaction kinetics under near-equilibrium undersaturated and supersaturated conditions, and transient reaction kinetics.

Thermodynamics of the solute-to-solid continuum. Reactions involving solutes, colloids, particles, and surfaces control the transport of chemical constituents in the subsurface environment. A rigorous structural, kinetic, and thermodynamic description of the complex chemical reality between the molecular and the macroscopic scale is a fundamental scientific challenge. Advanced techniques are needed for characterizing particles in the nanometer-to-micrometer size range, combined with a new description of chemical thermodynamics that does not rely on a sharp distinction between solutes and solids.

TECHNICAL AND SCIENTIFIC IMPACT

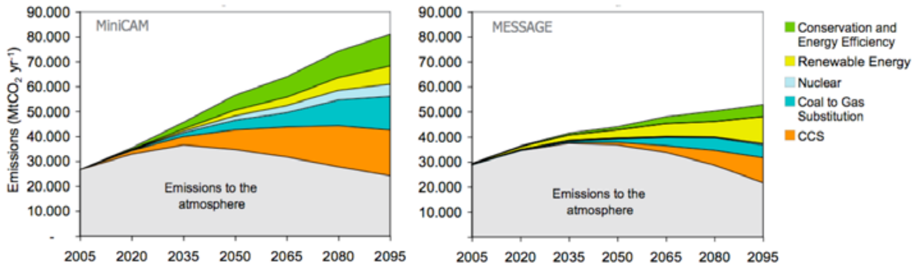
The Grand Challenges, Priority Research Directions, and Crosscutting Issues described in this report define a science-based approach to understanding the long-term behavior of subsurface geologic systems in which anthropogenic CO_2 and nuclear materials could be stored. The research areas are rich with opportunities to build fundamental knowledge of the physics, chemistry, and materials science of geologic systems that will have impacts well beyond the specific applications. The proposed research is based on development of a new level of understanding—physical, chemical, biological, mathematical, and computational—of processes that happen at the microscopic scale of atoms, molecules and mineral surfaces, and how those processes translate to material behavior over large length scales and on ultra-long time scales. Addressing the basic science issues described would revolutionize our ability to understand, simulate, and monitor all of the subsurface settings in which transport is critical, including the movement of contaminants, the emplacement of minerals, or the management of aquifers. The results of the research will have a wide range of implications from physics and chemistry, to material science, biology and earth science.

INTRODUCTION

Worldwide energy consumption is projected to double by mid-century as the population grows and rapidly developing economies increase *per capita* energy use. Energy technologies being developed around the world to meet this projected demand all assume that we will be living in a carbon-constrained world. Most plans envision that subsurface rock formations will be used to sequester vast amounts of energy byproducts. Underground formations are an attractive place to store large quantities of material because they have the requisite size and are relatively accessible. However, rock formations were not designed by nature as storage vaults, and yet there will be stringent and highly varied demands on them if their new contents are to be effectively sequestered for hundreds to thousands of years. Fundamental improvements in our understanding of how these rock systems will perform as long-term storage systems are critical to developing new energy technologies in a timely fashion, while guaranteeing public safety.

Although the expectation is that renewable energy resources will be used increasingly in the future, a substantial period of time will pass before they become a significant fraction of worldwide energy use. Meanwhile, the energy systems in large-scale use still depend heavily on fossil carbon resources. Approximately 12 terawatts, or 85% of current worldwide power consumption, is based on fossil carbon. Increased use of carbon-based fuels to meet expanding demand could lead to increased accumulation of carbon dioxide and other greenhouse gases in the atmosphere, which is widely seen as highly undesirable. To reduce global carbon emissions to the atmosphere, especially if the use of carbon-based fuels increases, requires that a significant

Scenarios for greenhouse gas emissions



Two scenarios for how greenhouse gas emissions to the atmosphere could be kept at low enough levels to ensure that the concentration of atmospheric CO_2 remains below 450 to 750 ppmv (1.6 to 2.7 times the pre-industrial value). The two graphs represent different scenarios for the total amount of emissions that are expected. Colored wedges correspond to contributions to lowered emissions from each alternative energy source, or through conservation and underground storage. **CCS** *stands for* ***carbon capture and storage****, where the storage is underground; it is also called* ***geologic storage*** *or* ***sequestration****. In the high-emission scenario (left panel), nuclear energy generation plays a significant role, and the emission reduction corresponds to an increase of nuclear power generation by 10 times the present value over the time period shown. For CCS, the target would be to sequester about 7 to 15 gigatons of CO_2 per year by late 21st century. (Metz et al. 2007—IPCC http://www.ipcc.ch/)*

fraction of the carbon dioxide produced from fossil energy conversion be captured and stored away from the atmosphere (see sidebar on *Scenarios for greenhouse gas emissions*). Porous, subsurface geologic rock formations offer potential locations for long-term storage of carbon dioxide.

Nuclear power is another component of the global energy equation. Nuclear power plants supply about 0.9 terawatts of the world's present rate of energy use, much less than fossil fuel-based systems, but a significant fraction—one that could increase to replace part of the fossil fuel-based energy production (see sidebar on *Scenarios for greenhouse gas emissions*). Nuclear energy produces no CO_2 but instead generates substantial amounts of radioactive materials, a fact that has both environmental and security implications. To sustain nuclear energy generation, and even more so to increase generation by a factor of up to 10 over the next century, it is necessary to safely store radioactive waste in underground repositories. Several countries, including the U.S., have programs in progress to develop underground nuclear waste repositories. If nuclear energy production is to expand, many more suitable sites for underground storage need to be identified and characterized, and suitable approaches to underground storage need to be engineered for each site.

SUBSURFACE GEOLOGIC STORAGE SCIENCE

This report outlines the scientific challenges that must be addressed if subsurface geologic systems are to be used to store safely the products of energy use, particularly those from electric power generation. The report covers issues that pertain to both CO_2 sequestration and nuclear waste isolation. Both issues are included as a basis for this report because the scientific communities involved in the relevant research overlap, as do the underlying fundamental science issues. The specific technical challenges are different (see Appendix 1: Technical Perspectives Resource Document).

Storage of carbon in the subsurface involves introduction of supercritical CO_2 into rock formations beneath the surface of the Earth, typically at depths of 1000 to 4000 meters. Although CO_2 is a relatively benign substance, the volume being considered is large. If developed to its envisioned potential, geologic sequestration will entail the pumping of CO_2 into the ground at roughly the rate we are extracting petroleum today. To have the desired impact on the atmospheric carbon budget, CO_2 must be efficiently retained underground for hundreds of years.

Storage of nuclear waste in the subsurface involves a smaller volume of material, and shallower burial depths of roughly 500 meters. But by virtue of its radioactivity and toxicity, nuclear waste must be confined carefully, and because of long half-lives, it must be sequestered for a long time, even by geological standards. Current regulations indicate that a U.S. repository will need to be effective for ten thousand to one million years.

Any underground storage system will have to account for the natural characteristics of subsurface rock formations; some are advantageous for storage, while others are not. The crosscutting consideration is that when foreign materials are emplaced in subsurface rock formations, they change the chemical and physical environment. Understanding and predicting these changes are important for determining how the subsurface will perform as a storage container. In the case of CO_2, a cold but low-density fluid is injected and is allowed to find its way into the rock formations. There are no barriers to the movement of the injected CO_2 except those that are provided naturally by the rock formations themselves. In the case of nuclear waste, the radioactive materials are encased in carefully engineered containers, and placed into particular geologic formations. The nuclear materials are therefore initially confined by the engineered containers, and become exposed to the geologic surroundings if and when the containers fail. Radioactive waste, however, heats itself and its surroundings due to the energy released by radioactive decay, and this modification to the local environment is one of the primary concerns in evaluating geologic formations as repositories.

Independent of the specific objective, storage site selection and design must be based on detailed understanding of the interactions that occur once the subject materials are placed underground. Although there is already basic knowledge adequate to begin some sequestration activities, the scale of the proposed operations, the fact that they will be carried out over a long time, and the likelihood that both efficiency and safety requirements will become more demanding with time, imply that fundamental advances in geoscience are needed for underground sequestration to be ultimately successful.

The specific scientific issues that underlie sequestration technology involve the effects of fluid flow combined with chemical, thermal, mechanical and biological interactions between fluids and surrounding geologic formations. Complex and coupled interactions occur both *rapidly* as the stored material is emplaced underground, and *gradually* over hundreds to thousands of years. The long sequestration times needed for effective storage and the intrinsic spatial variability of subsurface formations provide challenges to both geoscientists and engineers. Accurate descriptions of combined chemistry, biology, flow and deformation constitute a fundamental scientific challenge with broad implications.

New research must be aimed at producing a major leap in our ability to predict the properties and behavior of complex natural materials, with the added—and essentially geological—feature that critical processes occur at spatial scales from the atomic to tens of kilometers, and time scales from nanoseconds to many millennia. We need to describe fundamental atomic, molecular, and biological processes in solids and liquids and at mineral surfaces, translate such information into accurate descriptions of macroscopic properties, and ultimately build accurate models of transport in the subsurface. We also need to monitor subsurface properties and processes with unprecedented space and time resolution, and use the evidence recorded in the minerals and structures of geological formations as a way to study time scales that exceed by orders of magnitude those accessible by direct experiment.

WORKSHOP STRUCTURE AND REPORT PREPARATION

This report summarizes the results and conclusions of the Department of Energy (DOE) Workshop on Basic Research Needs for Geosciences: Facilitating 21st Century Energy Systems, held in Bethesda, Maryland, February 21–23, 2007. The purpose of the workshop was for geoscientists to identify basic research needs and opportunities to facilitate energy systems of the 21st century. Highlighted basic research areas include behavior of multiphase fluid-solid systems on a variety of scales, chemical migration processes in geologic media, characterization of geologic systems, and modeling and simulation of the behavior of geologic systems.

Recommendations of priority research directions and long-term grand challenges for the geosciences were developed.

The workshop was sponsored by the DOE Office of Basic Energy Sciences (BES). It follows the format of several previous BES workshops that dealt with other important aspects of energy futures. Those workshops examined overall energy challenges during “Basic Research Needs to Ensure a Secure Energy Future” (October 2002), the production, storage, and use of hydrogen during “Basic Research Needs for the Hydrogen Economy” (May 2003), “Basic Research Needs for Solar Energy Utilization” (April 2005), “Basic Research Needs for Superconductivity” (May 2006), “Basic Research Needs for Solid-State Lighting” (May 2006), and “Basic Research Needs for Advanced Nuclear Energy Systems” (August 2006). Reports from those and related workshops are available on the BES web site at http://www.sc.doe.gov/bes/reports/list.html.

The workshop included 127 invited attendees from U.S. universities, national laboratories, and government agencies, as well as representatives of academia, industry and government from foreign countries. The report was prepared by the 84 members of five topical panels. The workshop program and attendee list are provided in Appendices 2 and 3.

A plenary session covered the technology needs and the basic research challenges for geoscience needed to support prediction of the behavior of geologic storage systems. The workshop then divided into four panels that investigated specific areas in more detail:

- Multiphase Fluid Transport in Geologic Media
- Chemical Migration Processes in Geologic Media
- Subsurface Characterization
- Modeling and Simulation of Geologic Systems

In addition, a separate panel considered crosscutting research issues and grand challenges. The panels included research leaders in the specific areas from universities, national labs, and other institutions. Other participants included observers from assorted government agencies, who rotated among the various panel sessions. Participants received in advance a document describing current technology perspectives and applied research needs. That document (the Technical Perspectives Resource Document) is provided in Appendix 1. The panels were asked to consider the gaps in current knowledge, opportunities for significant advances in basic knowledge with a pathway for impact on geoscience in general, as well as the potential for impact on uses of geoscience to support future energy technologies. Each panel recommended a set of priority research directions to address these opportunities and challenges to the assembled participants at a final plenary session at the end of the workshop.

This report was prepared by core writing teams from the Multiphase Fluid Transport, Chemical Migration, Characterization, Modeling, and Crosscutting panels. Their reports outline in detail the research needs and the scientific issues that will have to be addressed systematically. The recommendations of those panels are summarized in four Panel Reports, three Grand Challenges, six Priority Research Directions, and three Crosscutting Issues. Taken together, these recommendations outline a program of geoscience research that will be of critical importance for the energy transitions that will take place in this century.

PANEL REPORTS

MULTIPHASE FLUID TRANSPORT IN GEOLOGIC MEDIA

CHEMICAL MIGRATION PROCESSES IN GEOLOGIC MEDIA

SUBSURFACE CHARACTERIZATION

MODELING AND SIMULATION OF GEOLOGIC SYSTEMS

MULTIPHASE FLUID TRANSPORT IN GEOLOGIC MEDIA

CURRENT STATUS

Important hydrocarbon fuels, like oil and natural gas, form in the deep subsurface of the earth. These fluids accumulate in the pore space of rock formations, and are extracted through wells drilled into the formation. Typical hydrocarbon-bearing formations usually contain several different fluids within the formation—for example, oil, gas and water—which collectively form a multiple fluid phase system. Such rock-fluid systems are often referred to as *multiphase flow systems*, where *multiphase* connotes the presence of more than one fluid, while *flow* implies that the fluids are capable of motion because the rocks are permeable.

At the pore scale, individual fluids occupy spaces that are bound by the solid surfaces, as well as by fluid-fluid interfaces that separate adjoining fluids from one another (Figure 1). These interfaces provide opportunities for mass exchange between phases, and can also support non-zero stresses. Mass exchange is important because dissolution, evaporation or other reactions occur along these interfaces, while the non-zero stresses are important because they allow the different fluids to exist at different pressures. Small-scale processes along fluid-fluid and fluid-solid interfaces, and within the fluid phases, ultimately control many of the properties and behaviors that are observed at larger scales.

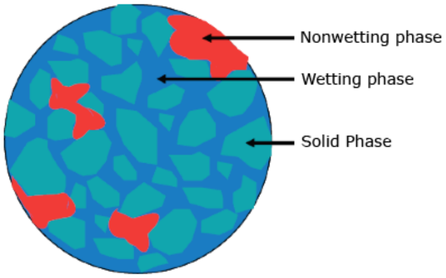
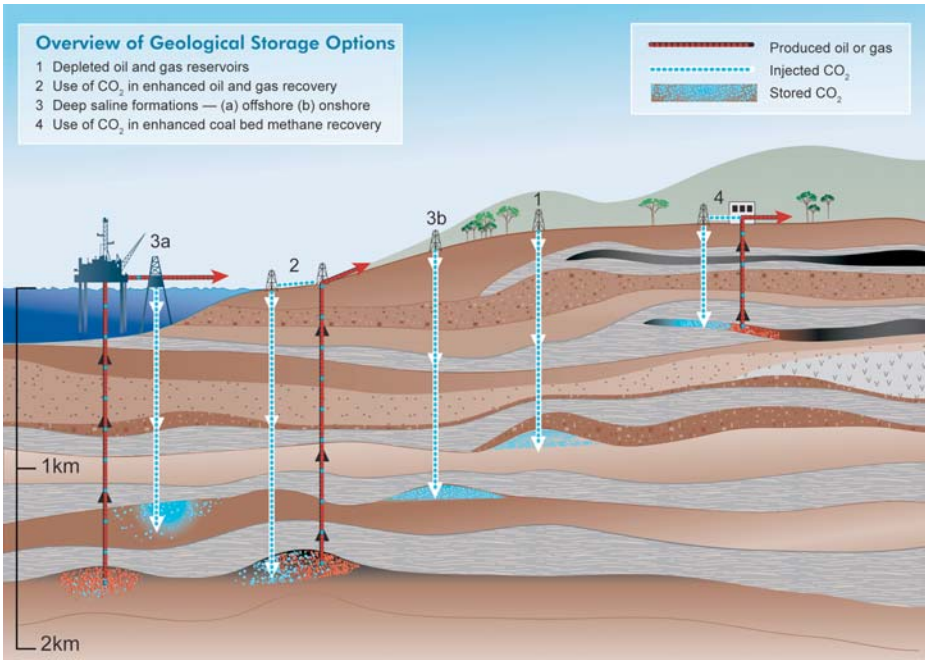


Figure 1. Two fluid phases, labeled *wetting* and *nonwetting*, and the solid rock, depicted at the pore scale (from Pinder and Celia 2006; reprinted with permission of John Wiley & Sons, Inc.).

Fluids and rocks at depth experience large pressures and stresses, and gradients in these quantities can lead to flow of fluids as well as possible deformation of the rock material. One of the standard ways that oil is taken out of the ground is through lowering the pressure in a well (via pumping), thereby inducing a pressure gradient that drives flow into the well. However, the presence of other fluids, especially water, tends to interfere with the flow of oil, and the entire system can exhibit quite complex, nonlinear, hysteretic and coupled behavior due to the presence of multiple fluid phases as well as any exchange phenomena across fluid-fluid or fluid-solid interfaces. Complex behavior and nonlinear feedbacks, from the pore scale to larger length scales, lead to oil recovery efficiencies on the order of 40%. That is, about 60% of the oil in a typical reservoir is left behind because it cannot be induced to flow into the well. This has not stopped the development of an impressive worldwide petroleum infrastructure: current global production of oil is about 80 million barrels per day, and production of natural gas is about 100 trillion cubic feet per year (Energy Information Administration 2006). Figure 2 shows locations of major oil and gas fields in the United States.

Carbon Capture and Storage

One of the most promising technologies to reduce carbon emissions is Carbon Capture and Storage, or CCS. This technology involves capture of CO_2 from large stationary sources of anthropogenic carbon, most of which are large power plants, before the carbon is emitted to the atmosphere. The capture part is most effective when modified processes such as coal gasification are used in the electricity generation, resulting in an essentially pure stream of CO_2, which is much easier to capture. Storage options include injection into the ocean and injection into deep geological formations. Injection into deep geological formations may involve depleted oil and gas reservoirs, including enhanced oil recovery operations, deep unmineable coal seams, and deep saline aquifers (see illustration below). Of these geological storage options, the largest storage capacity exists in deep saline aquifers; estimates of capacity range from 100 gigatons to 10,000 gigatons of stored carbon. These geological formations need to be permeable enough to allow large amounts of carbon to be injected, while being overlain by a low-permeability cap rock that will prevent the CO_2 from leaking upward. Depths are expected to be sufficient to reach high temperatures and pressures, such that the CO_2 will exist in a supercritical stage, although the high temperatures cause the CO_2 density to be less than the density of brine, with density ratios being on the order of 0.5. Overall, the resulting system involves multiple fluid phases, mass exchange between phases, geochemical reactions, and possible complex flow pathways that could involve different kinds of leakage pathways. Successful implementation of CCS systems will allow for widespread use of zero-emission power plants, which can have a very large impact on the global carbon problem.



Courtesy of CO2CRC, http://www.co2crc.com.au/

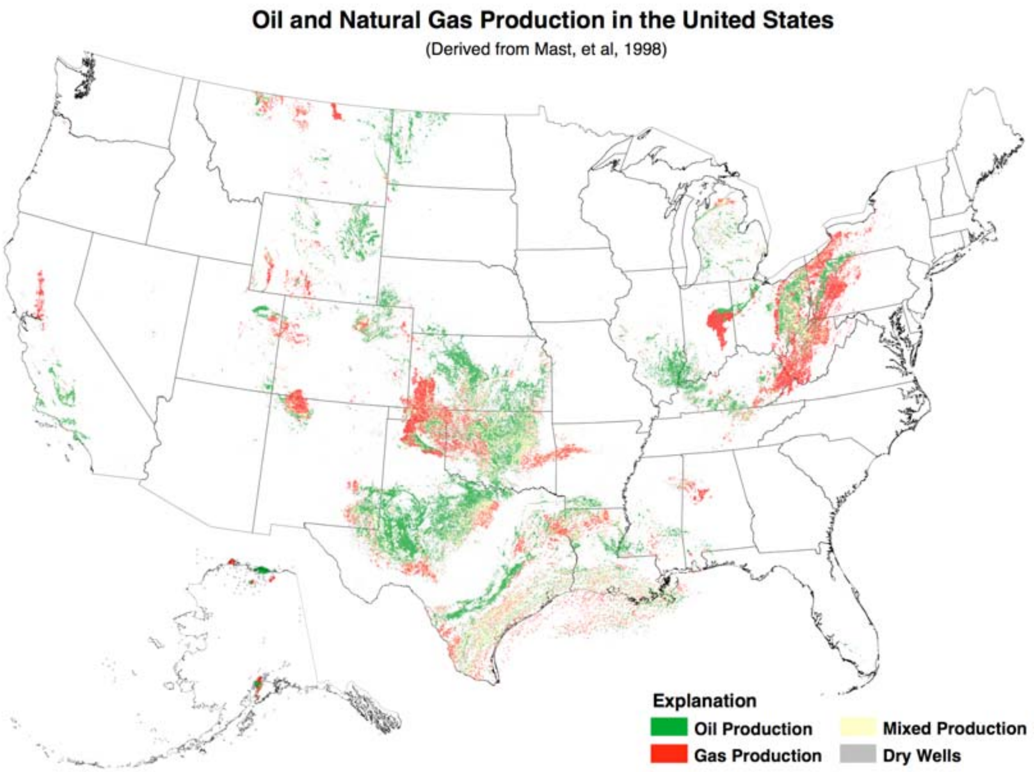


Figure 2. Oil and gas production in the United States (from the U.S. Geological Survey's National Oil and Gas Assessment website 1998).

Significant scientific discovery underpins the development of the oil and gas energy sector, much of it based on analysis and modeling of multiphase flow systems. Recent advances in imaging techniques make pore-scale analysis and modeling practical (see, for example, Lindquist et al. 2000; Blunt 2001). However, current limitations restrict the sample sizes to about a cubic centimeter. Translation of observations at these small scales to the much larger scales for practical applications continues to be a major challenge. At the larger scales, natural material heterogeneity strongly affects flow behavior and remains a major source of uncertainty, although advances in some subsurface imaging techniques have led to a better understanding of rock structure over a range of scales. Finally, improved computing power has allowed expanded use of computational simulations, which have provided additional insights into multiphase flow systems.

In addition to oil and gas production, there are other multiphase flow systems that are important to the energy sector, including systems in shallow zones that involve oil-water-air mixtures. An emerging area that involves multiphase flow, over unprecedented scales and with unique characteristics, is the storage part of Carbon Capture and Storage (CCS). CCS refers to the process of capturing anthropogenic carbon dioxide before it is emitted to the atmosphere, and then injecting the captured CO_2 into deep geological formations. The CCS concept could allow fossil-fuel-based power plants with essentially no emissions, which are often referred to as Zero-Emission Power Plants. To have any significant impact on the global carbon problem, a large amount of carbon emission avoidance is necessary—over the next 50 years, on the order of 500 billion metric tons, or Gigatons (Gt), of carbon dioxide. A typical coal-fueled power plant produces about 5 million metric tons, or megatons (Mt), of CO_2 per year, which means hundreds to several thousand zero-emission power plants must be brought on line over the next decades. Currently the U.S. has 1,552 coal-fueled power plants (336,000 MW) and 5,467 natural gas-fired power plants (437,000 MW) (Energy Information Administration 2006)

Carbon dioxide, perhaps with other combustion products like oxides of sulfur and nitrogen (SO_x and NO_x), persists as a separate fluid phase when injected into deep subsurface formations, thereby leading to a multiphase flow problem. However, this problem is now driven by fluid being injected, rather than extracted as it is for oil production. While CO_2 has been injected into depleted oil reservoirs for about 30 years, and a relatively mature infrastructure exists in places like West Texas, the amount injected to run all of the enhanced oil recovery operations in this region is about 20 Mt/yr of CO_2, which corresponds to emissions from about three large power plants. Direct experience with megaton-scale CO_2 storage, not involving enhanced oil recovery, is limited to two commercial-scale projects, one in the North Sea and one in Algeria (see sidebar on *Current CO_2 storage projects: The Sleipner and In Salah projects*). Solution of the carbon problem will require a much larger effort.

BASIC SCIENCE CHALLENGES, OPPORTUNITIES AND RESEARCH NEEDS

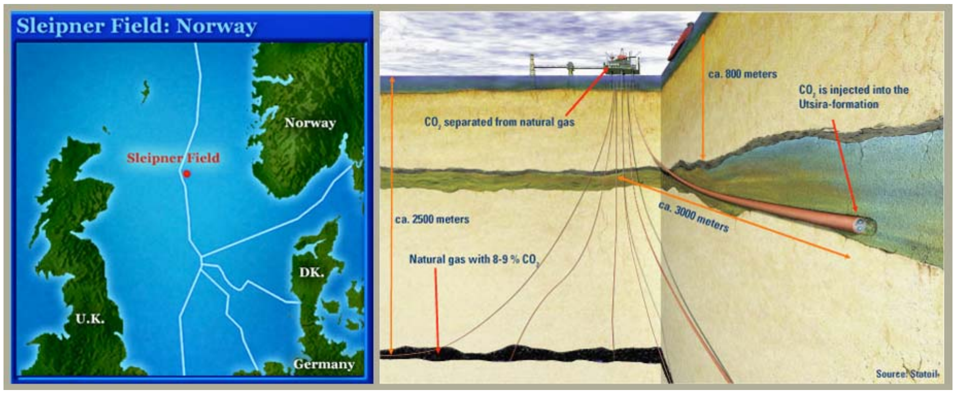
While scientists have studied subsurface multiphase fluid systems for many decades, and important scientific challenges remain, the carbon problem introduces fundamentally new scientific challenges that must be addressed to provide the proper foundation for meeting critical technical needs. The enormous scale of the carbon problem, the fact that a variety of geologic media will need to be used, and the fact that the flow system will fundamentally be driven by overpressurization (injection) rather than underpressurization (extraction), all lead to challenges that require fundamental scientific inquiry. The importance of the carbon problem and its new challenges leads to a new set of basic science questions, and to associated research opportunities. We highlight five important research areas.

Emergent behavior in multiphase systems due to physical and chemical heterogeneity from the pore scale to basin scale

Modeling subsurface systems is a formidable task because of the wide disparity in length scales ranging from pore to basin. Furthermore, many of the fluid phases are composed of multiple components; for example, crude oil has hundreds of different components. Research approaches to analyze this highly complex problem require new conceptual and theoretical models of multiscale, multiphase, and multicomponent processes, with their numerical implementation ultimately involving high-performance computing and model validation with corroborating laboratory and field experiments. Theoretical models range from pore-scale models that can be approached by existing descriptions, e.g., Navier-Stokes equations and their solution through techniques like lattice Boltzmann methods, pore-scale network models, Darcy-scale continuum models, and larger-scale continuum models based in part on stochastic theories (for example, Reeves and Celia 1996; Oren et al. 1998; Prodanovic and Bryant 2006). Development of theories to bridge this wide range of scales is still in its infancy. The enormity of the CO_2 problem and its impacts up to the basin scale make the issue of proper mathematical representation of processes and phenomena across disparate scales an important grand challenge. Four outstanding challenges are identified as follows.

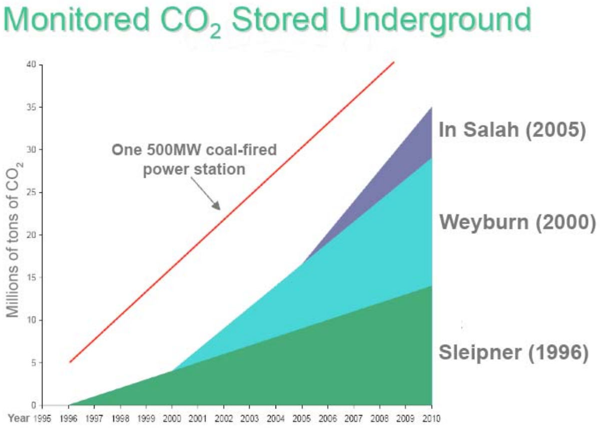
Current CO_2 storage projects: The Sleipner and In Salah projects

At the Sleipner gas field in the North Sea, the produced natural gas has a high CO_2 content. To prepare the gas for market, the CO_2 is stripped from the gas. The stripped CO_2 gas would normally be emitted to the atmosphere, However, because Norway has a CO_2 emission tax for off-shore emissions, in 1996 Statoil decided to inject the CO_2 back underground, into the Utsira Formation, rather than emitting it to the atmosphere. The amount injected is about one million metric tons per year. The Utsira Formation is overlain by a thick cap-rock formation, which limits upward migration of the buoyant CO_2 plume. The figures below show the location of the field in the North Sea, and a schematic of the CO_2 injection well and the deeper wells that produce natural gas.



Courtesy of Statoil

In addition to the Sleipner project, a newer injection, also on the order of a million tons of CO_2 per year, has begun at the In Salah field in Algeria. This is also for the purpose of emission avoidance, although in this case there is no taxation structure driving the decision. Both of these injections are being monitored by surface geophysics surveys. The Enhanced Oil Recovery (EOR) project at Weyburn is also being monitored—no other EOR projects currently involve imaging of the subsurface CO_2. The figure below shows the amounts involved in these three injection projects, as compared to the emissions from a single coal-fired power plant.



Courtesy of John Gale, IEA Greenhouse Gas R&D Programme, http://www.ieagreen.org.uk; see Gale 2006.

Buoyancy-driven flow at all scales

For problems like CO_2 injection into deep brine-filled formations, the less-dense CO_2 is driven upward by buoyancy. It is also driven laterally by pressure forces, and further influenced by capillary forces associated with the small-scale fluid-fluid interfaces. While each of these driving forces is reasonably well understood on its own, the interactions and interplay among these can lead to highly complex behavior, especially when the natural heterogeneity of a geological formation is included in the analysis.

In such cases, new behavior and new characteristic time scales emerge as the macroscale CO_2-brine interface interacts with heterogeneities in the permeability field. An example of these kinds of behaviors is presented in the sidebar on *Buoyancy, capillarity, and heterogeneity: Buoyancy-driven flow at all scales*. A suitable theoretical and computational framework for this behavior does not exist.

Impact and coupling of interfacial phenomena and reactive flow at all scales

Interfaces between fluid pairs, and between fluids and solids, are fundamental to all multiphase flow and reactive transport in geologic systems. A sound understanding of interfacial behavior, and how it is manifested across the range of length and time scales appropriate for practical flow problems, remains an open question. Couplings between fluid movement and interfacial phenomena, such as precipitation/dissolution reactions and their feedback to the flow system, make modeling the system particularly challenging. Such couplings often manifest themselves across different scales. A comprehensive understanding of how behavior at one scale affects behavior at larger (and smaller) scales remains one of the most difficult challenges for understanding and predicting multiphase flow.

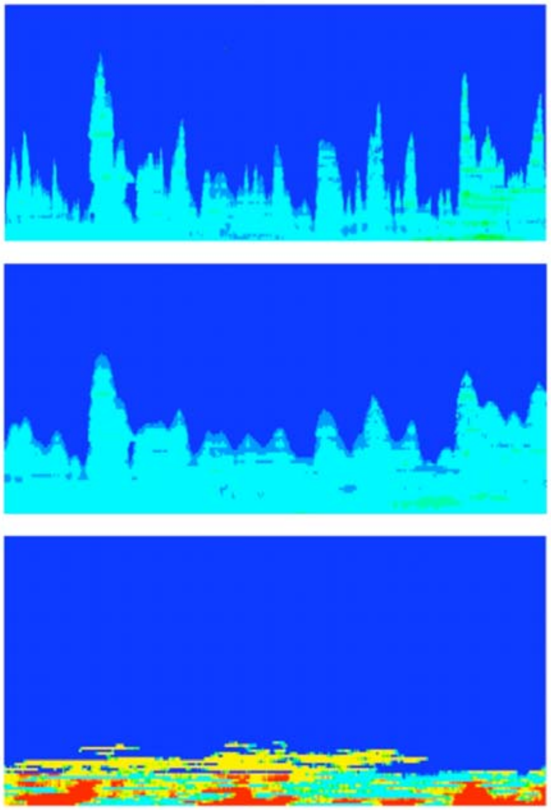
Seamless transitions between mathematical descriptions of flow at multiple scales in heterogeneous media (pore level to basin scales)

A grand challenge for multiphase flow in the subsurface is a satisfactory mathematical description of behavior that is self-consistent across many length and time scales. Well-known examples include the transition from molecular statistical dynamics to the equations of fluid flow, such as the Navier-Stokes equations, and the transition from Navier-Stokes flow with an individual pore to the Darcy equation at a laboratory column scale. Inclusion of multiple fluid phases and their associated interfaces leads to much more complex problems. Further transitions from the core scale to the field scale introduce extreme challenges. Efforts to place multiphase flow on a more rigorous foundation have begun, but much work is needed to develop these to the level needed. Intensifying the challenge still further is the effect of heterogeneous properties—chemical, interfacial, transport—across the wide range of length and time scales. Variations in properties can trigger a number of important mechanisms that lead to different physical/chemical phenomena impacting different parts of the geologic system at different times. Ideally, this seamless transition framework will allow the scientific community to understand the emergence of patterns, trends and behaviors at larger scales arising from behaviors at smaller scales.

Buoyancy, capillarity, and heterogeneity: Buoyancy-driven flow at all scales

Multiphase flow regimes and behavior are poorly understood when buoyancy is the dominant force. The instability inherent in buoyant flow is well known, but when the fluids occupy a porous medium, new behavior and new characteristic time scales emerge as the interface interacts with heterogeneities in the permeability field. Because capillary forces often exceed buoyancy forces in geologic systems, still more complicated behavior emerges as the fluid/fluid interface encounters heterogeneities in the capillary pressure characteristics of the domain. As the length scale traveled by the plume increases, the behavior can undergo yet another transformation. A suitable theoretical and computational framework for this behavior does not exist.

Examples of emergent behavior for buoyant flow in a heterogeneous geologic system:



Top—If less dense fluid initially occupies the bottom part of the domain, the flow pattern follows connected paths of higher permeability when capillary pressure is negligible.

Middle—If a single capillary pressure curve applies to the domain, capillarity smoothes the pattern established by the permeability field.

Bottom—If capillary pressure varies spatially, a qualitatively different displacement occurs.

Courtesy of Steven Bryant, University of Texas at Austin. From Sadaatpoor et al. 2007.

Correlating processes and heterogeneity on the basis of length and time scales

Many processes associated with multiphase flow and reactive transport occur at characteristic length and time scales. Heterogeneity inherent in geologic systems occurs at all length scales. A fundamental challenge is that the type of heterogeneity that strongly influences a particular process need not occur at the scale characteristic of that process. For example, multicomponent diffusion in the gas phase can give rise to pressure gradients that cause advective flow. While this process is important over the length scales on which the concentration gradients exist, over larger scales, buoyancy-driven or injection-driven flow will dominate the advective process.

The fundamental challenge is to identify and delineate the scales at which connections between *process* and *heterogeneity* are found. Constraining the links between process and heterogeneity would lead to a more seamless description of multiphase flow and reactive transport, and allow an organized description of emergent behavior useful for developing the next generation of models applicable over the full range of relevant length scales.

Multicomponent, multiphase properties and interactions of mineral-fluid-microbial systems

Multiphase flow systems commonly involve complex, multicomponent fluid phases that can react with one another and with the rock minerals. For example, when CO_2 is injected into a geological formation, reactions between silicate minerals, water, and injected CO_2 can produce calcite-group carbonates (e.g., calcite, siderite, dolomite, and magnesite). These and many other kinds of reactions must be understood over broad ranges of temperature, pressure, and phase composition. In addition, the presence of subsurface microbial communities can produce additional complexities due to their influence on reactions and surface properties. Proper inclusion of these fundamental reactions, over appropriate space and time scales, is crucial for meaningful model formulation and system prediction. Three areas have been identified as especially significant for general multiphase flow systems that are relevant to energy needs.

Phase behavior and partitioning between CO_2 and brine, organic, and gas and solid phases

Flow of geologic fluids, including gases, liquids, and supercritical solutions, serves to transport mass and energy in the natural environment. These fluid phases also act as both reaction media and reactants. Among the many different types of geologic fluids, those containing volatile carbon, oxygen, hydrogen, nitrogen and sulfur (C-O-H-N-S) species, and those enriched in chloride salts (brines), are of particular interest. They occur widely in varied geochemical settings, commonly contain significant quantities of dissolved and suspended compounds (complex hydrocarbons, organic macromolecules, colloids/nanoparticles), play a crucial role as primary reaction media, and are important sources and sinks of greenhouse gases. The relative strengths of complex molecular-scale interactions in geologic fluids, and the changes in those interactions with temperature, pressure, and fluid composition, are the fundamental basis for observed fluid properties. A comprehensive and technically rigorous understanding of the volumetric properties and energetics of C-O-H-N-S fluids is needed to correctly interpret fluid-fluid and fluid-solid interactions expected in various sequestration settings. Because many subsurface systems involve the presence of hydrocarbons, there is a clear need to investigate complexation and binding of organic molecules (e.g., humic acids) in aqueous solutions, with or without CO_2.

Although we have gained important quantitative insight into the speciation, stability and kinetics of many organic-based systems of geological relevance, we still lack a fundamental understanding of the effects of mixed-salt composition, elevated pCO_2 and temperature, and Eh/pH conditions on the equilibrium and kinetic properties of key organics and biomolecules. Moreover, we are just beginning to understand how molecular-specific interactions among solutes and solvents eventually lead to homogeneous nucleation, crystallization, and aggregation of colloidal nanoparticles which could participate in and influence transport behavior. Understanding these solvent-mediated interactions for broad classes of solutes and suspensions in natural systems over the range of conditions typical of geologic fluids will greatly improve our ability to model and predict fluid behavior, reactivity, and the partitioning of elements and isotopes between coexisting species and phases relevant to geological sequestration.

Rates of dissolution and mineral reactions involving CO_2

Kinetics of dissolution and mineral reactions can have enormous impacts in many fields of energy sciences. For CO_2 injection, the long-term efficacy of subsurface sequestration depends on our fundamental understanding of the extent and rate of CO_2-mineral interactions and the associated effects on the fate of the injected carbon and rock characteristics. Injection of CO_2 lowers the pH of the brine that it contacts by several pH units, leading to rapid dissolution of calcite and possibly other minerals. Some of these CO_2-mediated dissolution reactions can produce solutes that buffer pH, thereby controlling the extent to which formation waters become acidified (Knauss et al. 2005; Kharaka et al. 2006a,b). These reactions also have the potential to alter the porosity and permeability of the formation. Such changes may impact the injection process, but more importantly they would change the long-term flow characteristics and storage capacity of the formation. At present, neither the equilibrium thermochemistry nor the kinetics of these reactions are well understood at the low temperatures and the high CO_2 loading rates expected. They also exhibit a wide range of molar volume change. Porosity development in nature results, in part, from such volume changes; consequently, these reactions will provide important insights into this process. The thermophysical properties of fluids under confinement are still poorly constrained for the temperature-pressure conditions relevant to subsurface disposal of CO_2. Novel *in situ* experimental methods such as neutron scattering are needed to assess the interfacial interactions between a complex fluid and heterogeneous matrix at pressure-temperature-composition conditions relevant to CO_2 sequestration. The overarching challenge is to understand the chemical and isotopic phenomena engendered by complex mineral-fluid interactions occurring over ranges of temperature, pressure, compositions, and length and time scales relevant to the sequestration systems that lead to robust predictive capabilities of coupled reactive-transport processes in nature.

Microbial processes relevant to CO_2 sequestration

Anaerobic, thermophilic microbial communities are known to exist at depths and in formations, reservoirs and aquifers being targeted for subsurface CO_2 injections (Onstott et al. 1998; Onstott 2005). These communities are composed of fermenters, metal and sulfate reducers, and methanogens. Fermenters tend to be concentrated in shales, while metal and sulfate reducers and

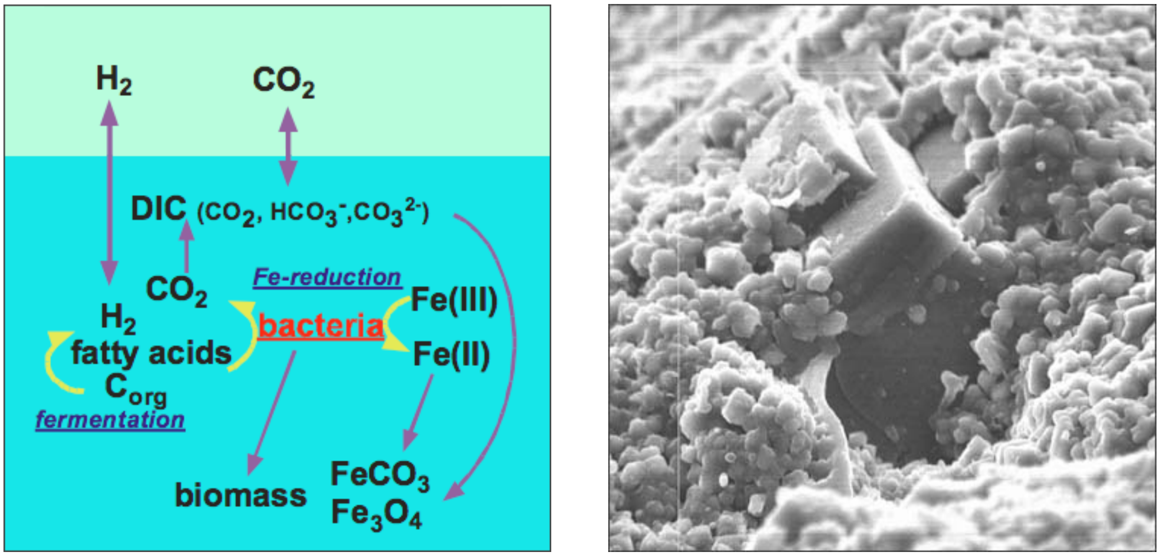


Figure 3. Schematic *(left)* illustrates the chemical processes associated with the microbial-mediated reduction of iron in solution in the presence of CO_2. The SEM *(right)* of a large siderite ($FeCO_3$) crystal co-precipitated with fine-grained magnetite in a bicarbonate-rich culture of iron-reducing thermophilic bacteria at 65°C (from Zhang et al. 2001).

methanogens are concentrated in sandstones (McMahon and Chapelle 1991; Fredrickson et al. 1997; Krumholz et al. 1997). Subsurface injection of CO_2 can impact this lethargic subsurface microbial ecosystem in a variety of ways, not the least of which could include iron reduction leading to biomineralization (Figure 3). For example, the mobilization of dissolved organic matter, as observed in the CO_2 injection into the Frio Formation (Kharaka et al. 2006a), may increase its availability for fermentation reactions; the increase in dissolved CO_2 may enable biogenic CH_4 formation; the decrease in pH may favor release of critical nutrients (e.g., phosphate and metals) and elevate cell membrane H^+ gradients, both of which promote cell growth and activity.

The rates and extent of microbial immobilization of CO_2, however, are difficult to predict since our knowledge of anaerobic microbial processes both in lab and field is based upon studies of water-saturated systems, not a mixed CO_2/water system at high pressure (Zatsepina et al. 2004). The challenge will be to parameterize this process at a scale that is useful for field-scale applications, based on comparison of laboratory microbial transformation of CO_2 under high partial CO_2 pressure in the presence of brine and various mineral/rock media for a range of microbial phenotypes with field observations.

Shallow crustal deformation and fluid flow driven by large anthropogenic perturbations

Understanding the physical and chemical responses of subsurface rock masses to large-scale perturbations like those associated with CO_2 injection presents substantial scientific challenges. Rock masses are highly heterogeneous with regard to lithology, texture, structure and strength. Discontinuities such as faults, joints and microfractures exist at all length scales, and they have significant impact on the coupled rheological and transport responses, which may be highly nonlinear and anisotropic. If other injection environments are considered, such as poorly lithified deep offshore marine sediments, then the challenges are magnified because geomechanical responses of these systems is a largely unexplored topic. Understanding of soft-sediment deformation requires interrogation of fundamental questions regarding coupled processes affecting pore pressure increases and resultant deformation of the sediments, and how these will affect fluid displacement. Indeed, the rapid and large-scale injection of a fluid like CO_2 into very soft sediments may be more akin to igneous intrusion than multiphase flow in porous media.

A variety of research approaches will be needed to address these challenges, including field studies of geomechanics in a variety of geologic settings, laboratory experiments to constrain rheological behavior of fluid-rock systems, discrete or continuum modeling of deformation, and development of novel theoretical frameworks where current approaches are inadequate.

Coupled pressure, stress, strain, and flow responses in multiphase fluid-rock systems

A multiplicity of deformation mechanisms at different scales may be activated by the anthropogenic perturbations in this geologic regime. In porous clastic and carbonate rocks, grain-scale deformation mechanisms such as microcracking, pore collapse, pressure solution, crystalline plasticity, and aperture dilation and contraction may be operative. The properties of fractures must also be understood across a range of scales, and must include both physical and chemical impacts. These include responses to effective stress, as well as feedbacks to the flow field and associated changes in fluid composition, and therefore geochemical reactions that can result due to changes in fluid flow. All of these processes can dynamically alter the already complex hierarchical architecture of fracture networks (e.g., Caine et al. 1996). The interplay of these factors controls whether a joint or fault system would provide conduits or barriers for the transport of a multiphase fluid in the shallow crust and the potential for fault reactivation. These are critical considerations for problems involving large-scale pressure perturbations, such as the CO_2 injection system. For injection into deep seabed sediments, a quite different approach must be developed, where very large deformations of the sediments may occur. The possible formation of CO_2 hydrates in these systems, which introduces an additional solid phase into the system, would lead to further complexities and represents a largely unexplored area of research.

Coupled geochemical and geomechanical responses

Mineral dissolution or precipitation can modify rock strength and pore structure. In turn, changes in stress and pore structure can modify the delivery of fresh reactants and removal of reaction products, influencing geochemical reaction rates and products. Over long time periods these local-scale coupled processes may impact large-scale fluid dynamics and deformation, creating a complex interplay between basin-wide processes and local-scale coupled geomechanical and geochemical processes. Chemical and hydrologic gradients in the fluid-rock system can significantly impact the kinetics of processes such as pressure solution, subcritical crack growth, and solution-precipitation. The interplay between space and time scales also enters into these mixed physical-chemical reactions, requiring new approaches to study the comprehensive system response across all of the relevant spatial and temporal scales.

Imaging of geomechanical processes and properties

Understanding complex geomechanical processes will require accurate measurements of stress, pore pressure, deformation, alteration to the solid matrix, and rock fracturing at a variety of scales, from the microscopic to the field scale. Available field-scale methods for imaging stress fields and deformation are limited by poor spatial coverage, particularly in three dimensions. Microscopic imaging of pore geometry and alteration of the solid matrix are limited by the sample size, spatial resolution of micro-tomography facilities, and experimental difficulties associated with creating controlled, representative and dynamic conditions needed for meaningful experiments in small experimental cells. Novel methods of *in situ* chemical imaging should also be explored to reveal complex behavior at fluid-matrix interfaces.

Flow and transport properties of seals, faults, and fractures

The sealing quality of cap-rock formations, including any faults or fractures, is arguably the most critical element controlling the vertical migration of overpressurized or buoyant fluids in the subsurface. These barriers to fluid flow typically consist of massive consolidated clay-rich sediments (shale) and evaporites such as anhydrite. Resistance to flow results from the small size of the pore and pore throats (nano- to submicron-scale) in the rocks, creating both viscous and capillary barriers to the nonwetting fluid during multiphase flow.

The quality of a seal depends not only on the texture of rock matrix, but also on faults, fractures and wellbores that penetrate the seal. Understanding the effectiveness of seals requires an integrated understanding of the microscopic interfacial stresses at fluid-fluid and fluid-solid interfaces, as well as a broader understanding of the depositional and postdepositional processes that created the modern-day architecture of the seal. Natural oil and gas seeps associated with hydrocarbon reservoirs around the world demonstrate the imperfection of many natural reservoir systems; these may be unacceptable in technological applications.

The presence of an oil or gas reservoir provides proof of the existence and effectiveness of a sealing formation, given that both oil and gas are buoyant relative to water. However, identifying strata that are effective seals for natural gas or CO_2 storage in brine-bearing formations, which have no apparent history of oil or gas residency, is a significant challenge. Basic research to identify the relevant pore-scale physics, long-term reaction rates, and response to pressure and fluid evolution, as well as the development of measurement techniques to identify small features (like fractures) within subsurface domains, will facilitate the success of large-scale underground storage of buoyant fluids such as CO_2. A concerted program of basic research addressing the following scientific areas is needed:

- Understanding the impact of interfacial and surface properties of fluids in fine-grained and fractured media at laboratory, reservoir, and regional scales and at slow transport and reaction rates
- Identification of the transmissivity of faults and fractures as a function of fluid chemistry, phase state, rock-fluid interactions, and pressure
- *In situ* measurement of fluid-rock interactions in fine-grained media (saturation, pressure, and flow)
- Identification and characterization of local high-permeability features in seals over large regional scales

Interfacial and surface properties of fluids in fine-grained and fractured media

Fine-grained materials lead to slow flow rates for single-phase fluid flow due to the high viscous resistance (low permeability) associated with the small pore spaces. In multiphase flow, capillary entry pressures may preclude a non-wetting fluid (like CO_2) from entering the pore spaces, thereby eliminating flow through the formation. However, heterogeneity of material properties, small-scale features like fractures, and the interplay between buoyancy, pressure, and interfacial forces (capillarity), make this invasion and subsequent flow of fluids like CO_2 through fine-grained materials highly uncertain and difficult to predict (see the sidebar on *Buoyancy, capillarity, and heterogeneity: Buoyancy-driven flow at all scales*). Possible reactions associated with fluid-solid interfaces can modify any invasive flows that develop (e.g., Johnson et al. 2004). All of these feedbacks and nonlinear processes must be understood in the context of flow suppression and leakage control to properly characterize and quantify the movement of injected fluids through sealing formations.

Transmissivity of faults and fractures

In addition to detection and characterization of the properties of faults and fractures at high spatial resolution, it is critically important to be able to predict whether faults will transmit or retain fluids as a function of fluid pressure, phase state, and chemical composition. A major source of uncertainty and disagreement centers on whether fault systems are sealing or transmissive. Even if the initial character of a fault system is known, anthropogenic perturbations can change its properties. Available wellbore-based characterization tools are either poorly suited or completely inadequate for characterizing these effects. Fault gouge properties and complex 3D fracture networks in natural systems are very difficult or impossible to reproduce in a laboratory setting, making field measurements a critical but expensive and time-consuming aspect of this research. Finally, the typically slow rate of fluid migration in these structures makes conducting measurements in a timely manner challenging, even under favorable conditions.

In situ measurement of fluid-rock interactions in fine-grained media (saturation, pressure and flow)

The performance of fine-grained barriers in multiphase conditions is complex because the active sealing mechanism varies with fluid composition and pressure, and the changes in geochemical behavior and stress can alter the properties of the seal. Tests of seal properties in the laboratory or from the wellbore are inherently limited in terms of their spatial coverage and validity when extrapolated to *in situ* pressure and temperature conditions. Improved field-deployable methods are required for accurate determination of the properties of flow barriers. If these measurements could be made *in situ* without major modification of the natural environment, then observations of seal properties as functions of changing fluid composition, pressure and stress during anthropogenic perturbations could be made.

Identification and characterization of local higher-permeability features in seals

Techniques to identify the existence of sealing strata, and to a lesser extent sealing faults, are currently available. However, techniques to locate and then quantify the properties of the weak points or flaws in these seals are poor to nonexistent. Especially challenging is the need to assess small features (fractures, sand-on-sand contacts) at the millimeter to the few-meter scale, when the total area of interest covers hundreds of square kilometers. Regions of heterogeneous permeability need to be identified. Even regions of slow leakage will need to be monitored over time.

Dynamic imaging for complex multiphase systems

The resolution of subsurface imaging methods must improve dramatically before we can track multiphase fluid movement and behavior *in situ*. Quantitative imaging of four-dimensional (three space dimensions plus time) variations in quantities like phase saturations and pressures requires a more fundamental understanding of how seismic and electromagnetic waves, and other remote sensing methods, depend on the spatial distribution, pressure, and interfacial properties of multiple fluid phases in porous and fractured media. Improved theoretical, mathematical and computational models for wave propagation in porous media must be developed, with explicit coupling to models of multiphase flow. Together, the coupled models form the basis for inverse modeling and imaging of relevant flow parameters.

Critical paths forward will:

(a) Determine remotely imaged features and properties sensitive to multiphase properties of interest

(b) Develop a theoretical basis for the constitutive relationships between material properties and how fields and waves interact with them

(c) Calibrate these relationships with quantitative laboratory data

(d) Demonstrate whether or not models accurately predict experimental behaviors at the field scale

For example, we know that the sensitivity of seismic velocity to increasing saturation depends on the distribution of the fluids in the pore space. In homogeneously saturated materials, P-wave sensitivity decreases appreciably with increasing gas saturation. However, we know very little about the sensitivity of seismic attenuation to saturation, and we cannot distinguish a residual phase saturation (trapped by capillary forces) from a mobile phase occupying the same volume fraction. Additionally, simulations in three spatial dimensions, for example seismic imaging, rely on complex numerical methods implemented on high-performance computers. Inclusion of multiscale heterogeneity, time-dependent properties, and the expanded list of parameters required for coupled models for wave propagation and flow in porous media, results in huge computational domains—perhaps hundreds of billions of nodes and petaflops of computing power with the accompanying complexities of adaptive and variable meshes, parallel algorithms, and challenges of quantifying uncertainties. Together these form an enormous scientific challenge.

Success in achieving a revolutionary breakthrough in imaging capabilities is expected to have substantial technological benefits, including improved oil and gas recovery, improved success in oil and gas exploration, and safer and more secure geological storage of CO_2. For example, the ability to detect and interpret the presence of vertically oriented gas distributions will improve leak detection from geological CO_2 storage reservoirs, as well as help to locate gas chimneys, which are signs of past hydrocarbon migration. Improved quantification of the fraction of pore space filled with a nonwetting fluid will provide more reliable inventories of hydrocarbon reserves and the mass of stored CO_2 in the subsurface.

Theoretical foundations for high-resolution spatial and temporal imaging of multiphase fluid distributions

Identification of local properties from global measurements is the key challenge for high-resolution geophysical imaging. This requires consideration of both the spatial and temporal scale of the global measurements, as well as the local properties of interest. The inherent multi-scale, multiphysics nature of this problem requires development of new theoretical approaches that preserve and reveal the relevant underlying physics, while volume averaging material properties over a spatial scale that is consistent with the resolution of the measurement. Limitations of current theoretical approaches will require inclusion of more comprehensive physical descriptions of wave interactions with the complex multiphase systems. For example, serious limitations in our current ability to image the spatial distribution of multiple fluid phases in rocks using seismic imaging can be overcome by moving beyond velocity-based tomography to methods that include wave attenuation and/or make use of the full wave form generated by the seismic source. Fundamental new understanding will be needed to develop the foundation for next-generation imaging approaches.

Constitutive relationships among waves, fields, and properties of multiphase flow systems

A comprehensive sequence of laboratory measurements at a variety of spatial scales is needed to establish a rich database to study the effects of fluids on bulk geophysical and flow properties. Examples include seismic compressibility, velocity, attenuation, electrical resistivity, dielectric constant, density, and saturation. These measurements, along with associated theoretical models, provide a robust scientific basis for relating geophysical measurements such as seismic velocity and attenuation to the amount and spatial distribution of fluid phases in the subsurface.

Coupled models for flow dynamics and imaging

This challenging problem requires development of integrated models that account for waves, potential fields, and flow and transport in porous media. Traditionally, each of these subdisciplines has proceeded in isolation, passing primarily abstractions of concepts and results from one group to the next. Progress in quantitative high-resolution imaging will require removal of disciplinary barriers, leading to rigorous cross-fertilization among subdisciplines by creating common theoretical and computational platforms. To this end, one must consider theoretical, mathematical and experimental (laboratory) activities that, in concert, seek to understand and quantify the relationships and sensitivities of image parameters to multiphase flow parameters of interest.

Large computational domains

Computational requirements for forward simulations and inverse models motivate the development of new computing paradigms, both algorithms and computer architectures. However, these new paradigms must carefully consider tradeoffs between capturing the relevant model descriptions and the computational loads. That is, new algorithms and architectures must consider the needs of the applications on a basis equal to the way applications have considered the limitations of modern architectures. We anticipate that forward and inverse modeling algorithms of the type we require here will need to drive development of new hardware architectures that are better suited to the applications at hand.

CONCLUSION

Understanding of multiphase flow of fluids in rocks builds on more than a century of development in oil and gas production, soil science, and geothermal energy production. Nevertheless, scientific challenges remain for applications such as geological storage of CO_2. In particular, the large injection volumes, long transport distances and long time frames raise new issues with regard to the reliability and robustness of current understanding. Carbon dioxide is highly mobile in subsurface environments due both to its low viscosity and density—and will tend to migrate along high permeability pathways, moving upward until it encounters capillary barriers in fine textured rocks. Complex and path-dependent behavior results from the interplay of buoyancy forces, natural rock heterogeneity, and capillary forces. Small-scale processes along fluid-fluid and fluid-solid interfaces, and within the fluid phases, ultimately control many of the properties and behaviors that are observed at larger scales.

Five critical fundamental scientific research needs have been identified.

1. New approaches are needed to accurately predict migration of multiple fluid phases in environments that are highly heterogeneous, from the pore scale to the basin scale—over large spatial scales and long time frames.
2. Methods to quantify and predict rates of geochemical reactions between multiphase, multicomponent fluids and minerals are needed to understand how quickly dissolution and mineralization will occur.
3. Fundamental scientific understanding of basin-scale geomechanical processes is needed to predict shallow crustal deformation and basin-scale brine displacement caused by large and rapid anthropogenic perturbations such as injection or extraction of multiphase fluids in the subsurface.
4. A new multidisciplinary approach is needed to assess the multiphase flow properties of membrane seals, faults and fractures to determine whether or not a geological reservoir has an adequate seal.
5. Dynamic field-scale imaging is needed to test and validate multiphase flow models.

A fundamental research program in these areas will significantly improve our ability to understand and predict multiphase flow in complex subsurface environments—and provide a strong scientific foundation for assessing the full potential of geological storage of CO_2 in deep geological formations.

CHEMICAL MIGRATION PROCESSES IN GEOLOGIC MEDIA

CURRENT STATUS

The ability to predict the transport of energy byproducts and related contaminants in geological systems over long times is one of the most important and daunting challenges facing the Department of Energy (DOE). For example, in the geological disposal of nuclear waste, the main scenario in which radionuclides could reach the biosphere and expose humans to unacceptably high radiation doses is through groundwater transport (Macfarlane and Ewing 2006). Groundwater may contact and corrode waste containers, leach radionuclides from wasteforms, and transport radionuclides as dissolved species or colloids (e.g., Kersting et al. 1999; Santschi et al. 2002) to wells used to extract drinking or irrigation water (Figure 4). As a second example, one mode of sequestering CO_2 in the earth is by injection into subsurface rock units. Evaluating the long-term integrity of these rock units, and therefore their ability to retain the CO_2, will depend on the chemical and physical interactions that occur among minerals, in-place pore fluid, and the CO_2. In all cases, forecasting how chemical byproducts and related contaminants may migrate through deep subsurface regions of the earth must be accurate and scientifically defendable. This requires that we understand the key chemical and transport processes that occur in geological systems.

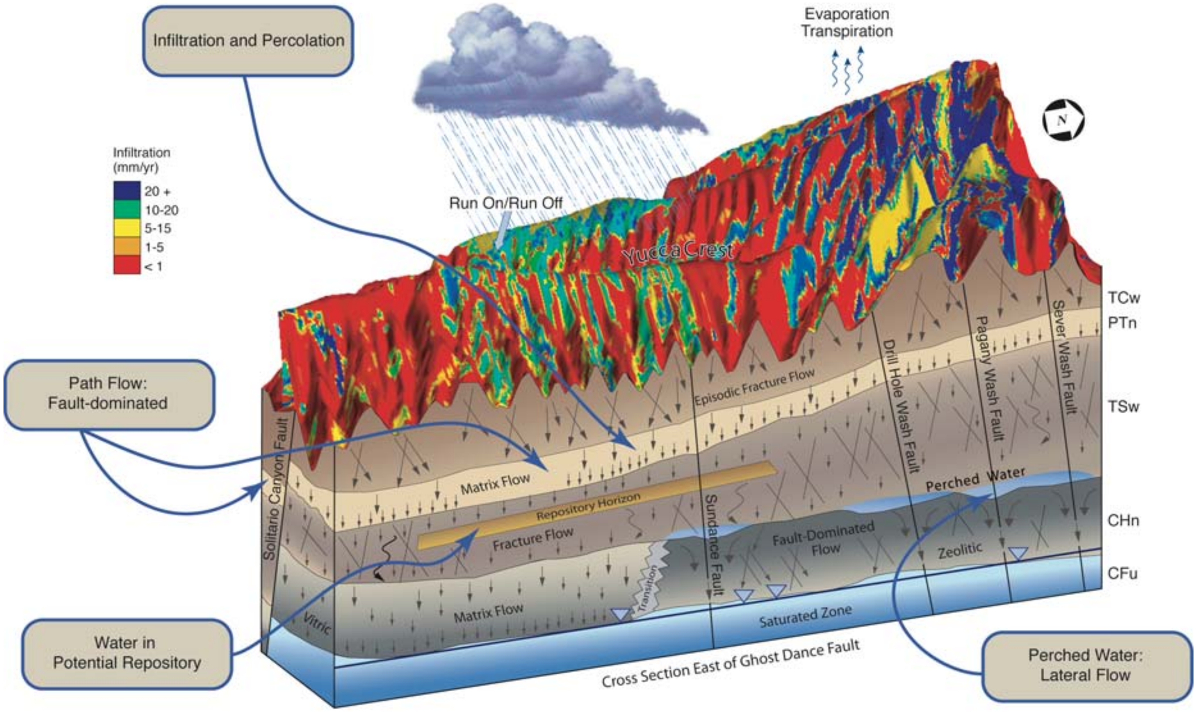


Figure 4. Illustration of possible contaminant migration pathways in the geologic system at Yucca Mountain, Nevada (CRWMS M&O 2000).

The objective of this panel is to identify important basic science challenges that, if met, would greatly enhance the reliability and scientific credibility of predictions of chemical migration in geologic media. These science challenges target five principal areas:

- Colloid migration
- Coupled chemical-hydrologic processes
- Complex and dynamic interactions at the mineral-water interface
- Biogeochemistry
- Reaction equilibria and kinetics in perturbed geochemical environments

The significance of each area in the overall context of chemical migration processes and specific proposed principal research directions are described in detail below.

BASIC SCIENCE CHALLENGES, OPPORTUNITIES AND RESEARCH NEEDS

Colloids as a critical mode of radionuclide mobility

Colloids, which range in size from 1 nm to 1 μm, are chemically, structurally, and temporally complex species that are critically important to understand as carriers of radionuclides, metals and other contaminants in geologic systems. Because colloids exist in many forms, understanding the processes that determine their formation, speciation, atomic-level structure, and interfacial properties is necessary before their migration behavior can be modeled in natural systems. Advances in sampling technologies, characterization, and computational approaches would enable acquisition of this information and lead to development of new conceptual models for how colloids behave at a microscopic level. Innovation is needed in these approaches at larger scales to enable the reliable prediction of the reactivity, fate and transport of colloidal particles in aqueous environments. Novel sampling techniques must be implemented that allow capture of representative colloids from natural environments without introducing artifacts.

Colloids are difficult to characterize because of their size range and chemical complexity. Colloids may have ill-defined, irregular structures and variable chemical compositions. Examples of colloids include more or less thermodynamically well-defined polynuclear hydrolyzed metal species, organic macromolecules, and clays. The broad range of sizes, structures, compositions, and heterogeneous atomic positions make modeling colloids at the molecular level a particular challenge. Computational approaches require advances in treating radionuclides, large nanoscale particles, and complex and heterogeneous species in solution and at interfaces. New reactive transport measurements at the pore, column and field scales will lead to new conceptual and mathematical models of colloid-associated contaminant transport in heterogeneous geologic environments. Scientific advancement on these fundamental issues will lead to lower uncertainty in predictive modeling of radionuclide transport, improved performance assessment of waste repositories, and improved engineered barriers around emplaced wastes.

Coupled physical-chemical processes from the mineral surface to the pore scale

Breakthroughs in modeling of reactive transport processes relevant to chemical migration will occur only by gaining fundamental understanding of coupled processes through a hierarchy of scales.

Basic research is required to:

- Develop robust multiscale, multiphase models that explicitly link mechanisms such as transport through thin films and complex reactions at mineral surfaces in different geochemical environments to the pore-scale and/or macroscale flow regimes
- Interrogate operative submicron- to pore-scale reactive-transport processes in natural and simulated systems through use of innovative experimental and analytical techniques for the purpose of testing new conceptual and mathematical models.

Many studies have documented orders of magnitude differences between mineral dissolution rates measured in the laboratory and rates derived from natural weathering environments. For example, White and Brantley (2003) demonstrated a strong dependence of the dissolution rates of common aluminosilicates (feldspars and biotite) on weathering “age.” Although the relative roles of surface reactions and diffusion processes on overall reaction rates are topics of active debate (e.g., Grambow 2006), it is clear that coupled processes influence multiple transport mechanisms and chemical reactions at grain surfaces and boundaries, and in fluid films, pore throats, and pores. Mineral reaction rates obtained from field observation and experiments apply only to the systems for which they were measured, and for which the extent of process coupling on transport is usually unknown.

In fine-grained and/or low permeability rocks (e.g., shales, bentonite, many igneous rocks), most fluid is present in nanometer-scale fluid films and submicron-scale pores, resulting in bulk reaction and transport rates that are governed by local fluid-mineral surface environments. Transport of contaminants into these microenvironments is therefore a crucial first step leading to immobilization on mineral surfaces or incorporation into minerals by precipitation or solid-state diffusion. Strong evidence for the role of such intergranular and intragranular processes on uranium immobilization as mineral precipitates has been documented (see sidebar on *Unique chemistry in intragranular microfractures and surface microstructures*).

Reactive-transport models are still in their infancy for multiphase fluids, yet multiphase systems are ubiquitous in nature and prevalent in engineered systems designed for subsurface waste storage. For example, documented effects of surface tension on thermodynamic properties of aqueous species and the partial pressures of gases are not usually accounted for in macroscale models. In addition to processes encountered in single-phase systems, mass transfer between fluid phases can alter the composition of the fluids. For example, supercritical CO_2 injected into a carbonate reservoir will displace water from the pore space, leaving brine films on mineral surfaces. Dissolution of CO_2 into the brine films will alter their pH values and drive surface reactions, such as carbonate dissolution and secondary mineral precipitation.

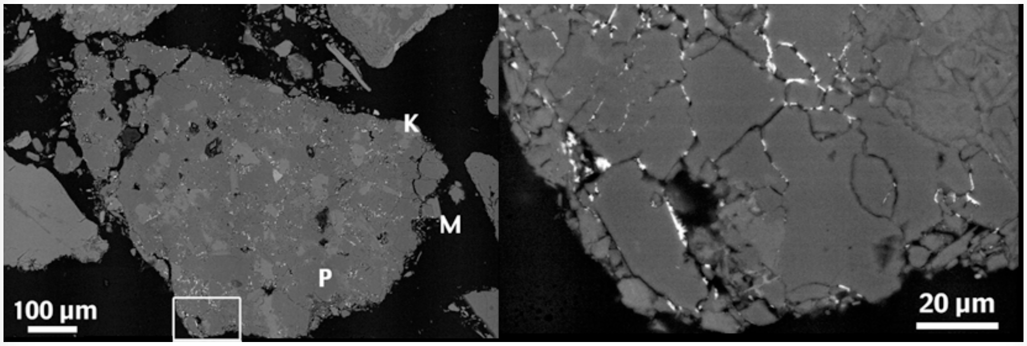
The primary objective of this research direction is to demonstrate the critical role that microstructural features and their associated geochemical environments play in basic coupled transport processes. This will lead to new evaluation of the limitations of large-scale models and to development of innovative approaches for capturing effects of site-specific processes by combining fundamental process-level models and site-specific data, and minimizing

Unique chemistry in intragranular microfractures and surface microstructures

Although contaminants in geologic systems usually have low bulk concentrations, they are not homogeneously distributed, but rather are concentrated in microscale phases or molecular clusters attached to solid surfaces. Chemical properties and geochemical behavior at these nano- to microscales can be dramatically different from those expected for contaminants evenly distributed as trace components in a bulk phase. Furthermore, these forms of contaminants tend to be localized in regions having geochemical characteristics atypical of average field conditions.

Certain properties of these microstructural environments and the nanophases within them have received considerable attention (e.g., Zachara et al. 2004; Sanchez-Moral et al. 2003). These regions can induce mineral precipitation or alter dissolution, and consequently sequester trace metals and radionuclides (see figure below). Such microstructures restrict fluid flow and/or solute transport, which ultimately causes isolation of specific regions (e.g., within micro-fractures or near microbes) from the bulk fluid system, and allows unique geochemical conditions and unexpected molecular processes to evolve. The unique conditions can lead to atomic to nanoscale properties of precipitates that are quite different from those expected for similar mesoscale solids. It is well known, for example, that nano-sized mineral phases are often polymorphs of the bulk material with different physical and chemical properties (e.g., Zhang and Banfield 1998; Navrotsky 2007). Also, the behavior of nanoparticles within chemical microenvironments can differ from the same nanophase outside the microenvironment.

Current geochemical models that have been used for decades to calculate how major species and contaminants change and migrate in natural systems (e.g., Jenne 1989; Loeppert et al. 1995; Arai et al. 2006; Payne and Airey 2006) are usually based on data obtained from macroscale laboratory systems. These models treat interfacial reactions as processes of adsorption/ion exchange, solid solution formation, or pure amorphous or crystalline phase formation. There are numerous examples of the failure of these simplified models based on large-scale chemical systems to successfully predict the fate of trace metals or contaminants in the environment. Chemical microstructures and microenvironments such as those illustrated below represent exceptional opportunities for considering the coupling of interdependent reactions, from the molecular level up to the micron scale. Geochemical models can be vastly improved by basic research on relevant molecular and hydrodynamic processes in confined systems at these scales.



These backscattered electron images of granitic rock fragments obtained from beneath a spill at the Hanford site show U(VI) (white) precipitated in microfractures within mineral grains. P = plagioclase; K = potassium feldspar; M = mica. Remarkably, these rock fragments account for <4% of the total sediment mass, yet contain >90% of the U(VI) (Liu et al. 2006). These results show that coupled multiscale processes (precipitation at localized surfaces, diffusion through thin films) must be represented in models used to predict subsurface reactive transport.

application of empirical calibrations. Quantifying site-specific processes will have direct influence on our capability to evaluate the potential extent of radionuclide immobilization or remobilization and trapping of CO_2 in mineral phases.

Mineral-water interface complexity and dynamics

A wide variety of geochemical processes are governed by elementary reactions occurring at the mineral-water interface. Adsorption, ion diffusion, growth, dissolution, precipitation, and electron transfer can change the composition of natural waters, alter the pathways of flowing solutions, affect colonization of microorganisms, control the geochemical cycling of elements, and determine the transformation and ultimate disposition of contaminants. Natural mineral-water interfaces are invariably complex in both their structure and reactivity, from the different atomic arrangements at dissimilar crystal terminations to imperfections such as defects, pores, or surface roughness. Variable distribution of sites with different reactivities at the atomic-scale is an intrinsic component of multiscale complexity, as is the accessibility of water and its dissolved components to specific sites in confined spaces. As a result, the reactivity of any mineral surface varies widely at different time scales, and overall dynamic behavior is difficult to predict. Furthermore, mineral surfaces can be partly or completely covered by residual organic, mineralogic, and/or microbial coatings. Therefore, chemical migration processes controlling geochemical cycling and element mobility operate in a complex and constantly evolving microscopic landscape (Figure 5). The rates and mechanisms of mineral-water interface reactions must be understood at the molecular level to adequately and accurately represent these reactions in reactive-transport models used for estimating the extent of chemical migration into the future.

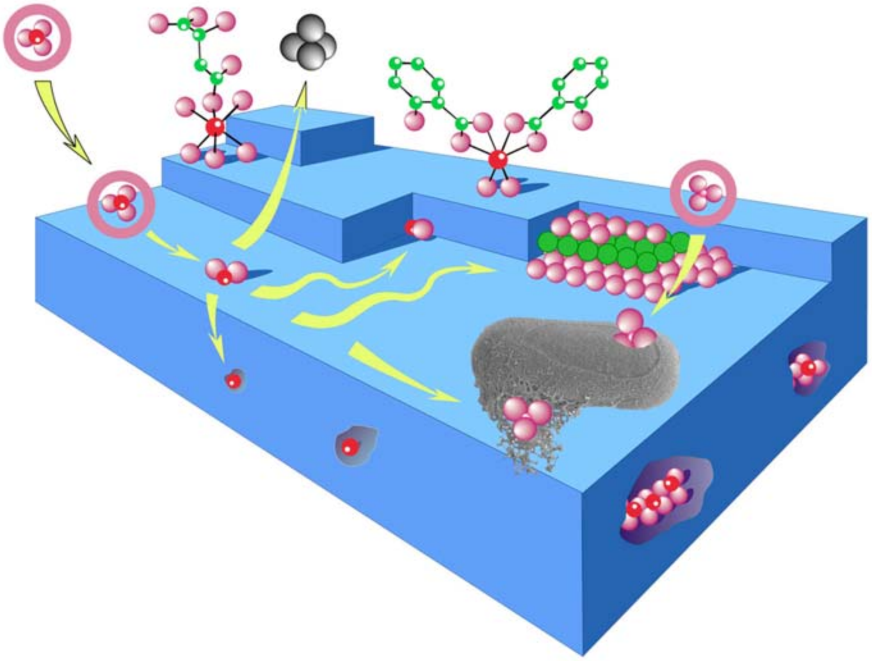


Figure 5. Schematic illustration of molecular-scale complexity at mineral-water interfaces, which includes variable topography and distribution of reactive surface sites, various kinds of adsorption, diffusion, incorporation, and precipitation reactions that define solute-surface and solute-cell interactions. (Manceau et al. 2002; copyright © 2002, the Mineralogical Society of America. All rights reserved.)

Although studies on perfect or near-perfect mineral-water interfaces are valuable for probing molecular-level structure, reaction mechanisms, and dynamics of elementary processes, the key scientific challenge is to reconcile this molecular-level information with the behavior of complex mineral-water interfaces expected in nature. There is a basic need to systematically examine the components of this complexity with increasing spatial, energetic and temporal resolution. For example, new knowledge of trace-constituent uptake in mineral surfaces can be obtained by determining how trace elements modify elementary step dynamics through processes such as changing the direction of step motion. Growth surfaces can acquire unique structures distinct from bulk mineral structures because of the changing composition of the interface that leads to variable dehydration rates of aqueous ions that attach to the surface and formation of vacant sites that are missing atoms. Such interface structures are difficult (if not impossible) to describe thermodynamically, and currently cannot be included in macroscopic thermodynamic models. Ion and charge transport in the solution and mineral on either side of the interface can couple in ways that makes their separate study irrelevant. Emerging advances in spectroscopic and microscopic capabilities, synchrotron X-ray and neutron sources, and computational hardware and modeling methods will be essential to make significant progress in understanding these complex dynamics at a robust quantum mechanical level. Realization of this science direction will also drive the development of next-generation capabilities and greatly enhance knowledge of the fundamental phenomena underlying element cycling and radionuclide mobility—important issues that continue to be characterized by orders of magnitude discrepancies in macroscopic reaction rates.

Biogeochemistry in extreme subsurface environments

Estimates of the distribution of life on Earth suggest that over 90% of Earth's biomass exists in the form of microorganisms in subsurface environments. These organisms are genetically and metabolically diverse, and mediate a host of globally significant chemical transformations (biogeochemical reactions) through their interaction with the lithosphere. Subsurface microorganisms can be distinguished (among other attributes) by their required source of carbon for biosynthesis: *heterotropic* (requiring organic carbon) and *autotrophic* (requiring CO_2). Microorganisms that are ubiquitous below ground can have a profound influence on: composition of subsurface waters; mineralogy and surface properties of subsurface sediments; valence; geochemical form; and mobility of radionuclide and trace metals. Certain microorganisms concentrate soluble metals or radionuclides in their periphery through biosorption to exposed biomolecular complexants, or by enzymatically driven electron transfer reactions that induce bioprecipitation reactions on the organism surface or within the cell periphery.

Subsurface microorganisms of many types can nucleate and form unique, high-surface-area biomineral phases including iron and manganese oxides of single and mixed valence states (e.g., ferrihydrite, goethite, magnetite, green rust, birnessites), carbonates (siderite, magnesite, calcite, aragonite, dolomite), and phosphates. Bio-precipitated solids can react strongly with trace constituents through surface and bulk substitution reactions, associating trace elements with the solid phase and significantly retarding their transport. A more specialized grouping of subsurface microorganisms, termed *metal-reducing bacteria*, can reduce oxidized, polyvalent radionuclides [e.g., Tc(VII), U(VI), Np(V)] in pore water, groundwater, or nuclear waste streams of different types, causing their precipitation and resulting in significant reduction in their solubility and far-field migration potential. Dissolved hydrogen gas and reduced carbon compounds serve as electron donors for biologic electron transfer to radionuclides and other redox-sensitive elements. Hydrogen is a likely byproduct of radiolysis and metal corrosion in environments near buried nuclear wastes. Reduced carbon species are likely to be entrained in plumes rich in CO_2 that may migrate in geological sequestration environments.

Individual microorganisms are typically 2-5 μm in size. These may co-associate in films of like organisms (*biofilms*) or in complex associations of different species with interdependent functions (*communities*). These biologic features populate reactive mineral interfaces and together concentrate nutrients, organic carbon, and mineral-derived electron donors that provide energy for metabolism and molecules for biosynthesis. Fluxes of metabolic products and the assembly of biostructures for geochemical functions create a unique and dynamic chemical environment at the microbe-mineral interface that can dramatically alter inorganic molecular and microscopic structures and compositions of the associated mineral surface. Biogeochemical processes have consequent large influences on chemical migration through their potential impact on all system variables and properties influencing solid-liquid distribution.

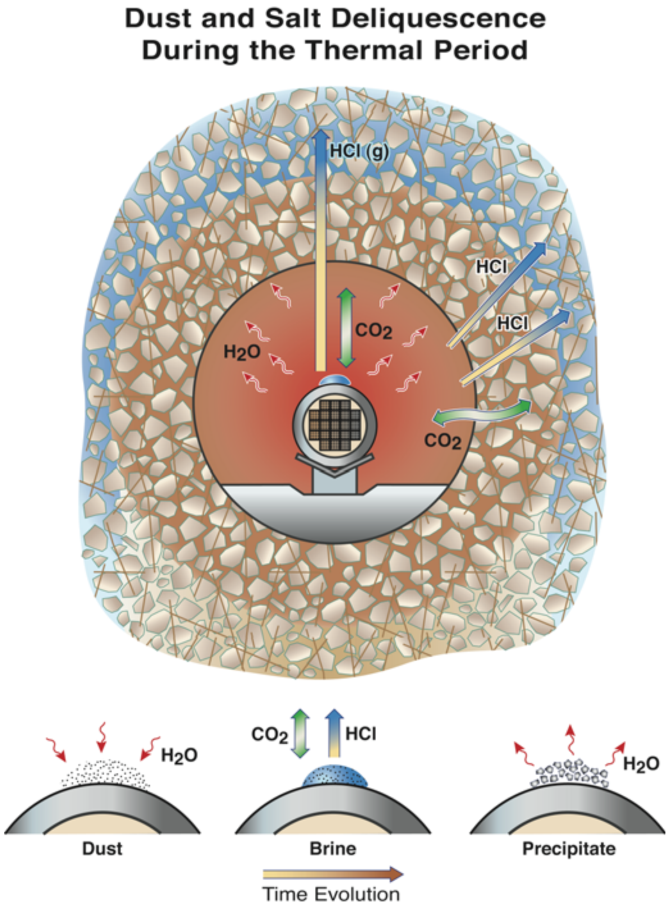
A high priority research area is understanding the dynamics of the biogeochemistry of extreme subsurface environments associated with nuclear waste and CO_2 sequestration. Central to this is the belief that perturbations in the indigenous microbial community by inoculation of surface microorganisms (during drift, shaft, or well emplacement), followed by the development of extreme conditions of temperature, radiation, water potential, and carbon dioxide concentration, will cause marked and unpredictable changes to the system's biogeochemistry that must be understood. Basic research targeting the evolution of the subsurface microbiologic community in response to environmental perturbation, and the molecular and microscopic nature, rates, and products of biogeochemical reactions that occur at the microbe-mineral interface under extreme conditions, holds particular promise for both discovery science and problem application.

Equilibrium and reaction rates in perturbed geochemical environments

Any geochemical environment that has reached a steady or equilibrium state over a relatively long time will respond to the emplacement of energy system byproducts through sudden or gradual reactions among minerals, pore waters, and the energy wastes. The reactions are triggered by perturbations to the original *in situ* conditions such as changes in temperature and gas pressure, chemical gradients, and oxidation-reduction conditions, or imposition of intense radiation fields. The reactions may be fast or slow, and may occur as single isolated events, be coupled, or have feedback effects on one another. They may have significant effects around the emplaced materials or at great distances. Matter and energy transfer between the geochemical environment and emplaced waste is expected with either beneficial or detrimental effects. As an example, the anticipated increased temperature near emplaced nuclear waste at the Yucca Mountain repository site may cause complex brines to form in moisture-laden dust that accumulates on the waste package surfaces (see sidebar on *The hypothetical perturbed environment near emplaced nuclear waste in a geologic repository*). These brine droplets will have different reactivity and corrosive effects than natural groundwaters, and their presence may lead to the release of contaminants to the surroundings. Therefore, over a wide range of scenarios, the thermodynamic properties of complex geological fluids and solids, and the reaction rates among phases and species, must be known to define the critical environmental parameters that control migration or immobilization of wastes.

The hypothetical perturbed environment near emplaced nuclear waste in a geologic repository

The longevity of engineered materials in proposed nuclear waste repositories such as Yucca Mountain strongly depends on the environments to which they are subjected (Steefel 2004). The pH, chemical composition, oxidation state, and transport of liquid water to the engineered materials, along with transport of organic and inorganic gases into the repository as a function of time and temperature, are critical parameters controlling environmental stability. Dust or rubble on engineered material surfaces may experience high temperatures, radiation fields and chemical gradients. Moisture and volatile gases may be added to or removed from the dust and rubble, possibly resulting in deliquescent brine formation and reactions that corrode the waste package materials, prevent corrosion, release wastes to the repository, sorb released species, or precipitate released contaminants. The surrounding geochemical environment is likely to be influenced by properties of the engineered materials, creating a feedback loop. Heat flow and rates of contaminant release, the degree of oxidation and generation of acidic gases from corrosion processes, and the effects on permeability and mineralogy of the surrounding rock must all be factored into the evolving environment.



Courtesy of Carl Steefel, LBNL

Above: Key processes within waste emplacement drift. Below: Surface processes on top of waste package.

Much has been learned about equilibria and reaction kinetics in complex geochemical systems over the past few decades, but our knowledge is far from complete. We lack basic data for many important compositional systems, and we have even less knowledge of reaction mechanisms, despite the recent advances in molecular-scale analysis and computation. For example, methods such as synchrotron X-ray, or neutron scattering and spectroscopy, or computational modeling have allowed us to advance our understanding of interfacial structure, dynamics, and reaction mechanisms, but rarely have these approaches been applied to determine reaction rates or equilibrium configurations of solid surfaces. The pace at which we can acquire knowledge of equilibria and reaction rates is limited by these approaches because they often require perfect mineral surfaces, simple solution compositions, and large time expenditures to implement. New thermodynamic and kinetic data must be obtained using new experimental techniques and approaches that rapidly and accurately handle complex compositional systems, concentrated solutions, and effects of variable time scales and solid surface characteristics. Almost any envisioned reaction between a geological repository and emplaced byproduct will result in chemical changes that are both kinetically and thermodynamically regulated, so theories that link relevant equilibria to reaction rates and mechanisms must be formulated. Experimental, analytical and computational approaches available today must be exploited and expanded to allow the progress needed to accurately and confidently predict risks associated with contaminant migration.

The goal of this research direction is to address critical gaps in our understanding of fundamental thermodynamics and reaction kinetics, and derive theoretical formulations relating the two, which are essential to accurately model effects of perturbations to the geochemical environment and emplaced energy system wastes that ultimately control contaminant migration processes. Specific objectives are:

1. Determine key thermodynamic data for solids and complex fluids, including effects of trace components.
2. Determine key data for mineral-solution reaction kinetics under the full range of saturation conditions and under transient conditions.
3. Investigate natural systems representing the expected perturbed environments for evidence of effects on chemical migration due to changes in specific parameters.
4. Apply advanced computational approaches to advanced chemical imaging capabilities, including neutron, synchrotron X-ray, NMR and other probes of surface reactions at the atomic scale, and *in situ* characterization of porosity/permeability and chemical/mineralogical heterogeneity in dense geologic media, whether in experimental or natural systems.

CONCLUSION

The fundamental reactions that control the migration of chemical constituents in geologic media take place at the interface between minerals and aqueous fluids, and in certain cases include significant effects of microbiological processes. Even at the atomic scale, this interface is a complex environment that challenges the geoscientist to make effective use of advances in geochemical, chemical, physical and biological knowledge. The complexity extends from the atomic to the pore scale, a range of scales over which fluid flow plays a progressively larger role in chemical migration. The likelihood is high that we are on the verge of being able to link reaction and transport across this scale range, both quantitatively and rigorously, through achievement of the research goals described in this panel report.

The five targeted areas for new basic research in the geosciences identified by this panel should produce the necessary knowledge that will allow the U.S. Department of Energy to fulfill its charge to accurately anticipate the long-term safety potential for any chosen repository of energy byproducts.

SUBSURFACE CHARACTERIZATION

CURRENT STATUS

Overview

The subsurface is spatially heterogeneous because of the complex geologic and biogeochemical phenomena that create and modify subsurface materials and processes. Since the first well was drilled, design and management of resource recovery or emplacement systems has been hampered by the difficulty of characterizing subsurface complexity. Consequently, predictions of mass transport and reactions are often too uncertain to provide meaningful estimates of risks in the contexts of human health, society, economics and the environment.

Subsurface characterization is a broad topic that could be construed to encompass most of the topics discussed in the other panel reports. The methods and research needs discussed herein pertain to the entire subsurface, including the vadose zone, fresh groundwater systems and deep saline systems. The panel focussed on those aspects of characterization that present the most difficult obstacles to progress in subsurface science and resource management:

1. Measurement or estimation at the appropriate scales of state variables such as fluid pressure, temperature, solute concentration, and fluid saturation, and geologic media properties such as permeability, porosity, capillary pressure or retention curves, geomechanical characteristics, and chemical reactivity. More effective subsurface characterization would not focus solely on the usual point- or local-scale measurement of these attributes, but rather on larger scale or multiscale measurements that might obviate the need for upscaling or downscaling, or provide unprecedented reduction in model non-uniqueness (e.g., spatially continuous measurement of pressure and temperature, *in situ* measurement of field-scale reaction rates with novel tracer methods).
2. Understanding the interaction of physical fields, such as elastic waves or electromagnetic disturbances, with geologic media sufficiently to use these physical fields in multiscale characterization of the state variables and media properties. These interacting physical fields are complicated because small-scale properties of the medium influence the behavior of the field at a much larger scale. Currently the theory that connects the small-scale properties to the larger-scale field is inadequate for many characterization purposes.
3. Fusion of disparate data types (e.g., geologic, geophysical, hydrologic, reservoir, biogeochemical) obtained at disparate scales to maximize reliability of characterization at appropriate scales. This hurdle requires substantial advances in forward modeling of coupled nonlinear processes, joint inversion of coupled process models, and evaluation of cumulative uncertainties stemming from local uncertainties contributed by each coupled model.
4. Characterizing the extremes in fluid flow fields—namely, zones of preferential flow in which fluids can migrate much faster than conventional estimates might suggest, and zones of extremely slow fluid movement. The former would include conductive faults and well-connected fractures or sand/gravel bodies. The latter would include confining beds, aquitards and seals. Because such preferential flow paths can be so consequential to material isolation efforts and exposure risk assessments, and because they are difficult to detect or anticipate, research focus on this area is paramount. Similarly, spatial structure and integrity of the

"slow" media are critical for containment and management of subsurface resources and are a primary reason why extraction of fluids, whether petroleum or contaminated groundwater, tends to be difficult and inefficient.

5. Remote observation of fluid flow, mass transport, fluid residence time, and reactions. Characterization of the complex subsurface is most hampered by its inaccessibility. We can achieve greater access to the subsurface by drilling more and more boreholes, but this is very expensive, typically not adequate, and is counterproductive when the objective is to maintain a naturally well-sealed storage site. Revolutionary change in our ability to characterize the subsurface will most likely come from techniques that provide much greater access with less dependence on drilling. Such techniques might include "smart" tracers capable of relaying their position without being sampled directly, the ability to measure local fluid residence time distribution (fluid age distribution) as a direct indicator of dispersion and preferential flow, enhanced geophysics including fusion with other data types (see Item 3 above), and the ability to monitor dynamic subsurface fluid processes remotely.

These obstacles can be organized under four broad, overlapping areas:

- Integrated characterization and modeling of complex geologic systems with large and diverse data sets
- *In situ* characterization of fluid trapping, isolation and immobilization
- Imaging flow, transport and chemical attributes
- Monitoring dynamic subsurface processes associated with large-scale anthropogenic manipulations

Integrated characterization and modeling of complex geologic systems with large and diverse data sets

Modern problems of coupled flow, transport and reaction require better coupled models, both forward and inverse, for resolving not only the dynamic phenomena but also for resolving the characterizations of spatial-temporal variations in relevant variables. In other words, more unified modeling approaches not only provide the means of simulating the relevant, coupled, nonlinear phenomena, but also potentially provide the means for better characterization through approaches such as joint inversion. No single data type (e.g., geologic, geophysical, hydrologic, geochemical, geomechanical) is sufficient by itself to characterize the complex subsurface. This is true even if one were trying to characterize only one aspect, for example, physical heterogeneity. Just as human perception of a 3D object requires observations from multiple perspectives, the complex subsurface can be better characterized by observing how the system complexity manifests through all the available physical and biogeochemical signals.

Current modeling practices decouple both scale and physics, and integrate data, in an *ad hoc* manner (Hill and Tiedeman 2007). A rigorous paradigm for treating these problems in the geosciences is missing. This is critical because incorrect treatment may lead to a gross accumulation of errors due to strong nonlinear couplings. Such strong nonlinearities are frequently encountered in multiphase flow, reactive transport, and geomechanics, although the

Hydrologic forcings and climate change

Subsurface fluid systems can be strongly influenced by magnitudes, rates and mechanisms of groundwater recharge and discharge, which in turn are affected by climate variability. Although the Characterization Panel focused mainly on measurement, monitoring and modeling of deeper subsurface properties and processes, subsurface models also rely strongly on characterization of boundary conditions at the land surface or the shallow subsurface (Scanlon et al. 2006; Flint et al. 2002; Bagtzoglou and Cesano 2007). Measuring or estimating the magnitudes as well as spatial and temporal variability of fluid movement through the vadose zone and groundwater recharge are therefore important challenges for DOE's research agenda in subsurface science. Furthermore, any long-term subsurface management operation must consider effects of climate change that will be translated downward via surface and shallow subsurface processes. A number of research frontiers exist in this area, including accurate measurement of precipitation and evapotranspiration across diverse landscapes and the development of geophysical methods for monitoring shallow hydrologic phenomena. Precipitation and evapotranspiration are the two largest components of the hydrologic cycle, yet we seldom can measure them with sufficient accuracy to adequately constrain estimates of groundwater recharge.

spatial and temporal scales at which these processes need to be resolved are different. There is a clear and urgent need to resolve these highly nonlinearly coupled processes in a way that preserves a theoretical and practical understanding of modeling and discretization errors.

At first order, the goal is to characterize the unknown spatial patterns in relevant properties and perhaps temporal changes in those patterns and properties. Top priority concerns are typically the extremes of preferential flow and very slow flow. At this first-order level, however, we still have a limited ability to predict the existence and characteristics of these features. While we can typically provide good estimates of mean fluid velocity averaged over certain volumes, the troublesome and almost ubiquitous extremes in fluid flow fields represent major deviations from the mean velocity. In the hydrologic sciences, modeling of such deviation has focused primarily on a diffusive model of dispersion that does not adequately represent these processes in the upscaled volumes (de Marsily et al. 2005; Zinn and Harvey 2003). More recently, workers have accounted for fluid transport more accurately by high-resolution modeling of the system heterogeneity, usually encompassing no more than one or two scales of heterogeneity (e.g., facies and sequence boundary scales) (LaBolle and Fogg 2001; Weissmann et al. 2002). Although high-resolution flow and transport models can provide more realistic representation of the relevant physical and chemical processes, this approach puts even more emphasis on quality of the characterization of heterogeneity and raises questions about whether the relevant scales of heterogeneity are represented adequately. In the presence of multiple fluid phases, the description of fluid transport is further complicated by multiphase flow phenomena, where the mobility of one phase depends on the presence and characteristics of other phases.

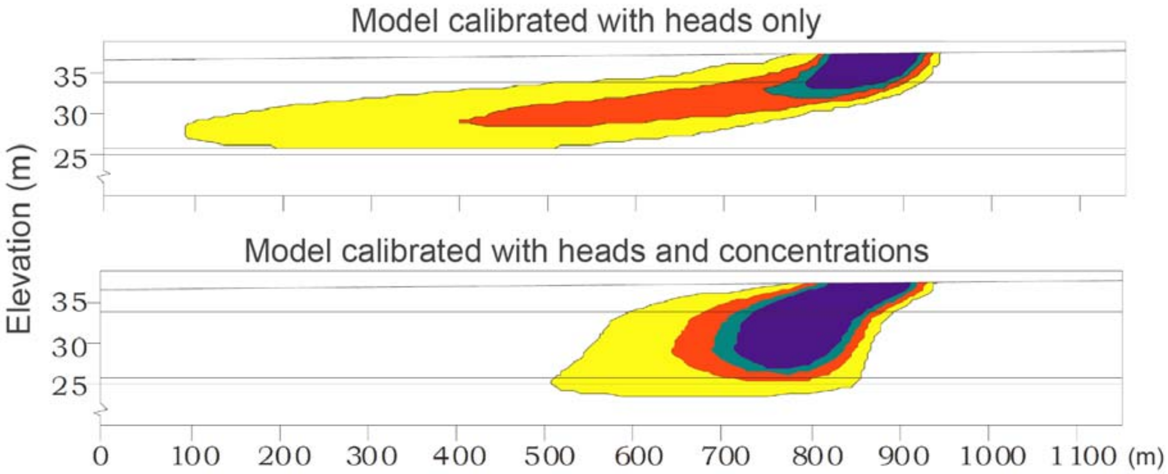


Figure 6. Simple example of benefits of data fusion (Barlebo et al. 1998). The modeled solute plume can differ dramatically when we add just one more observable, such as concentration, in the calibration procedure.

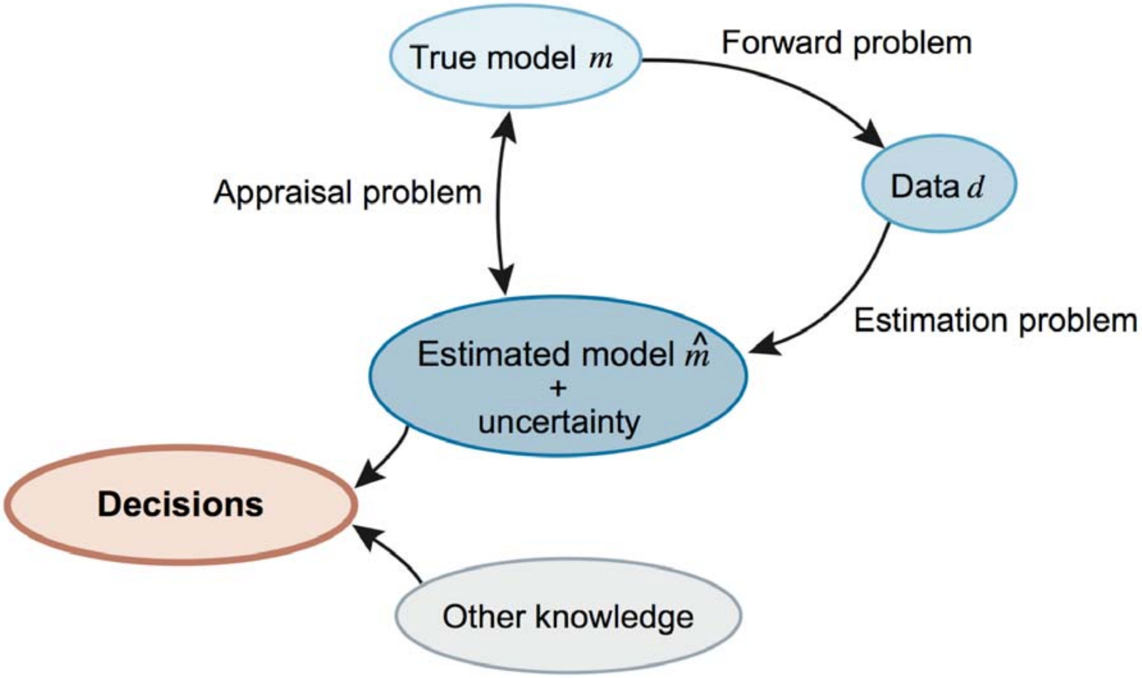


Figure 7. The role of uncertainty in decision making (Snieder et al. 2007).

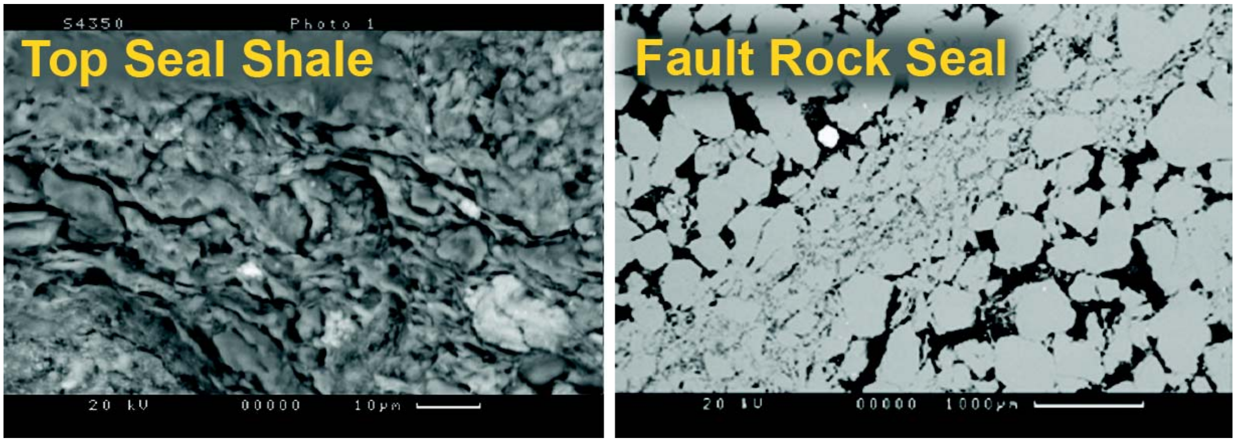
The problem of estimating the unknown spatial-temporal patterns of relevant properties is ill-posed unless one has information on the processes that created the patterns (Fogg et al. 2000). As an analogy, consider the problem of medical imaging of the human body with, for example, X-ray, CT scan or NMR methods. The effectiveness of these approaches would be dramatically less if the physicians interpreting the image data did not have in-depth knowledge of human anatomy. Similarly, any application of imaging technologies to the subsurface will be, at best, severely limited if the geologic origins of the deposit (e.g., depositional environment, structure, diagenesis) are unknown. Thus, information on geologic origins of the system is and will remain essential for characterization.

A pervasive limitation in the implementation of complex models is the problem of uncertainty (Poeter and Anderson 2005; Poeter and McKenna 1995). The estimated model has uncertainties that are due to data errors, limitations in resolution, and, sometimes, the poorly known relation between the probing field and the local physical and/or chemical properties. Yet the uncertainties in the data are essential for wise decision-making. To complicate matters, the uncertainty usually is scale-dependent, and often difficult to quantify because the uncertainties in the physical and chemical processes that underlie the model estimation are often poorly known. Combining multiple data sets (data fusion) usually reduces the uncertainty but, paradoxically, can complicate the estimation of uncertainty (see Figures 6 and 7). Because of nonlinearity, there is no general theory for the estimation of uncertainty (Snieder 1998). Moreover, visualizing the uncertainty (Sambridge et al. 2006) and communicating the uncertainty to the nonspecialist (Baddeley et al. 2004) is a largely unsolved problem.

In situ characterization of fluid trapping, isolation and immobilization

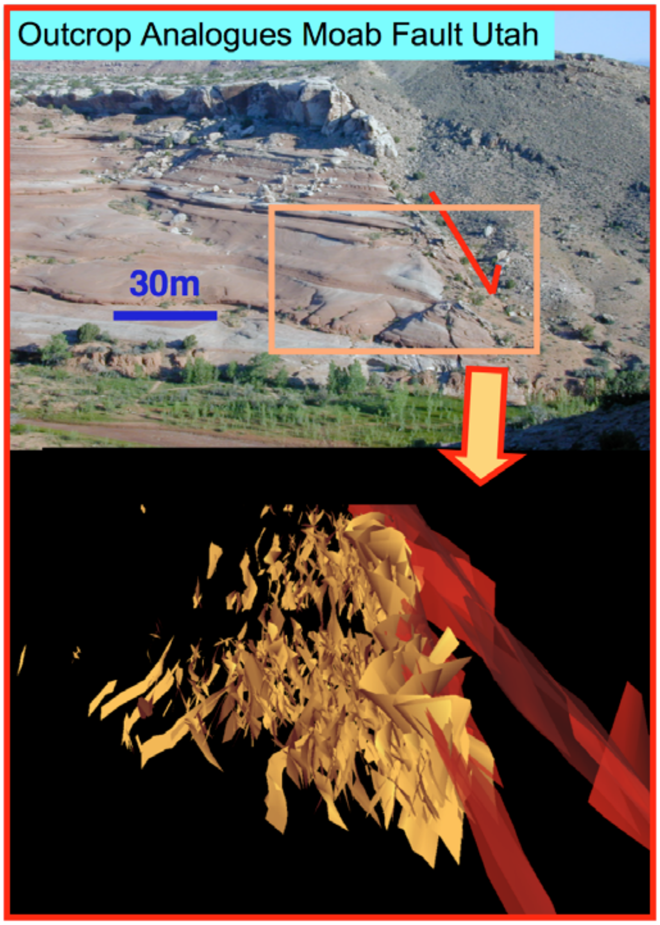
The transport of contaminants and storage products occurs predominantly through fluid transport. For this reason the trapping of fluids is essential for containment issues. Faults and impermeable, overlying rock units, including salt, can form effective traps. The trapping can occur through a variety of different mechanisms. A critical distinction is that porosity and permeability are not necessarily closely related in areas of relatively low porosity. The crystalline structure of salt and other minerals prevents fluid migration. Perhaps, surprisingly, most seals are porous to some degree, as shown in the microphotographs of a top seal and a fault zone in Figure 8. For multiphase flows, these rocks are sealing as long as the fluid pressure is less than the capillary entry pressure. The sealing properties depend in this case on the details of the pore-space distribution, as well as on the properties of the (multiphase) pore fluid. The pore space distribution is influenced by the constituents of the seal, the past deformation history, mineralization phenomena, and the formation of cracks. Overall, seals are complicated and dynamic structures. Their properties are affected by changes in the stress field, with fracture formation, by ongoing deformation (formation of clay smear), by disruptive events (earthquakes), and by mineralization or dissolution processes. The latter processes depend, in their turn, again on fluid migration.

The interplay of several processes makes the characterization of seals difficult. In general, the assessment of fault integrity is easiest in hydrocarbon reservoirs where the seal integrity can be established from the long-term accumulation of oil or gas. In environments where a buoyant fluid is absent, such as saline aquifers, the characterization of a seal must be established remotely. The local properties of a seal can sometimes be established from boreholes, but because of the cost of boreholes, and the potential risk of creating a future pathway for the fluid, one aims to minimize the number of boreholes. Furthermore, a seal is only effective when laterally uninterrupted, and local measurements usually do not establish the continuity of seal integrity. As shown in Figure 9, the geometry of minor faults near a major fault can be complicated. These minor faults can leave a significant imprint on the macroscale deformation and fluid conductivity properties of the fault system.



Courtesy of R. Knipe, Rock Deformation Research, rdr@leeds.ac.uk

Figure 8. Microstructure of top seal shale (left image) and fault rock (right image).



Courtesy of Rob Knipe, University of Leeds

Figure 9. An outcrop of the Moab fault (top panel), and the 10 million fractures and subfaults that have been mapped (bottom panel) for the region indicated with the orange box in the top panel.

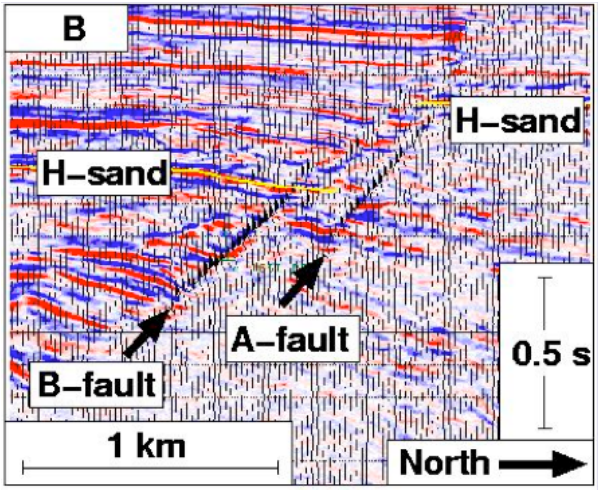
Imaging flow, transport and chemical attributes

Geophysical imaging of the subsurface has grown through spectacular advances made with the advent of 3D seismic surveys. Figure 10 shows a vertical cross section through a three-dimensional seismic image in a reservoir in the Gulf of Mexico. The different geologic strata and their spatial delimiters by faults are clearly visible. The phrase “high-resolution imaging” should be taken with a grain of salt. Employed wavelengths are often about 30 meters, which is much larger than the thickness of strata, and also much larger than the length scale of the microscale characteristics of the rocks that are crucial for understanding and predicting their bulk properties (Figure 8).

The complicated relation between microstructure and bulk properties is illustrated in Figure 11, which shows the seismic velocity measured in a laboratory experiment (Cadoret et al. 1995), where a porous rock is first infiltrated with a fluid and then drained. During infiltration (blue dots) the velocity steadily decreases until the last blue dot (near maximum saturation), which indicates an abrupt increase in velocity. During drainage (red dots), the velocity ultimately increases. Note that the shear wave velocity is not a unique function of fluid saturation. The colored circles show the fluid saturation on the microscale as measured by X-ray tomography. During the infiltration the fluid has a fine-scale distribution (bottom circle), whereas during the drainage the fluid distribution is patchy (upper right circles). This means that the deformation field on the macroscale (the seismic waves) does not uniquely depend on the water saturation; it also depends on the *spatial pattern* of the saturation on the microscale. This is only one example of the poorly understood relation between microproperties and bulk properties. Other examples include the relation between seismic anisotropy and fracture networks (Grechka and Kachanov 2006), and the relation between seismic attenuation (Q), microscale structure, and pore fluid behavior (Pride et al. 2003).

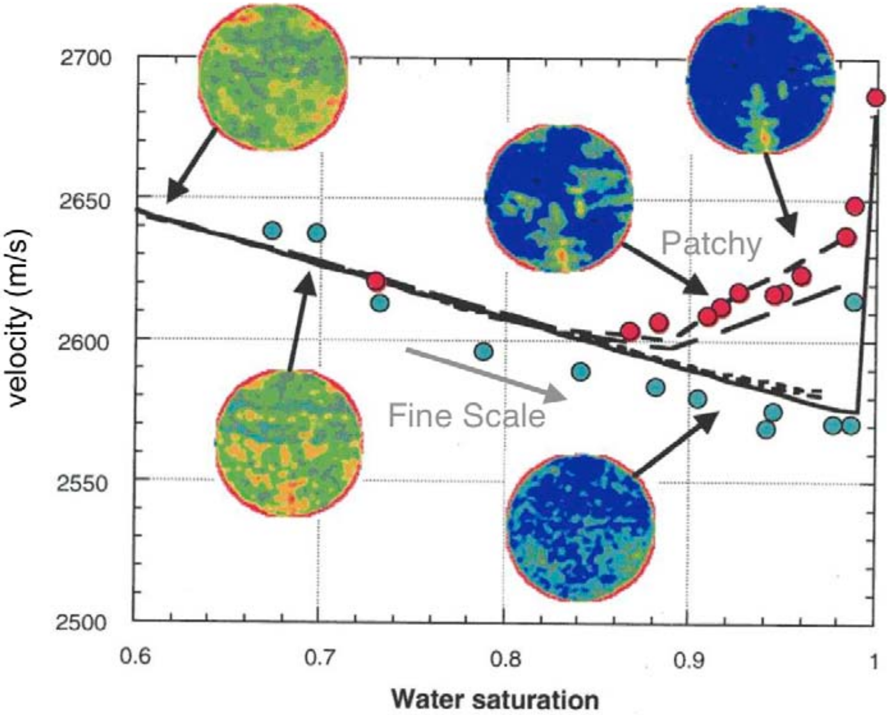
A comparison of the current state of subsurface imaging with medical imaging is of interest. Medical imaging started with X-ray transmission photography. The technique evolved into X-ray Computed Tomography (CT scans). This imaging method shows the structures in the body. In other fields, X-ray spectroscopy is now used to measure the details of molecular processes through the energy transitions in excited states of molecules. In Positron Emission Tomography (PET scans), the particles that are detected and used for the imaging are tagged to bio-chemical tracers. This makes it possible in medical imaging to probe the spatial and temporal distribution of the chemical process of interest.

In the geosciences, the geometry of structures at a length scale down to about 10 m can be constrained, as well as several attributes of these images, and some properties of the subsurface can be estimated from these attributes. Other geophysical fields, such as electromagnetic fields, supply complementary information, such as the electrical conductivity, but are even more restricted in spatial resolution. The smallest length scale that can be resolved is much larger than the small-scale structures and processes that determine the bulk properties of the subsurface. To bridge the large span of length scales over which subsurface physical and chemical processes operate, it is necessary to diagnose these processes over a much larger range of spatial and temporal scales than currently is possible.



Courtesy of Roel Snieder, Colorado School of Mines

Figure 10. Cross section through a 3D seismic image of the South Eugene Island field in the Gulf of Mexico. Colors indicate the horizontal reflectors, while black wiggles display the reflectivity of two fault zones (Haney et al. 2004).



Courtesy of Gary Mavko, Stanford University

Figure 11. The extensional velocity in a limestone sample as a function of water saturation during imbibition (blue dots), and drainage (red dots). The colored circles show the water saturation on the microscale measured with computerized X-ray tomography. From Cadoret 1993 with T. Cadoret's permission; Cadoret, T., Marion, D., and Zinszner, B. Influence of frequency and fluid distribution on elastic wave velocities in partially saturated limestones *Journal of Geophysical Research* **100**, 9789–9804 (1995). Copyright © 1995 American Geophysical Union. Reproduced/ modified by permission.

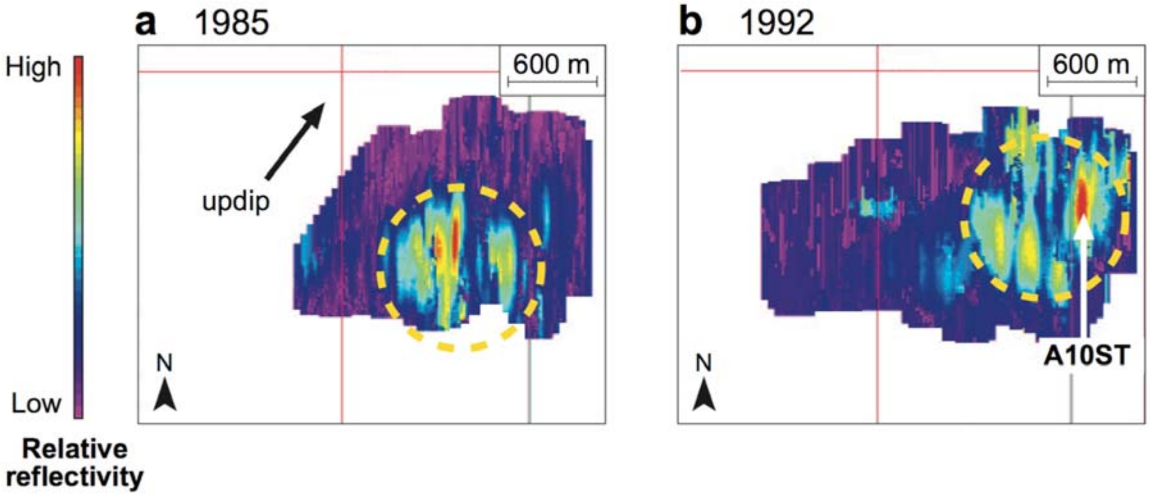


Figure 12. Plan view of the reflectivity of the B-fault in Figure 10 from two time-lapse seismic surveys. High reflectivity corresponds to large pore-fluid pressure in the fault. This region of high reflectivity propagates up-dip, and shows transport of fluid along the fault zone with a velocity of about 140 m/y Reprinted by permission from Macmillan Publishers Ltd: *Nature* **437**, 46 (2005).

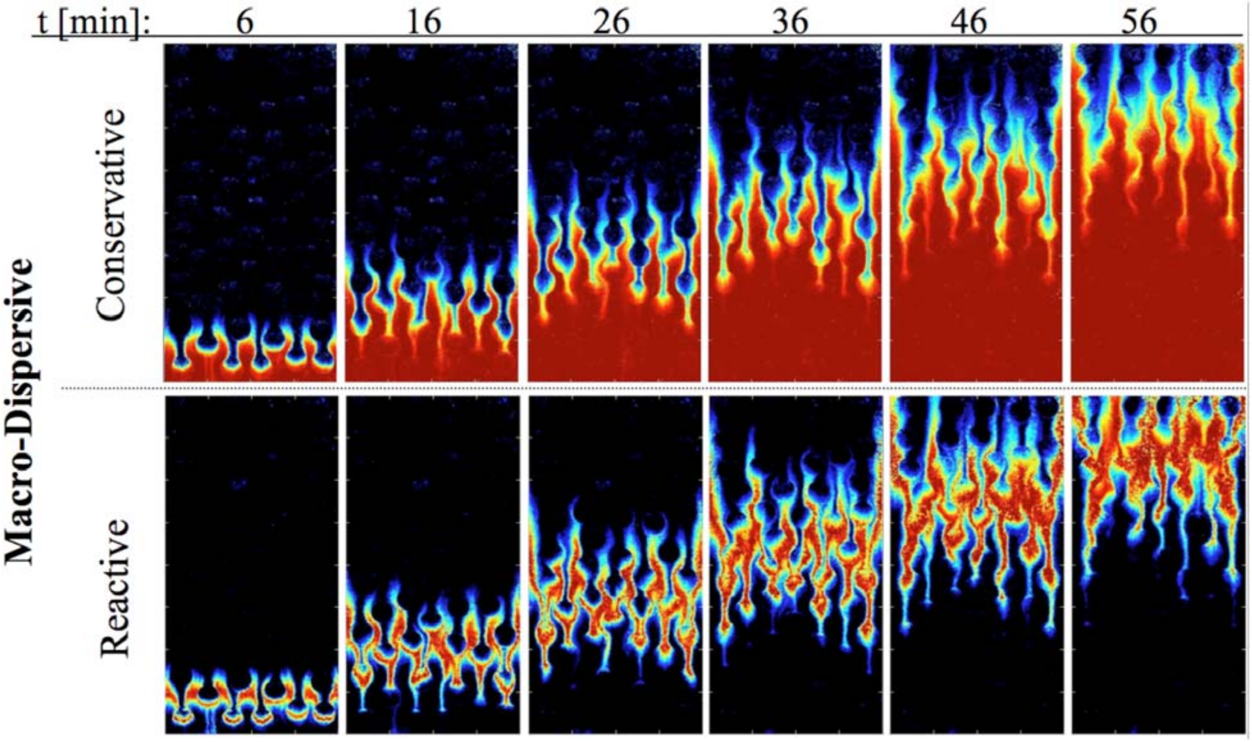


Figure 13. Optical measurements of the presence of a conservative tracer (top panels; red color) and a reactive tracer (bottom panels; red color) for different times. Fluid propagates from the bottom to the top of the figures through a porous medium consisting of glass spheres (Oates 2007).

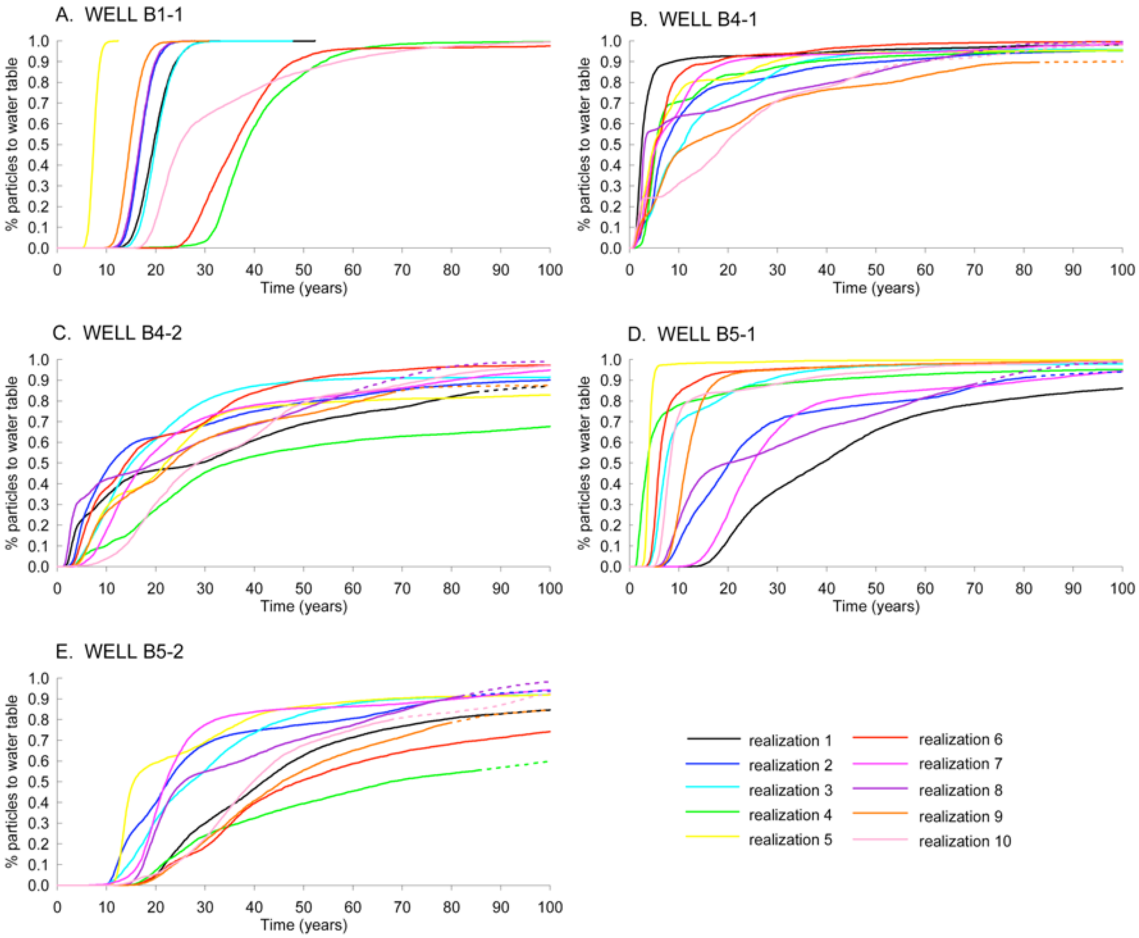


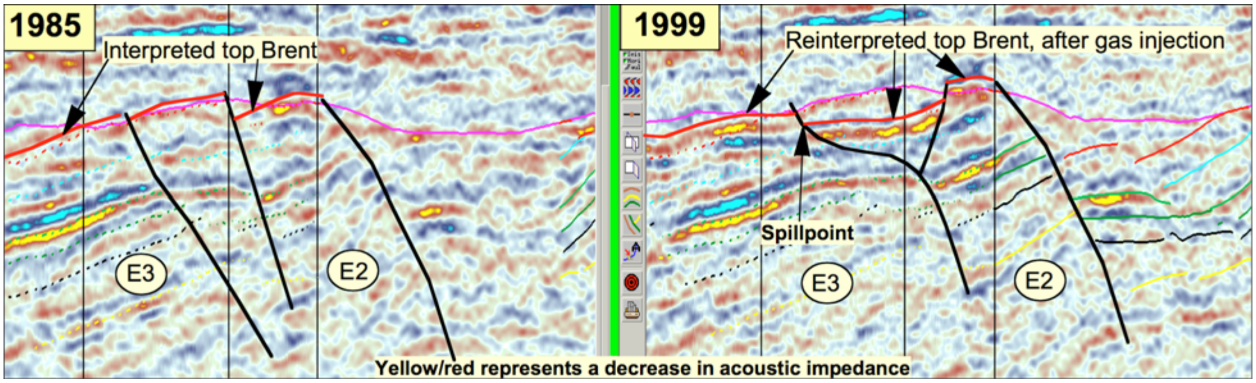
Figure 14. Simulated groundwater residence time distributions from the midpoint of selected well screens for each of the 10 realizations, Kings River alluvial fan aquifer system, CA (Weissmann et al. 2002). Local mixing of groundwater age is ubiquitous and more extreme than previously thought. Models show that the same phenomenon occurs at greater depth, but potentially with far greater ranges in ages. Predominantly old water (e.g., 10^3 y) that contains a young fraction (e.g., 10^1-10^2 y) is a direct indication of preferential flow. The travel time distributions are typically non-symmetric (non-Fickian). Weissmann, G.S., Yong, Z., LaBolle, E.M., and Fogg, G.E. (2002). Dispersion of groundwater age in an alluvial aquifer system. *Water Resources Research* 38(10), 16.1–16.8. Copyright © 2002 American Geophysical Union. Reproduced/modified by permission.

Detecting the presence of a fluid and possibly its movement over time (see Figure 12) is different from measuring its flow and the chemical reactions that take place within the fluid, or between the fluid and the rock matrix. Oates (2007) made laboratory measurements of the reactions of moving fluids by injecting fluid into a porous medium (Figure 13). Conservative tracers show the complicated invasion pattern of the flow, whereas reactive tracers create images of reactivity and the diffusion of reactants. The reactivity depends on the chemical properties of the reactants, as well as on the small-scale properties of the flow pattern that brings the reactants into contact. This experiment was carried out in the laboratory where optical techniques can be used for diagnostics. Measuring reactivity remotely in the subsurface is a much more formidable task.

In addition to geophysical methods, chemical and isotopic tracers can be used to characterize subsurface properties and structures. Environmental tracers (Cook and Herczeg 2000) are either anthropogenic or naturally occurring substances that, with the appropriate model, can provide estimates of the mean residence time of the sampled water. Examples include isotopes (e.g., ^{14}C, ^{36}Cl, ^{3}H-He) as well as anthropogenic compounds such as chlorofluorocarbons (CFCs) and sulfur hexafluoride (SF_6) (Phelps et al. 2006). Recent work (e.g., Weissmann et al. 2002; Bethke and Johnson 2002; DePaolo 2006) indicates that these methods tend to provide a biased estimate of the mean age of a typically broad distribution within the groundwater sample (Figure 14). The broad distributions of age are indicative of the multiple scales of complexity that cause scale-dependent dispersion, preferential flow (including leakage along faults), physical and chemical anthropogenic transients, and, in some cases, chemical reactions. Unfortunately, environmental tracer methods are currently insufficient to estimate the full range of groundwater ages within a sample and to thereby deduce the actual age distributions. In particular, methods are needed for reliably estimating groundwater ages in the range of 40 to ~3000 years. When methods exist to cover virtually the full range in most ages within groundwater samples (10^0–10^4 years), it will be possible to estimate actual age distributions, which will represent a powerful tool for characterization of multiscale heterogeneity via model calibration and for validation of these models.

Monitoring dynamic subsurface processes

Measuring time-lapse changes (monitoring) is especially critical for understanding processes in the subsurface. In the seismic image of Figure 10, clear fault zone reflections are visible. Figure 12 shows the reflectivity of the B-fault in map-view as inferred from two seismic surveys recorded seven years apart. A zone of high reflectivity is moving in the northeast direction, which is the up-dip direction. This moving zone of high reflectivity is indicative of fluid migration along the fault (Haney et al. 2005). Another example of fluid migration is shown in Figure 15, where CO_2 changes the reflectivity of the seismic image during enhanced oil recovery. Note that in the examples of Figures 12 and 15 the spatial and temporal scales of this observed moving fluid migration are low. Within the limits of this low resolution, the presence of the fluid pulse can be established, but details of the interaction of the fluid with the subsurface structure are lacking.



Courtesy of Martin Landro and Statoil.

Figure 15. Time-lapse seismic images of a reservoir in which CO_2 is injected. The yellow and red regions indicate low acoustic impedance; this indicates the presence of fluid or gas.

The issue of sensitivity is especially important for early identification of time-lapse changes in the subsurface. Early identification of changes can be important for effectively managing subsurface reservoirs. The capability to detect minute changes is also of importance for early warning and mitigation of natural hazards. In many monitoring problems, one seeks to detect a minute change in the properties. For example, if 1% of the CO_2 leaks from a sequestration site in one year, then 70% of the CO_2 will escape in a century. In this application it will be necessary to monitor with a much smaller detection threshold than currently is possible. It is possible in the laboratory to measure changes in the seismic velocity with an accuracy of about 0.01% using interferometric techniques (Snieder et al. 2002), but these accuracies cannot yet be achieved under field conditions.

BASIC SCIENCE CHALLENGES, OPPORTUNITIES AND RESEARCH NEEDS

Integrated characterization and modeling of complex geologic systems with large and diverse data sets

Subsurface geologic structures are complicated but not random. For sedimentary rocks, for example, there is a wealth of data and models that relate sediment transport by rivers and ocean currents to the mineralogy, texture, and large-scale structures of the resulting sedimentary rocks. Such geologic process descriptions can and must be used to develop better conceptual models of subsurface heterogeneity, including preferential flow paths and various scales of heterogeneity that may be difficult to detect or represent with statistical methods. Such geologically informed models are also needed for determining the consequences of neglecting certain features in upscaled or more conventional models of heterogeneity. This is one strategy for defining which system properties, attributes and scales are most relevant to a particular problem.

The translation of geological processes into spatial patterns and scales of relevant properties (basin, formations, core scale) can be achieved using physical and numerical models of depositional, diagenetic and structural processes. The field of depositional process modeling is still in the early stages, but with greater computational capability, and the optimal use and integration of disparate data sets, it can evolve into a powerful predictive tool for the 3D geologic structures at various length scales, the microproperties that govern the bulk behavior, and the temporal evolution of these structures.

One of the main challenges in creating a 3D scale-bridging description of geologic structures is to relate geophysical, geochemical and bio-geochemical measurements to *in situ* properties and processes. The relation between the measurements and the *in situ* properties is scale-dependent and needs to bridge different temporal and spatial scales. The quantification and reduction of uncertainties play a special role because measurements and inferences from these measurements are useless when the associated uncertainty is unacceptably large. The determination of the required thresholds of uncertainties needs to be addressed. Ultimately, it is necessary to develop a fundamental understanding of the relevant upscaling and downscaling laws for flow, transport properties, reaction rates, and mechanical properties.

Scaling laws for flow, transport, reactions and coupled processes

The scale-dependence of subsurface processes is so complicated that the laws that govern behavior are not easily established (e.g., Gollub 2003). An example is fracture propagation (Scholz 1990). Fracture behavior can be described at a crude level by the surface energy of the fracture. This description, however, hides the complexity of the formation of the damage zone near the crack tip, and the way the fracture propagation may be influenced by, for example, the surface chemistry on the microfractures in the damage zone. In this case, an adequate description of a process applicable to a particular time and length scale can be obtained by a simple analysis, but because it ignores essential aspects of the process, it may not be useful at other scales. Another example is shown in Figure 11. The principles of linear elasticity that govern the propagation of seismic waves are well-known, and predict that seismic velocity should be a simple function of saturation state. But as the example shows, two different states of fluid saturation may correspond to the same velocity, depending on the spatial distribution of the fluid, which in turn depends on the history of the sample. The difficulty in accounting for the physical/chemical behavior of Earth systems is most pronounced when coupled processes occur at different temporal and/or spatial scales. The laws for upscaling and downscaling need to be addressed by a combination of laboratory measurements, numerical simulation, and field experiments using different diagnostic methods.

Data fusion, instrumentation, tracers and uncertainty

No single approach or data type is adequate for characterizing subsurface structure and properties. However, adding additional data types is complicated because the sensitivity and resolution for each data type may be different. For example, seismic imaging can provide the subsurface architecture down to a scale of several meters in optimal situations, but this method cannot directly distinguish between water and hydrocarbon as a pore fluid. In this case, electromagnetic measurements provide additional information (e.g., Constable and Srnka 2007), but with different spatial resolution.

The process of combining different data sets (data fusion), and possibly *a priori* information as well, is a problem that needs further theoretical, numerical research as well as application to field examples. Disparate data sets, and other information, can only be combined meaningfully when the uncertainty in the different pieces of information as well as the resulting combination can be evaluated. This is especially challenging because the uncertainty depends on the different length scales for different data sets.

It is imperative to increase the spatial resolution in imaging and characterization. Because of the attenuative nature of the physical fields used for interrogating the subsurface, the resolution obtained degrades with distance. New instrumentation that can be used at depth in boreholes or wells is needed to achieve the required increased resolution at depth. Distributed subsurface sensor networks at the micro- or nanoscale may have the potential to provide images at unprecedented length scale. Permanent sensors, or sensors that roam the subsurface—for example by moving with the flow—can further enhance the temporal sampling of the subsurface.

New measurement techniques can be especially powerful in combination with smart tracers. As shown in Figure 13, the combination of conserved and active chemical tracers provides insight in the reaction rates, as well as the spatial and temporal pattern of reactivity. Tracers that respond to external fields (e.g., pH or pressure) by changing their response to probing fields, or by emitting an electric or acoustic signal, may open up new avenues for understanding processes. These tracers could be chemical or electro-mechanical, possibly in combination with biological components. Subsurface relay stations in some form are needed for the required transmission of information. Recent developments in micro/nanotechnology are promising and may play an important role in distributed sensors networks in the subsurface.

New tracers of groundwater age are needed that can be used to estimate the full spectrum of fluid residence times within individual water samples representative of large subsurface control volumes tapped by production wells or of local points within the subsurface. Our current inability to estimate water ages in the 50 to ~3000 year range is particularly limiting.

Lastly, methods of measuring state variables such as pressure, temperature, saturation and concentration continuously in space rather than mainly at points or over finite volumes are needed. Linear measurement technologies such as fiber optics may provide the means of accomplishing this (e.g., Selker et al. 2006).

Improved geophysical imaging techniques

Geophysical techniques which remotely probe the properties of the subsurface at their critical length and time scales are still generally unavailable. Despite spectacular advances in 3D seismic imaging, current imaging techniques are still limited. The current resolution is too low to identify many of the smaller-scale structures and processes believed to be relevant to the critical properties of the subsurface and their response to anthropogenic perturbations. The sensitivity of current monitoring methods is not sufficiently high to match the detection threshold desired for effectively managing the subsurface. Seismic waves are primarily sensitive to seismic velocities and density. From measurements of these properties other quantities, such as porosity, can sometimes be inferred. In practice, many important properties of the subsurface cannot be estimated from seismic data, although combining different receiver configurations at the surface and down boreholes, or through vertical seismic profiling, can improve results. For some properties, such as hydraulic conductivity, the combination of seismic data with electromagnetic data is promising. Many (bio)geochemical properties, such as the pH or the redox potential, cannot be probed remotely with current imaging techniques.

Imaging may be more effective by introducing contrast agents into the subsurface in such a way that it is more sensitive to probing fields. This approach is akin to the use of tracers in medical imaging. An example is the CO_2 injection shown in Figure 15 that can be used to determine the flow pathways in a reservoir. More advanced applications may include, for example, the use of organometallic tracers. The organic part of the tracers makes it possible to track (bio)chemical properties, while the metallic part of the tracers creates the opportunity to detect the presence and concentration of the tracers with electromagnetic fields. Well-designed methods to manipulate the subsurface may increase the effectiveness of geophysical imaging techniques to monitor structures and processes in the subsurface.

To adequately probe the subsurface remotely with imaging techniques, it is necessary to:

- Enlarge the number of physical, chemical, and biological properties to be analyzed remotely
- Enhance the spatial and temporal resolution of geophysical imaging techniques to help bridge the gap between the length and time scales that can be imaged and the length and time scales of the relevant structures and processes in the subsurface
- Increase the sensitivity of remote monitoring methods to match detection thresholds needed for managing the subsurface effectively
- Establish a more accurate connection between imaged properties and the microstructure of the subsurface
- Develop methods to manipulate the subsurface to increase the effectiveness of imaging techniques

In practice this will require including combinations of measurements of different physical and chemical fields, and combinations of surface measurements with down-hole and other probe measurements. This requires effective data fusion methods as described earlier. Developments in micro-instrumentation are needed to measure properties of the subsurface in more detail. Interferometric techniques need to be further developed to use the sensitivity of time-lapse measurements (Snieder et al. 2002) and to use ambient fluctuations as a source for imaging techniques (Curtis et al. 2006; Larose et al. 2006). Combined with permanent instrumentation, interferometric techniques may open up new opportunities for continuous monitoring. A combination of laboratory measurements and computer simulation is needed to relate the imaged properties at the resolution of the imaging technique to the relevant microscale properties.

CONCLUSION

Impacts in the geosciences

Restrictions in our current ability to characterize physical, chemical and biological properties of the subsurface at multiple length and time scales form a major hurdle that prevents us from understanding subsurface processes and managing subsurface systems. The research activities described here can impact water resource management, energy and mineral extraction or storage, geologic waste disposal or storage, site location and subsurface characterization for sensitive construction projects (e.g., nuclear power plants), and environmental remediation. For these systems, hazard assessments in general can be improved by more effective characterization methods.

New and improved subsurface characterization and imaging techniques will help in managing oil, gas, coal, hydrate and geothermal resources in a more effective and safe manner. The ability to be confident in early detection of problems and remediation of environmental consequences will be enhanced, and the benefits, costs, and impact of corrective action can be identified more rapidly.

Enhanced characterization and imaging systems will provide new and more detailed information for improving the siting, design, performance assessment, and management of geologic disposal sites, including carbon dioxide storage and radioactive waste disposal. Such improvements will increase political and public acceptance of geologic waste storage. Licenses for operation can be assigned more rapidly. The ability to detect, diagnose, and remediate leakage problems depends critically on effective characterization and monitoring.

Finally, the broad area of subsurface monitoring and environmental remediation will benefit from new and diverse measurement technologies and more integrated instrumentation, and by ensuring that all types of man-made disposal and storage processes in the subsurface have predictable consequences. In civil engineering, more effective methods can improve our ability to monitor new or aging underground infrastructure, and reduce the cost and risk for managing the subsurface.

Impacts for other fields

The challenge of effectively describing complex systems is also faced in other fields of science. Among the problems that share the complex, multiscale behavior found in subsurface systems are: the Earth's climate system; turbulence, stirring and mixing in fluids; and reactive flow. The research described in this report on imaging, data fusion, uncertainty estimation, and uncertainty reduction has consequences for other fields such as medical imaging, non-destructive testing, process monitoring, and material science. The proposed work on smart tracers, in particular, interfaces with medical research (treatment and diagnostics), materials science, manufacturing, and process control.

MODELING AND SIMULATION OF GEOLOGIC SYSTEMS

Everything should be made as simple as possible, but not simpler. – Albert Einstein

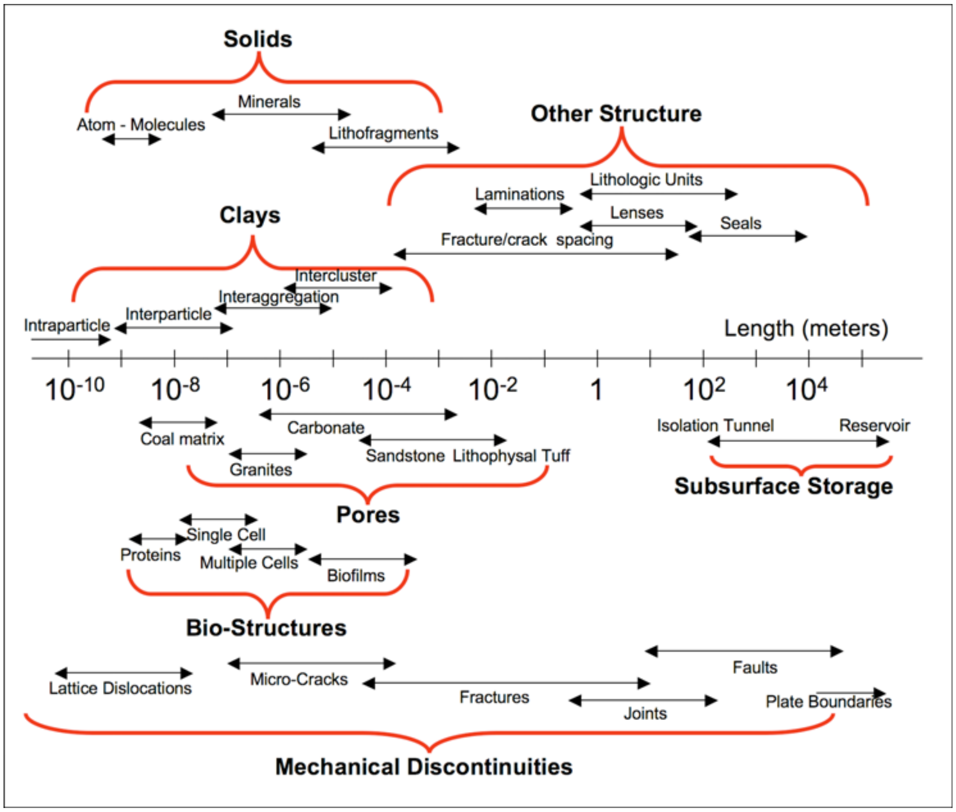
Computer modeling of subsurface systems has been practiced for over 50 years and in many respects is a mature technology. However, modeling capabilities fall short of application needs in areas such as nuclear waste disposal or carbon storage, where the long time scales needed for safe containment and the subtlety of interacting processes place far greater demands than can be satisfied with present capabilities. There are opportunities to develop multiscale, multiphysics, nonlinear modeling capabilities that will take advantage of evolving petascale computing platforms. These will provide qualitative improvement in the ability to simulate and understand subsurface systems, resulting in large technical and economic benefits for design and operation of waste disposal facilities, improved environmental protection, and higher recovery rates of energy resources. To accomplish this requires an additional research objective to develop first-principles-based approaches to chemical speciation, thermodynamics, and reactivity in aqueous and nonaqueous systems.

CURRENT STATUS

Computer modeling of subsurface flow systems, such as groundwater aquifers and oil and gas reservoirs, has been performed at increasing levels of sophistication since the 1950s (Peaceman and Rachford 1955). Much is known about the physical and chemical processes in such systems. Equations have been formulated that relate process dynamics and equilibria to fundamental driving forces, such as fluid pressure and chemical potential (Aziz and Settari 1979; Firoozabadi 1999). Algorithms have been developed for solving these equations and have been incorporated into sophisticated computer programs routinely used by engineering professionals in applications for recovery of subsurface resources and environmental protection.

In groundwater modeling, methods integrating modeling of complex systems with large and diverse data sets can build on a substantial legacy, which started with the work of, for example, Cooley (1979) and Yeh and Yoon (1981). Hill and Tiedeman (2007) review more recent work that addresses understanding and accounting for heterogeneity (e.g., Hyndman et al. 1994; Hyndman and Gorelick 1996; Kolterman and Gorelick 1996; Carle et al. 1998; Chen and Rubin 2003; de Marsily et al. 2005), integrating many kinds of data (e.g., Rubin et al. 1992; McKenna and Poeter 1995; McLaughlin 2002; Binley and Beven 2003; Sanford et al. 2004; Hunt et al. 2006), sensitivity analysis (e.g., Yager 1998; Saltelli et al. 2004; Barth and Hill 2005; Tiedeman et al. 2003, 2004), quantifying uncertainty (e.g., Moore and Doherty 2005; Meyer et al. 2004), and model discrimination (e.g., Poeter and Anderson 2005).

Software currently available to address some of these issues includes, for example, PEST (Doherty 2005), UCODE_2005 (Poeter et al. 2005), iTOUGH2 (Finsterle 2004, 2006; Kowalsky et al. 2005), MMA (MultiModel Analysis; Poeter et al. 2007), OPR-PPR (Observation-PRediction and Parameter-PRediction statistics; Tonkin et al. 2006), and DAKOTA (at Sandia National Laboratory). In addition, relevant environments for constructing such software are becoming available. For example, the USGS and EPA recently produced JUPITER (Banta et al. 2006), while the EPA is producing the COSU API.



Courtesy of Laura J. Pyrak-Nolte

Figure 16. Multiscale heterogeneity in geologic systems.

BASIC SCIENCE CHALLENGES, OPPORTUNITIES AND RESEARCH NEEDS

In many ways, computer modeling of subsurface flow systems has a well-established approach. Yet it also has shortcomings that severely limit scope and reliability of current simulation technology. These shortcomings relate primarily to two pervasive and interrelated aspects of subsurface systems: (1) the importance of coupled processes, and (2) the presence of structures and interactions on a vast range of space and time scales that are not compatible with space and time resolution of the models (Figure 16). *Coupled processes* denote the interplay of fluid flow, solute transport, heat transfer, and chemical and mechanical interactions between rocks and fluids. These processes are typically played out in environments that involve structure on scales from the mineral grain to a geologic region. In some cases there may be a natural *separation of scales* that would justify certain approximations and simplifications within some scale range; in other cases no such scale breaks exist, and processes may evolve through a continuum of scales, from below the pore scale all the way to the regional scale.

Current approaches to modeling natural or anthropogenic processes in subsurface systems are adequate for many tasks encountered in resource recovery (oil and gas production, groundwater management), but may fall short of application needs in areas such as nuclear waste disposal or carbon storage. 50% oil recovery from an oil reservoir is exceptionally good, while loss of 50% of a sequestered material is exceptionally bad. The long time scales needed for safe containment and the subtlety of potential failure mechanisms impose much more stringent demands on models as the foundations of performance assessment. In addition to the challenges pertaining to multiscale modeling of coupled processes, difficult issues arise when attempting to build detailed models for specific sites that are based on a diverse set of hard and soft data. These issues include:

1. Determining the optimal level of detail in geological-scale modeling
2. Incorporating large and diverse data sets into models
3. Quantifying model predictive uncertainty with consideration of data errors, model approximations, scale effects, nonlinearities, and coupled processes

Modeling multiple processes at interacting scales

The present level of understanding and modeling of complex properties and processes in the subsurface is often insufficient for predicting potential responses to anthropogenic perturbations. A fundamental gap in the knowledge base is how to accurately couple information across scales, i.e., accurate accounting of small-scale effects on larger scales, and of large-scale forcings on small-scale processes. For example, in a fracture, chemical interactions between pore fluids and the fracture walls occur locally on the submicron scale but affect fluid flow and wave propagation along the length of the fracture, on a typical length scale of meters or more. For a porous medium that is partially saturated with gas and water, the distribution of these two fluid phases is affected not only by the intrinsic length scales of the pores but by length scales associated with fluid-fluid and fluid-solid interfaces, as well as by time-dependent processes that alter fluid pressures (e.g., pumping, fault displacement, reactive events). In both of these examples, the problem is complicated by the fact that there are no obvious scale separations. This leads to the demanding challenge of determining not only the appropriate mathematical and numerical representations at each scale but more importantly the interactions across scales.

In addition to complex processes, the properties of natural geologic formations rarely display uniformity or smoothness. Instead, they usually show significant variability and complex patterns of correlation across a wide spectrum of interacting scales. For example, mechanical discontinuities range in scale from a few microns (microcracks) to centimeters-meters (fractures, joints) to kilometers (faults). They can occur singly or in sets producing heterogeneity from the pore scale to the reservoir scale that varies temporally because of participation in hydrogeologic, geochemical, biogeochemical and tectonic cycles, in addition to any human activities or interference. Geologic characterization models are usually constructed using sparse data, which come from different sources with varying quantity and information content. We are faced with the scientific challenge of developing stochastic mathematical and numerical frameworks that capture the nonlinear dynamic (physical and chemical) processes in geologic formations. Any probabilistic description must account for uncertainty in models, inaccessible length scales, scale-dependent statistical description of physical phenomena (e.g., diffusion, mechanical dispersion), and measurement errors.

Subsurface systems are not static, but evolve over time because of natural processes or human influences that lead to nonlinear processes with complicated feedback mechanisms. For example, the evolution of transport characteristics of fractures is controlled by competition between chemical and mechanical effects. These either generate (e.g., dilatant shear, microcracking, thermal cracking, focused dissolution) or destroy (shear and hydrostatic compaction, fracture healing, dislocation creep, pressure solution, free-face diffusion) fracture porosity. Crucial in this understanding of chemical effects are the mechanisms in which mechanical deformation contributes to changes in permeability, and by which, in turn, the mechanical response is modified. These effects are known to be important at relatively modest stresses and temperatures, and are typical in systems pushed far from chemical equilibrium, such as in geothermal or hydrocarbon reservoirs, or around waste repositories. A key challenge is the accurate representation of multiple processes that vary in strength and exhibit feedback that may be self-enhancing or self-limiting. Nonlinear processes cannot be modeled with simple scale-averaged descriptions, but require the resolution of nonlinear interactions spanning a multiplicity of scales. It also requires an understanding of the physics of systems pushed far from equilibrium. New linear and nonlinear solvers are needed to enable accurate simulation of evolving geologic systems on petascale computing facilities.

Coupling information across scales requires the appropriate governing equations for given spatial and temporal scales, as well as knowing how to appropriately transfer information across scales. For many subsurface applications, the model must adapt to use real-time information to update predictions, inform field-scale deployment of monitoring methods, and be able to quantitatively assess the results. Because of the range of scales, data integration will require understanding measurements from the laboratory scale to the field scale. On the laboratory scale, experiments need to be designed to access the data required under controlled conditions (e.g., pressures, temperature, material properties, fluids) over known scales (e.g., specific pore structures, molecular scales), and over time to determine how the structure/system/processes evolve. For example, the principal challenge of upscaling techniques for multiphase fluid dynamics in porous media is to determine which properties on the microscale can be used to predict macroscopic flow and the spatial distribution of fluid phases at core and field scales.

First-principles theoretical formulations over the past decade have been derived from volume averaging theorems in which microscopic interfacial behavior is explicitly incorporated. These theories have proposed that interfacial area per volume directly affects macroscopic behavior, and that this variable may govern the observed hysteresis in the capillary pressure-saturation relationship. Direct visualization of interfaces with high resolution is only possible on the laboratory scale. Transparent two-dimensional porous media (Cheng et al. 2004) with a resolution of 0.6 microns per pixel edge length and total sample length of 600 microns have been used to visualize and quantify the behavior of interfacial geometry, while concurrently measuring fluid pressures (globally and locally) to test the volume averaging theorem. Any upscaled models must be calibrated to ensure that fine-scale influences are properly captured. Thus, laboratory techniques can provide a basis for validating theorems and calibrating numerical methods for complex media over a range of length scales.

While the laboratory can describe physical phenomena over two to three orders of magnitude in length, testing of coupling across multiple scales will require mesoscale data and field-scale data integration. Structural information on the field scale is often difficult to obtain, and tends to be spatially sparse and temporally infrequent. A major scientific challenge is the development of models that can examine the state of a system when initial conditions are unknown, but time-lapsed data are available (e.g., time-lapsed seismic monitoring, well head pressures, strain from tilt meters). This requires developing feedback between model formulation and data acquisition. Modeling will inform the field characterization and monitoring process on the scale of data needed, on required spatial and temporal coverage of a field site, and on data interpretation. The field data in turn will enable the development of dynamic and adaptive models that can update predictions based on newly obtained data from a site. Integration of model development and data acquisition will make it possible to answer the principal question of how to appropriately simulate and measure information and processes across scales in a structurally complex dynamic system.

Subsurface storage of CO_2. A practically important aspect of CO_2 storage in saline aquifers is the process of Dissolution-Diffusion-Convection (DDC), which spans a vast range of scales from pore level to site scale, with continuous progression over time, and no scale separation (Ennis-King and Paterson 2003; Riaz et al. 2006). CO_2 injected into saline aquifers at supercritical conditions (pressures above $P_{crit} = 7.38$ MPa) is immiscible with water, and forms a separate phase with gas-like viscosity and liquid-like density. For convenience we refer to this CO_2-rich phase as “gas.” At typical subsurface conditions of pressure and temperature, CO_2 is less dense than aqueous fluids, hence experiences an upward buoyancy force, and migrates towards shallower horizons whenever permeable pathways are available. Over time some CO_2 becomes trapped in the pore space by capillary force so it is no longer mobile. Further, some CO_2 dissolves in the aqueous phase, whereupon the density of that phase increases by a small amount, on the order of 1%. CO_2 dissolution and its associated density increase are very desirable effects, as they remove the upward buoyant drive and thereby increase storage security. Once dissolved in the aqueous phase, CO_2 may react with formation minerals to form carbonates of low solubility, achieving a yet more permanent and desirable form of storage. Due to the obvious impact on CO_2 containment and storage security, time scales and quantitative aspects involved in the partitioning of CO_2 between these different storage modes are of great practical interest (Figure 17).

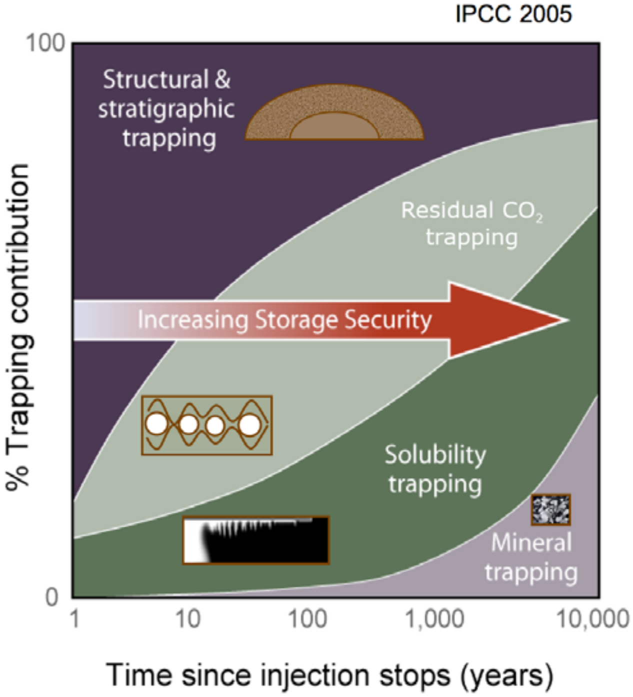


Figure 17. Schematic of CO_2 partitioning between different storage modes (adapted from IPCC 2005).

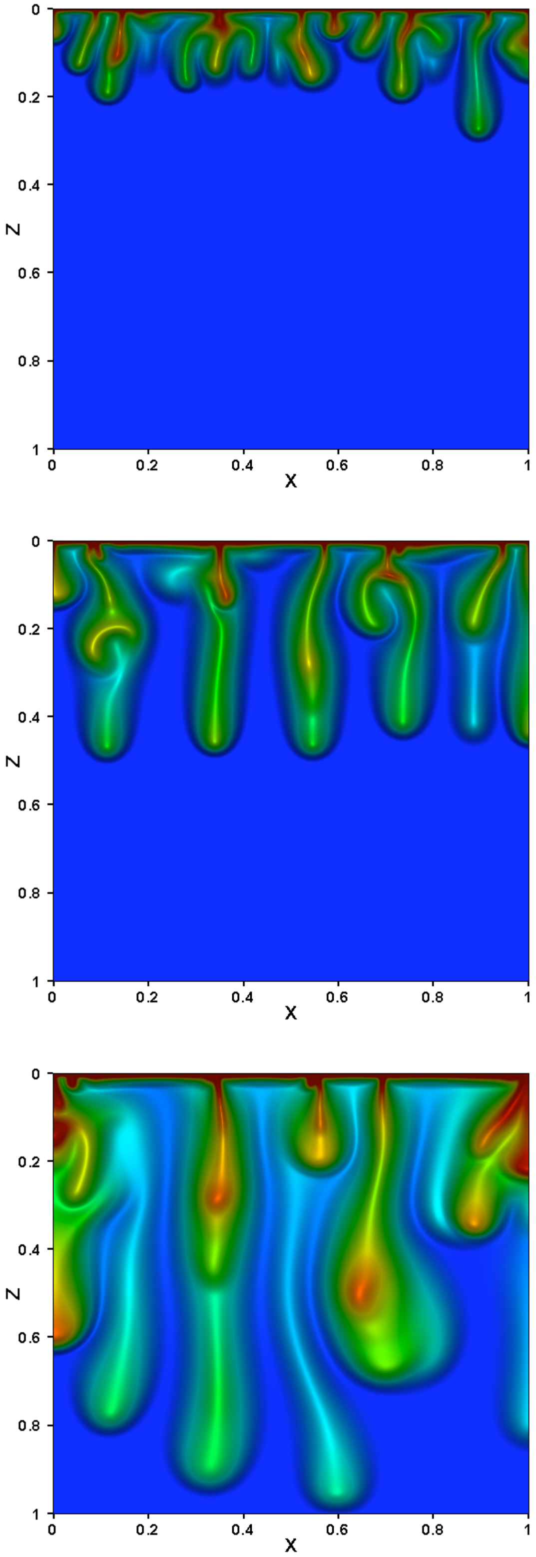


Figure 18: Time sequence of convective plumes induced by a density-driven instability (Riaz, A., Hesse, M., Tchelepi, H.A., and Orr, Jr., F.M. (2006). Onset of convection in a gravitationally unstable diffusive boundary layer in porous media, *Journal of Fluid Mechanics* **548**, 87–111; Copyright © Cambridge University Press, reprinted with permission).

CO_2 dissolving into the aqueous phase at early stages migrates away from the phase boundary by molecular diffusion in the aqueous phase, which is a very slow process. Indeed, effective aqueous diffusivities in porous media are of the order of $D_{eff} = 10^{-10}$ m^2/s, so that a time period of $t = 10^{10}$ s (≈ 300 years) is required to achieve a penetration depth of $z = \sqrt{(Dt)} = 1$ m. As had been mentioned, CO_2 dissolution gives rise to a small increase in aqueous phase density, which after a certain "incubation time" can induce convective currents in the aqueous phase, which remove CO_2 from the phase boundary and mix it throughout the permeable thickness of the aquifer at rates that can be orders of magnitude larger than those from molecular diffusion. The DDC process of CO_2 dissolution, diffusion away from the phase boundary in the aqueous phase and subsequent convective transport of CO_2, is a typical example of a multiscale process (Ennis-King et al. 2005). The early onset of convective instability occurs on the scale of a few pores. Convective plumes can continually grow over time until eventually they reach a scale of tens of meters or more. The process has been analyzed by applying stability theory to idealized geometric shapes subject to highly simplified boundary conditions. High-resolution numerical modeling for onset and growth of the convective instability has been performed for similarly idealized systems (see Figure 18; Ennis-King and Paterson 2003; Riaz et al. 2006). We currently have no methods that would allow an accurate modeling of the process for a field-scale domain. "Brute force" approaches using high-resolution space discretization are not expected to be feasible with any foreseeable increase in computing power. Indeed, if 1 cm spatial resolution is required, 1 billion grid blocks will provide coverage for only a $10 \times 10 \times 10$ m^3 domain, which falls far short of the several-kilometer scale required for design and performance assessment of CO_2 storage systems.

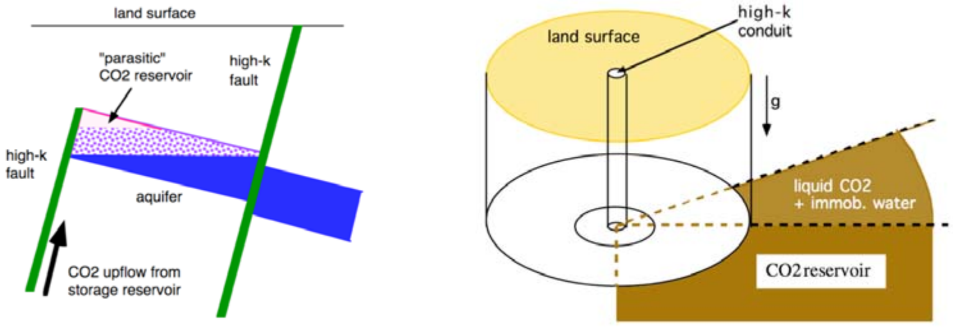
A key concern with geologic storage of CO_2 is secure containment. However, in industrial-scale storage systems some leakage may be expected (see sidebar on *CO_2 leakage*), which may give rise to complex, coupled, physical and chemical processes on a broad range of space and time scales. Multiscale, multiphysics problems are also at the heart of understanding solute transport in heterogeneous media, especially when reactive processes are involved, such as sorption, redox, or colloid formation.

Focused research efforts are needed to develop modeling capabilities for subsurface processes across multiple space and time scales to evaluate hazards and risks that may be associated with the design, operation and monitoring of storage facilities and operations. Among the potential benefits of such research is a better understanding of rare events with potentially large consequences; i.e., can a large volume of high-pressure CO_2 stored underground give rise to a rapid, large volume leak (Pruess 2007)? The modeling capabilities need to accurately represent coupled equilibrium and nonequilibrium processes with nonlinear feedbacks. Thermophysical properties of liquid-gas-solid mixtures need to be described accurately, using first-principles-based predictions of chemical speciation, thermodynamics and chemical reactivity (see below). Stochastic effects need to be included in a realistic fashion. Scaleable algorithms are needed to allow efficient simulation on petascale computing platforms.

CO_2 leakage

Subsurface storage of CO_2 from large fossil-fueled power plants will generate large plumes that over the lifetime of the plant may reach linear dimensions on the order of 10 km or more (Pruess et al. 2003). On this scale it seems likely that in most geologic environments, cap-rock imperfections, such as thin or permeable intervals, fracture zones or faults, may be encountered that provide potential pathways for some CO_2 to escape from the primary storage reservoir. CO_2 leakage may also occur along pre-existing and improperly plugged wells (Nordbotten et al. 2004). Different scenarios are being studied (i.e., Lewicki et al. 2007) to gain insight into the physical and chemical processes that govern leakage behavior (see below). Studies of natural CO_2 discharges in volcanic areas suggest that the most likely manner in which CO_2 may reach the land surface is through *diffuse degassing* over a large area rather than in a single location (Barnes et al. 1978; Sorey et al. 1998; Chiodini et al. 2004). However, at present the possibility of a localized high-energy discharge from an anthropogenic CO_2 storage reservoir cannot be ruled out. Modeling studies have suggested that CO_2 leakage may be subject to a combination of self-enhancing and self-limiting feedbacks (Pruess 2007). The lower density and viscosity of CO_2 as compared to aqueous fluids may cause leakage rates to increase over time. Gas exsolution upon pressure decline can also give rise to increasing CO_2 leakage rates. A number of effects can limit CO_2 leakage rates, including depletion of dissolved gas, Joule-Thomson cooling upon depressurization as CO_2 rises, and phase interference and latent heat effects when pressures become subcritical, and separate liquid and gaseous CO_2-rich phases may evolve (Pruess 2005). Chemical interactions between rocks and fluids can either increase or decrease formation porosity and permeability (Gherardi et al. 2007), providing a potential for both self-enhancing and self-limiting effects.

Assessing the potential for a high-energy discharge of CO_2 from underground storage reservoirs poses extremely challenging multiscale, multiphysics problems, the solution of which may provide important benefits for understanding volcanic and other natural hazards.



Courtesy of Karsten Pruess, Lawrence Berkeley National Laboratory

Scenarios for CO_2 leakage. (Left) A blind fault may allow CO_2 to escape from the primary storage reservoir and form a secondary accumulation at shallower depth that could induce a discharge at the land surface. (Right) High-permeability conduits, such as improperly abandoned wells, or fault intersections, may provide pathways that could enable CO_2 to leak from the primary storage reservoir and directly migrate to the land surface.

Modeling complex systems with diverse data sets

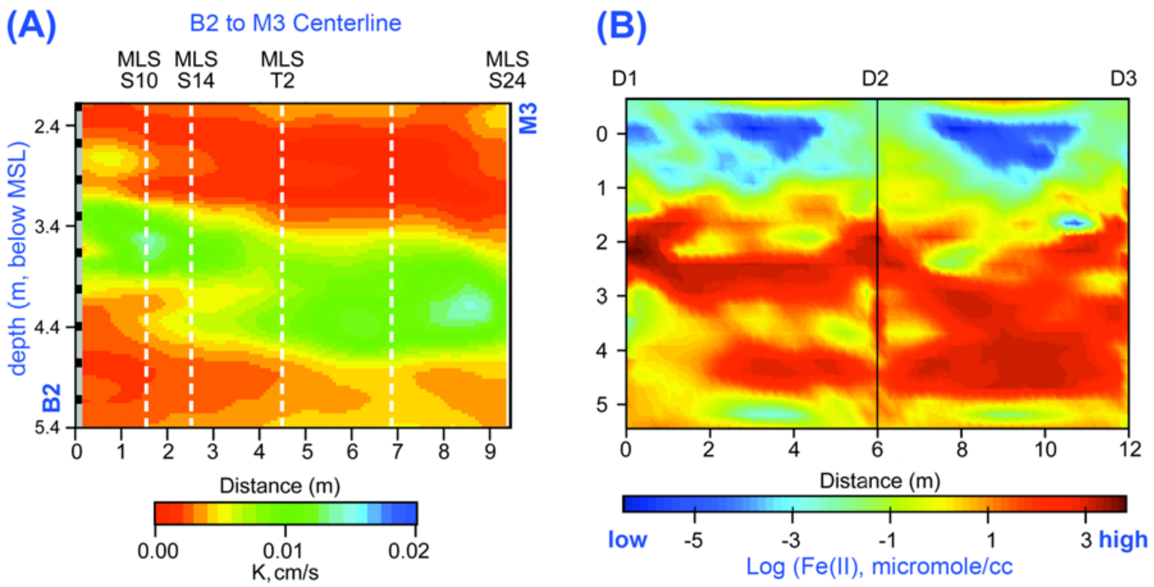
Current practice in inverse modeling tends to decouple processes, to aggregate parameters across scales, and to include only a limited amount of the available, real data. It is anticipated that advances in characterization methods will produce increasingly larger data sets as the spatial extent and the spatial and temporal resolutions of measurements increase. In addition, with the development of new measurement devices, data types not currently commonplace may become routinely available. The scientific challenge is to incorporate these larger data volumes and disparate data types into inverse modeling while simultaneously satisfying diverse physical and chemical constraints. In particular, in the context of monitoring perturbed geological systems, models will have to handle streams of different data types measured over a variety of spatial and temporal resolutions, including data that are only indirectly related to system state variables of interest and model parameters. The computational burden of such comprehensive inverse modeling requires fundamental advances in mathematical methods and numerical algorithms. Revolutionary advances in the modeling workflow are required to achieve automatic, real-time incorporation of diverse data sets into models.

Hubbard and Rubin (2005) described several obstacles that hinder the routine use of geophysics for quantitative estimation of subsurface properties, including limitations inherent in geophysical data inversion and associated artifacts, integration or joint inversion of datasets that sample different properties, petrophysical models, scaling issues, and non-unique geophysical responses to heterogeneities. In spite of these obstacles, recent synthetic and field studies have illustrated how geophysical data improve the prediction of transport and contaminant remediation in natural systems through better model parameterization and validation (e.g., Scheibe and Chien 2003; Scheibe et al. 2006). For example, geophysical methods have been used to provide high-resolution estimates of subsurface properties; some examples of hydrogeophysical estimation are shown in Figure 19.

Quantifying and reducing predictive uncertainty

Uncertainty in model results arises primarily from lack of information, inconsistencies between the available information, and the modeled quantities, and errors in the existing information. Quantifying the uncertainty requires a careful accounting of these contributions, numerical methods that are accurate and robust, use of optimization methods for model calibration, and use of sensitivity methods to reveal important information deficiencies. Recent and anticipated advances in data collection are expected to increase the demands on this process. Despite significant advances in recent years, the fields of model calibration, sensitivity analysis, data needs assessment, long-term monitoring, and uncertainty evaluation require fundamental improvements to optimally use anticipated data sets while fully accounting for multiscale features and nonlinearly coupled processes.

At the more practical level of decision making in a regulatory context, additional benefits would accrue from the development of these methods. In both CO_2 storage and nuclear waste disposal, operators are obligated to demonstrate that decisions based on models are appropriate. In today’s terminology, this generally means that models must be demonstrated to be “valid,” that is, shown to be consistent with data. The concept of model validity is fraught with philosophical



Courtesy of Susan Hubbard, LBNL

Figure 19. Hydrogeophysical examples. (A): Estimation of hydraulic conductivity obtained using crosshole seismic and radar data conditioned to flowmeter data within a Bayesian framework (datasets and methods described in Hubbard et al. 2001). (B): Estimation of sediment geochemistry obtained using crosshole radar amplitude and wellbore measurements within a Markov chain Monte Carlo approach (Chen et al. 2004).

difficulties related to provability of a scientific hypothesis (e.g., Oreskes 2000). A data-driven modeling paradigm, with continuous updating and error assessment, will move the dialog beyond theoretical discussions of model validity to a much more useful discussion of the state of knowledge of a particular system, and to a process of continual model improvement. Such a change of perspective would greatly improve the communication process between scientists, managers, regulators and the public in planning these often contentious projects by providing much-needed context for discussions of model validity.

Computational chemical thermodynamics—Equilibria and reactions

The chemical properties of aqueous and nonaqueous fluid phases, their mixtures, and their interactions with solid mineral phases are central to the safe storage of nuclear waste and the sequestration of CO_2 in geologic formations, the transport of ore-forming and toxic materials, the exploitation of geothermal energy, and many others. Our knowledge of the relevant subsurface systems is adequate for some engineering applications, but a better understanding of the complex structure of many species in solutions is needed as demands on engineered geological systems become more complex.

In recent years there have been dramatic advances in both the theory available to calculate the properties of complex mixtures and in the performance of computational platforms available for simulation. These developments, coupled with new high-resolution, analytical measurements made possible by high performance light sources and neutron sources, have led to advances in the understanding of complex materials at an unprecedented level of atomic specificity. A major, new scientific challenge is to build on the remarkable development of these technologies to achieve a new level of understanding and control of processes as diverse as self-organization in colloids, the catalytic biochemistry of signal transmission in eukaryote cells, and the prediction of the chemistry that occurs under extreme temperature and pressure conditions which may be experienced in the operation of advanced nuclear power systems.

The complexity of the processes of interest (e.g., bond breaking and formation, changes in bond valence and polarization) requires reliable, predictive simulation methods based on first principles (i.e., the electronic many-body Schrödinger equation). The problem is made more difficult by the amorphous structure of many species of interest (e.g., solid solutions), thus requiring treatment of many atoms to provide a complete description of chemical processes. *Ab initio* calculation of chemical equilibria, speciation and reactions poses a grand challenge computational problem.

Equation-of-State (EOS) models and data. Regardless of the state of understanding and calculations at the atomic level, to translate these advances into useful applications at the macroscopic level, efficient equations must be available that succinctly summarize experimental and computational data for use on the macroscopic level (e.g., a rate equation or more commonly an Equation of State, or EOS). The free energy summarizes all the thermodynamics of the system and usually is chosen as the basis for EOS development. The development of EOS representations is dependent on the availability of a succinct representation of the thermodynamics of the system that can capture the variation of the free energy for a wide range of intensive variables. There has been considerable research effort in this area. However, there are very few EOS that represent thermodynamic behavior with the accuracy that is required for problems such as nuclear waste disposal and CO_2 sequestration. It is likely that the required accuracy may be achieved from models that are tailored to describe specific states (e.g., solids, liquids, gases, polyion colloids, solid solutions), rather than from a quest for a single EOS representation that will describe all physical states.

EOS for compressible mixtures. For systems composed of water and gases, the most convenient variables are usually the temperature, volume (or density) and the composition. The appropriate thermodynamic function on which to base an EOS is then the molar Helmholtz free energy. All other properties (e.g., the enthalpy) may be derived from this function by the appropriate derivatives. To provide optimal interpolation and extrapolation of mixing properties, the functional form of the free energy should be based on a reasonably accurate molecular-level description of the system. The thermodynamic perturbation theory originally introduced by Pople (1954) provides a framework from which such an EOS may be generated. To provide the high level of accuracy necessary for quantitative description of thermodynamic data, empirical corrections must usually be added to the EOS. This type of approach was successfully applied to the analysis of mixtures of polar and nonpolar fluids, including soluble solids that may dissociate.

Geochemistry in the absence of an aqueous phase. Injection of CO_2 into aqueous environments will not only give rise to CO_2 dissolution in the aqueous phase, but also induce partitioning of water into the gas (CO_2-rich) phase. Over time this will produce a complete dry-out of the region around the injection well, with potentially important ramifications for chemical interactions between CO_2 and *in situ* mineral assemblages that may affect important practical aspects, such as the mechanical stability of the injection well. Currently there is little knowledge of rock-fluid interactions in the absence of an aqueous phase. Experimental and modeling studies of CO_2-rock chemistry in the absence of an aqueous phase are needed. These may open up new approaches for CO_2 storage in mineralogical settings that could be highly reactive with CO_2, such as basalts with their large abundance of magnesium and iron (McGrail et al. 2006).

EOS for liquid density complex mixtures of aqueous electrolyte solutions and mixtures with other nonaqueous solutions. For nearly incompressible aqueous mixtures, highly accurate EOS providing the mixing behavior of the system are available (Pitzer 1987; Weare 1987; Christov and Moller 2004). These approaches are largely phenomenological. To implement them, a high level of understanding of the speciation in solution and a sufficient database must be available. The principal limitation to the development of accurate EOS models of the fluids encountered in the application of energy strategies is the lack of understanding of the speciation (e.g., the structure and dynamics of polyions and colloids) present in the liquid phase. For example, even for the aluminum system, one of the most common elements in the Earth's crust, we still have a very incomplete understanding of the speciation in solution. The development and application of new approaches to chemical systems involving brine-CO_2 mixtures could greatly enhance our ability to predict the chemical changes in deep geologic systems of importance for CO_2 storage.

EOS for solids, solid solutions and absorbed phases. Present-day EOS for mineral systems are essentially empirical. For pure minerals this is not a problem as long as data exist to parameterize the pressure-temperature dependence. On the other hand, even commonly encountered systems such as dolomite can be very complex solid solutions, with like-like and like-unlike clustering, microcrystallization, defect structure, etc. Of course, solids under extreme conditions of radiative flux, high temperatures and pressures, etc., can develop extreme defects. These systems are at best at equilibrium locally. Without a more refined understanding of these materials on the atomic scale, it is difficult to reduce this behavior to an EOS representation required for the analysis of subsurface problems.

Typically colloidal systems contain hundreds of thousands of atoms. Such systems might be expected to be described by thermodynamic potentials. However, as in the solid solution systems, effects of clustering, local structure, surface compositional variation, etc., are difficult to quantify. In addition, for these systems the large ratio of surface area-to-bulk volume requires special treatment. Simulations of structure are today limited to 500 or so particles; however, with the availability of many more processors on next-generation computers, it will be possible to treat on the order of 1000 particles or more. New methods should be explored to treat problems such as colloidal coarsening and surface structure (including local ordering) and chemical reactions at interfaces. The state of species absorbed on solid and colloidal surfaces and their chemistry is a problem of great importance to solute transport, mineral formation and dissolution, oxidation and reduction of solute species, and others. Currently, quasi-thermodynamic models of surface complexation have been invoked on an *ad hoc* basis. These models work remarkably well when there is sufficient data for parameterization. New surface probes now provide a much more precise atomic level view of the surface interface region. This is a fertile region for the application of first-principles methods of simulation using approaches described above. As in the other areas in which these methods might be applied, the objective would be the development of an atom-based structural and dynamic view of the interface region (effects of local structure and defect structure as absorption sites, formation of surface islands, etc.). This level of understanding would be used to develop more accurate phenomenological models for the interface region.

Developing coupled in silico biogeochemical models

The fate and transport of radionuclides and metals (Charlet and Polya 2006; Kretschmar and Schaefer 2005; Lloyd and Oremland 2006; Roden and Scheibe 2005; Steefel et al. 2005), the corrosion of nuclear waste forms and packages (Bruno and Ewing 2006; Burns and Klingensmith 2006; Ewing 2006; Grambow 2006), the performance of engineered barrier systems, the storage of CO_2 in deep aquifers (Bachu et al. 1994; Bruant et al. 2002; Elliott et al. 2001; Gaus et al. 2005; Gunter et al. 1993; Johnson et al. 2004; Rochelle et al. 2004), and the global elemental and nutrient cycles (Berner 1995; Berner et al. 1983; Van Cappellen and Gaillard 1996) are all influenced by biogeochemical processes. In many cases, the rates of these processes are directly mediated by microbial activity. In other cases, new reactions may occur, or the extent of reactions may be altered, relative to an analogous abiotic system through the participation of cells or their byproducts in the reactions. Microbially mediated environmental processes rarely result from activity of a single group of organisms, but instead are the result of a diverse group of organisms that may reside as biofilms in the subsurface. Competitive and/or symbiotic communities may be present. Microbial metabolism and growth can directly or indirectly impact important geochemical processes, including electron-transfer, precipitation and dissolution, and sorption.

Specific bacterial populations are known to catalyze the reactions of certain redox-couples, e.g., the respiration of acetate with iron(III) as an electron acceptor. Moreover, there are feedback mechanisms between the geochemical environment and bacteria that lead to gradual changes in microbial functions as the environment changes. For example, the bacterial community may switch from iron(III) reduction to sulfate reduction as iron(III) reaches limiting (but non-zero) concentrations in a porous medium (Chappelle and Lovley 1992). A variety of competitive and cooperative bacterial community processes generally lead to a shift in predominant species when an evolution of geochemical conditions occurs. The transition of the bacterial community from one electron acceptor to another is an important topic with regard to bioremediation or the natural attenuation of redox-sensitive radionuclides, but also in marine sediments where steep redox gradients control the cycling of iron, manganese, and carbon (Thullner et al. 2005; Van Cappellen and Gaillard 1996).

Current microbial-biogeochemical models for reactive transport lack a suitable mechanistic treatment of these processes at the cellular level. This seriously hampers our ability to predict behavior under a range of conditions and environments. The few existing models that couple the processes are largely empirical and do not account for effects of the local geochemical environment (especially nutrient and solute fluxes) on metabolic rates, even though these ultimately govern the overall rates of subsurface reactions. For example, these simulators typically include “yield factors” in their kinetic rate laws that specify the partitioning of the nutrients between growth and metabolism as a constant. Or the switchover from the use of one electron acceptor to another (e.g., iron(III) to sulfate) is handled with empirical “inhibition” functions that do not capture the dynamic interaction between the bacteria and their environment and between biotic and abiotic chemical cycles (Brun and Engesgaard 2002; Thullner et al. 2005).

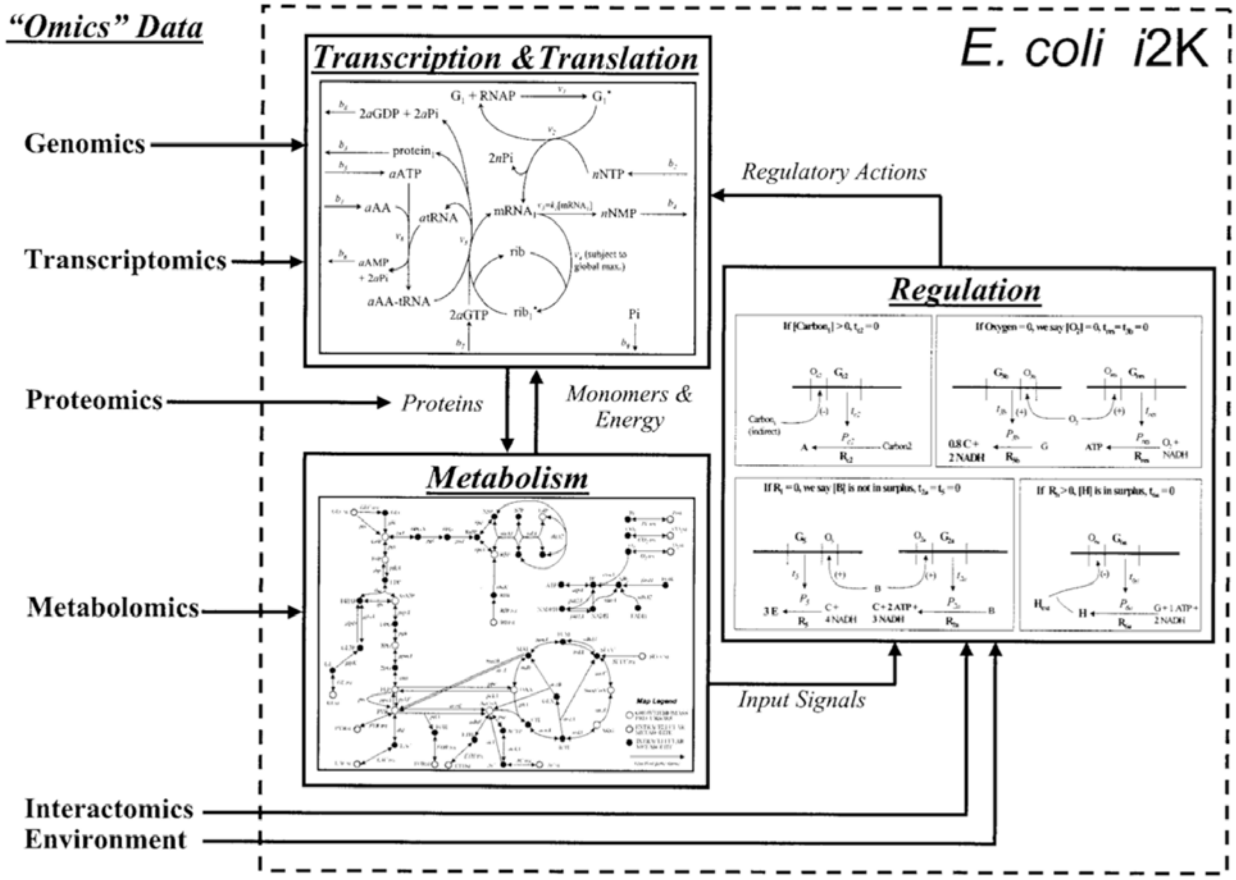


Figure 20. Integrated constraint-based model of *E. coli*. Modeling frameworks for metabolism, regulation, transcription, and translation have been developed; connectivity between these models is shown. The model can be used to reconcile diverse "omics" data. (Reed and Palsson 2003; Copyright © 2003, the American Society for Microbiology. All rights reserved.)

Experimental investigations of the mechanisms and rates of energy/electron-transfer across the microbe-mineral interface have been initiated. These processes can be implemented in numerical models to simulate biofilm dynamics in porous media coupled to extracellular geochemical reactions such as sorption, precipitation, and redox alterations. Other microbial community responses such as signaling and motility can be implemented numerically as well to capture the functioning of the biofilm as a whole as it interacts with its pore environment. In this way, metabolic activities that take place at the cellular level can be extended via modeling to the biofilm scale.

In silico methods are being developed that allow for the incorporation of "omics" data (see Figure 20), including genomics, proteomics, transcriptomics and metabolomics (Allen and Palsson 2003; Palsson 2002; Reed and Palsson 2003). The coupled *in silico* biogeochemical model developed in this research effort will be linked with next-generation pore-scale models for hydrodynamic flow, transport, and geochemical reactions (see Figure 21). Combined with petascale computing, it will be possible, and increasingly useful, to simulate the interactions between the biotic and abiotic geochemical cycles at increasingly larger spatial scales.

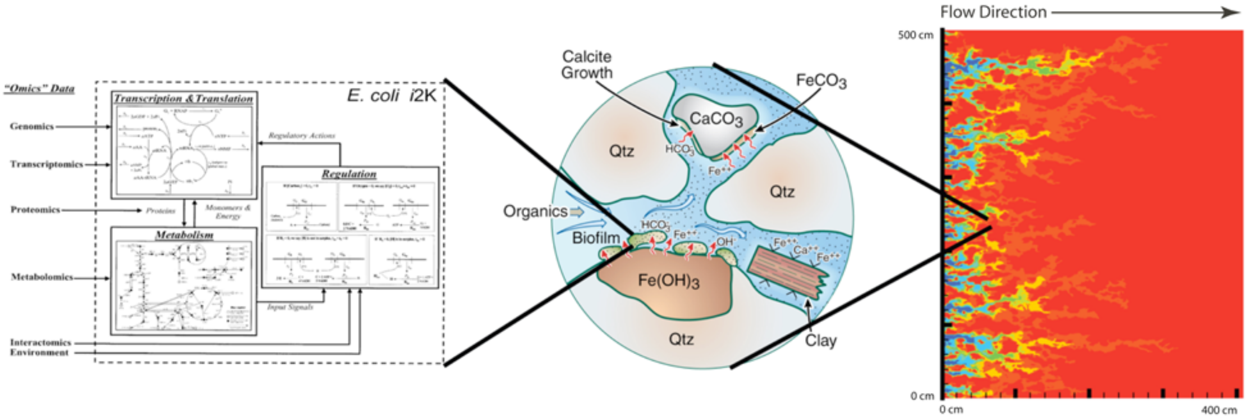


Figure 21. Coupling of *in silico* models with biogeochemical processes (Fe(III) reductive dissolution, carbonate precipitation, transport and sorption) at the pore scale, with upscaling to the continuum (cm to meter) scale. (Merged figures from Reed and Palsson 2003, copyright © 2003, the American Society for Microbiology, all rights reserved (left); Steefel et al. 2005 (middle); and Steefel 2007 (right).)

CONCLUSION

Underground storage of carbon and geologic disposal of nuclear waste involve processes on time scales of hundreds to hundreds of thousands of years, and spatial scales up to tens of kilometers. The large time and space scales involved make modeling and simulation essential tools for design, performance assessment, operation, and monitoring of such facilities. The complexity and multiscale nature of the physical and chemical processes that would be induced by these systems place demands on modeling capabilities that go far beyond the current state of the art in oil and gas reservoir engineering and groundwater hydrology.

There is a need and an opportunity for developing modeling capabilities that, by establishing a fundamental understanding of the response of complex geologic systems to strong anthropogenic perturbations, can provide a sound scientific basis for engineered storage and disposal facilities. The key to such understanding is representing interacting processes on the scales on which they actually occur, using parameters derived from first principles that are appropriate for the scale on which they are used. Much research is needed to establish mathematical descriptions for multiscale physical and chemical processes, and to derive needed thermophysical, chemical and constitutive properties from first principles. Numerical implementation of such multiscale process descriptions for field systems constrained by diverse sets of hard and soft data will require revolutionary advances in scaleable algorithms to be able to take advantage of future petascale computing facilities. A basic science program driven by these objectives will yield broad technical and economic benefits for utilizing and protecting subsurface resources and underground space.

In addition, the geoscience community needs the capability to incorporate and quantify the interactions between microbial populations and their geochemical environments in models of natural and perturbed geologic systems. These biogeochemical interactions may impact the evaluation of CO_2 storage, and the fate and transport of metals and radioactive elements.

GRAND CHALLENGES

COMPUTATIONAL THERMODYNAMICS OF COMPLEX FLUIDS AND SOLIDS

INTEGRATED CHARACTERIZATION, MODELING, AND MONITORING OF GEOLOGIC SYSTEMS

SIMULATION OF MULTISCALE SYSTEMS FOR ULTRA-LONG TIMES

COMPUTATIONAL THERMODYNAMICS OF COMPLEX FLUIDS AND SOLIDS

ABSTRACT

New modeling strategies for geochemical systems at the fundamental scale (atomic to single pore) are required to analyze the long-term storage of greenhouse gases and nuclear waste. The chemical complexity of the principal actinide components of spent nuclear fuel (e.g., the presence of highly correlated and poorly screened *f* and *d* electrons) and the complex nature of their transport in aqueous formation fluids requires the development of simulation tools based on interactions calculated directly from the electronic Schrödinger equation (i.e., first-principles methods). Further improvement of the efficiency of present methods based on the Density Functional Theory (DFT) and new higher level approximations to the solution of the Schrödinger equation will be required to provide quantitative estimates of the geochemical processes involved in waste mobilization and migration. However, even with optimistic projections of improvements in performance of first-principles simulation tools, the time scales required for analysis of these processes may be several orders of magnitude longer than can be achieved. For these situations strategies must be developed to extend the time frames of simulations while retaining the chemical specificity of the materials involved.

For CO_2 sequestration problems it is likely that very high accuracy empirical interactions at the molecular level could be developed from high level theoretical calculations and data. Nevertheless, to achieve the accuracy required for thermodynamic predictions under the extreme conditions expected in applications will require a large simulation effort and development of highly scalable free energy or Gibbs ensemble algorithms. Experimental data for mixed systems will be needed to complement simulation approaches.

Even with the development of fast solvers and methods to upscale the calculations, computed and experimental data will have to be incorporated in Equation of State (EOS) models for application to real problems (e.g., for use in hydrological simulators). EOS methods need to be further developed to treat the reactive and multiphase chemistry of complex mixtures. For closed shell inert gas systems (e.g., H_2O, CO_2, N_2, O_2 mixtures), simulation may be used to supplement experimental data. However, for more chemically complex systems such as the actinides, the principal contribution of simulations will be to analyze complex solution speciation and oxidation-reduction chemistry. This information is essential to develop empirical EOS for parameterization with laboratory data. There is a critical lack of data in many systems, and it is essential that this information be expanded to facilitate development of more reliable models.

EXECUTIVE SUMMARY

Strategies are being developed to sequester both CO_2 and radioactive waste in geologic formations. An unusual feature of these containment strategies is the extraordinary length of time that the integrity of the storage facilities must be maintained (hundreds of years for CO_2 storage/sequestration and 10^6 years for nuclear waste storage). Since these time frames are orders of magnitude longer than any laboratory simulations and the effects of many unpredictable subsurface processes (e.g., seismic events) cannot be simulated in the laboratory, highly accurate models of geochemical interactions that span these time scales must be developed.

The principal mechanism for the transfer of nuclear waste materials into the biosphere is via aqueous phases contacting the containment canisters. The transfer of toxic species from the solid waste form to formation fluids is controlled by processes such as: speciation of radioactive solutes (e.g., UO_2^{2+}(aq) and Pu(IV) hydroxides) in the fluid phase; solubility of associated mineral phases; sorption of these species onto formation minerals; their sorption and subsequent transport on colloidal particles in the formation fluid. While the observed behavior of geological processes is on time scales of hundreds to thousands of years, the processes that are the origin of this behavior occur on atomic time and length scales of tenths of picoseconds (10^{-12} s) and several angstroms (10^{-8} cm). In addition, these processes retain the atomic specificity (chemistry) characteristics of their position in the periodic table (e.g., the complex chemistry of uranium and the transuranic elements). As a relevant example, spent nuclear fuel is 95% UO_2; the formal oxidation state of U in this species is +4 (U(IV)). However, the most abundant uranium oxidation state in aqueous solution species containing U is the formal +6 valence (U(VI) as UO_2^{2+}(aq)). The oxidation process that changes the insoluble (immobile) U(IV) species into soluble (transportable) U(VI) solution species is dependent on poorly understood atomic scale processes at the solution/solid interface.

The critical challenge of the model development required to insure the safety of waste storage strategies is both:

- To predict the complex chemistry of these system on the fundamental atomic scale
- To provide reliable tools to translate these behaviors to the many orders of magnitude larger scales of geological storage problems without loss of their fundamental atomic character

To reliably predict behavior of the actinide (uranium, thorium, plutonium, etc.) waste products of nuclear power production over the large range of conditions possibly encountered in a storage facility requires a theory based at the most fundamental level on the electronic Schrödinger equation. Many evaluations of this equation are required in any method that expands length and time scales. This is a grand challenge computational problem. However, remarkable improvements in the methods available to solve the Schrödinger equation, and the computational power available to implement such methods, have been made. In addition, new experimental methods based on advanced synchrotron light sources and new neutron sources are becoming available that will provide highly informative data at the atomic level to calibrate the accuracy of predictions. Considerable development still needs to be done to provide the level of accuracy required and to develop simulation tools that will be able to fully exploit the computational power of the new leadership class of computers soon to be in place.

The chemical issues involved with the prediction of the outcome of CO_2 sequestration are more manageable. The chemistry of these systems is typically much less complex, and interaction potentials at the molecular level can be developed using existing quantum chemistry methods. However, even for very commonly encountered systems such CO_2-H_2O, there are many regions of pressure, temperature and composition (P-T-X) variables required for storage applications that have not been explored, and the interactions of these materials with geological formations is

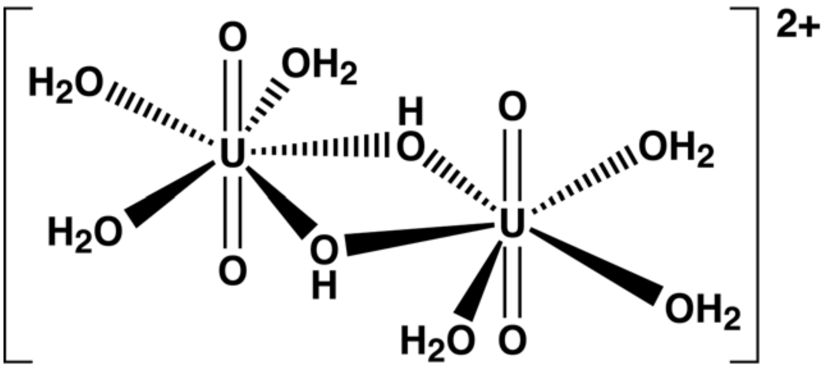


Figure 22. The structure of $[(UO_2)_2(\mu\text{-}OH)_2(OH_2)_6]^{2+}$. In a solution this would be solvated with four to five waters in the first shell and many in the surrounding region (Richens 1997, *The Chemistry of Aqua Ions,* copyright © 1997 John Wiley & Sons).

poorly understood. Direct simulation of the properties of these mixtures may be the most effective way to develop the required data. These simulations usually require free energy properties and therefore demand very large computational resources. New parallel algorithm development will be required to exploit the computational power of new classes of computers.

Even with the development of first-principles predictive capabilities, it must be kept in mind that while atomic detail is an essential starting point, averaged (i.e., thermodynamic) behavior is required for practical long-term prediction. Equations of State summarize the averaged behavior at the atomic level by providing thermodynamic potentials (here we are including irreversible thermodynamic properties, e.g., reaction rates, diffusion constants) and other properties (e.g., chemical rates) as a function of P-T-X that are required in higher-level predictive tools (e.g., reactive flow simulators). While the development of EOS has been a topic of research for many years, adequate EOS for many of the key mixtures encountered in storage applications are not available. Obviously these equations must incorporate the yet-to-be-discovered behavior of the complex systems that will be encountered in these storage problems. Unfortunately, because present EOS methods are poorly based in theory, they do not provide a very large range of extrapolation or interpolation, and are highly dependent on the availability of data. A key synergistic role of theory is to inform the development of EOS. Appropriate equations need to be developed that can more efficiently describe the chemical and physical properties of gaseous, liquid and solid mixtures. Nevertheless, it must be kept in mind that reliable EOS will, for the foreseeable future, have to be heavily based on experimental data.

SCIENTIFIC CHALLENGES

Understanding the chemical properties of aqueous electrolyte and nonaqueous solution phases, their mixtures and their interactions with solid mineral phases is central to the interpretation of energy applications, such as safe storage of nuclear waste (Ewing 2006; Bruno and Ewing 2006), sequestration of CO_2 in geologic formations, the transport of ore forming and toxic materials, the exploitation of geothermal energy, and others. For many systems the structure of species in solutions is complex and still very poorly known. For example, the presence of charged ions in aqueous solutions creates local structure (hydration shells) and local changes in the chemistry of the solution, such as changes in the acid/base chemistry, which may in turn create new species in solution. Examples of such species are oxyhydroxo polyions (e.g., $AlO_4Al_{12}(OH)_{24}(H_2O)_{12}$ and

$(UO_2)_2(\mu\text{-}OH)_2(OH_2)_6{}^{2+}$; see Figure 22), which have been shown to be the dominant Al(III) and U(VI) species for intermediate pH and concentration conditions (Richens 1997; Baes and Mesmer 1986; Soderholm et al. 2005; Clark et al. 1995). Their stability and chemistry influence transport, the kinetics of reactions in the solution phase, and interactions with solid phases, such as adsorption and other reactions in the interface region (Figure 23). The measurement of the structural and reactive properties of these species is difficult because of their amorphous and fluxional nature (Soderholm et al. 2005; Clark et al. 1995).

Fortunately, in recent years there has been a dramatic advance in both the theory available to calculate the properties of complex many-body materials and in the performance of computational platforms available for simulation. This was made possible by the DOE-sponsored high performance light sources and new neutron sources (e.g., X-ray, EXAFS, HEX spectroscopy, neutron scattering) and by the development of high resolution measurements (Brown 2001; Soderholm et al. 2005). The challenge is to continue the remarkable development of these technologies which will lead to a new level of understanding and control of processes as diverse as self-organization in colloids, the catalytic biochemistry of signal transmission in eukaryote cells, and the prediction of the chemistry that may occur under the extreme temperature and pressure conditions encountered in advanced nuclear power systems.

The complexity of the processes of interest (e.g., accurate treatment of the highly correlated and poorly screened *f* and *d* electrons in actinide and transition metal elements, complex bond breaking and formation, changes in bond valance and polarization, etc.) requires reliable predictions with simulation methods based on first-principles evaluation of forces (the calculation of forces directly from the electronic Schrödinger equation) (Marx and Hutter 2000; Valiev et al. 2002). The problem is made more difficult by the amorphous structure of the species of interest (e.g., the solvated uranyl dimer illustrated in Figure 22; the absorbed species in Figure 23), thus requiring many atoms to provide a complete description of chemical processes. Together these problems lead to a grand-challenge-level computational problem.

RESEARCH APPROACHES

Dynamical methods at the atomic time scale and upscaling

Currently the most efficient approximations to the solution of the electronic Schrödinger equation are based on the Density Functional Theory (DFT) approximation (Marx and Hutter 2000; Valiev et al. 2002). While simulations with this approximation are very efficient and the results adequate to provide reliable interpretations for many systems, there are limitations to the much wider applications of these simulations to more realistic models of technology problems. The most important of these are:

1. The DFT level of approximation to the electronic Schrödinger equation is not sufficiently accurate to treat many materials problems (energies and bonding in transition and actinide elements and long range (van der Waals) forces).
2. The scaling of existing solution methods is not sufficient to exploit the performance of the next generation parallel computers (tens to hundreds of thousands of processors).
3. Even with the improvements in scaling of these methods, the particle and time scales of many interesting processes are orders of magnitude larger than can be directly simulated.

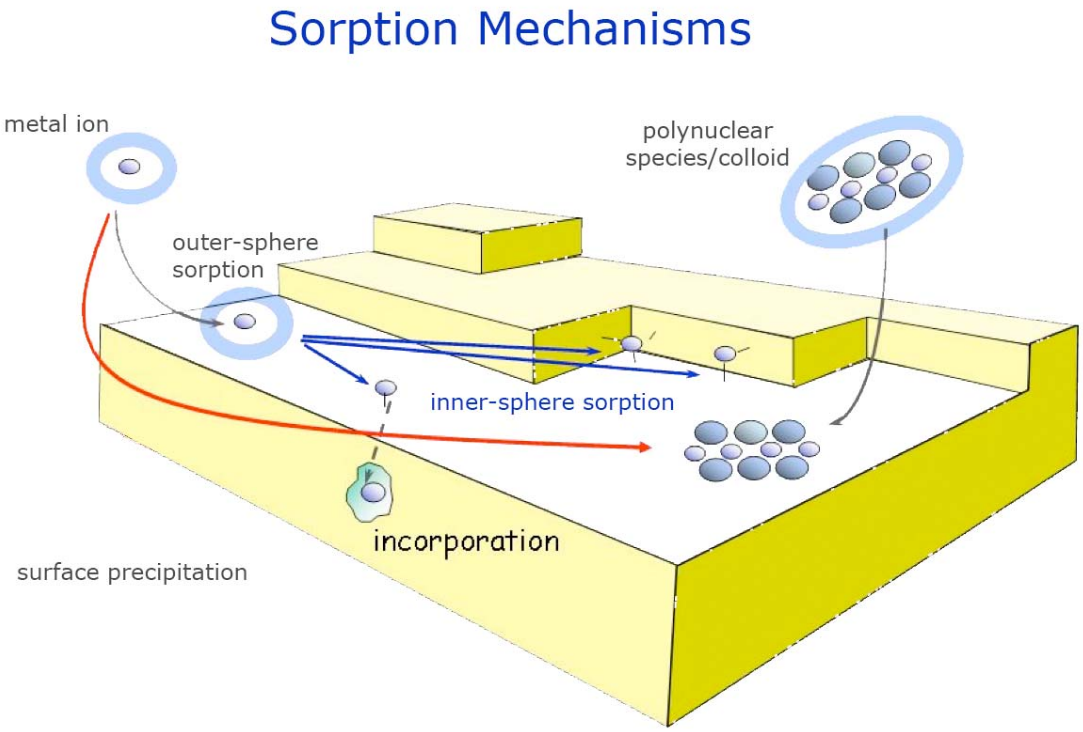
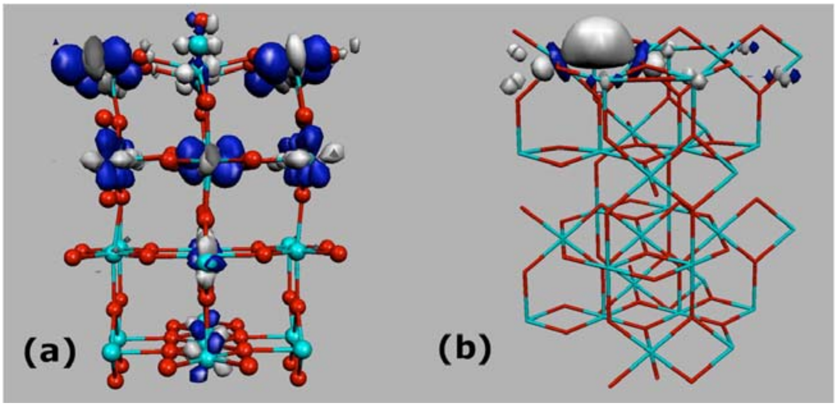


Figure 23. Schematic illustration of the numerous chemical species and processes that may occur at the mineral-water interface. (Manceau et al. 2002; copyright © 2002, the Mineralogical Society of America. All rights reserved.)



Courtesy of J. Weare (UCSD), E. Bylaska (PNNL), and K. Tsemekhmam (U Washington)

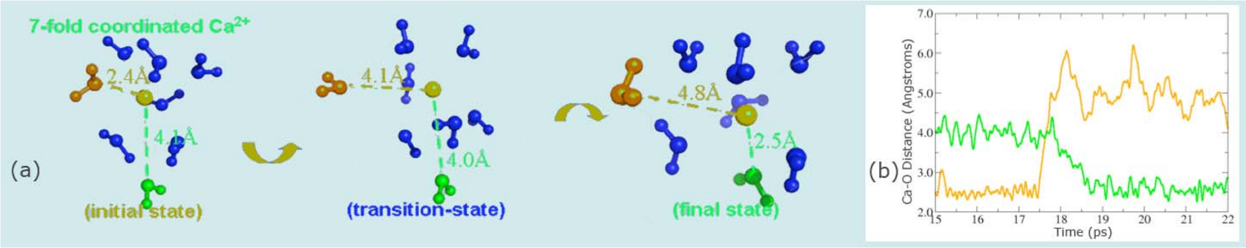
Figure 24. (a) TiO_2 hole delocalized around defect; DFT with no exchange. (b) Same as (a) with exchange-corrected DFT.

The first two of these problems require innovative improvements in solver methods and implementations. For example, the exchange-correlation functionals used in DFT approaches must be generalized to treat actinides and transition metals and oxides with highly localized *d* and *f* electrons in their valence shells. Existing DFT approaches which include electron exchange in a self-consistent way (e.g., exact exchange, Self Interaction Correction (SIC), LDA+U) (Kudin et al. 2002; Kulik et al. 2006) provide at least semi-quantitative accuracy and relatively high efficiency. An example of the effect of exchange on electron localization in a mineral system is given in Figure 24. In this problem, DFT calculations (Figure 24a) yield a completely delocalized spin density (incorrect), in contrast to the predictions of an exchange localized spin density when self-interactions are taken into account (Figure 24b; correct). The proper inclusion of exchange may have a dramatic effect on the reactivity of surface defects. Scalable algorithms that include exact exchange need to be developed for first-principles dynamics.

A more difficult problem with the DFT method is that long-range non-bonded (van der Waals) interactions are not included formally in the theory. These interactions dominate many problems of interest to subsurface modeling. The inclusion of exact self-consistent exchange as above is not sufficient to improve the accuracy for these problems. They can be treated by using high accuracy molecular orbital-based methods, e.g., MP2, or CCSD(T) (Bartlett 2005), or Quantum Monte Carlo methods (Grossman et al. 2001). However, these methods are currently too costly. New techniques may broaden their applications to much more complex systems (Kowalski and Valiev 2006; Valiev and Kowalski 2006). A critical research area is the development of higher levels of approximation for the electronic Schrödinger equation that can be used with dynamic methods in a computationally efficient manner.

Significant improvements in algorithm performance, scalability and implementation are required to treat important energy applications using any level of solution to the Schrödinger equation. For example, currently an *ab initio* molecular dynamics simulation of 128 water molecules for 0.1 picosecond (ps) requires about 1000 CPU hours, 30 ps about 34 CPU years! The projected size of the next generation supercomputers (10,000–100,000 processors) suggests that simulation times and particle size limitations could be overcome by brute force increases in computer size. However, there is a substantial problem in the parallelization of the Fast Fourier Transform (FFT) method that is critical to solving the electronic motion problem with plane wave DFT. Available implementations of present methods do not scale much beyond 1000 processors. There are fundamental reasons for this limitation which are difficult to overcome. The question of proper approximation in terms of discretization and the (separate) question of proper choice of iterative methods need to be addressed. More efficient and/or better scaling methods could be based on the use of completely unstructured simplex finite element or wavelet techniques (Harrison et al. 2004) built adaptively (Bank and Holst 2003) using a multilevel solve-estimate-refine iteration. Scaling can also be improved by finding methods to hide the latency in the calculation (Sorenson and Baden 2006).

The third problem demands new methods of upscaling both in number of particles tracked and time. The particle numbers included in a calculation can often be greatly increased by dividing the problem into a region in which quantum chemistry is required and a region in which a much more efficient molecular mechanics description of the forces is adequate, referred to as QM/MM (Quantum Mechanics/Molecular Mechanics) approaches (Field et al. 1990; Eichinger et al. 1999). These methods need to be made more efficient by coupling to faster solvers of the electronic Schrödinger equation. A promising way to upscale time is the introduction of rare event strategies. These approaches recognize that the important dynamics of a system—those that dramatically change the structure of the system as in a chemical reaction—occur rarely (see Figure 25). There are a number of ways to search for rare events. However, most of these have been designed for problems with only a few degrees of freedom. One class of methods accelerates or makes more efficient the exploration of phase space either by using higher



Courtesy of John Weare, UC San Diego

Figure 25. Water exchange in the hydration shell of Ca^{2+}+64H_2O first-principles simulations. Note that in the trajectories in the right panel the change in structure occurs in a few ps, whereas the process occurs on a time scale of greater than 40 ps.

temperature dynamics or by modifying the energy landscape so that rare events become more probable (Laio et al. 2002; Voter et al. 2002). This class of methods has the advantage that local minima in the system do not have to be determined before the search starts. In another class of methods, it is presumed that the local minima are known (very often this is the case in chemical reactions with known mechanisms), and the focus of the method is on determining the barrier to transition. There are several methods for doing this; for example, the Nudged Elastic Band (NEB) method (Henkelman and Jonsson 2000). This method works well for systems with few degrees of freedom. However, in a noisy system with many degrees of freedom, a method of averaging out unimportant environmental variations in the structure is necessary. New methods need to be developed that search for reaction pathways, including minima in noisy, many-dimensional environments. An example of such a method combines minimum free energy path finding and sampling to average out the environmental noise (Weinan et al. 2005). Given rare event paths, methods may be introduced to calculate the free energy and estimate the reaction rate using absolute rate theory. With these rate estimates, much longer time scales can be simulated using kinetic Monte Carlo dynamics (Voter et al. 2002).

Equations of State for complex systems

To translate the advances in atomic level dynamical simulation described above into useful applications at the macroscopic level, efficient equations that succinctly summarize experimental and computational data for use on the macroscopic level must be available (e.g., a rate equation or, more commonly, an EOS). The EOS should provide a succinct representation of the thermodynamics of the system that can capture the variation of the free energy, including changes in phase, speciation in solution, etc., for a wide range of intensive variables. There has been considerable research effort in this area. However, there are very few EOS that represent thermodynamic behavior with the accuracy that is required for energy applications. For many of these problems the molecular understanding is so poor that it is not possible to develop thermodynamic models at the macroscopic scale. The best way to begin to obtain this understanding may be through molecular level simulation as discussed above. It is likely that to obtain the required accuracy it will be necessary to develop models tailored to describe specific states (e.g., solids, liquids, gases, polyions, colloids, solid solutions) rather than search for a single EOS representation that will describe all physical states.

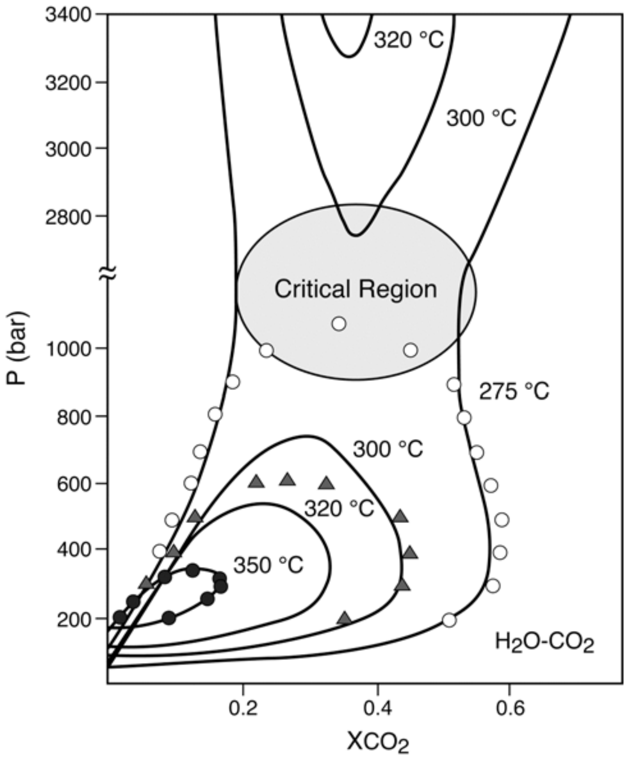
Essential data collection for Equation of State (EOS) development

In applications to real-world problems, EOS formulations must be parameterized from highly accurate data sets for fluid mixtures over a range of pressures, temperatures and compositions (P-T-X) that are as close to the intended application as possible. It is surprising that even for common systems (e.g., CO_2-H_2O-CH_4, Al^{3+}-H^+-H_2O-salt), sufficient data do not exist to parameterize a model. In fact for the aluminum system (the most abundant metal in the earth) there is insufficient information to even uniquely define the aqueous solute species and their activities for temperatures from ambient to critical temperatures of water. Yet the aluminum system is one of the most complete data sets. There are fewer data for other charged systems, such as Fe^{3+} and UO_2^{2+}, that are encountered in applications such as carbon sequestration and nuclear waste isolation. Solid mineral stability data are also not available for essential systems. For these materials the likely future contribution of modeling methods (simulations) will be to identify the speciation in solution. This is an essential step in the development of an EOS that succinctly reproduces the behavior of the system and can be parameterized from the limited data that are likely to be available. A short list of essential data needs includes:

- Equation of State and thermodynamic mixing properties of the system CO_2-H_2O-CH_4 over a wide P and T range
- Thermodynamics of gas hydrates, with the possible exception of methane hydrate whose properties are reasonably well known
- Properties of two phase mixtures of aqueous brines and high CO_2 gas phases, including densities, over a wide P-T-X range
- Solubility of minerals in aqueous electrolytes and nonaqueous mixtures with emphasis on expanding the database for the modeling of aluminum silicate minerals (feldspars, zeolites, etc.) for a range of temperatures up to 300°C and for important species encountered in natural and anthropogenically altered waters (SO_4^{2-}, F^-, etc.)
- Descriptions (including theoretical equations) of activities in concentrated multicomponent salt solutions over a wide P-T-X range
- Thermodynamics of major component solid solution mineral phases, including those such as carbonates, in which order-disorder phenomena are important
- Thermodynamics of clays and zeolites, including their ion exchange properties
- Thermodynamics of incorporation of minor and trace elements (including actinides) into mineral solid solutions
- Thermodynamics of mineral phases with ions of variable valence, including iron
- Thermodynamics of corrosion products of nuclear fuel, including U(VI) phases

The fact that most of these are old problems does not make their solution less necessary. There are opportunities here for the interaction of modern experimental and computational approaches, and there is a need for complete and easily accessible databases.

For some systems (e.g., CO_2, H_2O, O_2, N_2, CH_4) it should be possible to develop molecular dynamics models that can calculate phase equilibrium and thermophysical properties from first principles. For these systems it would be worthwhile to pursue the development of very high accuracy interaction models at the molecular level (i.e., for CO_2-H_2O, CO_2-CH_4 interactions). These could then be used to simulate thermodynamics for these systems via molecular dynamics and Monte Carlo methods. While this is not a difficult simulation *per se*, the magnitude of the problem grows quickly when desired results are thermodynamic data, especially free energy data. The scaling of present day simulation algorithms is not good, and it is important to develop highly scalable algorithms, including those that directly simulate free energy, for implementation on future generation computers.

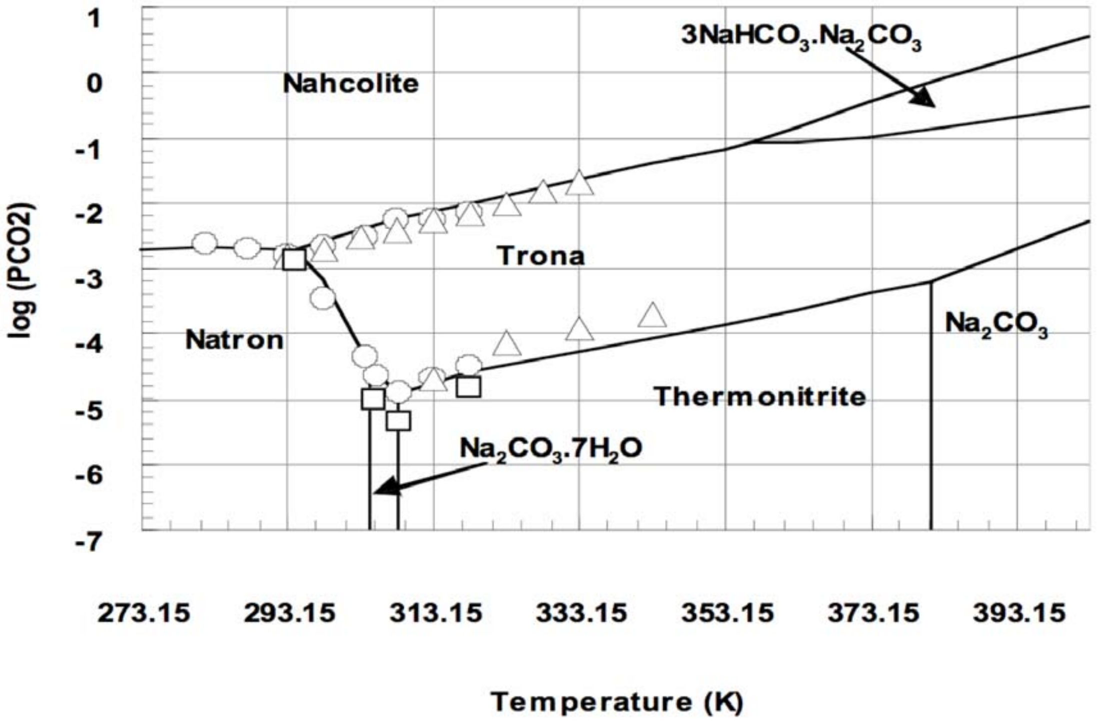


Courtesy of John Weare, UC San Diego

Figure 26. Pressure-composition predictions of EOS for the CO_2-H_2O system. Curves represent EOS predictions and symbols represent experimental data.

EOS for compressible mixtures. For these systems the most convenient variables are usually the temperature, volume (or density), and the composition. The appropriate thermodynamic function on which to base an EOS is then the molar Helmholtz free energy. All other properties, e.g., the enthalpy, may be derived from this function by the appropriate derivatives. To provide optimal interpolation and extrapolation of mixing properties, the functional form of the free energy should be based on a reasonably accurate molecular-level description of the system. The thermodynamic perturbation theory originally introduced by Pople (1954) provides a framework from which such an EOS may be generated (see Gubbins 1985 for a review). To provide the high level of accuracy necessary for quantitative description of thermodynamic data, empirical corrections must usually be added to the EOS. This level of the theory was successfully applied to the qualitative analysis of polar fluids and has been used to treat polar systems including those containing associated ions. An example of the accuracy that can be obtained from such an approach is given in Figure 26 (Weare, unpublished results based on the EOS of Duan et al. 1992). Note the poor behavior of the EOS in the critical region. Special scaling methods must be developed to treat this region (Kiselev and Friend 1999). The development of these methods will be required for application to complex speciation in mixtures.

EOS for liquid density complex mixtures of aqueous electrolyte solutions and mixtures with other nonaqueous solutions. For nearly incompressible aqueous mixtures, highly accurate EOS are available provided the mixing behavior of the system can be described (Pitzer 1987; Weare 1987; Christov and Moller 2004). Examples of the results of these models for complex mixtures are illustrated in Figure 27.



Courtesy of J. Weare

Figure 27. Solubility of carbonate minerals as a function of temperature and pCO_2. Triangles, squares and circles represent experimental data; lines represent EOS predictions (Moller et al. 2005).

The principal limitation to the development of accurate EOS models of the fluids encountered in the application of energy strategies is the lack of understanding of the speciation (e.g., the structure and dynamics of polyions and colloids) present in the liquid phase. For example, even for the Al system, one of the most common elements in the Earth's crust, we have a very incomplete understanding of the speciation in solution.

EOS models for mixtures of aqueous electrolytes and nonaqueous mixtures also have important applications to CO_2 sequestration in salt formations. Recently there has been progress in the development of Mixed-Solvent Electrolyte (MSE) models that have been shown to accurately predict the thermodynamics of electrolyte solutions extending to the fused salt limit and over a broad range of temperatures in aqueous-solvent mixtures. The development and application of such new approaches to chemical systems involving salt brines-CO_2 mixtures could greatly enhance our ability to predict the chemical changes in deep geologic systems of importance in CO_2 disposal. As in other areas, there is an important need for the development of more first-principles-based EOS methods in this area. EOS based on a fundamental understanding of the species present in the phases are important to reduce the dependence on data and extend the extrapolation of the EOS region of reliability outside the range of the data.

EOS for solids, solid solutions and absorbed phases. Current EOS for mineral systems are essentially empirical. For pure minerals this is not a problem as long as data exist to parameterize the temperature-pressure dependence. On the other hand, even commonly encountered solid phases such as dolomite can be very complex solid solutions, with like-like and like-unlike clustering, microcrystallization, defect structure, and other non-ideal properties. Of course, solids under extreme conditions of radiative flux or high temperatures or pressures can develop numerous internal defects. These systems are at best only at local equilibrium. Without a more refined understanding of these materials on the atomic scale, it is difficult to reduce this behavior to an EOS representation as required for the analysis of subsurface problems.

Local thermodynamic EOS for colloids and surface adsorption. Typically colloidal particles suspended in aqueous solutions contain hundreds of thousands of atoms. For systems this large the possibility of developing a finite system thermodynamic description should be investigated. As in infinite solid solution systems, the effects of clustering, local structure, and surface compositional variation are difficult to quantify. For these systems the large ratio of surface area to bulk volume should be included in a thermodynamic treatment. However, recent calculations of the stability of atmospheric aerosols using models based on bulk thermodynamics have shown remarkable agreement with available measurements (Moller and Weare, unpublished results).

The chemical interaction of the surface of aqueous colloidal particles with solutes and solvent species (e.g., sorption, dehydration, surface reactions, etc.) may be simulated with the first-principles methods discussed above. Because of the complexity of the chemistry in the surface region, many particles in the surface and interface must be included in the simulation. While such simulations are today limited to 500 or so particles, the processor scaling issues that are discussed above as limitations are less of a problem if the system size is increased. This means that with the availability of many more processors with next generation computers, it will be possible to treat on the order of 1000 particles using present software. Other ways to expand the size of the system without loss of accuracy, such as the QM/MM approach discussed above, should be explored. In addition there are ways to upscale time to provide rate information using free energy simulations and transition state theory (Voter et al. 2002). Extensions of such methods should be explored to treat problems such as colloidal coarsening and surface structure (including local ordering) and chemical reactions at the interface.

The state of species adsorbed on solid and colloidal surfaces and their chemistry is a problem of great importance to solute transport, mineral formation and dissolution, oxidation and reduction of solute species, etc. To treat these systems, quasi-thermodynamic models of surface complexation have been invoked on an *ad hoc* basis (Dzombak and Morel 1990). These models work remarkably well when there are sufficient data for parameterization. With the development of the new surface probes discussed above, a much more precise, atomic-level view of the surface interface region is becoming available. This is again a fertile region for the application of first-principles methods of simulation using the QM/MM methods described above. As in the other areas in which these methods might be applied, the objective of these calculations is the development of an atom-based structural and dynamic view of the interface region (effects of local structure and defect structure as adsorption sites, formation of surface islands; see Figure 23). This level of understanding would be used to develop more accurate phenomenological models for the interface region.

Data collection vs. molecular simulation for EOS development. It is important to emphasize that for reliable application to real problems, EOS must be parameterized from the largest data sets possible in intensive parameter regions close to the region of application. This is because high accuracy, theoretically-based EOS with good extrapolation properties are not available for even slightly complex systems (Gubbins 1985). It is surprising that even for common systems (e.g., CO_2-H_2O-CH_4, Al^{3+}-H^+-H_2O-salt), sufficient data do not exist to develop an accurate EOS. For example, for systems containing aluminum, the most common metal in the earth's crust and an ubiquitous component of natural waters, there is insufficient information to even uniquely define the speciation in solution (e.g., the formation of polynuclear hydroxide species, etc.) (Baes and Mesmer 1986). This is also the case for solutions containing other charged ions important to DOE applications, such as Fe^{3+}, UO_2^{2+}, etc. Without this knowledge, the development of reliable thermodynamic models with good interpolation and extrapolation properties is not possible. For these systems the likely contribution of simulation methods in the next generation will be to understand the relative stability, composition and structure of species (e.g., ion pairs, metal ion polymers) in the solution. This is an essential step in the development of an EOS that reproduces the behavior of the system with near-experimental accuracy and can be parameterized from the limited data likely to be available.

For closed shell uncharged molecules (e.g., CO_2, H_2O, O_2, N_2, CH_4), it should be possible to develop molecular dynamics models that can calculate phase equilibrium and thermophysical properties from first principles. For these systems it would be worthwhile to invest in the development of very high accuracy interaction models at the molecular level (i.e., for CO_2-H_2O, CO_2-CH_4 interactions; see Cao et al. 2001). These could then be used to simulate thermodynamics for these systems via molecular dynamics and Monte Carlo methods. While this is not a difficult simulation, the magnitude of the problem grows quickly when the desired result is thermodynamic data, especially free energy data. Even for these systems the scaling of present day simulation algorithms is not good (less than 200 processors) (Fitch et al. 2006). It is important to develop highly scalable simulation algorithms, including those that directly simulate free energy for future implementation on next-generation computers.

INTEGRATED CHARACTERIZATION, MODELING, AND MONITORING OF GEOLOGIC SYSTEMS

ABSTRACT

To seriously consider geological opportunities for waste sequestration, public health and safety demand a uniformly excellent characterization of potential subsurface sites. Subsurface systems pose some of the most challenging characterization and modeling problems in science. The challenges arise largely from the inaccessibility and complexity of the subsurface system, a wide continuum of relevant scales of variability, the potential role of coupled nonlinear processes, and the importance of detailed results to human health, society, and ecological systems. Progress in simulating subsurface performance of a potential disposal site requires improved understanding of geological processes and the effective integration of high-resolution geophysical measurements into model development and parameterization. In addition, to fully integrate characterization and modeling will require advances in methods for joint inversion of coupled process models that contain important nonlinearities, scale effects, and uncertainties.

Advanced monitoring approaches are needed to improve our understanding of subsurface system responses to large-scale manipulations and to detect releases associated with the manipulations that may pose a risk to living organisms and earth systems. Scientific advances in the integration of disparate monitoring datasets and in the coupling of monitoring and modeling approaches are expected to lead to an unprecedented ability to quantify and predict subsurface system transformations associated with large-scale anthropogenic manipulations over relevant spatial scales and over decadal to century time frames. Technological advances will include the development of systems that can be routinely used to detect and quantify phenomena that provide the earliest indication of anomalous responses that may portend impending failure of a manipulated system.

EXECUTIVE SUMMARY

Modeling practices in geosciences currently deal with variations in length scales (from atoms to planets), variations in observable data, and variations in physical, chemical and hydrological constitutive relationships, in a piecemeal, *ad hoc* and disparate manner. If significant progress is to be made in understanding reservoir-scale geological systems and predicting the behavior of these systems under anthropogenic perturbations, then forward and inverse modeling must integrate across scales, data types, and geological processes. Increasingly large and disparate data streams need to be incorporated into modeling systems in a comprehensive and adaptive way. Furthermore, new techniques are needed to quantify uncertainty in model predictions and conclusions that arise from data limitations, modeling approximations, and non-uniqueness.

The datasets that must be integrated for large-scale, complex geologic systems come from a combination of local measurements and remote sensing techniques. Subsequent monitoring approaches will be based on repetitive collection of similar data. Hence, characterization of the subsurface, modeling of processes occurring there, and monitoring of these processes are inextricably linked. The basic science challenges involve developing improved theoretical, mathematical and computational approaches for using multiple hydrological, geochemical, geomechanical and geophysical datasets into a cohesive subsurface understanding of dynamic system behavior. Particular challenges are associated with:

- The ability to use remote datasets to provide quantitative estimates of subsurface processes
- The integration of multiple types of monitoring datasets that sample different parameters over different time and space scales
- The coupling of advanced monitoring and multiphase modeling to improve our understanding and predictability of subsurface responses to large-scale anthropogenic manipulations over decadal to century time scales

Such a revolutionary improvement in geosystem modeling will require breakthroughs in applied mathematics, computational science, numerical methods, and inverse theory; a simple retooling of existing codes will not achieve the desired results. Coupling relationships between critical geophysical, geochemical and geological properties need to be established and quantified through new efforts in laboratory studies, *a priori* modeling, and examination of field data. The impact of this work will be an ability to generate meaningful interpretations from large and disparate datasets through a data-driven modeling approach, along with model-driven data collection and monitoring focused by insights obtained from the modeling. Examples of scientific impacts include:

- An unprecedented quantification of coupled hydrogeological-geochemical-geomechanical processes under both natural and perturbed conditions that will lead to a new understanding of critical behavior at relevant scales
- Improved imaging, inverse, and coupled monitoring-simulation capabilities that promote a better understanding and prediction of complex and coupled subsurface responses to perturbations over decadal to century time scales
- Identification of rare, extreme mechanisms that may be triggered by large-scale manipulations, but may not have been recognized during the development of the initial conceptual model

An important technological advance of integrated characterization and monitoring will be the development of systems that can be routinely used to detect and quantify phenomena that provide the earliest indication of processes that are unexpected in the manipulated system. A particularly important example is the development of monitoring technology and strategies for early identification and quantification of CO_2 leaks, so that the hazard can be mitigated or remediated before the overall storage system integrity is compromised.

SCIENTIFIC CHALLENGES

Optimal detail in geological modeling

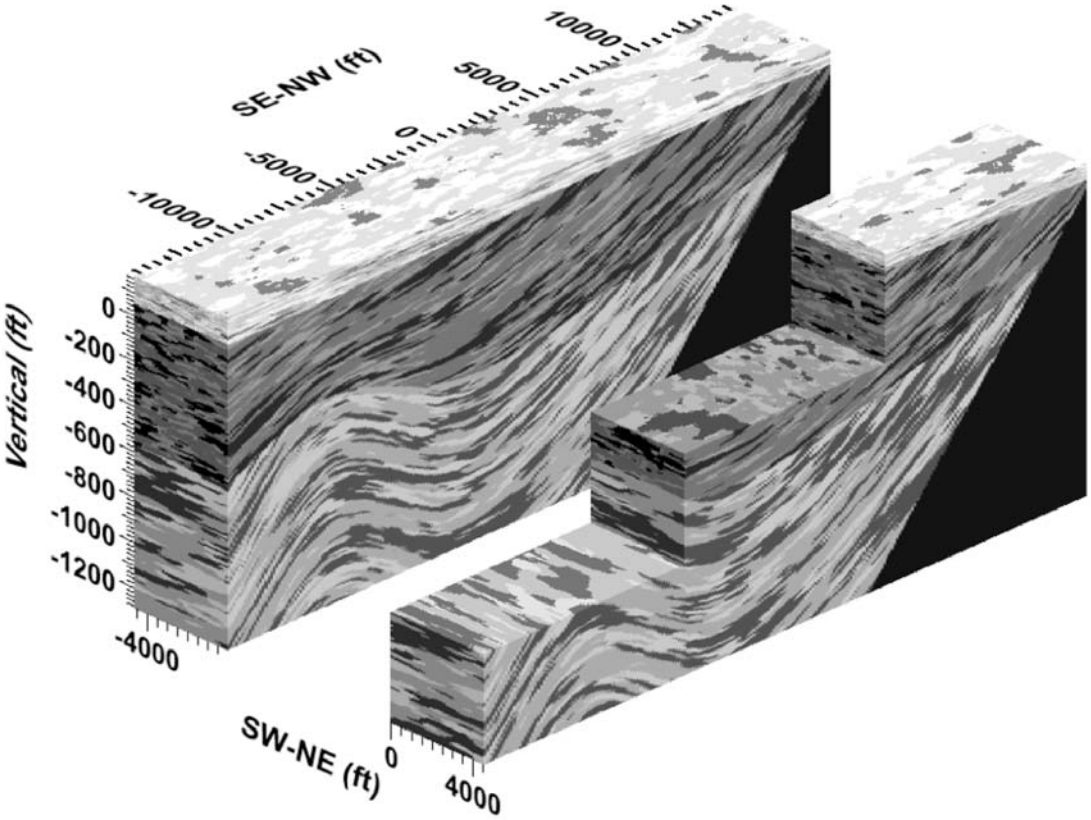
Energy-related problems in the geosciences involve consideration of a multitude of physical and geochemical processes that are active over a wide range of spatial and temporal scales. A comprehensive simulation framework must be flexible enough to exploit and adapt actively to integrated coupling of processes over this continuum of scales. The characteristics of such a framework are described elsewhere in this report. There are currently fundamental limitations in the ability of models to represent all necessary scales and processes of interest in an integrated manner. These limitations are compounded by constraints in available computational resources. Even with anticipated advancements in modeling theory, numerical methods, and computational capabilities, practical limitations in modeling the complex systems of interest in the geosciences are likely to remain.

Current modeling practices decouple both scales and physics, and integrate data, in an *ad hoc* manner. A rigorous paradigm for treating these problems in the geosciences is missing. This is critical because incorrect treatment may lead to a gross accumulation of errors due to strong nonlinear couplings. Such strong nonlinearities are frequently encountered in multiphase flow (including partially saturated flow in the vadose zone), reactive transport, and geomechanics, although the spatial and temporal scales at which these processes need to be resolved are different. There is a clear and urgent need to resolve these highly nonlinearly coupled processes in a way that preserves a theoretical and practical understanding of modeling and discretization errors. The scientific challenge is to determine the optimal level of modeling detail required to answer specific questions with minimum violation of underlying physics and chemistry. Model error is thereby constrained, enabling models to provide an adequate representation of observed system behavior. One way to explore what levels of geologic detail are optimal is to work with models that are rich in details. Such geologic modeling is a challenge in itself, and is addressed in the next section.

Geologic process models of subsurface structure and heterogeneity

Large-scale injection of fluids into the subsurface will drive a major new research agenda focused at understanding geological architecture and geomechanics at spatial scales ranging from the radius of the wellbore to the scale of basin-wide aquifers. At the local scale, the research will be driven by concerns about injectivity of the fluids, its subsequent near-field migration path, and potential fluid trapping mechanisms. At the large scale, the research will need to extend the principles of basin analysis that have evolved in the oil industry and academia over the past few decades (e.g., sequence stratigraphy, deep basin fluid circulation, 3D basin modeling).

Substantial uncertainty is inherent in defining variable spatial patterns in rock properties at relevant scales. This uncertainty can be reduced through collection of additional data and new measurement technologies, but it can almost never be eliminated. Subsurface scientists have made important strides in dealing with uncertainty through the use of stochastic (geostatistical) descriptions of subsurface heterogeneity (e.g., Deutsch and Journel 1998; Carle et al. 1998; Figure 28). The stochastic methods suffer, however, from limitations in their ability to include certain geologic structures (e.g., meandering patterns, faults, and permeability heterogeneity) that can be crucially important in mass transport analyses (e.g., Western et al. 2001; de Marsily et al. 2005; Zinn and Harvey 2003). For example, the two spatial patterns in Figure 29 have the same probability densities and omnidirectional variograms, yet their connectivity is much different. Such spatial organization arises from the geological processes that laid down or modified the rocks, and will ultimately be best incorporated through a new generation of stochastic or stochastic-deterministic methods that account for the geologic processes themselves (de Marsily et al. 2005). Relatively new geostatistical approaches, such as the transition probability Markov chain approach (Figure 28 and Carle and Fogg 1997; Carle et al. 1998) and multiple-point



Courtesy of S. Carle, Lawrence Livermore National Laboratory

Figure 28. Conditional simulation of Quaternary to Holocene sediment heterogeneity beneath Orange Co., CA, including sequence stratigraphic framework, nonstationarity, and surface soils data. Produced with transition probability Markov chain approach. (S. Carle, personal communication; see Tompson et al. 1999.)

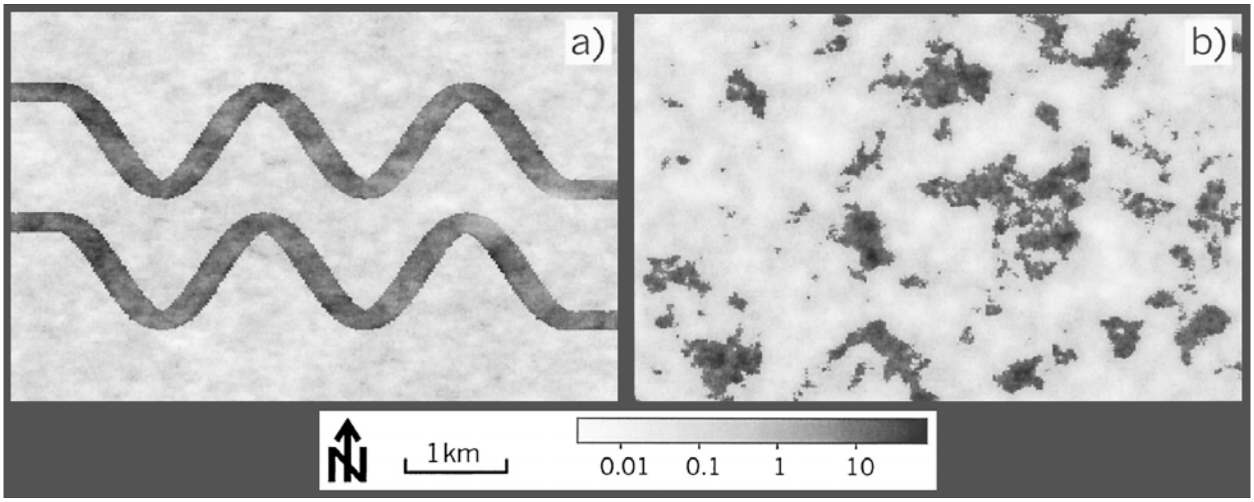


Figure 29. Spatial patterns of two hypothetical systems with different degrees of connectivity but virtually identical probability density functions and omnidirectional variograms (from Western, A.W., Bloschl, G., and Grayson, R.B. (2001). Toward capturing hydrologically significant connectivity in spatial patterns. *Water Resources Research* **37**(1), 83–97. Copyright © 2001 American Geophysical Union. Reproduced/modified by permission).

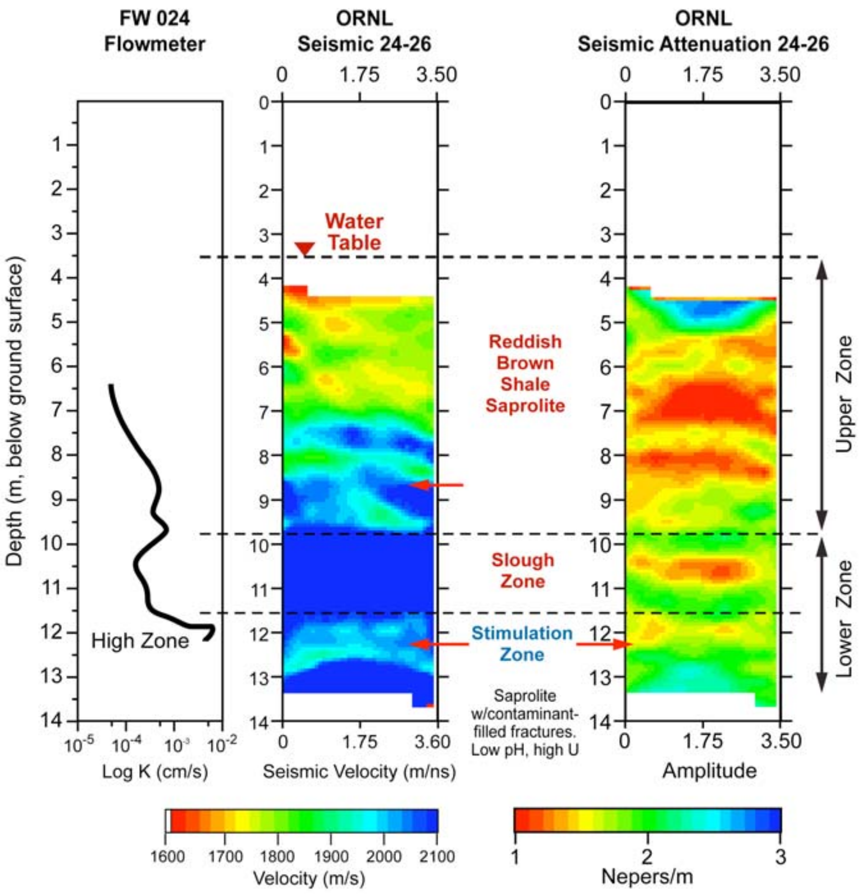
geostatistics (Strebelle 2002), provide important improvements for incorporation of hard and soft geologic information, but these are still “structure imitating” techniques (Koltermann and Gorelick 1996) and are therefore limited in their ability to account for important geologic processes which, for example, can give rise to unanticipated preferential flow paths.

The geological architecture (distribution of rock permeability, connectivity of high and low permeability media, fractures and faults) determines flow pathways. Modern geology, including knowledge of depositional systems, sequence stratigraphy, structural history, and diagenesis, illustrates that the distribution of architectural features is not random. Rock mechanics documents that fracture distribution relates to strain from stretching, bending or tearing, and to the distribution of anisotropy elements (e.g., bed thickness). One challenge is to link the hydrodynamics of sediment deposition, erosion and transport to the spatial dimensions and reservoir properties of the resulting deposits, predict reservoir body stacking patterns in response to base-level changes, and document their degree of connectivity at successively larger scales (from pore to basin scale).

Early attempts at such 3D geologic process modeling can be found in Tetzlaff and Harbaugh (1989), Koltermann and Gorelick (1992), and more recently Teles et al. (2001) and Euzen et al. (2004). The newer models are improved in part by enhanced computer hardware and governing equations. Much work, however, remains to be done to make quantitative geologic depositional models theoretically rigorous and to reach their potential in subsurface characterization. Because the boundary conditions (including sediment supply, tectonic history, and climate) will never be known precisely, these geologic models may be most useful as hypothesis-testing, rather than predictive, tools. One important byproduct might be improved geostatistical models or process-geostatistical hybrids. Another might be improved understanding of which geologic features are most important for certain fluid flow and transport processes, providing a means of estimating optimal levels of geologic detail (discussed in the prior section).

Incorporating large and diverse datasets into models

Hill and Tiedeman (2007) describe the current state of inverse modeling in groundwater flow and transport. Current practice in inverse modeling tends to decouple processes, to aggregate parameters across scales, and to include only a limited amount of the available data. It is anticipated that advances in characterization methods will produce increasingly larger datasets as the spatial extent and the spatial and temporal resolutions of measurements increase. In addition, with the development of new measurement devices, data types not currently commonplace may become routinely available. The scientific challenge is to incorporate these larger data volumes and disparate data types (see Figure 30) into inverse modeling while simultaneously satisfying diverse physical and chemical constraints. In particular, in the context of monitoring perturbed geological systems, models will have to handle streams of different data types measured over a variety of spatial and temporal resolutions, including data indirectly related to system state variables and model parameters. The computational burden of such comprehensive inverse modeling requires fundamental advances in mathematical methods and numerical algorithms. Revolutionary advances in the modeling process are required to achieve more automated, real-time incorporation of diverse datasets into models.



Courtesy of Susan Hubbard, Lawrence Berkeley National Laboratory

Figure 30: Example of diverse datasets described in Chen et al. (2006a). Seismic velocity and attenuation of subsurface media at the Oak Ridge Field Research Center showing high resolution estimates of subsurface zonation that correspond well with measured hydraulic conductivity measurements. From Hubbard et al. 2006.

Relating geophysical measurements to in situ properties/processes

The data required to predict the impact of deep subsurface emplacement of anthropogenic fluids at the basin scale include 3D seismic reflection data cubes and potential fields (gravity, magnetic). On the aquifer scale, these data may be augmented with geoscience data from well logs and core-derived rock properties. Fluid communication pathways in the subsurface are identified using chemical tracers, time-lapse monitoring of geochemical changes in oil and brines, and pressure transients. Phase changes in the fluids in response to pressure changes can both be imaged and directly measured in wells.

A key scientific challenge addressing deep subsurface disposal consists in part of applying these state-of-the-art tools to probe the volume under investigation for a range of physical and chemical properties (e.g., density, bulk modulus, porosity, viscosity, permeability, saturation, concentration). Part of this challenge is to identify new methodologies to represent these properties at all scales to predict system performance after perturbation. The performance of this system relative to the process of storage will be critically defined by the geological properties associated with fluid flow, geomechanical status (stress, fractures and faults), and their distribution within the system. Not all this information is available at the level of detail required. Consequently the system is underconstrained as to its properties, which requires experimentation and additional investigations to reduce uncertainties associated with the key parameters to provide suitable convergence of prediction and performance.

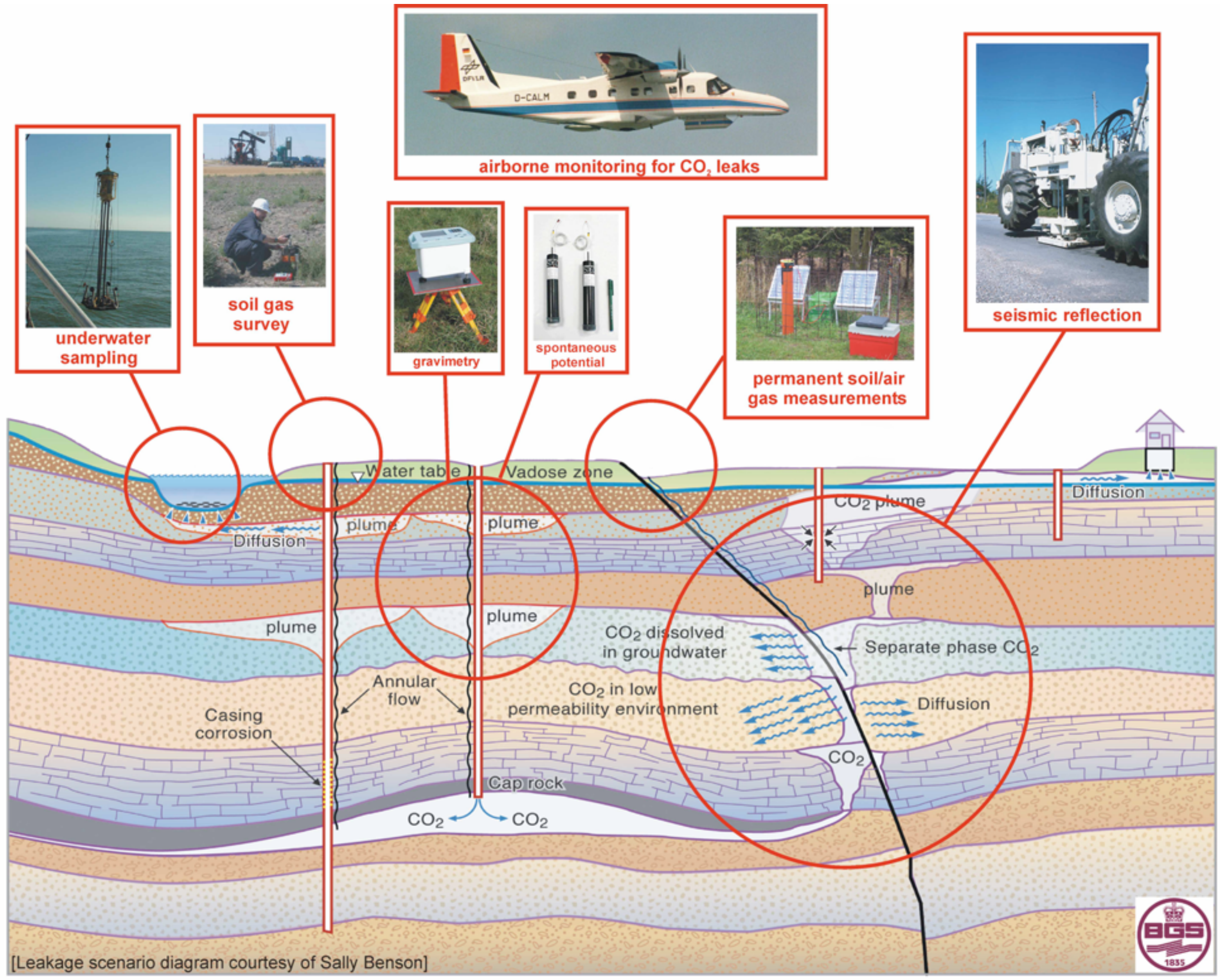
The performance of the system at the macroscale is determined by the accumulated processes acting at microscale and mesoscale. Heterogeneities that will dictate dynamic performance at the macroscale exist at all scales, and may occur in a fractal way. Identifying new methodologies to represent these properties at all scales will be critical to the prediction of system performance.

It is well recognized that natural heterogeneity of hydrogeological-geochemical-geomechanical parameters is typically great and can have multiple spatial scales of variability. Conventional sampling techniques for characterizing these properties typically involve collection of measurements or samples from boreholes. When the size of the study site is large relative to the scale of the heterogeneity, data obtained using wellbore methods may not be sufficient to characterize the heterogeneity of the system. Just as biomedical imaging procedures have reduced the need for exploratory surgery, integrating more spatially extensive (yet indirect) geophysical datasets with direct borehole measurements hold promise for improved and minimally invasive characterization and monitoring of the subsurface. Geophysical methods have been used in recent years to provide high-resolution estimates of subsurface properties, including water content, permeability, sediment geochemistry, and hydrogeological zonation, but are hindered by limited scales of investigation, geophysical data inversions, inversions of datasets that sample different properties, and non-unique geophysical responses to heterogeneities.

Developing integrated monitoring approaches

Another key challenge is the development of approaches for (1) interpreting indirect monitoring datasets in terms of critical system responses, and (2) integration of hydrological-geomechanical-geochemical datasets into a comprehensive interpretation of the system response to manipulation. As illustrated in Figure 31, monitoring technologies are available to measure specific hydrological-geochemical-geomechanical properties. However, challenges exist in both the interpretation of some of these datasets in terms of flow, transport, and deformation processes, and in the integration of disparate monitoring datasets that sample different properties over disparate space and time scales.

As an example, the use of geophysical methods is of particular interest for monitoring effective changes in hydrological, geochemical, and geomechanical properties associated with large-scale manipulations, because these methods have the capability to probe subsurface systems over large spatial areas and often in a minimally invasive manner. However, many challenges exist in using time-lapse geophysical information to obtain quantitative estimates of system transformations. It will be necessary to tackle resolution issues (described above), to develop the petrophysical models that link the geophysical attributes to the particular transformational end-products, to investigate scaling issues associated with using disparate measurements and phenomena, and to develop integration frameworks that can incorporate the time-lapse imagery and petrophysics with direct measurements to produce an integrated interpretation. Recent examples illustrate that



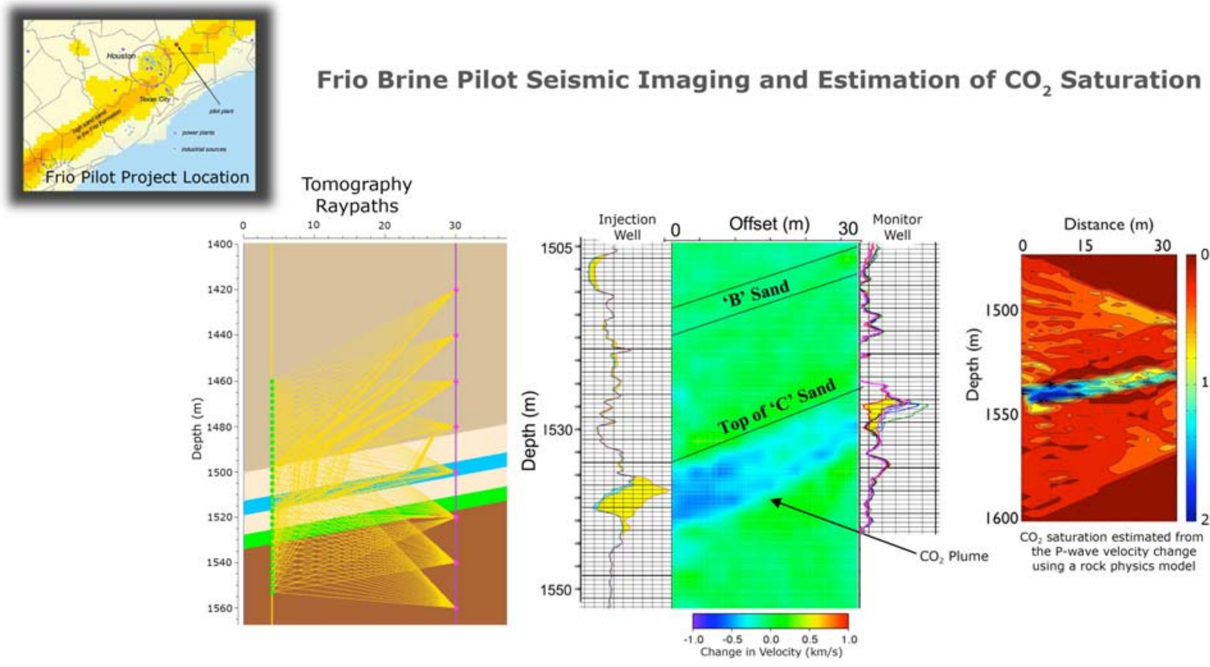
[Leakage scenario diagram courtesy of Sally Benson]

Courtesy of Sally Benson, Stanford University, and Andy Chadwick, British Geological Survey

Figure 31. Example of the varied approaches used to measure geochemical-geophysical-hydrological subsurface properties and processes, modified from David and Elewaut (2006) and Benson and Hepple (2005), and with measurement approaches from Chadwick (British Geological Survey).

we are at a threshold in developing such geophysical monitoring approaches. An example of the use of time-lapse seismic crosshole data with petrophysical relationships to estimate the CO_2 saturation associated with the Frio brine CO_2 injection pilot test is shown in Figure 32. For the purpose of monitoring CO_2, it is vital to be able to detect small amounts of leakage (Wells et al. 2006). For example, leakage of only 0.5% per year over 200 years leads to a loss of 66%. Monitoring must be sufficiently sensitive and cover sufficient volumes of the subsurface to detect such small leakage.

Because anthropogenic manipulations often result in complex flow-reactivity responses, and geophysical attributes can be sensitive to various properties, the use of multiple methods can greatly reduce uncertainty associated with the use of geophysical datasets to quantitatively monitor system transformations. Figure 33 illustrates the use of time-lapse geophysical datasets to provide quantitative, time-lapse estimates of biogeochemical transformations associated with a manipulation experiment in the laboratory. Although these recent studies illustrate the potential



Daley et al., *Environmental Geology* (in press, 2007)

Figure 32. Example of the use of time-lapse crosshole seismic velocity information and petrophysical relationships to estimate percent of CO_2 saturation associated with injection of CO_2 into a brine reservoir at the Frio Pilot Study Site in Texas (Daley et al. 2007). The estimated saturation values obtained using 2D, time-lapse seismic datasets agreed favorably at the wellbore location with the CO_2 concentration information obtained using the Schlumberger reservoir saturation tool (RST).

of remote methods for informing us about transformations associated with manipulations, significant research on petrophysics, fusion, joint inversion, resolution and scaling is needed to advance these monitoring approaches to a level where they can be used to interrogate subsurface system responses to perturbations.

Seismic interferometrics have been shown to be a highly sensitive monitoring tool (Snieder et al. 2002). It also has been shown that the response of a system can be retrieved from ambient fluctuations (Curtis et al. 2006). This obviates the need for using active sources for monitoring purposes. A combination of these two approaches has been used for daily monitoring of volcanoes and fault zones (Sens-Schonfelder and Wegler 2006; Wegler and Sens-Schonfelder 2007). This methodology has been implemented so far only for seismic approaches, but can in principle be extended to a large class of physical systems that includes coupled processes (Wapenaar et al. 2006) such as the seismo-electric effect.

Coupled monitoring and modeling approaches

Iterative *comparison* of time-lapse information and advanced simulations can be used to improve both monitoring and modeling approaches. For example, advanced monitoring data can be used to constrain, update or validate modeling approaches, and monitoring predications can be used to reduce the uncertainty associated with the interpretation of system transformations using indirect datasets, such as time-lapse geophysical data (e.g., Hubbard et al. 2007).

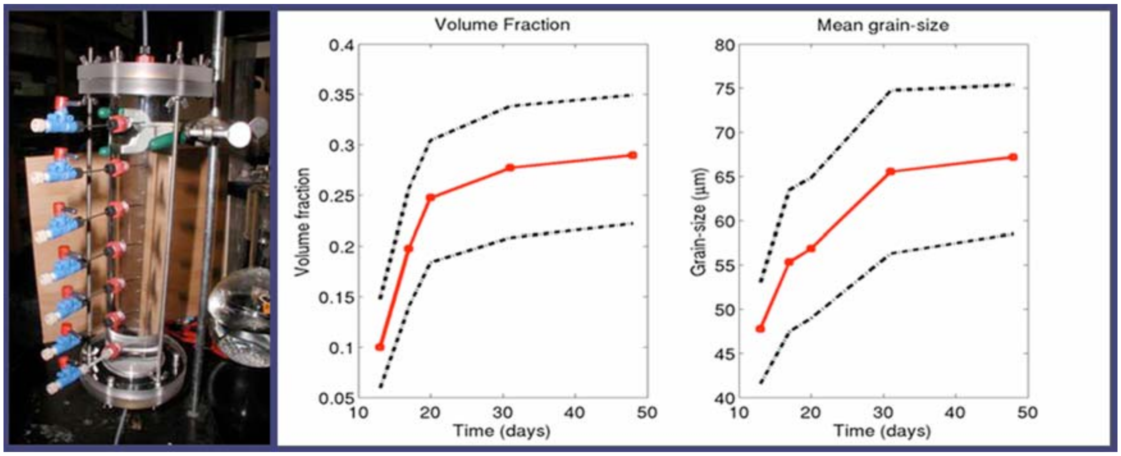


Figure 33. Example of use of time-lapse seismic amplitude and complex resistivity phase data, together with petrophysical models and a Markov chain Monte Carlo approach, to estimate temporal evolution and uncertainty associated with volume fraction and mean grains size of sulfide precipitates that formed in response to a biostimulation lab experiment (Chen et al. 2006b).

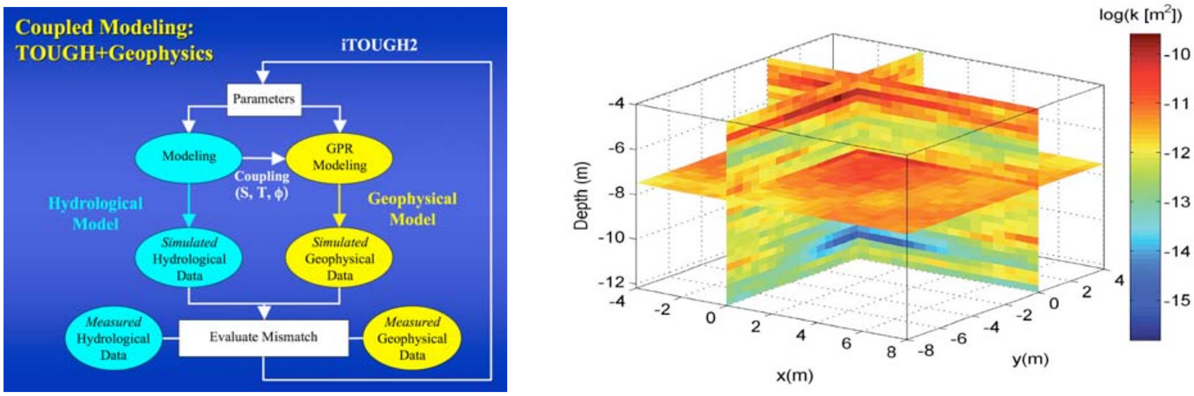


Figure 34. An example of the approach and estimate of permeability obtained through coupling time-lapse hydrological and ground penetrating radar (GPR) phenomena and datasets (modified from Kowalsky et al. 2005, 2006).

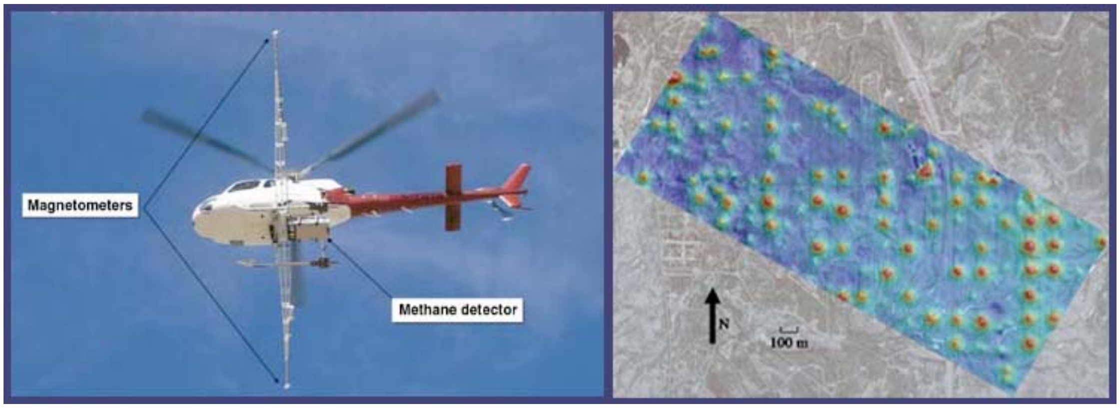


Figure 35. Example of the use of remote sensing approaches to detect gas leaks and potential leak pathways associated with wellbores (Wells et al. 2006).

A particular challenge is the *direct coupling* of advanced monitoring and modeling approaches through joint inversion or simulation to permit calculation of the relevant properties or processes of interest. This challenge could be tackled through the development of a common computational framework that jointly honors phenomena associated with waves, potential fields, flow, transport, and deformation. Such coupling is expected to lead to improved insights about system transformations and emergent phenomena, which in turn will lead to the evolution of improved predictive models. Several recent examples have illustrated the benefit of coupling geophysical solvers with numerical flow and transport algorithms to improve inversions or simulations of hydrological properties, including the coupling of time-lapse ground penetrating radar (Kowalsky et al. 2005, 2006) and self-potential (Revil et al. 2007b) formulations within the TOUGH2 family of codes. An example of the estimation of permeability obtained through joint inversion of hydrological and geophysical datasets is shown in Figure 34.

Computational challenges are associated with the development of advanced monitoring and with the coupling of monitoring and modeling approaches. For example, forward and inverse modeling using three-dimensional seismic datasets requires high-performance computers. The computational requirements are expected to increase significantly with the potential need to quantify uncertainty and to augment such datasets with additional time-lapse datasets (hydrological, geomechanical, biogeochemical, and geophysical datasets) and associated coupled phenomena in the presence of multiscale heterogeneity.

Quantifying and reducing predictive uncertainty

Uncertainty in model results arises primarily from lack of information, inconsistencies between the available information and the modeled quantities, inherent uncertainty or instability in measurements, and errors in the existing information. Quantifying a model's uncertainty requires a careful accounting of these contributions, numerical methods that are accurate and robust, use of optimization methods for model calibration, and use of sensitivity methods to reveal important information deficiencies (e.g., Neuman and Wierenga 2003; Helton et al. 2006; Saltelli et al. 2004). Recent and anticipated advances in data collection are expected to complicate this process. Despite significant advances in recent years, the fields of model calibration, sensitivity analysis, data needs assessment, long-term monitoring, and uncertainty evaluation require fundamental improvements for optimal use of anticipated datasets while fully accounting for multiscale features and nonlinearly coupled processes. Additional challenges include improving the representation of model structural uncertainties, consistent propagation of uncertainties across scales, and systematic methods for using uncertainty information in data collection and model development.

Early identification and quantification of anomalous behavior

Another monitoring challenge is the development of systems and protocols to detect and to quantify significant hazards associated with large anthropogenic manipulations. A particularly important hazard is the potential leakage of waste into overlying groundwater systems, ecosystems, and the atmosphere. Although technologies exist to sample groundwater, ecosystem and atmospheric chemistry individually, and to remotely detect subsurface ruptures once they are sufficiently large, these techniques currently cannot provide information with both the spatiotemporal resolution and sensitivity needed to detect and quantify leaks in a cost-effective manner. Particularly challenging is the identification and quantification of vertical fluid features (chimneys), residual oil or gas chimneys (dispersed fluids), and the ongoing migration of buoyant fluid (continuous fluid phase) associated with leaked CO_2. A recent example of a remote sensing technology specifically developed to detect potential leakage paths as well as gas concentration is illustrated in Figure 35. Analogous challenges are posed by localized leakage of fluids from nuclear repositories.

RESEARCH APPROACHES

A revolutionary approach for multiprocess simulation of flow and transport over a continuum of scales in porous media will require breakthrough results at the interfaces between applied mathematics, computational science, and geoscience engineering. Retooling of existing modeling codes will not achieve the desired results. Only a top-to-bottom redesign of modeling systems will suffice.

Numerical and computational algorithms with input from the geological, geophysical, geochemical, hydrological, and reservoir engineering communities need to be developed. These should integrate modeling tools that accept a variety of parameterizations and predict a variety of responses. Laboratory studies, *a priori* modeling, and examination of data to develop coupling relationships between critical geochemical and geophysical properties should be included, allowing joint inversion and forward modeling.

Improved understanding and descriptions of spatial and temporal heterogeneity should come with models including upscaling and downscaling of measurements and processes from pore to field scales. Examples are how depositional/diagenetic heterogeneity impacts spatial distributions of saturation and mineral reactivity, how biological activity impacts fluid flux, and how the depositional environment, diagenesis and structural history constrain model inversions both at and below resolution scale.

Direct coupling of advanced monitoring and modeling approaches through joint inversion or simulation could be tackled through the development of a common computational framework that jointly honors phenomena associated with waves, potential fields, flow, transport and deformation.

Conceptual models, numerical model sensitivity analyses, and case studies associated with manipulated and natural analogue sites should be useful for guiding the choice of parameters and phenomena to be monitored, and for identifying thresholds or regions that might mandate enhanced monitoring effort. To advance the use of remote datasets for quantifying subsurface transformations, it is necessary to:

- Tackle resolution issues
- Develop the petrophysical models that link the geophysical attributes to the particular transformational end-products
- Investigate scaling issues associated with using disparate measurements and phenomena
- Develop integration frameworks that can incorporate the time-lapse imagery and petrophysics with direct measurements to produce an integrated interpretation

Improved sensitivity and uncertainty analysis methods are needed for a better understanding of models, data and assumptions so as to improve the quality of the evidence and the transparency of the results. Advanced methods should explore all sources of uncertainty simultaneously across scales and should apply to nonlinear models so as to capture singularities and interactions.

SCIENTIFIC IMPACTS

Integration of models and data. Model results will be improved by making the best use of all available data. Evaluation of model data structures and uncertainty has to be matched in complexity and resolution. Data collection will be improved by using models to identify the most valuable data, an iterative process that might be referred to as "data-driven model development and model-driven data collection." Using a diverse set of data that simultaneously provide information about different characteristics of the system can be expected to reduce the non-uniqueness of inverse modeling results. The result will be improved imaging, and inverse and coupled monitoring-simulation capabilities that promote a better understanding and prediction of complex and coupled subsurface responses to perturbations over decadal to century time scales, including their uncertainties.

Enhanced prediction of rock and fluid properties. This will include better techniques for imaging geologic features that enhance or inhibit flow and better characterization of statistical properties at a variety of scales. Images of surface properties will have enhanced resolution and accuracy. Breakthroughs could include remote detection of chemical and biological processes, and dramatically improved mapping of rock type, mineralogy, porosity, permeability, temperature, pressure, saturation, and fluid movement and transport.

Improved understanding of coupled processes in geologic systems. Advancements in measuring and imaging techniques will be built upon discovering and understanding links such as:

- Geophysical signals from biological, chemical and mechanical processes
- Geochemical links to porosity, permeability, mineralogy, fluid fluxes
- Geomechanical causes/consequences of fluid transport and geochemical activity
- Chemical and fluid impacts on faulting, fracturing and seismicity

Better resource allocation in model development and application. By identifying and isolating the sources of errors in model results, resources can be optimally allocated between site characterization, conceptual model development, improvements in modeling methods and simulation codes, and application of additional computational capabilities.

Increased model defensibility. Predictive uncertainty will be reduced by identifying significant contributing errors and data deficiencies and through the collection of relevant data and the modification of models. Quantification of uncertainties will facilitate better communication of the reliability of model results. Explicitly accounting for model limitations will increase the transparency of the modeling process and improve acceptance of model results. In addition, the close coupling of characterization, modeling and monitoring will permit identification of rare, extreme mechanisms that accompany large-scale manipulations and that may not have been realized during the development of a conceptual model.

TECHNOLOGY IMPACTS

More predictable consequences of subsurface storage and containment. Improved description of the *in situ* geologic/chemical/mechanical system, and improved understanding of the storage characteristics and their dynamic response of the *in situ* system to natural (e.g., climate, earthquake) and anthropogenic (e.g., injection, withdrawal) perturbations, will lead to improved simulation and reduced uncertainty and risk.

Real-time model adaptation. Given the time-consuming nature of today's model-building process, restructuring model development will improve the discovery process by freeing the scientist to experiment with the system, rather than manage data and tune models. The continually evolving system would be linked to a model that is updated in real time. Accompanying analyses of all sources of error would enable scientists to make decisions regarding data collection and adjustment of operating variables to maximize the information content of the data.

Model validity and improved communication. The concept of model validity is fraught with philosophical difficulties related to provability of a scientific hypothesis (e.g., Oreskes 2000). A data-driven modeling paradigm, with continuous updating and error assessment, will move the dialog beyond theoretical discussions of model validity to the much more useful discussion of the state of knowledge of a particular system, and improved communication between scientists, managers, regulators, and the public.

Unified modeling architecture. An integrated approach involving applied mathematicians, computer scientists, and geoscientists is required. This can only happen in a unified framework that replaces the current splintered research approach. A unified modeling architecture would encourage a community software environment in which large portions of software would be reused, updated regularly, and controlled. Active management of the intellectual output and software projects would enable rapid advances in software codes and numerical methods.

Integrated, diverse measurement technologies. Development of novel instrumentation and procedures will lead to simultaneous measurements of geological, geophysical, hydrological and geochemical processes. Examples might include (i) miniaturized sensors to simultaneously sample fluid chemistry while recording geophysical signals; (ii) new geophysical measurements that can sense changes in enhanced mineralization; (iii) field protocols for accurate and cost-effective simultaneous measurements. Sensors will be smaller, cheaper and faster to deploy.

Early detection of anomalies. Development of much improved techniques for characterization, modeling, and monitoring of the subsurface will allow creation of systems that can be used routinely to detect and quantify phenomena that provide the earliest indication of unexpected processes or signs of impending failure of the manipulated system. In the implementation phase, the primary system performance indicator will be the ability to detect and quantify anomalous events in near real-time, so that hazards can be mitigated or remediated before overall storage system integrity is compromised.

Increased cost efficiency and effectiveness of enhanced oil recovery, groundwater remediation and related industrial processes. New instrumentation, imaging tools, and modeling approaches will impact the enhanced oil recovery and groundwater remediation industries in a very positive way. Sweep efficiency of the injected fluids will be better understood, potential bypass via fluid fast paths can be avoided, and production can be better optimized with respect to the reservoir architecture.

Improved management of groundwater reservoirs. Because few new surface reservoirs are likely to be built in the future, demand for more intelligent, optimized use, and management of subsurface reservoirs will increase. This will require a new level of subsurface characterization and modeling that would be provided by the research discussed herein.

SIMULATION OF MULTISCALE GEOLOGIC SYSTEMS FOR ULTRA-LONG TIMES

ABSTRACT

One fundamental gap in the knowledge base for modeling complex processes in the subsurface is accurate coupling of information across scales, i.e., accurate accounting of small-scale effects on larger scales, and capturing the effects of fast processes as well as the ultra-slow evolution on very long time scales. The latter is an unprecedented requirement dictated by the need to sequester materials in the subsurface for hundreds to hundreds of thousands of years—time scales that reach far beyond standard engineering practice. Mathematical and numerical frameworks must capture the stochastic nature of geologic media and the nonlinear dynamic physical and chemical processes that occur in geologic formations, and must recognize that subsurface systems may or may not be in equilibrium. Conceptual model development from the pore scale upward as guided by observations and data from laboratory and field experiments will be used to define a mathematical framework amenable to computation. Traversing spatial and temporal scales requires the appropriate mathematical and numerical representations at each scale and across scales for dynamic processes. Refinement of theoretical and numerical frameworks must also use data integration to calibrate numerical models, validate theorems, and test multiphysics cross-scale coupling models. Cross-scale modeling of complex, dynamic subsurface systems requires the development of new computational and numerical methods of stochastic systems, new multiscale formulations, data integration, improvements in inverse theory, and new methods for optimization. The fundamental importance of heterogeneity on all scales in natural systems suggests that research in this area will have broad scientific impact on subsurface science. On the technology side, the resulting advanced modeling framework will find a wide range of applications, from improving the design and optimization of fluid injection and storage to monitoring programs and risk assessment. The ultimate objective is reliable, long-term predictions of subsurface processes that span multiple spatial and temporal scales, with significant improvement in the quantification of uncertainty.

EXECUTIVE SUMMARY

Subsurface geologic systems are open systems that participate in the hydrologic, geochemical, biogeochemical and tectonic cycles of the Earth. Storage of anthropogenic waste products, recovery of energy resources, and management of aquifers will perturb these subsurface systems. The anthropogenic perturbations can occur over tens of years, which is a standard time scale for engineering design, prediction, and monitoring. However, regulatory requirements demand that the performance of these perturbed systems be predictable for time periods of hundreds of years for CO_2 sequestration, and for up to a million years for nuclear waste isolation. For models to provide decision-level predictions of such ultra-long-term behavior, an unprecedented understanding is needed of the geologic structure, the processes that occur within the structure, and how the structure and processes evolve over time scales that are very long in comparison to the relaxation time of normal chemical and hydrological systems.

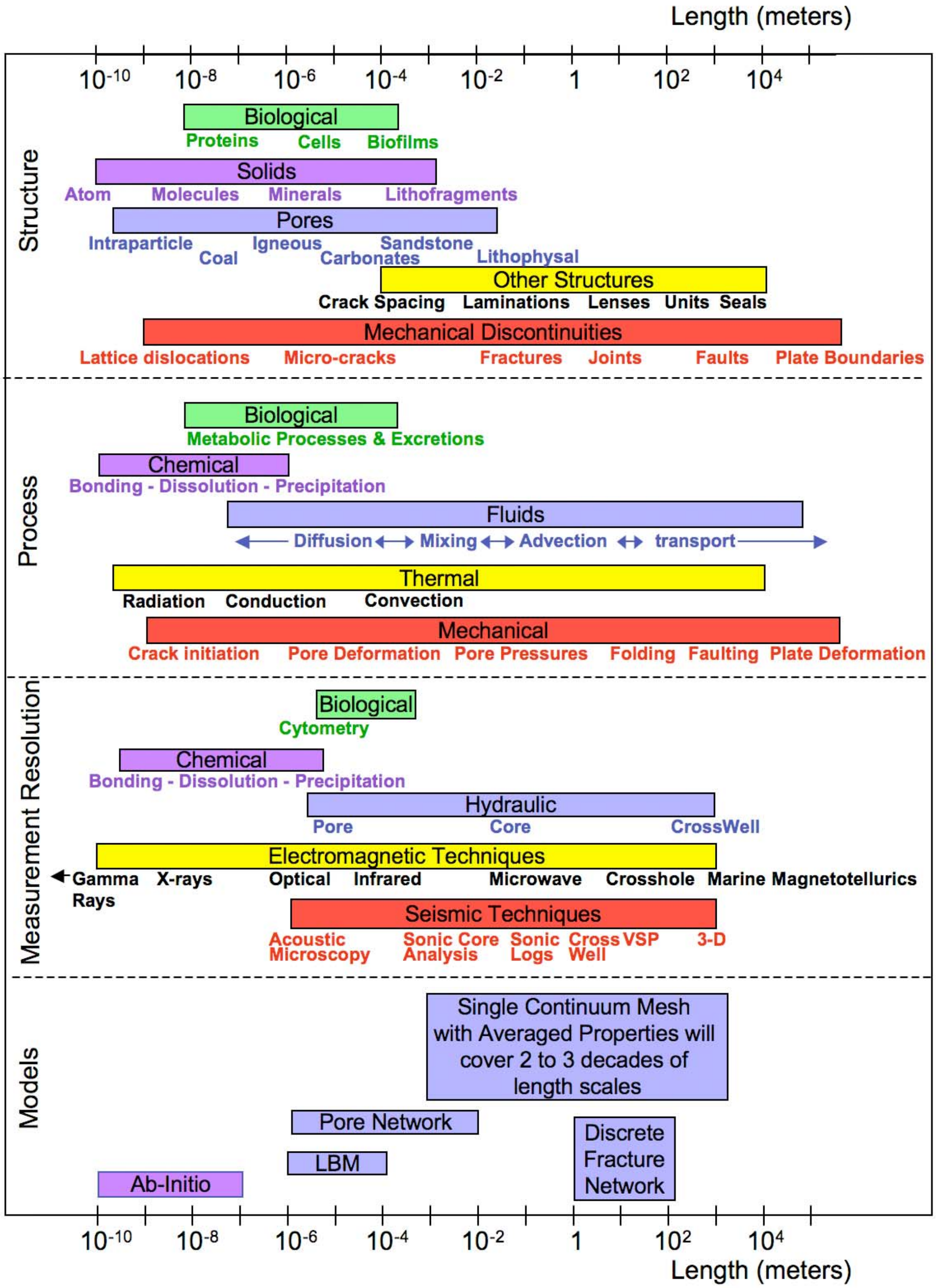
Challenges in modeling geologic systems arise from the large range of scales, both temporal and spatial, that any subsurface site encompasses, and from the coupling of processes on multiple scales. For example, injection of fluids into the subsurface affects not only fluid pressures within the reservoir, but can result in deformation of the rock that affects permeability through pore/fracture closure or opening, the initiation of chemical reactions that result in dissolution and/or precipitation of minerals, the enhancement/death of microbial life, the simultaneous flow of different fluid components and phases resulting in fluid fingering from viscous, capillary, gravity and thermal forces. Geologic storage of CO_2 generates buoyancy forces that act on all scales, producing potentially simultaneous pore-scale, reservoir-scale and basin-scale effects. Simulation of leakage from repository sites will require predicting flow paths and geochemical reactivity at low hydraulic gradients and low concentrations. Heterogeneity, multiphase interfacial and phase interference effects, and geochemical reactions add further complexity to the system and demand advances in understanding and modeling capability. Advances can be achieved through development of a seamless, multiscale framework for modeling coupled multiphysics processes in heterogeneous systems.

Thus the fundamental challenge for model simulation of subsurface processes is accurate representation of physical processes, not only at specific scales but also across scales. The development of general stochastic mathematical and numerical frameworks of large-scale dynamic nonlinear systems is needed to rigorously quantify the uncertainties and risks associated with site selection, operation, and long-term monitoring of large-scale subsurface storage projects. The fundamental importance of heterogeneity on all scales in natural systems suggests that research in this area will have broad scientific impact on subsurface science. The primary impact on technology is the development of multiphysics simulation capabilities that offer seamless modeling of processes over multiple scales. From the improved forecasting of long-term fate of sequestered materials will come numerous improvements in applications, such as design and optimization of injection and storage strategies, monitoring programs, remediation techniques, and risk assessment.

SCIENTIFIC CHALLENGES

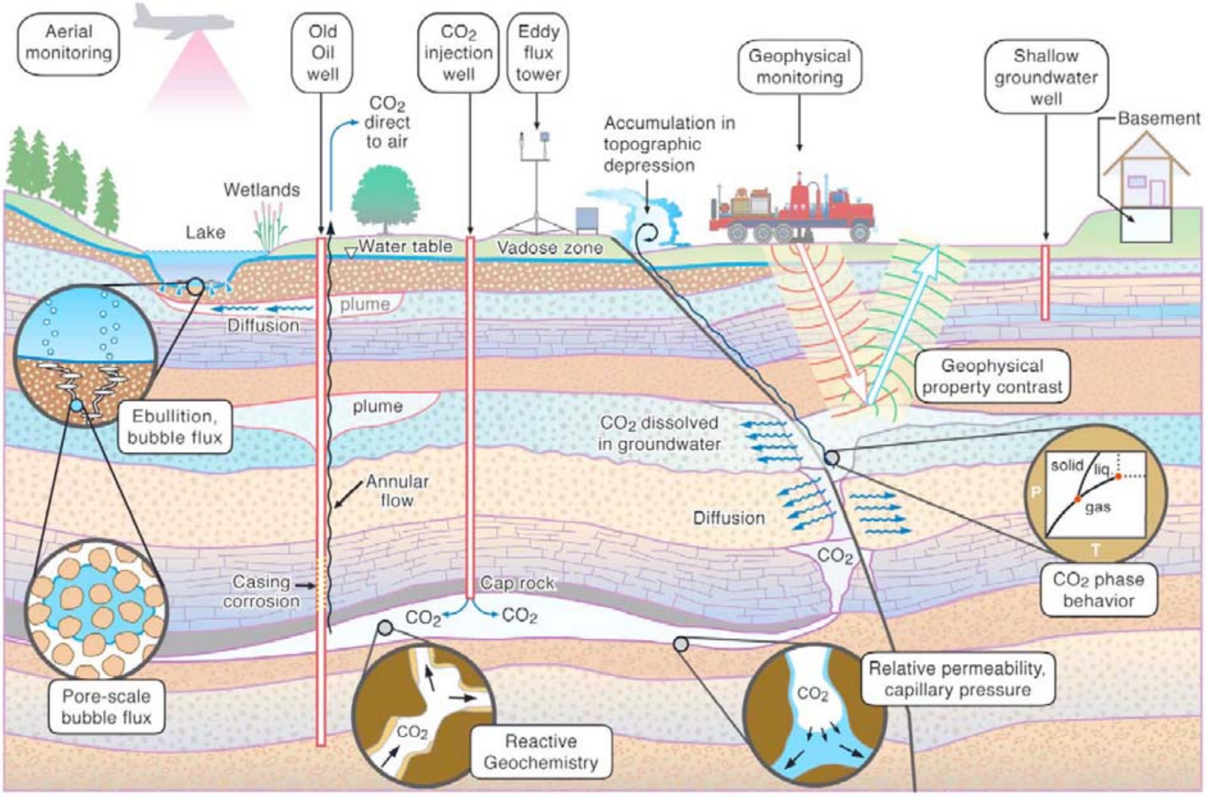
The subsurface is composed of a hierarchy of structures and processes that span a wide spectrum of length and time scales (Figure 36). Any subsurface response is a function of this dynamic multiscale spectrum, which includes reinforcing and damping feedbacks of a variety of strengths. Important feedbacks are often those that traverse scales. Multiscale modeling is necessary to correctly represent the dynamic evolution of the geologic system. Modeling requires the parsing of behaviors and interactions observed at microscales to define the response at the field scale. These behaviors are controlled by transport mechanisms driven by a complex interplay of viscous, capillary, gravitational, inertial, reactive, diffusive, geochemical, biological and geomechanical forces.

Flow of multicomponent, multiphase fluids, such as mixtures of CO_2 and brines, is poorly understood when buoyancy is the dominant driving force. The instabilities inherent in buoyant flow are well known, but when the fluids occupy a porous medium, new behavior and new characteristic time scales emerge at the pore scale, and as interfaces interact with heterogeneities in the permeability field. Because capillary forces often exceed buoyancy forces in geologic systems, still more complicated behavior emerges as fluid interfaces encounter heterogeneities in the capillary pressure characteristics of the domain. A suitable theoretical and computational framework for multiscale buoyancy-driven flow remains an outstanding challenge.



Courtesy of Laura J. Pyrak-Nolte

Figure 36. Length scales associated with structure and physical processes in geologic systems. (LBM—Lattice Boltzmann methods.



Courtesy of Sally Benson and Curt Oldenburg, Lawrence Berkeley National Laboratory

Figure 37. Processes affecting geologic CO_2 storage and monitoring occur over a wide range of length scales, from subpore scale to reservoir and basin scale. Aggregated pore-scale processes can give rise to larger-scale emergent phenomena. Well-known examples include the upward rise of CO_2 plumes by buoyancy forces, and residual phase trapping as water imbibes into a mobile CO_2 plume. The ability to predict emergent processes over the full range of length and time scales using seamless modeling frameworks remains a fundamental scientific challenge.

Processes occurring at interfaces between fluids and between fluids and solids are fundamental to multiphase flow and reactive transport in geologic systems (Figure 37). While some interfacial phenomena are understood, local couplings of interfacial phenomena with flow are less well known. Linkages between interfacial phenomena and flow as scales increase are hard to demonstrate. Consequently, the understanding of how behavior at one scale affects behavior at both larger and smaller scales remains one of the most difficult challenges.

A grand challenge for multiphase flow in the subsurface is a mathematical description of behavior that is self-consistent across many length and time scales. A familiar example is the problem of relating the Navier-Stokes description of flow at the pore scale to the Darcy's law description at the core-to-reservoir scale. Introducing multiple fluid phases greatly increases the difficulty because capillary forces must then be accounted for. An indication of the inadequacy of the art is that continuum descriptions still routinely use an empirical modification to Darcy's law parameterized only by the volume fraction of the fluid phases. Efforts to place multiphase flow on a more rigorous foundation have begun, but much work is needed to develop these to the level where reliable macroscale predictions can be made. Intensifying the challenge still further is the effect of heterogeneous properties across a wide range of length scales. Variation in properties is perhaps the most important feature for causing different physical/chemical phenomena to be important in different parts of the geologic system at different times. A seamless multiscale framework would allow the scientific community to understand the emergence of patterns, trends and behaviors observable at larger scales that may arise from structures and processes at smaller scales.

Many processes associated with multiphase flow and reactive transport occur over characteristic length and time scales, while heterogeneity inherent in geologic systems occurs at all length scales. The fundamental challenge is to identify and map the scales at which connections between *process* and *heterogeneity* are found. Such a map would inform efforts to describe multiphase flow and chemically reactive transport in a seamless way and allow an organized description of emergent behavior useful for developing the next generation of models applicable to the full range of relevant length scales.

The scientific challenges are:

- Accurate accounting of small-scale effects on the larger scales. The problem is complicated by the fact that in many cases there may be no obvious scale separations. Challenges include the appropriate mathematical and numerical representations at each scale and across scales for dynamic processes.
- Development of stochastic mathematical and numerical frameworks that capture the nonlinear dynamic physical and chemical processes in geologic formations. The probabilistic description must account for uncertainty due to (1) incomplete knowledge of inaccessible scales, (2) imperfectly understood physical phenomena, and (3) measurement errors.
- Accurate representation of physics, including nonlinear interactions spanning a multiplicity of scales which are not amenable to scale-averaging. The complexity of the representation is amplified in systems pushed far from equilibrium.
- Limited characterization of geologic structure on the field scale due to difficult, spatially sparse and temporally infrequent sampling, and continually changing conditions.
- Developing iterative feedback loops between model formulation and data acquisition.

Significant computational challenges exist because the computational resources required to solve these problems using Direct Numerical Simulation (DNS) at the required scale are not attainable even with predicted increases in computing power. The computational challenges are:

- The upscaled model typically includes fewer degrees of freedom at the expense of more complex (difficult to model) constitutive equations.
- Upscaled models must be calibrated to ensure that fine scale influences are properly captured.
- Accuracy estimates for the upscaled models need to be developed (Wallstrom et al. 1999). This will require running ensembles of statistically equivalent realizations of the model.
- Scaleable linear and nonlinear solver algorithms for very large-scale computations must be developed.

RESEARCH APPROACHES

Research approaches to understanding processes relevant both to CO_2 geologic emplacement and storage and to very long-term leakage from nuclear waste storage involve development of new conceptual and theoretical models of multiscale and multiphysics processes. Numerical implementation ultimately requires high-performance computing and model validation using both laboratory and field experiments. Theoretical approaches range from pore-scale models that can be approached with existing methods, e.g., Navier-Stokes equations and their solution through lattice Boltzmann (Kang et al. 2006) and smooth particle hydrodynamics techniques, to pore network and Darcy-scale continuum models (e.g., Pruess et al. 1999). Accurate tracking of interfaces is critical to modeling pore-scale processes, a capability that can be provided by Level Set methods (e.g., Prodanovic and Bryant 2006). Hybrid formulations, involving coupling of pore-scale and continuum models or viscous and Darcy flow (e.g., Oldenburg and Spera 1992) across disparate scales may be required as well.

Injection of supercritical CO_2 into deep underground reservoirs introduces unique computational challenges arising from the formation of multiphase buoyancy-driven flow, fingering instabilities as CO_2 dissolves into groundwater, and viscous fingering as supercritical CO_2 displaces water. Understanding these processes requires development of models that can resolve instabilities and fingering patterns that originate on the pore scale but grow to produce emergent effects possibly extending to the basin scale.

One possible approach to representing multiscale processes is the dual or multiple interacting continuum model. Multiple continuum formulations appear adequate for sufficiently slow reaction rates where concentration gradients within a single pore remain small (Lichtner 2000). As rates and concentration gradients within a single pore increase, dramatic dissolution processes are possible (e.g., Golfier et al. 2002), and hybrid approaches that resolve viscous boundary layers and related transport processes (e.g., Taylor dispersion; see Taylor 1953) in the pore space are needed.

A significant challenge to developing and implementing multiscale models is obtaining the appropriate properties and parameters for each scale. One approach is to perform simulations at the pore scale and then upscale the results to the continuum scale. In so doing, the most appropriate continuum formulation is determined along with values for its system parameters. Carrying out the pore-scale modeling requires an accurate representation of the pores and their heterogeneity. Recent advances in pore-scale imaging (e.g., focused ion beam) can achieve micron to submicron resolution. Upscaling will be essential for obtaining effective parameters for basin-scale applications.

To model processes on a wide range of scales, observations and data are needed from laboratory and field experiments. Experiments must be designed and carried out to aid in conceptual model development and to validate resulting models. An iterative approach will be required to test, calibrate, and refine models against lab and field experiments. Innovative microfluidic experiments will need to be designed for multiphase systems to investigate multiphase interfacial phenomena.

Coupling methods used for different scales

The mathematical models for each fundamental length scale are reasonably well understood (Figure 36). However, the link between models and their parameters at different scales is largely missing. Geologic characterization models are usually constructed using sparse data, which come from different sources, have different spatial and temporal coverage and resolution, and are of varying quality and information content. Uncertainty in the characterization leads to uncertainty in forward predictions of dynamic behavior. The development of techniques that couple different scales and different physics incorporating stochasticity requires the four following aspects.

1. *Methodology concept and computational*

Scaling over a range of fundamental scales can be achieved through a combination of numerical approaches:

- Via coupling of models, each tuned for computation at specific scales. (e.g., lattice-Boltzmann computations feeding accurate, computed, pore-scale parameter information into a network flow model, which in turn feeds computed core-scale parameter information into a continuum-scale model.) *This direction requires an understanding of accurate "information passing" (Fish 2006) from one model to the next; that is, from one scale to the next.*
- Via efficient means for solving very large systems of equations on high performance computers. New adaptive hierarchical and multilevel methods are essential. *It is a critical need to migrate the computational geoscience community towards petascale computing facilities and software capable of utilizing such hardware.*
- Via "adaptive upscaling" techniques (local upscaling, model hybridization) that apply spatially variable resolution dynamically over the domain of computation (resolve fine scales locally).

2. *Mathematical theory*

The mathematical challenges to subsurface modeling require much more detailed information from microscale phenomena:

- The development of techniques that couple different scales and different physics in the same simulation, e.g., precalculated or adaptively computed parameterization of the coarse scale representation (Weinan et al. 2003; Kevrekidis et al. 2003).
- Development of techniques that seamlessly integrate nonseparable scales (Caffarelli et al. 1996; Owhadi and Zhang 2007).
- Solution of hybrid systems of differential equations.
- Stochastic formulations, e.g., the development of Probability Density Functions (PDFs) of the dynamic properties of interest (Pope 2000), development of statistical moment equations (Dagan 1985; Neuman 1990, 1994; Zhang 2002; Li and Tchelepi 2003), smart Monte Carlo (Sarma et al. 2005), and discrete network approximation (Borcea and Papanicolaou 1998; Berlyand and Kolpakov 2001).

3. *Data Integration*

For many subsurface applications, the model must be capable of using real-time information to update predictions, to inform field-scale deployment of monitoring methods, and to quantitatively assess the data. Data integration requires measurements from the laboratory to the field scale. In particular:

- Laboratory experiments need to be designed to provide scale-appropriate information under controlled conditions. These provide the best potential for validating mathematical formulations and calibrating numerical methods for complex processes and media.
- Coupling across multiple scales needs to be tested, which will require the integration of data acquired at multiple scales—from the laboratory to the field scale.
- Time-lapsed data has to be integrated into the numerical models.

4. *Coordination with other priority research directions*

Coordination with other priority research directions is required to achieve an accurate representation of the physics, chemistry and biology at different scales for development of models that will couple information across scales. Specific length and time scale information will include (but is not limited to): quantitative chemical reaction rates, the role of interfaces (fluid-fluid / fluid-solid) on multiphase transport, microbial-solid interaction rates, chemical migration, and time-lapsed data of evolving systems.

SCIENTIFIC IMPACTS

The fundamental importance of heterogeneity on all scales in natural systems suggests that research in this area will have broad scientific impact on subsurface science. For example, insofar as permeability heterogeneity controls fluid flow, heterogeneity exerts a profound control on key processes in a wide range of subsurface systems. From the pore scale to the basin scale, heterogeneity may lead to emergent behavior not readily predicted from process descriptions restricted to one scale or another.

Research into impacts of heterogeneity over multiple scales will aid in the understanding of the origin of residual saturation, a key mechanism of CO_2 trapping. At the pore level, fluid phases are subject to entrapment and bypassing of existing fluids. Predicting residual saturations and their evolution with time across multiple scales is important for estimating the capacity of CO_2 storage sites and predicting brine displacement. From pore-level studies, we can derive accurate parameterizations (e.g., hysteretic relative permeability and capillary pressure curves) needed for reservoir and basin-scale models.

Critical to reactive transport modeling at the pore scale is accurate modeling of pore-fluid composition. The spatial averaging concepts inherent in Darcy’s law do not suffice for describing fluid composition at fluid-mineral interfaces where reactions occur. Feedback of reactions on pore geometry and fluid compositions propagates to larger length and time scales.

The importance of reactive multiphase flow processes at various scales depends to a large degree on the questions being asked and the data available. Research in this area will allow identification of dominant processes and length and time scales over which they operate, potentially leading to simplifications in predictive modeling. The prospect exists for discovery of a new set of simpler models applicable to very long time and length scales appropriate to basin-scale investigations of CO_2 trapping and migration.

The onset and form of density-driven flows in CO_2 storage reservoirs at all scales are controlled by the interplay between fluid dynamics and heterogeneity. Multiphase effects in the former further complicate the processes as interfacial forces come into play. Through improved understanding, better models of density-driven flows will be developed that are applicable to a wide range of hydrogeologic problems beyond CO_2 storage.

New conceptual models of multiscale flow will likely involve Navier-Stokes equation descriptions of viscous flow in the pores coupled with Darcy formulations for larger scales. The resulting seamless mathematical description of reactive flow over the full range of scales relevant to CO_2 storage systems will provide a scientific basis for developing process models appropriate for whatever length and time scales are of interest.

Advanced modeling capabilities that can accurately describe multiscale processes will have the following scientific impacts:

- Improved understanding of the fundamental physics of flow and transport in geologic systems
- Reliable long-term simulations and predictions across multiple spatial and temporal scales with uncertainty quantification
- Stimulating advances in computational and numerical methods for multiscale dynamics, data integration, system identification, and optimization
- Deeper understanding of the dynamics of multiscale, multiphysics stochastic systems
- Increased integration between data acquisition and modeling

TECHNOLOGY IMPACTS

The desired product is the next generation of reactive transport simulators that explicitly account for the influence of multiscale physical and compositional heterogeneity on multiphase flow and chemical mass transfer processes, and are capable of forecasting the long-term isolation performance of geologic storage over the broad range of compositional, hydrological, and structural parameters that characterize proposed disposal sites. Explicit inclusion of multiscale heterogeneity in key physical properties (e.g., porosity, permeability) will significantly improve forecasting of CO_2 or nuclear waste plume migration, which defines the spatial framework of residual-phase and geochemical trapping mechanisms. Analogous inclusion of multiscale compositional heterogeneity will permit more accurate prediction of geochemical trapping mechanisms as well as related porosity/permeability evolution. Improved forecasting of plume migration will enable more accurate prediction of aqueous migration paths and their evolution, which is required to predict reservoir/seal responses.

Because the advanced reactive transport simulation capabilities outlined above provide improved predictions of CO_2 plume migration and trapping, brine displacement, and pressure evolution, they also provide tools for designing injection strategies, monitoring programs, and remediation techniques—as well as for quantifying the uncertainties that bound such predictive and design optimization efforts. Specifically, the next-generation computational tools can be used to design disposal strategies that explicitly correlate storage requirements and reservoir capacity while engineering the pressure perturbation that is unique to CO_2 sequestration such that maintenance of cap-rock/wellbore seal integrity is ensured. This is particularly important in the context of managing storage sites within a given basin, where explicit account must be taken of interference between multiple injection projects. In terms of verifying predicted containment performance, on both individual and multiple site scales, the advanced simulators can be used to identify appropriate suites of geophysical and geochemical monitoring techniques, and imaging and sampling strategies. With respect to remediation strategies that may be needed, the new computational capabilities can be used to design appropriate corrective actions (e.g., brine withdrawal to reduce or laterally smooth the injection-triggered pressure perturbation). Finally, next-generation simulators can play a critical role in risk assessment by quantifying the uncertainties that bound performance prediction though comprehensive sensitivity analyses that establish the impact of key uncertain model parameters.

Pursuit of these research directions is expected to have the following impacts:

- Improved science-based decision making for site selection, licensing, operation, and long-term monitoring.
- More efficient and economic management of subsurface systems for storage of anthropogenic byproducts, energy production, and aquifer management.
- The proposed development of general stochastic mathematical and numerical frameworks for large-scale dynamic nonlinear systems will allow rigorous quantification of the uncertainty and risk associated with site selection, operation, and long-term monitoring of large-scale subsurface storage projects.

PRIORITY RESEARCH DIRECTIONS

MINERAL-WATER INTERFACE COMPLEXITY AND DYNAMICS

NANOPARTICULATE AND COLLOID PHYSICS AND CHEMISTRY

DYNAMIC IMAGING OF FLOW AND TRANSPORT

TRANSPORT PROPERTIES AND *IN SITU* CHARACTERIZATION OF FLUID TRAPPING, ISOLATION, AND IMMOBILIZATION

FLUID-INDUCED ROCK DEFORMATION

BIOGEOCHEMISTRY IN EXTREME SUBSURFACE ENVIRONMENTS

MINERAL-WATER INTERFACE COMPLEXITY AND DYNAMICS

ABSTRACT

Over the past two decades, molecular level information on the structure and reactivity of idealized mineral-water interfaces has become available in unprecedented detail. However, natural subsurface materials do not have ideal mineral surfaces, but rather surfaces that are often structurally complex with variable composition, topographic roughness, defect content, and mineralogic and organic coatings. This complexity is usually accompanied by spatially variable reactivity operating over a wide distribution of time scales. These aspects of mineral-water interfaces make it difficult or impossible to extrapolate information, such as the adsorption behavior of highly dispersed radionuclides, gained using idealized interfaces in laboratory systems to the field environment. The issue of time dependence is especially important given the need to extrapolate such data thousands of years into the future in performance assessment and other disposal safety analyses. This Priority Research Direction has the objective of determining how the spatial and dynamic complexity of mineral-water interface reactions influence the cycling of elements and the ultimate chemical disposition of radionuclides in subsurface environments.

EXECUTIVE SUMMARY

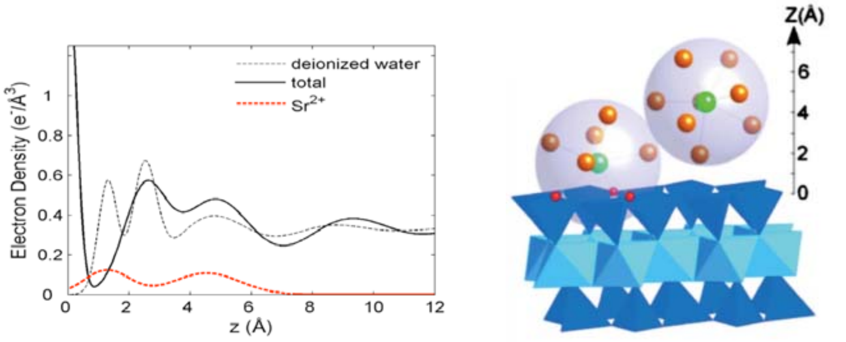
Natural mineral-water interfaces are invariably complex both in terms of structure and reactivity. Complexity exists at natural mineral-water interfaces across a range of length scales, from atomic-scale structure at crystallographic mineral terminations to multiscale variability associated with imperfections such as defects, pores, or even fractal topography. This complexity is accompanied by spatially variable reactivity operating over a wide distribution of time scales leading to overall dynamic behavior that is difficult to predict. Furthermore, mineral surfaces can have partial or complete coverage by various kinds of coatings. Inorganic coatings can evolve either by precipitation or sorption of material from solution to the surface, or via dissolution of more soluble parts of the material, leaving behind more insoluble coatings that impact the adsorption of ionic species. A significant fraction of mineral surfaces in natural environments are coated by organics or extensively colonized by microbial organisms, which creates complex interfaces with the surrounding aqueous solution. Biofilms may obscure the mineral surface from solution, or create microenvironments in which the local solution conditions are different from those in the bulk solution. In addition, bacterial activity may catalyze the transformation of toxic metals into less or more toxic species, affect their mobility through redox chemistry and biomineralization, or enhance the dissolution of the underlying mineral substrate. Therefore, most processes affecting the cycling of elements and radionuclide mobility, such as adsorption, diffusion, growth, dissolution, precipitation and interfacial redox reactions, operate on a very complex microscopic landscape with a high degree of spatial and temporal heterogeneity (see the sidebar on *Intrinsic structural complexity at mineral-water interfaces*).

Investigation of idealized mineral surfaces, such as those using prepared single crystal terminations, has provided unprecedented insight into the structure and reactivity at the molecular level. There is a pressing need to drive these kinds of investigations towards

Intrinsic structural complexity at mineral-water interfaces

The ability to observe molecular-scale processes at mineral-water interfaces is derived directly from the availability of advanced national scientific user facilities. High brilliance hard X-ray sources provide unique opportunities to probe mineral-water interface processes *in situ* and in real-time, making use of the highly penetrating nature of X-rays. X-rays can probe interfacial processes through various approaches, ranging from spectroscopy and diffraction to microscopy-based techniques.

Recent advances provide new opportunities by combining the benefits of these different approaches. Resonant anomalous X-ray reflectivity (RAXR) has the elemental and chemical sensitivities of X-ray spectroscopy combined with the structural sensitivity and interface specificity of X-ray scattering techniques. Applied to the case of ion adsorption at the mica-water interface (e.g., as a model clay mineral), a comprehensive understanding of ion adsorption was obtained (Park et al. 2006a). These results revealed that the interfacial binding of even simple ions (e.g., Sr^{2+}) can be complicated by the balance between the electrostatic attraction and the energy cost of ion dehydration, resulting in coexisting adsorption configurations. These results also directly revealed that the hydration structure immediately adjacent to the interface was disrupted by adsorption of the ion, thereby demonstrating the inherent coupling and interplay between molecular-scale structure and the associated processes.



Interfacial electron density within 0.01 M $Sr(NO_3)_2$ *in contact with muscovite (black solid line) compared with that of deionized water (blue dashed line) is shown as a function of height above the surface (left panel). The element-specific Sr profile (red dashed line) reveals two distinct ion heights corresponding to the coexistence of "inner-sphere" and "outer-sphere" adsorption complexes, shown schematically in the right panel. (Park et al. 2006a)*

incorporation of increasing structural, compositional and physical complexity to strengthen their link to conditions expected in natural settings. Research needs to take advantage of advances in surface analytical spectroscopies and microscopies, the emerging improvements in synchrotron and neutron capabilities, and the continually increasing power of computational facilities to enable next-generation insights.

SUMMARY OF RESEARCH DIRECTION

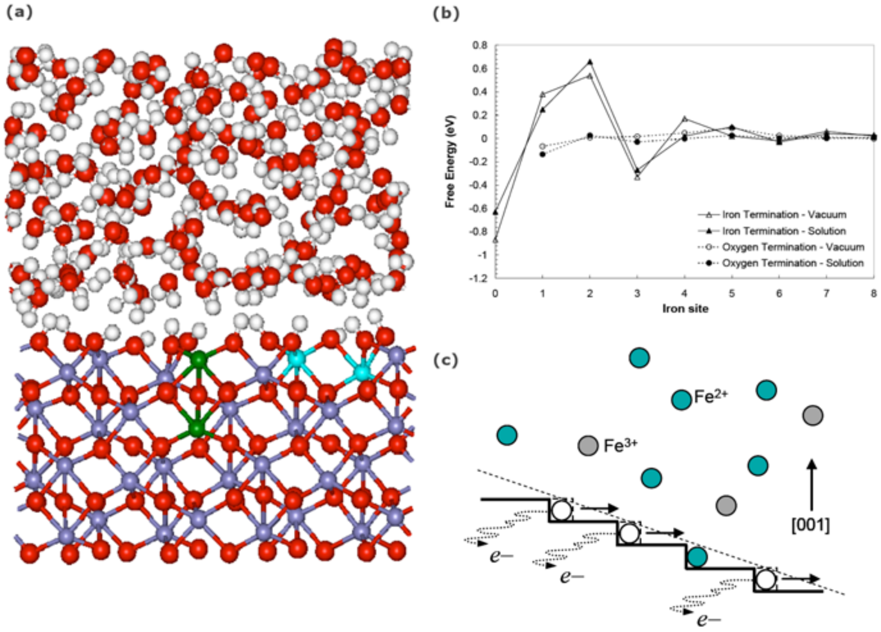
There is an overarching need to interrogate the complex structure and dynamics at mineral-water interfaces with increasing spatial and temporal resolution using existing and emerging experimental and computational advances. Scanning probe microscopic methods, and synchrotron (Fenter et al. 2002) and neutron sources (Wenk 2006) allow mineral-water interfaces to be investigated *in situ* with unprecedented detail. Such studies have recently shown, for example, that the atomic structure of surfaces is sensitive to the presence of water and aqueous species at the interface, and to temperature/pressure, that a complex interplay of surface hydration/hydroxylation processes and ion desolvation/ligand exchange reactions can dominate nominally simple sorption reactions of ions on well-defined mineral surfaces, that electronic feedback between surface electron transfer processes and bulk electronic structure properties of semiconducting minerals supports spatially coupled site reactivity, and that leached layers commonly develop on mineral surfaces during dissolution (Brown et al. 1999). It is crucial to improve the spatial, energetic and temporal resolution capabilities of *in situ* spectroscopies and microscopies to facilitate distinctions between various possible sorption structures and compositions at mineral-water interfaces. Next-generation sources and computational hardware and methods will help to develop an understanding of this complexity and these dynamics at a robust quantum mechanical level. Fundamental studies on idealized mineral-water interfaces are critical for providing a means to probe molecular-level structure, reaction mechanisms, and dynamics of elementary processes.

To strengthen the link between these studies and the complex conditions expected for natural mineral-water interfaces, a great deal of research is required to understand the role of non-idealities and the time-dependent behavior of the interface. For example, the incorporation of trace impurities alters growth kinetics through the modification of elementary step dynamics by mechanisms such as the pinning of step motion. Changes in interfacial composition during growth due to, for example, differential ion dehydration kinetics as the rate-limiting step for incorporation or by incorporation of vacancies, lead to the development of lattice strain that can change both the conformation of the growth (island vs. film) and self-limiting interfacial reactions. Furthermore, defects can dominate the thermodynamic stability of surfaces and the kinetics of growth and dissolution, affecting the incorporation or release of minor constituents. Ion and charge transport processes both on the solution and mineral sides of the interface can couple in ways that makes their separation impossible or irrelevant (see the sidebar on *Solid-state charge transport at mineral-water interfaces*).

Extension and development of new molecular probes using next-generation sources for understanding the structure and dynamics of complex mineral-water interfaces are needed to better understand mechanisms and kinetics of element cycling and radionuclide mobility in the subsurface. Advances in computational methods are also needed to provide feedback in support of experiments and to gain insights into processes that will remain difficult to experimentally probe. Traditional computational methods involving *ab initio* optimization of surface structures have been useful but yield only a static description of the interface; techniques and computational resources are needed that allow a better understanding of surface dynamics (Cygan and Kubicki 2001). Large-scale computer hardware and efficient algorithms for *ab initio* molecular dynamics at the density functional theory level need to be advanced to the stage of

Solid-state charge transport at mineral-water interfaces

Heterogeneous electron transfer is the basis for much of interfacial geochemistry, controlling processes such as metal cycling, contaminant transport, and microbial activity. For example, reductive transformation of iron oxide minerals is a key part of the iron biogeochemical cycle. Reduction of lattice Fe^{3+} to Fe^{2+} leads to dissolution of the solid mineral phase, but the electronic structure of many iron oxides allows for electron transport within the lattice. Thus iron surface sites undergoing reduction do not necessarily correspond to the locations of iron release. Using state-of-the-art molecular modeling tools such as Density Functional Theory coupled with molecular dynamics simulations, the mobility of electrons at various low-index hematite surfaces has been evaluated, with some surprisingly high electron hopping rates predicted (Kerisit and Rosso 2006). These findings point to the possibility of lattice self-diffusion of electrons as an explanation for, for example, the transfer of electrons from the points of microbial cell attachment to reactive sites through the hematite lattice. Thus electron transfer at mineral-water interfaces is complicated in many cases by the electronic structure of the solid phase.



Combined quantum mechanical and molecular dynamics simulations reveal an intrinsically high self-diffusion mobility for electrons donated to iron atoms in the mineral hematite (Kerisit and Rosso 2006). (a) A simulation cell for the hydroxylated hematite (001)-water interface (red—oxygen ions, blue—iron ions, white—hydrogen ions) showing two possible electron migration pathways (green—iron pair and light blue—iron pair). (b) Free energy calculations show that the mobility is sensitive to the crystallographic termination and the structure at the interface, and reveal iron sites in the uppermost few Ångstroms of hematite (001) that preferentially trap mobile electrons. (c) New mineral-water interface models must incorporate a link between interfacial redox reactions and solid-state electron migration to describe processes such as the autocatalytic growth of hematite (001) by adsorption of Fe^{2+} and subsequent electron transfer into the solid.

being able to simulate thousands of atoms over sufficiently long time scales to determine time-averaged mineral-water interface stabilities. Continual improvement in the scalability and implementation of such methods across emerging petascale computing resources could allow at least a factor of ten increase in both numbers of atoms and simulation time scales over current capabilities (see sidebar on *Solid-state charge transport at mineral-water interfaces*). To make reliable kinetic predictions, it is critical to not only be able to provide good energies, but also to be able to sample the phase space of the system well enough to be able to predict consistent reaction paths, mechanisms, and rate constants along with the entropy of the system. Whereas this can be accomplished for single molecules, it is far more difficult to do for solutions, surfaces and interfaces. Progress is being made in this area, but substantial advances are needed for the prediction of reliable parameters for use in higher scale models.

Specifically for radionuclides, generally applicable electronic structure methods for the reliable prediction of the properties of molecular systems and materials with active *f* electrons need to be developed. These systems with actinides require relativistic treatments because of the high atomic number. New theoretical approaches, including advances in Density Functional Theory to deal with the strongly correlated electron problem, techniques to deal with the multiplet problem, and new methods to predict important properties of materials and chemicals with known error limits, need to be developed. These techniques need to be applicable to heavy elements in solution, in the solid state, and at surfaces, and need to be useful for predictions to chemical accuracy of the thermodynamics and kinetic processes for complex interfacial systems.

SCIENTIFIC CHALLENGES

Fundamental challenges involve the ability to:

1. Translate a molecular-scale description of complex mineral surfaces to thermodynamic quantities for the purpose of linking with macroscopic models
2. Follow interfacial reactions in real time to separate out the roles of kinetic and thermodynamic phenomena
3. Understand the mechanisms by which minerals grow or dissolve, and how these mechanisms dynamically couple to changes at the interface
4. Understand the interrelationships between hydration structure and mineral reactivity at the same level of detail with which we currently understand aqueous ion reactivity
5. Observe elementary oxidation state changes of mineral surfaces and reactants, and determine the kinetics of associated electron transfer reactions
6. Isolate element-specific aspects of interfacial reactions with high spatial and temporal resolution

A key goal will be to understand how these molecular-level aspects of interfacial phenomena depend on temperature and solution composition, and how they are related to macroscopic observables so that the results can be connected to larger-scale experimental and theoretical characterizations. It will be necessary to apply these objectives to conditions beyond highly idealized mineral-water interfaces near equilibrium to appreciate the role of complexity under reactive conditions where the interfacial composition and structure may be dynamically changing with time.

SCIENTIFIC IMPACTS

Ultimately this research direction will achieve a robust understanding of the intrinsic heterogeneity of mineral-water interface chemistry at the molecular scale, including the coupling among structure, hydration, impurities, defects, redox reactions, interfacial dynamics and transformations. Research in this area will introduce new scientific methodologies for preparation and characterization of mineral surfaces in ideal and complex structural and chemical environments. The need to understand molecular-scale structure, function, energetics and dynamic processes at mineral-water interfaces will also help drive the development of advanced computational methodologies. Collectively, the focus on mineral-water interface complexity and dynamics will lead to a fundamental understanding of phenomena underlying mineral transformations (e.g., movement of redox boundaries, anthropogenic changes in the subsurface associated with the sequestration of energy byproducts, those driven by biologic activity), and will provide a bridge between laboratory studies and field studies where there continues to be orders of magnitude discrepancies in measured reaction rates.

TECHNOLOGY IMPACTS

Practical contributions to chemical migration in geologic storage sites include fundamental new knowledge to enable the design of modern engineered barrier systems that function via contaminant-surface interactions, and improved understanding of the role of mineral-molecule interactions that will advance modern science-based predictive capability for contaminant transport models. This research direction will yield a scientific basis for how to improve and optimize the design of geological repositories, including those for nuclear waste from tailored fuel cycles.

Advances in modeling, imaging, and spectroscopic interrogation of mineral-water interfaces will improve our fundamental understanding of a range of complex geological systems, and may also aid in the design and optimization of heterogeneous catalysts, nanoparticles and ceramic feedstocks, batteries, solar cells, fuel cells, and hydrogen storage media.

NANOPARTICULATE AND COLLOID CHEMISTRY AND PHYSICS

ABSTRACT

Understanding particle-facilitated transport of radionuclides and other trace contaminants is essential to reliably predict the impacts of energy production and long-term isolation of energy-system wastes on subsurface geological environments. Geochemical reactions between injected fluids such as CO_2 and the subsurface minerals and ambient aqueous fluids may also generate mobile particulates that affect porosity and permeability evaluation within a porous formation. The fundamental questions central to attaining this goal include the following:

- Which environmental processes lead to the formation of nanoparticles and colloids?
- What are the atomic-level structures of these particles?
- How are contaminants distributed within these particles?
- What are the dominant solution and interfacial factors governing stability, reactivity and ultimate fate of these particles, and how do they interact with heterogeneous natural systems?

Advances on these scientific questions will ultimately help to ensure the safe, long-term isolation of nuclear and other wastes.

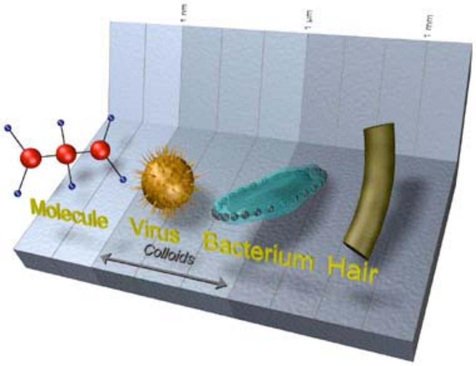
EXECUTIVE SUMMARY

Nanoparticles and colloids (which by International Union of Pure and Applied Chemistry (IUPAC) definition include nanoparticles—see sidebar on *What is a colloid?*) have sizes ranging from 1 nm to 1 μm and are composed of inorganic and/or organic matter. Radionuclides and other contaminants can attach to the surface of pre-existing colloids or can themselves form colloids. Thus, all colloidal forms play a critical role in the dispersion of contaminants from energy production, use, or waste isolation sites. Because colloids are complex species, they must be studied in detail at the molecular level to provide the data to reduce uncertainty in larger-scale transport models. New advances in characterization, sampling technologies, and computational approaches are needed to acquire these data from which new conceptual models of the microscopic nature of colloids could be developed. The reactivity, fate and transport of colloidal particles in aqueous environments over larger scales also require advances in these areas.

Colloid characterization is difficult because of their small sizes, chemical complexity, and structural variability. A single colloid may be a composite of irregular structures with differing compositions which further complicates characterization. Improved sampling methods for capturing representative colloids, including those transporting contaminants, from natural environments without introducing artifacts are critical to develop. Modeling colloids at the molecular level is a particular challenge. Advanced computational methodologies must be able to treat actinides, large nanoscale particles, and complex and heterogeneous species in solution and at interfaces. New and better approaches to measuring reactive transport at the pore, column and field scales are necessary to develop conceptual and mathematical models of colloid-associated transport of contaminants. Fundamental research on colloidal particles will lead to better models of radionuclide and other contaminant transport with lower uncertainty, improved performance assessment of isolation sites for nuclear waste and other energy byproducts, and improved engineered barriers for waste isolation.

What is a colloid?

According to IUPAC, colloids are nanoparticles and macromolecules in the defined size range between 1 nm to 1 µm (Buffle and van Leeuwen 1992). Colloids occur in two forms: *intrinsic colloids*, which have the same metal-ion or binding group(s) over the entire structure, and *pseudocolloids*, which are effectively intrinsic colloids with a different chemical coating. In the former, radionuclides can comprise the colloid, often as the hydroxide, oxyhydroxide or oxide nanoparticle. In the latter, frequently one of the structures is organic and the other most often inorganic. For example, iron (hydr)oxide colloids may be covered by a coating of natural organic matter (humic or fulvic acid) and radionuclides such as actinides will bind to the coating and not to the central $(Fe_2O_3)_x$ core. Humic and fulvic acids can have sufficiently large structures that they can be classified as colloids. They are common in soils, groundwaters, terrestrial lakes, and rivers.



Source: http://www.grimsel.com/crr/crr_intro.htm
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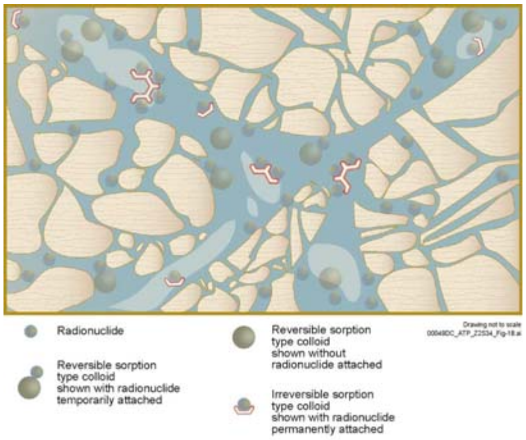
Colloids, both as intrinsic colloids and as pseudocolloids, can bind actinide cations and be a factor in actinide behavior at most environmental sites (McCarthy and Zachara 1989). Humic acid can even reduce some metal cations (e.g., PuO_2^{2+} to Pu^{4+}). The surface properties of colloid and aquifer solids or fracture surfaces govern colloid attachment and retention. The potential importance of colloid-facilitated transport in the geologic environment has been long recognized but is difficult to predict and model. Strongly-sorbing and/or highly insoluble radionuclides are likely to be transported in the subsurface only in association with colloids.



Source: http://www.ocrwm.doe.gov/documents/ser_b/figures/chap4_2/f04-136.htm

SUMMARY OF RESEARCH DIRECTION

The overall goal is to develop new approaches for the characterization of colloids and prediction of their behavior in natural environments. This will involve:

- Improving techniques to reliably sample the distribution of colloids in natural systems
- Developing new experimental and analytical methods to measure and characterize the structure, stability, and reactivity of synthesized and natural colloids
- Constructing new conceptual models and simulation methodologies across the range of temporal and spatial scales relevant to the chemical interactions and physical transport of colloids

Completion of these objectives will require access to national user facilities including light sources, neutron sources, mass spectrometers, NMR spectrometers, nanoscience and technology centers, and high-performance computers.

SCIENTIFIC CHALLENGES

To address the above issues, the following advances in basic science must be achieved:

- Formulate a fundamental theory for the formation, structure, and stability of colloids derived from organic, inorganic and microbial sources
- Develop new methods to measure and predict the interaction and reactivity of colloids with radionuclides, and inorganic and organic ligands
- Develop novel approaches to characterize and predict the mobilization and transport of colloids in heterogeneous natural systems

Colloids (see sidebar on *What is a colloid?*) are ubiquitous, occurring even in distilled water (Bundschuh et al. 2001) due to leaching from container walls and introduction during processing. Colloids can either be intrinsic or pseudocolloids, inorganic or organic, crystalline or amorphous. Inorganic colloids of interest include metal oxides and clays. Recent studies of intrinsic actinide colloids have shown that the distribution of the radionuclide (Pu) among dissolved, colloidal, and solid phases and among various oxidation states can be described using equilibrium thermodynamics; however, thermodynamics alone may be inadequate to describe the colloidal behavior of other contaminants.

Organic colloids are composed of biopolymers or geopolymers. Biopolymeric colloids include exopolymeric substances (EPS) excreted by microorganisms (MW = 10–1000s kDa). EPS help microorganisms attach to surfaces within biofilms or aggregates, but it is not known how microbial communities regulate the attachment properties of their EPS, nor how fast different EPS molecules are degraded and/or transformed by exoenzymes. Geopolymers include humic and fulvic acids, which are residues of biogenic organic matter (MW = 1–10 kDa) (Trumbore 2000; Backau et al. 2004). In general, fulvic acids have high mobility, and humics and EPS have lower mobility. Both bio- and geopolymers have good complexing properties for trace metals and radionuclides, as well as amphiphilic properties, i.e., hydrophilic and hydrophobic regions or moieties, which give them special surface-active (e.g., surfactant, emulsifying) properties. Hydrophobic regions of aquatic colloids are often “hidden” from the water by conformational changes of the molecule, such as those that control folding of protein groups or humic micelle formation. Drying can make soil organic carbon more hydrophobic, potentially affecting the mobility of colloids in the unsaturated zone.

Overall, the physico-chemical interactions between the different molecules that make up “dissolved” organic matter, including humic substances, are not well understood. All colloid-sized particles, including minerals, organic polymers, and bacteria, have a high capacity for adsorbing a variety of contaminants and trace components, including radionuclides and toxic metals.

Sampling

A variety of sampling systems are used to collect and concentrate colloids and colloidal contaminants (including radionuclides) from surface or groundwater for analytical purposes (size or molecular weight separation). Current knowledge of sampling, characterization, and interaction mechanisms for colloids with metals or radionuclides was recently reviewed by IUPAC (Wilkinson and Lead 2007, and references therein). Sampling techniques include (1) ultrafiltration (cross-flow, tangential flow, stirred cell); (2) field flow fractionation; (3) reverse osmosis; (4) electrophoresis; (5) combined electrodialysis and reverse osmosis; (6) chromatographic (HPLC, or High Performance Liquid Chromatography) and resin techniques, including size exclusion, hydrophobic resins or ion exchange. *In situ* approaches for sampling groundwater are challenging, because they often have to be conducted under reducing conditions. Such approaches need to have minimal disturbances due to artifactual colloids introduced during well sampling, and minimal aggregate formation or fractionation processes (e.g., anion rejection) at the membrane during processing. In laboratory experiments, when working at picomolar levels (or below) for a species of interest, special attention has to be paid to artifactual colloids introduced by reagents, from aerosols, or from wall leaching.

Atomic-scale characterization of colloid structure

Because of the site heterogeneity of natural colloids, stability constants for metal complexation increase with decreasing metal-ion concentration, making it a challenge to probe binding constants, speciation, and structure at environmentally relevant concentrations. Recent advances in colloid characterization are reviewed for IUPAC in Wilkinson and Lead (2007). New techniques for determining the chemical composition and structure of single molecules or compounds include multidimensional NMR and mass spectrometry with electrospray sources. Imaging and surface probing techniques include transmission electron microscopy (TEM) of samples embedded in hydrophilic resins, cryo-TEM on frozen solutions down to < 10 nm, atomic force microscopy (AFM) techniques for imaging, and measuring adhesion forces and charge distribution on colloidal sized inorganic nanoparticles and organic macromolecules, and the correlative use of imaging techniques with different length scales. Dynamic size determination techniques include fluorescence correlation spectroscopy (FCS) and dynamic light scattering (DLS) to quantify aggregate size as a function of time (i.e., aggregate formation).

Recent developments associated with DOE user facilities, when combined with other available structural techniques, now provide the tools needed to probe structure across the length scales of colloids. Structural characterization techniques have largely been limited to probing either short-range correlations (< 5 Å) or long-range ordering (> 40 Å), so colloid-scale correlations occur at length scales currently inaccessible for study. This historically unavailable window of information is crucial to the development of a predictive understanding of colloid structures in solution and their aging and precipitation reactions as well as providing input for modeling dissolution energetics and migration phenomena. The current probe of choice for short range correlations in non-crystalline systems is XAS (X-ray absorption spectroscopy), which includes both XANES (X-ray absorption near-edge structure) and EXAFS (extended X-ray absorption fine structure). XAS is a single-ion probe that can be used to target metal-ion speciation, at concentrations down to submillimolar, in a complex system, through selectivity provided by characteristic X-ray absorption lines. The technique provides information about speciation including oxidation state and near-neighbor coordination environments out to distances of about 5 Å.

For long-range correlations (> 40 Å) that exhibit periodicity (order), X-ray diffraction is the method of choice. The challenge, within the context of colloid characterization, is finding ways to synthesize or isolate molecular crystals suitable for structural characterization. Rarely available, this information constitutes the ultimate structural characterization.

Small angle and high-energy X-ray scattering has been applied to the study of solute correlations in aqueous solution, providing the missing bridge for structural characterization of intrinsic colloids. Although not extensively employed to date, small angle scattering (SAXS (Small Angle X-ray) and ASAX (Anomalous Small Angle X-ray)) potentially provides important information about colloidal morphologies, particularly for heavy-metal containing nanophases, where the contrast with the aqueous solution is optimal. Under favorable conditions, high-energy (> 60 keV) X-ray scattering (HEXS) experiments can be used to probe solute correlations at length scales to distances of 20 Å or longer, precisely the size-range important to an understanding of aggregate formation. Information about interactions over this crucial length scale is not currently available from any other technique. Recent advances in X-ray imaging are extending the spatial resolution down to 30 nm or less, well within the length scale of importance to colloid characterization by diffraction, fluorescence or transmission imaging (Nilsson et al. 2005).

Theory, modeling and simulation

Modeling colloids at the molecular level is a challenge because of the broad range of sizes, structures, compositions, and heterogeneous atomic positions. There are specific issues due to differences between intrinsic colloids and pseudocolloids in the area of radionuclide transport. A colloidal particle can react and effectively adsorb contaminants, but these may be only a very small fraction of the number of atoms in the actual colloid. This leads to significant questions in terms of the size of the aggregate that should be used to model colloids important in natural systems. Furthermore, colloids relevant to geochemistry and radionuclide activation and transport are essentially metastable “phases” that exist in aqueous solution. Modeling of colloids, their formation, and their reactivity requires the inclusion of the solvent. Besides size, there are considerable problems in dealing with the evolution of the colloid from its formation and reactivity through its aging to its transport, all of which span many orders of magnitude of time scale, making computations difficult. Time is inherently a linear process and the number of time steps scales linearly with processor speed. Current and planned computer architectures show large numbers of processors, but no single processor will have high performance. One can take advantage of massively parallel computer architectures in terms of system size, but not in terms of making predictions of the system over the long time scales necessary for modeling geochemical processes involving colloids. Also, there is need for improved accuracy in simulations from the perspectives of the data needed for models at larger scales and the ability to predict electronic structures as system size increases.

Computational methods for describing particles greater than 2 nm in size (500 to 1000 atoms) do not currently have the accuracy that can be obtained for molecular systems at or below this size. This is especially true for molecular systems containing radionuclides, notably the actinides, which require relativistic treatments due to the high atomic number (Vallet et al. 2006). Methods must be developed to predict the electronic structure of large systems, including relativistic effects, with the accuracy necessary for developing predictive models at the molecular to nanoscale and at higher scales. These could include new exchange-correlation functionals for Density Functional Theory and basis set-free methods as well as improvements in *ab initio* molecular dynamics and solvent models to deal with long-range interactions. New approaches will be needed for force-field-based methods to predict the behavior of much larger systems at longer times, including improved formulations for long-term dynamics, sampling of phase space, force fields for all atoms in the Periodic Table, and mixed electronic structure/force-field methods based on theoretical or empirical parameters. Reactions within colloids and on their surfaces will require novel ways to predict solvation/desolvation and reactivity in complex systems. Innovation is essential for the modeling of reaction kinetics, including transition states and other rare events, and thermodynamics in solution, which must include appropriate sampling of phase space for reliable predictions of entropy in complex, heterogeneous systems. New statistical physical approaches will be needed to predict the chemical behavior and motion of large colloids that may or may not be charged in solution.

At the next set of scales, approaches suitable for predicting the movement of colloid-associated contaminants through the vadose zone and into groundwater environments rely on advances in our understanding of colloid mobilization, transport, and deposition within water-saturated and unsaturated porous media. Mobilization, which describes the release of colloids into pore water, is driven by fluctuations in flow and perturbations in pore water chemistry. Quantitative inferences on mobilization rates are limited by too few observations of the phenomenon. Laboratory measurements made at the Darcy (column) scale are needed to elucidate how mobilization rates are linked to measurable properties of the porous media, pore water, and colloids. Pore-scale observations that identify mechanisms that govern mobilization are needed to guide the development of a theory for colloid release in unsaturated and saturated geologic solids. Once mobilized, colloids move by advection and dispersion and are susceptible to removal from the pore water (deposition) by reactions that take place near solid-water and, in the case of unsaturated media, air-water interfaces. Knowledge of colloid transport and deposition in ideal systems must be extended to account for complexities associated with real subsurface environments. In particular, the presence of organic coatings on colloid surfaces, and heterogeneity in the physical and chemical properties of the porous media, should be evaluated for their roles in influencing colloid transport and deposition. Also, parameters and models from smaller scales must be incorporated into the scale describing colloidal transport in natural systems. Thus, new and improved reactive transport approaches need to be developed to deal with the transport of these nanoscale particles. Collectively, developments from research at the pore, column, and field scales are critical to the development of conceptual and mathematical models of colloid-associated contaminant transport through the heterogeneous geologic environment.

The above topics are all great challenges that will require substantial computational resources. Advances will require new mathematical and theoretical approaches, and implementation of software for high performance architectures, if we are to be able to make reliable predictions on the colloidal systems of interest. Such developments will require the interaction of geoscientists, domain specialists, mathematicians, and computer scientists working in teams.

SCIENTIFIC IMPACTS

Anticipated scientific impacts from the proposed research include:

- The capability to predict the chemical and physical behavior of nanoparticles and colloids in the environment
- New geochemical models for colloid formation and colloid-contaminant interactions
- A fundamental theory of colloid transport in variably saturated media

TECHNOLOGY IMPACTS

These scientific advances will provide new knowledge for use in improving:

- Models of radionuclide transport with lower uncertainties that specifically include the role of colloids
- Performance assessment of isolation sites for nuclear wastes and other energy system byproducts
- Engineered barriers for waste isolation
- Remediation technologies for environmental contaminants

DYNAMIC IMAGING OF FLOW AND TRANSPORT

ABSTRACT

Managing waste and resources in the subsurface critically depends on predictions of fluid flow, mass transport and reaction rates. Our current capabilities to measure these phenomena and properties are extremely limited, especially *in situ*. To develop the capability for dynamic imaging of flow, transport and reactions, it is necessary to measure state variables continuously in space and time, rather than locally or at fixed scales. This needs smart tracers that are capable of relaying their locations and concentrations remotely, or providing chemical reaction rates at the appropriate scales. Improved resolution in space and time measurements of phase saturations, new means of estimating groundwater age distributions within individual fluid samples, and better understanding of the interaction of physical fields with fluid-filled porous media on a variety of length scales are all required.

EXECUTIVE SUMMARY

Waste disposal, environmental remediation, and the efficient exploration, production, and management of the earth’s resources depend critically on the migration of fluids in the subsurface, and the geochemical reactions that occur in the subsurface. Presently, some of the properties and processes can be measured in the laboratory or *in situ*, but current science and technology is not sufficiently far advanced to measure certain properties *in situ* at depth. Open questions exist in the details of the transport of multiphase reactive flow in porous media that cannot be addressed adequately even at the laboratory scale because of a lack of adequate diagnostic methods.

Subsurface science used to predict behavior of transport processes is based on local values of state variables (e.g., pressure, temperature, concentration, phase saturations) in heterogeneous media. Models of those media used to make predictions typically are not sufficiently constrained by local measurements. As a result, the models are non-unique and are typically considered more appropriate for hypothetical analysis than for *bona fide* prediction. *In situ*, multiscale measurement of state variables, flow, transport, fluid age, and reaction rates would dramatically improve both our understanding of subsurface fluid processes and our ability to produce predictive models.

Research is needed in four areas to make further progress:

1. There is wide scope for the development of smart tracers. These can be chemical tracers (active or conservative), reactive tracers whose presence, or state, can be probed with physical fields (e.g., organo-metallic tracers), or miniature sensors that can be distributed through the subsurface. Coupling these tracers to microbes as a transportation vehicle, or even as a source of energy, might create new opportunities.
2. Measured or estimated fluid age distributions within individual fluid samples would provide a leap forward in our ability to characterize fluid flow pathways, rates, sources and multiscale dispersion, and to create predictive models of local-to-regional scale flow and transport. Key breakthroughs in the science of environmental tracers are needed to make this happen, particularly concerning our current inability to reliably date fluids in the 50–3000 year range.

3. Methods are needed for measuring state variables such as pressure and temperature continuously in space and time, rather than as local averages at points or within conventional well bores.
4. To diagnose and image flow, transport, and reaction rates, it is necessary to understand much better the interaction of physical fields, such as elastic waves or electromagnetic disturbances with fluid-filled porous media. This is especially important to advance our understanding of relevant upscaling and downscaling laws.

This research will have spin-offs for optimal management of fluids in the subsurface, which include waste disposal, enhanced oil recovery, and environmental remediation. Because of the fundamental nature of this research, much interaction with physics, chemistry and biology is envisaged. Technical spin-offs include the continued development of miniature sensors and distributed sensor networks. Because of the common importance of fluid transport, one may also expect interactions with research and engineering in medical imaging and diagnostics.

SUMMARY OF RESEARCH DIRECTION

To design or evaluate facilities for waste storage and to assess the impacts of chemical spills, transport of injected fluids, or leaks of radionuclides on the subsurface environment, it is necessary to measure and image subsurface physical and chemical properties that determine fluid flow, mass transport, and geochemical transformation. This is a difficult problem in geologic media because of the complex geometry and incompletely known history of subsurface rocks and sediments, as well as the high degree of spatial variability (heterogeneity) of the many physical and chemical properties. The variability is not simple because it is neither homogeneous nor statistically homogeneous. The variations are also, in general, neither random nor statistically stationary. Instead, the properties appear to vary differently at different spatial scales of measurement, so one often speaks of “multiscale heterogeneity,” and heterogeneity is viewed as “evolving,” in some sense, from the pore scale all the way to the basin scale. In reacting flows actual heterogeneity evolves over time.

In addition to the difficulty of characterizing an inaccessible, complex subsurface environment, research is limited by methods of measurement that are either confined to particular space or time scales, or provide results that are only indirectly related to properties or processes of interest. For example, we can measure single values of average fluid pressure and temperature within a control volume accessed by a well screen. These state variables measured at points in space or over limited control volumes must typically be interpolated in space. More importantly, the interpretation of their meaning must be done with models that incompletely and non-uniquely define the multiple scales of properties or forcings that dictate the local values of the state variables, which are also used to calibrate the models. Seismic velocities are an example. They are known to depend not only on the saturations and properties of phases present in the pore space, but also on the microscopic spatial distribution of the phases with the pores. A leap forward in both model calibration and our ability to observe complex phenomena in the subsurface would be provided by new methods of measurement that span multiple space and time scales, as well as better models for scale translation, as described in more detail in the Grand Challenges. Selker et al. (2006) provide an example of how spatially and temporally continuous measurement of temperature with fiber optics can open a new window into stream-streambed dynamics. It is time to start looking beyond traditional point measurements and to develop new methods for continuous spatial-temporal measurement of temperature and pressure in the subsurface. Similarly, measurement of solute concentrations or phase saturations continuously in space (e.g., along linear transects) and time should be explored.

Another important measurement or observational limitation is the difficulty of tracking or tracing actual fluid or mass movement within the subsurface. We can inject conservative tracers, but we virtually never know exactly where they go because of limitations in our ability to measure them at the appropriate scales and times. The time has come for major research efforts on *smart tracers*, where *smart* means that the tracer either tells us where it is or how long it has been in the system, may probe chemical, physical or biological properties, and store or relay that information. With a smart tracer, one could detect the location and concentration of the tracer remotely without having to rely entirely on local, *in situ* measurements. Another type of smart tracer is a substance that transforms at a known rate, providing information on residence time in the system. Groundwater age tracers are examples of this, but the methods of dating groundwater and the potentially wide distribution of ages within a fluid sample are in need of development. Research (e.g., Weissmann et al. 2002; Bethke and Johnson 2002; DePaolo 2006) shows that the local distribution of fluid age or residence time is much more broad (e.g., decades to millennia) and complex than previously assumed, and models demonstrate that such age distributions are sensitive to solute dispersion, preferential flow, leakage, and anthropogenic influence. Yet the lack of methods for comprehensively estimating different ages of groundwater, and deconvolving the results into local age distributions, limits the application of groundwater age for site characterization.

In addition to smart tracers, geophysical methods for direct estimation of fluid flow need further development. The presence of fluids can currently be detected by geophysical methods (seismic, electromagnetic). An example is shown in Figure 38, in which the electrical conductivity in Volcano Island, Italy, is shown to correlate well with the CO_2 flux, temperature and self-potential. In time-lapse images it is possible to monitor the change in fluid content with time (Haney et al. 2005), but this still does not constitute a direct measurement of flow.

The streaming potential is generated by a charge separation between moving fluid and the walls of the solid that contains the fluid. In the subsurface this is the rock matrix. For near-surface applications the streaming potential can be measured and used to infer the flow velocity directly. Since the measured electrical potential is influenced by chemical potentials as well, it is in practice necessary to unravel the streaming potential from the redox potential. This has successfully been achieved by Naudet et al. (2004), who measured the self-potential near a landfill and unraveled the contribution of the flow (through the streaming potential) from the chemical potential in the near-surface.

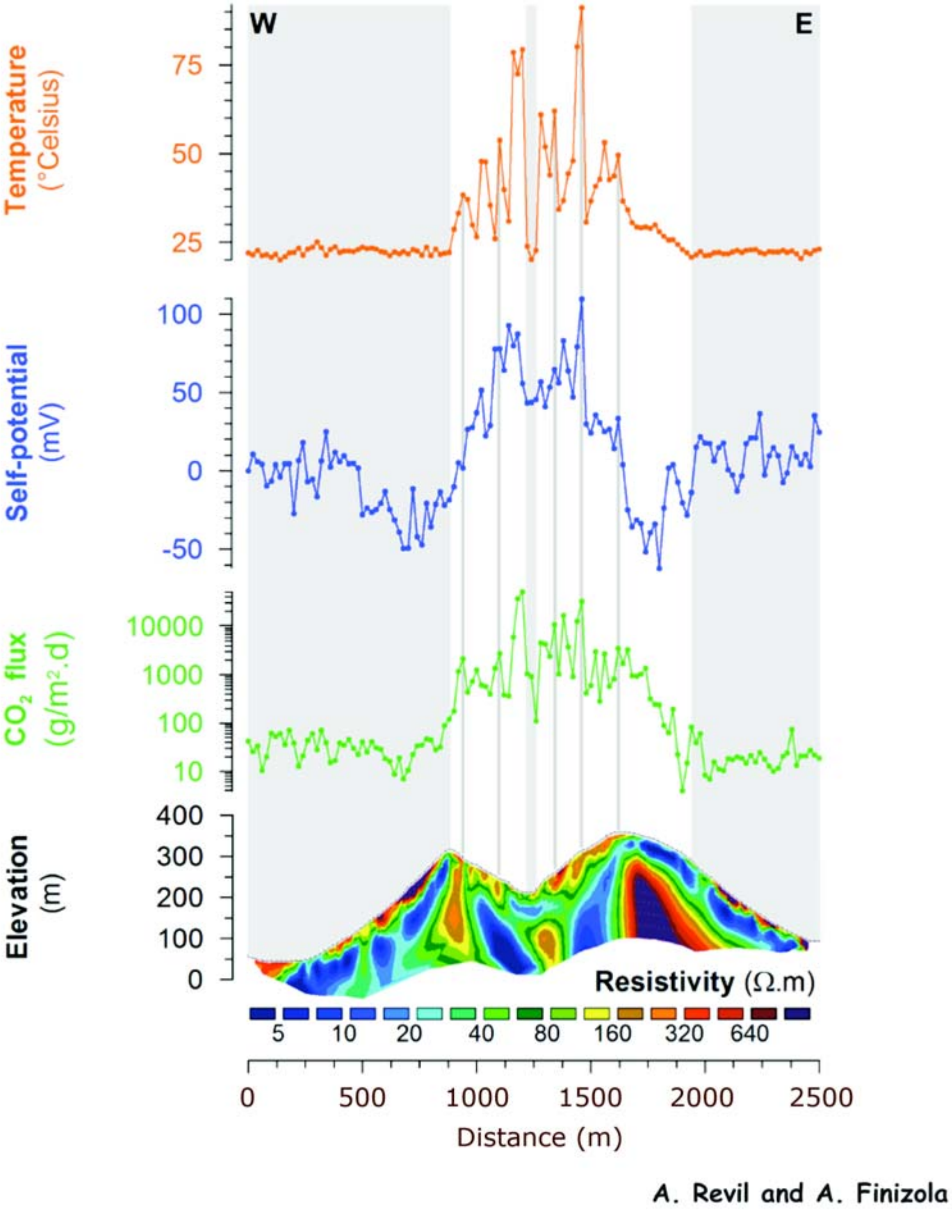


Figure 38. The temperature, self-potential, and CO_2 flux measured along Volcano Island (Italy). Bottom panel show a cross section of the electrical resistivity through the volcano (Revil et al. 2007a). Blue areas are conductive, indicating the presence of fluids. *Courtesy of A. Revil, CNRS-CEREGE.*

SCIENTIFIC CHALLENGES

It is currently possible to measure flow directly at the surface or in the shallow subsurface (e.g., Naudet et al. 2004). Our ability to measure flow directly at depth is currently extremely limited. Similarly, measuring reaction rates *in situ* is of particular importance because the reaction rates depend on the microstructure of moving and mixing reactants, as well as on the chemical properties. In a porous medium, surface processes play a particular role in this respect. The community needs to develop the diagnostic tools to measure flow, transport, and reaction *in situ*.

To overcome current limitations, two major future scientific challenges must be met. One is to improve the far-field visibility of reservoir attributes that drive flow and transport systems from the pore scale to the basin scale, and a second challenge is to develop the ability to describe flow, transport, and chemical reactions from observations of subsurface materials and fluids from a limited number of wells.

Meeting these challenges requires the development of a more thorough understanding of the natural variability of geologic media, as well as the refinement of existing geophysical methods and the development of new technology and methods of data analysis. The goal is to obtain detailed information concerning the chemical reactions that occurred in the medium or are presently occurring. The properties and geologic structure that control flow and transport phenomena need to be observed on a variety of scales, and scales appropriate to a particular problem need to be identified. Ideally, flow, fluid mixing based on tracer tests, and active chemical reactions need to be sensed and visualized directly.

In summary, the following research needs appear most critical:

- Understanding the hierarchy of linear and nonlinear principles that govern the propagation of physical fields through geologic media
- Advanced technologies for measuring physical, chemical and biological attributes that affect propagation of physical fields from the core scale to the molecular level
- Methods to quantify flow and reaction regimes from physical and chemical observations of fluid and solid phases
- Advanced measurement techniques based on improved theoretical, mathematical, and computational models for wave propagation

Spatially and temporally continuous measurement of state variables

It is currently possible to measure pressure and temperature adjacent to screened or open intervals within a well or at points in space (Figure 39). Recently, it has also become possible to measure temperature on the surface or shallow subsurface along continuous transects using fiber optics. The latter technique has provided a leap forward in measuring spatially complex phenomenon because it greatly reduces the need to integrate or interpolate point data on critical state variables, thereby providing vastly enhanced ability to detect critical phenomena and to constrain models. An important scientific challenge is to measure pressure, temperature, and possibly other variables, such as fluid electrical conductivity and phase saturation, continuously along transects emplaced via vertical or horizontal drilling in the subsurface.

Smart tracers

The level of instrumentation of hydrocarbon reservoirs is steadily increasing, and the phrase, *instrumented oilfield,* is used regularly (Tura 2005). With current developments in micro- and nanotechnology, and the advent of *smart dust* (e.g., Kahn et al. 2000) new opportunities exist for massive instrumentation of the subsurface. New tracers could be miniature measurement and data-relay devices, a combination of passive and active chemical tracers (Oates 2007), chemical tracers that respond to physical fields (such as organo-metallic tracers), or a combination of these. All of these are considered tracers as *smart tracers*.

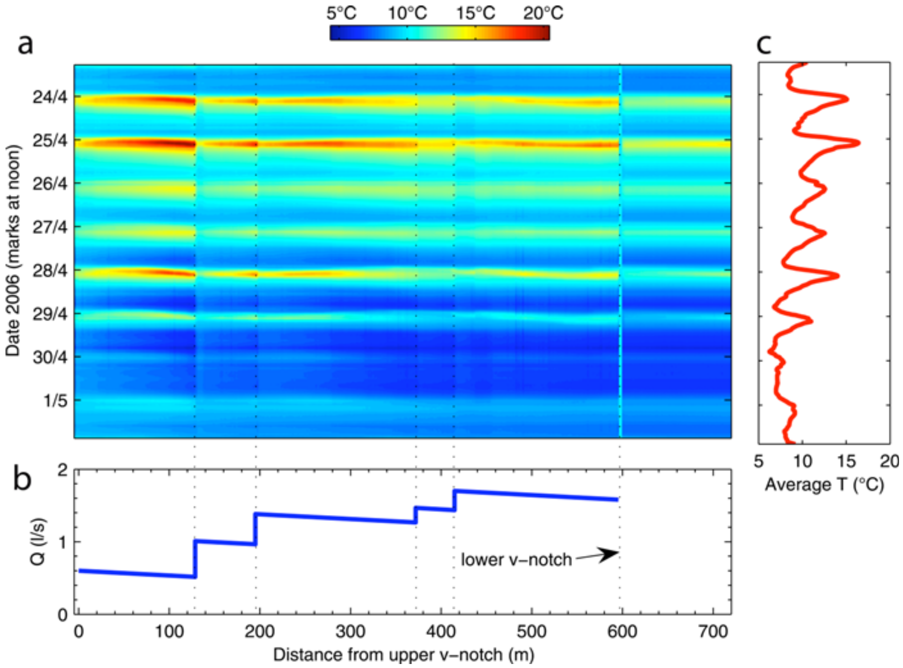


Figure 39. (a) Temperature distribution over time (vertically) and space (horizontally). (b) Amount of water flowing through the stream with the gains from the different sources and the losses as inferred from the temperature profiles and the up- and downstream v-notch measurements. (c) Average temperature over time with sunny days early on and cloudy days toward the end of the measurement period. From Selker, J., van de Giesen, N., Westhoff, M., Luxemburg, W., and Parlange, M.B. (2006). Fiber optics opens window on stream dynamics. *Geophysical Research Letters* **33**, L24401. Copyright © 2006 American Geophysical Union. Reproduced by permission.

Smart tracers may be developed to interrogate the biogeochemical reactivity, and physical or biological properties of formations. Tracer injections are conventionally used in subsurface science to track flow paths, and the ideal tracer for this purpose is nonreactive. Solutes with known reactivity could be used in addition to nonreactive tracers to acquire already upscaled measurements of reaction coefficients. Tracers could be designed to characterize small-scale mixing processes, quantify different phases, and measure the chemical and biological characteristics of formations that control chemical transformations.

Development of some smart tracers has already begun. Partitioning tracers that preferentially dissolve into oil are used to quantify remaining oil saturation in oil-bearing formations, and surfactants can quantify the interfacial area between phases. Conservative tracers with different diffusion coefficients can be used to quantify the role of diffusion and transfer between regions of high and low fluid velocity. Tracers can potentially be used to enhance the response to probing geophysical fields.

The opportunity now exists to develop new tracers that target the geochemical characteristics of a formation where chemical transformations and retardation occur. First, simple reactive solutes can be used to quantify the small-scale mixing process that drives complex geochemical reactions. By using well-understood and easily measured reactants, descriptions of small-scale mixing processes can be derived that are specific to a given formation. These empirically based models of chemical mixing and segregation would greatly improve our ability to model much more complex geochemical transformations. Second, reactants can be designed to target important geochemical characteristics of rock formations. For example, redox-sensitive solutes could gage the reductive or oxidative characteristics of a formation, thus providing important information for modeling transport of many contaminants. In the long term, sophisticated tracers could be developed that target specific characteristics of formations. Solutes that chelate specific elements and solutes that transform over different time scales under different conditions could be used to collect detailed information along a flow path that is then "delivered" to a sampling well where the solutes are retrieved.

Nonreactive tracers that can identify flow paths may be derived based on the emerging developments in the field of nanotechnology. Such tracers would be sufficiently small to move freely through a formation while communicating their positions and, possibly, measured variables to an observer. Such information might be propagated by releasing a continuous stream of nanobodies and having such bodies communicate with each other in an organized manner. The result could provide much more detail concerning the geometry of flow paths through geologic media, and vital mixing information.

Ultimately, it might be possible to attach microscopic measurement devices to microbes. When these microbes are (bio)engineered to move in specific spatial patterns, for example by following chemical gradients, they could be used as a transportation vehicle. By tapping into chemical potentials, the metabolism of these microbes could potentially be used as a power source for the sensor.

Groundwater age distribution

The molecules within a water sample from the subsurface have a distribution of ages that can range widely (e.g., years to centuries, or decades to millennia) and that is diagnostic of the fluid flow history, including flow pathways, sources of the fluid, dispersion, characteristics, preferential flow and leakage from adjacent media—all happening at the relevant multiple space and time scales. Data on groundwater age distribution within fluid samples therefore can be tremendously powerful for characterization and for calibrating or validating multiscale flow and transport models. The distribution of groundwater ages within a fluid sample, however, cannot be measured directly at present. It can only be inferred from models, and vaguely defined by a very limited set of age-dating tools.

Environmental tracer technologies currently exist to estimate residence times over time scales of about 0 to 50 years and over time scales of about 10^3 to 10^5 years, but there remains a fundamental gap in dating tools over time scales of 50 to ~3000 years (Figure 40). While several tracers could theoretically fill this gap (e.g., ^{39}Ar), advances in measurement technologies are still needed due to the very low concentrations of such tracers in natural waters. Suites of tracers that respond to various travel times are needed to resolve the travel time distribution. By measuring both mean and travel time distributions, an integrated characterization of flow rates, storage volumes, and mixing processes could be obtained with the help of flow and transport models.

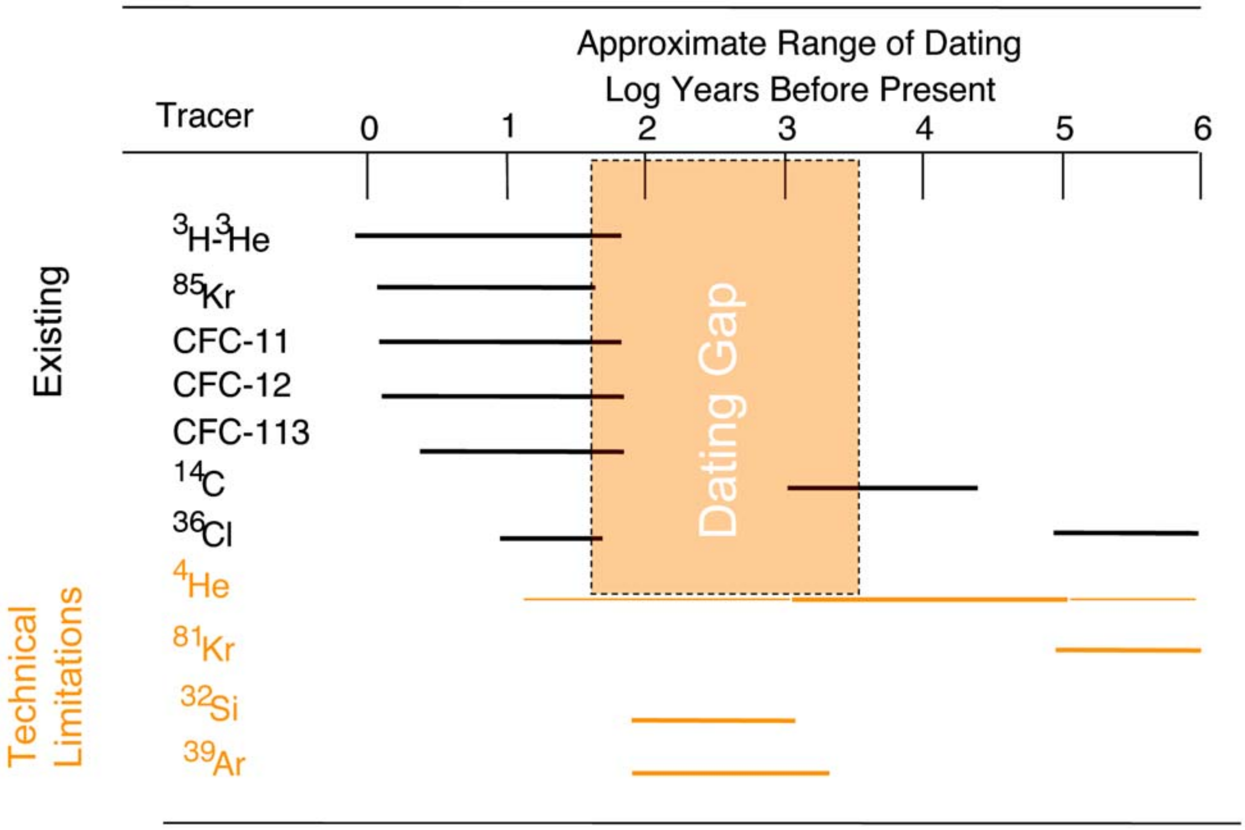


Figure 40. Illustration of available tracers and the current "age gap" that exists in dating the age of fluids in geologic reservoirs. Courtesy of K. Solomon, University of Utah (personal communications). Modified from L.N. Plummer, USGS (personal communications; see also Plummer et al. 1993).

The interaction of physical fields with fluid-filled rocks

Advances in the basic understanding of how physical fields (i.e., acoustic and electromagnetic waves) interact with subsurface materials and fluids are needed for better inversion of geophysical data. Seismic and electromagnetic data are rich in information, but the ability to map this geophysical information into physical, chemical and biological processes is hampered by gaps in understanding of how these fields interact with the subsurface. For example, the state of stress in the subsurface changes the propagation of seismic signals, but the direct relation between the velocity and attenuation of seismic waves with the microscale properties of fluid-filled fractured rocks is poorly understood. The problem becomes more challenging when including interactions of rock heterogeneity and fabric with pore fluid pressure and anisotropic stress fields. An improvement in the fundamental knowledge of how microscale responses to stress fields influences wave propagation needs to be developed and would enable inversion of data to determine the stress state in the field. Similar questions arise regarding seismic and electromagnetic response to changes in temperature. Advanced experiments using, for example, X-ray spectroscopy, will improve understanding of the microscale physical properties that control geophysical responses. Links between many geophysical responses (e.g., seismic attenuation, travel time, compressive-to-shear-wave ratio, electrical and magnetic fields) and rock/fluid properties have yet to be fully understood and exploited. Coupled models for flow dynamics and imaging could be based on a common framework for waves, potential fields, and flow and transport in porous formations.

SCIENTIFIC IMPACTS

Subsurface science relies on local measurements of state variables (e.g., pressure, temperature, concentration) in heterogeneous media and models of that media that typically are not sufficiently constrained by the local measurements. As a result, the models are non-unique and considered more appropriate for hypothetical analysis than for *bona fide* prediction. *In situ*, multiscale measurement of state variables, flow, transport, fluid age and reaction rates would dramatically improve both our understanding of subsurface fluid processes and our ability to produce predictive models. Such measurement allows for a better understanding of fluid flow and dispersion of pollutants, deepens our understanding of fluid-rock interaction, and helps address long-standing scientific questions concerning the details of reactive flow in porous media. Flow and reaction rates depend critically on the processes occurring at the microscale, and the proposed research therefore has implications for a better understanding of upscaling and downscaling laws to govern the behavior of the subsurface. The diagnostic methods to be developed will draw heavily on new research in physics, chemistry, biology, electronics, and data networking; significant cross-fertilization in these fields can be expected, especially in the field of micro/nanoscale structures.

TECHNOLOGY IMPACTS

Direct measurement of flow, transport, and reaction rates is highly valuable for improving the siting, design, performance assessment, and management of geologic disposal sites. Such improvements result in better-supported performance assessments and a resulting increase in political and public acceptance of geologic waste storage. Environmental remediation would become a much better defined process and hence more economical to perform. Also, improved imaging techniques would result in enhanced recovery of energy resources.

Better diagnostic tools are valuable for a wide range of problems that concern the behavior of fluid-filled rocks. Potential spin-off can be expected for enhanced oil recovery, environmental remediation, and optimizing the management of aquifers. Application can also be expected in civil engineering in the area of developing new underground infrastructure, or monitoring and managing the existing ageing underground infrastructure.

Work on miniature instrumentation is expected to benefit, and benefit from, other work on micro/nanotechnology and distributed sensor networks. Much of the work proposed here has parallels in biology and medical technology. Additional value can be expected by carefully coordinating these efforts.

TRANSPORT PROPERTIES AND *IN SITU* CHARACTERIZATION OF FLUID TRAPPING, ISOLATION, AND IMMOBILIZATION

ABSTRACT

Immobilization of fluids within pores and/or beneath impermeable stratigraphic intervals dominates a range of natural processes within the earth's crust, including the migration of fluids along fault zones, the creation and maintenance of natural geothermal systems, the emplacement of ore deposits, and the trapping of hydrocarbons. Fluid immobilization is also the single most important factor for assessing a proposed geologic CO_2 storage location. However, our current state of knowledge about fluid-trapping mechanisms and the flow properties of slow/no permeability intervals (seals), faults, and fractures under *in situ* conditions is limited, as is our ability to measure and characterize the spatial and temporal variations in the trapping mechanisms operating within a reservoir. Ground-breaking improvements in quantifying the relevant pore-scale physics, slow chemistry, response to pressure and fluid evolution, and remote measurement of mineralization and other changes in rock pores will lend needed insight into natural processes and ensure the success of large-scale energy byproduct storage.

EXECUTIVE SUMMARY

Various mechanisms play a role in the immobilization of radionuclides and fluids within the Earth. Mechanisms include trapping of fluids by geologic seals in the form of impermeable strata or faults, deposition of minerals due to interactions of fluids with rocks, formation of bubbles within rock pores that inhibit the migration of fluids, density differences between pore fluids that prevent one fluid from moving above or beyond another, and the sorption of radionuclides to the surfaces of fractures. These mechanisms interact with each other at different temporal and spatial scales. However, the operable mechanisms and the interplay among them are poorly understood even in the laboratory, and are virtually unknown under *in situ* conditions. For example, mineralization is expected to occur by interaction between dissolved CO_2 and local mineral phases. While there is a general agreement on the process, the conditions under which mineralization will occur, and the rate at which it will occur, are largely unknown. As mineralization occurs, the resulting changes in porosity may cause changes in the flow regime within a region and change or alter immobilization processes at nearby locations. Detecting such changes using remote imaging techniques is crucial for the effective management of fluids and the chemistry of what they carry in the subsurface.

Even small aperture flaws in a seal or the spatial variation in the immobilization mechanism can allow rapid fluid transport. The injection or natural infusion of fluids into a zone can have profound impact on the state of the surrounding rock, altering its trapping ability. Figure 41 depicts a situation in which the injection of fluids alters the local stress field that may lead to instability within surrounding strata. Figure 42 shows a field example where the occurrence of an earthquake caused significant changes in productivity due to the likely changes in pore fluid-flow processes in a reservoir. This reveals the sensitivity of fluid flow and possible fluid mobilization mechanisms to small changes in externally applied reservoir conditions.

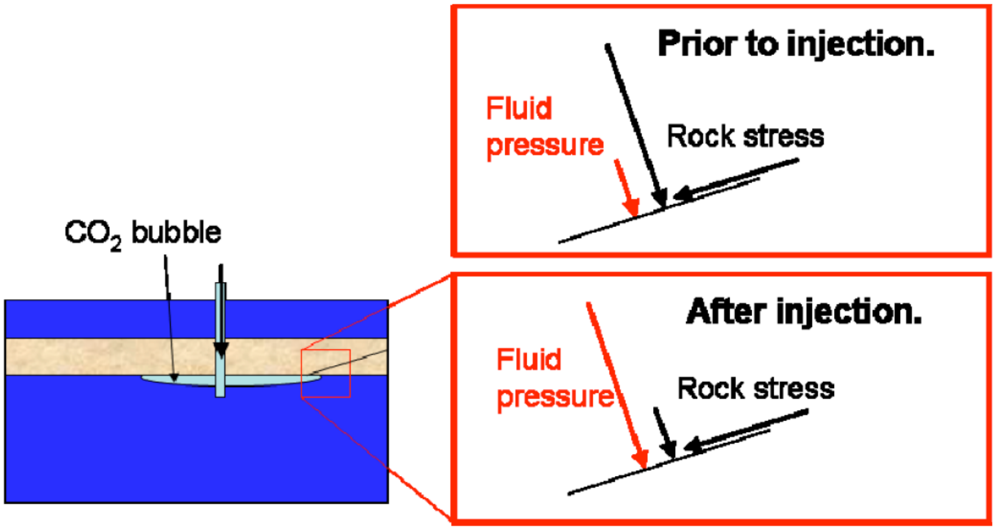


Figure 41. Pressure buildup in a fluid bubble and in surrounding brine changes the stress state of faults and fractures which may compromise mechanical stability of the cap rock and its isolating properties.

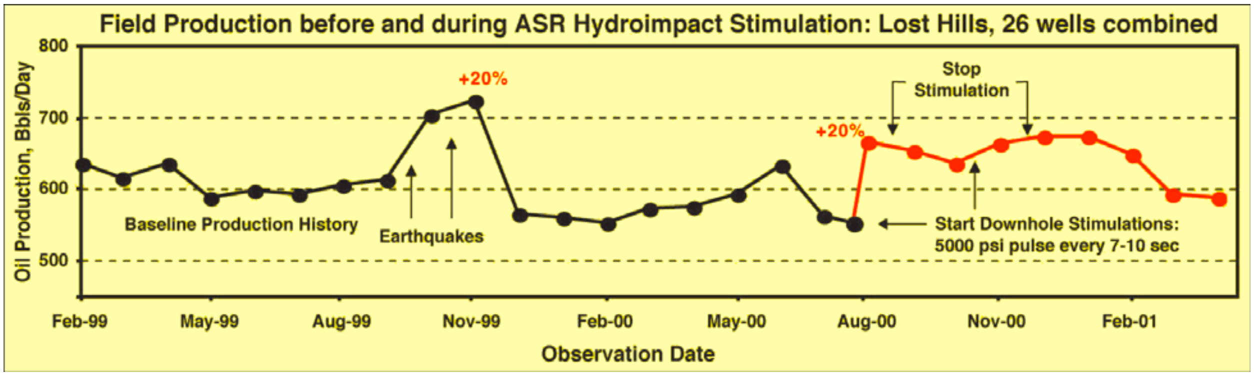


Figure 42. Oil production from a field in California *vs* time showing the improved productivity that resulted from a sequence of earthquakes that occurred at a distance of 400 km (after Roberts et al. 2003).

We need a major improvement in our understanding of fluid trapping mechanisms and our ability to detect the dominant mechanisms that are operating both spatially and temporally within a reservoir to advance our basic understanding of several naturally observed phenomena and to allow the required validation necessary for confirming the successful human-induced sequestration of waste.

SCIENTIFIC CHALLENGES

Spatial and temporal variations of flow and transport properties can be caused by multiscale interaction of injected fluids and ambient pore fluids, the geochemical, textural and structural characteristics of the rocks, or the heterogeneous distribution of porosity and permeability. Natural spatial and temporal variations in flow and transport properties within the earth play a dominant role in fluid migration resulting in the creation of petroleum reservoirs, ore deposits, and geothermal systems. Understanding the mechanisms, and being able to remotely detect which mechanisms are operating as a function of location and time within a reservoir, is essential to our ability to successfully engineer a manmade repository for energy waste. We currently have limited understanding of how trapping mechanisms operate under *in situ* conditions. Our ability to detect and characterize the dominant mechanisms within a given reservoir at depth is similarly limited.

Interfacial and surface properties of fluids in fine-grained and fractured media

Interfacial tension between fluid phases and surface tension between fluid and solid are the fundamental forces that control the flow of multiphase fluids through porous media. As pore size decreases, the radius of curvature of fluid interfaces decreases, causing interfacial forces to rise to levels that are a significant fraction (ranging from > 10% to several times) of the gravitational forces that drive fluid flow. When the surface forces are greater than the gravitational forces, fluids can be trapped in porous media.

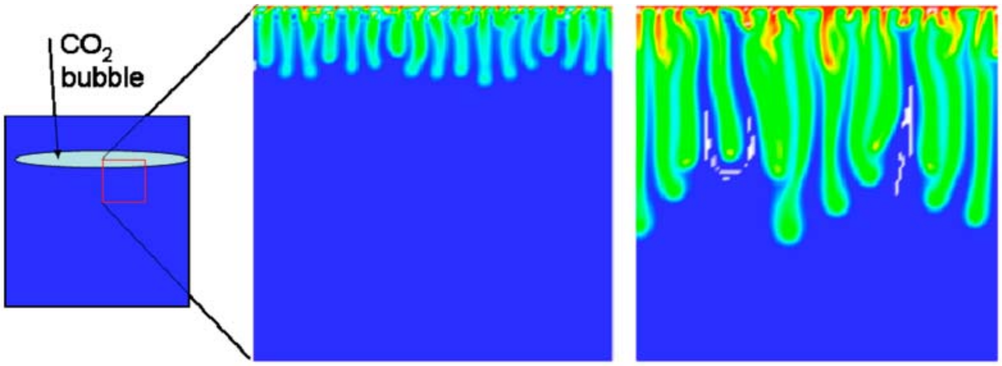
Interfacial and surface tension of multicomponent fluids is rarely measured, and is one of the poorly predicted physical parameters in currently available simulators of thermochemical and physical properties of fluid mixtures and fluid-rock properties. In addition, interfacial processes are dramatically impacted by abiotic and biologically mediated chemical reactions. Also, the kinetics of many mineral-fluid and fluid-fluid reactions are slow, making examination of their impacts on interfacial properties exceedingly difficult.

Conductivity of faults and fractures

It is critically important to be able to predict whether faults or other local crosscutting heterogeneities (e.g., clastic dikes, etc.) conduct or retain fluids as a function of fluid pressure, phase state, and chemical composition. Furthermore we need to be able to predict the impacts of anthropogenic perturbations on the conductivity of these structures to buoyant fluids (see Figure 43). Presently available wellbore-based characterization tools are either poorly suited or completely inadequate for characterizing these effects. Fault gouge properties and complex 3D fracture networks in natural systems are very difficult, or even impossible, to reproduce in a laboratory setting, making field measurements a critical but expensive and time-consuming aspect of this research. Finally, the typically slow rate of fluid migration in these structures makes conducting measurements in a timely manner challenging, even under favorable conditions.

In situ measurement of fluid-rock interactions in fine-grained media

Low-permeability media (barriers to flow) are elements that define the pathways of fluid migration at the basin scale in many subsurface settings. Fine-grained rocks, low permeability salt or anhydrite, and faults with gouge are examples of barriers. These features compartmentalize pressure, trap buoyant fluids, and isolate compositionally different fluids. The performance of these barriers in the presence of multicomponent fluids is complex, because the active sealing mechanism varies with fluid composition and pressure, and geochemical and stress changes can alter the properties of the seal.



Courtesy of Jesus Carrera

Figure 43. Dissolution of CO_2 in brine increases its density and creates an unstable condition (bottom brine lighter than top brine) that promotes downwards fingering. As a result, dissolution goes from being diffusive (rate decreasing as $t^{-1/2}$) to advective (constant rate). The time to onset of instability and actual dissolution is sensitive to modeling details (Hidalgo and Carrera 2007).

Because seal properties are variable under different fluid and stress conditions, measurements may perturb seal properties. Tests of seal properties in the laboratory or from the wellbore are inherently limited in terms of their spatial coverage and validity when extrapolated to *in situ* pressure and temperature conditions. Rock samples retrieved from the field have been unloaded, cooled, and their fluid conditions radically altered. Seal rocks near wellbores are highly perturbed during well construction. Measurements of small flows or small changes in properties within or across seals may be dominated by well properties (casing, cement, damaged zone) rather than the true properties of the seal. These inaccuracies, extrapolated to basin scale and long time frames, lead to potentially large errors in prediction of migration paths and inaccurate assessment of seal continuity and integrity.

Improved field methods are required for accurate determination of the properties of flow barriers. If these measurements could be made *in situ* without major modification of the natural environment, then observations of the seal properties—fluid composition, pressure, and stress change—during anthropogenic perturbations could be made. The temporal changes in these seal properties during fluid injection must be measured to obtain reliable information about the performance of the seal in the presence of changing fluid properties.

Identification and characterization of local flaws in sealing structures

Identification of impermeable strata and to a lesser extent prediction of impermeable faults are relatively mature techniques. However, techniques to locate and to quantify the properties of the weak points or flaws in these seals are poor or nonexistent. Where a buoyant fluid such as oil or gas has been trapped, this trapping is *a priori* evidence of the quality of the seal (although the exact sealing mechanism may not be described). However, in other cases, such as introduction of buoyant CO_2 or assessment of the dynamics of another fluid system, new conceptualization, approaches, and techniques need to be developed. Especially challenging is the need to assess small features (fractures, sand-on-sand contacts) at the millimeter to a few meter scale over areas of hundreds of square kilometers.

Prediction of the distribution and efficiency of in situ trapping processes

Current geophysical techniques are moderately successful at detecting the presence of fluids within a reservoir, but are less capable of reliably determining the volume fraction of gas and liquid. The ability to remotely detect the changes that occur in rocks as mineralization occurs would add substantially to our understanding of many natural processes that occur within the Earth. Experiments are needed to understand the chemistry of CO_2 phases and mineralization, the geophysical signatures, and the possible impacts of biological processes that may be used to observe the progress of mineralization. High-confidence detection of relevant trapping mechanisms within a given storage site, and the spatial and temporal variations of these mechanisms, will allow for better management of the repository and for confirmation that the fluid has been successfully sequestered. Such detection must be done without physical penetration of the repository so that no new potential leak paths are created. This means that some geophysical (e.g., remote sensing) approach must be employed. To achieve the required level of detailed information will require major advances in our ability to both characterize the earth’s subsurface in addition to our ability to interpret spatial-temporal changes detected from remote sensing.

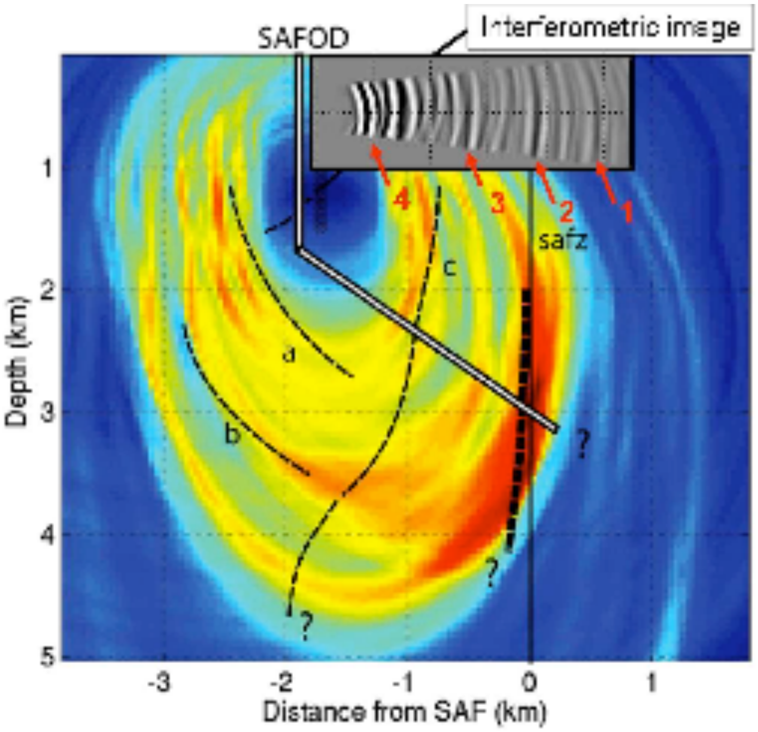
RESEARCH APPROACHES

Sedimentological process models can be a powerful tool in predicting the continuity of sealing strata and efficiently developing an approach that verifies this assessment. Seal thickness may be a poor proxy for estimating the quality of a seal. Linking of depositional characteristics—such as bedding thickness with diagenetic effects, compaction or cementation, tectonic and burial histories with information on stress states—will provide better information on the effectiveness of the seal as a barrier to the migration of injected fluids.

Laboratory measurements and simulations are needed that provide new concepts and methods that link large-scale multiphase flow and reactive transport behavior to interfacial properties of multicomponent fluid-solid systems. Studies of the impacts of dissolution-precipitation reactions and possible microbial communities on interfacial properties are critically needed. Impacts of molecular-scale interfacial mass transport processes, such as removal of interlayer water in swelling clays into supercritical CO_2, are needed to better predict the impacts of clay desiccation on the capillary properties of originally impermeable intervals.

Laboratory experiments can be carried out using physical models that investigate trapping and isolation mechanisms simultaneously with use of characterization methods, so that relevant geophysical signatures of trapping can be investigated. Such experiments may include the simultaneous use of neutron scattering and acoustic measurements of rocks undergoing mineralization to investigate the relation between mineralization/cementing within pores and observable geophysical parameters. Other spectroscopic approaches for detailed characterization of changes induced within rocks may provide valuable information to help understand trapping mechanisms and their remote detection with geophysical techniques.

Fundamental research is needed on propagation, scattering, nonlinear effects, and attenuation of continuous and pulsed waveforms in geological media over a wide range of electromagnetic and acoustic frequencies and amplitudes. The objective is to be able to locate and resolve fault and fracture structures, and to estimate multiphase flow and transport and characteristics within the pores with the spatial resolution required (on the order of meters) for evaluation of the processes that are occurring within the reservoir. New concepts should be explored involving combinations of methods that produce complementary excitations, new resonance modes, and/or waveform constructive/destructive interference over a range of spatial scales. To assess the wide range of scales required to characterize the heterogeneous reservoir will require new analysis approaches and the integration of deterministic and probabilistic methods. Some investigations may be initiated by using existing datasets, particularly those available from industry, or from scientific projects like the San Andreas Fault Observatory and Depth (SAFOD) project.



Modified figure courtesy of Roel Snieder

Figure 44. Image of the San Andreas fault and adjacent subfaults obtained from natural earthquakes (color image from Chavarria, J.A., Malin, P., Catchings, R.D. and Shalev, E., A look inside the San Andreas fault at Parkfield through vertical seismic profiling: *Science* **302**, 1746–1748 (2003); reprinted with permission from AAAS), and from drill-bit noise (interferometric image from Vasconcelos et al. 2007). Reflection 2 is caused by the San Andreas fault.

SCIENTIFIC IMPACTS

This area of research will generate a step change in the platform needed for the understanding and prediction of complex multiphase and reactive flow systems, including the effects of capillarity, pore-scale, reservoir-scale and basin-scale properties. The advances will allow the generation of a new level of integrated understanding (and management) of complex hydrogeological flows in the subsurface. The basic science at the core of the activity relates to the characterization and quantification of the interactions and feedbacks between competing flow processes and mechanisms in an evolving complex, multicomponent, multivariable and multiscale system. The dependence of the large-scale system behavior on local or transient perturbations of flow is common to many fluid dynamic problems.

Characterizing the detailed multiscale coupling between flow, geomechanics, fluid pressure and reactive flow processes will impact the identification of the key dependencies and uncertainties. In addition, the research will advance the understanding of flow path and stress path evolution that controls the future strength, deformation, permeability and flow behavior in a system.

The research area has the potential to affect a broad range of research fields where multiscale, spatial and temporal variations in flow control a host of critical geological processes: groundwater flow, contamination, remediation, fluid-controlled mineralization or dissolution, focused flow migration along high permeability pathways (lithology, faults and fractures), and fluid trapping/storage critical to locating hydrocarbon accumulations and mineral ore deposits.

TECHNOLOGY IMPACTS

Modeling, design, construction, and operation of CO_2 sequestration facilities require defining parameters such as the total volume of CO_2 to be injected, the rate of injection, and operating rules. These include criteria for injection rates (so as to maximize mixing and mineralization processes), potential additives (so as to promote capillary barriers or capillary retention mechanisms), and other aspects of managing reservoirs and waste disposal.

In the short term the limiting factor for injection is most likely pressure buildup. Continued isolation, before dissolution and mineralization become the dominant storage mechanisms, is largely dependent on the integrity of the cap rock. Excessive pressure may compromise mechanical stability. Over time mechanical properties of the rock will change because of dissolution of resident minerals and precipitation of new mineral phases. Understanding of how CO_2 injection affects mechanical properties is required for site selection, for design, and for long-term performance assessment.

Pressure buildup depends on overall reservoir flow rate and permeability. Flow rate can be controlled during operation. Permeability is site specific, but will change in response to geochemical changes on both rock (dissolution/precipitation) and fluids (viscosity and phase saturation). Therefore, it is necessary to quantify these for site selection and operations.

Dissolution, mineralization, and capillary trapping processes can be accelerated by enhancing mixing rates. This can be achieved by promoting temporally fluctuating pressure gradients, but the rates of actual mechanisms depend on the local fluid interactions with heterogeneous mineralogy (Dentz and Carrera 2003). Therefore, proper understanding of how these mechanisms act at the local scale will impact how injection technology is employed.

Understanding trapping and isolation processes involves situations that are common in many subsurface aquifers or oil fields. In fact, they are similar to those affecting Enhanced Oil Recovery (EOR). Therefore, an improved understanding of these processes has direct application to improved EOR and production efficiency. Less direct, but equally likely, are the links with contaminant hydrogeology, soil science, or mineral exploitation (dissolution mining).

It is reasonable, therefore, to expect significant advances to occur in these fields in response to improved understanding in:

- Quantification of long-term storage capacity, leakage and uncertainties
- Robust site selection criteria, workflows and improved risk assessment
- Advanced injection and monitoring methodologies
- Improved predictive hydrogeology, mineral resource exploitation, and soil and environmental remediation schemes
- New insights for improved EOR and production efficiency

FLUID-INDUCED ROCK DEFORMATION

ABSTRACT

Geologic carbon sequestration presents scientific challenges associated with the large pressure transients induced by CO_2 injection, which affect the thermal, mechanical, hydrological, and chemical state of subsurface volumes that span hundreds to thousands of km^3. Accurate forecasting of the effects requires improved understanding of the coupled stress-strain and flow response to injection-induced pressure and hydrologic perturbations in multiphase-fluid saturated systems. Such effects manifest themselves as changes in rock properties at the centimeter scale, mechanical deformation with length scales that reach tens of kilometers, and modified regional fluid flow. Improved understanding of rock hydromechanical properties over this range of scales would lead to more accurate geomechanical modeling of multiphase-fluid saturated systems, permit improved coupling of chemical, mechanical, and hydrological processes, and potentially provide new theoretical constructs for understanding shallow crustal deformation.

EXECUTIVE SUMMARY

Commercial-scale carbon capture and geologic storage requires injecting large volumes of impure CO_2 into the shallow crust for many decades. The volumes will be enormous: to reduce annual global greenhouse gas emissions by one gigaton of carbon requires cumulative subsurface injection that exceeds current global oil production. This injection program will produce very large pressure transients that will deform the shallow crust and possibly displace ambient fluids over large regions, thereby modifying regional hydrology. For example, faults may be activated and fractures formed or opened, seismicity may be induced, and groundwater quality might be degraded. Consequently, understanding shallow crustal deformation and multiphase fluid flow driven by commercial-scale CO_2 injection is a priority research need.

Innovative research in this area should focus on improved understanding of multiscale geomechanical processes in the shallow crust, but must also include explicit account of the dependent thermal, hydrological and geochemical processes. The fundamental goals are:

- Improved understanding of coupled stress, strain, and flow response to injection-induced pressure transients in multiphase-fluid saturated systems at all scales
- Improved geomechanical modeling of multiphase-fluid saturated systems
- Improved coupling of chemical, mechanical, and hydrologic process descriptions
- Improved understanding of permeability evolution due to concomitant geomechanical and geochemical processes

These improvements will directly impact technical programs in carbon capture and geologic storage by providing advanced simulation capabilities and reservoir management tools, improved monitoring and verification techniques, and new inputs, constraints, and methodologies for hazard and risk evaluation. More broadly, these improvements would significantly impact our ability to model and monitor shallow crustal deformation caused by other perturbations, both natural and engineered.

SCIENTIFIC CHALLENGES

Commercial-scale carbon capture and geologic storage requires injection of large volumes of impure CO_2 into the shallow crust for many decades, and efficient trapping of the CO_2 for hundreds of years. The introduced buoyant fluid phase will partially displace ambient fluids, induce large local pressure transients, and establish new regional-scale multiphase fluid flow regimes. To be successful, the reservoir storage capacities must not be compromised by leakage through cap-rock faults and fractures that could be activated by the stress-strain response to the injection-induced pressure evolution. Furthermore, maintenance of shallow groundwater quality must be ensured, and the hazards and risks associated with potential uplift and induced seismicity must be quantified and managed. Hence, improved understanding of shallow crustal deformation and multiphase fluid flow triggered by commercial-scale CO_2 injection is a priority research need.

The physics of coupled rock deformation and multiphase fluid flow has been a subject of study for many years, but still presents a substantial scientific challenge due to complexity of materials and processes. Rock masses are highly heterogeneous with regard to lithology, texture, structure and strength, while the presence of multiscale discontinuities (faults, joints, and microfractures) has a significant impact on the coupled rheological and transport response to injection-induced pressure and dependent stress perturbations. Under the ambient pressure and temperature conditions most pertinent to CO_2 storage—generally, < 0.5 kb (< 5 km depth) and < 100^{o}C—this often nonlinear coupled response is particularly challenging to quantify because the rocks undergo brittle failure when stressed. Deeper in the Earth, where temperature and pressure are higher, rock deformation is easier to model in some respects because the behavior is viscous or plastic, but still challenging to model when fluid is present and heterogeneously distributed, and mineral-fluid chemical reactions proceed at faster rates.

Understanding geomechanical processes and properties at all scales

A multiplicity of deformation mechanisms at different scales may be activated by CO_2 injection. In porous clastic and carbonate rocks, grain-scale deformation such as microcracking, pore collapse, pressure solution, and crystalline plasticity may be operative. Although our understanding of these processes in rocks saturated with a homogenous fluid is adequate (e.g., Guéguen and Boutéca 2004), many questions remain for rocks saturated with multiphase fluids. For example, the mechanical effect of pore pressure changes on the elastic, inelastic, and failure behavior of rocks saturated with a single fluid phase are commonly described using the effective stress principle. To what extent this formulation applies to a rock saturated with brine and CO_2 is not well known. Further, although it is likely that interfacial tension will influence the kinetics of subcritical crack growth and pressure solution in multiphase fluid-saturated rocks, this hypothesis requires demonstration. Finally, some studies have indicated that seismic velocity is highly dependent not only on bulk CO_2 saturation, but also on how it is distributed in the pore space. Thus, systematic investigation of rock properties, including seismic velocity, seismic attenuation, and electrical conductivity in multiphase-fluid saturated rocks, will provide useful insights into the interpretation of geophysical imaging.

The shallow crust is permeated with fractures on all scales. The mechanical stiffness, strength, and hydraulic transmissivity of these fractures depends on their aperture, roughness, and connectivity, which can be modified by cataclastic and chemical mass transfer processes. These discontinuities can have a hierarchical architecture with significant geometric complexities (e.g., Caine et al. 1996). The interplay of these factors controls whether a given fracture system provides a conduit or barrier for multiphase fluid flow in the shallow crust.

Understanding coupled stress, strain, and flow response to pressure and hydrological perturbations in multiphase-fluid saturated systems

Subsurface injection of impure CO_2 can induce significant pressure perturbations and dependent multiscale stress-strain evolution, partially displace ambient fluids, and in this manner establish a new multiphase flow regime that facilitates migration of the introduced buoyant fluid on regional scales. The migration paths are highly dependent on this stress-strain evolution, which may significantly alter the permeability field; e.g., the pore space and rock matrix may compact or dilate, multiscale fractures may form or undergo aperture evolution, and inelastic bulk deformation can develop, either in a distributed or localized manner.

Many of these coupled processes are nonlinear and some are hysteretic. For multiphase-fluid saturated rocks, additional complexity derives from the interplay of fluids with contrasting density, viscosity, compressibility, and interfacial tension. Further, to explicitly incorporate the multiscale geometric complexities and key geomechanical and hydraulic attributes of such systems, it is necessary to develop models based on both continuum and discrete approaches, which provide complementary insights.

Understanding permeability evolution due to concomitant geomechanical and geochemical processes

Subsurface CO_2 injection induces concomitant pressure-dependent stress-strain evolution and disequilibria-dependent chemical mass transfer that together modify the pore structure and permeability of reservoir, cap-rock, and well-bore environments. While mechanical stress-strain response can cause deformation and failure of weak structural features (i.e., dilation of faults and fractures), chemical disequilibria along their fluid-rock interfaces can lead to alteration of bounding matrix blocks (i.e., mineral dissolution/precipitation and dependent volume change). Integrated permeability evolution caused by these conceptually distinct yet interdependent processes may result in significant modification—degradation or enhancement—of pre-injection reservoir, cap-rock, and well-bore integrity, which may significantly affect CO_2 migration within and beyond the reservoir (Johnson et al. 2005). Understanding this interplay of geomechanical and geochemical processes represents a fundamental challenge to predicting the long-term isolation performance of geologic CO_2 storage.

Quantifying interdependence of these processes is also a key challenge. For example, fluid-rock compositional evolution impacts the kinetics of deformation mechanisms such as pressure solution and subcritical crack growth, mechanical properties such as fracture stiffness, and the seismic and electrical attributes of multiphase-fluid saturated rocks.

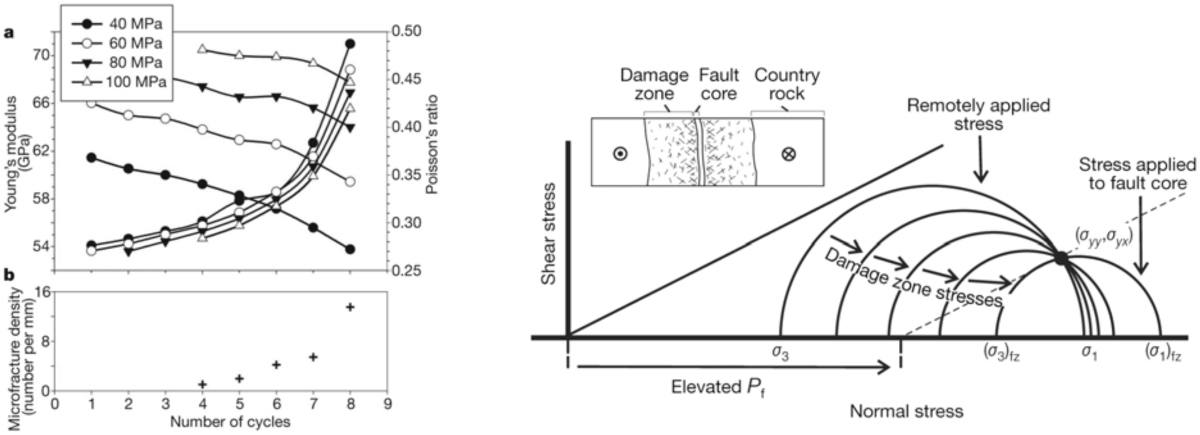


Figure 45. Example of nonlinear, history-dependent property response to pressure. Left: Measured changes in rock elastic modulii as a function of microfracture density under different pressure cycles. Right: Mohr-circle representation of associated stress rotations and failure envelopes. From Faulkner et al. 2006; reprinted by permission from Macmillan Publishers Ltd: *Nature* **444**, 922-925 (2006).

RESEARCH APPROACHES

New scientific insight and advanced simulation capabilities can be achieved through a set of complementary technical approaches that span the range of relevant length scales. The ultimate goal of this integrated research area is to develop coupled field-scale models that fully capture the fundamental physical and chemical processes. The research will be is grounded by experimental laboratory studies designed to constrain the fundamental processes that control the rheological behavior of fluid-rock systems. Recent advances in X-ray computed tomographic imaging and enhanced spectroscopic techniques applied to cores under reservoir conditions can provide new data to constrain the evolution of perturbed fluid-rock systems. The laboratory work will help design field studies of geomechanical processes where innovative geophysical/hydrological techniques can be used to monitor the integrated system response to commercial-scale CO_2 injection over the relevant range of geologic settings. Building upon and constrained by the laboratory experiments and field studies, fundamentally new modeling approaches must be developed that effectively represent coupled mechanical, chemical, and hydraulic processes in deformable, brittle media. Both discrete and continuum modeling approaches may be applied to these problems, but the ultimate objective of either approach is to explicitly represent process coupling over the full range of length scales. These models will require improved constitutive relationships or upscaling techniques for representing coupled processes from the pore scale to the field scale.

SCIENTIFIC IMPACTS

New experimental results, field data, and process coupling techniques will lead to the emergence of novel mathematical and computational approaches for representing and simulating fully integrated geomechanical and multiphase flow processes. These advanced simulation capabilities will permit more accurate long-term forecasting of injection-induced geomechanical effects that range from poroelastic deformation to dynamic fracturing over the full range of length scales that characterize multiphase-fluid saturated reservoir/cap-rock/well-bore systems. Moreover, the development of improved mathematical formulations and computational techniques for representing and modeling explicitly coupled geomechanical, hydrological, and geochemical processes will facilitate fully constrained long-term predictions of the energy and mass redistribution catalyzed by commercial-scale CO_2 injection. All of the above will help spawn development of new theoretical constructs for understanding shallow crustal deformation, multiphase flow regimes, and geochemical alteration triggered by subsurface perturbation events.

TECHNOLOGY IMPACTS

A fundamental challenge of geologic CO_2 storage is to accurately forecast the injection-induced pressure, hydrologic and chemical perturbations, interdependent stress-strain, multiphase flow, and mass transfer responses, respectively, of the reservoir/cap rock/wellbore system. Advanced capabilities that permit such forecasting are needed to optimize injection strategies, to predict long-term CO_2 storage capacity, spatial distribution, phase partitioning, and reservoir containment, and to design effective monitoring programs for verifying anticipated isolation performance.

Integrated laboratory, field, and modeling studies will directly impact technical programs in carbon capture and geologic storage by providing next-generation predictive capabilities. Such forecasting tools can be used to optimize deployment strategies and reservoir management, to predict long-term cap-rock/well-bore permeability evolution (reservoir containment) due to coupled mechanical deformation and chemical mass transfer processes, and to design effective monitoring programs (geophysical imaging and geochemical sampling techniques, locations, frequencies) for isolation performance verification.

Advanced computational models based on integrated geological process understanding can be used to predict injection-induced changes in basin-scale hydrology, as well as to develop new inputs, constraints and methodologies for hazard and risk evaluation (induced seismicity, fracture failure, leakage, and subsidence). Finally, simulation tools are directly applicable to many geoscience and engineering disciplines beyond geologic CO_2 storage, such as the behavior of fault zones, the generation of earthquakes, and other aspects of shallow crustal deformation due to both natural geologic processes and engineered modifications to subsurface hydrology and structure.

BIOGEOCHEMISTRY IN EXTREME SUBSURFACE ENVIRONMENTS

ABSTRACT

Biological processes that are ubiquitous below ground can have a profound influence on: the geochemistry of subsurface waters; the mineralogy of subsurface sediments; and the valence, geochemical form, and mobility of radionuclide and trace metals. Existing and future proposals for the subsurface isolation of radioactive waste and carbon dioxide will greatly perturb subsurface environments leading to locally and regionally extreme subsurface conditions in terms of heat, chemistry, radiation, and other variables. These changes will drive and accelerate unknown biogeochemical processes that may enhance or reduce the long-term effectiveness and potential risk of these critical activities. Basic research on the influence of biological processes on the long-term chemical speciation of radioactive elements, and the mineralogic, interfacial and hydrogeochemical conditions in severe, deep environments is needed to resolve these concerns. Moreover, fundamental research on these bio-directed processes may identify unique chemical pathways and mechanisms that may provide unforeseen benefits to other energy technologies.

EXECUTIVE SUMMARY

Microorganisms strongly influence the mineralogy and chemistry of near surface geologic systems (e.g., banded iron deposits), contribute to regional zones of metal enrichment and concentration through adsorption and precipitation reactions (e.g., ore formation and uranium roll-front deposits), and drive globally important elemental cycles of life-supporting major elements (e.g., C, N, S, and P) and trace metals (e.g., Mo, Co, Zn). Estimates of the distribution of life on Earth suggest that over 90% of Earth’s biomass exists in the form of microorganisms in subsurface environments.

The proposed use of deep saturated or unsaturated water-rock systems for nuclear waste and carbon dioxide isolation will perturb these environments and modify biologically mediated processes. Radioactive waste isolation introduces heat, radiation, electron donors (metals and hydrogen gas), and external-source organisms to the subsurface. Carbon sequestration will change water activity, composition, pH, and other variables. These sequestration strategies will give rise to new forms of extreme environments. Some of these parameters will globally stimulate microbiologic activity (e.g., moderate heat and electron donors), while others will be lethal to certain species (e.g., radiation) and encourage selection of potentially unique individual survivors and communities tolerant to radiation, salt, acid, low water potential, and other severe conditions.

Great opportunities for basic research exist in the study of biogeochemical processes and their effects on system geochemistry (water, solids, and surfaces) and trace element/radionuclide chemical distribution in harsh, perturbed deep subsurface environments. Of importance are the microbiologic communities that evolve and flourish and the fluid-rock geochemical interactions that they promote; the biologic machinery that they assemble at the mineral-microbe interface and the associated bio-directed reactions that occur to accomplish their genetically programmed geochemical mission; and the unique biogenic products that form or phase transformations that occur in microscopic regions surrounding them as a result of extracellular metabolic fluxes. New microbe-mediated phenomena of potentially broad application and significance may be discovered. For radioactive waste isolation specifically, the research will provide knowledge underpinnings to evaluate microbiologic influences on waste form stability through corrosion and similar processes, and down-gradient migration of radionuclides through bio-influenced speciation changes, precipitation, and surface chemical processes.

SUMMARY OF RESEARCH DIRECTION

Research is needed at different scales using laboratory model systems, field-derived geologic materials, microorganisms isolated from relevant environments, and in-field observations at analogue or real sites. Pervading the research is an emphasis on the extreme characteristics and system variables of the target deep subsurface environments that motivate and distinguish this topic. Integration of experimental studies and measurements with state-of-the-art or newly developed models of different types is essential to unravel and understand the complex linkage of geochemical and biologic processes at the fundamental level required.

SCIENTIFIC CHALLENGES

Research over the past ten years has shown that microorganisms can strongly influence the valence, solubility, mineral association, and migration potential of actinides and other important radionuclides (e.g., ^{99}Tc, U) and inorganic chemical contaminants (Cr). Often, microorganisms concentrate soluble metals or radionuclides through biosorption or bioprecipitation reactions on the organism surface (see Figure 46) or within the cell envelope's periphery where metabolic products and biostructures create a unique and unexplored chemical environment. These same organism types can also nucleate and form unique, high surface area, major element biomineral

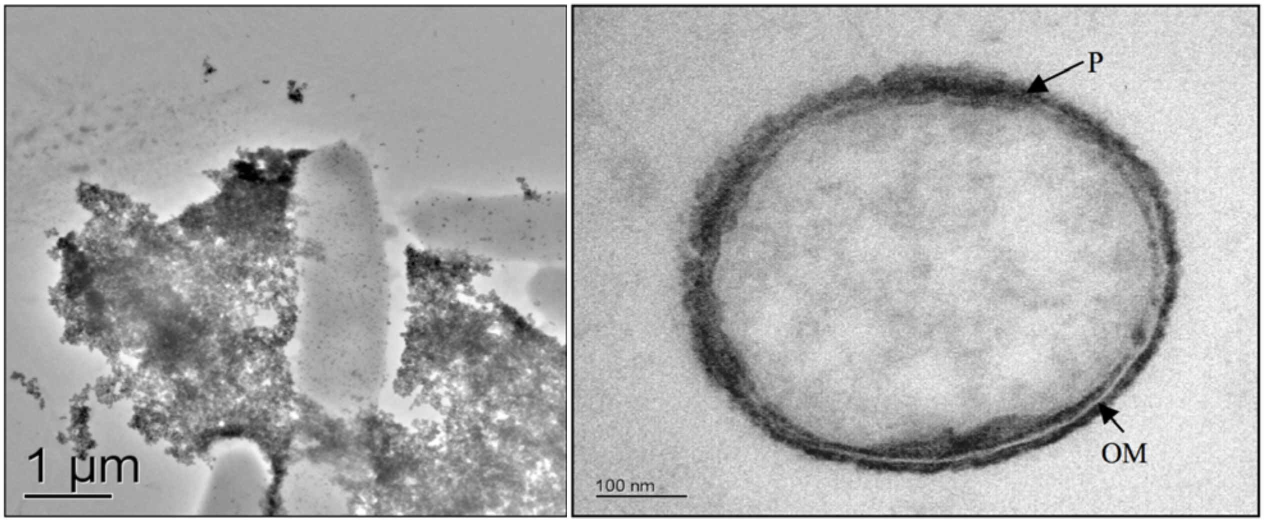


Figure 46. Two forms of microbiologic radionuclide precipitates generated under reducing conditions. *Left:* Extracellular uraninite (UO_2) produced by *Shewanella* resulting from the reaction of U(VI) with externalized cytochromes on exopolysaccharide. *Right:* $TcO_2 \cdot nH_2O$ precipitated within the periplasm (P) and on the outer membrane (OM) of *Anaeromyxobacter* (Marshall et al. 2006, 2007).

phases such as metal oxides (Fe and Mn), carbonates, and phosphates that are strongly reactive with trace constituents both through surface and bulk substitution reactions.

The biogeochemistry of natural extreme environments, such as thermal springs, oceanic vents along spreading centers, and deep, hot, geologic formations, has been investigated to provide insights on bioadaptive processes and functions under stressful conditions. Subsurface microbes have remarkable adaptability and ability to flourish in and extract energy from a variety of apparently stark, lithotrophic environments. Extremophilic organisms exhibit diverse chemical function and mediate complex geochemical reactions that influence pore water chemistry, the chemical and physical nature of reactive surfaces, and the composition of newly-formed solid phases that function as repositories for trace species. These reactions and processes can differ markedly from those occurring under ambient conditions because of temperature, kinetic, and/or specific organism effects. An important general observation for understanding this research area is that organism diversity (e.g., number of different species) greatly decreases as the environmental conditions become more extreme.

Given this background, four critically important fundamental science challenges can be articulated as follows:

1. How do characteristic, deep, low-diversity subsurface microbial communities (e.g., probably gram-positive dominated) evolve in response to parameter changes resulting from energy use such as inoculation by near-surface organisms and increases in radiation, temperature, hydrogen, and carbon dioxide? Do evolved organisms and/or communities have greater or lesser effects on system geochemistry and minor element (e.g., radionuclide), speciation, biogeochemistry, and migration potential? These observations will inform more fundamental studies at smaller scale.
2. What are the reaction rates and products of important biogeochemical reactions under relevant conditions as function of organism type, population, and metabolic rate? How are these moderated or controlled by coupled parallel or sequential abiotic reactions (precipitation, dissolution, surface complexation) with associated bulk mineral phases or reactive interfaces?
3. What are the molecular processes, mechanisms, and biostructures that occur on or near the cell surface of extremophiles that influence metal/radionuclide speciation via electron or other chemical transfers, that precipitate trace or major element biomineral phases, or that alter solid surfaces?
4. Can new biogeochemical models for single cell and biofilm scales be conceptualized and formulated to: integrate complex intracellular biochemical pathways, biodirected reactions at the cell surface, and extracellular, nonlinear abiotic reaction networks; improve coupled process understanding; quantify biologic-geochemical interdependencies and feedback relationships?

RESEARCH APPROACHES

The fate and transport of radionuclides and metals (Charlet and Polya 2006; Kretschmar and Schaefer 2005; Lloyd and Oremland 2006; Roden and Scheibe 2005; Steefel et al. 2005), the corrosion of nuclear waste forms and packages (Bruno and Ewing 2006; Burns and Klingensmith 2006; Ewing 2006; Grambow 2006), the performance of engineered barrier systems, the storage of CO_2 in deep aquifers (Bachu et al. 1994; Bruant et al. 2002; Elliott et al. 2001; Gaus et al. 2005; Gunter et al. 1993; Johnson et al. 2004; Rochelle et al. 2004), and the global elemental and nutrient cycles (Berner 1995; Berner et al. 1983; Van Cappellen and Gaillard 1996) are all influenced by biogeochemical processes. In many cases, the rates of these processes are directly mediated by microbial activity. In other cases, new reactions may occur or the extent of reactions may be altered relative to an analogous abiotic system through the participation of cells or their byproducts in the reactions. Microbially mediated environmental processes are rarely due to activity of a single group of organisms, but instead are the result of a diverse group of organisms that may reside as biofilms in the subsurface. Competitive and/or symbiotic communities may be present. Microbial metabolism and growth can directly or indirectly impact important geochemical processes, including electron transfer, precipitation and dissolution, and sorption. For example, bacteria can:

- Drive the rates of thermodynamically favorable redox reactions, such as those of iron, sulfur, uranium, and plutonium, which in the absence of biological mediation would be kinetically inhibited (Chappelle and Lovley 1990, 1992; Christensen et al. 2000; Jakobsen and Postma 1999; Lovley and Chappelle 1995; Park et al. 2006b)
- Produce nanosized precipitates with unique geochemical properties (Banfield and Navrotsky 2001; Banfield and Zhang 2001; Suzuki et al. 2002)
- Indirectly influence the rates and extent of sorption, dissolution, and precipitation processes via biofilm formation, the exudation of extracellular materials, and the geochemistry of the pore solution

Despite the universally recognized role of microbes in regulating geochemical cycles, there is still relatively little understanding of the actual mechanisms by which microbial communities interact with their geochemical environment. Specific scientific questions include the following:

- What environmental factors affect the metabolic pathways of individual bacterial species and their rates?
- What are the controls on the rates of electron transfer across the cell wall in the case of redox reactions?
- How are the microbial community dynamics influenced by the flux of nutrients at the pore scale, and how do these affect the partitioning of energy between growth and metabolism and the competition or symbiosis between individual communities?
- How do microbially mediated mineral precipitation or oxidation-reduction rates change as nutrient fluxes change, going for example from “banquet” to “starvation” levels?
- How do biofilm properties, growth, and function affect extracellular geochemical reactions like adsorption, precipitation and dissolution?
- How does the pore environment affect the interactions between mobile aqueous and solid phases, immobile reactive phases, and the microbial communities that reside there?

For the geoscience community, there is a need to incorporate and quantify the interactions between microbial populations and their geochemical environment in models of natural and perturbed geologic systems. This is necessary because the interactions may control or strongly couple with processes that need to be modeled as a part of important technological applications, including the remediation of contaminants and the promotion of precipitation reactions in the case of CO_2 sequestration.

Mechanisms of biogeochemical reactions

Specific bacterial populations are known to catalyze the reactions of certain redox couples, e.g., the respiration of acetate with iron(III) as an electron acceptor. Moreover, there are feedback mechanisms between the geochemical environment and bacteria that lead to gradual changes in microbial functions as the environment changes. For example, the bacterial community may switch from iron(III) reduction to sulfate reduction as iron(III) reaches limiting (but non-zero) concentrations in a porous medium (Chappelle and Lovley 1992). A variety of competitive and cooperative bacterial community processes generally lead to a shift in predominant species when an evolution of geochemical conditions occurs. The transition of the bacterial community from one electron acceptor to another is an important topic with regard to bioremediation or the natural attenuation of redox-sensitive radionuclides, but also in marine sediments where steep redox gradients control the cycling of Fe, Mn, and carbon (Thullner et al. 2005; Van Cappellen and Gaillard 1996).

Current microbial-biogeochemical models for reactive transport lack a suitable mechanistic treatment of these processes at the cellular level. This seriously hampers our ability to predict behavior under a range of conditions and environments. The few existing models that couple the processes are largely empirical and do not account for effects of local geochemical environments (especially nutrient and solute fluxes) on metabolic rates, even though these ultimately govern the overall rates of subsurface reactions. For example, these simulators typically include “yield factors” in their kinetic rate laws that specify the partitioning of the nutrients between growth and metabolism as a constant. Or the switchover from the use of one electron acceptor to another (e.g., iron(III) to sulfate) is handled with empirical “inhibition” functions that do not capture the dynamic interaction between the bacteria and their environment and between biotic and abiotic chemical cycles (Brun and Engesgaard 2002; Thullner et al. 2005).

Cellular level models

At the cellular level, a new class of computational models is currently under development. These are referred to as *in silico* models (Covert et al. 2003; Palsson 2000, 2002; Price et al. 2003). The most widely used approach to date is the *constraint-based approach*, which eschews the full computation of all of the metabolic pathways taking place at the cellular level in favor of a reduced set of key metabolic and transport processes that honor that constraint space of the organism and its local environment.

These constraints include (Covert et al. 2003):

- Environmental constraints—these include nutrient availability and fluxes, since these control the extent to which the organisms can obtain and synthesize biomass components. In natural porous media, the kinds of nutrients that are available are considerably more limited than what could be provided in a laboratory setting. Symbiosis and competition produce additional constraints, since multiple communities may have to exist in the same limited pore environment.
- Physicochemical constraints—these include thermodynamics, mass and energy balance considerations, enzyme capacity, stoichiometric constraints associated with biochemical (intracellular) and geochemical (extracellular) reactions, the balance between osmotic pressure and the maintenance of electroneutrality.
- Self-imposed constraints—these include constraints that the cells impose upon themselves (in contrast to the environmental and physicochemical constraints discussed above). These include regulatory constraints, where the organisms are able to control, to some extent, which genes are expressed, which proteins are present, and even the activity of proteins in cells (Covert et al. 2003), and evolutionary constraints, whereby the microbes may reconfigure their genomes gradually via mutations and adaptive evolution over many generations.

To date, stoichiometric, thermodynamic, enzyme capacity and energy balance constraints have been successfully incorporated into genome-scale models of metabolism for such organisms as *E. coli* (Price et al. 2003). This effort continues today, with constraint-based models being expanded to form an integrated description of cellular metabolism, transcriptional regulation and protein synthesis. *In silico* methods are being developed that allow for the incorporation of “omics” data, including genomics, proteomics, transcriptomics, and metabolomics (Figure 20).

Similar constraint-based *in silico* models need to be developed for the most important subsurface microbes involved in contaminant immobilization, enhanced CO_2 mineral sequestration, and nutrient and elemental cycling. These models then need to be coupled to biogeochemical models that describe the extracellular thermodynamic, kinetic, and flux constraints at the pore scale. The goal should be to integrate experimental data derived from single microbial species to model diverse interactive communities. Model complexity will parallel experimental endeavors that span scales from single cell investigations to complex biofilms. Modeling efforts should focus on quantifying the rates and pathways of microbial metabolic processes involved with subsurface processes via the full range of available “omics” data. In this regard, new capabilities in cataloguing the gene sequence (genomics) and the protein expression of specific proteins (proteomics) or even metabolites (metabolomics) offer the intriguing possibility of ultimately establishing markers for the metabolic pathways and their rates for microbial communities of interest in subsurface science. It appears likely that the choice of metabolic pathways included in a coupled *in silico* biogeochemical model will depend in part on the protein expression or metabolite accumulation that can be *actually measured* and how effectively they can be *associated with the key pathways of interest*. Measurements of this kind should provide the basis for calibrating and/or validating model rates, thus providing an important constraint on modeling the metabolic pathways relevant to subsurface geochemical transformations.

Biofilm dynamics

Experimental investigations of the mechanisms and rates of energy/electron transfer across the microbe-mineral interface have been initiated. These processes need to be synthesized in numerical models to simulate biofilm dynamics in porous media coupled to extracellular geochemical reactions such as sorption, precipitation, and redox alterations. Other microbial community responses such as signaling and motility also should be modeled numerically to capture the functioning of the biofilm as a whole as it interacts with its pore environment. In this way, metabolic activities that take place at the cellular level can be extended via modeling to the biofilm scale.

We envision that the coupled *in silico*-biogeochemical models will be linked with next-generation pore-scale models for hydrodynamic flow, transport, and geochemical reactions (see Figure 21). The objective is to simulate the interactions between the biotic and abiotic geochemical cycles at increasingly larger spatial scales.

Modeling efforts should build upon recent experimental investigations that assess molecular-scale biofilm processes utilizing Flat-Plate, Channel Flow (FPCF) reactors that contain mineral phases with a face that is mounted flush with the floor of a channel through which an aqueous phase is passed by the exposed mineral surface (Geesy and Mitchell 2007). The top of the FPCF contains a window for microscopic viewing of the mineral surface without interrupting flow. The system has been used in the past to determine the influence of mineral surface-associated microbial activities on secondary mineral formation and the influence of mineralogical properties on the behavior and activities of bacteria colonizing the mineral surface under well-defined hydrodynamic conditions (Neal et al. 2001, 2003). The aqueous phase effluent from the reactor can be chemically and microbiologically analyzed (e.g., microarray analyses for community structure and activity) to assess dynamic transformations and metabolistic processes occurring on the mineral surface. Solid phase transformations and metabolic processes can further be deciphered using high-resolution surface interrogation methods such as X-ray microtomography (Holman et al. 1998, 1999; Hansel et al. 2005), auger electron spectroscopy (Geesey et al. 1996), X-ray photoelectron spectroscopy (Neal et al. 2004, 2001), Mössbauer spectroscopy (Dong et al. 2003), and X-ray absorption spectroscopy (Benner et al. 2002; Gonzalez-Gil et al. 2005). Modeling efforts may also take advantage of recent advances in magnetic resonance microscopy (MRM) that has historically been used to define water behavior and movement through complex heterogeneous porous media at high spatial resolution (Callaghan 1991; Seymour et al. 2004, 2007). The approach has been recently used to define the local density of biomass based on magnetic relaxation and diffusion of the water molecules entrained in a microbial biofilm, and the translational dynamics for water at the pore scale (i.e., μm^2-mm^2 range) (Seymour et al. 2004, 2007). MRM offers the opportunity to experimentally follow and map new sites of biomass accumulation as a result of diffusion- and advection-controlled dissemination of individual cells through porous geological media. It also offers the opportunity to detect and follow sloughing of cell aggregates and aggregate-induced plugging of flow paths (Geesey and Mitchell 2007). In these applications, the distribution of protons associated with protein and polysaccharide components of bacterial cells that accumulate in different flow paths can be distinguished from those of surrounding water molecules, and used to map and follow biomass accumulation in porous media (Seymour et al. 2004, 2007).

SCIENTIFIC IMPACTS

The proposed research will expand our understanding of biogeochemical processes, properties, and possibly discover new organisms with distinct function and geochemical impact under extreme conditions. Exploration of the biogeochemistry promoted by these microorganisms at the most fundamental level will certainly identify novel enzymatic and bio-interfacial reactions that impact the speciation and chemical form of trace constituents and radionuclides, and the topography and chemistry of associated reactive surfaces.

At a higher scale, the research will develop new, basic knowledge of how subsurface microbes, biofilms, and communities develop, evolve, and select under modified conditions (T, Bq, H_2, CO_2) resulting from deep geologic waste isolation. Microorganism influences on radionuclide valence and distribution between fluid and immobile phases under extreme conditions will be elucidated for comparison to established knowledge bases for geomicrobiological processes under ambient conditions. The development of new microscopic models that explicitly couple intracellular energetics and metabolism with (i) biodirected reactivity at the cell- or biofilm-mineral interface and (ii) linked extracellular abiotic reactions of different types will provide fundamental new insights on the interplay of geomicrobiologic and geochemical processes.

TECHNOLOGY IMPACTS

The described basic research on geomicrobiological processes in perturbed deep environments will provide insights and knowledge necessary to develop:

- Waste form stability and release models that incorporate potentially significant microbiologic influences
- Reactive transport models for radionuclide or other contaminant transport downgradient of repositories that account for geomicrobiological influences on solids, surfaces and waters, radionuclide valence, and tendency of radionuclides to associate with immobile solids by precipitation or adsorption

Overall, more robust and realistic performance and risk assessment will emerge, and will account for the importance of ubiquitous subsurface life forms.

While primarily focused on migration of radionuclides, this topic will also contribute to the resolution of geomicrobiological issues associated with carbon management. These issues include, but are not limited, to microbial influences on reservoir permeability and carbonate precipitation. Knowledge will be developed that will allow explicit modeling of biogeochemical processes for performance assessment.

A research focus on molecular and microscopic processes at the mineral-microbe interface represents a new, important direction for geomicrobiology that has traditionally been an observational science. New discoveries related to microorganism biomachinery and structures that control the rates and products of subsurface biogeochemical reactions will occur that will transform the field. Applications of this information to other energy-related uses of the deep subsurface are inevitable.

CROSSCUTTING ISSUES

THE MICROSCOPIC BASIS OF MACROSCOPIC COMPLEXITY

HIGHLY REACTIVE SUBSURFACE MATERIALS AND ENVIRONMENTS

THERMODYNAMICS OF THE SOLUTE-TO-SOLID CONTINUUM

THE MICROSCOPIC BASIS OF MACROSCOPIC COMPLEXITY

SUMMARY

Classical continuum mechanics relies on the assumption of a separation between the length scales of microscopic fluctuations and macroscopic motions. However in geologic problems this scale separation often does not exist. There are instead fluctuations at all scales. The resulting macroscopic behavior can then be quite complex. The underlying cause is invariably a kind of microscopic disorder. The challenge is to determine the nature of the microscopic disorder, and, ultimately, how it affects macroscopic observables.

SCIENTIFIC CHALLENGES

Geologic systems are disordered. Reactions within and transport through geologic media are therefore inhomogeneous. In a typical porous rock, this disorder begins at a sub-micron scale. Chemical reactions occur at the molecular level, while most physical processes occur at the scale of pores and pore networks. Both can be highly intermittent in time and space. Each level of heterogeneity may create a range of microenvironments for the next lower scale of processes.

One manifestation of disorder is the roughness of fluid-grain boundaries. At the scale of many pores, one finds a distribution of pore sizes, representing another kind of heterogeneity. At still larger scales, macroscopic heterogeneities in volume-averaged properties such as porosity and permeability are common.

Consider, for example, the roughness of pore-grain interfaces. Here the disorder can arise from the microscopically random (Brownian) motion of solute that precipitates on interfaces. Depending on reaction rates and diffusivities, precipitation can be either diffusion-limited or reaction-limited. In the former case, dendritic structures occur; in the latter, the pore-grain interface is relatively compact, but its roughness increases with the scale over which one measures it. Moving upward in scale, at least two kinds of disorder are relevant: the pore-space geometry itself, and the heterogeneity of mineral surfaces.

The case of immiscible two-phase flow is particularly instructive. Randomness of pore sizes can have a profound effect on flow because surface tension can impede the motion of interfaces through pores. Such phenomena have been well studied in their quasistatic limit. The work has been a triumph of percolation theory, in part because some of the most interesting behavior can be unambiguously related to fractal phenomena at the percolation threshold. The resulting patterns are significant, because they show that there is no scale at which one may reliably measure fluid saturations that can be extrapolated upward to another scale.

Dynamic phenomena are considerably less well understood. There is a tendency for small pores to be filled by wetting fluid, and a tendency for large pores to capture whatever flow there is. How these two processes interact dynamically, however, is not well known. In practice, static models are naively applied to dynamics. The problem becomes especially interesting when one takes account of the unusual correlations imposed by tortuous flow paths within a rock, and the dynamic nature of the paths themselves. There is a possibility of extreme events—i.e., breakthrough phenomena—not only in the approach to steady state, but possibly also within it.

Also poorly understood is the effect of inhomogeneous wetting. If the inhomogeneities are microscopic (smaller than a grain) and uncorrelated, then they would merely manifest themselves in the average wetting properties. However the inhomogeneities are more likely to manifest themselves from grain-to-grain, and may even cluster. In this case there would be effects due to their spatial correlations.

Chemical kinetics can also be altered by disorder. For example, phenomena as diverse as the weathering of silicate minerals, the recrystallization of carbonates (Fantle and DePaolo 2006), and the degradation of organic matter in soils and sediments (Middelburg 1989) have been found to exhibit apparent reaction rate constants that decay inversely with time, like *1/t*, at time scales ranging from less than a year to more than millions of years. The reasons underlying such time-dependent reactivity are unclear, but they probably depend on a combination of inhomogeneities of the reactive substrate and differences in the accessibility of the substrate to reactants in solution. That the decay of reactivity is so simply expressed as a power of time suggests the existence of a simple mechanism common to all such problems.

RESEARCH APPROACHES

The essential need is to develop a scientific basis of "emergent" phenomena relevant to predicting geological processes at a technologically relevant scale. To reach this goal, we must first develop a fundamental understanding of physical and chemical processes at the molecular scale. Such small scales are important because of the unusual mineral-fluid interactions that can be expected to occur in geologic environments impacted by human intervention.

Conversely, there is a need to develop methods that link changing macroscopic properties (e.g., chemical concentrations and flow properties) to changes at mineral-fluid interfaces. Thus we expect that mineral surfaces will be the most important point of contact between microscopic and macroscopic dynamics. Changes in chemistry can influence surface properties (roughness and surface area), and the surface properties in turn can influence flow (e.g., by clogging or dissolution).

Progress with such coupled problems requires a hierarchy of approaches. One is theoretical and includes the use of computer simulation. From basic considerations of physical dynamics and statistical mechanics, one seeks simple idealized models that show how macroscopic observables can be related to microscopic dynamics. Similarly it is appropriate to construct laboratory experiments that explore the effects of microscopic disorder on macroscopic dynamics. Our understanding of immiscible two-phase flow in porous media has greatly benefited from this approach. The challenge now is to construct similarly useful experimental analogs that show how mineral-fluid interactions are influenced by molecular scale disorder, and how changing surface properties influence flow. Experiments, theory, and simulation should be aimed at developing a predictive theory that directly connects microscopic disorder to macroscopic properties.

SCIENTIFIC IMPACTS

Environmental complexity is pervasive but an understanding of its microscopic foundation is not. Thus any insight gained from these studies would have an impact throughout environmental science. Specifically, there is a great need to better understand the interactions of physical processes, chemical reactions, and biological communities across all scales.

More specifically these studies offer the opportunity to identify the key variables that control the evolution of geological systems, especially those perturbed by human intervention. These variables change from scale to scale, in both time and space, but merely being able to identify those that exert the greatest control often represents major scientific progress.

TECHNOLOGY IMPACTS

These studies offer many opportunities for practical applications. Perhaps foremost among them are scaling laws that could help predict relations between microscopic properties and macroscopic flows. We also expect these studies to directly impact how information arriving from small, possibly nanoscale, subsurface sensors can be integrated to represent larger scale processes. Small sensors individually probe small environments. An understanding of the collective information they provide can only be derived from knowledge of how small scales connect to large scales. More generally, we seek a fundamental basis for characterization, monitoring, and prediction of human-impacted geologic environments.

HIGHLY REACTIVE SUBSURFACE MATERIALS AND ENVIRONMENTS

SUMMARY

The emplacement of energy system byproducts into geological repositories perturbs the existing geochemical environment and causes reactions that alter the minerals, pore fluids, and emplaced materials. Perturbations include changes in temperature and pressure, imposition of chemical gradients, and creation of intense radiation fields. Effects of perturbations may be short in duration or last thousands to millions of years. The effects may be dominant near the emplacement site or most significant at great distances. Strong interactions between the geochemical environment and emplaced materials are expected. The thermodynamic properties of complex geological fluids and solids, and the reaction rates among phases and species must be known to define the critical environmental parameters that control migration or immobilization of wastes.

New insight is needed on equilibria in compositionally complex systems, reaction kinetics in concentrated aqueous and other solutions, reaction kinetics under near-equilibrium undersaturated and supersaturated conditions, and transient reaction kinetics. Equally important, unifying theories linking kinetics and thermodynamic equilibrium for real-world solids and fluids are virtually nonexistent. Experimental, analytical, and computational approaches available to the geochemical community today are merging at the atomic and microscopic scales, and are poised to allow significant advances that will lead directly to quantitative macroscopic models of fluid/solid interactions with a high degree of confidence in the ability to accurately predict risks associated with contaminant migration.

SCIENTIFIC CHALLENGES

Geologic fluids (gases, liquids, and supercritical solutions) act as reaction media, reactants, and carriers of energy and matter in the natural environment. Among the many different types of geologic fluids, those containing volatile C-O-H-N-S species and those enriched in chloride salts (brines) are of particular interest. They occur widely and commonly contain significant quantities of dissolved and suspended compounds. The relative strengths of complex molecular-scale interactions in geologic fluids, and the changes in those interactions with temperature, pressure, and fluid composition, are the fundamental basis for observed fluid properties. Complexation and binding of organic molecules (e.g., humic acids) in aqueous solutions with or without CO_2, and the thermal stabilities of organic acids at high CO_2 loadings in the presence and absence of metal or surface binding will also be important. Although we have gained important quantitative insight into the speciation, stability, and kinetics of many organic-based systems of geological relevance, we still lack a fundamental understanding of the effects of mixed-salt composition, elevated pCO_2 and temperature, and Eh/pH conditions on the equilibrium and kinetic properties of key organics and biomolecules. Moreover, we are just beginning to understand how molecule-specific interactions among solutes and solvents eventually lead to homogeneous nucleation, crystallization, and aggregation of colloidal nanoparticles which could participate in and influence transport behavior. Understanding these solvent-mediated interactions for broad classes of solutes and suspensions in natural systems over the range of conditions typical of geologic fluids will greatly improve our capability to model and predict fluid behavior, reactivity, and the partitioning of elements and isotopes between coexisting species and phases relevant to geological sequestration.

Corrosion at metal, metal alloy, and waste form surfaces, deliquescent brine formation and evaporation on reactive surfaces, and condensation of volatiles into liquid films can result in highly concentrated and/or complex aqueous solutions and complex solids, whose chemical and physical properties are unknown. Much of the existing geochemical database is best employed to calculate equilibrium solubility of pure mineral phases in dilute aqueous solutions. Activity coefficient effects in liquid, crystalline, and amorphous phases are lacking for many solid and solution compositions critical to chemical migration issues. Little is known about the volatility of acids in complex brines. Competitive adsorption effects are ill-defined, particularly for trace levels of exotic species in complex brines.

The efficacy of subsurface sequestration depends on our fundamental understanding of the extent and rate of CO_2-mineral interactions and the associated effects on the fate of the injected carbon and rock characteristics. CO_2-mediated dissolution reactions produce solutes that buffer pH, thereby controlling the extent to which formation waters become acidified. These fluid-mineral reactions also have the potential to alter the porosity and flow permeability regimes. These changes may impact the injection process, but more importantly they would change the long-term flow characteristics and storage capacity of the aquifer.

Studies of mineral-solution reaction kinetics have been focused on steady-state dissolution rates and mechanisms in highly undersaturated aqueous solutions. Few investigations of near-equilibrium reactions have been undertaken and even fewer of mineral precipitation kinetics. Systematic investigations of solution composition effects are rare. Attempts to derive empirical or theoretical linkages between multiple regions of solution saturation state are rare (Nagy and Lasaga 1992; Dove et al. 2005). No theory has yet been formulated to apply to all minerals in all solutions. While a multitude of experimental systems could be investigated, the first major challenge is to identify key fluid and solid compositions that will lead to an integrated empirical and/or theoretical framework for predicting mineral-dissolution and precipitation rates in the multi-compositional environments of interest. The second major challenge is to develop fast methods for quantifying rates as a function of composition and saturation state (Bénézeth et al. 2007). Finally, reaction mechanisms must involve the structure, dynamics and electrostatics of mineral/water interfaces, but there have been few attempts to link heterogeneous reaction rates with the atomic-scale properties of the interface (Oelkers et al. 1994; Ludwig and Casey 1996; Dove 1999; Brantley 2004; Bickmore et al. 2006).

Superposed or fluctuating environmental perturbations could cause feedbacks that are unpredictable based on models using empirical reaction rate laws from simple systems. Short-lived coupled processes, such as simultaneous adsorption and solid dissolution reactions, can result in surface precipitation of new phases that rapidly and irreversibly immobilize contaminants, which would have a positive impact on performance assessment. Alternatively, cumulative release of an element by non-steady-state reactions can be orders of magnitude higher than those estimated with steady-state rates (Samson and Eggleston 2000), effectively increasing risk. Trace components derived from reactions triggered by perturbations can dramatically change the rate of subsequent reactions, for example by initiating autocatalysis or poisoning sorption at specific structural surface sites. The challenge is to be able to identify and quantify rate-limiting mechanisms of transient reactions and the cumulative effects of composite reactions.

The impact of perturbations on chemical migration may be much greater in fluids located in tight grain boundaries or within single mineral grains compared to fluids flowing through open cracks. Nanoscale confinement will alter the physiochemical properties of complex fluids, and highly-localized fluctuations in chemical conditions may occur due to leaching of mineral surfaces, nucleation and growth of new solids, and introduction of exotic elements from the repository. Recent advances in chemical imaging capabilities offer excellent opportunities for a fresh look at mineral-solution reactions in confined spaces. These tools include neutron, synchrotron X-ray, NMR, and other probes of surface reactions at the atomic scale, along with tomographic methods for *in situ* characterization of porosity/permeability and chemical/mineralogical heterogeneity within dense geologic media from either laboratory experiments and or natural systems (Fenter et al. 2002; Wenk 2006).

It is probable that the equilibrium state between a fluid in a nanosized pore and the confining solid phases is significantly different from that between the bulk fluid and minerals at the same solution composition, temperature and pressure, due to the effects of confinement on thermodynamic properties. It is also likely that reaction mechanisms will change when the structure and solvating properties of fluids change under confinement. The influence of confinement on the structure and dynamics of geofluids is now starting to receive more attention (e.g., Sposito et al. 1999; Wang et al. 2004a, b 2006; Mamontov and Cole 2006). Many factors dictate how fluids, and with them reactants and products of intrapore transformations, migrate through nanoenvironments, wet, and ultimately adsorb and react with the solid surfaces. These include the size, shape, distribution and interconnectedness of the confined spaces, and composition and physical properties of the solids and fluids (Cole et al. 2004, 2006). The dynamical behavior of fluids and gases in confined spaces is controlled by processes occurring at the interface with solids. A fluid can exhibit unexpected confinement-promoted phase transitions, including freezing, boiling or condensation, immiscibility, and other phenomena which are intrinsic to the fluid-confining surface interactions (such as layering and wetting) (e.g., Gelb et al. 1999; Melnichenko et al. 2006).

RESEARCH APPROACHES

A combination of unique and novel experimental and analytical techniques coupled with theoretical and modeling approaches is required to gain a fundamental understanding of the structures, dynamics, and reactivity of geologically representative fluids. Complex intermolecular interactions of C-O-H-N-S fluids (H_2O, CO_2, H_2, H_2S, N_2, CH_4) result in their unique thermophysical properties, including large deviations in the volumetric properties from ideality, vapor-liquid equilibria, and critical phenomena. The scaling from molecular to macroscopic properties of these fluids can be obtained by first making accurate determinations of these properties over wide ranges of temperature, density and composition, using novel methods such as densimetry (Blencoe et al. 1996) or synthetic fluid inclusions (Bodnar et al. 1985). These results can be used construct more robust Equations of State and to validate results obtained by *ab initio* modeling and molecular dynamics simulations of binary, ternary and complex mixtures of simple molecules in the C-O-H-N-S system. Scattering and spectroscopic methods can be used to identify local clustering and short-range ordering that affect deviations from ideal mixing as well as phase separation and critical phenomena. In addition, isotope effects in the C-O-H-N-S system will be a useful probe for investigating intermolecular forces, as well as the motion of molecules in condensed phases. Accordingly, experimental, theoretical, and simulation studies on the isotope effects (liquid/solid-vapor fractionation, pressure effects) are needed to understand the fundamental behavior of fluid species in the C-O-H-N-S system and to better use isotopes as tracers of subsurface fluid processes.

Studies are required that measure and assess rates of dissolution-precipitation in time-series where the controlling parameters (T, P and fluid composition) are varied in such a way as to promote reaction—i.e., at conditions both close to and far from equilibrium. In particular, novel approaches such as H^+ relaxation can be used to quantify near-equilibrium rates for key pH dependent dissolution-precipitation reactions (Bénézeth et al. 2007). Novel chemical imaging (e.g., Secondary Ion Mass Spectrometry, SIMS) and characterization tools (e.g., ICP-MS) are available to assess not only the chemical and isotopic signals resulting from mineral transformations, but also chemical and isotopic communication (e.g., ^{18}O, D, ^{13}C, ^{41}K, ^{26}Mg) between fluid species and mineral surfaces from the nano to pore scales. Neutron and X-ray scattering methods are particularly well suited for interrogating the structural features of starting minerals, reaction products, the reaction zone, and the reaction interface as complements to the chemical interrogation of mineral-fluid systems. These analytical techniques will provide crucially important information on the structural and dynamic properties of the fluids confined within micropores. In particular, the penetrating capability of neutrons, and their high sensitivity to hydrogen isotopes, will be useful in tracking the mobility of water and other H-bearing species during reactions. Quantifying structural and chemical patterns at the reactive interface can also utilize advanced microscopy techniques such as Atomic Force Microscopy (AFM) and High Resolution Transmission Electron Microscopy (HRTEM). Most importantly, studies of specific mineral suites from natural systems (e.g., sedimentary basins and geothermal resource areas) that exhibit micro- to macroscale reaction features analogous to those produced at the bench scale will complement and verify results from laboratory-based investigations.

SCIENTIFIC IMPACTS

A comprehensive and technically rigorous understanding of the volumetric properties and energetics of C-O-H-N-S fluids is needed to correctly interpret fluid-solid interactions relevant to key sequestration scenarios. Previous PVT and activity-composition studies of mixed-volatile fluids containing H_2O-CO_2-CH_4-N_2-H_2 coupled (Anovitz et al. 1998; Blencoe et al. 1996, 1999, 2001, Seitz and Blencoe, 1999; Seitz et al. 1996) with Equations of State (EOS) modeling (Blencoe 2004) has demonstrated that departure from ideal mixing can be profound, particularly at near-critical conditions. While theoretically robust EOS have been developed to represent experimental results, a molecular-level understanding of complex fluid behavior is lacking, which in turn severely limits the predictive capability needed to model fluid behavior in subsurface geochemical environments. Additionally, it is becoming increasingly clear that organic molecules in aqueous and mixed-volatile fluids—ranging from simple hydrocarbons and carboxylic acids to branched and cyclic compounds, to proteins and humic substances—may also play a major role in controlling deviations for ideality.

Despite the utility of the equilibrium approach in quantifying the elemental and isotopic behavior in mineral-fluid systems, there is mounting evidence that chemical (and isotopic) heterogeneity and disequilibrium are common features of the rock record. Highly spatially-resolved imaging techniques have documented chemical, mineralogical and isotopic disequilibrium features preserved over varying length scales (Å to mm) in both experimental and natural materials which represent different snap-shots in time (e.g., Cole and Chakraborty 2001; Labotka et al. 2004). The discrepancy between reaction rates (both chemical and isotopic) predicted for natural systems and those determined in the laboratory is a major limitation in our ability to unravel the time-dependent evolution of mineral-fluid interactions. The factors contributing to this discrepancy are manifold and complex, and include mineral structure and composition, solids preparation, nature of reactive surface area, the chemical affinity or saturation state of the solution, fluid to solid ratio, and the temperature and pressure history (cf. White and Brantley 1995; Brantley 2004; Lüttge 2004; Maher et al. 2006). Successful bridging of this gap between laboratory and field rates will have a profound impact of our ability to assess the spatial and temporal evolution of mineral dissolution-precipitation and associated permeability changes.

Additionally, a fundamental understanding of mechanisms and rate behavior of mineral-fluid interactions provided a means to address the feedbacks on mineral trapping due to geomechanical stresses distributed throughout the system.

- Development of steady-state kinetic rate laws for mineral-solution reactions under the full range of saturation conditions
- Quantification of rates and identification of mechanisms that control transient reaction kinetics
- Determination of thermodynamic properties of complex solutions and solids, including the effects of nanoscale confinement and trace components

TECHNOLOGY IMPACTS

Research on highly reactive environments could lead to improved carbon sequestration efficiency through better understanding of dissolution and mineral trapping in CO_2 storage reservoirs, and by developing methods for accelerated trapping. The results would also be critical for predicting the long-term effects of CO_2 on seal integrity, and for improved geochemical modeling and risk assessment. Improved understanding of highly reactive environments also pertains to predicting the longevity of engineered barriers and materials, describing the evolution of fluids in geologic repositories, and evaluating the safety and risk over the extremely long time scales needed for effective nuclear waste isolation. Fundamental results obtained on complex fluids will also contribute directly to our understanding of such diverse processes as mineral and gas solubilities, fluid hydrodynamics, hydrocarbon generation and persistence, and the metabolism of subsurface microbial communities.

THERMODYNAMICS OF THE SOLUTE-TO-SOLID CONTINUUM

SUMMARY

Reactions involving solutes, colloids, particles, and surfaces control the transport of chemical constituents in the subsurface environment. A rigorous structural, kinetic and thermodynamic description of the complex chemical reality between the molecular and the macroscopic scale is a fundamental scientific challenge. Advanced techniques for characterizing particles in the nanometer-to-micrometer size range, combined with a new description of chemical thermodynamics that does not rely on a sharp distinction between solutes and solids, will have a wide range of implications from physics and chemistry, to material science, biology and earth science.

SCIENTIFIC CHALLENGES

Chemical phases in geological environments range from water containing dissolved solutes to mineral grains visible by eye. Of these, nanoparticles and surface nanophase systems can account for most of the adsorption of trace and toxic elements, as well as for the bulk of chemical reactivity. In both precipitation and dissolution, nanoparticles or nanophases are often intermediates and their high surface areas provide a rich spectrum of reactive sites. Traditional theoretical approaches in colloid and surface chemistry, developed using concepts borrowed from continuum mechanics, have been applied to the nanoscale regime with some success. But, a number of important phenomena cannot be captured because these approaches describe only average properties for small systems. New computational and experimental methodologies provide opportunities to resolve on spatial and temporal scales the complex landscape of chemical configurations and their thermodynamic and kinetic consequences. *Ab initio* calculations should soon allow us to resolve the collective interactions of hundreds of atoms. The structure and dynamics of surfaces and small particles can be probed with increasingly powerful spectroscopic and X-ray scattering techniques, many of which require synchrotron and neutron facilities. Laboratory studies of solubility, reaction kinetics, and thermodynamic properties will provide detailed data to be used, together with computational results, to describe the complex and gradual transition from isolated dissolved species to bulk solid phases.

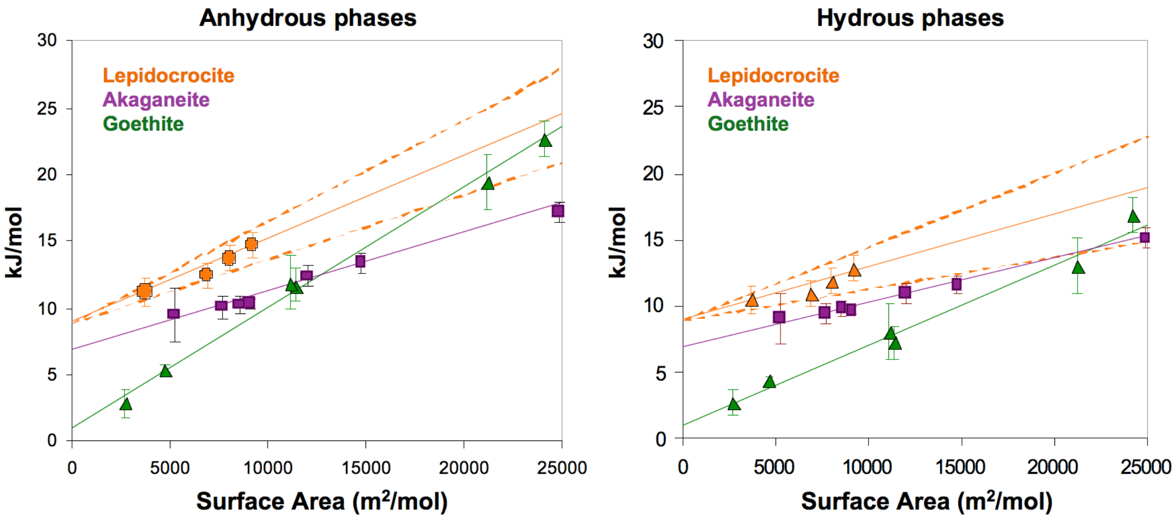
A new thermodynamic formalism, which explicitly takes into account the gradual change from solute to solid phase, and includes the microscopic abundance of local surface environments, needs to be developed. The challenge is to make this formalism both rigorous at the level of statistical thermodynamics and useful at the level of applications. A more fundamental description of the heterogeneity of small particle and surficial processes will lead to a better understanding and prediction of radionuclide transport, reactions of CO_2 with minerals, and the potential use of nanoscale sensors. Such an approach is also needed for applications to physics, chemistry, nanotechnology and biology, where similar nanoscale complexity is encountered.

The fundamental scientific challenge is to develop a rigorous structural, kinetic and thermodynamic description of this complex chemistry from the molecular to the macroscopic scale. There is increasing evidence that a continuum exists between dissolved aqueous molecular and ionic species on the one hand and macroscopic crystalline phases on the other. This continuum between solute and solid is populated by molecular clusters, nanoparticles (colloids), and small crystals with large surface areas. For example, the speciation of aluminum ranges from isolated Al^{3+} species to clusters containing 13 and 30 aluminum atoms bridged by water molecules and hydroxide ions, to nanoparticles, to a variety of hydroxides, oxyhydroxides, and oxides (Casey 2006). Not all material passing through a filter is truly in solution, and thus apparent solubility may represent the sum of species of different sizes. Furthermore, the small particles, having large surface areas, may adsorb the majority of trace elements, including heavy metals and radionuclides. The mode of what is collectively called adsorption (or sorption) may vary from ions separated from the surface by water molecules to bound metal atoms on the surface, to surface precipitates of new phases, to solid solutions within the particles. Additional inorganic, organic, or biogenic materials coat the particles and change their chemical reactivity. The particles evolve with time and solution conditions; they may dissolve, coarsen, or transform. This complexity raises a number of fundamental scientific questions and limits our ability to understand and model the transport of chemical species in the subsurface environment.

RESEARCH APPROACHES

Because nanoparticles and nanophases are neither small molecules nor extended solids, the very definition of a phase, and therefore of phase equilibria, solubility, and phase diagrams in the classical sense, becomes clouded. A particle 1 nm on a side contains a few hundred atoms, one 10 nm on a side contains hundreds of thousands. Both are too small to give full X-ray diffraction patterns, yet both contain significant ordering of atoms that may differ from larger bulk crystals. Spectroscopic probes (NMR, EXAFS) provide local structural information. Small angle scattering (X-ray and neutron) provide information on structural correlations at the 1-2 nm scale. Imaging with X-rays and electrons, and the spatially resolved chemical analyses associated with these measurements provide information on structure, morphology and composition at the nanoscale. All of these techniques are evolving rapidly, and many require the capabilities of the most advanced synchrotron and neutron facilities. With better synthesis and characterization methods, well-defined nanophase materials can be used for thermochemical and kinetic studies. *Ab initio* calculations are on the verge of being able to handle several hundred atoms, but particles of thousands of atoms, still different from bulk periodic solids, are not yet accessible to rigorous computation. The local environments of adsorbed species can be probed by spectroscopic, X-ray scattering, and computational techniques, but species interactions at longer distance in and on the particle, and their evolution with time, are harder to access. On a fundamental theoretical level, the statistical mechanics of assemblages of such particles must be explored.

A major question is to what extent the evolution of systems containing nanoparticles or colloids can be described by thermodynamics or requires a full kinetic description. In nature at low temperatures, particles formed by precipitation often coarsen slowly or not at all. The interplay of surface energies, polymorphism, and surface hydration (or other types of surface coating) can create a steady-state which has a reasonably well defined free energy and local equilibrium between the particles and their environment. The stable crystal structure (phase) at the microscopic scale may be different from that in the bulk (Figure 47), but the equilibria of such particles with the aqueous phase, surface adsorption of minor species, catalytic properties, magnetic and electrical properties, and other physical properties, may in fact be reasonably well



Courtesy of Alexandra Navrotsky, UC Davis

Figure 47: Experimentally measured enthalpies of formation for a variety of iron oxide minerals relative to bulk hematite plus liquid water as a function of surface area. The crossovers in energy for both anhydrous and hydrous conditions show that different phases become stable at the nanoscale. This reflects competition among the closely balanced energetics of polymorphism, surface energy, and hydration and indicates a complex energy landscape of accessible states (more discussion is found in Majzlan et al. 2003 and Mazeina et al. 2006).

defined, though again different from those of the bulk phase. Thus, for example, in the iron oxides, which are common in the geological environment, maghemite rather than hematite, and ferrihydrite rather than goethite, may dominate the chemistry and transport of minor constituents, such as actinides, which may themselves also form colloidal phases.

Colloid chemistry was developed by applying concepts borrowed from continuum mechanics to the nanoscale: electrical double layer, point of zero charge, Gibbs-Thomson effect, etc. These concepts work amazingly well considering that they relate the notion of uniform distributions of force and charge on spherical surfaces to particles which are inherently atomistic, faceted, and heterogeneous. If one distinguishes nanoscience from colloid science, it is that the former focuses more on molecular scale interactions and structural heterogeneity through its use of modern spectroscopic and computational techniques to build an atomistic description. But the challenge remains to link this microscopic structural description to thermodynamics and dynamics.

A specific example of a quasi-thermodynamic description of chemical reactions at the solid-solution interface is given by so-called “surface complexation models.” These models quantify reactions between solutes and surface species with free energy changes that include, in addition to an intrinsic chemical term, a coulombic term calculated on the basis of electrical double layer theory. In effect the coulombic term is an activity coefficient for the surface species that is neither unity (as that of a pure solid phase) nor that of a solute surrounded by water molecules. This approach also has worked remarkably well in that the average electrical potential calculated for a continuous smooth surface is applied to individual molecules. But these models are limited in their applications since they do not explain the “chemical reality” of many surface phenomena. For example, the adsorption of solutes on surfaces can result in the formation of clusters that change the local chemistry in a way that cannot be accounted for by surface complexation models. Such clusters may be the precursors to surface precipitates.

A concerted approach using a variety of modeling studies and experiments defining structures, thermodynamics and reactivity is needed to provide the basis for a thermodynamic description of the gradational regime between solutes and solids. The molecular scale insights derived from modern spectroscopic techniques must be accounted for in this description. The computational challenge is in both the computing power and algorithms for dealing with systems containing more than a few hundred atoms. The experimental challenge is to attain higher resolution in concentration, space, and time for the study of structures and their evolution. To further these ends, large facilities must be developed and exploited, including large parallel processors, new techniques at light sources, and new capabilities at neutron-scattering facilities.

SCIENTIFIC IMPACTS

A unified fundamental description of the transition from isolated molecules in solution to extended solids has a wide range of implications from physics and chemistry, to material science, biology and earth science. What is sought is a description of chemical thermodynamics that does not rely on a sharp distinction between solutes and solids. The impact of a new paradigm will be as wide as the present range of application of chemical thermodynamics. In terms of kinetics, a description of the full diversity of chemical states and local environments will lead to a reformulation of rate laws for chemical transformations. Rather than focusing on average properties, this approach will identify the energy landscapes through which reactions will occur.

TECHNOLOGY IMPACTS

In addition to developing an enhanced capability to predict the migration of radionuclides and other components in natural systems, there are increasing opportunities to use nanotechnology in monitoring subsurface environments. When nanoscale or molecular sensors (as passive tracers, as active sensors for changes in pH or redox fronts, or as “smart sensors” which are attracted to “hot spots”) are placed in the environment, they become part of the geologic system. Their transport and survival in the harsh environment, and their potential role as contaminants or transporting agents for other contaminants, must be characterized. Such characterization will involve many of the same thermodynamic and kinetic issues described above.

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APPENDICES

APPENDIX 1:
TECHNICAL PERSPECTIVES RESOURCE DOCUMENT

APPENDIX 2:
WORKSHOP PROGRAM

APPENDIX 3:
ALL ATTENDEES AT WORKSHOP

APPENDIX 4:
ACRONYMS AND ABBREVIATIONS

APPENDIX 1: TECHNICAL PERSPECTIVES RESOURCE DOCUMENT

OVERVIEW

The Department of Energy has at least a dozen program areas in which the Geosciences form the foundation for applied program activities. All energy production starts with resources extracted from the earth, either directly, as in hydrocarbon production and the mining of coal and uranium, or via raw materials like metals and silica that are needed for the infrastructure of energy production. Energy byproducts are then released in controlled ways back into the environment—into air, water or ground—and this aspect of the energy cycle is proving to be as important and challenging as energy production.

The Office of Science seeks the continual improvement of scientific knowledge with which existing energy technologies can be enhanced, new energy technologies developed, and environmental impacts of energy production efficiently and economically reduced. These objectives provide impetus for the series of “Basic Research Needs” workshops that the Office has undertaken over the last four years. Several were focused on individual technology areas, such as Solar Energy, the Hydrogen Economy, or Nuclear Energy. Others are more broadly based with significant impacts envisioned for multiple DOE mission areas, such as the current Basic Research Needs for Geosciences workshop and the upcoming workshops on Basic Research Needs for Materials in Extreme Environments and Basic Research Needs in Catalysis.

To guide discussion, the Basic Research Needs for Geosciences workshop will focus on the scientific challenges in Geosciences that are posed by two revolutionary technologies recently proposed. The first is the “FutureGen” integrated gasification combined-cycle power plant concept that will fully sequester all greenhouse gases by deep earth injection. The second is the new nuclear fuel cycle which will use two kinds of reactors, providing power as well as consuming some long-lived radionuclides.

These two technologies require understanding two fundamentally different types of geological systems (Table 1), but ultimately have in common the implicit need to further advance the current state of knowledge of subsurface geologic processes to foster future improvements as these technologies are implemented over the coming decades (Table 2).

Geological sequestration of carbon dioxide will occur through pumping of supercritical CO_2 fluid down several kilometers into deep porous rock formations that are completely unusable for other purposes. In the simplest terms, industrial scale CO_2 sequestration requires a stronger foundation for our understanding of multiphase (CO_2-water-possibly diverse hydrocarbons) fluid transport and stability in the deep subsurface, although workshop discussions are free to expand that simplistic description as needed. Isolation from the surface environment is provided both by depth and by impermeable geologic formations capping the sequestration site. Although sequestration involves emplacing anthropogenic CO_2 in deep formations, CO_2 is also a natural component within many existing natural gas and oil deposits where it has been generated by processes similar to those that generate hydrocarbons. Current understanding of deep geological formations has been developed primarily through experience within the oil and gas industry through reservoir investigations lasting a decade or more. Injection of CO_2 has also been used in enhanced oil recovery, which gives additional understanding of how it reacts within deep geological environments.

Most nuclear materials disposal or isolation will occur within several hundred meters of the surface, either within the zone of sediment and rock that are unsaturated by ground water, or within the sediment or rock that is fully saturated with ground water, but above any deep geological aquifers. Again, in simplest terms, disposal of nuclear waste requires developing better understanding of chemical (radionuclides, metal corrosion products, and other waste-derived materials) migration processes within complex geological media outside the engineered disposal system in case of leaks. The geological disposal approach provides a deep location to prevent human intrusion at some point in the future since isolation has to be maintained for many thousands of years. A critical scientific aspect is that the emplacement of the engineered disposal canisters will occur in unpressured environments at depths that may communicate with the atmosphere and/or the hydrosphere if the engineered barriers are breached. Understanding the scientific basis for nuclear materials disposition will also contribute to challenges faced by DOE in its environmental cleanup mission.

The scientific challenge for these two technologies is to build systems-level understanding that can provide unprecedented public safety margins. Systems-level understanding is ultimately based on knowledge of the systems' components and processes at spatial scales ranging down to the atomic level and time scales up to thousands of years. Scientific understanding today is adequate to begin to move forward with the proposed technologies, but it is our responsibility to continue research to provide the best possible implementation of these technologies over the succeeding decades. Some uncertainties about the evolution of the isolation environments over the long-term will remain, even in state-of-the-art designs. Thus, continuing improvements in understanding the chemical and physical changes to geological systems potentially will reduce risk and cost, and expand confidence in predicted performance.

Success in reaching this new understanding will have a much broader impact on DOE's applied programs than just in these two energy areas, because of the commonality of challenges diverse offices face, for example in geothermal energy, oil and gas development, environmental remediation and waste management. The improved understanding of the critical processes associated with these two new energy technologies will be used to design advanced geochemical, hydrologic and geophysical measurement technologies, enhance our ability to predict and monitor subsurface processes at a much higher resolution, and enable us to use measurements and monitoring capabilities for verifying system behaviors.

Table 1. Differences between geologic carbon sequestration and nuclear waste disposal

	Geologic Carbon Sequestration	**Nuclear Waste Disposal**
Volume	Very large	Small
Local footprint	Very large	Very small
Regional footprint	Many locations	One location
Lethality	Very low	Very high
Risk over time	Decreases over time	Increases with time
Operators	Industry	Government
Regulatory	Government mandate	Government license
Reprocessing	Highly unlikely	In new technologies
Physics	No thermal anomaly	No pressure anomaly
Chemistry	Largely inert	Highly reactive
Monitoring	±100 years	>1000 years
Initial liability	Private industry	Government
Public opinion	To be determined	Negative

Table 2. Shared research activities for geologic carbon sequestration and nuclear waste disposal

Site Characterization

- Determine fracture geometry and transmissivity
- Determine fracture-matrix interaction
- Determine fault geometry and tortuosity
- Determine geochemical conditions (mineralogy, fluid chemistry, reactive surface area) over range of scales
- Predict relative permeability and bulk permeability fields
- Evaluate uncertainty of subsurface parameter measurements

Predictive Modeling

- Couple thermal, hydrological, chemical, mechanical and biological processes
- Upscale and downscale processes over space and time
- Propagate uncertainty
- Calibration and boundary conditioning
- Validation methods

Monitoring

- Develop robust sensors to monitor subsurface conditions
- Multivariate inversion of data for parameter estimation
- Proxy data interpretation
- Rapid interpretation and recursion of monitoring results

Subsurface Engineering

- Determine perturbation of natural systems
- Characterize interfaces between natural and engineered systems
- Optimize natural and engineered systems
- Determine effect of engineered system on fluid flow

TECHNOLOGY AND APPLIED RESEARCH AND DESIGN NEEDS FOR GEOLOGICAL CARBON SEQUESTRATION

INTRODUCTION

In the global energy system, fossil fuels currently comprise 85% of all energy supply. Combustion of these fuels releases greenhouse gases to the atmosphere, chiefly CO_2. Every year, ~27 Gt of man-made CO_2 enter the atmosphere (7.3 Gt C), nearly all of it from fossil fuel combustion. Concerns have increased about the risks of greenhouse gas emissions and attendant climate change impacts. This has prompted renewed focus on reducing emissions through efficiency improvement, renewable energy supplies, and nuclear fission. Still, even with new carbon-free sources of energy, reduction in worldwide emissions may not decrease as much as hoped because fossil energy use will continue and grow. Providing a technology foundation for reduced carbon or carbon-free economic energy development for the rest of the world is another highly worthwhile objective for research in this area.

Carbon sequestration is the long-term isolation of carbon dioxide from the atmosphere through physical, chemical, biological, or engineered processes. Geological carbon sequestration appears to be one of the more promising options for major greenhouse gas reduction in the next 20–50 years, particularly when coupled with improvements in energy efficiency, renewable energy supplies, and nuclear power. The basis for this interest includes several factors:

- The potential capacities are large based on initial estimates. Formal estimates for global storage potential vary substantially, but are likely to be between 800 and 3300 Gt of C (3000 and 10,000 Gt of CO_2), with significant capacity located reasonably near large point sources of the CO_2.
- Geological carbon sequestration can begin operations with demonstrated technology. Carbon dioxide has been separated from large point sources for nearly 100 years, and has been injected underground for over 30 years.
- Testing of geological carbon sequestration at intermediate scale is feasible. In the U.S., Canada, and many industrial countries, large CO_2 sources like power plants and refineries lie near prospective storage sites. These plants could be retrofitted and begin CO_2 injection today, though it is important to keep in mind the scientific uncertainties and unknowns.

As the concepts for geological carbon sequestration are proven to be reliable for current power plant technology, improved power plant designs, such as the integrated gasification combined cycle approach to clean coal power generation, are expected to be able to bring down sequestration costs dramatically by incorporating the requirements for sequestration in the power plant design from the beginning rather than treating it as an add-on technology.

To achieve substantial greenhouse gas reductions, geological storage needs to be deployed at a large scale (Friedmann 2006), there must be minimal leakage from the underground storage reservoirs back to the atmosphere, and there must be minimal impact on other uses of the subsurface environment and the resources it contains. With regard to scale, 600 large pulverized coal plants (~1000 MW each) will produce 1 Gt C/y (3.7 Gt CO_2/y) requiring sequestration. This is 3600 times the injection of Statoil’s Sleipner project (Pacala and Socolow 2004), which has injected 1 MMt of CO_2 per year for ten years (Arts et al. 2004). In that context, the technical needs for geological carbon sequestration involve questions of scale (both spatial and temporal).

Greater scientific understanding is required to develop tools, regulations, and operational protocols for deployment of multi-million ton injections in thousands of wells nationwide and worldwide across a range of geological settings. This need requires that future suitable sites are confidently identified, atmospheric isolation of CO_2 is effective during injection and long after, and that the subsurface environment is effectively monitored. These expectations in turn require that large volumes of subsurface rock formation can be adequately characterized, and that the performance of the storage reservoir can be predicted, simulated, and verified. Hazards that present potential risks must be identified and the risks quantified. Underlying these concerns are questions of fundamental petrophysics, hydrology, geochemistry, and reservoir characterization. Given the limited data sets from geological carbon sequestration operations at scale and the heightened interest in the technical feasibility of sequestration, additional fundamental research should lead to significant enhancements in the scientific and technical understanding needed for large-scale deployment. While substantial understanding currently exists, it can be better quantified, characterized, used, and validated through addressing remaining important scientific and technical questions.

CARBON CAPTURE AND STORAGE OVERVIEW

Carbon capture and storage involves three components: capture and separation, transportation, and geological sequestration. Industry has substantial experience with each of these components, chiefly from operation of hydrogen plants, fertilizer plants, refineries, and natural gas processing facilities, as well as from enhanced oil recovery operations. CO_2 has been separated from industrial flue streams at scales greater than 1 MMt CO_2/y (270,000 t C/y), large pipelines transport millions of tons of CO_2 hundreds of kilometers, and millions of tons of CO_2 and other acid gases are injected into geological formations every year. Similarly, CO_2 has been separated from small-scale power plants, and technology to scale these operations to plants of 200 MW or greater exists.

In considering the technical needs for geological carbon sequestration deployment, it is helpful to consider a reference case of a 500 MW coal-fired power plant with its carbon capture and storage needs (MIT 2007). Such a plant, burning bituminous coal with an 85% capacity factor and 90% capture, will require injection of 3 MMt CO_2/y and approximately 200 MMt CO_2 over its expected lifetime of roughly 60 years. For targets of interest and a normal geothermal gradient, this mass will require a storage volume equivalent to 60,000–100,000 bbl/d (~10,000–16,000 m^3), and ~1.4–2.3 billion barrels (~200–400 million m^3) over the same time. For injection into a sedimentary rock layer of 30 m thickness, 70% net injectivity, 10% porosity, and where only 5–50% of the pore volume can be accessed effectively due to heterogeneity, the resulting CO_2 plume would have a 7–70 km final radius and displace an equivalent volume of pore fluid. For plants where the sulfur species are co-sequestered at ~0.03% of the injected volume, ~8500 tons/y of sulfur could be injected as SO_x or H_2S.

There are over 1500 coal-fired power plants in the United States today generating 330,000 MW of electricity. There are over 5,500 natural gas fired power plants generating over 430,000 MW of electricity. To achieve substantial reductions of CO_2 emissions, well over 1 Gt C (emissions from 600,000 MW of electricity $\approx$ 3.7 Gt CO_2) must be injected annually. Injection will be proposed for a range of geological formations, including those with some understanding based on previous oil and gas operations, but mostly in deep saline aquifers with limited direct local information. Operators, investors, regulators, financiers, and other key stakeholders will require additional information that cannot be addressed with existing scientific knowledge and capabilities. With these considerations, it is prudent to presume that continued technology development will be critical to the long-term success of commercial carbon capture and storage, and that scientific advances will be necessary to facilitate such technology development (DOE 2006b; IPCC 2005).

CO_2 capture and separation

The first step in carbon capture and storage is the separation of CO_2 from industrial flue streams and concentration to CO_2 purities of 95% or greater (Thambimuthu et al. 2005). This step is necessary to limit compression costs and to make effective and efficient use of available subsurface pore volume. Natural mineralization and dissolution trapping mechanisms of CO_2 in deep sedimentary rock formations will be most effective at this high purity.

Currently, three technology pathways exist for commercial CO_2 capture and separation:

- Post-combustion capture: This involves separation of CO_2 from nitrogen, commonly with chemical adsorption processes (e.g., monoethanolamine (MEA)).
- Pre-combustion capture: This involves conversion of fuel feedstocks (e.g. coal) into syngas via gasification, steam reformation, or partial oxidation and then shifting the syngas chemically to hydrogen and CO_2, and then separating the H_2 from CO_2. Currently, this last step is commonly done with physical adsorption (e.g., Selexol, Rectisol).
- Oxy-firing combustion: This involves combustion of fuels in a pure oxygen or O_2-CO_2 rich environment such that effectively no nitrogen is present in the flue gas (separation of O_2 from air (N_2) is required).

Each of these approaches requires substantial power to run adsorption and air-separation units, raising operating expenses and increasing the amount of CO_2 emissions simply to drive the sequestration process. They also require more capital in plant construction and have differing operational costs and energy penalties. At present, each technology pathway appears equally viable from an economic and thermodynamic standpoint (Thambimuthu et al. 2005; MIT 2007).

CO_2 storage (sequestration)

The issue of scale dominates implementation of geological carbon sequestration deployment. The first scenario of the Climate Change Technology Program’s Strategic Plan (CCTP 2006) assumes that geological carbon sequestration could store between 75 and 300 Gt C (260–1000 Gt CO_2) over the next century. Edmonds et al. (2004) places the potential abatement of CO_2 emissions by geological carbon sequestration at 55%, with McFarland et al. (2004) estimating the abatement potential of sequestration at 70%. These volumes would have geological carbon sequestration providing 25–75 Gt C over 50 years, or 15–43% of the emissions reduction needed to stabilize atmospheric CO_2 levels at 550 ppm (Pacala and Socolow 2004)

STORAGE BASICS

CO_2 behavior at depth

Storage of large CO_2 volumes in geological formations requires that the CO_2 be relatively dense, so that storage capacity is efficiently used. Given typical geothermal gradients and hydrostatic loads, CO_2 is likely to be in a supercritical state (Figure 1) at most target sites (e.g., Bachu 2000). This requirement means that CO_2 will be injected typically at depths greater than 800 m.

At the likely range of injection pressures and temperatures, CO_2 density would range from 400 to 800 kg/m^3 (Table 3). Gravitational (buoyant) forces will drive CO_2 upward from the injection point to the formation cap rock. Consequently, trapping mechanisms (listed in next section) are needed to store CO_2 effectively. CO_2 viscosity will be less than most oils (~ a factor of 10); this raises the concern of viscous fingering by the CO_2 through any reservoir into which it is injected, thereby potentially bypassing much of the potential pore storage space. CO_2 dissolves slowly into brines and then forms carbonic acid, which lowers pH. Both the carbonate alkalinity and the change in pH can influence chemical reactions among the CO_2 (gas), the brine and the minerals in the rock matrix. At the same time, water dissolves into the CO_2, effectively drying out the pore volume within the body of the plume and reducing reaction rates therein. This process may also supersaturate pore brines and induce salt precipitation. These physical and chemical properties are summarized in Annex 1 of the IPCC Special Report (Freund et al. 2005) and references therein.

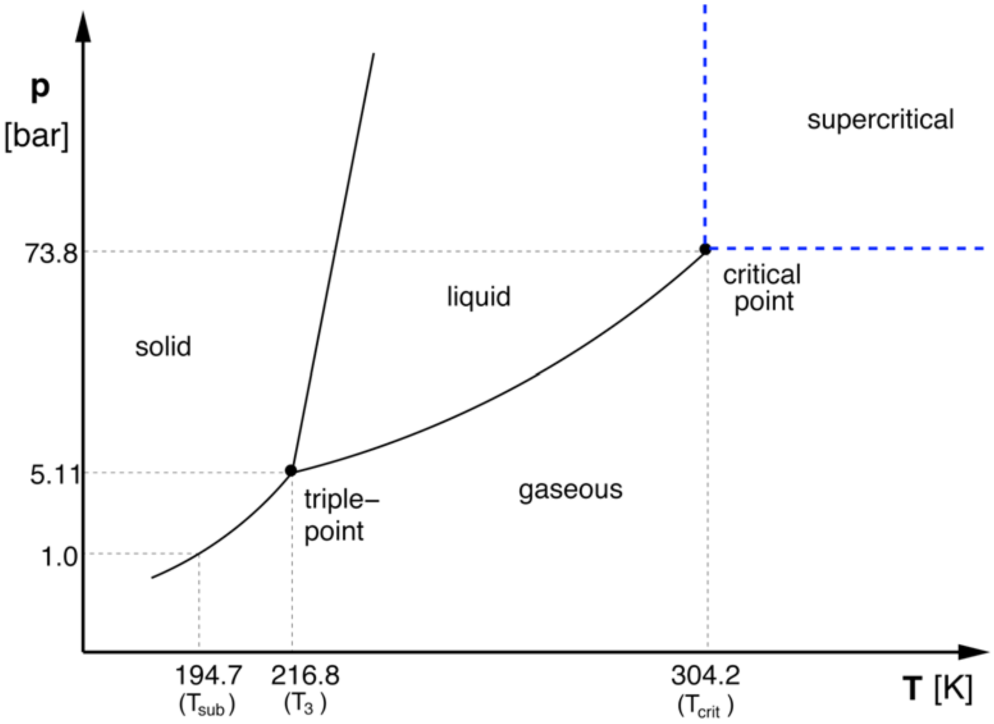

Figure 1. CO_2 phase diagram (Bielinski 2006)

Table 3: CO_2 properties at likely injection conditions

CO_2 property	**Likely minimum T (35°C) and P (8 MPa)**	**Likely maximum T (80°C) and P (40 MPa)**
Density: kg/m^3	419	823
Viscosity: mPa/s	0.030	0.076
Solubility: weight % in fresh water (wt.% in 50,000 ppm TDS water)	5.2% (4.1%)	5.8% (4.7%)

Data from NIST chemistry webbook (http://webbook.nist.gov/chemistry/fluid/) and Spycher and Pruess (2005).

Over time, injected CO_2 remains within the target reservoir and will dissolve and react with the local rock volume (see below). If CO_2 leaks from the reservoir, it will migrate towards the surface and will change phase from supercritical fluid to gas at approximately 800 m depth. The gas phase will expand and cool. At very high rates of ascent, Joule-Thomson cooling of CO_2 could be sufficient to solidify the CO_2 and either plug or divert flow temporarily (Pruess 2006). Though this is unlikely under most geological conditions of interest, it may be important in the well bore or near-well environment.

Substantial process uncertainties remain in how CO_2 interacts with other pore fluids. For example, uncertainties persist in how CO_2 interacts and mixes with gas, water, and oil in the same pore. Changes in solubility, equations of state, dynamic composition, fluid properties, and interfacial tension make it difficult to predict sweep, dissolution rate, and mixing front trajectories (e.g., Stalkup 1987; Jessen et al. 1998; Yang et al. 2005). Initial modeling work has explored how the introduction of CO_2 might affect existing subsurface microbial communities (e.g., Onstott et al. 2005). Enhanced microbial activity could lead to the development of biofilms, which could reduce pore and fracture permeability. These uncertainties ultimately affect questions of CO_2 fate, and the rates and importance of other pore-scale processes (e.g., drying and salting of intra-pore brines). Focus on some of these questions would lead to improved simulations and predictive capabilities.

Trapping mechanisms

A number of geological reservoirs appear to have the potential to store many 100's–1000's of Gt of CO_2 (Benson and Cook 2005). The most promising reservoirs are porous and permeable rock bodies at depth (Figure 2).

Saline formations contain brine in their pore volumes, commonly with salinities greater than 10,000 ppm.

Depleted oil and gas fields have some combination of water and hydrocarbons in their pore volumes. In some cases, economic gains can be achieved through enhanced oil recovery or enhanced gas recovery (Stevens 1999; Oldenburg et al. 2004; Jarrell et al. 2002). Substantial CO_2-enhanced oil recovery already occurs in the US with both natural and anthropogenic CO_2. These fields provide much of the knowledge base we have about the potential issues related to CO_2 sequestration. Although oil and gas fields have the broadest knowledge base, they are also already breached by all of the oil and gas wells that have made them economic, but potentially provide leakage pathways.

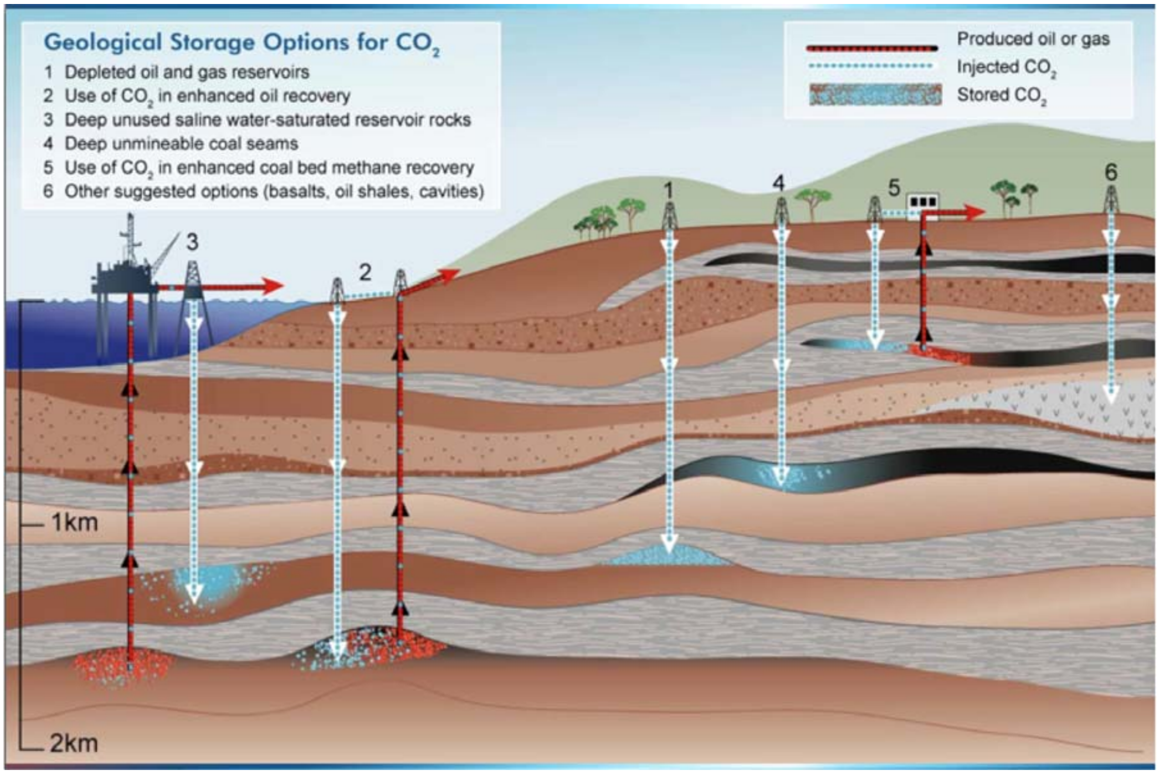

Figure 2. Options for storing CO_2 in underground geological formations. After Benson and Cook (2005).

Deep coal seams, often called unmineable coal seams, are composed of organic minerals with brines and gases in their pore and fracture volumes that can preferentially adsorb and bind CO_2 as well as store it in pores and minor fractures.

It is likely that most geological sequestration will occur in saline formations due to their large storage potential and broad distribution. However, initial proposals are for depleted oil and gas fields, accompanying enhanced oil recovery, due to high density and quality of subsurface data and potential for economic return. Although there is some economic potential in enhanced coal bed methane recovery, much less is known about this style of sequestration (IPCC 2005).

For these three sequestration classes, expected CO_2 storage mechanisms are reasonably well defined and understood (Figure 3). CO_2 sequestration targets will require *physical barriers* preventing CO_2 migration to the surface. These barriers will commonly be impermeable layers (e.g., shales, evaporites) overlying the sequestration target, although CO_2 may also be trapped dynamically by regional aquifer down-flow. This storage mechanism is highly or directly analogous to that of hydrocarbon trapping, natural gas storage, and natural CO_2 accumulations. Storage through physical trapping allows for very high fractions of CO_2 within pore volumes (80% or greater), and act immediately to limit vertical CO_2 migration. Physical trapping can be compromised or minimized by either a breach of the physical barrier (e.g., permeable fractures) or far-field migration away from an area lacking closure.

At the pore scale, *capillary forces* can immobilize a substantial fraction of a dispersed CO_2 bubble, commonly measured to be between 5 and 25% of the CO_2-bearing pore volume. The volume of CO_2 trapped as a residual phase is highly sensitive to pore geometry, and consequently is difficult to predict; however, standard techniques can measure residual phase trapping directly. If a CO_2 plume does migrate from the injection point, residual phase trapping will attenuate the plume and may eventually immobilize a substantial fraction. This mechanism acts over long time scales and CO_2 trapped this way may be considered permanently trapped because active injection is required to displace it.

Once in the pore volume, the CO_2 will *dissolve* into other pore fluids, including hydrocarbon species (oil and gas) or brines. Depending on the fluid composition and reservoir condition, this may occur rapidly (seconds to minutes) or over a period of tens to hundreds of years. The volume of CO_2 that may be dissolved into brines commonly ranges from 1–4% of the pore volume—this mechanism and these ranges served as the basis for many of the earliest estimates of geological storage capacity potential (e.g., Bergman and Winter 1995). Once dissolved, the CO_2–bearing brines are denser than the original brines, and so the strong buoyant forces of free-phase gas are replaced by small downward forces.

Over longer time scales (hundreds to thousands of years) the dissolved CO_2 may react with minerals in the rock volume to *dissolve or precipitate* new carbonate minerals. For the majority of the rock volume and major minerals, this process is slow, and may take hundreds to thousands of years to achieve substantial storage volumes (e.g., Wilson and Monea 2004). However, recent experiments demonstrated that a small fraction of the mineral volume has rapid kinetics that may dissolve and precipitate on the time scale of seconds to hours (Knauss et al. 2005b). Subsurface microbial activity might also accelerate mineralization or dissolution kinetics; additional research

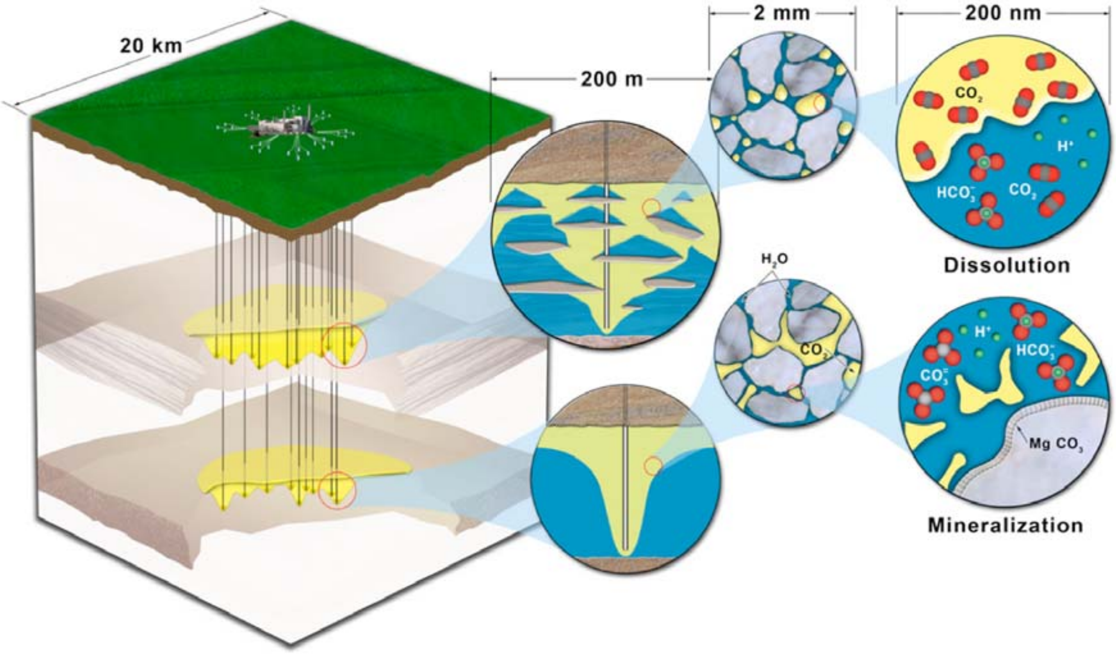

Figure 3. Schematic diagram of large injection at 10 years time illustrating the main storage mechanisms. All CO_2 plumes (yellow) are trapped beneath impermeable shales (not shown). The upper unit is heterogeneous with a low net percent usable porosity, whereas the lower unit is homogeneous. Central insets show CO_2 as a mobile phase (lower) and as a trapped residual phase (upper). Right insets show CO_2 dissolution (upper) and CO_2 mineralization (lower). After MIT (2007).

in this area is needed to evaluate the potential impact that this process might have. Precipitation of carbonate minerals permanently binds CO_2 in the subsurface; dissolution of minerals generally neutralizes carbonic acid species and increases local pH, buffering the solutions and trapping CO_2 as an ionic species (usually bicarbonate) in the pore volume. Substantial mineral dissolution could lead to deterioration in the integrity of the cap-rocks that prevent migration of CO_2.

Last, in the case of organic mineral frameworks such as in coals or organic shales, the CO_2 will physically *adsorb* onto the rock surface. This displaces other gases (e.g., methane, nitrogen) within the coal. The amount of CO_2 adsorbed onto organic surfaces is a function of the kerogen type, maturation, gas saturation, and pressure-temperature conditions. Storage volume estimates are commonly made through adsorption isotherm experiments. This trapping mechanism is also considered permanent, as active pumping and decompression of these beds is necessary to desorb CO_2 from the coal. Although substantial work remains to characterize and quantify these mechanisms, today's level of understanding can be used to develop estimates of the percentage of CO_2 that can be stored over some period of time. Confidence in these estimates is bolstered by studies of hydrocarbon systems, natural gas storage operations, hazardous waste injection, and CO_2-enhanced oil recovery. In the case of enhanced oil recovery, CO_2 has been injected underground for over 30 years. Although there are examples of CO_2 wellbore blowouts, there appear to be few cases of catastrophic or long-term leakage. Finally, the range of length and time scales on which trapping mechanisms act suggests that over time the system may become more effective at sequestering CO_2 (Figure 4).

An important source of geological information on key processes and long-term fate are studies of naturally occurring CO_2 accumulations world-wide. These including the CO_2-bearing domes of the central Rocky Mountains, high CO_2 gas fields, and the carbo-gaseous provinces of Europe

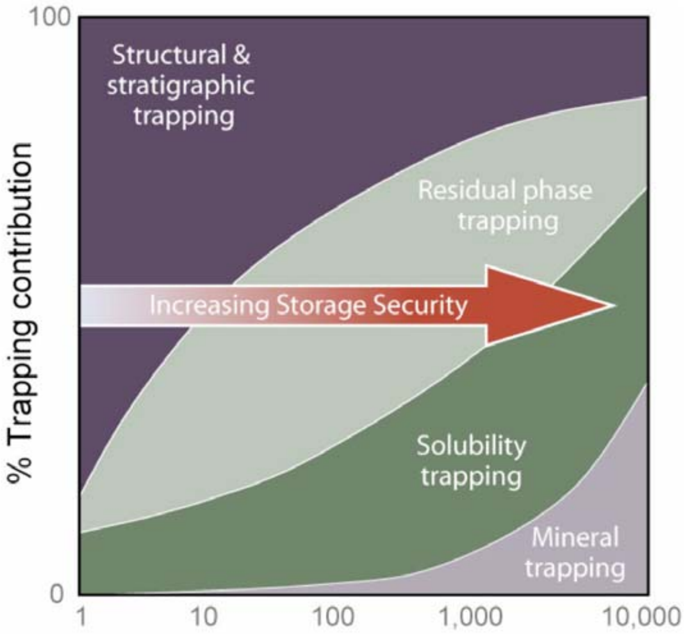

Figure 4. Multiple trapping mechanisms of GCS. Note that over time the physical processes of residual trapping and chemical processes of solubility and mineral trapping increase in importance and sureness. After Benson and Cook (2005)

and Australia (Allis et al. 2001; Czernichowski-Lauriol et al. 2002; Watson et al. 2004). In these regions, accumulations have held large volumes of CO_2 for tens of millions of years. These systems show evidence of CO_2 leaks through fault networks, natural CO_2 springs, and evidence of fossil leakage (e.g., Shipton et al. 2005) but apparent cap-rock fractures have been sealed through mineral precipitation and porosity reduction (Wilson and Monea 2004). Ultimately, these are either time-integrated or steady-state systems, and as such, information concerning the physical and chemical transients related to CO_2 storage can only be inferred from these systems.

Large uncertainties remain in the behavior of coal exposed to CO_2. Many experiments have produced coal adsorption isotherms, which underlie estimates of enhanced coal bed methane potential. However, most experiments have used powdered coals instead of continuous plugs, and have only preliminarily characterized the physical and chemical response to gas exchange. For example, CO_2 adsorption causes coals to swell, which in turn reduces permeability within cleats (coal fractures) and micropores (e.g., Reeves et al. 2003). This in turn affects total injectivity, capacity, and economic potential. Some workers also theorize or observe structural changes in the coal matrix, plasticization, which reduces transmissivity, and adsorption (e.g., Larsen 2004). These uncertainties present challenges to operations, prediction, and simulation of coal-CO_2 systems.

Current evaluations for risk estimation must be based on present understanding of trapping mechanisms through experimentation, analog analysis, and simulation. Specifically, it is estimated that more than 99.9% of injected CO_2 can be reliably stored over 100 years, and it is likely that 99% of CO_2 can be reliably stored for 1000 years (Benson and Cook 2005). While these estimates are predicated on the assumption of careful siting and due diligence before injection, it reflects the view that the crust contains sites that are generally well configured to store CO_2 effectively.

Other potential geological target classes have been proposed and discussed by various workers. These include oil shales, flood basalts, and salt domes (Figure 2). They will require substantial scientific inquiry and verification before commercial deployment because the storage mechanisms are less well tested and understood and there is much less commercial technology or experience for the tasks of simulation, monitoring, verification, and risk assessment (see below).

Monitoring and verification (M&V)

Once injection begins, a program for monitoring and verification of CO_2 distributions will be required. Scientific objectives in the short term will require such monitoring to understand trapping mechanisms, validate previous simulations and their predictions, and to discover new and important local features, events and processes. Longer term monitoring and verification will serve additional technical, regulatory, and economic needs:

- Provide constraints for probabilistic risk assessments
- Manage the injection process
- Delineate and identify leakage risk and surface escape pathways
- Provide early warnings of failure near the wellbore or above the reservoir
- Provide assurances to insurers and investors in geological carbon sequestration operations
- Verify storage for accounting and crediting

Monitoring and verification studies are thus a chief focus of many applied research efforts. The US Department of Energy has defined M&V technology development, testing, and deployment as a key element to their technology roadmap, and one new European Union program (CO2ReMoVe) has allocated €20 million for monitoring and verification. The International Energy Agency has established an M&V working group aimed at technology transfer between large projects and new technology developments. Because research and demonstration projects are attempting to establish the scientific basis for geological sequestration, they will require more involved M&V systems than future commercial projects.

Monitoring and verification must detect and track CO_2 in the deep subsurface near injection targets, in the shallow subsurface, and above ground. Some form of M&V will be required at commercial sites, but the extent of monitoring required by regulators, operators, or financiers remains uncertain.

Tools and approaches

A number of methods to monitor CO_2 near the reservoir and the near-surface have been proposed, deployed, tested, and validated to varying degrees. Perhaps surprisingly in the context of these and other research efforts, there has been little discussion of what are the most important parameters to measure and in what context (research/pilot *vs.* commercial). Rather, the literature has focused on the current ensemble of tools and their costs. This discussion is limited to a small set of the broad and expanding list of possible M&V tools and approaches.

Time-lapse (4D) reflection seismic surveys: 4D seismic has emerged as the standard for comparison, with 4D surveys deployed at Sleipner, Weyburn and likely to be deployed at In Salah (e.g., Arts et al. 2004). This technology excels at delineating the boundaries of a free-phase CO_2 plume, and can detect small saturations of conjoined free-phase bubbles that might be an indicator of leakage. Results from these 4D-seismic surveys are part of the grounds for belief in the ability to monitor the long-term effectiveness of geological sequestration.

Other geophysical methods: Several other approaches have been tried with varying degrees of success. These include other acoustic methods (vertical seismic profiling and cross-well seismic), potential field measurements (microgravity), electrical surveys (electrical resistance tomography and induced electromagnetic induction), ground deformation (tilt-meter and interferometric synthetic aperture radar) and passive teleseismic surveys (microseismic) (e.g., Daley and Korneev 2006). These have not yielded outstanding results, but neither have they made large-scale efforts to design highly tailored systems focused on specific sites.

Tracers: A number of tracers have been proposed for co-injection with CO_2. These include perfluorocarbons, SF_6, noble gases, and stable isotopes (Phelps et al. 2006). Limited field deployments suggest that tracers could serve to identify both cross-well migration and small leakage volumes; however, none has been validated adequately for those unique purposes.

Surface surveys: The most comprehensively tested surface detection method is soil-gas surveys, which have been deployed at the Weyburn and Rangely fields as well as the Frio pilot. Airborne and truck-mounted aeromagnetic surveys have proved to have value in identifying lost or mislocated boreholes that may become leakage pathways, but they do not identify CO_2 leakage sites. Other surface methods include airborne hyperspectral surveys, LIDAR-based detection, and atmospheric eddy-covariance towers (e.g., Benson and Cook 2005; Miles et al. 2005).

Integration: Many workers have expressed a need to formally integrate monitoring approaches, particularly as a means of improving accuracy or reducing operational cost. This was identified at Weyburn through formal gap analysis as a key need. A joint inversion of cross-well electromagnetic and seismic monitoring has been attempted at the Frio brine pilot. Multi-variate inversion had successfully been tested at a CO_2-enhanced oil recovery project using stochastic inversion and integration (Ramirez et al. 2006), but no other integration attempts have been made at a CO_2 storage project.

Coal Sequestration Monitoring: Knowledge on the monitoring of geological carbon sequestration in coal seams and enhanced coal bed methane recovery is extremely limited. Most of the monitoring technologies proposed operations have not been tested in coal injections. The Allison project, a commercial enhanced coal be methane program in New Mexico, did not employ geophysical monitoring. Even conventional coal bed methane operations commonly do not employ much geophysical or geochemical monitoring.

Hazards and risks

Since supercritical CO_2 is buoyant, it will seek the earth's surface. Therefore, despite the fact that many deep geological formations may be well configured for geological carbon sequestration, free-phase CO_2 carries the possibility of leakage, which would negate some of the benefits of sequestration (Herzog et al. 2003) and introduce elements of risk. Importantly, CO_2 leakage risk will not be uniform across all sites, thus CO_2 storage sites will have to demonstrate minimal risk potential in their site characterization plans (Bradshaw et al. 2004). A small percentage of sites might end up having significant leakage rates during injection, which will require mitigation efforts. Based on analogous experience in CO_2 injection such as acid gas disposal and enhanced oil recovery, these risks appear to be less than those of current oil and gas operations (Benson and Cook 2005).

Table 4: Carbon capture and storage-related earth and atmospheric hazards and primary component risk elements

Atmospheric release hazards	**Groundwater degradation hazard**	**Crustal deformation hazards**
Well leakage	Well leakage	Well failure
Fault leakage	Fault leakage	Fault slip/leakage
Caprock leakage	Caprock leakage	Caprock failure
Pipeline/operational leakage		
	Water displacement and far-field saline intrusion	Induced seismicity
		Subsidence/tilt

The list of potential earth and atmospheric hazards that present substantial risk to carbon capture and storage operations is limited (Table 4). These hazards can be grouped by area of consequence—atmospheric release, groundwater contamination, and crustal deformation—and related to features, events and processes that present key elements of those hazards (e.g., well-bores, faults, chemical leaching, induced seismicity). Biogeochemical effects may also impact the long-term stability of caprocks. These hazards present a concern only if CO_2 leaks in sufficient flux and reaches sufficient concentrations to threaten health, safety, environment, or economics.

CURRENT LARGE PROJECTS

Today there are three well-established large-scale injection projects with an ambitious scientific program that includes monitoring and verification (Table 5): Sleipner in Norway (Arts et al. 2004), Weyburn in Canada (Wilson and Monea 2004), and In Salah in Algeria (Riddiford et al. 2004). Each project has injected CO_2 at the rate of ~1 MM tons/y (~280,000 t C/y). Each project has had a substantial supporting science program or anticipates one. Substantial information can be found on each project in the literature, and summaries can be found in Benson and Cook (2005).

These projects have sampled a wide array of geology (Table 5) with varying trapping mechanisms, injection depths, reservoir types, and injectivity. Each of these projects appears to have ample injectivity and capacity for success, and none has detected CO_2 leakage of any significance.

The monitoring and verification program at each site varies substantially. Weyburn has supported the most comprehensive program, including multi-channel time-lapse seismic surveys, quarterly geochemical sampling, soil-gas surveys, and limited microseismic monitoring. In contrast, Sleipner relies almost exclusively on time-lapse seismic surveys, and all other planned monitoring programs have not yet been implemented. While this presents an opportunity for scientific discovery, many technical issues remain unsettled due to the limited investigations to date.

A significant number of large-scale injection projects are expected to begin within the next five years, which will provide dynamic new opportunities to design and implement and test new monitoring strategies (Table 5). These projects will sample a substantial range of geology and on a global basis will be able to provide the opportunity to learn about the scientific, technical, and operational concerns.

The injection tests proposed for Phase III of the Department of Energy's Regional Carbon Sequestration Partnership program have not yet been selected or sited. The program will support up to seven large injection projects of between 100,000–1,000,000 tons CO_2/y, with one being investigated in each partnership region. Although the geology and project consideration are still under review, the program is likely to sample a wide range of geological configurations.

In addition to these targeted sequestration projects, there are many industrial applications that have injected large volumes of CO_2 into the subsurface. Enhanced oil recovery operations in West Texas, New Mexico, Colorado, Wyoming, Oklahoma, Mississippi, Trinidad, Canada, and Turkey have individual injection programs as large as 3 MM t CO_2/y (~820,000 t C/y) and cumulative anthropogenic emission injections of ~10 MM t CO_2/y (2.7 MM t C/y) (Kuuskraa et

Table 5: Current and pending large CO_2 injection projects

Site	Location	Reservoir class	Reservoir type	Permeability	Seal type	Start date*
Sleipner	Norway	Offshore Saline Fm.	Deep-water Sandstone	V. high	Thick shale	1996
Weyburn	Canada	Onshore EOR	Ramp carbonate	Moderate	Evaporate	2000
In Salah	Algeria	Onshore Sandstone	Fluvial/tidal sandstone	Low	Thick shale	2004
FutureGen	US	Onshore Saline Fm.	Fluvial sandstone or shelf carbonate	Moderate	Thick shales or evaporites	2012
ZeroGen	Australia	Onshore EOR/Saline	Fluvial/deltaic sandstone	Low-moderate	Shale	2011
Snohvit	Norway	Offshore Saline Fm.	Fluvial sandstone	Moderate	Shale/evap.	2007
DF1/Miller	UK	Offshore EOR	Deep-water sandstone	Moderate - high	Thick shale	2010
DF2/Carson	US	Onshore EOR	Deep-water sandstone	Moderate - high	Thick shale	2011
Latrobe Valley/ Monash	Australia	Offshore EOR/Saline	Fluvial/deltaic sandstone	High	Thin and thick shales	2011
Gorgon	Australia	Offshore Saline Fm	Deep-water sandstone	Moderate	Thick shales	2008
Hauten/ Draugen	Norway	Onshore/ Offshore Saline Fm.	Deep-water sandstone	High – V. high	Thick shales	2010
Phase III Regional Partnerships	US	Varying, but mostly Saline Fm.	Varying	Varying	Varying	2011

** = date of first injection or planned first injection of* CO_2

al., 2006). Several of these operations have injected continuously for over 30 years. Similarly, although of smaller volume, acid gas disposal operations have also injected large volumes of CO_2 and H_2S for over 10 years (Bachu and Haug 2005). In all cases, there have been no reported cases of apparent or detected leakage of CO_2 from deep formations.

Given the limited deployment of geological carbon sequestration, challenges remain in generalizing current experience to large system-level effects. For example, the large volumes of injection for a conventional carbon capture and storage plant would displace a substantial water volume. This could become a major constraint for a small region or single disposal aquifer system with many injection efforts. Displaced brines could potentially intrude into fresh water aquifers up-dip or along high-transmissivity pathways. Operation of hundreds or even thousands of wells in a larger region could result in unanticipated pressure interference and geomechanical concerns. Injection and production of large volumes of fluids into and out of producing geothermal and oil and gas reservoirs has resulted in induced seismicity (Phillips et al. 2002). Although the risks of substantial induced seismicity appear small (e.g., Raleigh et al. 1976), similar effects are possible for large-scale CO_2 injection. Studies around a regional deployment have not yet provided answers to these and similar questions.

TECHNOLOGY AND APPLIED RESEARCH AND DESIGN PERSPECTIVES AND NEEDS

Although much commercial oil-related technology exists for geological carbon sequestration pilot efforts, there remain important scientific and technical challenges to large-scale commercial deployment. These challenges can be summarized as being able to understand the complex geology of any given site and how each of the geological variables will affect the performance of a site. Sequestration of greenhouse gases from the atmosphere for substantial periods of time is required, but possibly perfect isolation or containment is not required. Sites must be able to accept large volumes of CO_2 over many decades and then hold the overwhelming majority of that volume for many decades, possibly centuries or longer. They must do so without substantial operational risk while maintaining health, safety, and environmental standards.

The following set of technical needs flows from the goals of effective geological storage (Figure 5). The research and development needs are derived from the specific technical and scientific challenges associated with the central elements of site characterization, selection, operation, and monitoring.

Site characterization

The first stage in a project life cycle (Figure 5) is site characterization. Siting viable geological storage projects requires substantial geological characterization prior to project deployment. The detail, degree of quantification, and precision of characterization will be driven by regulatory, legal and insurance requirements, and cost effectiveness. These needs and goals will change as the project proceeds through different stages of operation and regulation. Initial site characterization will focus on locations with low overall risk and high chance of success, short- and long-term. It will provide data for planning, including safe and successful operations, deployment of monitoring and verification tools, and risk quantification and management.

While many possible goals and terms may be pursued in site characterization, it is difficult to imagine the success of a large-scale injection project without knowledge of three parameters. These are *injectivity*, *capacity*, and *effectiveness* (Friedmann 2006). In general terms, injectivity and capacity may be estimated by conventional means, such as special core analysis, regional and local structural and stratigraphic mapping, and simple multi-phase fluid flow simulations. However, there are few explicit standard measures of effectiveness. Ultimately, characterizations must rely on estimates of geomechanical integrity, hydrodynamic stability, and seal continuity for the rock system, fault system, and well system (e.g., Hovorka et al. 2006). Some aspects of effectiveness characterization (e.g., continuity and thickness of cap-rock, presence of multiple seals, structural closure) may be easily defined with limited suites of data and analysis. Other

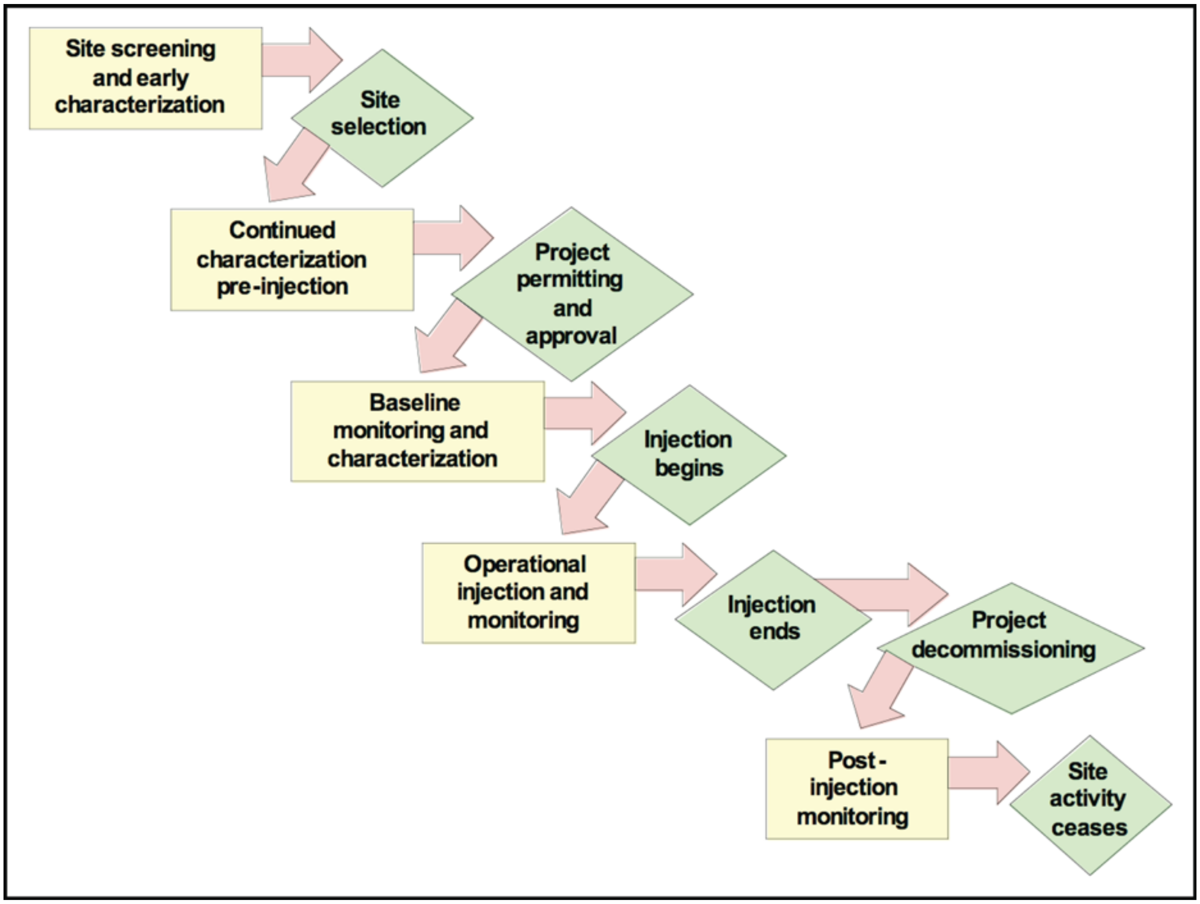

Figure 5. Hypothetical operational life cycle for GCS project (Friedmann 2007).

aspects (e.g., Mohr failure criteria, capillary entry pressure) are straightforward but require basic measurements of relevant rock types (Streit and Hillis 2004). Still other aspects require more significant geological sophistication (e.g., fault reactivation potential, fault-seal analysis, *in situ* stress tensor characterization; Wiprut and Zoback 2002; Gibson-Poole et al. 2005; Chiaramonte et al. 2006). Some elements of the analysis are extremely difficult to define deterministically (e.g., well behavior in 50–100 years) and cannot be unambiguously circumscribed in any reasonable operational context.

Given this complexity, it is not broadly accepted today what terms constitute effective storage. The FutureGen project's request for proposals (FutureGen Alliance 2006) laid out a set of minimum criteria for acceptance. These criteria are based on expert opinion, laboratory experimentation, analog studies, and simulations. However, there is no empirical data set from multiple geological carbon sequestration deployments that provides a standard for characterization of site effectiveness.

Co-contaminant storage

To date, most studies have assumed pure CO_2 and focused on pure CO_2-rock-brine systems. Very little work has focused on gas streams with variable concentrations of other gases, in particular SO_x, NO_x, and H_2S. However, it is likely that all existing carbon and separation technology pathways will produce storage gases with some of these components in varying degrees. Even small volumes (~1%) of these co-contaminant gases have the potential to alter the chemical response of a gas-brine-rock system (e.g., Knauss et al. 2005a). Understanding purity requirements will save capital and operating expenses. A focused study of laboratory reactive chemistry and numerical simulations is needed to provide insight into how these gases might affect storage effectiveness and additional types of site characterization.

M&V design and integration

Given the natural variation in storage site geology and the uncertain regulatory requirements *a priori* today, it is difficult to predict the requirements for standard monitoring and verification systems. Many geophysical and geochemical methods are sufficiently well understood for them to be used to make reasonable performance predictions at candidate storage sites (e.g., Benson et al. 2004). Testing which of these approaches will be the most valuable for a given geological environment remains to be determined. It will require that multiple approaches to testing be compared robustly in terms of performance and cost, and validated in the field.

Multivariate hydrogeologic and geophysical integration and inversion provides one approach to this problem. Unfortunately, there are very few examples from industry or CO_2 storage experiments where multiple data sets have been integrated robustly. Often these techniques involve geostatistical characterization (e.g., Goovaerts 1997; Pawar et al. 2003) that can require large data volumes and produce mixed results. Multivariate inversion is a more difficult problem, with very few successful demonstrations (e.g., Hoversten et al. 2003; Ramirez et al. 2006). Ultimately, addressing this technical need will require that many comparable data sets are collected simultaneously and inverted in a common platform or framework.

Risk assessment methodology and quantitative basis

Several frameworks have been proposed for geological carbon sequestration risk assessment (e.g., Stenhouse et al. 2006; Saripalli et al. 2003). The most comprehensive published risk assessment work to date comes from Weyburn (Wilson and Monea 2004), which used a combination of long-term simulation with analysis of features, events and processes. A 5000 year interval was selected, and the risk metric was CO_2 returned to the biosphere over that time interval. This choice of risk end state and metric was ultimately not technically based.

While simulations and studies generally show that risk should decrease post injection (Figure 6), there is little quantification of what the magnitude, rate, or trajectory of risk reduction is. Ultimately, such a characterization will evolve from probabilistic risk assessments methodology and a larger empirical data base. Until then, a scientific basis is needed to choose risk end states, select metrics for risk assessment, and develop methodologies that can be regularly applied to conventional data sets.

Wellbore integrity

The many wells penetrating oil reservoirs represent a risk of both gradual and catastrophic leakage of CO_2 to the atmosphere (e.g., Gasda et al. 2004; Celia et al. 2006). For reservoirs older than 30 or 40 years, locations of old capped wells are a major concern. Incorrectly constructed or abandoned wells increase potential for substantial CO_2 leakage due to elevated likelihood of poor cement, advanced corrosion, or ineffective plugging (Ide et al. 2006). Groundwater can also be affected by CO_2 leaking from its storage site into shallower aquifers without any surface

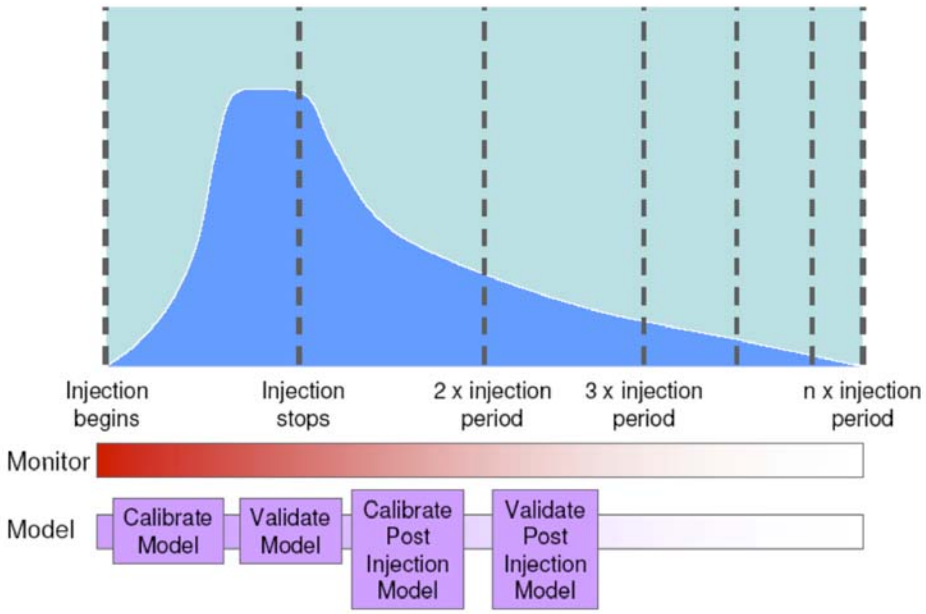

Figure 6. Conceptual risk profile of a geological carbon sequestration site. Vertical axis is leakage risk. Overall, risk decreases dramatically post-injection and then more gradually. Courtesy of S. Benson 2006.

manifestation. In addition, rapid mineral dissolution and release of metals and volatile organic compounds may result from such leakage (e.g., Kharaka et al. 2006). Cement carbonation around wellbores can change physical and rheological properties (e.g., Carey et al. 2006). Aging, corrosion, and shifting of completion materials can cause leaks (IEA GHG 2006), and mechanical well failure by shear on bedding and fault planes presents a real hazard to long-term operations and storage effectiveness (Bruno 2001).

Wells in CO_2-enhanced oil recovery areas do not appear to have high failure rates, and many technologies exist to plug and mitigate leakage even from major well failures (e.g., Lynch et al. 1985). However, “sweet” corrosion (no sulfur) and an increased incidence of blowouts in CO_2-enhanced oil recovery areas have grown as concerns over the last 10 years (Skinner 2003), although there are proactive operational measures to prevent and mitigate CO_2 blowouts. In general, the reported events generally have not received scientific study, and it is possible that processes with long time-scale effects (e.g., well-bore corrosion) have not yet reached key thresholds. Major issues that will need to be considered are location and construction of existing wells, methods used to seal old wells, availability of methods to seal surface leaks, and the atmospheric risk associated with releases as a function of location and weather conditions (e.g., Bogen et al. 2006).

Substantial uncertainty remains around the nature of the long-term wellbore environment at depth, the presence and stability of fractures within formations near wells, the condition and distribution of cement around well casings, and the static and dynamic relationships between rock, casing, cement, and plugs (IEA GHG 2006). Key processes remain poorly parameterized, such as the degree and nature of formation damage in the wellbore environment, the bonding process, and permeability dynamics in CO_2-rock-brine-casing-cement systems.

Protocols and standards

Understanding risk requires understanding the controlling parameters in the geological environment elected for the sequestration sites. The risk elements described so far for earth and atmospheric hazards suggest the need to systematically rank, quantify, and respond to those potential hazards. **Protocols** will be developed to inform operators and regulators on preparing and opening a site, and will serve as the basis for operational standards.

Operators will also have to establish a protocol for decommissioning or decertification of any site, the last stage in the geological carbon sequestration operational life cycle (Figure 5). This involves the completion of storage injection according to all regulatory requirements and protocols such that the site operator can close and properly abandon the site. This protocol is likely to involve a post-injection monitoring requirement of uncertain length after which all site operations cease. Ambiguities remain about the process of site decertification that revolves around these unanswered technical questions, and includes mechanisms for termination or transfer of liability (MIT 2007).

Planning for operation geological carbon sequestration will be based on scientific studies (Wilson et al. 2007 in press) from the large projects discussed above; however, few of these have planned, gathered, or integrated the data with a vision to underpinning practices and protocols.

ADDITIONAL CROSS-CUTTING NEEDS

In addition to research needed to develop and quantify central elements to an operational flow, additional cross-cutting areas have applied research and development needs.

Accurate characterization of rock volumes

In many cases (i.e., saline formation targets), available well and geophysical data is likely to be very limited. This creates a substantial challenge in the accurate characterization of many important aspects of a rock volume. Some of the more fundamental include:

- Presence/distribution of target formation
- Formation thickness
- Formation composition over the area of significance to injection
- Formation porosity and permeability
- Formation connectivity and heterogeneity
- Distribution of small structures and fracture networks

To develop reasonable and hopefully accurate estimates of injectivity, capacity, and effectiveness, potential operators will rely on geological concepts (e.g., facies models, sequence stratigraphy) to constrain subsurface characterization and simulations. In some cases, transfer functions may be used to interpret geophysical data or phenomena in terms of rock properties, but this is often non-unique and difficult to employ. Measures are needed to clarify what constitutes sufficient accuracy at different stages of the project life cycle.

Definition and management of uncertainty

Uncertainties in rock properties can dramatically affect the magnitude, sign, and detailed behavior of subsurface system responses. In most contexts, including in many commercial oil and gas applications, this uncertainty is neither characterized initially nor propagated through successive elements of work flows because it is not critical to current operations. New data commonly are not integrated with prior data in a fashion as to reduce or manage the initial uncertainty. Various approaches, including stochastic inversion (Ramirez et al. 2005) provide tools and approaches to address this task; however, they require large computational resources and expert capability, and have not been broadly applied to common subsurface operations. Improved technology development and deployment in uncertainty rendering and management would dramatically improve the accuracy of site-specific work and the ability of operators to select monitoring and characterization tools that would reduce uncertainty.

Fracture systems and geomechanics

Fracture networks may be critical components to geological carbon sequestration targets for several reasons:

1. They can play a substantial, sometimes dominant, role in the hydrological flow field
2. They can represent potential migration fast paths through cap-rocks and along fault networks
3. Their transmissivity may be dynamic, responding to both pressure transients and chemical disequilibria

The response of existing fracture networks to pressure and stress transients are of special importance in saline formations where the pre-injection pressure is likely to be hydrostatic. In addition, overpressures generated by the CO_2 injections may generate new local fracture systems with different properties. In unmineable coal units, the rock volumes swell in the presence of CO_2, closing fractures (cleats) and dramatically reducing injectivity. Fracture orientation and density have been successfully inferred from observations of seismic anisotropy from shear-wave splitting (e.g., Li 1997), but seismic characterization of fracture permeability remains a key research objective for the oil and gas industry. In rendering fracture networks and their process response, substantial uncertainties remain in fracture orientation, length, transmissivity, and response to stress.

Mineral chemical kinetics

Mineral carbonation has been regularly observed in natural analog systems, and laboratory experiments provide thermodynamic and kinetic constraints for some key minerals or mineral assemblages. These constraints greatly impact the accuracy and precision of complex reservoir simulations (e.g., Johnson et al. 2005). At least three important technical needs remain:

1. A more comprehensive suite of kinetic and equation-of-state data sets, particularly aimed at the small fraction of the rock volume with rapid reaction kinetics (e.g., metal oxides and hydroxides; Kharaka et al. 2006)
2. An improved theoretical and experimental basis for determining the reactive surface area within a rock
3. The effects of trace (co-contaminant) gases on phase equilibria and kinetics

Simulation and modeling

Short- and long-term modeling is central to many aspects of planning, operational control, analysis, risk assessment, and site decommissioning. At present, simulation and modeling are the primary tools for providing qualitative or quantitative assessments of the long-term fate of CO_2

in geological formations. Many applications exist that serve investigators studying geological carbon sequestration, and preliminary code inter-comparisons have produced generally similar results (Pruess et al. 2004). Several codes now attempt to integrate hydrodynamic, geochemical, and geomechanical processes (e.g., Johnson et al. 2005; Rutqvist et al. 2006). It is widely considered that current simulation capabilities cannot render simultaneously all of the key processes and heterogeneities at relevant length and temporal scales (MIT 2007).

Some of the simulation limitations are due to limitations in key inputs both throughout a formation, and in local areas within formations (e.g., uncertainties in reservoir properties, chemical kinetics, and mechanical response). These research needs are identified above. Other concerns include:

1. Quantification and propagation of reservoir parameter uncertainties
2. Incorporation of low-probability, high impact events
3. Comprehensive system level simulation, e.g., multiple simultaneous injections with both near-field and far-field effects
4. Rapid incorporation of monitoring data and other deterministic information into sequential models

Mathematical and computational challenges are substantial, since geological carbon sequestration involves multi-scale, multi-phase, and multi-temporal systems involving coupled flow, reactive transport, and geomechanical processes. Ultimately, validation of complex reactive transport models will play a critical role in both scientific verification and public acceptance of carbon capture and storage technology.

Mitigation and active reservoir management

Very little research has focused on effective mitigation options for problems should they appear. Although operators now have a handful of mitigation options (Benson and Cook 2005), they may face new challenges requiring novel mitigation approaches, techniques, and materials (DOE 2006b). Some of these concerns and risks can potentially be mitigated through active reservoir management, e.g., circulating brines *in situ* (Keith et al. 2004) or depleting water volumes during injection. There is substantial room to investigate novel physical, chemical, biological, or reservoir engineering approaches to risk reduction and hazard management.

TECHNOLOGY AND APPLIED RESEARCH AND DESIGN NEEDS FOR NUCLEAR WASTE GEOLOGIC DISPOSAL

INTRODUCTION

Nuclear fission is a carbon-free source for the production of electrical energy. In addition to potentially meeting a significant fraction of the world energy demand, nuclear energy can be a critical source of energy for the production of transportation fuels (hydrogen and synthetic fuels) and desalinated water. For nuclear energy to be more generally acceptable as a long-term energy solution, several requirements must be met. These include widely accepted safety and efficiency standards, proliferation resistance, sound nuclear materials management, and minimal environmental impacts (greenhouse gas emissions and nuclear waste products).

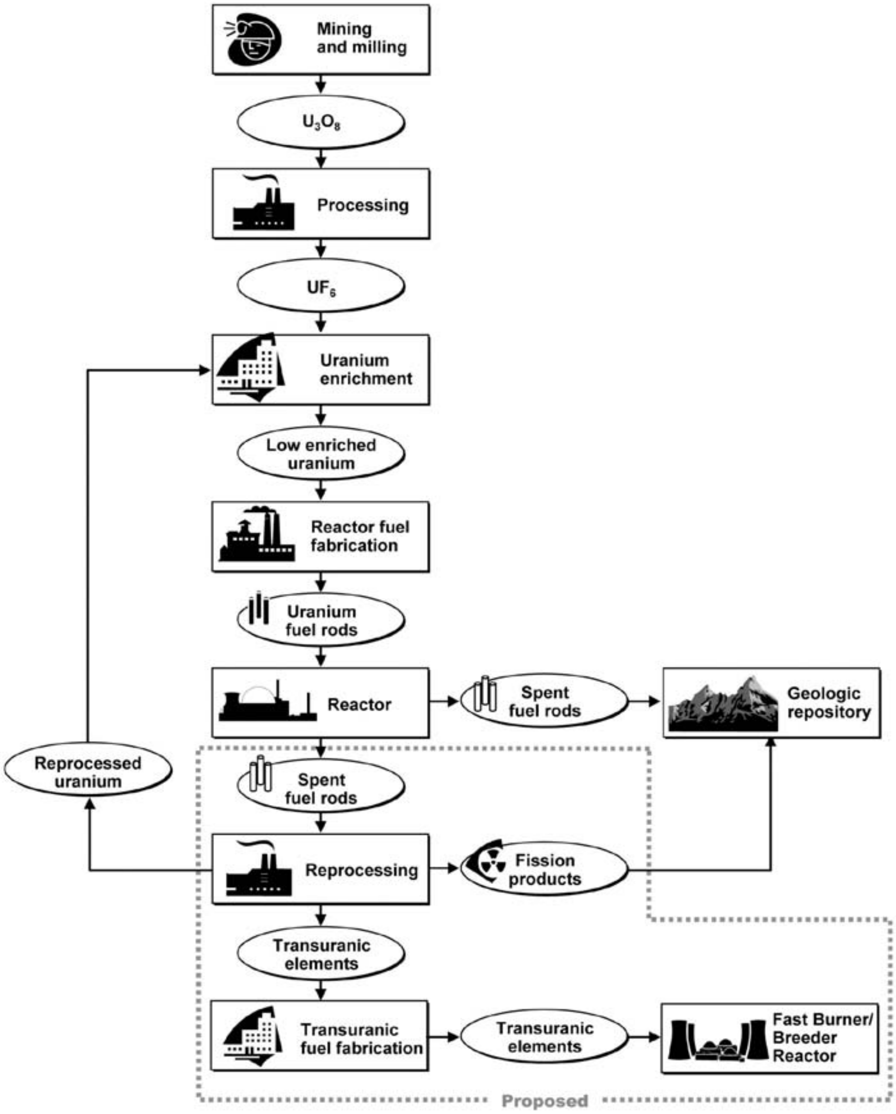

Figure 7. The existing U.S. nuclear fuel cycle. Also shown are proposed modifications involving fuel reprocessing to the back end of the fuel cycle, involving fuel reprocessing (from DOE 2006a).

The nuclear fuel cycle is a key concept when discussing a sustainable future for nuclear energy and nuclear waste management (see Figure 7). To the first order, there are two approaches to the nuclear fuel cycle. An open (or once-through) fuel cycle, as currently planned by the United States, involves simply disposing of spent nuclear fuel as waste within a geologic repository. New nuclear fuel is only derived from mined uranium. In contrast, a closed (or recycle) fuel cycle, as currently planned by other countries (including France, Russia, and Japan), involves reprocessing spent nuclear fuel by separating useable actinides to put into new fuel rods and disposing of other elements that are inappropriate for nuclear fuel in a geologic repository.

It is important to note that regardless of the fuel cycle approach, a geologic repository is required to dispose of long-lived radioactive material. The constraints for a repository design are primarily the type of waste form(s) to be disposed of and the inventory of radionuclides they contain. Recycling spent nuclear fuel can prove beneficial in terms of managing nuclear waste by reducing the quantity of waste needing to be isolated. A given repository size can thereby accommodate waste that has produced more energy per ton of original nuclear material.

The total waste capacity of any geologic repository will be constrained by many factors such as available physical space, waste volume, waste thermal density, and most importantly, post-closure repository performance requirements (effective dose to the public). In particular, significant thermal benefits could potentially be achieved through separation/recovery of actinides and key fission products from spent nuclear fuel. Reduced thermal densities may provide flexibility in the ability to optimize the design of subsurface facilities while meeting thermal criteria and goals.

Removing the actinides and key fission products from the waste may also potentially reduce long-term environmental risks. The benefits of an advanced nuclear fuel cycle that includes reprocessing of spent nuclear fuel depend on the density with which waste can be loaded into new waste forms, and on the repository design and its ability to accept all waste forms.

There is scientific consensus that the disposal of spent nuclear fuel and high-level radioactive waste in deep geologic formations is potentially safe and feasible (National Research Council 2001; International Atomic Energy Agency 2003), provided that sites are chosen and characterized well, and that the combination of engineered and natural barriers is designed appropriately. However, as illustrated by the history of decisions on radioactive waste disposal in the U.S., many issues still need to be resolved.

Although the U.S. has decided that it will sequester waste in volcanic formations in an arid region with a thick unsaturated zone, other possibilities were previously entertained. Salt formations were originally considered to be the most promising hosts for a repository. Such formations would theoretically prevent transport of liquid and would become self-sealing in the event of fracturing. Another possibility considered was the thick basalt lava sequence in the Columbia Plateau region. Each geologic environment generates specific technical and scientific challenges, but there are many issues common to all.

The primary goal of waste management is to ensure that the health risks of exposure to radiation from spent nuclear fuel discharged from nuclear reactors and other high-level wastes over time remain below an acceptable level (Table 6). To meet this goal, most disposal strategies rely on a succession of multiple, robust safety barriers. This barrier system can be subdivided into engineered and natural components.

Table 6. EPA regulatory limits associated with geologic disposal of radioactive waste.

Radionuclide or type of radiation emitted	**EPA limit**
Combined Ra-226 and Ra-228	5 pCi/L
Gross α activity (including Ra-226, but excluding Ra and U)	15 pCi/L
Combined β- and photon-emitting radionuclides to the whole body or any organ, based on drinking 2 L/d from the representative volume	4 mrem/y

Table modified from DOE 2002a (Table 5-9).

NUCLEAR WASTE GEOLOGIC DISPOSAL SYSTEM

Geologic systems are considered suitable for radioactive waste disposal because of their stability over long time periods, their ability to physically and chemically isolate the waste canisters, their property to limit or significantly retard the release of radionuclides, and their relative inaccessibility, preventing unintentional or malevolent interventions (Long and Ewing 2004). For geologic repositories, the main scenario of possible pathways for radionuclides to reach the biosphere and expose humans to unacceptably high radiation doses is the transport by groundwater that contacts and corrodes waste containers, dissolves the waste form, and leaches the radionuclides into the water, where they migrate in dissolved or colloidal form towards locations where the contaminated groundwater is used as drinking water or for agricultural purposes. Other release and transport mechanisms (such as volcanism, earthquakes, erosion, meteors, and human intrusion) also need to be considered.

The discussion below provides a more detailed description of a geologic repository system (consisting of engineered and natural barriers), in many instances using the proposed Yucca Mountain repository as an example. The Yucca Mountain site is unique in that it is the only unsaturated zone site being considered worldwide for high-level waste disposal and has some unique engineered components (e.g., drip shield). A number of different disposal strategies are being considered in other countries with different geologic settings (e.g., Lidskog and Andersson 2002; Witherspoon and Bodvarsson 2006). The hydrologic and geologic environments associated with these potential geologic repository systems are summarized in Table 7.

Table 7. Potential geologic repository environments

Hydrologic Environment	Rock Type	Key Features	Countries considering this option
Unsaturated	Ash-flow tuff	Limited seepage, fluid flow predominantly in fractures, zeolitic units have high sorptivity, oxidizing environment	USA
Saturated	Crystalline rock	Low porosity and permeability, fluid flow predominantly in fractures, reducing environment	Canada, Finland, France, Germany Hungary, Russia, Sweden, S. Korea, Spain, Switzerland
	Clay	Low permeability, high sorptivity, reducing environment	Belgium, France, Germany, Hungary, Russia, Spain, Switzerland
	Salt	Low-permeability, self-sealing, reducing environment	Germany, USA*

The Waste Isolation Pilot Plant in the US began receiving transuranic waste in 1999. Data from Swift and Corbet 2000; Lidskog and Andersson 2002; and Witherspoon and Bodvarsson 2006.

For example, in Sweden, the proposed repository design (KBS-3 method) involves storage of spent nuclear fuel assemblies within copper canisters (Figure 8). The waste canisters would then be emplaced in vertical holes drilled into crystalline bedrock at depths of around 500 m. The holes are to be backfilled with bentonite clay to retard the transportation of radionuclides outside of the canisters (Lundqvist 2006). The disposal of radionuclides within the saturated zone will result in the ubiquitous presence of water, but will also ensure that the waste will reside in a reducing environment, which will significantly reduce the solubility of many radionuclides.

While the elements of the proposed Yucca Mountain repository design differ from those being considered in other countries, the engineered and natural components for the Yucca Mountain site and how they function together are still illustrative and provide the required context for the more general discussion of technology and applied R&D perspectives and needs. Much of the discussion below is taken from DOE (2002c), and the reader is referred to that report for much more detail. Information available in Witherspoon and Bodvarsson (2006) and on the web describing international high-level waste management sites illustrates the common themes and the different geologic, hydrologic, and geochemical settings being considered worldwide (e.g., unsaturated zone sites in tuff and saturated zone sites in granite, salt, or clay; see Table 7).

The barriers important to waste isolation are broadly characterized as engineered barriers and natural barriers associated with the geologic and hydrologic setting. The engineered barriers are designed specifically to complement the natural system in prolonging radionuclide isolation within the disposal system and limiting their potential release. Natural barriers would contribute to waste isolation by (1) limiting the amount of water entering emplacement drifts, and (2) limiting the transport of radionuclides through the natural system.

In addition, the natural system provides an environment that would contribute to the longevity of the engineered components (disposal canisters and waste forms). The components of the engineered system are designed to complement the natural barriers in isolating waste from the

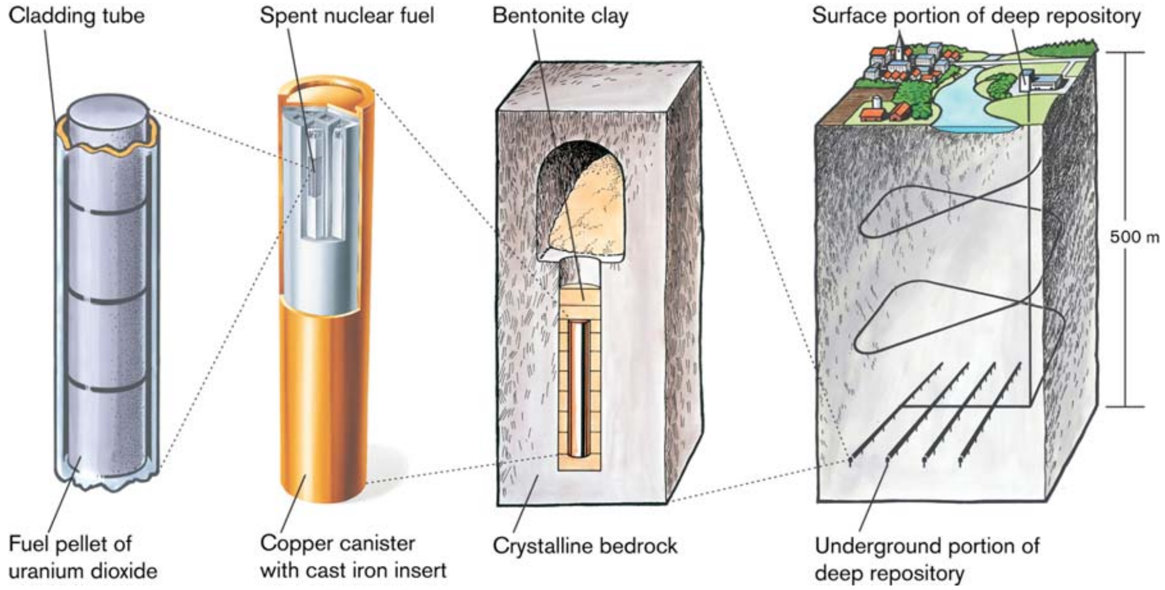

Figure 8. Schematic illustration of the Swedish concept for a deep geologic repository (Lundqvist 2006).

environment. A repository design includes, at a minimum, the waste package and the waste form. A variety of engineered barrier systems have been proposed (e.g., NEA 2003) to enhance long-term isolation of spent fuel and other high-level radioactive waste within geologic repositories (Table 8). Figure 9 depicts waste packages within an emplacement drift for the proposed Yucca Mountain repository design concept as an illustrative example. The engineered barriers would contribute to waste isolation by (1) using long-lived engineered components to keep water away from the waste forms, and (2) limiting release of radionuclides from the engineered barriers through components engineered for optimum performance in the expected geochemical environment. This requires a clear understanding of the chemical composition and behavior of the radioactive waste, the physical and chemical processes that would act on the repository system's barriers, and how the parts of the system would work together to isolate waste. Table 9 provides a summary of possible radionuclide inventories that might be represented within typical pressurized-water reactor and boiling-water reactor fuel assemblies. Figure 10 presents a summary of the interdependent processes that may affect the repository's ability to isolate waste, again using the proposed Yucca Mountain repository as an illustrative example.

Table 8. Proposed engineered barrier systems for different international programs

Country	Waste type	Waste matrix	Container / overpack	Buffer / Backfill	Other components
Belgium	HLW	Borosilicate glass	304 SS container, 316L SS overpack	Clay, bentonite, quartz sand, graphite mixture	Disposal tube, tunnel lining
	Spent fuel	UO_2	Supercontainer with carbon steel overpackage, concrete matrix, and outer SS cylinder		Concrete gallery lining
Canada	Spent fuel	UO_2	C steel inner container with Cu outer shell	Bentonite/sand buffer, clay or crushed rock backfill	Tunnel with shaft seals
Czech Republic	HLW	Glass	Steel	Bentonite buffer	Clay seals
	Spent fuel	UO_2			
Finland	Spent fuel	UO_2	Cu-iron	Bentonite buffer, compacted crushed rock and bentonite backfill	Bentonite and concrete plugs
France	HLW	Borosilicate glass	SS container, steel overpack	Optional bentonite buffer	Bentonite seals
	Spent fuel	UO_2 and MOX	SS with metal insert	Bentonite buffer with metal disposal tube	
Japan	HLW	Glass	C steel overpack	Bentonite-sand mixture	Tunnel sealing plugs and grout
Korea	Spent fuel	UO_2	C steel inside, Cu or SS outer container	Bentonite or bentonite-sand mixture	
Spain	Spent fuel	UO_2	C steel	Bentonite	Concrete and bentonite seals
Sweden	Spent fuel	UO_2	Cu-iron	Bentonite	Tunnel backfill
Switzerland	HLW	Glass	Steel	Bentonite	
USA	HLW	Borosilicate glass	Inner SS canister, outer	No backfill	Ti alloy drip shield, granular

			Ni-based alloy container		invert
	Commercial spent fuel	Fuel rods, Zircaloy or SS cladding, UO_2 fuel pellets	SS inside a Ni-based alloy outer container		
	Defense spent fuel	Many types, including MOX, ceramic–Pu, Pu/U alloy	Standardized cask inside Ni-based alloy package		

Table adapted from NEA 2003 (Table 3.1), with additional information from DOE 2002b, ONDRAF/NIRAS 2007.

SS = stainless steel

C steel = carbon steel

Table 9. Radionuclide half-lives and activities for typical reactor fuel assemblies

Isotope	**Half life (y)**	**Curies per PWR fuel assembly**	**Curies per BWR fuel assembly**
Hydrogen-3	12.3	9.76×10^{1}	3.37×10^{1}
Carbon-14	5.7×10^{3}	6.41×10^{-1}	3.04×10^{-1}
Chlorine-36	3.0×10^{5}	5.38×10^{-3}	2.20×10^{-3}
Cobalt-60	5.3	1.46×10^{2}	3.74×10^{1}
Nickel-59	7.6×10^{4}	1.29	3.53×10^{1}
Nickel-63	1.0×10^{2}	1.77×10^{2}	4.55×10^{1}
Selenium-79	6.5×10^{4}	2.26×10^{-1}	7.92×10^{-2}
Krypton-85	10.7	9.31×10^{2}	2.91×10^{2}
Strontium-90	29	2.13×10^{4}	7.08×10^{3}
Zirconium-93	1.5×10^{6}	1.16	4.8×10^{1}
Niobium-93m	16	8.21×10^{-1}	3.51×10^{-1}
Niobium-94	2.4×10^{4}	5.8×10^{-1}	1.91×10^{-2}
Technetium-99	2.1×10^{5}	7.14	2.55
Ruthenium-106	1.0	4.76×10^{-3}	6.69×10^{-4}
Palladium-107	6.5×10^{6}	6.35×10^{-2}	2.37×10^{-2}
Tin-126	1.0×10^{6}	4.35×10^{-1}	1.54×10^{-1}
Iodine-129	1.7×10^{7}	1.75×10^{-2}	6.27×10^{-3}
Cesium-134	2.1	1.61×10^{1}	3.39
Cesium-135	2.3×10^{6}	2.55×10^{-1}	9.99×10^{-2}
Cesium-137	30	3.13×10^{4}	1.07×10^{4}
Samarium-151	90	1.85×10^{2}	6.61×10^{1}
Actinium-227	2.2	7.81×10^{-6}	3.08×10^{-6}
Thorium-230	7.5×10^{4}	1.53×10^{-4}	5.83×10^{-5}
Proactinium-231	3.3×10^{4}	1.58×10^{-5}	6.01×10^{-6}
Uranium-232	69	1.85×10^{-2}	5.51×10^{-3}
Uranium-233	1.6×10^{5}	3.29×10^{-5}	1.07×10^{-5}
Uranium-234	2.5×10^{5}	6.58×10^{-1}	2.38×10^{-1}
Uranium-235	7.0×10^{8}	8.39×10^{-3}	3.00×10^{-3}
Uranium-236	2.3×10^{7}	1.40×10^{-1}	4.76×10^{-2}
Uranium-238	4.5×10^{9}	1.46×10^{-1}	6.23×10^{-2}
Neptunium-237	2.1×10^{6}	2.29×10^{-1}	7.27×10^{-2}
Plutonium-238	88	1.67×10^{3}	5.45×10^{2}
Plutonium-239	2.4×10^{4}	1.83×10^{2}	6.27×10^{1}
Plutonium-240	6.5×10^{3}	2.69×10^{2}	9.54×10^{1}
Plutonium-241	14	2.05×10^{4}	7.47×10^{3}
Plutonium-242	3.8×10^{5}	9.92×10^{-1}	3.98×10^{-1}
Americium-241	4.3×10^{2}	1.71×10^{3}	6.82×10^{2}
Americium-242/242m	1.4×10^{2}	1.05×10^{1}	4.57

Americium-243	7.4×10^{3}	1.25×10^{1}	4.90
Curium-242	0.45	8.70	3.79
Curium-243	29	8.30	3.10
Curium-244	18	7.05×10^{2}	2.51×10^{2}
Curium-245	8.5×10^{3}	1.80×10^{-1}	6.31×10^{-2}
Curium-246	4.8×10^{3}	3.80×10^{-2}	1.28×10^{-2}

Data from DOE (2002a; Tables A-8, A-9, and A-11). PWR—pressurized water reactor; BWR—boiling water reactor.

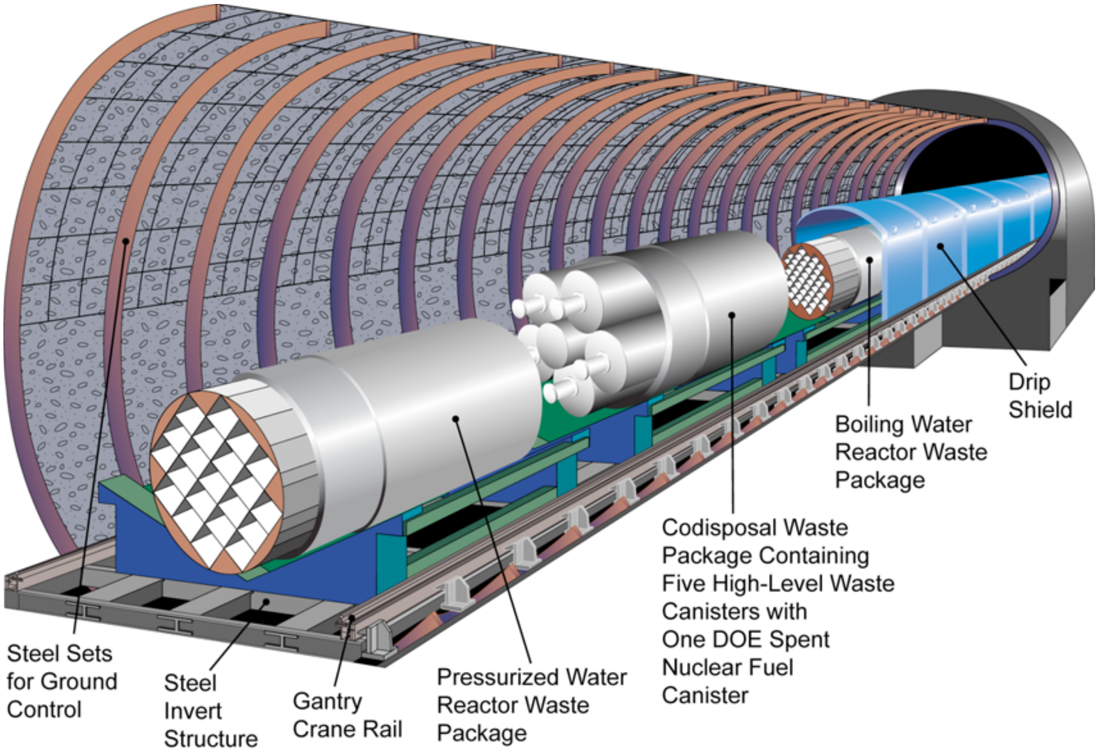

Figure 9. Schematic illustration of the emplacement drift, with cutaway views of different waste packages for the proposedYucca Mountain design concept (from DOE 2002b).

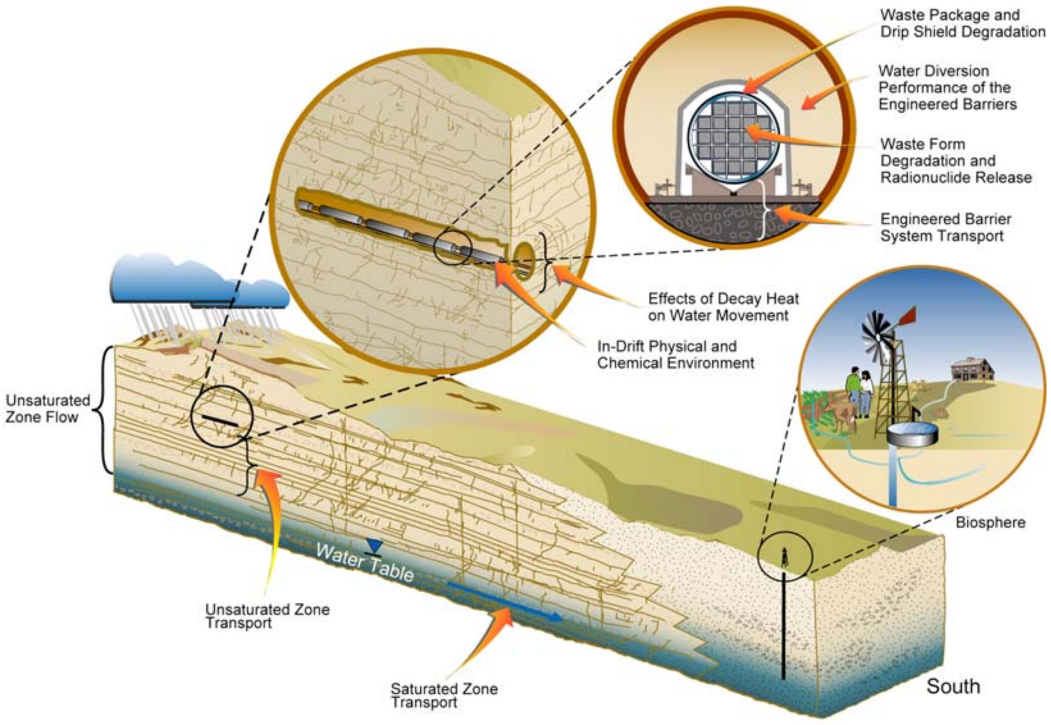

Figure 10. Schematic illustration of the natural and engineered system processes for proposed Yucca Mountain repository (from DOE 2002b).

TECHNOLOGY AND APPLIED RESEARCH AND DESIGN PERSPECTIVES AND NEEDS

The grand technical challenge for nuclear waste disposal is the need to understand and predict with sufficient confidence flow and transport processes and performance of materials (engineered and geologic) over geological time scales (at least to a million years), with long-term climate changes and the impact of extreme events taken into account. It is important to enhance the interaction of engineered barriers with natural systems, to maintain retrievability and monitoring, and to prioritize/address the performance in a regulatory framework. The longevity of engineered barrier components depends on the quantity and chemistry of fluids in the surrounding natural system. Finally, there is a need to establish a sound foundation for model abstraction and stochastic approaches used for performance assessment (e.g., Helton et al. 1999).

The following subsections address technology and applied research and development needs for geologic disposal, focusing on the engineered and natural systems, cross-cutting areas, and questions primarily addressed by geosciences. The research needs are derived from technological and scientific challenges associated with each element of the repository system.

Engineered systems

1. Engineered materials performance

A major component of the long-term strategy for safe disposal of nuclear waste is, first, to completely isolate the radionuclides in waste packages for long times, and then, to greatly retard the egress and transport of radionuclides from breached packages. The materials used for isolating waste in the repository are an important component of the overall approach to the design of the repository system.

Corrosion is a primary determinant of waste package performance in any storage or disposal environment and will control the delay time for radionuclide release and transport from the waste package. Intact waste packages fully contain and isolate radionuclides. Corrosion is the most likely degradation process that will determine when waste packages will be penetrated and the shape, size, and distribution of those penetrations. Thus, corrosion resistance is important to the long-term performance of waste packages. The waste packages are manufactured from highly corrosion-resistant metals, and the surface of these metals is protected by the formation of a self-healing, passive layer. Based upon previous measurements of corrosion rates of passive metals, if the passive film remains stable, the waste packages can remain intact with no penetrations resulting from corrosion for durations of tens of thousands and even hundreds of thousands of years (DOE 2002a; DOE 2002b).

Materials optimization must be realized through a coordinated program of targeted, applied research. Areas of materials research needed are:

- Long-term behavior of protective, passive films
- Composition and properties of moisture in contact with metal surfaces
- Rate of penetration and extent of corrosion damage over extremely long times

2. Radioactive waste form (which is the source for radionuclide releases)

There are two important reasons for understanding radioactive waste form and near-field behavior. First, almost all of the radioactive elements are initially within the waste forms, mainly in the spent nuclear fuel and vitrified waste. Therefore, the waste form character itself places both initial as well as long-term limits on radionuclide release. Possible interactions of the waste forms with the near-field environment, such as the corroded waste packages, place additional constraints on the long-term behavior and mobility of radionuclides (see Grambow et al. 2000 and references therein; Poinssot et al. 2001 and references therein). An enhanced understanding and realistic estimates of the extent to which radionuclides will be retained in the waste form or near-field environment reduce the demands on the performance of subsequent, far-field barriers. Realistic estimates of radionuclide release will also reduce the uncertainty in the total system performance assessment. Second, over long periods, after the engineered barriers have degraded, the waste form is a primary control on the release of radioactivity. Thus, it is essential to know the physical and chemical state of the waste form after hundreds of thousands of years.

The goal of source term research is to enhance the understanding of the performance and evolution of nuclear waste forms (mainly spent nuclear fuel and nuclear waste glass) and to quantify the release of radionuclides in the evolving near-field environment expected in the repository. A basic understanding of the fundamental mechanisms of radionuclide release and a quantification of the release as repository conditions evolve over time, particularly at longer times ($>10^5$ years), must be developed. Radionuclide release will be sensitive to variations in temperature, the radiation field, redox conditions, pH, P_{CO2}, surface area-to-solution volume, and the presence of near-field materials. Among the important processes that can control radionuclide release are:

1. The kinetics of waste form corrosion
2. The formation of secondary, alteration phases
3. The reduction and sorption onto the surfaces of near-field materials (see Figure 11)

In addition, biogeochemical processes and microbial activity may influence the geochemical environment and promote colloid formation with resultant impacts on waste form stability and radionuclide transport.

The prediction of the long-term behavior of nuclear waste forms cannot be based entirely on models of laboratory results that are extrapolated to long periods; hence, integration of multiple lines of evidence (e.g., results from natural analogue studies) is required to clarify the scientific basis for waste form degradation mechanisms in relation to source term models (see Lutze and Ewing 1988 and references therein).

The nuclear waste forms, spent nuclear fuel and nuclear waste glass, may serve different functions at different times in the multi-barrier system of a geologic repository (see Grambow et al. 2000 and references therein; Shoesmith et al. 2003 and references therein; Lutze and Ewing 1988 and references therein; National Research Council 1996; Van Iseghem 2001 and references therein). The waste form may be:

1. the sole barrier to release of radionuclides to the biosphere
2. an effective, but not the primary, barrier to radionuclide release
3. a solid-medium for transportation and temporary storage (National Research Council 1996.)

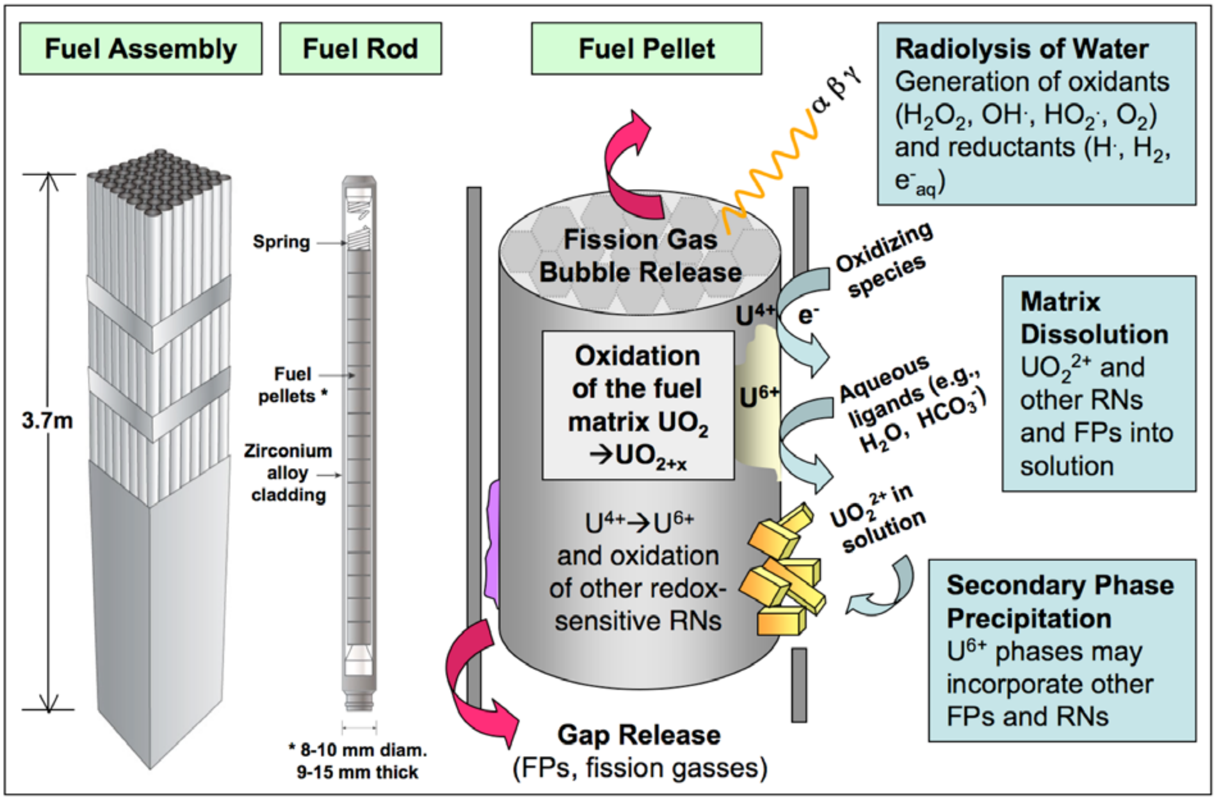

Figure 11. Schematic illustration of the fundamental processes used as a framework for definition of the source term for spent nuclear fuel waste form (after Bruno and Ewing 2006). The fuel assembly represents one used in a typical light water nuclear reactor.

At Yucca Mountain, for example, the waste form is one of a series of barriers, engineered and geologic, to the release of radionuclides. The effectiveness of these barriers varies over time, as does the inventory of radioactive elements, the temperature, and the radiation field. Immediately after emplacement in a geologic repository, the waste forms are protected from contact with water by the waste package. During this time (hundreds to thousands of years), the waste forms experience the highest temperatures and most intense radiation fields, but the waste forms are not in chemical contact with the surrounding geologic medium. The waste forms are only exposed to outside water after the waste package has been breached. At intermediate times (thousands to tens of thousands of years), some fraction of the waste packages is assumed to have failed, and the waste forms will be in contact with water (or water vapor) and air. This represents the first possibility for release of radionuclides from the waste forms. At the longest time periods (tens of thousands to hundreds of thousands of years), most of the waste forms will be exposed to the ambient, geochemical/hydrological conditions. At this stage, one may expect extensive alteration of the waste form and hydrochemical interactions with corroded waste packages and the surrounding geology (Allan and Nuttall 1997).

By focusing on the changing conditions over time, identifying the processes within each time interval, and with attention to the radionuclides that are the major contributors to dose, new research will be able to improve fundamental understanding of source term processes. The research addresses the need to understand the physical and chemical processes as a function of time (see Figure 11 for a portrayal of potential processes). The research needs presented here are focused on spent nuclear fuel; other waste forms (e.g., glasses, ceramics, metals) would have similar needs but some specifics would change (e.g., no role of cladding for other waste forms).

A closed fuel cycle requires a geologic repository for disposal of long-lived fission products and potentially very small amounts of actinides, the latter being from minor separations process losses. Potential waste form materials—oxides, glasses, and/or metals—containing radionuclides are key components of the repository system. The potentially significant doses from the encased radionuclides require long-term isolation in durable waste forms. As part of efforts in the U.S. and worldwide to develop advanced nuclear fuel cycles, additional research is required to identify potential advanced waste form materials (see Lutze and Ewing 1988 and references therein; Ewing et al. 2004). If candidate advanced waste form materials are further developed, focused work to increase understanding of waste form performance in complex geologic settings is needed. Prediction of geologic repository performance to 10^4 years (and even 10^6 years), and the role of the source term in long-term safety, represent unprecedented scientific challenges.

To provide durable waste forms and demonstrate their long-term performance, the behavior of materials must be understood at a level of fundamental knowledge and predictability that could allow for reduction in the conservatism of engineered system designs, while still achieving the required safety margins, and perhaps lowering repository costs. The waste form materials form complex multi-component dynamic systems that evolve in time over a wide range of conditions including high radiation fields, high temperatures, and potentially corrosive chemical environments (see Lutze and Ewing 1988 and references therein; Smith et al. 1992). Fundamental understanding of the properties of waste forms is essential to predicting their long-term behavior and can only result from closely coupled theory, modeling, and experimentation.

A fundamental and integrated experimental and modeling approach to source term processes, as described above for spent nuclear fuel, can also be readily applied to development of advanced waste forms as part of a closed nuclear fuel cycle. Specifically, a fundamental understanding of the stability of candidate advanced waste form materials in high temperature/high radiation environments and near-field geochemical/hydrologic processes could enable development of waste forms “tailored” to specific geologic settings (Lutze and Ewing 1988). Closing the fuel cycle will generate a new class of waste forms with a different chemical composition, different thermal and radiation profiles and time evolutions, and different requirements for waste packaging, interim storage, and long-term disposition. Technical challenges include:

1. Immobilization of high-heat fission products (cesium, strontium) and long-lived fission products (iodine, technetium) in tailored storage/waste forms
2. Higher fission-product loadings for ceramic waste-form technologies
3. Determination of thermodynamic and thermophysical properties of actinide-containing waste forms, including radiation effects, transport, and interfacial interactions
4. New geologic waste-form materials tailored for reduced actinides and increased fission products

See DOE 2006a for detailed discussions.

The development of these “tailored” waste forms would also be contingent on an integrated systems analysis of the closed nuclear fuel cycle. Such a systems analysis would allow for optimization of the entire separations/storage/disposal process. Key elements are:

1. Development of an optimal separations process to minimize separations process losses
2. The production of the required product form for advanced nuclear fuel fabrication and storage form for short-lived fission products
3. The tailoring of waste forms to specific geologic settings (Peters and Ewing 2007)

Optimization of the geologic repository design, combined with the total amount of waste that would be disposed and the volume of the waste, could result in different sub-surface repository configurations. These factors, plus the long-term behavior of the engineered and natural barriers, affect the forecast annual dose to the public. It is expected that waste form research and development could lead to new waste forms that perform as well as, and likely better than, borosilicate glass and spent nuclear fuel in a geologic environment.

Natural systems

The term “geologic disposal” highlights the key role that the natural system plays in isolating the waste from the biosphere for as long as it poses significant risks. Assessment of the barrier capability of the natural system and demonstration of its significance for repository performance need to be based on:

1. An understanding of the features, events, and processes that could transport radionuclides from the repository to the accessible environment
2. Laboratory experiments and field observations and tests to appropriately characterize the relevant properties at a potential repository site
3. Conceptual, mathematical, and numerical models that predict the behavior and performance of the repository system given its site-specific characteristics and properties
4. Natural analogs, which help build confidence that the model predictions can be reliably extrapolated to the long time scales required for waste isolation

Figure 12 schematically shows some of the issues that need to be addressed to understand the behavior of the natural system at Yucca Mountain, Nevada. Similar issues are relevant for repositories located in other host rocks and different hydrogeochemical environments.

1. Climate

Water is the predominant transport medium of radionuclides from geologic repositories to the accessible environment. Availability, distribution, and chemical composition of water flowing through the geosphere are critically affected by the hydrological and geochemical conditions applied at the repository system boundaries. These boundary conditions are determined by global climate and related regional water cycles. The influence of climate conditions on repository system behavior applies to disposal sites in arid regions, in the saturated zone, as well as sites close to marine environments. Climate change not only directly impacts hydrological boundary conditions, but also may indirectly affect geomorphological processes, geothermal regimes, and geochemical conditions. Long-term global climate change over the timescale of 100,000s of years, its primary impacts on the regional water cycle, and its secondary effects on geomorphology need to be analyzed and predicted, requiring novel approaches that combine

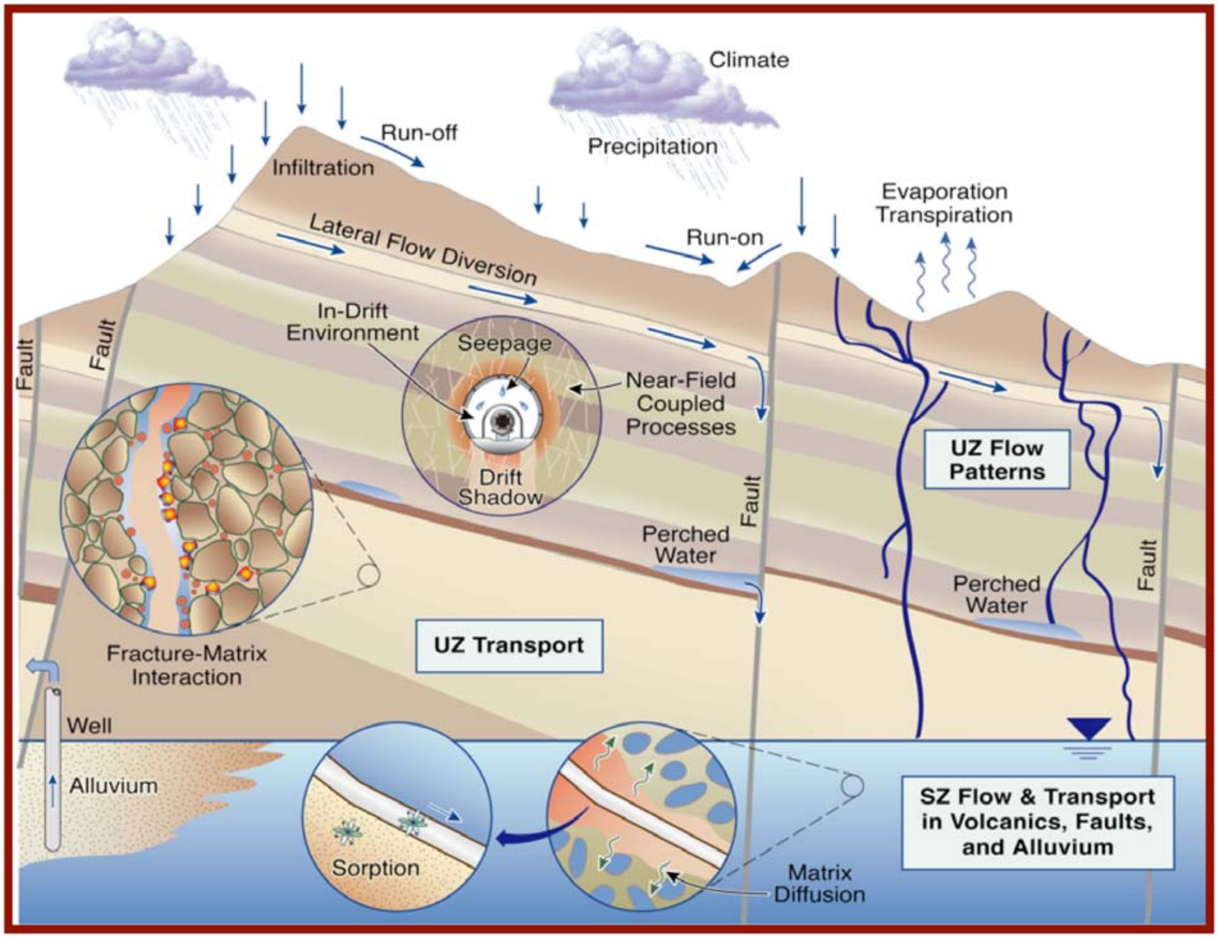

Figure 12. Schematic of features and processes relevant for the understanding of the natural system and its impact on repository performance at Yucca Mountain (from Bodvarsson 2005).

information from paleoclimatic and paleohydrologic data (Petit et al. 1999) with appropriate predictive tools that allow for the development of relevant climate scenarios. Moreover, potentially dramatic changes in climate induced by very high levels of atmospheric CO_2 (Houghton et al. 2001) may pose additional scientific challenges regarding the long-term prediction of atmospheric conditions and their direct and indirect geological, hydrological, and geochemical impacts.

2. Recharge and discharge

Regional and local groundwater flow patterns are primary factors determining site suitability and repository performance. Groundwater flow fields are strongly affected by the hydrologic boundary conditions, which in turn are influenced by climatic states and their impacts on precipitation, evapotranspiration, run-off and run-on, sea level, erosion, and other factors. Estimating the magnitude and spatial distribution of recharge and discharge for different climate states on the scale of a repository system is a significant challenge, specifically for arid sites. A methodology needs to be developed to estimate magnitude, spatial distribution, and episodicity of recharge and discharge conditions over a very long time period. These approaches need to include the quantification of aleatory and epistemic uncertainty in long-term estimates of recharge and discharge.

3. *Percolation and groundwater flow fields*

The integrity of the engineered barrier system as well as waste dissolution, release, and transport of radionuclides to the accessible environment depend on the availability, amount, and distribution of groundwater flow towards, into, and away from the repository. Delineation of groundwater flow paths through complex geologic media (i.e., porous and fractured rocks and sediments with complex stratigraphy which potentially contains faults) remains a major challenge in subsurface hydrology that strongly affects the predicted performance of a geologic repository (Berkowitz 2002). Specifically, there is a need for robust methods for detecting and identifying main flow features. This requires advances in science and technology to enable:

1. Site-specific, high-resolution characterization of relevant hydrogeological properties
2. Estimation of spatial and temporal distribution of water flow through these features under unsaturated and saturated flow conditions
3. Appropriate upscaling, downscaling, and averaging procedures for hydrogeologic parameters, processes, and the resulting flow fields

In addition, there is a need to develop alternative models that include non-Darcy flow processes (e.g., film flow, rivulet flow, evaporation/condensation effects, liquid islands, flow across fracture intersections, non-equilibrium flows, etc.). Given the inherent difficulty to directly observe subsurface flow patterns, approaches need to be developed that estimate flow paths using combined hydrological, geochemical, and geophysical data. Finally, the long-term stability of identified groundwater flow paths needs to be assessed or predicted in response to geochem–ical and mechanical changes imposed by natural processes or the presence of the repository.

4. *Near-field effects*

The performance of a geologic repository is critically affected by the mutual impacts of the natural and engineered systems. The geochemical and hydrological conditions of the natural system affect the integrity of the engineered barriers. Conversely, the engineered barrier system may strongly affect natural processes in the near field, specifically through coupled thermal-hydrological-chemical-mechanical-biological mechanisms. Potential effects include flow field alteration, evaporation, condensation, and the development of deliquescent brines, the generation of an excavation-disturbed zone, thermal effects, development of a drift shadow zone, and impacts of introduced materials on the biogeochemical environment. There is a need to develop models that describe, predict, and control the transport of fluids, radionuclides, chemicals, and heat across the interface between the natural and engineered systems. In addition, methods are needed to optimize the repository design such that stable, passive, self-supporting, or self-healing mechanisms are induced at the interface between the natural and engineered barrier systems such that they are beneficial to repository performance.

5. *Radionuclide transport*

The accurate prediction of radionuclide release and transport from the repository to the accessible environment (including transport through and accumulation in the biosphere) is a key element of performance assessment calculations. Research is needed to identify the relevant processes and related hydrogeochemical properties affecting radionuclide transport (specifically advective transport pathways and transport velocity, fracture-matrix interaction, sorption kinetics, and colloid-facilitated transport). Moreover, methodologies are needed to upscale, downscale, and appropriately average the highly heterogeneous transport parameters, processes, and resulting radionuclide breakthrough curves. Finally, alternative conceptual models need to be developed, capable of analyzing anomalous transport behaviors such as early arrival of radionuclides as well as multimodal and heavy-tailed breakthrough curves.

6. *Disruptive events*

Disruptive events (such as volcanic and seismic events) may affect repository performance in a way that is fundamentally different from features, events, and processes described in the nominal case. Disruptive events are fundamentally different in terms of their occurrence probability, their consequence, and their discreteness. Challenges in geosciences in need of further research include the prediction of the occurrence of low-probability disruptive events, their impact on the natural and engineered systems, their aleatory and epistemic uncertainty characteristics, and mathematical and computational methods to embed them into a performance analysis (e.g., Woods et al. 2002; Ho et al. 2006).

Additional cross-cutting needs

In addition to research needs for the repository system elements, there are several cross-cutting areas that have technology and applied research and development needs. These are discussed next in more detail.

1. *Repository design and nuclear fuel cycle*

Changes in repository design or the consideration of alternative nuclear fuel cycles (which may include reprocessing of spent nuclear fuel and waste partitioning and transmutation technologies) may significantly affect the requirements for and performance of the natural barrier system. Possible variants in repository design could include a low temperature (sub-boiling) *vs.* high temperature (boiling) waste configuration, backfill *vs.* no backfill in the emplacement drifts, and the use of an extended period of ventilation in the drifts. A technology is needed to fully couple and optimize decisions on the nuclear fuel cycle and repository design as they relate to overall system performance. (Note also that uranium ore exploration and mining is an essential part of the nuclear fuel cycle that is addressed by geosciences.) Alternative disposal technologies (e.g., the deep borehole approach, Kuo et al. 1995) need to be evaluated as well.

2. *Monitoring*

Monitoring the natural system during the early stages of repository operation is a critical aspect of a defensible nuclear waste disposal strategy. The rationale for monitoring a variety of variables representing the state of the repository system is to: (1) provide early warning of unforeseen system behavior and consequences of repository operation, and (2) provide data for confirming site conditions and previous model predictions, or for progressively adjusting the parameters of such models. Designing a monitoring system suitable for adaptive repository management is expensive and challenging, because of: (1) the variety of performance-relevant parameters that need to be observed, (2) the size and inherent complexity, heterogeneity, and discreteness of the natural system, (3) the fact that the system to be monitored may exhibit previously unknown or unanticipated behavior, and (4) the need to minimize the risk of not detecting a performance failure. There is a need to design robust, efficient, comprehensive, and cost-effective monitoring systems of large natural and man-made systems. These approaches must evaluate the scope of monitoring, identify observable variables, and optimize measurement frequency and location. Technical issues associated with monitoring include instrumentation, data acquisition system, data management (storage, retrieval, dissemination), and data interpretation.

3. *Reversibility and retrievability*

While geologic disposal of radioactive waste is based on the principle that waste will only be emplaced in a repository when there is high confidence in the ultimate long-term safety without relying on actions following the closure of the repository, most repository development programs include the possibility of post-closure activities for security and monitoring purposes (Nuclear Energy Agency 2001). Reversibility denotes the possibility of reversing one or a series of steps in repository planning or development at any stage of the program. Retrievability denotes the possibility of reversing the action of waste emplacement. This flexibility is needed to be able to respond to new technical information regarding the site or repository design, new technological advances regarding waste treatment and waste management, and changes in the societal, political, and regulatory environment. The ability to retrieve nuclear waste depends on the repository design and its interaction with the natural system. Design concepts that hinder or promote waste retrievability need to be examined, and related criteria for the geologic system and repository design need to be developed. In addition, techniques and equipment need to be developed for the mining of waste at potentially high temperature and radiation levels.

4. *Natural analogs*

The study of natural analogs is a potentially powerful method to understand the long-term behavior of natural and engineered systems (IAEA 1989; Murphy 2000; DOE 2004). Natural analogs exhibit materials or processes that resemble those expected in a geologic repository. They can be used to develop or test methodologies and models, or (more directly) to analyze the long-term behavior of an approximate system, which is not feasible by active testing. A methodology needs to be developed for selecting and analyzing natural analogs, and to assess their representativeness for a specific waste disposal site.

5. *Modeling*

Long-term repository performance is largely assessed through the use of numerical models (Bredehoeft 2003). There are many scientific and technological challenges for development, calibration, validation, use, and uncertainty of numerical models (Oreskes et al. 1994; Lemons 1996). These challenges lead to a variety of research needs, including the development of approaches and tools to:

- Accurately simulate highly nonlinear, coupled processes at multiple spatial and temporal scales
- Identify the most appropriate model structure suitable for the prediction needs, given limited characterization and calibration data, and identify opportunities for additional characterization and calibration data collection to enhance the predictive model structure
- Infer process-relevant, scale-dependent, and model-related parameters
- Resolve inherent inconsistencies in scale and data type between characterization data, model parameters, and prediction variables
- Characterize aleatory uncertainty and quantify and reduce epistemic uncertainty
- Propagate aleatory and epistemic uncertainty through prediction models

- Incorporate low-probability, high-impact events into performance assessment analyses
- Incorporate alternative conceptual models into uncertainty assessments
- Develop appropriate model abstractions
- Perform comprehensive simulations on the system level

Mathematical and computational challenges are also associated with these modeling needs (see DOE 2006c for more detailed discussions).

6. *Geological criteria for site selection*

In siting repositories, it is important to select a hydrological and geochemical environment that ensures low solubility and high retardation of radionuclides. The needed repository capacity is closely coupled with the waste inventory, future use of spent fuel with advanced fuel cycles, and the national energy policy on reprocessing and recycling. Both options should be considered: the potential siting of additional repositories in different geological media, and the potential expansion of capacity of existing sites with different design configuration optimized with the natural surrounding. There is a need to develop criteria and to identify site characterization needs and approaches for future geologic repositories based on previous experiences and new developments.

NUCLEAR WASTE HISTORICAL BACKGROUND—ADDITIONAL INFORMATION

The U.S. has had a longstanding and ongoing technical and policy discussion on the importance of geologic disposal to nuclear waste management. To place the technical aspects of geologic disposal in the proper context, it is useful to review the history of the technical and policy discussions. This is discussed in some detail below. Much of this discussion is taken directly from Office of Technology Assessment (1985). The reader is also referred to Cotton (2006) for a more recent, thorough review of this subject.

High-level radioactive waste was first produced in the United States on a large scale in the wartime effort of the early 1940’s to produce plutonium for atomic weapons. Spent fuel from defense reactors was routinely reprocessed to recover uranium and plutonium, and liquid high-level waste from reprocessing was stored in storage tanks at federal facilities—first at Hanford, Washington, and later at Savannah River, South Carolina, and Idaho Falls, Idaho. It was assumed that disposal could take place later, possibly at these same sites.

In 1954 the Atomic Energy Act opened the nuclear power industry to private enterprise, and the first contract for a commercial reactor was issued two years later. Unlike defense reactors, commercial reactors were designed primarily to produce electricity. Spent fuel discharged from commercial reactors was stored in water-filled basins at reactor sites, pending development of a commercial reprocessing facility.

The Atomic Energy Commission (AEC) first addressed the problem of waste disposal in 1955 when it asked the National Academy of Sciences (NAS) how to structure research to establish a scientific basis for the waste management program. Under the assumption that the waste to be disposed of would be dissolved at relatively low concentrations in liquid, NAS stated in its 1957 report (National Research Council 1957) that disposal was technologically feasible and that stable salt formations appeared to be the most promising repository medium. Such formations would theoretically prevent transport of liquid and would become self-sealing in the event of fracturing. The commitment to salt became a cornerstone of waste disposal policy for the next 20 years.

In the 1960’s, improved reprocessing techniques reduced the volume and increased the thermal and radiation content of reprocessed wastes. To test the effect of these new characteristics on salt, 14 spent fuel assemblies and several heaters to raise the temperature of the salt were emplaced from 1965 to 1967 in the abandoned Carey Salt Mine at Lyons, Kansas. The experiment, called Project Salt Vault, was conducted in an atmosphere of goodwill among federal, state and local officials. State and local officials were consulted about various aspects of the experiment, public tours of the mine were given during the experiment, and the wastes were removed at the end of the experiment, as promised. The results of this experiment showed no measurable evidence of excessive chemical or structural effects on the salt.

AEC announced in 1970 that, pending confirmatory tests, the Lyons site had been selected for the first full-scale repository. Although the degree to which AEC had consulted with state and local officials before this announcement is in dispute, AEC’s decision did not have full endorsement from these officials. Moreover, state and local political opposition to the Lyons site was intense, particularly when technical problems with the site became apparent. The federal government abandoned plans for Lyons two years later because AEC was unable to convince critics that the many mining boreholes throughout the site could be plugged reliably and because no one could account for the disappearance of a large volume of water flushed into a nearby mine.

Left without a repository, AEC requested the U.S. Geological Survey (USGS) to search for additional repository sites for defense wastes. It also proposed building a series of above-ground structures, called retrievable surface storage facilities (RSSFs), to store commercial high-level wastes for a period of decades while geologic repositories were developed. The environmental impact statement issued by AEC in support of the RSSF concept drew intense criticism from the public and from the Environmental Protection Agency (EPA) due to concerns that the RSSFs would become low budget permanent repository sites. As a result, AEC abandoned the RSSF concept in 1975.

After the mid-1970’s, significant changes occurred in nuclear waste management. EPA issued its first standards—those for the preparation of reactor fuel, for reactor operations, and for reprocessing of spent fuel—and announced its intention to develop standards for the disposal of nuclear waste. The Energy Reorganization Act of 1974 abolished the AEC and distributed its developmental functions to the new Energy Research and Development Agency (ERDA), later changed to the Department of Energy (DOE), and its regulatory functions to the new Nuclear Regulatory Commission (NRC). These events marked the change to a formal process of regulating the storage and disposal of high-level wastes. Thus, ERDA (later, DOE) would select a disposal site and design a facility to meet regulations promulgated by NRC in accordance with EPA standards.

By the late 1970’s, the problem of waste isolation had captured the attention of the federal government, which began to allocate substantial personnel and funds to its solution. Although many decision makers still contended that managing high-level radioactive wastes was not technically difficult, they increasingly recognized the nontechnical aspects of the problem and worked to develop a firmer technical basis from which to make decisions.

For disposal of commercial high-level waste, ERDA developed the National Waste Terminal Storage (NWTS) program in 1975. The program involved a multiple-site survey of underground geologic formations in 36 states and was designed to lead to the development of six pilot-scale repositories by the year 2000—the first in salt, the rest in other geologic media. This change from preoccupation with salt reflected new views about what constituted an effective repository. As formally expressed in 1978 in “Circular 779” (Bredehoeft et al. 1978) by several USGS scientists and also in a study by the American Physical Society (APS 1978), the effectiveness, or integrity, of a repository could be considered dependent on the combination of the emplacement medium and its environment, rather than on the emplacement medium alone. With that view, salt, although still a strong contender, might not be the only choice for a geologic repository. Moreover, the staff of NRC contended that “it would be highly desirable to place major, if not primary, importance on the waste form itself, its packaging, and the local waste rock interface.”

Because of lower-than-requested funding and political opposition from the states, schedules slipped repeatedly as the federal government was forced to cut the program drastically. By 1980, active site evaluation research was being undertaken only in Louisiana, Mississippi, Nevada, Texas, Utah, and Washington. The watershed action for United States nuclear waste policy followed shortly thereafter with the passage of the Nuclear Waste Policy Act (NWPA) in 1982. The Act established a schedule for the DOE to nominate at least five sites in a first round of repository selection and recommend three of them to the President for further characterization before selecting one for the first repository. A similar process for selecting a second repository site was also required. Since most of the first round sites were in the west, it was expected (though not explicitly stated) that this second round choice would focus on sites in the east to provide geographic equity.

The sites already under consideration when the NWPA was passed formed the basis of site screening for the first repository. In 1983, the DOE identified nine potentially acceptable sites—six in the west (four in bedded salt, one in basalt, and one in tuff) and three in the south (all in domed salt). Later in 1986, three sites were designated for characterization: a basalt site in Hanford, Washington; a tuff site at Yucca Mountain, Nevada; and a salt site at Deaf Smith County, Texas. However, with the rise in political opposition to specific repository sites and the escalation of the estimated cost of characterizing multiple sites, Congress in 1987 passed the Nuclear Waste Policy Amendments Act. The Amendments Act terminated consideration of the first round salt and basalt sites and directed the DOE to study only one site—Yucca Mountain—to determine its suitability as a repository. It also required the DOE to deliver a report to Congress on the need for a second repository between January 1, 2007 and January 1, 2010.

Following selection of Yucca Mountain for detailed evaluation, the DOE issued a Site Characterization Plan for review and comment by the State of Nevada, the NRC, and the public, as required by law. Once that was done, the DOE was allowed to begin site characterization, which, by law and regulation, had to include testing in an underground facility at the site. The site characterization phase ended in 2002 when the Secretary of Energy recommended the Yucca Mountain site to President Bush as suitable for further development (DOE 2002c). Following the process laid out in the NWPA, Congress voted in July 2002 to approve the site, overriding a veto by the State of Nevada.

DOE is required by the NWPA to submit a license application for a repository to the NRC. This is currently expected to occur by June 2008**.** The NRC has three years to decide on the license application once it receives it from the DOE, with the possibility of a one-year extension.

LIST OF ACRONYMS AND ABBREVIATIONS

AEC	Atomic Energy Commission
Bbl/d	Stock-tank Barrels per day
BWR	Boiling Water Reactor
CO2ReMoVe	CO2 Research Monitoring Verification project (http://www.co2remove.eu/)
DOE	U.S. Department of Energy
EOR	Enhanced Oil Recovery
EPA	Environmental Protection Agency
ERDA	Energy Research and Development Agency
FPs	Fission Products
GCS	Geologic CO_2 Sequestration
Gt	Billions of tons
IAEA	International Atomic Energy Agency
IEA	International Energy Agency
IEA-GHG	IEA Greenhouse Gas Program
IPCC	Intergovernmental Panel on Climate Change
LIDAR	Light Imaging Detection And Ranging
M&V	Monitoring and Verification
MIT	Massachusetts Institute of Technology
MMt	Millions of tons
NAS	National Academy of Sciences
NEA	U.S. Nuclear Energy Agency
NWPA	Nuclear Waste Policy Act (1982)
NWTS	National Waste Terminal Storage
PWR	Pressurized Water Reactor
RNs	Radionuclides
RSSF	Retrievable Surface Storage Facility
USGS	U.S. Geological Survey

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APPENDIX 2:
WORKSHOP PROGRAM

BASIC RESEARCH NEEDS FOR GEOSCIENCES:
FACILITATING 21ST CENTURY ENERGY SYSTEMS

Tuesday, February 20, 2007 • EVENING

Pre-meeting: panel co-leads and workshop organizers only

6:00 pm - 6:15 pm	Welcome and purpose of meeting	Eric Rohlfing
6:15 pm - 6:30 pm	Overview of agenda	Co-Chairs Don DePaolo and Lynn Orr
6:30 pm - 7:00 pm	Discussion of breakout sessions	Co-Chairs Don DePaolo and Lynn Orr
7:00 pm - 8:00 pm	Working dinner: Workshop report and discussion	

Early Registration

6:00 pm - 8:00 pm	Early Registration

Wednesday, February 21, 2007 • MORNING

7:30 am - 8:30 am	Registration and continental breakfast

Plenary Opening Session

8:30 am - 8:45 am	Introductory remarks	Pat Dehmer / Chairs

Session 1: Multiphase Fluid Transport in Geologic Media

8:45 am - 9:25 a	Industry Perspectives	Charles Christopher
9:25 am - 10:10 am	Technology Needs and Research Frontiers	Sally Benson
10:10 am - 10:30 am	Break	

Session 2: Chemical Migration Processes in Geologic Media

10:30 am - 11:00 am	Technology Challenges	Abraham Van Luik
11:00 am - 11:30 am	International Perspectives	Thomas Fanghänel
11:30 am - 12:00 pm	Research Frontiers	Rod Ewing
12:00 pm - 1:30 pm	Working lunch—breakout sessions	

Wednesday, February 21, 2007 • AFTERNOON

Four Panel Breakouts

1:30 pm - 3:30 pm	Series of presentations by panel
3:30 pm - 4:00 pm	Break
4:00 pm - 6:00 pm	Initial discussion of one-sentence proposed research directions
6:00 pm - 7:30 pm	Working dinner
7:30 pm - 9:00 pm	Prioritize 3-5 one-sentence proposed research directions

Thursday, February 22, 2007 • MORNING

7:30 am - 8:00 am	Continental breakfast

Four Panel Breakouts

8:00 am - 10:00 am	Draft 3-5 one-sentence proposed research directions (one viewgraph for each)
10:00 am - 10:30 am	Break

Thursday, February 22, 2007 • MORNING (continued)

Plenary Midpoint Session

10:30 am - 12:30 pm	Presentations of draft proposed research directions	*Four 30-minute blocks of time for presentations and discussion*
12:30 pm - 1:45 pm	Working Lunch	

Thursday, February 22, 2007 • AFTERNOON

Four Panel Breakouts

1:45 pm - 6:00 pm	• Further discussion as needed • Draft "five"-viewgraph panel report • Draft executive summary paragraph • Create a 1000-1500 word draft and one viewgraph for each proposed research direction • Begin drafting panel report (3000-5500 words)
6:00 pm - 7:00	Reception
7:00 pm - 9:00 pm	Dinner on your own

Friday, February 23, 2007 • MORNING

7:30 am - 8:00 am	Continental breakfast

Panel Breakouts

8:00 am - 10:15 am	Finish drafting panel report (3000-5500 words)
10:15 am - 10:45 am	Break
10:45 am - 12:00 am	Finish drafting panel report (3000-5500 words)

Friday, February 23, 2007 • AFTERNOON

12:00 pm - 1:00 pm	Working Lunch/Opening Remarks

Plenary Closing Session

1:00 pm - 1:30 pm	Multiphase Fluid Transport in Geologic Media	Leads: Sally Benson and Michael Celia
1:30 pm - 2:00 pm	Chemical Migration Processes in Geologic Media	Leads: Andy Felmy and Kathryn Nagy
2:00 pm - 2:30 pm	Characterization of Geologic Systems	Leads: Graham Fogg and Roel Snieder
2:30 pm - 3:00 pm	Modeling and Simulation of Geologic Systems	Leads: James Davis and Karsten Pruess
3:00 pm - 3:15 pm	Break	

Plenary Closing Session (continued)

3:15 pm - 3:45 pm	Crosscutting and Grand Challenge Science Themes
3:45 pm - 4:00 pm	Final closing remarks
6:00 pm - 7:00 pm	Working dinner for writing groups

Saturday February 24, 2007
Writing groups and workshop organizers only

7:30 am - 8:00 am	Continental breakfast

Final Writing of 4 Panel Reports

8:00 am - 10:00 am	Selected writers, panel co-leads, and workshop co-chairs complete writing and integration of panel reports, proposed research directions, crosscutting research directions, and technology assessment into the final workshop report.
10:00 am - 10:15 am	Break
10:15 am - 12:30 pm	Continue with tasks
12:30 pm - 1:45 pm	Working lunch
1:45 pm - 3:45 pm	Finish up

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APPENDIX 4:
ACRONYMS AND ABBREVIATIONS

AEC	Atomic Energy Commission
AFM	Atomic Force Microscopy
ASAX	Anomalous Small Angle X-ray Scattering
Bbl/d	Stock-Tank Barrels per Day
BWR	Boiling Water Reactor
CCS	Carbon Capture and Storage
CCSD(T)	Coupled Cluster Method With Non-Iterative Triple Excitations
CFCs	Chlorofluorocarbons
CO2ReMoVe	CO_2 Research Monitoring Verification project (http://www.co2remove.eu)
C-O-H-N-S	Carbon, oxygen, hydrogen, nitrogen, and sulfur
CT	Computed X-ray Tomography (i.e., CT scans)
CUAHSI	Consortium of Universities for the Advancement of Hydrologic Sciences, Inc.
DOE	U.S. Department of Energy
DLS	Dynamic Light Scattering
DDC	Dissolution-Diffusion-Convection
DFT	Density Functional Theory
DNS	Direct Numerical Simulation
EOR	Enhanced Oil Recovery
EPA	U.S. Environmental Protection Agency
ERDA	Energy Research and Development Agency
EOS	Equation of State
EPS	Exopolymeric Substances
EPS	ExoPolySaccharide
EXAFS	X-ray Absorption Fine Structure
FCS	Fluorescence Correlation Spectroscopy
FFT	Fast Fourier Transform
FPCF	Flat-Plate, Channel Flow
FPs	Fission Products
GCS	Geologic CO_2 Sequestration
GPR	Ground Penetrating Radar
Gt	Billions of metric tons, or Gigatons
HEXS	High-Energy X-ray Scattering
HPLC	High Performance Liquid Chromatography
HRTEM	High Resolution Transmission Electron Microscopy
IAEA	International Atomic Energy Agency
ICP-MS	Inductively Coupled Plasma Mass Spectrometer
IEA	International Energy Agency
IEA-GHG	IEA Greenhouse Gas Program

IPCC	Intergovernmental Panel on Climate Change
IUPAC	International Union of Pure and Applied Chemistry
LBM	Lattice Boltzmann Methods
LDA	Local Density Approximation
LIDAR	Light Imaging Detection And Ranging
M&V	Monitoring and Verification
MIT	Massachusetts Institute of Technology
MMt	Millions of tons
MP2	Second Order Moller-Plesset Perturbational Method
MRM	Magnetic Resonance Microscopy
MSE	Mixed-Solvent Electrolyte
Mt	Metric tons, or Megatons
NAS	National Academy of Sciences
NEA	U.S. Nuclear Energy Agency
NEB	Nudged Elastic Band
NMR	Nuclear Magnetic Resonance
NWPA	Nuclear Waste Policy Act (1982)
NWTS	National Waste Terminal Storage
PDF	Probability Density Functions
ps	Picoseconds
PVT	Pressure, Volume, Temperature
QM/MM	Quantum Mechanics / Molecular Mechanics
PWR	Pressurized Water Reactor
P-T-X	Pressure, Temperature and Composition
RAXR	Resonant Anomalous X-ray Reflectivity
RNs	Radionuclides
RSSF	Retrievable Surface Storage Facility
RST	Reservoir Saturation Tool
SAFOD	San Andreas Fault Observatory and Depth project
SAXS	Small Angle X-ray Scattering
SIC	Self Interaction Correction
SIMS	Secondary Ion Mass Spectrometry
TEM	Transmission Electron Microscopy
USGS	U.S. Geological Survey
XAD	Trade name of proprietary resins manufactured by Rohm and Haas Corp
XANES	X-ray Absorption Near-Edge Structure
XAS	X-ray Absorption Spectroscopy

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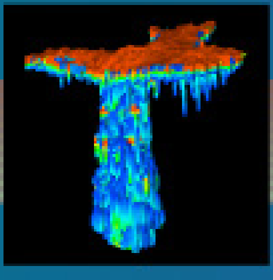

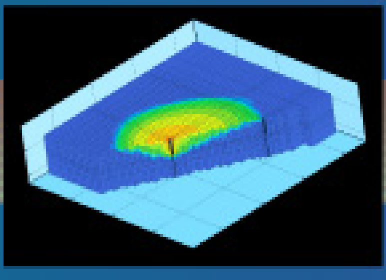

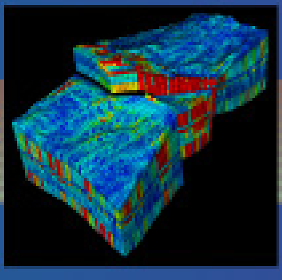

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