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NUCLEAR REGULATORY COMMISSION

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ADVISORY COMMITTEE ON NUCLEAR WASTE
172ND MEETING

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TUESDAY,
JULY 18, 2006

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ROCKVILLE, MARYLAND

The meeting convened at the Nuclear Regulatory Commission, Two White Flint North, Room T-2B3, 11545 Rockville Pike, at 8:30 a.m., Michael T. Ryan, Chair, presiding.

COMMITTEE MEMBERS PRESENT:

MICHAEL T. RYAN	Chairman
ALLEN G. CROFF	Vice-Chair
JOHN T. LARKINS	Executive Director
JAMES H. CLARKE	Member
WILLIAM J. HINZE	Member
RUTH F. WEINER	Member

PANEL MEMBERS PRESENT:

RACHEL J. DETWILER	Braun Intertec Corp.
LESLIE DOLE	ORNL
EDWARD GARBOCZI	NIST
FRED GLASSER	Aberdeen University, UK
DAVID S. KOSSON	Vanderbilt University
CHRISTINE A. LANGTON	SRNL
BARRY SCHEETZ	Pennsylvania State University

ACNW STAFF PRESENT:

ANTONIO DIAS

LATIF S. HAMDAN

MICHAEL P. LEE

DEREK WIDMAYER

NRC STAFF PRESENT:

DAVID ESH	NMSS/DWMEP
JOHN FLACK	ACRS
BRET LESLIE	NMSS/DWMEP
A.C. RIDGE	NMSS/DWMEP

VIA TELEPHONE:

LANE HOWARD	CNWRA
LINDA LEHMAN	Stanford

C-O-N-T-E-N-T-S

C-O-N-T-E-N-T-S

P-R-O-C-E-E-D-I-N-G-S

8:31 a.m.

CHAIRMAN RYAN: Okay, if we could come to order, please. The second day of the 172nd Meeting of the Advisory Committee on Nuclear Waste. During today's meeting, the Committee will conduct a working group meeting on predicting the performance of Cementitious Barriers of Near Surface Disposal. The meeting is being conducted in accordance with the provisions of the Federal Advisory Committee Act.

Latif Hamdan is the Designated Federal Official for today's session. We have received no written comments or requests for time to make oral statements from members of the public regarding today's session. Should anyone wish to address the Committee, please make your wishes known to one of the Committee staff.

It is requested that the speakers use one of the microphones, identify themselves and speak with sufficient clarity and volume so they can be readily heard. It's also requested that if you have cell phones or pagers, that you kindly turn them off. I'd like to add a note of welcome to all of panel participants today. I know you've traveled from far and wide to be with us and we appreciate you sharing your expertise with us today and giving us you insights on this important topic to the Committee.

Vice-Chair Allen Croff is chairing our working group meeting, so without further ado, I'll turn that meeting over to Allen.

VICE-CHAIRMAN CROFF: Thank you, Mike. Good morning, all. On behalf of the ACNW, I too would like to welcome our speakers and the audience to the working group meeting. By way of background, cementitious materials have been used to stabilize and isolate radioactive waste for many years. However, it's only recently that organizations responsible for the waste have decided to try to take credit for the beneficial characteristics of the cementitious materials. The most visible example of this, I think, is in the Department of Energy in their Tank Waste Management Program, where they're using it to stabilize the tanks and low activity waste both in the near surface.

There are also signs that credit may be taken for the beneficial effects of cement in decommissioning applications, although that's a little bit further out on the horizon. All of this raises the issue of how much credit can be taken for the cementitious barriers and for how long. That is, what do we know about predicting the performance of cementitious barriers into the future. The purpose of this working group meeting is to address this issue by considering three questions.

Where are cementitious materials being used in radioactive waste disposal, and what are the potential beneficial effects of the cements? What are the failure modes of the cementitious barriers relevant to the performance over long times, centuries out to the millennia and what's the current state of technology for predicting the performance of these cementitious materials?

Information gathered here today will provide the basis for the Committee to provide technical advice to the Commission concerning the reliance on these barriers and identify areas where additional information is needed. I might add that I hope it will produce some information that's relevant to the performance of concretes in applications such as nuclear power plants, which is of interest to the ACRS. This working group meeting will have three sessions corresponding to the questions I outlined earlier. To address these questions, we have a very distinguished group of scientists and engineers. They have extensive experience concerning cementitious materials. But before launching into the program, per se, I'd like to highlight a few items on the structure of the meeting.

Within each of the three sessions, we're going to have two or three speakers followed by a panel discussion where the Committee members, Committee staff, other speakers and NRC staff can ask the panelists questions. It would be useful if the questions for the speakers could be held until the panel discussion, that is try not to interrupt the speakers and their flow.

After the three sessions, later in the afternoon, there will be a panel session involving all of the speakers for us to catch up on anything that happens later that needs to be addressed to earlier speakers. And then, as Mike has said, there's an opportunity for the public to weigh in and if you want to do so, you need to sign in and let a member of the staff know.

Before going into the agenda, I think we have some folks on the phone. Would you introduce yourselves?

MS. LEHMAN: Linda Lehman at Hanford.

MR. HOWARD: This is Lane Howard, the Center for Nuclear Waste Regulatory Analysis in San

Antonio.

VICE-CHAIRMAN CROFF: Okay, anybody else? Hearing nobody else, I think that's it. Welcome. These introductions out of the way, I'd like to begin the first session concerning the applications of the materials and how they're important to performance assessment. Our first speaker is Dr. Chris Langton from Savannah River National Laboratory. Dr. Langton is a Senior Fellow Scientist at SRNL. Her areas of expertise include waste treatment, cementitious waste form designs, construction grout design, and the geo-chemistry of cementitious systems.

She has a master's degree in geo-chemistry and a PhD in material science and engineering from Penn State. Dr. Langton.

DR. LANGTON: Is this the format, stand here or sit?

VICE-CHAIRMAN CROFF: You can sit there as long as you speak into the microphone or we have a portable mike if you want to use that, someplace.

DR. LANGTON: Well, I was asked to speak on designing cement waste forms and the use of cementitious materials for contaminant management in the environment. I'll review some applications for use of cementitious materials in this -- in managing contaminants. I guess I should look at this. I can't figure out what to look at. The applications include waste treatment, containment, which would include vaults or casks, drums, culverts made out of concrete, environmental remediation, I'm not going to speak too much on that. I'm not really going to touch on that today, just to list it. Facility closure, I'll include some information on functional requirements as I see them from a person designing waste forms, go over material requirements for performance and processing and laboratory qualification of materials, field testing of materials.

And then I've included the landfill also because in order to design a waste form, any kind of waste form, including a cementitious waste form, you need to know something about the landfill or disposal environment that that waste form will be placed in. And then I'll talk, just briefly mention uncertainties and touch on risk reduction. The applications for waste include treating liquids, aqueous liquids, sludges, slurries and wet solids, in addition to some particulate material. Another application of cement based containment, the Savannah River site in South Carolina, we use concrete vaults. We also have culverts and casks.

Concrete at Savannah River site is used as a component for backfill in certain disposal applications and then it can also be used for trench liners and trench covers. For environmental restoration at the Savannah River site, we've used cementitious materials in basin and soil stabilization and in grout curtains for managing the flow of contaminated groundwater, for containing contaminated groundwater. And the grout curtain designs include gates to let the groundwater out after it has been treated or filtered in situ.

We've also done some facility closure at Savannah River site. The one that most people know about or the biggest one has been high level waste tank closures. We've also filled some small 20,000 gallon tanks that were buried underground in our disposal facility. We're looking at decommissioning another facility that was used to make the Plutonium 238 fuel pellets for the space program for heat sources to generate electricity in the space program. That program is just in the infancy stages right now.

As far as -- in this slide, I've just shown a schematic of how the materials are used. The saltstone facility -- why don't I not stand there. I'll stand here. The waste form is a saltstone in a concrete vault and then we also have a clean cap. The ground material -- the ground material in the slide would be like a containment or a fill material that's not radioactive and that's an example where three applications are used in just one disposal scenario.

This is a slide -- these are photos of the saltstone facility. This is the processing room. The mixer is up here and it goes through a series of pumps and finally pumped out to a concrete vault. There are two vaults in this picture, Vault 1, which is a single -- it's got six cells and then the second vault, a set of 12 cells. This is a picture of that first vault under construction. That landfill is very important in the waste form design. If you know what you have and you know where you're going to put it and what -- how the two sets of requirements interact, you can design in the middle to achieve your goals.

Currently, we're designing another type of vault for the saltstone facility that's a one million gallon prefabricated tank and that will be our -- that's the new concept for future designs. This is a schematic drawing of a facility closure. In this case the facility is a high level waste tank. We used several different kinds of cementitious materials. The one that's in contact with the waste which is this orange material at the bottom and this is residual waste. This is chemically adjusted to control the leaching, minimize the leaching in the -- of the waste on the bottom or the residual heal, a film material, an intruder barrier and then some just engineered features to protect the openings into the tank.

This is some photographs of a facility closing. This is one of the 1.3 million gallon waste tanks at Savannah River that's under construction. We had a portable grout plant set up to prepare the film material. These are two 30-cubic yard an hour plants. This photograph at the bottom is the grout going in, the first layer of grout going in. There was a pore over here, another pore and this pore is happening in the center where it's -- and this is the residual, tank residual material that was on the bottom. This is in the same tank closer to the top where we're putting in the bulk fill. That's this line but we had a -- we designed a flowable, self-leveling grout that flowed over the 80-foot diameter -- flowed 45 feet in each direction to make a fairly uniform surface.

These are some examples of waste and waste forms. This is a picture inside of a tank. This is not one of the tanks that we closed. This is one that has cooling coils. The salt waste in this tank is dissolved to a salt solution which is pre-treated, decontaminated and then intimately mixed with a cementitious set of reagents to form a slurry. This is a picture of the slurry after it's gelled. The picture on Slide 2 is a picture of the slurry as it's being -- after it was poured and -- after it's been prepared and being poured into the sample containers. It's very fluid material that, within 60 minutes gels to look like this and it sets within two days.

This last slide -- this last photograph is a picture of the residuals. This picture was taken from a test, a field test that we did before putting cementitious material in a tank. A small amount of the cementitious material did go under the waste. These are the solids. There was a little bit of liquid on top that was top dressed with dry grout and you see that material in here and then we -- the addition of more grout resulted in covering it up, encapsulating the waste. So those are some examples of our approaches to radioactive waste treatment that we've used at Savannah River site.

Now, the functional requirements of waste forms, of cementitious materials used for contaminant management and mitigation of mobility in the environment, in disposal environment include stabilization, fixation, we reduce the mobility of the soluble contaminants by either changing the chemical form and/or reducing the surface area that's exposed to the environment. Another function of stabilization fixation is to reduce the mobility of dispersable particles by macro encapsulation and increasing the particle size, again, to decrease the exposure to the environment. And then there's another function that we like to accomplish and that's to create a recognizable material that's distinct from the environmental media with the idea of reducing exposure and dispersion by human intrusion.

Waste form solidification, sometimes we treat liquid waste, tritiated water for example, to eliminate the liquid nature of that waste so it qualifies for disposal in a landfill. And then the functional requirements of landfills in which -- of concrete materials or cementitious materials that are used in landfills are to provide engineered barriers and those engineered barriers are intended to reduce infiltration of water and human intrusion and support the over-burdens to maintain the integrity of the capping material.

The waste form plus the landfill plus the environment make up the disposal system. And those disposal systems also have requirements. One of them or two of them are that they can be operated and that they can be constructed. I guess in the opposite direction, they can be constructed, and then they can be operated. And finally, that they perform for the required duration.

Now, if we talk about the design process for designing waste forms or other disposal applications using cementitious materials. First, we need to characterize the waste and get a waste classification. The waste classification is very important to determining the path that's chosen. We also need to select a disposal unit. Different disposal units come with different concentration limits, packaging requirements, handling requirements, and once we get through this process, we would down select a type of waste form based on an alternative study or some testing, past experience, and down selecting the waste form involves identifying potential materials for the waste form and processing for the waste form.

The processing depends on the amount of material that needs to be processed, the rate at which it needs to be processed, the location of the disposal site relative to where the waste is generated. And the material requirements typically depend on the contaminants. The next thing we do is test the waste forms to optimize waste loading and to measure properties. Properties are important with respect to demonstrating that we meet the regulatory requirements and properties that are important to the overall performance of the landfill.

The disposal -- the treatment disposal system is designed, that means, designing the processing building or the process equipment for making the waste form and making changes or modifying the disposal site if necessary. Backfill performance, we run performance assessment, modeling, calculation that evaluate how the waste form containment in the landfill and the environment interact. We address the risks and approaches to risk reduction and determine if there's a need for additional specifications or modifications. Sometimes we're in this process for a long time and if there's regulatory or -- regulatory guidelines that we meet easily, we're in this loop for a couple of years, two years. If we're in new territory, it could be a few decades.

Waste form testing; the important thing to get out of this slide is that the testing protocols that are in blue are in the literature. They're standard. We don't have any problems running those tests and we run the tests. You need to characterize the waste, again, select the ingredients and the proportions. Cure the samples, curing the samples, we cure according to ASTM methods. Sometimes we have to modify those methods but I'm talking about laboratory curing, not field testing here.

We test the samples. Processing properties, that's straightforward. Rheology measurements, leachability on a crush sample, we do EPA TCLP. Sometimes we change the leachate but run a similar type of test. There's an ASTM test where the leachate can be selected but again, it's a crushed sample. Monolithic sample, on the monolithic sample, we get an effective diffusion coefficient. Sorption is going the other way, from extraction. We take a material like a concrete and put the contaminants in simulated groundwater and absorb them or sorb them onto the material to get numbers, values for our predictions. Mechanical properties are straightforward.

The next one, the hydraulic properties, we have issues in measuring permeability, hydraulic conductivity of our materials or our waste forms, especially the waste forms that contain salts that interact with the leachate and in getting moisture characteristic curves for materials like concrete and our waste forms in the cases where they have very low hydraulic conductivities. Thermal properties, we know how to do that. I don't know if they're ASTM methods. We don't use ASTM methods, but we feel we have the general properties down.

Degradation to susceptibility, there are ASTM methods for concrete and there are standard concrete practices for designing materials that have low susceptibility to degradation for a variety of mechanisms. The one thing to point out here is that waste form are not concrete. They may have cement in them but they're not concrete. There's a whole body of literature, extensive literature on concrete but that's not the same as a -- as waste forms.

Long term aging; accelerated test methods and the evaluation and effects of the long term aging. A lot of these concrete methods, there might be a length change or usually it's an expansion that indicates cracking has occurred. Now, that's susceptibility -- that measures susceptibility to degradation, not exactly how that's going to perform in the long term or the rate at which that effect is going to take place. And property geometry changes we call cracking geometry changes, whether it's independent or coupled with -- independent, just one mechanism being evaluated or coupled with several mechanisms.

Now, in the landfill evaluation, again, there are standard practices. For the material property characterization and testing, for the cementitious materials and for the environment, there are standard tests. Constructability and offerability, there are engineering practices, there are codes, available materials, ALARA considerations and costs. Performance of the landfill, we evaluate landfills with lysimeters. At Savannah River we've had a series of lysimeters over the years. Some were -- we had three 30-ton blocks of our saltstone material and then some smaller 20-pound blocks, 30 of those 20-pound blocks disposed of in the environment where different parameters were measured over time.

The performance of the landfill can be evaluated in terms of sampling and monitoring of the waste form and barriers and the environment as the landfill is being used before it's closed. And then to evaluate the landfill again, we use this predicted modeling. We use flow and contaminant transport. We do this evaluation by commercial computer codes. We use deterministic to do the base case and sensitivity cases and we're using -- we've started to use probabilistic or uncertainty analysis. This predictive modeling besides data that's produced in the waste form and environmental characterization studies, the predictive modeling relies on scenarios and a number of assumptions, many assumptions.

There are uncertainties in the waste form design and data collection. At the top of the list is the analysis of the waste. Often we have limited samples or we design the waste form based on pilot scale or laboratory scale processing. There is sample variability. Detection limits, we have problems with low detection limits, low concentrations, and interferences. We have in the leaching absorption category, contaminant distribution and interaction between contaminants, competition between contaminants, the chemistry of the leachate. We can have leachates from groundwater to rainwater, the TCLP leachates, the ionized water.

In some aspects the chemistry leachate has a significant effect and in other -- on other parameters, it has very little effect. So there's no -- there's no worst case because -- or there's no conservative case for all parameters that are of interest. And then we have laboratory versus field conditions. There are issues with equilibrium, attainment of equilibrium, evaporation, flux extremes, exposure to leachate, and coupled effects.

For hydraulic properties, the low permeability makes the measurements difficult. The poor size distribution in the cementitious materials also makes the measurements and interpretation of the measurements over the long term difficult. There are scaling factors, hydraulic conductivity of a laboratory sample is not the same as a hydraulic conductivity over a 100 by 100 by 25-foot block in the ground enclosed in concrete. There's again, laboratory versus field aging. The curing conditions used in the laboratory are standardized to eliminate a variable so that other parameters can be studied.

Field aging is field aging. It's variable through the course of the time that the sample is exposed. And again, there are the coupled effects; hydraulic properties effect leachate chemistry, leachate chemistry effects hydraulic properties and all this is taking place over time. Thermal properties are not a particularly big problem or insurmountable problem. The impact of thermal transients during curing on the other properties -- the curing time is short. For concrete we would think of a few months. For the waste forms we might think of a few months to a few years. But the bottom line here is the effects of those thermal transients can be measured in a relatively -- in a reasonable amount of time and incorporated into the modeling. However, this isn't always done, again, because field conditions and laboratory conditions are different.

The durability, we have chemical and physical durability. There are events that occur, catastrophic events, continuance events. The timing of the catastrophic events is significant and the rate at which continuous events, if they are continuous in fact, are difficult to determine. It's relatively easy to identify susceptibility to degradation, but it's difficult to turn that susceptibility into a rate and extrapolate for years, 1,000 to 10,000 years.

There are coupled effects and that's the manifestation and the impact on the rates of other changes that are taking place. And I just -- I listed a few, again, mineralogical changes impact the mechanical properties, the hydraulic properties, the leaching properties. There's alkaline environment in some of our waste forms. There's a chemically reducing environment, all of which -- some of these specs could lead to cracks, the crack location, pattern, dimension, inter-connectivity and in-filling. Healing of the cracks is a good possibility over long time periods.

Now, I included the landfill because it is an important part of the overall objective here which is disposing of certain wastes. The landfills, performance time is up to 10,000 years or the time of maximum contaminant -- the maximum of the peak concentration in the compliance well, wherever the compliance well happens to be. The factors that effect that, extrapolate field conditions, there are seismic events, climate change, landfill use, intruder scenarios, toxicology, and we joke about it at Savannah River, but maybe in some 1,000 years, people will have evolved to be radiation resistant. We may be doing something, over-kill here with our requirements.

Also there are programmatic changes and regulatory and public perception changes that we have to deal with and these last two are not technical but they do impact the design of waste forms. Now, approaches to risk reduction; this is what we're doing at Savannah River site. We're statusing our current state of knowledge and our programs with respect to the current state of knowledge. Technical information on rates of change, I don't want to say degradation, just rates of change of materials over long time periods. We're reviewing regulations and DOE orders and interpreting how those changes impact our programs. We're reviewing to improve -- we're reviewing our strategy with the idea of improving our current and future disposal systems, performing sensitivity analysis for our current and proposed units, disposal units.

An example of a way of reducing the risk is to better capture the initial conditions and the initial material properties. So right now we have an emphasis on better descriptions and incorporating those descriptions into our long-term predictions, as a starting place for long-term predictions. Where there's a need is to develop innovative approaches for aging and waste form testing and then to develop a framework for interpreting the test results. This is probably -- this is a bigger issue than one would think.

Obtain peer review approvals for the current and future work and establish priorities for future work. And I've summarized it in this slide.

We know the waste treatment requirements. We know the disposal site requirements. We pre-treat the waste to get from here to here. We may need to modify a disposal unit. We design a waste form, a waste form production process and a packaging process, packaging system, perform the performance assessment and through testing and inputting that would be testing models. Then we evaluate the risk and if we find there's acceptable risk, we can treat and dispose and if we don't we come back up here, start with the pre-treatment.

Pre-treatment is really inventory reduction. We can remove some contaminants, remove bulk waste, remove waste, and start the process over. Now, this looks simple but issues to be pointed out here are that it's unclear at this time what it takes to get through this risk, acceptable risk decision point to a yes. We don't have a clear set of criteria. This would be like going into court and you'd need to know what evidence needs to be presented to get a certain verdict or what level of evidence, how much of that evidence. And I'm not sure that we have this right now. For example, what case needs to be made for this yes decision.

Right now, we're looking at using

predictions, using scenarios for intruder analysis, using extrapolations of groundwater contaminants, but we don't look at the ability to remediate and is our situation that we're coming up with if there was a problem, if we didn't fully address the risk or if we didn't analyze the testing, if we didn't do a complete set of testing and I don't know how you'd do a complete set of testing for 10,000 year predictions, but if we could do that, what if we come up to the acceptable risk and find out that remediation, if there is a problem is known technology and people have been remediating groundwater for 50 years using the technology.

Remediation is not included in this risk analysis to get us over here. And risk reduction -- I'm sorry, remediation is a viable strategy for shallow land disposal, maybe a lot more so I would think than for geologic disposal. But we know sort of who makes this analysis, it's DOE, NRC, National Academy of Sciences, and other state and federal regulators, the public, our peer group. We know who the judges are, and that's expert witnesses, our peer reviews, but they can come down on either side of an issue. I mean, how you present enough case to get into the -- to go -- to treat and dispose is unclear to me. And that's something I pose to this Committee is to help us figure out. That's it. Are there any questions?

VICE-CHAIRMAN CROFF: Thank you very much. If we could, I'd like to defer questions until after out next speaker and then we'll have at it. I suspect we'll have one or two.

Before moving on, to the speakers, you have your choice up front. You can either stand fairly fixed as Dr. Langton has done and speak into the microphones that are there, which means you can't move around. Or there is a portable microphone there, if you like to wander around a bit when you speak, that's an option also. So it's your choice.

With that, our next speaker is Dr. David Kosson. Dr. Kosson is a Professor and Chairman of Civil and Environmental Engineering at Vanderbilt University. He's carried out research on leaching processes and performance assessment including cementitious and other waste forms for approximately 20 years. Dr. Kosson will talk on conceptual models and approaches of understanding long-term performance of cementitious waste forms.

DR. KOSSON: I have trouble standing still so I might as well use this one. Okay, what I wanted to do was to lay the framework for how -- oh, that's no good at all, can't get too close -- about how we think about the various waste forms and their long-term performance with respect to leaching. I want to acknowledge that the work I'm presenting today and the concepts come out of collaborations within my own group at Vanderbilt and the department, other faculty members there, collaborations that we've had with the Netherlands Energy Research Center for about 20 years as well, working very closely, DHI in Denmark and then also working with some folks at the Savannah River National Lab. You just heard from Chris, and also from Pacific Northwest National Lab, dealing with some of the Hanford programs over the various years.

When looking at it, Chris gave an overview of the various disposal scenarios involved but what I wanted to make a point with this slide is that you're looking at the performance of an overall disposal system and that system includes both the waste form, it can be concrete structures that the waste form is deposited into and other barriers and caps and drainage layers that can be important. So you're looking at overall performance, not only the waste form and the influence of the external conditions on that waste form, but also migration of constituents from that waste form such as sulfate or chloride which may, in fact, influence the containment structure such as degradation of reinforced steel and concrete systems.

The motivation why we look at these things is for a number of reasons. I'm sure you're familiar with many, if not all of these, but the perform assessments and the waste incidental to reprocessing determinations or 3116 determinations and Chris went through a number of these different applications. But what I also think is important is to recognize that cementitious waste forms are one of many waste forms that are being considered for near surface land disposal systems and as a result, you need an equal comparison base to understand what the performance of these are. And frequently what's used as over-simplified methods, do not give you a good understanding of the various processes the occur over time and their interactions to give you a comparative base say between a cementitious waste for and say a steam reforming waste form that may be under consideration.

So ultimately, then you have the performance assessments, but then you have your waste acceptance criteria which can be backed out of that.

Your operational controls, how do you deal with day-to-day quality control and performance and then also when you're trying to make decisions about future waste forms. We're at a time right now where the country is considering reprocessing again. We're considering different future nuclear fuel cycles. Looking forward, these fuel cycles are going to generate waste. Some of those wastes are going to be targeted for near surface land disposal and how do we evaluate them?

Often for the waste that we see right now, the constituents of concern are some are long-lived and mobile. Tc-99 is certainly one of the key ones that's of concern. Iodine 129 often. And then in the mobile and not as long-lived cesium-137, strontium-90 and then often at some of these wastes we see nitrate in very high concentrations and tritium which are not radio nuclides but also have the potential to impact both the performance of the system and some of the constituents of interest down gradient.

So some of the broader questions that you're typically trying to address is what is the appropriate type of waste form disposal system and location for specific waste, because, as I mentioned earlier, it's that overall system and the local conditions become important; to estimate the long-term waste form performance and disposal system performance, to establish the treatment criteria and to define monitoring requirements. If you understand the mechanisms, I would suggest what you want to do is to monitor pre-cursors to impact so that you can be pre-emptive in your system rather than going into remediation mode after the fact.

So what I want to do then is overview what we consider to be the primary factors and mechanisms that you have interactions as you view these systems and one is your system integrity and you've got to look at the coupled effects of the engineered and institutional systems. And often you see in the regulatory environments and some of the other regulatory programs, you engineered barriers are separated in terms of performance monitoring, integration from your institutional performance and bring those two together, I think is very essential as you look at the integrated system.

From the waste form performance itself, I'm going to talk about the physical integrity, water contact, the moisture status, your oxidation rates and extent and the chemistry and mass transport and then sum that up with how we view it in an integrated approach.

So with the physical integrity, you can start off with an attack monolith but over time, you go to a stressed matrix and you have some micro-cracking, macro-cracking occurring and then ultimately a spalled matrix. So what may become initially a diffusion controlled release, your mechanisms of release vary in your varying degrees of infiltration over time as you look at the system degradation. So over time you may see convective flow through it and your ultimate release at this end state may be based on what the equilibrium conditions are, local equilibrium in that long-term, even though your initial release and for some considerable period of time, may be dictated by the boundary conditions and those diffused responses.

With moisture transport, it is an important controlling variable which I think is often overlooked in these systems. The reason why it's important is not only because of the percolation through the system, but your moisture status in the system, your pore structure and whether you're saturated, say a capillary saturation or whether you're unsaturated has an important impact on the transport processes that occur.

You can go through several different scenarios. One is where you're saturated and you have a continuous liquid phase and discontinuous gas phase. At that point, you have liquid diffusion processes which become very important and gaseous diffusion processes become relatively unimportant because it's in isolated pockets of vapor space. However, you have a transition phase where you have continuous liquid and a continuous gas process phases and at that point, your liquid diffusion and your vapor diffusion become important because you can have gasses for example, oxygen or carbon dioxide infiltrating into the material both through the liquid phase and through the gaseous phase.

And then you have completely dry or -- which you'd probably never get to in field conditions, but you have what's also referred to as insular saturation where you have a discontinuous liquid phase and a continuous gaseous phase. When you have a discontinuous liquid phase, you don't have leaching occurring obviously, because you have no complete pathway but you still have vapor transport occurring so you have oxidation, carbonation, other reactions still occurring.

And if you look at this from an overall

perspective, if you look at the physical resistance or D/D0 for your diffusivity, what you see is you go through these boundary conditions. As you increase saturation, your liquid diffusivity increases and your gaseous diffusivity decreases.

Now, how is that impacting? If we look at oxidation rates, and that's been a very important aspect with respect to Tc-99 looking at the overall performance of that because of the difference in mobility under reducing conditions where it's relatively immobile, we're under oxidized conditions, it's much more mobile. And what you find here is your oxygen is really -- has to consider two-phase system that depends on the moisture content, as I mentioned earlier, and your oxygen transport via gaseous diffusion can be important depending on the saturation.

If you're in a less than saturated state and you have a continuous vapor pathway, then your diffusion flux of oxygen in the gaseous phase can be up to five orders of magnitude greater than diffusion through a liquid phase. So you've got a great disparity between the two diffusive rates. If you're in a continuous liquid phase and discontinuous gaseous phase, then only liquid phase diffusion should be considered. But understanding the moisture content and the moisture status becomes very important, as I mentioned where you are in that curve.

In most cases from what I've seen that moisture status is not well-defined or well understood under the field conditions. Carbonation again, your moisture impacts it and the way that that does is your carbonate formation, you're basically reacting carbon dioxide with the alkalinity of the matrix and forming a carbonate or under extreme conditions a bicarbonate precipitate. If you are under saturated conditions, that tends to be on the exterior boundaries that that occurs. If you're in partially saturated conditions, then you get migration further in.

The actual rate and extent that this occurs is a consequence of the alkalinity of the material and your external carbonation, carbon dioxide source, be it through soil gas, which can be elevated over basic atmospheric gas because of biological processes in the adjacent soils or also you can be talking about coming from carbonate saturation in groundwater such as some of the systems that you see out at Hanford, for example. You have a carbonate saturated groundwater and that will react and precipitate with that.

Now, what is the impact of the carbonation? One is that it can change the speciation or the absorptive sites that you have in the matrix. I illustrated this here looking at a cement matrix, one that is uncarbonated and the arsenic liquid solid equilibrium that occurs, that typical curve. And then under the carbonated circumstance, you see that this was the typical curve for that same material. It can be very dramatic. It's ph dependent behavior. Also, you have the potential for pore blocking because of precipitation that occurs at the interface and it changes the ph grading within the system.

So that also if your release is coupled to ph in your system, then that's changing in a gradient within the material itself. So your carbonation can either have positive or detrimental impacts on the long-term performance of a material. The leaching of major constituents, basically, you've got to look at it in terms of gradients that you have within it and your local chemistry is controlled by the major constituents; your alkalinity, your calcium, other major constituents that are being released and that, in turn, is setting up what you have in terms of your pour water chemistry, oxidation fronts and ph gradients that you have within the system.

So when you look at this, if you don't consider that, then you can lose the effectiveness of some of these highly non-linear processes within the material and some of the boundary layer effects. The trace constituents, then follow some of the bulk constituents and that local pour water equilibrium chemistry. So your release would then be dependent on the moisture conditions because that effects your diffusivity, your continuity of your liquid base, your ph gradients and your oxidation or your redox chemistry within the material itself, and boundary layer formation. I'm going to talk more about that in a few minutes.

But I just wanted to illustrate the complexity of the process a little bit and how over-simplification can result in misleading results. If you took -- this is a cement stabilized waste form, a sariate (phonetic) waste form that was analogous to one that's being considered out at Hanford. And in turn we did monolith or tank leaching for more than a year on that study. And what you see here, this green line, is the projection that you would get off of using ANSI 16.1, a short-term rapid study and a simplified diffusivity that would come out of that or leaching index and if you projected that over for a year, and then the actual data as to what the flux conditions are. And what you find is after just one year, you're off by two orders of magnitude. So and if we're looking at projecting much longer, if you don't take into account the coupled effects within the matrix, and that pour water chemistry, those two projections diverge considerably.

So ultimately, what you're look at is integration of the chemical degradation and the physical stress and they have integrated effects. They are synergistic. Some are antagonistic that you have to look at and you see the physical stresses in terms of loading, drying, shrinkage, seismic effect, settlement, but then also you have expansive reactions which can couple with that, including carbonation, sulfate attack or corrosion reactions that are happening at rebar. And those expansive reactions both change the local chemistry and can open up cracks, micro or macro cracks, within the system.

So what I want to do is just illustrate a few of these and wrap it up with how we look at these as an integrated system. And this is just an example where we were using the Tc-99, Iodine 192 and secondary waste from vitrification with a prototype matrix to understand the different factors that would be involved and using a reducing grout and we used rhenium as the surrogate for Tc-99 and stable iodine as the surrogate for iodine-129 to simplify the laboratory handling. Also I want to point out, we're using distilled water as one leaching extractant as is typically used in ANSI 16.1 but also we're using a synthetic groundwater which is a stimulant that's often used at Hanford to reflect the carbonate, bicarbonate effects that you see out there.

Now, when you look at equilibrium, what we -- the way we view this is understanding that leaching behavior as a function of ph, and then what we do with that is back infer from looking at the whole range of constituents that are present, a geochemical speciation model for that system so that you can look at the coupled chemistry within it that considered both solid phase dissolution and saturation, solid phase dissolution kinetics, absorption processes on the iron, aluminum, silica type surfaces, iron exchange processes and coupled with redox and the various ionic strength effect. So for example, looking at high ion strength that you have initially in the pour water using a modified pitzer (phonetic) type of approach.

So what you see here, just to illustrate, for strontium for example, your initial waste form is about ph 11.5 to 12.5 and you'd see initial solubility constraint of strontium or leaching at about 100 micrograms per liter but as you go towards the fully carbonated waste over time, you would shift along that curve and that can increase by two, three orders of magnitude. Here you see it at about 10,000 micrograms per liter. And you seem some, the rhenium does not have that characteristic behavior. Uranium, for example, has also a very typical characteristic behavior, not impacted in speciation by the carbonation as I'd shown earlier for the arsenic case, but is impacted dramatically by the ph changes that are occurring.

When you look at the mass transfer results and these are again, in the distilled water type testing, here I'm just comparing again, for various species, the rhenium, the selenium, calcium and strontium, the difference between the ANSI 16.1 projection and what you actually see over a year of testing in that matrix. And again, you can see up to two orders of magnitude variance over just one year of testing.

Then when you go to synthetic groundwater, it gets interesting. What we're looking at over here, and I just want to focus on selenium because it's the best example to illustrate it quickly, is over time you see the carbonate precipitation on the material. Here you see a little bit of the white on the edges of the surfaces that are occurring and we saw that carbonation that precipitation beginning right around the six leachate and what you see here, this is the distilled water line, for ANSI 16.1. This is your simulated groundwater and you see the dramatic effect of the precipitation in terms of pore blockage and the change in some of the chemistry at that interface.

The typical ANSI 16.1 type models are effected and cannot capture these boundary layer effects and what you see here in comparison where before with distilled water we were about two orders of magnitude, now we add on about another two orders of magnitude of variance from that type of projection that can occur. So how do you pull all this together and begin integrating these different processes. One thing that I want to make sure to separate in people's mind is the difference between the observational experiments that are used to develop the conceptual model, your parametric experiments that are used to parameterize models and projections and integrative experiments which are independent to do validation of models, because often we see model verification but not validation, even short-term validation over one to 10 years, given what the field conditions are allowed much less none of us are going to wait around to see validation over 10,000 years.

So then once you have at least short-term validation that you've coupled the processes correctly, then I think it's appropriate to look at your field scenarios and your long-term performance estimates, sensitivity analysis and uncertainty analysis. We published an overarching framework for leaching assessment which is currently under adoption by EPA right now as well as the European EU DG environment is concerning a framework under a number of applications over regulatory development and what this framework does is it looks at integrated approach to leaching assessment. It says that you measure the intrinsic leaching characteristics of a material and then you use that in conjunction with mass transfer and geochemistry models to project different field scenarios.

So you're looking at the leaching is a function of ph and liquid to solid ratio or tank leaching monoliths as I showed earlier and coupling out of that what your model would be and your model parameters for the various conceptual models. Then what you're doing is you're evaluating the release in the context of the field scenario. What are your important external factors such as carbonation, oxidation, mineralogical changes and hydrology and then using coupled geochemical speciation, mass transfer models to estimate release for alternative scenarios.

Why this integrated approach? TCLP, for example, may have regulatory standing for some of these applications, has no valid technical basis for application to cementitious waste forms in these applications. Similarly, oversimplification and some other approaches, as I pointed out, can lead to some misleading results. But importantly from this approach, you can take multiple scenarios from a common data set and project them out. So what we do is use coupled laboratory testing to get model parameterization and then develop that into a geochemical equilibrium model that considers the various factors I mentioned earlier and then take that into field scenarios and mass transfer modeling. You've got this so you can look at it.

The way that we do it, we use a program

that's been developed and in development right now called Leach XS which is based on ORCHESTRA as the geochemical speciation reactive transport modeling, couple it with a materials data base, a scenarios data base, and then regulatory criteria and ultimately that models the various materials and scenarios. EPA is evaluating this right now as a decision support pool, looking at it going forward in some of its applications.

Why? If you take a look, what it allows us to do is to follow the speciation, the geochemical speciation, as a function of ph and location and conditions at each location in a matrix over time. This is just an example of how you can follow the chromium speciation, the aqueous phase, and see the difference between the contributions of the calcium chromate, for example, that's dissolved, the chromium 3 that's dissolved at various conditions, comparing it to the experimental data, the bright red dots, but also, it's a partitioning between a liquid and a solid phase, where it takes into account the free dissolved which is this is that whole thing in the green over here, but then, for example, that which is absorbed onto iron oxides.

This yellow fraction over here, for

example, is barium sulfate chromate speciation over there and over in here you see the ettringite formation with the chromium. Now, if you couple that with your reactive transport, then you start capturing the boundary conditions. If you start looking, for example, that interaction between the Hanford groundwater and the matrix interface, and here I've got the leachate cement material, simulating that but what you see is that that interface you get brucite precipitation and calcite precipitation, again shutting off the pore structure and capturing those changes over time that I showed experimentally.

And then when we couple this fully, we look at all of the different species that are present and can do it in a layered effect and then for example, for this case, we were looking at cement MSW bottom ash and soil, but you see areas where you get precipitation, where you get the boundary layer effects and you're tracking the full speciation at each point in the matrix over time. So that that allows you to capture these various long-term effects that are occurring.

So just to wrap it up, then the suggested path forward from my perspective is to process a continuous improvement, trying to capture the state of the art in these assessments and both for current assessments and to future nuclear waste management, and to define both the short term and the long term needs and to look at experimental studies, coupled with model development and validation. I can't say that validation being important enough. And really trying to capture the formation, the effect of the boundary layers. The moisture transport and status, I think is critical and often overlooked.

The oxidation rates are closely coupled with that. And to bring that together in terms of a full geochemical model that couples your local equilibrium mass transfer for the key systems and then as you go down, trying to couple that with the physical effects as well as you change from and intact matrix to a spalled matrix progressively.

So in conclusion, there are a number of these processes currently aren't included in the current DOE performance assessments that can impact constituent release. In some cases, I think it's over-simplified being very conservative. I showed several orders of magnitudes difference. In some cases it may not be conservative such as if oxygen diffusion is important in this moisture status or these materials and the effect of technicium potentially. So it's important over time to improve the understanding for both near term and long term DOE waste management decisions and we've been working with Savannah River National Lab as well as others, as I mentioned earlier, to develop the various system components and integrate this for model systems. So thank you very much for your attention. I know I went through this quickly but it was a lot of ground to cover.

VICE-CHAIRMAN CROFF: Thank you. I'll give you a moment to be seated and then we'll go with the questions.

Dr. Hinze?

MEMBER HINZE: Well, I was very much struck with Dr. Kosson's comment that over-simplification can lead to misleading results. I think that's the bottom line to what you've said here today. The -- I was also struck with your concern about short-term versus long-term validation in the performance assessment and that's really where the rubber is attached to the road. Can you give us your expert opinion on the major sources of uncertainty in the long-term validation and what are their impacts and how do you know this?

DR. KOSSON: Right now, the major

uncertainties that I've seen -- I'm sorry, does that help?

MEMBER HINZE: That helps.

DR. KOSSON: All right, the major sources of uncertainty that I've seen looking at these various systems and how they're implemented, one is dealing with the boundary layer effects, which could be very important. The second is the neglect of the geochemistry within the pore matrix and the boundary and the gradients that actually exist which are highly non-linear in these systems. A third is understanding the moisture status of these systems over time, both initially and over time and how that impacts vapor phase processes, both in terms of carbonation, oxidation. And then in terms of validation, there has been very limited comparison of modeling results both with data that may be in hand or obtainable in the short term meaning one year to a decade type data, which to me is reasonable time frames when we're looking at the lifetimes that we're looking at on these and the rate of movement on some of these processes.

The long-term is extraordinarily difficult. You can look at historic systems. We've looked at concrete, for example, from Roman ruins and things of that sort to validate different pieces of it, but I think long-term, you don't know the initial conditions well, you don't know your boundary conditions well. So getting back to your question, those are what I think are your major uncertainties.

MEMBER HINZE: Hardly any at all.

DR. KOSSON: Hardly any at all. But I tried to point out the magnitudes that some of these have.

MEMBER HINZE: That's very important. Let me ask about the vapor aspect of it and the mobility through the cement. We see -- whenever we see the picture of the cement we see this model and you've shown how the cracking can lead to spalling and so forth. How well do we know those mechanical/hydrologic properties and their change and how well can we model those in cement?

DR. KOSSON: I think some of the other speakers are going to address that in more detail but the micro cracking and the larger cracking has been a separate area of model development in cement based system reliability. The integration of those models with the chemistry, the coupled effect, is very limited in its implementation right now, I believe.

MEMBER HINZE: I was very struck with both you and Dr. Langton commenting about the coupled processes which is a major factor in the whole uncertainty in the performance assessment.

DR. KOSSON: If I can just add one more comment; it's what you'll see typically in models, either strength comes from the physical durability side or strength comes from the leaching side. Getting the coupled strength from both of those, is much less prevalent.

MEMBER HINZE: Yeah, thank you.

CHAIRMAN RYAN: Dr. Langton, on your Slide 16, you had the diagram there for acceptable risk and you talked a little bit about that. Have you ever used a probabilistic risk analysis technique to try and get at what the range of risks might be and you know, based on what you know and don't know and how that might help?

DR. LANGTON: We have -- yes, at Savannah River we have but I was getting at a larger issue that -- at Savannah River we have started using probabilistic analysis. I was trying to get at an even larger issue and that would be -- an example would be, so exactly what is the risk of exceeding four millirem at the monitoring well, hypothetical monitoring well, for technicium, for groundwater that contains --

CHAIRMAN RYAN: Sure.

DR. LANGTON: What is that risk at 5,000 years? Is it one -- well, what is it and how do we go about mitigating it. All of the modeling contains a series of assumptions and scenarios that are hypothetical scenarios.

CHAIRMAN RYAN: Well, I think that's one of the values of PRA is that you can actually analyze that and you can evaluate each parameter for its contribution to the total system risk.

DR. LANGTON: That's right, but if you -- when we do that, some of the scenarios result in failure and I don't know if those scenarios are valid or -- I mean, we can always come up with scenarios that result in failure.

CHAIRMAN RYAN: Sure.

DR. LANGTON: It's who's going to evaluate that evaluation? I guess that's my question.

CHAIRMAN RYAN: Yeah, no, and I understand the point that sometimes the -- a regulatory requirement tends to be deterministic and it's hard to match a probabilistic analysis against a deterministic requirement. That's fair enough. But I think it's hard to gain insight into what risks are and what uncertainties are without doing some kind of a more rigorous analysis, say a one off, a boundary case.

DR. LANGTON: No, we agree with that --

CHAIRMAN RYAN: Okay.

DR. LANGTON: -- and we're doing that type of analysis but the question is even -- is bigger than that. Again, we don't take any sort of remediation strategy into account to mitigate any risk. We just -- just looking at risks, not just, we are identifying risks and we're making improvements but that doesn't mean we can't even improve our scenario that resulted in negative risks.

CHAIRMAN RYAN: There's lots of good work to do. Sure. No, I appreciate that point. Turning to the second presentation, Dr. Kosson, your Slide 16, I took away from -- 16 and 17 actually, it's your curve showing mass transport tests and synthetic groundwater tests, I took away from that, that your prediction, your green line, which is a prediction of the model, maybe we could throw that up on the screen, is that possible? 16 or 17 either one. Thank you, Michelle.

All the data diverged from the model in every case. Wait a second, let's get it up there. No, that's not it. There it is. Slide 16, please.

There we go. And as you pointed out, you know, it rapidly becomes orders of magnitude of deviation, in this case in probably the positive direction. It's less getting out than the model predicts but I would say a model that has that pattern of divergence isn't conservative. It's just flat out wrong. It doesn't match the data. So help me understand these results in the context of uncertainty analysis.

DR. KOSSON: Sure. What I was trying to do was the green line is the model that is typically applied in these cases, the ANSI 16.1 projection of constant diffusivity.

CHAIRMAN RYAN: Right.

DR. KOSSON: So I wanted to compare what -- even over a short term, over one year, what the typically assumed model that's implemented would project in comparison to what actual data is. If you looked at the full coupled geochemistry mass transfer model which I didn't have time to really get into in detail here, just gave you an overview, that would track with the -- that's a very different type of modeling approach.

CHAIRMAN RYAN: Gotcha.

DR. KOSSON: My goal in putting up that slide and the next is to show some of the deviations between -- that can be caused by over-simplification some of which is occurring now. That's your green line which you typically see and what reality is or at least on one year, you know, short term experiment --

CHAIRMAN RYAN: And I --

DR. KOSSON: -- which is longer than usually carried out.

CHAIRMAN RYAN: I take that as a real important caution that, you know, unless you have some fairly detailed understanding of your uncertainties and their behaviors, for lots of reasons, phenomonologic reasons, chemical, physical, scale, you know, all those reasons, you really don't know -- you really have the risk of not knowing whether you're diverting from what reality is when you model and that's a great caution to carry away.

And I guess maybe we'll get into it later on through the day is to think a little bit more and talk a little bit more, and I'd be curious to hear all of your views on how do you get at system risk or system uncertainty. That's a big question, I know.

DR. KOSSON: Do you want me to comment?

CHAIRMAN RYAN: If you want to take a crack at it now, have at it.

DR. KOSSON: Okay, just a little bit, I

think you start off to get to system risk and you're starting point is the best conceptual models that you can have for the system and then look at the individual uncertainties and lump them together trying to get an overall system uncertainty.

CHAIRMAN RYAN: Step-by-step.

DR. KOSSON: Step-by-step.

CHAIRMAN RYAN: Gotcha. Okay, thanks. It's great, appreciate it.

MEMBER WEINER: I'd like to thank both of you for something that -- for very interesting and revealing presentations. I'd like to ask Dr. Kosson, since you get transport through the concrete, transport of solutions basically, can you use that to bring about chemical reactions which will stabilize your waste? In other words, can you -- can you make a precipitation reaction happen in the grout itself?

DR. KOSSON: I believe that by understanding the chemistry in some of these reactions that occur, you can design and control your systems to take those into account and to -- without going too far in the way I want to comment, but I think what you're suggesting, Dr. Weiner, is indeed possible but if you're basing your evaluation on models or evaluations that don't even capture these effects, then there is no incentive to design in that way because you can't take credit for it.

MEMBER WEINER: Well, shouldn't we be looking at models that do -- I'll tell you what prompted the question is that many years ago in a study of how do dispose of nerve gas at an arsenal in Denver -- outside Denver, Rocky Mountain Arsenal, the suggestion was made and it was quite a good one, drop it in the ocean because the salt water infiltrates and hydrolyzes the stuff and make a relatively benign product. Certainly, you get rid of the toxicity. So I was just thinking, couldn't you use the opposite effect and shouldn't that be incorporated into some models?

DR. KOSSON: I think so, yes.

MEMBER WEINER: Okay.

DR. LANGTON: At Savannah, we're looking at landfill amendments. The schematics that we're shown are simple but there are other features that could be added to make improvements and then the follow-up on that would be that there are amendments that could be made post-closure, post-completion of the landfill which would fall into the remediation category and yes, that's out there as something that's available and uses the same chemistry and known engineering practice but is not to the point of being included in any modeling or risk assessment at this time.

MEMBER WEINER: Which brings me to the question that I have for you, Dr. Langton. And I suppose you've partly answered it. What is preventing you from including remediative factors? Is it regulation, is it approved modeling, why can't you go there?

DR. LANGTON: It's at least a perception that we will -- we need to design today and construct today so that when the landfill is closed or 100 years after it's closed at some period into the future, a short time into the future, we can walk away from it. It doesn't require any maintenance and it's a big problem in durability assessment because one way of defining durability is performance of design function for design lifetime with a certain amount of maintenance, however much maintenance is decided upon up front and we, for some reason, historically, don't know for some reason, have the idea that that's zero maintenance.

And 10,000 years is a long time to design for and to address risk over that time period and eliminate maintenance at the same time.

MEMBER WEINER: I think you've raised a really interesting point to look at in designing regulation, both of you have. I just had one more question for Dr. Kosson. And that is that I'm a little surprised that with uranium the ph effects overshadow the carbonate effects. Is that what you've observed? Have you done this with other actinides?

DR. KOSSON: The results that I showed for this matrix was the first matrix that we did uranium evaluation on. When you look at the geochemical modeling of this system, that's not surprising for the system, but we have not scored it more broadly for other waste systems.

MEMBER WEINER: I see, thank you.

MEMBER CLARKE: I have a few questions and I think they may be a little premature, because I know we have several more talks. Allen has planned a full day of really interesting stuff, but let me just kind of give you a heads up of some of the things I'm interested in. One of them was that until Ruth asked her question, I had yet to hear the term maintenance from either of you. And I would suggest that at least in an ideal world, free from other constraints, that it would go containment, intervention, and remediation would be the last resort.

So in other words, if we want the systems to perform for a long time, I can't see anybody doing that without intervening at times and maintaining them and that suggests to me that we should design them to facilitate that. Now, I know that goes against the school of thought that says we don't want to burden future generations with things that we've done and we want to design these facilities so that we can implement them and they'll take care of themselves. So I'd just throw that out as kind of food for thought.

And the other thing I didn't hear much about was monitoring. And Dr. Kosson raised the importance of moisture content. That is being looked at as something that can be monitored in landfill covers and there is a prototype systems, there's a prototype at Hanford and I think there's a full-scale system at Fernald, where moisture content is being monitored in the landfill cover. Is that something that could be done in these vault systems, in these concrete containment structures? Like I said, I just throw that out for both of you.

DR. LANGTON: I don't see why not.

VICE-CHAIRMAN CROFF: Microphone.

DR. LANGTON: Yes, it certainly could be

done. We are not doing -- we are not monitoring our concrete vault moisture characteristics currently or the saltstone, but I don't think it's impossible. I think it's doable. For the longer time periods that we're interested in, which a long time period for field monitoring might just even be a year, longer would be better but certainly programs that need to be developed and implemented.

MEMBER CLARKE: That is certainly the case, I'm sorry, David. Certainly the case from what we've seen at landfills that if they're going to fail the high probability of failure is assumed because they weren't constructed properly, they weren't designed properly.

DR. KOSSON: I just wanted to comment, Jim, that it's also important to keep in mind that it's easy to project these as steady state conditions or constant conditions, but we've got to recognize that moisture as well as infiltration and other -- a host of other conditions area periodic or intermittent type of effects in response to climate cycles, you know, winter/summer type effects but also precipitation events, for example, impact the moisture content.

MEMBER CLARKE: Episodic.

DR. KOSSON: These episodic events are very important, I think to be captured because your outcome from an episodic event modeling can be very different than what you get from continuance average event.

CHAIRMAN RYAN: Can any other panel members address Jim's question?

VICE-CHAIRMAN CROFF: Barry?

DR. SCHEETZ: Your concern about monitoring; through FHWA there are programs going on through our organization at Penn State right now, where we are instrumenting bridge decks with a 25-year monitoring plan where the embedding instrumentation has a -- is connected to a cell phone which calls home every day or every week or every month and then automatically downloads. So these autogenous sensors and the ones that you referenced out at Hanford are available for pressure, for tilt, but they're just now coming on line for moisture. I don't know of any decent moisture sensor, particularly one that you're going to be able to embed long-term and leave it there for 20 years or more. Rachel may have -- it looks like she has some ideas there.

The specific conductants that the folks at Hanford are using are very good. They're very durable, but they're -- you know, they're not going to function in the long term that we're looking at there. These so-called intelligent aggregates is something that needs to -- you know, that's a very specific need that is out there to be developed that you can put into concrete and just applications here are one application but they're in -- in the civil infrastructure they'd be invaluable.

MEMBER CLARKE: Thank you. How are we doing on time, Allen? Can I ask one more question?

DR. DETWILER: I would like to add something on monitoring, just as a general conceptual look at it. I think that over the long term, Dr. Scheetz is right, you're not going to be able to use instruments over an extended period. For example, if you embed something in the concrete, you can expect that after a certain time, whether the battery runs out or the leads corrode or whatever it is that makes it impossible for it to continue to work and it may be something as simple as electronic computational methods that we use just become obsolete and so they can't talk to each other any more.

And so I think if you were really -- if you really wanted to look at long-term modeling as in decades and centuries, you're not talking about active systems but more like passive systems where, for example, you have access ports that you can put different kinds of probes in when you want to or you put benchmarks that you can sight on and then you use whatever instruments you have that -- you know, in that year or that century but you have something permanent that you can sight on so that that's always the same. And your records, then, may be something very different from electronic records or something that you use in addition to electronic records, like pencil and paper because you can keep those longer or you have -- you can still read them 10 years, 20 years, 50 years later even though it may have faded ro started to deteriorate. At least it can be read much longer than say a floppy disk.

So you really would have to consider some of those long-term things as well and then have some overlap when you're switching from one measurement to another so that you at least are satisfied that you're still getting the same thing.

MEMBER CLARKE: Those are good comments. I appreciate them. I think the approach that is being taken in the way of recovery is just to put in access ports and incorporate that into the design. As I recall, I think in another site they actually retrofitted the moisture content measurements. You know and it strikes me that even if we couldn't do this for, you know, short-term versus long-term, what does that mean? You know, if we did it for as long as we could, it would be valuable information on some of these systems as we begin to implement them and look at their performance. So my concern is that everything that's being done up front is good stuff and it's good science, but if we don't get it right up front, then where do we go from there and I'd hate to go right to remediation. So I'm raising questions about monitoring, designing to monitor, which I don't think we do, and designing to maintain, which I don't think we do either.

So those are my comments. Thank you.

VICE-CHAIRMAN CROFF: I've got a couple of questions here. I think the first one I may struggle to articulate but I'd like to address this to Dr. Langton. In one of your early slides you had a list of applications of cements, where they have been used. It focused on Savannah River but I know you're familiar with what's going on in a lot of other places. What wasn't so clear to me is in how many of those applications did the Department of Energy or whomever try to take credit for more than just filling up a void space, try to take credit for the hydrologic barrier or the chemical barrier or something like this.

DR. LANGTON: I don't think we have tried to take credit for hydrologic barrier for waste forms. We've taken credit for chemical stabilization of specific radio-nuclides and by taking credit it's reduced the leaching in our low level waste disposal facility. Physical integrity, we've taken credit for waste forms maintaining their integrity and that would be drummed waste forms that went into this low-level waste disposal facility.

Taking credit for hydraulic conductivity is typically the function of the concrete vault, the barrier in our disposal facility, not the saltstone facility but in our low level waste disposal facility. That -- the concrete structure is intended to reduce infiltration.

VICE-CHAIRMAN CROFF: And the performance assessments reflect some credit for this?

DR. LANGTON: Yes, the -- it's the E area performance assessment takes credit for that, yes.

VICE-CHAIRMAN CROFF: Okay. So --

DR. LANGTON: There are two places, E area and Z area performance assessments for the concrete vault -- we have several different types of concrete vaults. We also have a disposal system referred to as containment ingrouts where we're poured grout around a large object that's disposed of, so that is an infiltration barrier also. But there are waste forms that we've made that are drummed where that's not taken into account. We solidify the liquid, stabilize contaminant, reduce the surface area but not so much -- it's not related to hydraulic conductivity, I don't believe.

VICE-CHAIRMAN CROFF: Okay, and in those cases it doesn't really factor into a performance assessment.

DR. LANGTON: Right, right. Small cement waste forms, small volumes that go into our disposal facility aren't included. It's only the large concrete vaults or the large volume waste form.

VICE-CHAIRMAN CROFF: Okay.

DR. LANGTON: One's a monofill of -- saltstone is a monofill essentially where one -- a large volume of a waste stream is solidified in a cementitious matrix but we do have small volumes, a few drums here and there over time.

VICE-CHAIRMAN CROFF: Okay, so is it fair to say that in much of this and in trying to take credit for the effects or the beneficial effects of cements beyond just, you know, sort of filling a void space or something, that we've started down that path, we've done some of it but it's a relatively new experience for us in how to do it and how much?

DR. LANGTON: Well, cementitious waste forms are best developed available technology for hazardous constituents. So EPA has a much broader application of cementitious waste forms for non-radioactive waste.

VICE-CHAIRMAN CROFF: I know they use them a lot on that side of the house, if I can call it that, but I didn't think they did much performance assessment. They sort of say use it and hope it works or --

DR. LANGTON: No, it's use it and it needs to go, depending on its characteristics, whether it's characteristic or listed waste, whatever the details are of its waste classification, it goes to a landfill, whatever kind of landfill, it goes to that landfill. It's monitored. It's got leachate collection. There's a plan. The plan doesn't extend that far into the future. I think it's 50 years, is that right, Les, or Subtitle C landfill but at the end of 50 years, it doesn't say it's closed. We haven't gotten to 50 years for any of these landfills yet.

So there is a leachate collection and a groundwater monitoring plan and it is regulated.

VICE-CHAIRMAN CROFF: Okay.

DR. LANGTON: Thirty years, yeah.

VICE-CHAIRMAN CROFF: Okay, Dr. Kosson, a very different question; if -- I sort of sweep across all of what you said and you know, let me suggest a broad generalization, it's sort of a true/false thing. It sounded like if the cement waste form was saturated with water, and it was carbonated, the carbon dioxide had reacted to sort of seal up the surface and this kind of thing as you described, it sounds like that would be a good thing, a desirable thing to have.

Are there any down-sides to this? In other words, at some point does carbonation begin degrading the waste form or the water or something like this?

DR. KOSSON: I think there are a number of different processes that you have to balance across that and let me give you a couple of examples that you just mentioned and why. Ideally, you would keep the matrix saturated to avoid vapor phased diffusion and to limit it, but at the same time, when you're saturated, you have to be concerned about not maximizing some of your liquid phased diffusion and if you're past saturation, suddenly you've got capillary -- I mean convective movement as well.

So there are careful balancing acts for the design conditions that you want there. Similarly, carbonation as a capping, a pore blocking phenomena can be very beneficial. Also the ph effects of it in some circumstances can be very beneficial the way it effects the leaching behavior of some constituents. However, for some constituents, as I pointed out earlier, it also can have detrimental effects so because of the ph geochemistry effects. So what you're really looking for is looking for your best operational window that you have of these combined processes and then designing to maintain that operational window.

VICE-CHAIRMAN CROFF: Okay, I was --

DR. DETWILER: May I add something here? Carbonation also causes shrinkage so that could result in cracking.

VICE-CHAIRMAN CROFF: Okay, I was struck, maybe generalizing off this specific point by something Dr. Langton said and that is that there is no conservative case for all parameters. It's, you know, your phrase is windows. It's something is good on one hand, bad on the other and that makes performance assessment very interesting kind of an exercise.

DR. LANGTON: Especially for 10,000 years work.

VICE-CHAIRMAN CROFF: Yes, at this point, I'd like to offer the other panel members. Do you have any questions of our two first speakers? All right.

DR. DETWILER: For Dr. Kosson, I saw you had a couple of slides in here at page 7 and also page 13, where you are showing cracking and the development of cracks and I was wondering how you put that into your model, because for the most part, that would be something that's not going to be continuously growing but either -- it's caused by something and that something is probably fairly short term. How are you incorporating this into your model, if you are?

DR. KOSSON: Well, I've got to be candid that that's a very high challenge in these kinds of modeling. The way that we're dealing with it right now is that micro-cracks are dealt with as they form from the structural perspective as localized effects on diffusivity because they're not through cracks. Larger cracks, the rate and formation of them, we have not been able to capture well, but what we've done is assume that they've formed as a matrix within the matrix and then basically what you do is you have a dual model where you have diffusion to the boundary of the macro-crack and then transport through the macro-crack.

MEMBER HINZE: May I ask a follow-up question to that? In terms of this monolithic cement, is the separate pours, are there at the interface between pours that may be separated in time by some -- by days or even longer, do we see a lot of micro-crack there? Is there infiltration along those pours?

DR. KOSSON: I would suggest -- we've done some observations and I would suggest some of the other folks here have done much more extensive work on the crack evolution and they'll probably talk about that later.

DR. LANGTON: I didn't quite understand your question.

MEMBER HINZE: Well, if you pour concrete in and you don't immediately pour in further concrete but then at a later time have another pour, what is the interface like at the position between the pours?

DR. LANGTON: There is an interfacial region, interfacial zone layer. It's more than a layer, it's got dimensions. What it looks like depends on the details of the situation. If drying takes place between pours, there's drying, shrinkage, cracking. If drying doesn't take place, in some cases there might be condensation of water, in our case we have vaults that have roofs and moisture will condense on the roof and fall back into the -- onto the surface. So if we have a day between placements, we have a wet surface.

So there's always an interfacial region. It could be a high water region. It could be a very dry region, with cracks. It depends.

MEMBER HINZE: Yeah, how do you handle that in the performance assessment?

DR. LANGTON: Right now, that's a de -- that's in the noise. That's a detail that's not handled. The performance assessments are built on so many assumptions that when we ask to have the assumptions listed, people just get weak kneed, there are so many assumptions.

VICE-CHAIRMAN CROFF: Peace. Okay, anybody from NRC staff have a question?

MR. FLACK: Yeah, John Flack from ACRS. Getting back to acceptable risk in the long-term, and I'm actually coming from reactors where they have safety goals and they talk about .1 percent of other risks that the individual is exposed to around nuclear facilities. Have you thought of, in the long-term that type of risk as exposure to individuals, certain frac percent of all the environmental risks that one would be exposed to at that time in the future and using that as some goal, then working backwards to see how one achieves that goal through this short-term monitoring that has extended into the long-term effect, that sort of thing, that sort of thinking?

DR. LANGTON: I don't specialize in the details of the performance assessments but I haven't seen anything that addresses what you're talking about.

MR. ESH: This is Dave Esh with the NRC staff. I have a question that might be for the two of you or it might be for the whole panel, but one of the items that was addressed was the use of standard method for particular materials or assessing the materials, I guess. In the working group's opinion, are the standard methods suitable for the very longer term performance that we're getting at or are they more focused on shorter term performance, common in low level waste applications where you're looking at a cesium, strontium dominated source where hazard is on the order of a few hundred years instead of longer term? So that's kind of my question is, are the methods suitable or is there a need for maybe some longer term methods or are there longer term methods to get at it?

I'm kind of thinking that some of the processes that occur, the standard methods you have now, they might be focused on the processes that the best response on the time scale that we're looking at in the laboratory but are there long term mechanisms, processes, that aren't really amenable to the short-term test that you might need this set of longer term procedures or tests to look at those long-term mechanisms?

DR. KOSSON: I think what we're seeing is standard methods in a number of cases from the leaching assessment, from things I talked about at least, were developed for other applications or for very short-term type of phenomena or over-simplified assumptions and are very inadequate for projecting a long-term behavior. Don't capture a lot of phenomena, don't capture a lot of processes.

For example, as I mentioned earlier, TCLP has regulatory standing, has no technical basis for its application here even though I know that, for example, Dr. Langton listed is as one of their evaluations because it's a regulatory standard. There's no basis for projecting off of that.

MR. ESH: Then a second question I had is related to scale. In the working group's opinion how much validity is there to testing laboratory samples on this very small scale when your application might be a much larger system that brings in all sorts of discrete engineered features and different conditions for those large scale samples compared to the laboratory samples? Is -- are you aware of any work that has been done to try to take results from the small sample -- small samples and show that they've accurately or at least over-estimated the deterioration compared to the larger scale, because I think that maybe the larger scale has some features that can be detrimental to performance that of course aren't represented in the laboratory analysis.

DR. LANGTON: We recognize the same issue. To take it out of the waste form business and into ordinary concrete construction, there are applications where concrete hydraulic conductivity is important. It's measured underwater concreting like the Chunnel or underwater tunnels. The material property is measured and it's something that the people that make the concrete, the suppliers of the concrete have specifications on or if they don't have specifications, they have a correlation between some other property and the permeability. So it gets to -- specifying a job and constructing the job. Material properties are important.

Performance of the final product is a separate issue and the two are related but one doesn't necessarily predict the other except in extreme cases. So we do need some sort of evaluation, I think, of the structure.

MEMBER CLARKE: If I could interject here, David has articulated very well, you know, of why 25 years of my in-system monitoring would be valuable, because now we have a large full-scale system. We've done our best in the front end to project long-term performance. If we can link the front end to what we're finding, what we're actually measuring, we can make that loop, design to get monitoring data that can help us build model confidence, which is the title of a working group meeting we're going to have in September, just throwing out a plug.

Then, you know, we can improve the models as we go. I mean, we don't have to do this everywhere but maybe we'll learn a lot if we do this, and that's the reason I keep raising monitoring. And the other reason is that I guess I'm not a believer. You know, I guess I'm just concerned that anything is going to last 10,000 years without intervention and if we have to intervene, then we ought to plan on intervening now.

DR. SCHEETZ: I think to address Dave's question, it's a matter of the crinkly green lubricant. If we look at the performance of large scale engineering structures in the civil engineering realm, you know, we've placed -- we have an investment of what, 1.7 or $1.8 trillion in placed concrete within the United States in the civil infrastructure realm. We looked at big structures. We built the Grand Cooley Dam. We've build enormous structures. So the engineering community has had to look at, they have been forced to look at, what you do in the short-term ASTM or ACI test protocol to place the concrete and then what the long-term performance is.

We have this so-called analogue, if you want, out there. What we don't have is the same thing in the nuclear community. No one has ever -- I mean, Chris is the only one that's ever placed a tank full, a 1.3 million gallon tankful to close a hazard -- or one of these storage tanks. We don't have that experience and the driver isn't there, hasn't been there from and economic standpoint to develop those understandings on these rather unique and unusual circumstances. But I think, you know, to answer Dave's question, some of the knowledge is there but we're going to have to pull it from the civil concrete.

MEMBER WEINER: Could I ask a final question? It's on another topic, so I don't want to interrupt the discussion but uranium is mined as we just learned, by leaching with an oxygenated carbonate solution. It seems to me that this is an intruder scenario that you might consider with grout because you get cracks and you have carbonate and you have water and here is a possible intruder.

VICE-CHAIRMAN CROFF: Okay, I think -- I'm sorry, is there a comment?

DR. DOYLE: I think I'll address that in a later -- I have a slide that addresses that because that's exactly the scenario that lay in grouts from Yucca Mountain. They failed to look at the aluminum silicate chemistry associated with that system and just isolated the carbonate and the ph. And you get a different answer when you do a little more complex geochemical model.

MS. RIDGE: This is Christian Ridge from the NRC and if I could follow up on something that Chris talked about a little earlier was the interface between various grout pours and the various ways that that interface can occur, a dry surface, a wet surface. I was wondering if work was being done with respect to the interface between the grout and the waste itself in a sort of DOE specific case of closing a tank if you have not just various grout pour interfaces to look at but also what to my mind seems like would be a more radical interface between cementitious material and the sludge itself, you know, of metal oxide precipitate and whether or not you think that that interface would be, perhaps more important to look at.

To me it seems like there would be for different physical properties of the two, which would facilitate cracking and separation of the materials, and I was wondering if there was work ongoing or if, in your opinion and the rest of the panel's opinion, if maybe I'm not understanding and that interface is not as much of a problem as it seems like it might be.

DR. LANGTON: Actually, I proposed doing work on actual tank residual material and cement and grout in a layered effect to get to look at the interface and a column effect. But that was -- that's primarily concerned with the chemistry of the system. As far as cracking is concerned, there are reasons for cracking.

Cracking is dimensional change, either from expansion or contraction -- well, not contraction but from expansion. So dimensional changes and I don't really see dimensional changes in the sludge as it exists now, which is soft material or not completely rigid material. It's solid but it's not bound together. It's a rigid mass, a particulate material. There's plenty of room for expansion in that material.

Now, whether it changes with time as a result of leachate chemistry or interaction diffusion of materials in a cement pour solution to form a rigid material that then cracks, that then could crack as a result of expansion, I don't know, but we have proposed work from a chemistry standpoint. There's talk of cleaning the tanks, removing more of the residual material from the tanks which would negate that need to do the work. So that's where we're at right now, but if we do leave material in the tanks, I think we would certainly be looking at the chemistry and the chemistry, in turn, impacts the dimension or creates dimensional changes or could create dimensional changes.

MS. RIDGE: Right.

DR. LANGTON: You would get that also.

MS. RIDGE: And then, I suppose, the temperature you'd expect after the curing would be fairly constant. I was thinking perhaps that with respect to any thermal gradient, the sludge would react very differently than the cement and you could get them -- a separation in that interface.

DR. LANGTON: We did thermal analysis for the next two tanks to be closed and there's such a small temperature rise from radioactivity in the waste. Now the temperature rise from the grout is something that we can -- if we find it's a problem or if we identify it as a problem, we can control but again, it's moving across the surface. It's expanding, contracting, whatever the grout is doing, it's happening on a surface that is not rigid.

MS. RIDGE: Right, thank you.

DR. LANGTON: We're not anticipating a big effect there in grout temperature.

MS. RIDGE: Right.

VICE-CHAIRMAN CROFF: I think with that, we're slightly over, not a problem. Let's take a break till about 10:35. I'd like to thank our two speakers this morning, look forward to your participation in the rest of the show. 10:35, please.

(A brief recess was taken at 10:23 a.m.)

CHAIRMAN RYAN: On the record. If we could come back to order please.

(Discussion off microphone.)

VICE-CHAIRMAN CROFF: Let's go ahead and proceed here with our second session and our first speaker here is Dr. Rachel Detwiler. Dr. Detwiler is a Senior Engineer at Braun Intertec Corporation in Minneapolis. Her areas of expertise involve the durability, transport properties, microstructure and test methods of concrete and cement based materials. She also previously served in an advisory role for the initial development of the grout formulation for the stabilization of radioactive and hazardous waste in storage tanks in Savannah River. Take it away.

DR. DETWILER: Thank you, Allen. I'll stand up too, so I don't have to be tied to one place. I have several areas that I'm going to try to cover in this talk. First of all, I just wanted to go quickly over the difference between grout and concrete because sometimes people who are not in this field, they get confused about which is which and it's nice to get it defined a little bit first. Then I'd like to talk more about getting concrete to do what we want and I'll use the term "concrete" throughout. To an extent, you can put grout in the same category but just for simplicity, I'll refer to concrete primarily. Then I have a few ideas at the end about monitoring. So the bulk of the talk actually is this central portion right here.

To distinguish between grout and concrete, first of all, grout is a mixture of cementitious materials with water. It may also contain fine aggregate which the rest of you know as sand and fresh grout would have a pourable consistency. So when, for example, you're doing that you're going to be able to pump it very easily and place it in a form and it's probably going to be more or less self-consolidating.

Concrete is similar, but it also contains coarse aggregates. That would be larger pieces of either gravel or crushed rock and you would probably use this in larger applications. So grout would tend to be for smaller things just because usually in normal construction we use the coarse aggregates because they are the cheaper ingredient. But it's also something to consider when you're doing applications like this where the cost of the materials is probably not the biggest issue. But the coarse aggregates also provide you with a lot of dimensional stability. So if you're concerned about the overall shrinkage of the material for example, you're going to get less overall shrinkage if you have concrete because you have this big component in here that is not going to shrink but instead will restrain the shrinkage.

As I mentioned, concrete is generally more economical and more stable dimensionally than grout and so probably on large pours that's going to be what you would rather use, although not necessarily. Generally speaking because the grout does not have the coarse aggregate in it, it has much more cementitious paste, it's going to have a greater tendency to crack and that can have a very significant effect on such things as the transport properties. It may not be that big a deal in terms of some of the structural characteristics because of the kinds of configurations that we'll be using it for. Either grout or concrete could be made as a waste form if that were desired.

Now how do we get concrete to do what we want? First of all, I would like to go over some hard facts about concrete. One is it almost always cracks and so when you're modeling transport characteristics, for example, you need to take that into account or you need to figure out what you're going to do to make it not crack or to limit the size of cracking which is probably more to the point.

It is subject to deterioration and that's what I'm going to go over. I call this talk, it has to do with durability. That's because it's durable against something. It's resisting deterioration hopefully.

Most of what we know about concrete comes from the construction industry. There are researchers who have done a lot of work in the area of specific applications for nuclear materials but they are far fewer than those who have done work in the construction industry and we in the construction industry have a great deal of advantage in that we actually build stuff.

VICE-CHAIRMAN CROFF: Rachel, we just had a problem here. Your slide vanished.

DR. DETWILER: You're on my screen. I don't know what your problem is.

(Laughter.)

DR. DETWILER: Okay. There it goes.

VICE-CHAIRMAN CROFF: There it is.

DR. DETWILER: Most of what we know about concrete comes from the construction industry. So that's sometimes good that you have people like me who mostly work in construction and occasionally dabble in nuclear applications that can sort of bridge the gap, but mostly people like Dr. Langton can review the literature and say, "This is what they're doing in construction and this may apply to us in the following ways."

But there are certain disadvantages about that. First of all, we are dealing with a very different context in the construction industry. For us, a long time is 50 years. Now we're starting to look at hundred year lives of structures, design lives. And nobody know whether we can actually make that. Yes, we have Roman concrete and some people even claim that the Egyptian pyramids were made of concrete which is kind of silly but there you go.

But the problem with that is that those things were made of a very different kind of material than we are using today. So in fact, we don't really have that long a track record with modern materials and modern concrete technology. In any case, when we talk about these 50 year lives or 100 year lives and actually we don't know if we can have a hundred year life, we're just talking about it at this point, we're specifying it, but we haven't actually seen that it lasts that long, we are considering that we are going to be doing regular maintenance. So that is very different.

This question has already been brought up, but we in construction assume we are going to be doing regular maintenance and what people are assuming in the nuclear area is that we're not going to touch it again or we may upgrade in 50 years or 100 years and then not touch it again. So that's a very different set of criteria than we would be using in construction and so there's a lot less experience in that.

Now because we are looking at much shorter life times in construction, when we mean durability or when we say durability, we're actually talking about generally postponing or slowing deterioration, not prevention and that's something else that's a very different mind set. It's good enough if you have to make something last for 50 years to simply postpone deterioration. You can slow down things like corrosion by just limiting the permeability or the diffusivity of the concrete to those harmful constituents.

For example, with corrosion, you want to keep chloride ions from reaching the steel. But that's relatively easy to do if you all have to do is make a thicker cover of concrete over it and that will work. But if you're talking about even 1,000 years, let along 10,000 years, postponement and slowing of deterioration are really not going to be that helpful unless you can say there are certain, say, very highly radioactive materials that will lose enough of their radioactivity over that time that in 50 years we don't care as much and then we can allow certain kinds of deterioration to have happened. So we may have to look a little bit more carefully at what the criteria are or decide that we can actually prevent deterioration but we really don't know a lot about that.

The other concern that is a little bit difficult when you're trying to use knowledge from construction to help in applications that it has not been designed for effectively is that there are certain criteria that matter tremendously for the Department of Energy, for example, that have no relevance to us. So we don't know what they are. So what that means is that in that case, you cannot draw from this larger group of people who are doing research in the construction industry. You really have to rely on those people who are looking specifically at applications that have to do with radioactive materials. So suddenly you have a much smaller pool of people and much less in terms of resources to look at them.

Now the next thing is what criteria are we imposing on the concrete. Now one thing that we do have in here is structural support. Now really this turns out in most cases not to be that difficult to do because if you are actually just using it, for example, as tank fill material, you could have used a completely incoherent material like gravel and that would have done if all you're trying to do is keep your cap from collapsing or keep that tank from collapsing after the fact. So you don't actually need much from your concrete to do this. In that case, you wouldn't care if it was riven with cracks because it would still hold it up.

You may need it as a barrier to intruders whatever those intruders are, whether they are plants or animals or humans. So in that case, you're talking about something that's hard to get your roots into or hard for an animal to dig into or just something that looks unnatural because humans can dig through almost anything if they're really determined.

Sometimes people want it as a physical

barrier to infiltration, in other words, hydraulic isolation from the environment. There may also need to be a chemical barrier to transport. This is where we get into the reducing capabilities and the pH and that sort of thing. Basically for most purposes, we want a high pH and a low E_h.

And I think often times you haven't brought up the politics of it, but really a lot of it is public perception. I think in a lot of cases especially for low level waste it probably isn't necessary but it makes people feel better because they thing concrete is really solid, even though every time you see it, it has cracks in it. But, hey.

Going back again to specific criteria, for structural support probably what we're going to measure is the compressive strength. That's usually something that's easy to measure and everybody understands that. We may care about the stiffness. That is the resistance to deformation when it's under load. And as I mentioned, these criteria are fairly easy to satisfy. We just need to make sure that cracking is controlled and we have the durability we need so that, for example, if we still need to have a certain measure of compressive strength in 100 years or 300 years or whatever that may be, that it has not deteriorated so much that we have lost that. And actually, it has to deteriorate pretty thoroughly before it doesn't have any compressive strength left.

Now as a barrier to intruders, if we're talking about plants, animals or humans, here we probably need to be more careful about limiting cracking because of course a plant can find its way in if there's something to be had and then the problem there is that once the root gets in it could start wedging it apart. So we need to get sufficient resistance which could be strength in or thickness, in other words, to make it difficult for an animal to burrow in and then you wouldn't care if there were some cracks in it. You would just have to have something that was solid enough and even really a thick enough layer or rubble would probably do for a lot of burrowing animals.

For humans, you might be looking more at things like adding a pigment or to do something to make it look really unnatural. And remember that after awhile, concrete that was pretty well broken up might not look as unnatural as all that. So you might really want to look at a pigment of some kind of stuff that was not seen locally so that people would know it was really unnatural.

Now concrete as a physical barrier to infiltration is probably not all that wonderful. Even without the cracks, the concrete is porous and permeable and all the models if they have any relation at all to reality will show this. I mean they're all talking about some sort of permeability or diffusivity. So you're always going to have even in the small scale if you have no effective cracking you're still going to have this. With cracking, of course, it is in orders of magnitude more permeable.

So if your barrier has to be completely impermeable, you really need to have some other system and you may be able to do a good deal with things like site grating so that the water runs off rather than leeching through. You may want to do a lot of things with clay barriers and other things like that that are more appropriate for that and also using vegetation to take up what water is there. So you're really looking at a total system, not that concrete is doing everything and I think it makes more sense to let it do what it's good at and not expect it to do what it really isn't capable of doing.

Now as a chemical barrier to transport in general as I mentioned, we want it to have a high pH and a low E_h to make the constituents as immobile as possible. Now Portland cement and concrete naturally has a high pH because of the calcium hydroxide which is one of the products of the hydration reactions. The reducing characteristics, this low E_h, would be imparted by slag cement. This is the ground granulated blast furnace slag.

Over time, leeching may alter these characteristics and that's where I'm not sure that we have as good an understanding of this as we really need and remember we know a fair amount about the pH because we care in construction about pH because high pH protects steel from corrosion. And so we do have a pretty decent understanding about that in the relatively short term, you know, the first few decades. We probably can say something sensible about that, maybe not everything you want to know, but at least something.

Reducing capabilities, if you ask most people in construction, they would have no clue what that even was. There just isn't any need for it in our normal lives. So we don't deal with this. I know about it because I've worked in nuclear things before. But that's the only reason.

Now going back to public perception and I'm not a politician, so I don't want to get too far into this but just to bring it up because it is part of the context and it is something that will often dictate what gets done. In a lot of cases, the use of concrete isn't really necessary. You could probably get away with especially in the case of low activity waste you could probably design your landfill very nicely without it. You don't really need it. But it does give people a good feeling about it.

In particular though, concrete is ill-suited as a long term barrier against water and this may seem counterintuitive if you're thinking of dams that hold back water. But in fact, they're not necessarily holding back all of it. It's probably getting through somehow and you don't particularly care. It's capable of fulfilling its function as a dam while still allowing some water through. But if we don't want any water through in the applications that we're talking about, then it's not concrete that's going to do this for you. It has to be something else.

It's probably appropriate as an intruder barrier. So it is a way of making it difficult for plants to get through and particularly burrowing animals. It can also provide structural support. That's something it fairly easily does, although there certainly are other ways to do this. So it isn't necessarily the first thing I would think of if I were trying to provide that.

So the criteria then we've sort of discussed. Now look at the kinds of characteristics of the concrete we're after. We probably want a certain measure of strength, although this is unlikely to be the controlling factor. In the construction industry, we have been able to make strong concrete for a long time and that's not really the issue anymore even for us. We tend to be much more concerned now about durability.

We want to do things to minimize the cracking and the reason I would like to de-emphasize strength is that normally the things that we do to get strong concrete ironically enough will tend to make more cracks. So we need to be careful that we don't decide if some is good, then more is better in terms of strength because the more things we do to get high strength the more likely we are to have some serious problems with cracking and that may be detrimental to the application that we're considering.

We probably also want minimal permeability and it happens a lot of times people use strength as a surrogate for permeability and that's a mistake.

They really need to look at the transport properties as directly as they can to obtain those and if it's done at the expense of strength, so what because we'll probably have plenty of strength anyway.

We are also concerned about favorable chemistry and this is obviously chemistry over the long term and also favorable microstructure which is to say as low permeability as we can, as low diffusivity as we can. We need to stabilize radionuclides and something that really hasn't been mentioned here but it is often an issue is the toxic heavy metals because a lot of times these wastes do have other components that are not radioactive, but they can be just as nasty to the environment and these don't go away. So it's not like you're going to -- These things don't have a half-life. They're just there unless they are transported somewhere and you don't want that either.

So these things have to be kept in mind and some toxic heavy metals actually do have certain effects on the ability of the cement components to set, for example. So you may have some sort of a waste form where you make it and it never sets because you had say too much lead in it. So there are things like that that will affect how these waste forms work.

Then the next question is how long do we actually want to the concrete to be able to do these things. It may be that we don't need structural integrity for the entire 10,000 years. It may be that it's good enough if we have it for the first 50 years and then it's so riven with cracks that maybe then we're concerned more with the chemistry or whatever. So I think we really need to look at this in more detail and it seems like some of the models that I've seen they are starting to do this in sort of a rudimentary way but I don't think they've really considered this as well as they probably need to.

Now if we look at how to minimize cracking which obviously is a big issue here, in a model cracks are, just as in real life, going to form for a specific reason and so it isn't just that you have deterioration over time and it's sort going on at a steady rate and you get so many millimeters of cracks per year or anything like that. A lot of it happens in a very short time and then those cracks may propagate, but they start for a particular reason and they propagate for a reason.

Now we have thermal cracking which is basically what happens when you get differences in temperature which will result in some of the concrete expanding and some wanting to contract. So they are basically fighting each other until the crack forms and that relieves the stress. This is relatively early on and basically what happens mostly is that it has to do with heat that is generated during the hydration of the cementitious components. So that's basically what you're dealing with there is how much heat are you generating and when it is being generated. But most of this is occurring within the first hours, days and weeks, not later. So that's something that you're going to deal with soon and then those cracks may propagate for other reasons, but this is early relatively speaking.

Plastic and drying shrinkage both occur due to the drying of your cementitious materials and that again is very early on. Plastic shrinkage happens before it sets and drying shrinkage will happen following setting usually within -- I mean you can still measure it after a year, but it's just so minimal by then you don't really care. It's again something that happens earlier and not so much later.

If you allow the concrete to shrink as much as it likes, then you will not generate stresses and you will not generate cracking. But normally in any real system, you have some degree of restraint and so basically if it wants to shrink and you don't let it, then you'll generate stresses that could result in cracking.

Structural overloading, again basically just something that would happen episodically. It could happen because of an earthquake. It could happen because during construction your construction vehicles drove over it. It could be that you're casting some sort of pre-cast concrete and the greatest stresses it ever sees are when you're assembling this thing and then just picking it up may be the most stressful thing you ever do to it.

So how do we control thermal cracking? This chart is an example of what we did. This happened to be from construction of a hospital MRI facility and they're using relatively thick concrete, approximately seven feet thick, as radiation shielding around the structure. So it forms the floors, the walls and the ceiling of this facility.

This shows you what are thermal couple measurements measured at different locations in the section over time and you can see this is something that -- Our peak in this case happened approximately at 200 hours. So you can see that this is a relatively short term phenomenon. But the design of this concrete was specifically developed for mass concrete. So it was supposed to generate relatively little heat. That was a good design.

Basically, what you're trying to do is keep the thermal stress less than the tensile strength at all times and so that's how to prevent any cracking actually is to keep the stress less than the strength. Here ACI has a short-cut method in which you just maintain the temperature difference between the surface and interior to less than 35 Fahrenheit degrees or 20 Celsius degrees and that's what we were doing here is just monitoring to make sure that happened and the reason that monitoring is useful in this case is that we know what the interior temperature is and then we can say, for example, if the contractor wants to remove the forms and we know what the air temperature is and we say that difference here is more than 35 degrees, no, you leave the forms. Or if you want to take them off, you can tent and heat the structure and you can keep the heat on so that you don't have more of a temperature difference than we can tolerate.

This is something that might conceivably be used in some of these applications because you certainly do have mass concrete. And basically the way you do this is you select materials that don't generate a lot of heat. That's one reason why you like slag and fly ash as opposed to lots of cement because it's cement that generates the most heat and the earliest heat.

You will also do things to minimize the amount of cementitious material overall. The aggregate does not generate heat at all. So the more aggregate you use the better off you are in this case. So you would look at things like can we use larger aggregate that takes up more space, can we get a more efficient aggregate grating that fills up more space. So there are ways to formulate these things that I think would be very relevant to a lot of the mass concrete that you're using in these applications.

How do we minimize the cement content? We have aggregate size and grating as I mentioned, fly ash and/or slag cement and preferably in large percentages. You don't really care about things like how fast does it gain strength. If it takes weeks or months, so what. But you can get a much better product if you use these materials that don't generate a lot of heat and react much more slowly. So they are generating their heat over a much longer time.

Another thing that you can do is have a

low placement temperature. There are ways of cooling concrete before you place it. The extreme case would be to use liquid nitrogen and people do that where they'll actually jet liquid nitrogen through there so that it cools it off considerably and you can place it at any temperature above freezing and you will be better off because of course just like any chemical reaction or most chemical reactions, the hydration reactions are a whole lot slower when it's cold and so if you can keep them slow, then the heat will be generated much more slowly over a much longer time. It gives it a chance to dissipate. So that's something that's relatively easy to do and again can be done commercially on a regular basis.

Insulation is also helpful. This is probably more of an issue for construction above ground. If it's underground and you're just casting against soil, the soil will be good enough insulation. You don't need to worry about it. But you probably have a free surface that's not against the soil and that would be good to insulate. Then you want to have insulation that can be removed gradually so that you can gradually lower the temperature on the cool surface rather than just take it off all at once.

Another thing that's really important is you need to protect it from rain because of course if you splash cold water on it, it will cool it very fast and you will probably see cracks because of that.

Plastic and drying shrinkage both result from drying and sometimes what will often happen in construction is that the crack will initiate by plastic shrinkage and propagate through drying shrinkage. You may not even see it during the plastic stage, but it has in fact already started to crack. So a lot of people will just call it shrinkage cracks because it is in fact hard to distinguish between them.

Plastic shrinkage will occur before it sets and as I say, you may not even see this but it's there and then the drying shrinkage is after the concrete sets. A colleague of mine sometimes says, "Plastic shrinkage occurs when the concrete is of the texture of a Three Musketeers bar and drying shrinkage occurs when the concrete is more the consistency of a Butterfinger bar." So it's actually brittle at that point.

Basically with this, you minimize both of these by preventing the drying and so that's mostly just good curing practices. If you're really concerned about this and you really want to do the best job you possibly can, you will also fog the air above the concrete even while you're placing it and finishing and other things just to keep it from losing water while it's being handled.

Now this is a little example of how restraint of shrinkage works. Concrete generally speaking does want to shrink and it will do so for a variety of reasons. If you just let it happen, it's not that big a deal. It gets smaller but it's not going to develop a lot of stress. But normally, we have some measure of restraint and that may be because we've cast the concrete against the ground or it has to be joining two things that aren't moving, say, it's a floor and it's going between two columns. So we actually do have measure of restraint.

And then of course, the aggregates themselves are a form of internal restraint too. Basically what happens is if it wants to shrink and it can't, then somehow the shrinkage has to be compensated and that's what it's going to do. So a lot of what we do in normal construction is just bow to the inevitable and figure out how we're going to handle the cracking rather than try to prevent this.

As a general rule, concrete is roughly ten times as strong in compression as it is in tension and because of some of the things I've talked about, it tends to develop cracks even before any load is imposed. Certainly the plastic and drying shrinkage could cause cracking before loads are imposed. So could the thermal stresses. So those are basically the things that would tend to cause cracking before loads are imposed.

Typically what we do is we minimize the crack width by closely spacing reinforcing bars and what that does is it gives us a lot of narrow cracks rather than a few wide cracks. We may also design in the structure and include prestressing or post-tensioning to keep the concrete in compression. So that's a way a structural engineer might handle it and that's something that's worth looking at. Note though that if you do have prestressing or post-tensioning that over time that will be reduced by creep. So it's more effective at the beginning than at any other time. Also this prestressing steel will be in tension and it will be more susceptible to corrosion because of that. So that's kind of a tradeoff.

Structural overload, you could have structural overloading occurring in construction or in service due to any one of a number of causes and you really need to consider all these possible sources of loading. A lot of them do take place only during construction and at no other time, but even things like driving construction vehicles over something and remember that the concrete is weakest when it's young. It's continuing to gain strength over time. So here you have big heavy vehicles driving over it early in its life. That's bound to be detrimental. Even before you put any other load on it, a structure has its own weight to carry and often that's more than any live load it will ever see.

You have bearing pressures from the soil and any groundwater that's there. Soil settlement can be a big problem because the concrete is rigid, the soil is not and so if you have differential settlement, that can be very problematic.

Earthquakes which would be of course a single event, but certainly in 10,000 years it's not difficult to imagine how you could have multiple earthquakes. And there probably are plenty of other things that I haven't thought of that you would need to.

Now going to permeability and durability which is probably more of an issue for most of the things that we're concerned about. This is something I found when reading through an old concrete engineer's handbook. You know, of course, remember that when something gets to a handbook it's already old news. But back in 1918, it was apparently well established that water penetration is directly or indirectly the cause of the majority of disintegrations in concrete and the degree to which water penetration is permitted by the texture of any concrete is a direct measure of its strength and endurance. And this is ironic because this happened to be the year when Duff Abrams developed the relationship between water-cement ratio and strength and so we've been concerned about strength since about 1918 and it's only been relatively recently that people have started to concern themselves again with permeability and durability. So now we're back to 1981 again.

This slide gives you some idea about the relationship among strength and permeability and porosity. Normally in concrete we're looking at porosities in this range, but you could conceivably have higher porosities. And you can see that the compressive strength tends to go fairly smoothly along. It gets lower and lower and lower as the porosity increases which stands to reason.

But the permeability is more interesting because you don't see a steady increase. What you see is a steady increase and then a sudden rapid increase. So basically what this is telling you, roughly speaking this break point is around 30 percent porosity. So in general what we would like to do is get the porosity below 30 percent if we're concerned about permeability and diffusivity and all that sort of stuff.

Now we reduce porosity, again here is our porosity and here is 30 percent. We have just for theoretical reasons this 100 percent hydration curve. This never happens. Ever. I have seen 100 percent hydration in the lab and it was not done in concrete. Basically they put cement and water in a bottle with some ceramic balls and keep turning it and turning it so those balls keep breaking up the hydration products and what you have at the end is something like a 100 percent hydration and nothing like concrete.

In real life, 75 percent hydration is probably as good as you're going to get in a real system where you give it a reasonable curing and for that then to get to 30 percent porosity you're looking at a water/cement ratio of about 0.45. So that gives you an idea. Once you get above 0.45, you probably will not see low porosities and therefore you will always have a continuous pore system no matter what else you do. So water/cement ratio is really key to getting this to work.

If we have a water/cement ratio below 0.45, we also need to get an extended moist curing time even to get to the 75 percent. If we had 0.45 water/cement ratio at 50 percent hydration, we're looking at almost 40 percent porosity. So that's not going to be acceptable.

Supplementary cementitious materials, again fly ash, slag and also silica fume can really help here, but again, they need this extended moisture curing time to be able to work.

Now looking at some of the deterioration mechanisms, we have carbonation which has already been mentioned and also leeching of soluble materials. We have cycles of freezing and thawing which probably is not an issue once the concrete is buried. We have sulfate attack. We have alkali-silica reaction. We have corrosion of reinforcement and we have irradiation. So these are all things that I'm going to go over fairly quickly to give you an idea of what we might do about some of them.

Carbonation has already been mentioned. Carbon dioxide and moisture in the air react with calcium hydroxide to form calcium carbonate. It is true that you might have also, you might get this from dissolved in water and some other things. So it is possible, but normally we'd see it in air. The result is shrinkage and also a reduction in pH and I would consider both of these things to be undesirable for this application because remember shrinkage probably means cracking.

Once the concrete is buried, this is probably not an issue unless you do happen to have water that's carrying carbon dioxide in it. If the concrete is above ground, a coating may be helpful and remember that for most of these systems if you starting with the concrete above ground, it's not staying there. It's going to be buried eventually. So your coating doesn't have to be a permanent thing. It could be something that lasts for just the time it takes you to build the thing and get it buried. So you don't have to have something that lasts 10,000 years. Five years is maybe enough. Maybe you need it for ten years.

The way we test for carbonation, you can actually see this, you squirt some phenolphthalene on a freshly broken surface and you can see where the color change has not happened. This is all carbonated and you can see that normally it's done, it comes from the surface and it will go irregularly into the concrete depending on whether there were cracks or other voids or other things for it to go in.

Leeching is an issue because some components of hydrated cement paste are solubles, primarily the calcium hydroxide which is soluble in both water and acid. So if you have any acidic water, your groundwater may be acidic or you may have acid rain, this is more of an issue even than just in water.

The loss of the calcium hydroxide will leave open pores and also locally reduce the pH. Over the long term, it really is best to keep the water out and you need to do that by some other means than just the concrete itself.

Cycles in freezing and thawing because water expands approximately nine percent on freezing, if you have saturated concrete when it freezes you're in trouble and you can see what happens here. It completely destroys the structure. Again, this is probably not going to be an issue once the concrete is buried because it's probably not going to freeze and hopefully it's not going to be that wet.

What we do to prevent freeze/thaw damage is we entrain air, you can see all these little air bubbles here, and that basically provides some place for the water to go. We also need to make sure though to get this that we have done our job in terms of mix design, mixing, transport and placement so that we get the air in and we don't take it out again. It's extremely difficult to do all of this in hot weather and do it properly.

Sulfate attack, this shows you a photo microgram of the sulfate front coming in in this direction and you see the kind of deterioration that occurs and these are, of course, cracks that would come in and that's obviously something that you don't want to have. The tricalcium aluminate in the cement is actually the component whose hydration product is vulnerable to this. You need to be careful that aluminates in some supplementary cementing materials is specifically Class C fly ash can also supply this and so you may end up with just as bad a problem wit them. There are certain kinds of Class C fly ash that can make the problem worse than it was.

If you have sulfates, for example sulfate groundwater, and water present, there's no preventing sulfate attack. It's just a question of postponing the deterioration or slowing it down. So this is something where you really want to make sure that you don't have this in your environment.

Alkali-silica reaction, you see an example here of the characteristic cracking that occurs. For your application, you would want to use nonreactive aggregates. What we normally do in construction is we'll use reactive aggregates and we'll mitigate the reaction by using fly ash or slag. Again, though that is a slowing down or postponement of the inevitable. It is not avoiding it and you need to avoid it for the applications you're looking at. So you really need to be aware that if you have a reactive aggregate you're going to have to import something else.

Corrosion of reinforcement, this is actually a familiar site for anybody who lives in northern states where it freezes and we use deicing salts on the roads. There are two problems with corrosion. One is the actual loss of the steel area. If you needed the steel for structural integrity, you've obviously lost that. What's probably more of a concern though is that corrosion of steel is an expansive reaction. The products of corrosion are anywhere from seven to ten times the volume of the original steel and of course, that causes a lot of spalling and that's much more of an issue for most people.

The high pH of the Portland cement when it's hydrated does help protect the steel, but chlorides are catalysts for the corrosion reactions and so that's something that you really have to be concerned about. If you have chlorides present, they will continue with this and they're not consumed. They are free to continue to do this.

Corrosion is slowest in the absence of oxygen or if there's a shortage of oxygen and that may pertain to a lot of the applications that you look at because most of these things would be underground. So there would be less access for oxygen. But there's always some corrosion going on. It's slower or it's faster. You may reduce the rate by a couple of orders of magnitude if you do the right things, but it's still happening. So eventually you will see this deteriorate.

Irradiation, if concrete receives sufficient gamma radiation, it can deteriorate. But what information I was able to obtain came from the use of concrete for radiation shielding where it's actually getting a lot more radiation than it would in our applications. So I'm not sure this is even an issue, but it's possible that it would be.

It would take the form of cracking and loss of strength and stiffness. Again, maybe that that doesn't matter too much over the long term depending on what the concrete was used for.

Carbon steel which is what you would be using for the reinforcement and prestressing can also lose ductility with irradiation. It may or may not be an issue. Here this application where they determined this information is very different from what we have. It may not be all that relevant and it may be worth investigating what are the effects at much lower levels of radiation over much longer times.

The best model that I know of for modeling deterioration mechanisms is at NIST and I think it's because it's been going on so long and they've made a very conscientious effort to keep it tied to the physics and chemistry and the material science and also to validate it against actual tests. I think they've done a really good job.

Otherwise in general, there seems to be rather little connection between the models and the material science. I see an awful lot of models that they just kind of assume things and you wonder how they get there and if you ask, they just kind of look embarrassed and wonder why you want to know.

Some of the assumptions that I've seen in the models that are being used by DOE are very conservative, but it's hard to estimate the safety factors even to the order of magnitude and I think that's just because our knowledge isn't that good in a lot of areas and some of the assumptions are kind of wild. There is naturally very limited knowledge of the long-term behavior because we're using a lot of short-term tests or no tests at all.

We have some recommendations coming up in our National Academy of Science's report that I'm participating in. I think it should be out any day. I'm not sure what's happened to it.

Just to quickly reiterate a few ideas that I had about monitoring. First of all, the instruments are not going to last decades let alone centuries. So you need to be aware of that and either decide that you're only going to monitor certain things for a short time or make provision for monitoring with something else and changing several times during the course of things.

Electronic data would need to be transcribed to some long-term formats just because you can't read old formats of electronic data for very long. The things themselves deteriorate or they're just so incompatible with what you have now that you can no longer read it. So I think that may end up pointing people to stuff that may be very old-fashioned and simple, but at least you can still use it.

It may be best to install access ports, benchmarks and so on, things that don't change very much over time and then let whoever is monitoring it use the instruments of their own day. So that way they can just get in there and cite on the benchmark or whatever they need to do citing on it, however they like.

Something else that could be done is you could put materials coupons in certain exposures just to see what happens over time and then you can observe them, pull them out and take a look and see what's happened to them.

I guess we weren't going to do questions at this point. So I'll just end.

VICE-CHAIRMAN CROFF: Okay. Thank you very much. Our next speaker is Dr. Barry Sheetz who is a Professor of Civil and Environmental Engineering at Penn State. His research activities focus on cementitious materials for civil infrastructure, reclamation and nuclear waste management.

PROFESSOR SHEETZ: Thank you, Allen. In preparing this presentation, I've talked to Allen and we did try and get an idea of where I fit into the grand scheme of things today and we were talking and he suggested talking about failure in cementitious materials and he suggested the potential of discussing cracking and you'll find out as Chris has pointed earlier in her conversation that there are synergisms throughout this entire process and considering that Rachel just gave one-third or more of my presentation you'll see the synergisms develop.

I'm going to talk about cracking but I'm also going to give you a disclaimer. As we discussed with Dr. Esh's question earlier, most of our knowledge, most of our intuition, most of our expertise, resides from civil infrastructure applications. We just haven't done enough of these types of tank closures in sequestration of nuclear materials in order to gain the broad scope of knowledge that we're wanting and that you're asking for right now.

So we have to go back to what we know. You always want to start with what you know and then extend it out into the unknown and we're starting with civil infrastructure. We have a very significant background in concrete. We have a very significant background in Portland cement concrete. We have a very significant background in construction and we have this to call upon.

A fundamental tenant of anything that we do with Portland cement concrete is that "all concrete cracks" and that's exactly what we heard. You expect it to crack. The civil engineers when they're designing, now I'm a civil engineer but I've been raised as a geochemist and my entire career up until about Thursday was in Materials. So I look at things differently than my colleagues in civil engineering. I look at it from chemistry and phase composition rather than how close to the functioning specs can you get your material. If it cracks they can engineer around that. But just because it cracks, that doesn't say that all cracks are bad. We can mitigate those. We can control them and this is what we need to discuss.

Why are cracks bad? Well, I'm not going to go through all of this, but generally if you're looking at hydraulic conductivity, the hydraulic conductivity is composed of two parts. It's composed of the matrix conductivity that David talked about it and of course, it's controlled by the crack and the flow of water through the crack. And what you'll find out is that this water flowing through this crack is the predominant force or the predominant factor controlling the movement of water through the concrete object.

The crack width becomes very important. You can see width down there versus hydraulic conductivity in centimeters per second and you get the linear relationship just from this and not taking in the permeability. ACI 224 on cracking, it's a committee on cracking, gives a guideline. It used to be more than a guideline until the lawyers go involved with it. But they give you crack widths, two sets of crack widths, one for water retaining structures and another one for protective membranes and these span the amount of allowable crack width within a structure and you can see that we're talking about hydraulic conductivities that are much, much higher than what we would consider acceptable for the applications that we're discussing today.

If it's a partially-saturated system, the Wabash equation comes in, we understand how this behaves and then we can determine the width of the crack that will drain water. Not all cracks will drain water. So not all cracks are necessarily bad.

And again, this is probably a third derivative of the 1918 Handbook that Rachel just talked about. We know that the premature deterioration of concrete structures, it can be traced to cracking. It can generally be traced to cracking and it allows ingress of deleterious agents into the interior of big cementitious bodies. That's how it fails. The hydraulic conductivity through the tortuous microstructure of a concrete is generally slow enough that if you go from a two inch cover over a rebar to a four inch cover over a rebar most of the corrosion of rebar disappears. So it's a relatively slow process in engineering time frames, but when it's crack, you get it through quickly.

We've heard from Rachel a little bit of the cracking and time frame. I've tried to give that in some sense here and I wish these were years, but they're hours and you can see that there's a thing called placement settling that will contribute to cracking and this is while it's still plastic aggregate flowing around objects, around rebars. You see this a lot in parapets where you're forcing concrete through a parapet and it will settle and flow around the rebar. But you get these various phenomena that contribute to cracking occur as a period of time in hours, tens of hours and in obviously my log scale and we get to the freeze/thaw and alkali-silica reaction and the sulfate attacks that we talk about and in these cases, you're talking about years to reach the full degradation effects of cracking associated with those.

The underlying reason is very straightforward. Rachel talked that as a general rule of thumb concrete is ten times stronger in compression than it is in tension. We know that. That's not a big deal. So that any time the tensile stresses exceed the mechanism strength, a crack develops. So the onset of cracking looks like this with time after drying and stress level.

If we did not take into consideration the behavior of creep in a concrete what you would follow is this kind of a behavior here where the stresses exceed the crack resistance and cracking would occur here. But because cement creeps, creep will locally diffuse the microcracking. It will locally disseminate this, the stresses, and we extend the age of cracking from basically here to here. So the residual stress level when we take into consideration creep has to be evaluated when you begin to design your structures.

Now how does creep respond to strength? It's important. That's what I just said. And creep is inversely related to strength. If you want to build a (Inaudible.) strength concrete, it's going to have very low creep. So in this particular case, I think we want creep. So what kind of a strength should be recommended to design into this? Basically, what we would recommend is you design the strength in there to be just enough for what you need. You don't need 15,000 psi compressive strengths. Basically you need something that's probably a compressive strength of a little over 40 psi for if you're going to fill an underground tank and I'm looking here like and I'm approaching the whole presentation focused on large cementitious bodies, a.k.a. underground tanks.

So creep's important. We know how to control it. We know what that creep will do for us. We know the benefits that it will give us. We don't need to make high strength cement.

When we sit down, we start looking at the factors that impact cracking in cementitious bodies. We see that there's chemical and physical properties of the cement itself. We have to look at the cement itself. This is becoming very, very important and then there are the external conditions. There's mechanical and there's environmental. I'm going to step down through these and when I started to prepare these, this I have 20 different mechanisms or 20 different things that can contribute to creep and that sort of sounds daunting like we could never make a big piece of concrete that would survive.

Properties of cement that impact the cracking. These are the cements itself. High tricalcium silicate content suggests that there's low dicalcium silicate content. With time, what has happened is the market who's using, this is the construction market who's doing the civil infrastructure, has demanded from the concrete manufacturers, demanded from the specifying agencies, that what we do is we want a concrete that we can pull the forms off of faster when we're constructing because the faster we pull the forms off, the more money I can put in my pocket.

So what they're doing is there's a subtle draw, there's a subtle market draw, on the industry saying faster concrete, faster setting, faster setting and what this does is it impacts the chemistry. These are not unrelated. You will find the fact that we're putting more tricalcium silicate in our cements means that the heat of hydration of tricalcium silicate is higher by also a factor of four than the dicalcium silicate. So we're producing more heats of hydration. If you go back, this ratio is changing and we'll talk a little bit about that.

We're also tending to get more tricalcium aluminate into the Portland cements and as a consequence, we're having to put in more sulfate to ameliorate the early age reactions of the hydration of tricalcium silicate. We're also finding that we're grinding, we're tending to grind, these cements finer and that means a higher surface area. That means a higher chemical reactivity. That means faster strength gain. That means I can get my forms off quicker.

The other thing that we're finding is that deleterious is a high alkali content and this is from the other end of things. This is from the environmental end of things. Most cement manufacturing in the United States has now shifted to the dry kilns as opposed to wet kilns and in dry kilns, what you end up doing or what you were getting -- I'm sorry. In the wet kilns and in the dry is cement kiln dust. You're getting dust that comes off and it's collected in the bag house during these processes.

In the wet kilns, you couldn't put that back into the kiln. You could only put a very small percentage in. But in the dry kilns, you can take this dust that you've collected and you can insulflate it back into the kiln. This insulflation gets rid of your waste product that you don't have to dispose of. But that cement kiln dust is very high in potassium and potassium is our killer in the alkali content of cements, potassium and sodium.

So a manufacturer today is saying I don't want handle. I don't have to deal with EPA. I don't want to have to deal with the local environments, environmental regulations on handling this separate waste stream. I'm just going to blow it back into my kiln and as a consequence what we're doing is we're raising the alkali content. This is good and it's bad. The problem with this game is that there's no black and white.

We did a study, an FHWA study, that was Della Roy was the lead author on it. It was Paul Takowski (PH) and I were also on this project and when we compared this data just to back to 1969 to Blaine's study, we found a 40 percent increase between 1969 and 2003 in the sulfate content. We found a 45 percent increase in the potassium and that directly reflects the conversion of going from wet kilns to dry kilns. We see the calcium, this ratio of dicalcium/tricalcium silicate, has gone much higher. We have a eight percent rise in the sodium equivalent and we found the cements are much finer.

In a lot of authors and Burrows is the one that I read in preparation, this is ACI Monograph No. 11, and Burrows is a hoot. If you haven't read it, you need to get that book and read it. Burrows, he has a quirky sense of humor and he's opinionated and it comes through very, very quickly and I respect a lot of what he says, but Burrows and a lot of other people think that what we're doing by catering to the construction industry to change and get the cement to hydrate faster and set up faster that we're making poorer quality cements. We're causing the microstructure to change because it's hydrating so fast the microstructure of this. The hydration products in concrete is poorer than it was back when in the `20s and `30s when we had a very high dicalcium silicate content and were hydrating much more slowly.

This is also stolen out of Burrows and you get an idea of how things have changed over this 70 year period. Sid Mendez in one of his publications have a very, very good graphic which I stole. I used in my classes and since I've moved offices recently, I can't find anything and I couldn't find it. But he found two inch cube strength data that span from like about 1870 through current times and it's a log linear increase. It's an increasing logarithmically of time and the strength and you can see that here. You can see the fairly significant changes that are taking place.

We made some pretty damn good concrete back here and why? Because it hydrated slower. Burrows would have you think it also was better because we didn't cure it as long. He would also have you believe that it was better because of the higher water to cement ratio. Now when you read Burrows, you have to take him with -- You have to understand him. There are some things in there that nah --

But the bottom line on it is that the cement that we're manufacturing today is changing. We may not in the applications that we're going to talk about if we do and use Portland cement, we may not have control over any of this. But you have to know it's changing and you have to know what these changes are doing to the performance. Cement that hydrates rapidly generally gives you a more poorly developed microstructure. Slower hydration is better, the moral to that story.

Let's look at practices. Water to cement ratios, we've been pushing. You used to if you specify FHWA it would specify a 0.5 water to cement ratio for bridge deck. Then it was down to 0.7. Then to 0.4 or 0.5, I'm sorry. 0.47, 0.45. We're doing an FHWA study at Penndot right not where some of our decks are down at 0.43. We're pushing it to lower, lower water to cement ratios and this may not be good. Once you get it down below 0.4 you tend to get into another situation where the hydrating cements will suck up all of the water that's there. It's called autogenous shrinkage and you'll remove all of the water. You'll severely reduce the pore structure, the pore fluids and then deleterious other reactions open up.

We are also adding accelerators in many cases because as soon as I can get these forms off I can make more money. So we're trying to accelerate these reactions. We'll go farther out into the winter season beyond the end of the concreting placement season and we can accelerate this by adding calcium chloride which would be a death knoll if you had any kind of reinforcements in there.

And then we're pushing for very long

periods of curing and I put this in there. This is a Burrows statement and I find it interesting because he's concerned in his statements about the use of hydrating all of the cement. Rachel has shown that with a 0.47 water to cement ratio in her graph you still have 25 percent unhydrated clinker phases in your concrete.

If you have hydrated everything, it's considered bad and Brian Mather is one who expressed a great deal of concern about the consumption of all of the anhydrous phases in your concrete because microcracking can be an autogenously healed. If you microcrack and you get water in and you have on hydrated cement present and one of these microcracks goes by an unhydrated part, a piece of Portland cement, one of the cement minerals and it gets wet, there's no reason why it won't rehydrate. So we have to be cautious and we can indeed recover a lot of our failure and a lot of our cracking by autogenous healing of concrete. Don't necessarily build that in, but it is a reality.

Let's talk about these external or the mechanical loading. I haven't stress a lot of this because I'm looking at a buried underground tank at Savannah River or a buried underground tank at Hanford and short of an earthquake, we're not going to get cyclic loading on it. We're not going to get a great deal of static loading on it. It's in a stainless steel tank or not a stainless -- It might be. It's in an iron tank. It's contained. The tank may have a hole in the floor. It may leak. But basically you have a rigid containment.

Loading is a problem because in a stress/strain space concrete is nonlinear and as soon as you load it in any manner it's going to start microcracking and when it fails, of course, is when all these microcracks coalesce into failure. So I'm done playing this for the scenario that we're talking about today. The one episodic event that we have to keep in mind which I didn't think of was earthquakes.

Shrinkage. There are two types we've heard about. We've heard about plastic and drying shrinkage. Plastic shrinkage is a short-term phenomena. It results in part from aggregate settling. It's in part from evaporation from a higher temperature and low humidity. You're doing this in Hanford. You could get high temperature and low humidity. It's something to be concerned about.

But are you going to get that in a tank where you're pumping this? Probably not. The temperature is going to be reasonably stable. It's going to be less than the -- I've been out there at 103 or 104 with about 20 percent relative humidity. It's actually fairly comfortable. It's not like outside today.

The other thing that we have to worry about is wind because wind is going to contribute to the evaporation rate and we need to control that. So any time you're doing these kind of placements whether it be in an open vault at Savannah River where the top is off while you're pouring you have to take this into consideration. And with the finest of cement, all of this tends to increase.

Drying shrinkage is a slightly longer term and it's basically related to evaporation. If you control the scenario and you control the environment of placement you have the chance of controlling this. If you're pouring it in a tank through a hole, most of this is a non-consideration. Just to give you an idea of the effects of shrinkage on evaporation, this is kilograms per meter squared and this is the measured shrinkage and we have fairly decent understandings and relationships to what's going on there.

Autogenous shrinkage is a consideration that in the `20s they never even thought of. We now need to take that into consideration because we're pushing for high performance cements and I think what you have to do is define what high performance is. High performance is not necessarily high strength, but most people correlate them. When you go to high strength concretes, you saw from one of Rachel's figures that you go to low water to cement ratios and you can get enormous strengths.

I have a concrete that I had patents on in the early `80s that had 70,000 psi compressive strength in a concrete. It didn't have any water in it. We cooked all the water out of it. So if you can push the water down, your strength goes up. But once you get down below 0.4 what will happen is that the influence of the hydration phase is going to pull that water and going to pull that water out of the pore fluids and you'll get cracking associated with this removal of the water and that's also with water to cementitious materials.

Silica fume is particularly noted for this. When Silica fume first came onto the market and was being used, they were pushing it at 30 percent, 25 percent. If you go back to that patent that I had in `83 or something like that, we said five to seven percent. And if you look today, it's in the three to five percent that people are recommending.

Thermal behaviors. Rachel did a marvelous job on this, so I'm going to go through it quickly. The equivalent alkali content has a strong impact on thermal cracking, fineness. The tricalcium aluminate which you heard, the tricalcium silicate content also has a fairly significant impact on it and we've discussed those.

Internal and external restraints we've talked about. This is I think going to be a big problem because the tanks that we're going to fill, you know you picture a tank and when the layman thinks of a tank, they think of a tank that's a right circular cylinder with nothing in it. In reality, we know that these tanks are penetrated by dozens of cooling vents and pipes and all of kinds of probe ports and whatnot and as the concrete or grout of whatever we put in here starts to dry, starts to cure, against these, these are going to act as restraints. These are going to act as points of restraints and these have the potential therefore to enhance cracking.

For external behavior, of course, it's contained in a tank. It's contained in this iron shell and it's going to thermally expand against that.

Preferably we won't have an -- Or maybe we want an expanse of concrete in there to put a positive force against that and we can engineer around this in many cases by having a positive internal stress left in the concrete when it finally does cool down.

Freeze/thaw. We've gone through this. Nine percent expansion. When that water expands in the pores, it puts a hydraulic pressure on the interconnected pore water and it has to go someplace. If it doesn't have a place to expand, you're pumping a hydraulic pressure on the inside pore structure and you're going to get microcracking. When these microcrack coalesce, you get failures.

What we do is we introduce bubbles. We introduce about five to nine percent bubbles that are about 100 microns with a less than 0.2 millimeter spacing and we give it a place for that water to expand into as the ice freezes. A well developed aerated concrete, freeze/thaw is a non-problem anymore. Are we going to see a freeze/thaw problem at Hanford? Probably not even if we're casting in the wintertime because we're going to be casting underground. So again, I don't think that this is a major concern.

Corrosion. I'm not going to go through.

I think Rachel did a wonderful job there. The corrosion is a problem. The corrosion products are expansive. You have to keep chloride out. There is a threshold in civil infrastructure concrete above which that we know chloride begins to initiate the corrosion of the rebar. But commensurate with that, we have to get the pH of the pore fluid down so that we go from a passive to an active surface. And there is a lot of, as Rachel pointed out, concrete engineers out there who don't know what slag does for them or don't really realize that it's controlling the E_h of that solution as well and extending the durability of it.

The alkali aggregate reaction, they come into two forms. They come as alkali-carbonate reactions and alkali-silica reactions. Basically this is the reaction that you've all seen where carbon dioxide is entering the pore fluids and reacting with calcium hydroxide. The reality of the matter is that there isn't one phase in the mineralogy of clinker that is stable with respect to carbon dioxide.

So let me put that another way. The thermodynamic end products given enough exposure to moisture and to carbon dioxide, the thermodynamic end products are calcium carbonate, quartz, silicon dioxide, aluminum oxide, water and calcium carbonate and Chris in her graduate student years had an opportunity to go over Crete and look at some of these with -- Who did you go with? Was that Geographic?

DR. LANGTON: Smithsonian.

PROFESSOR SHEETZ: Smithsonian study to look at these old concretes as a function for long term use in the applications that we're talking about and the Colosseum is glued together with calcium carbonate and silica. So carbonate chemistry is a very interesting concern, however, it's all relative humidity driven. So if we can keep the relative humidity up, it's a non-problem. If we keep it up in the 50 to 100 percent range, we minimize the effects of the deleterious carbonation effect.

(Microphone noise.) labs they've actually had a program out there where they are specifically carbonating Portland cement in order to change its properties and enhance its properties and they were basically making a moral when they finished their reactions. But we do have some experience with rate kinetics and things like that from those studies.

The alkali-silica reaction you've seen as these polygonal cracks. Basically what happens here is that the rock contains forms of silica that are more water soluble. The pore fluids, we've talked about the pore fluids being controlled by calcium hydroxide at 12.45. The reality of the matter is that it's not controlled by that, at least not initially. It's controlled by the alkali, mostly the potassium hydroxide content and the pore fluids are actually up at about 13.3 or 13.4. That's why if you play in concrete with your bare hands at the end of the day your hand feels like a piece of sandpaper because you're dissolving. It's dissolved all the fluids out of your hand, the oils out of your hand and you become rough.

These high pHs will dissolve certain forms of silica, crystabolite for instance, and they tend to have a higher solubility and they'll take those into solution. What they'll do is the whole process is fairly complex. I'm not sure that the model is fully developed, but what you'll find is it gets an osmotic pressure in this silica gel. Water is absorbed. As that water comes in, the gel expands and microcracks. Sid Diamond found that there's this pessimum and I sort of like that idea. There's an optimal value of silica where it favors the deleterious expansion and again that's something you can determine.

You can minimize it. You can generally

eliminate it by the use of blended cements and these are the supplemental cementitious materials that are put in and that will stop it. Size of the aggregate also affects the alkali-silica reaction and the use of lithium. Lithium does a lot of things, but it also cures ASR.

One of the other carbonate reactions is the so-called dedolomitazation where the alkali hydroxide if you have any amounts of dolomite in your aggregate you can get it to decompose and form brucite, an alkali carbonate and calcium carbonate. Brucite is not necessarily very good because if it goes from magnesium oxide to brucite there's a very significant swelling in it. That's how we seal geothermal wells with the paraclay brucite reaction.

There are other environmental effects from sulfate attack. There is alkali ingress into the concrete. Magnesium ingress. The so-called delayed ettringite formation and that may be a can of worms. When I speak, I'll open it and then duck and ettringite formation. I'll go through these really quickly.

The ingress of sulfates will react with the tricalcium aluminates and the tricalcium aluminates are in the cement but as Rachel pointed out, you have to look at very carefully your applications with other supplemental cementitious materials because a Class C fly ash has a mineralogy that has a lot of the cement phases in it and that could put that into it. So you could get some tricalcium aluminate from your supplemental cementitious material.

But generally they form gypsum, ettringite and monosulphoaluminate and if these are formed while the cement is a plastic, while it's fluid, ain't no problem. But let it get hard, let a structure set up, and let them begin to form and now you have a problem. They'll start to expand. Their molar volume is larger than their constituent starting materials and you'll initiate microcracking. I don't need to go through the chemistry of all that. I'll go through it very quickly, but you can have it there as a reference. And you can assume that the rate of sulfate attack is almost directly proportional to the calcium aluminate content.

Magnesium attack is particularly onerous because what magnesium does is magnesium attacks the C-S-H. It attacks the glue that's holding your structure together. So what will happen is the magnesium sulfate solutions will come in. They'll react (Microphone noise.) gypsum or you form -- Something's not right there. Yes, you form gypsum and magnesium hydroxide and you'll get a double whammy from the expansion of the magnesium hydroxide and the loss of the glue that's holding your structure together.

Delayed ettringite was a big phenomena here a few years ago and I'll be very gentle here I think. Basically we need to have ettringite in our Portland cements. It controls that reaction rate with tricalcium aluminate. So we have to have it formed. But it's not stable above 65 degrees. So above 65 degrees, it decomposes and it decomposes, ettringite will decompose to maybe hydrogarnet, depending again on how hot it gets, some form of a hydrated calcium silicate, either one of those four polymorphs, and water.

So it sits in these forms and they're in spacial or they're in a close spacial relationship because they just fell apart. So if your concrete is sitting here, it's gotten very warm. First of all, you've deteriorated the microstructure and you're going to have long-term problems with the loss of that microstructure. But what will happen is if upon rehydration water gets back into these, this is going to be generally taken out into the microstructure, if water gets back into these what you do now is you have a hardened structure and you're reconstituting the ettringite and it expands and it cracks and it fails.

Tank closures aren't unique. Chris has done two. She's going to do two more. How many 20,000 gallon tanks did you do?

DR. LANGTON: Oh a lot. Twenty-five.

PROFESSOR SHEETZ: Lots. You know they've done the vault. We have experience within the community. We have a broader experience in mass concrete in the civil engineering community. We have bridge piers. We have all kinds of structures. So this isn't unique. But what is unique is that we have all these damn things in there. We have to take that into consideration. We have to be aware of it.

So size and geometry. We've talked about this. We started to bump up against this, what we do in the lab versus what we do in the field. We have to be aware of that. I can make the best concrete in the lab, but if I don't have my proper QA/QC in effect, the engineer in the field will say, "Gee, what did he know" and he's going to do his own thing and you get a different product and then you now don't know the performance.

Do we know the scale factors for all of the concerns that we have? No. Can we guess at them? Yeah. We have, the engineering community has, ideas on what to do. Geometry is a very, very interesting question that we haven't talked about. Most of what we've talked about and most of our knowledge on cracking comes from lenticular slabs, lenticular structures, not from mass concrete pores. We've done a lot of these but we've done an awful lot more. We've laid a lot more highway and bridge decks than we have big massive structures.

So we've done bridge decks, parapets, foot walls, slab grades. These are where we're getting a lot of our data from, but we do know how to do the big stuff. So if you were going to go and you were going to do a 1.3 million gallon tank closure, who would you go to? Take out a piece of paper and a pencil. This is a quiz. Who would you go to? What component of the engineering community out there is interested in producing mass concrete that doesn't leak? Dam. You'd go to the dam builders. Right? These people are out there. We know we do this. These guys are concerned about leakage. They know how to handle the infiltrating water. They know how to handle the heat. So we should engage them.

Are there a lot of those guys out there? We're not building dams anymore.

PARTICIPANT: Then you go to Brazil.

PROFESSOR SHEETZ: We go to Brazil. Go to China. Maybe not. But the point is that we have a body of knowledge to look at. So are there unknowns and I'm here to tell you that there are and the unknowns are this. We're going to use Portland cement. It's going to hydrate and I'm using tobermorite as the surrogate because it's easy because it has stoichiometry. But this is the formula for tobermorite and we can substitute crystal chemically into that.

So David is going to be putting all kinds of sluck from radioactive material into his waste forms into this grout to sequester and it's going to take up different mobile, labile species into the structure and it's going to do it according to this. Do we know what the properties are? No. Will there be significant effects on the mechanical performance of the concrete? Maybe. Maybe not. Has anybody looked at building structures with this kind of substitution into it? Yeah, but not nearly as complete as what we're talking about and what we need.

Ettringite, we have to have ettringite

into our cements. David talked about the uptake of the hexavalent chrome, oh no, trivalent chrome into the ettringite. These will all go into ettringite. There are some of the nitrates that will go into ettringite. Iodides will go into ettringite. In fact, you can't put iodide into ettringite. It will oxidize. It will take it to iodate going into ettringite.

Do we know its performance and the behavior of these? Not really. But let me give you an example. Ettringite is a crystal with symmetry 6m and 2m 2m. It's a dihexagonal dipyramid. It looks like this and this is where the problem comes because it elongated along the zed direction and if you have a hardened concrete structure and this starts to grow, this can put enough forces that it will exceed the tensile strength of concrete and crack.

However, what we found in that Della Roy project of `03 is if we substitute trivalent iron for trivalent aluminum we change the morphology. The morphology doesn't go elongate. It goes something like this. We suppress the growth in the zed direction. So I can get rid of ettringite degradation just by raising the iron content in my cement and it works. So this was an unintended consequence of that study, but it's the surprise and I'm presenting this just to give you an idea of what we don't know. I don't know what would happen to this morphology if we substitute trivalent chrome into it. Maybe instead of going from a clam to a needle, it goes somewhere in between. There is some unknowns.

Let me wrap up. So there's a list of the factors. I didn't even include wet/dry cycling in here and efflorescent salts. So let me just quickly go through this. Tricalcium silicate, we may not be able to have any control over. Because if you're buying cement at Savannah River, they're not going to reburn the cement for you. So you have to live with it.

The sulfate that sort of came and went, same deal. May not be a problem.

Fineness, we can probably get them to grind it for us the way we want it if we really insist. If you tell them you're going to buy their total year's production if they grind it the way you want it, they'll knuckle under.

Alkali content, again you're not going to have much control over. You're going to have to live with it.

Low water to cement ratio, you can control it. You can engineer that.

Accelerating add mixtures you can certainly engineer that. You don't care if this thing hydrates in ten hours or if it hydrates in ten months as long as it gets hard and as long as it gets 40 psi, you don't care.

Long-term thermal cracking, that may be a concern. How do we control that? Can we control that? That's going to be one of the bigger concerns.

ASR, you can control that. You can control that by the choice of aggregates that you use. You can control it by the choice of supplemental cementitious materials you use.

Sulfate attacks, this is going to be a tank and it's a lot likely that you're going to get external groundwater into this tank until that tank dissolves.

Sulfate attack from magnesium, sulfate attack from ettringite.

DEF may be a problem. If you can't control the thermal behavior you may have future susceptibility for the delayed ettringite attack. How long those sleeper cells are going to remain in place in there and be reactive is anybody's guess at this point.

Drying shrinkage is probably not going to be a problem because you're going to place this in a tank underground in a relatively constant temperature and constant humidity. Plastic shrinkage, likewise.

Thermal contraction is a problem.

Freeze/thaw, if you do it and you do it underground, it's probably not going to be a problem.

Corrosion, as long as you keep the pH up it's not going to be a problem. I don't see really that you're going to reinforce these tanks with anything. So that's probably not a problem.

Static loading, cyclic loading, they may be a problem. The only problem you get with mechanical loading may come from earthquakes and frankly I didn't look at any of that.

And internal and external restraint is I think going to be your biggest problem

So if we look at these, what can we do? That's going to go away. I just said that you really don't have any control over that. The alkali content you really don't have any control over. The long-term contraction you may have, you may be able to handle. So DEF, my guess is that DEF's not going to be a concern.

So what we're left with is we're left with the thermal contraction that you have to be concerned of once this thing heats up and then it's going to swell because of heating and it's going to shrink when it cools down and of course, the external/internal restraints associated with the tank. These I believe are going to be the two things that we really have to be concerned about for closure of these large tanks in order to minimize the cracking.

I believe we can control everything else. I believe we can control these. I think it's going to take a bit of effort to control this because of all of the pipes and protrusions and things inside, but I believe it's possible. They do it with dams. They pump liquid nitrogen through cooling pipes in dams and they pump water through it to cool the individual components. If we really need to, we could probably do that.

Everything you wanted to hear about cracking.

VICE-CHAIRMAN CROFF: Thank you very much. It was just a tad long here and I do want to adjourn for lunch at 12:30 p.m. as planned because the lunchtime is relatively short even at that. But we'll try a few questions here. Jim.

MEMBER CLARKE: I had a question I wanted to ask before but we were running short on time on that and we're hearing a lot of interesting stuff and a lot of the pieces and I'm sitting here trying to put the pieces together that both of your talks, I think, were very helpful in identifying what we could be concerned about and what we need to be concerned about if those are any different.

The question I wanted to ask was about accelerated testing that you mentioned, Christine, and the question is if Rachel can give me 25 years of monitoring data and I can keep that in an information management system that we can all understand and I think that's possible, what do we get out of the accelerated testing? What tests are available and how far do they accelerate? David showed us a model and real data and after one year, there were two orders of magnitude apart. So how can the accelerated testing help us with this?

DR. LANGTON: I just identified the need for accelerated testing.

MEMBER CLARKE: Okay.

DR. LANGTON: I didn't say what they were.

PROFESSOR SHEETZ: Accelerated testing is obviously something that is of interest elsewhere than just here. There are some procedures that are floating around the literature right now where you raise -- I mean how do you accelerate any reaction. You can do it three ways. You can add a catalyst, you can increase the surface area or you can increase the temperature.

DR. LANGTON: Or you can increase the concentration.

PROFESSOR SHEETZ: Or we can increase the concentration. So we can't increase the concentration here. We're not adding catalysts. We can't grind this thing up. We're left with increasing the temperature. There is a procedure that is being circulated in the literature where you would take your ASTM protocols, let's say if you want to compressive strength, and you cure it for seven days at room temperature and then you take and you cure it for another seven days at 38 degrees Centigrade. That will give you about 3X acceleration in time and then you go crack it and there's very good correlation that that accelerated test works and you can just spend the time and take the room temperatures for the period of time and the values are pretty reasonable, I mean, within the limit of error of the particular test method. They will accelerate.

But you're only accelerating a factor of

3X. If you go to 68, you accelerate by about, what, 7X or 8X. So what we need is a test that's going to accelerate by orders of magnitude not by --

MEMBER CLARKE: Maybe, but I still think the further out we go the better off we are and we're not going to go to 10,000 years. So I'm not looking for that, but I'm looking for ways to get monitoring data and correlate it with model predictions and improve the model and go through that cycle.

PROFESSOR SHEETZ: I believe we can probably -- Some of that data is out there.

MEMBER CLARKE: And then I just keep saying that because I don't see it being done.

DR. DETWILER: One concern you have though when you accelerate phenomena is that you may eventually get to different failure mechanisms than you had or that would happen in real life or it may just be that if you had multiple mechanisms already occurring, that by your acceleration method you may favor one over another and so that it becomes a poor representation of what's going to happen.

So it's not simple and especially when you're -- You know it's one thing if you're dealing with just chemical reaction. But if you're also dealing with things like diffusion and a number of physical phenomena at the same time that you may end up with something that's very, very different. I think that's where maybe using your accelerated test to choose from among several formulations to decide this is the best one and then making an effort to do some of these long-term monitoring things so that you can kind of verify your models and go back and see does this make sense or do we need to adjust or correct and then if we have the possibility --

I mean I've seen even in something like when I was in my first job. I went out to a precasting plant where the people who had started this plant were very interested in investigating things. They instrumented every member that they had. Their plant was built of prestressed concrete and they had instrumented absolutely everything so that they would have long-term data and then later they could go back and look and that kind of thing then if you did it in a systematic way and you shared it you could provide a lot of useful information for yourselves and other people who were doing that same kind of thing.

MEMBER CLARKE: That's where I'm coming from and help sorting out which because the complexity is obvious and if you were focusing on one property, the accelerated test would probably be extremely helpful, but sorting out which ones are the ones you can focus on.

PROFESSOR SHEETZ: To supplement Rachel's statement, what you're doing from the materials standpoint, when you accelerate you have to stay within the same compositional range, the same mineralogical stability range when you're accelerating and if you exceed that range and you go into the stability range for another mineral phase in your concrete, then all of a sudden all bets are off because you're not really, you're accelerating it into something that doesn't exist.

MEMBER CLARKE: I understand. In the interest of time, thank you. Ruth.

MEMBER WEINER: Would you prefer that I just wait, hold my questions till we have the roundtable?

MEMBER CLARKE: Your choice. I'll give you one.

MEMBER WEINER: Okay. They're quick questions. But the first is, Dr. Detwiler, you mentioned that you go out to 100 years. How about 500 to 600 which is 20 half lives of strontium-90 and cesium-137? Do you think you could have structures that could be predicted to retain something for that long?

DR. DETWILER: I'm just saying what our experience is and that's well beyond our experience. You could predict anything. I won't be around to see it.

MEMBER WEINER: Nor will I.

DR. DETWILER: One job that I was on where one of the geologists that was consulting on it said and he was probably in his 60s already, he said, "I don't care about 500 years. I only care about five years." So we could say anything, but as far as do we have a solid basis, no we do not.

MEMBER WEINER: The other question I have is what about, you mentioned gamma degradation of concrete, what about alpha degradation?

DR. DETWILER: I don't know of any information about that.

MEMBER WEINER: Dr. Sheetz, do you have any?

PROFESSOR SHEETZ: Alphas don't penetrate very much. They'll just -- I mean they won't even penetrate your skin.

MEMBER WEINER: Thank you.

CHAIR RYAN: I'll defer.

VICE-CHAIRMAN CROFF: Okay.

MEMBER HINZE: Briefly. In the face of this blizzard of information, I have taken away several things and one is that there's concrete and then there's concrete.

(Laughter.)

MEMBER HINZE: And the concrete that one might use in Savannah River versus Hanford versus Minnesota, you might wish to have considerably different attributes. And one of the things I'm taking away from this is that there is the possibility of custom blending of concretes.

To focus it on the Hanford problems, for example, you might want to change the rigidity of the concrete because of the seismic hazard there, but you don't have the problem associated with all of the moisture that you have. So it seems to me that what I'm taking away and tell me if I'm right or wrong is that there is a lot of potential here for customizing concretes to the particular environmental attributes that you anticipate over a 10,000-year time period.

PROFESSOR SHEETZ: You are correct. Concrete is an engineering substance.

DR. DETWILER: Basically even for things that are much less complicated, we still design it. It's basically custom designed for anything. So certainly with this, you would do the same. I mean if you do that to make a box store, you have a different mix design for the footings and for the columns and for the stab on-grade. You could certainly and you should do this in this kind of application, but you're probably going to be looking at more sophisticated criteria and criteria that not everybody deals with. So there may be things where we really need to do some very different kinds of testing, very different kinds of investigations to come up with how best to meet those criteria. But that's well within the purview of what normal concrete engineering is about.

CHAIR RYAN: Bill, if I may just add on. There's an important, I think, addition to your thought which I think is right on target and that is that if you can somehow do that tailoring of the material and then take credit for it in a modeling and performance sense and then add Dr. Clarke's comment about if I can now figure out a way to monitor it over some reasonable period of time and see that if it's behaving in that environment as tailored, as anticipated, now we have something where confidence is a possibility.

MEMBER HINZE: (Inaudible.)

CHAIR RYAN: Absolutely. So I just wanted to throw that in.

MEMBER HINZE: I don't want to get at this now because we don't have time, but one of the things that perhaps we can take up in the final is the direction and status of research in concretes and Barry tangentially hit that.

VICE-CHAIRMAN CROFF: You'll hear a lot this afternoon.

MEMBER HINZE: We will hear that. Okay. Thank you.

VICE-CHAIRMAN CROFF: I think a couple of points. First, I've taken away from two or three of these talks that air is the enemy of cement. Cement is not stable in front of the CO_2 in air in particular and over time it will degrade, air and water, humid air, which tells me air ingress is a problem and that leads to a couple of thoughts and that is whether any consideration has been given to let's say sealing a tank or a saltstone vault or something like that, sealing it to air. We think a lot about water ingress, not so much about air, but I'm hearing that's fairly important over the long term.

Secondly, we're talking about monitoring and we're talking about penetrations. The penetrations are avenues for air to get into this thing potentially and so I'm sort of seeing a possibility of a tradeoff there. Any thoughts on that?

PROFESSOR SHEETZ: Carbonation attack in concretes in northeast is pretty rare. Would you agree?

DR. DETWILER: Well, I think that of course that's part of that and I think where people really see lots and lots of carbonation is more in Europe where there's a lot less cement in their cement. After World War II, there was a real shortage of cement because they were trying to rebuild. So there was a tremendous demand and basically what they did was they intergrounded a lot of unburned limestone into the cement and so that was basically a dilution. That's where you really saw a lot of carbonation.

But it is nothing like that bad when you're talking about the amount of cement that we have in ours. It's almost all clinker and we should have enough residual in there to deal with that. So I don't see it as a huge problem and remember that if it's an underground tank you don't have that much access to air. I mean the soil around it or the steel while the steel is there and the soil around it, it's not something where you have lots and lots of air and chances are some of these other things that you hope are not in the soil like sulfates would definitely be worse.

PROFESSOR SHEETZ: As long as the humidity is up in the pore fluid, it's a non-problem and nothing is independent of one another. But if the pore fluid in that 50 to 100 percent range and it's sealed off, there won't be any problems. If it's up and there's carbon dioxide present, it still probably won't be a problem.

We've looked at some structures from a parking garage at Duquesne University. It's been in 25 years and did the phenolphthalene test and you can see some effect on the surface. It's not quite clear if it's carbonation or if it's just rain and other events washing out of the surface, but the measurement on that is just a millimeter or two after 25 years.

DR. KOSSON: I think it's very important that you differentiate between structural concretes and waste forms because in waste forms you do see significant carbonation and the outcome carbonation often is in the 60 to 80 percent relative humidity range and when you talk about these very long time frames where you do have cyclic wetting and drying conditions, then you may be talking slow processes relative to your 50 year duration of structural concrete. But when you're starting talking hundreds of years into a waste form which is not designed like a structural concrete the carbonation ingress can be rather significant.

PROFESSOR SHEETZ: Yes, the cyclic wetting and drying we see efflorescence coming out of concrete and that's limestone. That's calcium carbonate. So you do have the potential of sealing your pores with the wet/dry cycling as well.

DR. LANGTON: I have to emphasize that when you're looking at the system -- Well first, waste forms are not concrete and our waste form at Savannah River, our saltstone waste form, already contains carbonate as sodium carbonate salt. I can't say that air is the nemesis of concrete. Air is not necessarily bad. That's the wrong conclusion to come to, air with carbonate.

The other thing to say is that monitoring units of a landfill is one thing, but so far all I've seen done is monitoring of the landfill. We're monitoring well either in near field or someone more distant, not too far away, is what's monitored and you can wait hundreds of years before you see anything in those wells unless something really catastrophic goes wrong. But what we need is monitoring of the components that go into the landfill, the soil. Well, even the soil is too far away to be affected when we've have large --

MEMBER CLARKE: Christine, if I can interrupt. The monitoring I was referring to is placing access probes inside the cover over the landfill and then monitoring -

DR. LANGTON: But we won't put the cover on for years, for 20 or 100 years.

MEMBER CLARKE: As you close this landfill.

VICE-CHAIRMAN CROFF: We need to terminate this.

MEMBER CLARKE: I just wanted to make that distinction. I agree with you on the --

VICE-CHAIRMAN CROFF: We can continue it on later on this afternoon. I think we'll hear some things that bear on it, but it's a very relevant discussion. Let's come back at 1:20 p.m. if we can. It's a quick lunch but thank you. Off the record.

(Whereupon, at 12:35 p.m., the above-entitled matter recessed to reconvene at 1:24 p.m. the same day.)

VICE CHAIRMAN CROFF: I'd like to come to order, if we could. We've got a number of interesting things to do this afternoon, and time is fleeting. I think we've got everybody here in the room.

All right. We're into the third session that's to address the state of the art in predicting long-term performance of cementitious materials. We've got three speakers here, although I suspect many of our former speakers are going to have more than a couple of opinions as we get into the question and answer later in the afternoon.

The first speaker in the session is Professor Fred Glasser from Aberdeen University in the United Kingdom. Professor Glasser received a Ph.D. in Geochemistry from Penn State. In his many years of service at the University of Aberdeen, he has directed a group working on ceramics, glass, and cement, with emphasis on fundamental and applied studies. He has been working on radioactive waste since the late 1970s, mainly on application of cementing, but also on longer term planning and repositories and their post-closure performance.

Professor Glasser, take it away.

DR. GLASSER: Thank you, Chairman. It's a pleasure to be here. I do have to say that almost everything that I wanted to say has in fact been said by previous speakers.

(Laughter.)

But I'll try to go through that part quickly. I think I have a few things that haven't been said, and I'll try to make my oral comments relate to some of the things that I think haven't been said.

I'll briefly talk about the role of cement in nuclear waste disposal, but I think I'm teaching my grandmother to suck eggs here.

(Laughter.)

Resistance to degradation, mechanisms and processes, some synergies with civil engineering and civil engineering practice. I want to talk about what we mean by "performance," what we mean by words like "durability," to give you some data on solubility studies, showing how cements perform in response to different aggressive substances in the natural environment, about the need to develop a new paradigm and to implement it about testing and test methods, some special hazards to cement studies in nuclear applications, to cements and the source term about which not much has been said, remediation activities, and, finally, conclude with a brief summary.

By "cement" -- and I'm going to talk about cement. When I do venture into mortars, grouts, and concretes, I'll try to use the appropriate correct term, but mainly the focus of durability studies is on the cement. It's the matrix that binds other materials together. And when that matrix is destroyed, the functionality of the resulting material, be it mortar or concrete, is destroyed.

Now, cement is a standard product. It's almost the same the world over. The detailed specifications in the United States, ASTM specifications, are mirrored very closely by worldwide practice, not surprising perhaps when you think that the bigger cement producers operate on a worldwide scale. The U.S. is one of the few places in the world where there's still lots of independent companies, but increasingly the market is being dominated by the big international players.

There are codes of practice that govern the composition of both cements and also blended cement specifications, and they are important. They're treated second only in importance to the Bible by civil engineers who work with cements and concretes. And you find that if you want to make changes you do so at your own risk.

In nuclear waste disposal, cements and

concretes have a long history of use. Obviously, it's primary matrix material for solidification and stabilization of liquids, sludges, or particulates. Because of their relatively high physical density and the possibility of including aggregates, they give good shielding for personnel and good protection against the exigencies of storage and transport.

They can be used in repository construction, both as liners and seals. Sometimes they're necessary to permit retrievability, which may be a requirement. But although cements are relatively similar in specification, they can be modified by adding supplementary materials as well as, of course, coarser aggregates. And we'll have course to deal with some of those in the not-too-distant future.

Now, cements are perhaps unique in respect of other barrier materials. Whereas other barrier materials, such as steel or glass or clay have primarily a physical function to play, cements also exhibit chemical activity, so it's not directly comparable with other barrier materials -- for example, metals that have a mainly physical role to play in the immobilization process, although as we will see there are certain factors in common between the deterioration of cements and those of metals.

This chemical conditioning role is always present and has both positive and negative implications for performance. For example, portent cements will react strongly with glass. They condition a high pH, and this is detrimental to the longevity and durability of glass wasteforms. And so it's important that the two not be mixed, or if they are mixed that there are special circumstances which will permit effective isolation of one from the other.

Now, we've talked about the change in cement, and many people will question whether this is inevitable. And I think the answer is yes. I think almost all environments that I can think of in which cement and concrete will be used, both in nuclear engineering and in civil engineering, they are in fact thermodynamically stable -- unstable, sorry. Therefore, they will change by reaction with their environment. So this is inevitable.

What we cannot always predict is the consequences of a reaction with the environment, which range widely, and we also cannot readily predict the rate at which these changes will occur. So a purpose of this meeting is to define and, if possible, quantify these changes, and I will try to stick, whenever possible, to generic considerations in presenting material to you.

I'm not going to present a vast amount of factual material. I don't want people to go on to overload. So the examples that I'll offer I hope are selective and easy to understand, although not always comprehensive.

Well, if we compare resistance to degradation of different materials, I have the feeling that many scientists are more comfortable with the degradation of metals than they are with the degradation of cement. Perhaps if I call it corrosion of metals, that will strike home exactly what I mean.

Now, there are differences between the behavior of corrosion of cement and corrosion of metals. Metallic corrosion clearly involves oxidation and with it electron transport, whereas cement corrosion does not generally involve oxidation reduction, although I would make an exception for slag cements and, of course, the materials that are embedded within cements.

But certain features are common to both. For example, we have the formation in some regimes of soluble corrosion products, and we -- and insoluble corrosion products. Now, in metallic corrosion, this gives rise to regimes of active corrosion where the products are soluble, and passivation where the products are insoluble and tend to accumulate at the surface of the metal undergoing change.

So we can see this analogy in the next slide. I've shown here on the left a metal which is partly active, soluble products are forming and going off into the aqueous phase, but there are also an accumulating layer of insoluble products of corrosion, the substrate metal being -- ah, yes, the substrate metal being, well, I think -- yes, the substrate metal being to the left and insoluble products of corrosion accumulating as well as some soluble products.

Now, this is mirrored by cement, which can also have these different regimes of corrosion. Here the aqueous solution is on the left. The unaffected cement is to the right, and we have insoluble products of corrosion accumulating at the surface as well as solid products going off into solution.

But a difference between metals and cements is that in aqueous solution water and salts that might be present in the aqueous solution can migrate into the rather more permeable and porous cement matrix. So alteration indicated by the hatched lines may extend to greater depth within the cement, whereas with the metal we generally see a clean contact, an interface, although not necessarily as geometrically perfect as I have shown it.

So the strength of this interaction between cement solids and water, or species that may be dissolved in water, or with atmospheric constituents varies greatly. As with metallic corrosion, there is a need to preserve local electrostatic charge balances.

So when we measured diffusion coefficients of species in and -- in and out of cement, we are measuring apparent diffusion coefficients, because the driving force may be partly dictated by the need to maintain local electrostatic balances to maintain the ionic potential of the pervading aqueous phase, and so on.

So it also is a difference between metals and cements that because these matrix diffusions occur in cements that there is a quality factor associated with the diffusion. It's a complex function of the matrix formulation -- for example, how much porosity there is and how interconnected this porosity is to give rise to permeation. It's a function of age of the material, and it's also a function of the thermal history of the cement, mortar, or concrete.

Now, this quality factor has been much

studied by engineers. You heard a lot about the influence of water cement ratio, for example, in previous talks. And, clearly, engineers have been looking for decades now for specific measurable features to -- with which to quantify the cement that they can introduce into equations relating to degradation in order to define the rate at which degradation occurs and its consequences.

Now, these relationships are almost entirely empirical. Again, we've had descriptions of some of them today. And the problem with these empirical relationships -- and this is one of the nubs of the problem -- is that although they are cherished by engineers, protected, beloved by engineers, they don't actually yield a predictive capability.

So that the questions that have been asked today over and over again, how do we -- but how do we -- all right. You've told us what happens in five years, but what happens in 500? We can't answer that question, by and large, from the existing body of knowledge. And that's a problem that we'll have to live with, and so I'll be talking later about new paradigms.

So given the long history of civil engineering, and the scientific study of cement and concrete, was begun well over a hundred years ago, famous names like LeChatelier, and so on, were very active, and Henry Sorbe, the discoverer of the petrographic microscope, these people very active in elucidating the constitution and deterioration of cement.

And one can understand, given the times, the qualitative nature of their approach. So although it might be expected that quantitative models now exist, this is not so, and there are a variety of reasons for this, some of which are valid, but some of which are -- really fall in the class of excuses.

So just to recap our durability standards in civil engineering, now, these stand like a great monolithic body. And if you're going to do anything new or different, you run into this obstruction on the highway of progress. The standards are legally binding, and they are prescriptive. And no self-respecting engineer will go against them, because his or her professional reputation is riding on the way in which they implement these.

So this experience of test standards, which themselves are often the products of experience, do have a lot to teach us. I'm not dismissing this body of wisdom. It has been acquired, much of it, in a hard way, and much of it is very useful. But we have another problem to overcome, and that is that cements and concretes are often made on the job at site, and they're not necessarily subject to the same rigorous quality assurance that you get if you bought, say, a steel column or eyebeam.

Another problem that we'll have to face is the extreme complexity of natural environments. Even steady-state environments are very variable from one spot to another on the face of the earth, the atmosphere, the oceans, the groundwaters, the earth.

Temperatures vary, and there are physical processes as well, which affect the durability and performance of cement, the phenomena like Freestar has been mentioned earlier, and they create a virtually infinite spectrum of service conditions that require to be tested. And, of course, the tests have not been done for this variety -- or infinite variety of conditions, simply because there's not infinite manpower and there's not infinite time.

So having said that, engineers fall back on a few simple measurable parameters -- for example, compressive strength. Again, we've heard that mentioned, and it is, after all, for material which is intended for use by engineers in structural. It's hardly surprising that compressive strength is a strong arbiter of your success in creating a proper structure, proper material. But as we'll see -- as we've seen in the nuclear field, compressive strength is not such an important parameter in many circumstances, not all but many.

All right. Now, I've been using words like "performance" and "durability," and I haven't defined them. And, indeed, I haven't heard them defined earlier today, and the reason for that is that some of these words like "performance" and "durability" are themselves rather abstract words, like patriotism or love or whatever. They're abstract words.

And the only way which you can define them is through separate attributes like, did I remember my wife's birthday?

(Laughter.)

No, for us the attributes may be a bit more complicated, and you may be able to express them numerically. And I think engineers have been good about realizing this. This overhead is borrowed from Professor Geyorv in Norway. And he would say that we -- we define performance or durability in terms of separate attributes.

And we plot a numerical value of the selected property. The selected property has to be one that is capable of quantification, and we plot this as a function of time. I'm sorry, that has gone missing off the lower axis here. This is time in this direction, possibly log time as you will. And we note an interesting feature about cements and concretes -- that after they are made they oftentimes improve in quality for quite a while.

I don't want you to be totally negative about cements and concretes. They oftentimes, with maturation, actually improve in properties for some time. But eventually, the value of the selected parameter declines, and we agree some lower limit of that parameter -- and that is the time to failure. A very simple concept, but a very useful one that enables you to relate words like "performance" and "durability" to actual measurable quantities.

All right. Let's change subjects slightly now and look at some conditions in which cement performs well and some conditions in which cement doesn't perform so well.

Now, my first example is to look at the durability of cement as modeled by taking a very simple substance -- calcium hydroxide -- and we know that one of the reasons why cement fails to perform over the long term is it dissolves. It's somewhat soluble in water, and so dissolution is an important reason for its failure.

Now, here on the left-hand side I've plotted the solubility of calcium hydroxide in millimoles at equilibrium. And you'll see that the solubility of calcium hydroxide actually decreases with rising temperature. So if you're looking at the impact of temperature alone, in the range up to 85 degrees, the solubility decreases by not quite half, from 20 millimoler down to 12.8.

This decrease in solubility actually carries on up to about 180 where the solubility curve then turns positive again. So this is unusual behavior, because relatively few substances have decreasing solubility with rising temperature.

Now, if we want to look at the impact of sodium chloride, a common constituent of many groundwaters and, of course, of the oceans -- and I've marked for reference the approximate seawater concentration sodium chloride, just a little bit less than a half-moler, you can see that -- and I've extended data points up to 1.5 moler sodium chloride, a little more than three times seawater concentration, you can see that there's a considerable increase in solubility.

But taking into account the overall scheme of things, not a huge increase, going to .5 moler sodium chloride. So the solubility at 25 degrees increases from 20.1 to 27.7 millimoler, and at 55 from 14.4 to 21.9, and so on. There is still the same tendency with rising temperatures for falling solubility, but the effect is about the same percentage-wise as it is in distilled -- initially distilled water.

But you see that if I go on to higher sodium chloride concentrations, the solubility is really very little affected. So the question about whether cements will perform well in brine is answered for you -- that certainly with respect to the dissolution they will not be significantly more affected by sodium chloride concentrations up to 1.5 moler. And, indeed, they will dissolve less at high temperatures than they will at low temperatures.

Now, I haven't put the data for pH onto this diagram, but because the solubility of calcium hydroxide is not greatly affected, and because calcium hydroxide continues to ionize in sodium chloride solution, the pH is -- at 25 degrees is virtually unchanged.

Now, it's true that the pH decreases at high temperature, but that's because the whole nature of the pH scale itself is temperature-dependent. And I don't want to get on to that in this discussion. We'll be bogged -- we'll be thoroughly bogged down. The ion product of water changes with temperature, so the basis of the pH scale changes.

But on a relative basis, at any conditions on this grid, the pH under comparable conditions, i.e. same temperature, the pH remains about 12.4, something like that, plus or minus .2 unit.

So these are conditions under which cement will perform well. Well, I've got the same data for CSH, which is -- makes -- the gel phase, which makes up 80 percent of cement. But the same lesson is true here as from the previous diagram. The trends are exactly the same, so I'll pass over this.

Now, the role of carbon dioxide has been touched on by almost all of the speakers today. Rainwater is saturated with respect to atmospheric partial pressure of CO_2, about $10^{-3.5}$ atmosphere at sea level. And when this water contacts cement, especially where the water can be sucked into pores in the cement, most of the CO_2 dissolved in rainwater will react with carbonation of cement and the reaction is as was depicted earlier.

So moist atmospheres carbonate cement, and all of the cement phases will react with formation of calcite, silica gel, alumina, and ferric oxide hydrates. And the rate of carbonation is quite dependent on relative humidity. The CO_2 has to dissolve in a film of water in order for it to react with cement. So humidities lower than 50 percent by and large don't generate this film of water.

At humidities above 80 or 85 percent approximately, water condenses, the pores are filled with water, and so the surface area available for transport of CO_2 from the atmosphere to water decreases. The geometric surface area remains the same, but the pore surfaces get filled, and so the rate of carbonation decreases.

For reasonable quality concrete, the rate of carbonation in normal air -- and I realize this varies with exposure. For example, north sides of buildings tend to carbonate faster than the south side, because they don't experience so much solar insolation. Depending on exposure, carbonation rates are sort of in the range .2 to 2 millimeters per year.

Now, the interesting thing about this

carbonation process is that the strength is not impaired. Indeed, in the past, possibly in the future, there has been quite a productive industry of taking fresh cement products, like brick and block, and so on, and letting them carbonate in flu gas. Not only does this help pay back some of the CO_2 penalty that you've incurred by making cement, but for relatively porous and permeable objects they are actually strengthened by allowing carbonation to proceed.

So it's not necessarily a bad process to happen in cements, although I'll show in some circumstances it is harmful. But, of course, the problem arises in that most cements are used as composite materials, not only in the form of concrete but also in the form of steel reinforced concrete. And there, of course, if the pH decreases, the passivation that these objects enjoy in the high pH regime of cements is lessened or eliminated and corrosion tends to be much more rapid.

Now, because calcium carbonate is several orders of magnitude less soluble than calcium hydroxide, or CSH, it tends to form a protective carbonate skin in or on the near surface layers of concrete. And this is the passivating film that I was referring to earlier, and it really does have a remarkable effect on improving and promoting the durability of constructional materials.

The medieval cathedral builders in Europe quickly learned by the 12th and 13th century not to make their lime for setting brick and stone from pure limestone, but to use impure limestones containing alumina and silica. So it was easier to build up a protective layer containing amorphous alumina, amorphous silica, as well as calcium carbonate. The properties of that layer were much more durable.

So, in general, with models of cement and concrete performance in the atmosphere, which rely on solubility in initially pure water, will tend to overpredict the importance of dissolution. So we don't find concrete bridge decks, for example, slowly dissolving away. They may wear away through abrasion, and solubility will contribute but only to a minor extent.

So rapid carbonation of these near surface layers will result in about a two order of magnitude decrease in solubility with the result that lime is -- particularly impure lime is a successful construction material, whereas gypsum, which has about the same solubility as lime, is not a successful construction material when exposed to rain or drip or whatever.

The only ones who have built successfully in gypsum were the ancient Egyptians who used it for facing pyramids that were built in the Nubian Desert where rainfall is typically a few millimeters a year. There it's successful, but otherwise not, because, of course, gypsum doesn't develop this self-protective skin on it.

Now, seawater contains a certain amount of dissolved carbon dioxide. Obviously, it picks up CO_2 from the free surface, the contact with the air, the waves, and so on. You get a lot of aeration at the surface. But on the other hand, there are organisms living in the ocean that very effectively extract carbon dioxide as carbonate from seawater and use it to construct their own homes, i.e. mollusks and snails and things of that sort.

And so the result is that the Henry's Law considerations that you might think would apply to the concentration of CO_2 in seawater don't really apply, because, first, the only place that seawater can pick up fresh CO_2 is at the surface, by and large. And, secondly, that CO_2 at greater depth is scavenged by shell-building organisms. So the actual effective CO_2 pressure in seas is somewhat less than atmospheric saturation, not much but somewhat.

Now, natural waters are a different case entirely, because in natural waters the rainwater filters through a biolayer in soil where CO_2 is an important metabolic product from -- coming from microorganisms. So the result is that groundwaters may start out life where water permeates the soil and hits the subsoil -- effective CO_2 pressure in those waters may already be 10 to 100 times higher than in rainwater.

Now, some of the CO_2 dissolved in groundwaters can be remarkably aggressive to cement and concrete. These aggressive conditions arise in several sets of circumstances, mainly chemically when there is more CO_2 than can be effectively combined with calcium as calcium bicarbonate, but also where the water is rendered acidic by passage through peat or other types of bioaccumulation.

There are special circumstances, of course, like mine drainage, but I won't go into those. So there are both empirical approaches to this question of CO_2 aggressivity, and there's also a mathematical model which we published in Advances in Cement Research some years ago. And we also demonstrated that computer-based interactions handle these calculations well, although, having said that, 1992 was a long time ago, and we probably ought to revisit this.

So summing up on CO_2, CO_2 can be neutral in passivating in some circumstances, but it can also be aggressive and cause rapid dissolution in cement components in others. So we mustn't stick labels on these substances. We mustn't say CO_2 is not aggressive or CO_2 is aggressive. It all depends on the physical chemistry of the situation that you faced.

Right. Having criticized existing test methods, and having said that these are to varying degrees inaccurate or inadequate, and let me give an example of this and talk about sulfate resistance. I don't want to condemn ASTM, so I've included our Canadian cousins in this.

(Laughter.)

But there's also a draft European standard on sulfate resistance, which will probably be published towards the end of this year, which is very similar in spirit to the ASTM. Naturally, being European, it can't be exactly the same as the U.S. standard, but there you are.

Now, what one does to test the sulfate

resistance of cement under the ASTM specifications is to make up prisms or cylinders of a known composition, and you immerse them in dilute sodium sulfate. Now, the first question is: well, why sodium sulfate? If you look at groundwater now, see, sodium is a common constituent in groundwaters. And so, too, is sulfate, but almost always balanced by a whole lot of other cations and antions.

So I don't know of any groundwaters anywhere in the world which are predominantly sodium sulfate. So why sodium sulfate? Why have they selected this? Well, the answer is -- and I've talked to some old timers about this -- and they say, "We didn't want to use sulfuric acid. We knew that was a non-starter." It's like testing the resistance of sugar cubes to putting -- immersion in pure water. We know what the outcome is. You don't have to do it. They'll all fail.

What we wanted is to combine the sulfate into a salt which was neutral or near neutral in terms of pH, but also one in which the cation did not interact strongly with cement, so we chose sodium sulfate. Well, you have to start out, then, in the knowledge that these tests are unrealistic with respect to the composition of almost any natural water.

All right. You say, "Okay. We'll do these tests." Well, what you then do is to measure the -- because there's usually an expansion in sodium sulfate, you measure length of your prisms or cylinders, and you measure the compressive strength as a function of time at a fixed temperature, typically up to one year.

Now, because it is difficult to make cement cylinders or cubes reproducibly, you need a large number of specimens to get statistical reproducibility. And because you're going to sample at perhaps different temperatures and perhaps different times, the number of samples rapidly grows extremely large.

So if you visit a typical testing center using these engineering protocols, you will see great big tanks known as swimming pools, which are filled up with cubes and cylinders and what not, and every so often they're taken out and wiped with a paper towel and weighed and measured for length and then put back to continue the test.

So obviously we're not going to get a huge variety of formulations, and we're not going to get a huge variety of temperatures, and we're not going to get a huge variety of sodium sulfate concentrations. And we're certainly not going to be able to pick up mixtures with other salts.

Now, besides what I've said, what's the matter with these tests? Well, first off, because the cement samples absorb sulfate out of the solution, you may have started out with a precise concentration of sodium sulfate, and it usually is prescribed in the test method you're following. The sulfate concentration will decrease with time.

So if your test has lasted three months, six months, or a year, what is the effective sulfate concentration in the life of the test? Is it what it was at the start? Is it what it was at the finish? Or is it what it was in between? I don't know the answer.

Sodium, on the other hand, is not depleted. Because it's a weekly interacting cation, it stays behind. Now, you can't have sodium in solution on its own. It's a positive charged ion. It requires some negative charge. So what happens, well, it takes hydroxide from the cement. That's the one soluble anide which the cement can contribute. So, bingo, you've got sodium and hydroxide ions in solution, and the pH goes up.

And in many of these simulations, if the sample is put into a sealed container, the pH will rise perhaps as high as 14. So have you seen the mineralogical changes that would occur in real cement? Because the pH is now 1.5 orders of magnitude higher than what it would be in the real cement. Well, you don't know.

Moreover, the situation is compounded by the fact that most tests do not require you to do the test in a sealed container. And when the container is left open to the atmosphere, as the pH goes up, the solution absorbs atmospheric CO_2 very rapidly. The kinetics of CO_2 absorption from the atmosphere increase with increasing pH, and the equilibrium concentration will increase with increasing pH.

So lo and behold, that carbonate that now appears in the solution reacts with the cement to precipitate calcium carbonate. And what's worse, the point at which precipitation occurs is not necessarily at the surface of the cement. You may get cement substance dissolving, going to near the surface where the CO_2 concentration is being increased and refreshed by absorption, and then it precipitates like a gentle rain of calcium carbonate.

So you've coupled a new leaching mechanism for removing calcium from the cement that you did not anticipate in the course of the test.

Well, I think I've told you enough to convince you that the sodium sulfate tests are not only extremely variable depending on the size of the container, the surface area available for contact with the atmosphere, and a host of other factors that are not specified in the test to indicate why you get such large interlaboratory variations. And even more important with respect to present cases, why these tests don't have any predictive ability.

Well, I've run ahead of myself. Well, we have looked at the physical chemistry of these tests, and we will be reporting to RILEM, the International Pre-Standards Committee on Cement Testing, in Quebec in September. So there will be a paper from us giving chapter and verse and numerical calculations related to these.

Well, just coming back to this depletion of sulfate, with time you generally come down to the -- at the end of the test, the depletion of sulfate stops, because you get down to the solubility that's controlled by gypsum, not the sodium sulfate, the solubility of gypsum at the relevant pH.

Right. Now, magnesium sulfate is an

interesting case, because here you have a cation and an antion that both react strongly with cement. And testing with magnesium sulfate is -- which is a standard test method is fraught with problems, because if you don't watch the solution concentration and monitor it continuously, and that's not generally a requirement of the test, you will get virtually quantitative removal of magnesium from the solution.

The equilibrium solubility of magnesium hydroxide at pH 12.5 is on the order of 10^{-7} moler, which means you will need a very sensitive analytical technique to detect any remaining magnesium in the solution.

So I hope I've given you enough evidence to convince you that standard tests and test methods are not the way to go if we're to set standards for cement durability and performance in the nuclear waste field.

I'm not suggesting that you ignore this body of knowledge. It represents experience in its identification of destructive agents and the mechanism of destruction, and it is going to be legally binding that the findings of those investigations are paid good and careful attention by any of the civil engineers you employ on design.

But it does not measure, I assert, reliability or quantitatively what it purports to do. So these tests are really in need of refreshment. We need supplementary calculations about how they work. We should analyze them from the physiochemical point of view, and focus them better if we're to extract any useful information from them.

Now, I want to say a little bit about thermal hazards to cements and concretes. People have mentioned delayed echingite formation in other words, and much of the problem arises -- and it's going to be particularly a hazard in nuclear waste immobilization -- where large masses of cement-rich formulations are used -- is the thermal excursion that results in the first few days or weeks of cement hydration.

It really is strongly exothermic. If you take a standard barrel, U.S. barrel, and fill it with a fresh mixture of cement and water in appropriate proportions, and keep a thermocouple in the center, you'll quick find the centerline temperatures will reach the boiling point, and cement won't set properly because steam will be evolved before the cement has had a chance to harden, not at the outside but at the inside.

And this -- the resulting cooling in the post-hardening stage of course then results in a thermal contraction to -- and then the result is cracking, and usually not microcracking but usually macrocracking. And, you know, we heard a lot this morning about microcracking, but I don't consider microcracking too serious a hazard to cement performance, because, first, the microcracks may not go right through the cement. And, secondly, the transport properties of torturous microcracks are not very good, but macrocracking is certainly at all costs to be avoided. You undo all the good that you've done.

So this has to be managed by attention to formulation design, sequential emplacement, and that entails problems. It's not free from problems and junction boundaries. But certainly the importance of thermal cracking on transport properties is, in my view, a neglected area of study and one which everyone needs to take into heart.

Now, there's also a situation that could arise, and that is that in some situations we may have heating as a result of discharge of heat from waste. I'm not aware that cements themselves will be used as a primary immobilization matrix for highly active, heat-generating waste, but the repository itself may be lined with concrete, the integrity of which is important.

And in the post-closure phase, we may get hazards to the concrete which include crystallization, if it's a concrete reaction between the cement and the aggregate. Now, we heard this morning about inert aggregates and reactive aggregates, but you must remember that with the exception of calcium carbonate aggregate no mineral aggregate is inert in the equilibrium sense in contact with cement.

No mineral aggregate is inert -- granites, schists, gneisses, sandstones, shales. All are potentially reactive with cement. You only get away with this in ordinary construction, because you don't raise the temperature. But when you have a prolonged thermal excursion you must expect reaction to occur in the course of time. If you're worried about it, you need to specify limestone aggregate concretes.

So we can consider briefly the consequences to mineralogy pH conditioning ability, resistance to dissolution, strength permeability, and dimensional stability.

Now, just to remind you briefly that 90 percent of cements are two solids. It's calcium hydroxide and there's this gel-like amorphous phase cryptically known as CSH, shorthand for calcium oxide, silica oxide, water.

Now, the CSH is nearly amorphous to X-rays, and although it doesn't necessarily have a fixed composition, in cement where it coexists with calcium hydroxide it is effectively calcium saturated, which means it has a moler calcium to silica ratio of about 1.8 to 2.0.

Now, we do in industry do a lot of work with autoclave cements. And to cut a long story short, we know that if you autoclave unmodified cements -- that is, they're not chemically modified by adding any other material -- they will emerge very porous and very weak, because at high temperatures the CSH phase crystallizes and the products of crystallization are denser than the CSH itself.

So the physical dimensions, exterior dimensions of a shape, remain the same, but the volume change is accommodated by increasing the porosity and with it the permeation of -- the permeability.

So that's not a good way to go, but we know that in industry what's done is to add around 50 mole percent of finely ground quartz silica. And then, when you autoclave you shift the bulk composition from the moler calcium to silica ratios of portent cement, which is typically about 2.7, 2.8 for most industrial products, you shift it down to about somewhere between 1 and 1.5, which means adding quite a lot of silica to it, and then you get crystallization phases like tobomoride, for example, with a calcium silica ratio of .87.

And the density of tobomoride is very similar to that of the mixture of CSH calcium hydroxide in quartz that you started with, and the result is that tobomoride autoclave products have good strength and low permeation. So we know some of the answers from industrial practice about what happens when you heat cements.

Now, the question is: what happens if a cement is used in a repository, experiences a prolonged thermal excursion, and then cools down again. What will its pH conditioning ability be? Will be it permanently affected, or will it not? And I've simplified a phase -- complex phased diagram for a lime silica water system only to show you the range of compositions bounded by yellow that will still contain, at the high temperature and upon cooling back down to room temperature, calcium hydroxide.

Now, commercial cements have a ratio about here. So you can see that after heating, while they might crystalize to have a brandite or jaffyite, I'm assuming no silicious aggregate is present -- that when they're cooled back down portandite calcium hydroxide will remain continuously stable throughout this region bounded by a ratio of 1.5 and stepwise function of temperatures close to 160.

So I conclude from this that all cements, provided they're not reactive with silica or aluminum materials, will, after prolong thermal excursion, come back down to room temperature and still have a good reserve of calcium hydroxide left with which to condition the pH.

Right. I think I want now to come to some conclusions. I won't say anything about the source term, except to remark that I'm very surprised that after decades of study of the interaction between cements and radioactive waste species that we don't have a library or an agreed dictionary of solubilities.

We don't know the nature of the solubility-limiting substance that represents the form of binding between cements and radionuclides. We don't know how that particular mineral or minerals respond to changes in temperature, to humidity, or CO_2 or other dissolved constituents in groundwater.

We don't have this information scattered throughout the literature. Never been pulled together into any sort of collective form, a real mission in our ability quantitatively to model cements, but one that could be partly repaired by a really good survey of the literature.

All right. QA -- enough has been said about QA in the course of this meeting to convince you that we're -- that laboratory concretes, so-called lab cretes -- are different animals than field concretes. What you make in the laboratory may not be duplicated in the field unless you take extraordinary precautions to see that that is done.

It's not enough -- and we've visited many sites that -- where concrete is being used. And what's happening? Well, Joe down on the job with his mixer is getting on with making the concrete. The engineer in charge is sitting in his construction shack drinking instant coffee and filling up timesheets and health and safety forms and God only knows what. But he's not checking the quality of the concrete.

And I have seen examples of this in documentation that has been sent to me for assessment by the U.S. Nuclear Regulatory Commission and its agents where this QA is not being done, to my mind at any rate, to proper satisfaction.

Okay. Summary. Well, it appears frustrating that we can't at present predict the lifetime performance of cement barriers or matrices for that matter. In fact, I think that people are oftentimes putting unreasonable demands on cement and concrete barriers. They're wanting to say, "Well, tell me how it will perform. I don't know what the conditions will be and to which -- particularly in shallow burial the conditions may fluctuate, there may be an Ice Age in a thousand years, it may turn tropical and people have got a banana plantation on top in another thousand years."

You know, we don't know what the conditions are. We don't know what the groundwater level is. We can tell you what the groundwater chemistry is now, but not in the future. Never mind, we don't have this information; just tell us how the cements will perform.

Well, you're not going to get good predictions unless the whole mechanism for evaluating repository performance is firing on all cylinders. People have got to work together on this, and they've got to come up with a holistic scenario.

So to conclude on an optimistic note, though, the purely chemical models of cement performance are reasonably well advanced. That's why so many people have been talking about the chemical alteration or the chemically-induced alteration of cements, including myself in that category, because these models are reasonably well advanced.

Okay. They're like a child taking their first steps. They can't yet run, but they can toddle, they can walk. Now, where we're not good and where we also have to improve the links, weak areas include linking the change in chemical and mineralogical changes with mechanical properties. We're not good at that.

The engineers say they don't understand the chemistry, and the chemists say, "Well, we're not terribly interested in what the compressive and tensile strengths are." You go away and sort that out, and the answer is nothing gets done.

We don't have a basis for accelerated testing that is free from suspicion that it doesn't alter the fundamental mechanisms involved. That's the rub of the problem. I can tell you from experience that the mineralogy of cement is remarkably sensitive to temperature. Even differences like between

5 degrees and 35 degrees are crucial. Big changes occur over short ranges of temperature.

So you can't just accelerate things by heating up the system. Sure things go faster, but are they really the things you want to know about? We have people that rely on computer-based model predictions, but we also need those same laboratories to develop methods for experimental verification of their computer-based results. You can't wait years for somebody else to pick it up and do it. You've got to have a dual capability in your laboratories.

And, finally, we need a better integration of data into deterministic performance models. I don't think very much of the probabilistic models -- I think situations are much better off as far as developing predictive capability if we can have a quantitative model. I feel much more comfortable with these than I do about probabilistic models applying to something where my gut feelings say we ought to be able to calculate this.

So that's -- thank you for listening. My final thoughts are that material performance in non-steady states will always be difficult to quantify, that performance has to be quantified by a subset of parameters, each of which can be determined and then modeled, and we need to all work together on this problem of delivering reliable predictions about cement performance in the longer term. We need more holistic whole of repository performance models.

Thank you very much for your attention.

VICE CHAIRMAN CROFF: Thank you.

With that, we'll take just a moment or two here to change speakers. And our next speaker is Dr. Les Dole from Oak Ridge National Laboratory.

Dr. Dole studied corrosion and nuclide propagation in Westinghouse nuclear powerplants, directed research on engineering barriers for some predecessors of the current Office of Civilian Radioactive Waste Management, served as the Technical Director of Call Tech, a Superfund remediation contractor, and led a group at Oak Ridge National Laboratory for more than 10 years that develops and tests wasteforms for various hazardous and radioactive waste from across the DOE complex.

Dr. Dole, take it away.

DR. DOLE: Allen is giving me the unique possibility here of having -- following people in the program from whose work I've stolen from for at least three decades.

(Laughter.)

So not surprisingly, you're going to hear some of these themes repeated. I thought maybe I'd give them cards and they'd hold up and put a number on it, and I could see what my score is for how much material I've stolen.

But nevertheless, Fred will be an empiric hard act to follow.

Basically, you know, it's like what a woman learns in marriage, you know. The secret of happiness is to lower your expectations.

(Laughter.)

So the question is: what do you really expect the cement to accomplish in the system? And basically, we're looking a the wasteform package, the bulk, the liner, whatever configuration we're looking at, as a system where different parts of the system contribute to the overall thing.

And some of those are -- some of those are mechanical, and some of those are just basically a geochemical buffer between essentially you influencing the local geochemistry to minimize the transport from that site. Now, whether that's 1 meter or 50 meters or 1,000 meters, you can at least include those concepts into your selection of materials. And that's what I'm really going to talk about.

Rather than go through a litany of pathologies that I've seen over my career, I thought I'd try to talk about the elements which we use to choose to try to avoid problems. And most of the problems are really the wrong choice of materials or poor mixing. And that's really not the issue we want to address here.

I think we want to look at the idea that cement is a complex material that forms sequentially, and that we have choices in what level of C3A or C3S we choose. We have a choice of the calcium to silica ratio. And based on the experience of my friends, we have a -- somewhat of a guideline, if not phenomenological, at least experiential guidelines to make the right decisions.

And so we really have a choice of how we adjust the calcium to silica ratio, the alumina silica ratio, and, you know, how that affects the permeability, how that affects the choice of high density or low density CSH, increase the internal ion exchange capacity or effect reducing conditions or to buffer the pH.

So all of these things, from a waste formulator standpoint, are controllable, perhaps unlike construction where you essentially have to work with a commodity material. In most cases in a waste management context the major cost is not a materials cost. It's an operational cost. So you can afford to go wide and far to find the material that meets your needs. And that's really going to be a small component of the overall cost of your disposal operation.

For instance, for years we have used a Type 1-2 low alkalized cement for the northwest, Washington State near Hanford. We're currently now happy with a Type 5 cement from Southern California which is now our favorite. So in waste management you have more luxury. The volumes are smaller. And like I say, relatively, the cost of materials is a smaller component.

Now, this is right out of the Barry Scheetz student's handbook. This is the Roy school of grout in Penn State. But the idea is that we have this suite of materials -- pozzolans, slags, and various types of cement. And we can blend those in such a way that we can achieve different properties in the wasteform.

Now, the question is: given that ability, what do we use? What do we want? We're looking for a tall ship and a star to guide her by. Well, this is the star I use more often than not is this phase diagram, so we may have to like refer back to it. But the idea is we want to steer the system into a phase -- part of the phase diagram that prevents the formation of calcium hydroxide, which is the most labile component.

And we usually formulate right about this upper line, because a lot of the times the materials we use we formulate based on total silica alumina and calcium. And because silica comes in a variety of minerals, not all of it participates in the pozzolanic reaction.

So by working up at this end there may be a fraction of unreactive material that keeps us actually effectively down in this region. But this is kind of the sweet spot which we use, and we'll talk about what we hope to achieve by picking this sweet spot, in addition to reducing the free calcium hydroxide.

Now, this is a formula -- now, I've always said that I've been a dirty water cement chemist in which I mix the waste directly with cement, and that there's a whole body of civil engineering experience out there that I call clean water cement. And I've never had much to do with them.

Suddenly, as a cruel twist of fate in my career, I'm suddenly trying to formulate an engineering material. And we're looking at coming up with a blend of live cement, blasfernous slag, Class F fly ash, and silica slew that controls over the sequence of curing the level of calcium hydroxide.

So, in principle, we want some calcium hydroxide, because that's what drives many of the reactions. It helps etch the aggregates, and so we want -- we don't want to eliminate calcium hydroxide immediately, but at the end of the curing cycle we want it all gone. So what we've done is we've found a blend of these components, these specific components, that give us the effect that we want.

So the idea, then, is that by the judicious selection of materials you can formulate a cement that avoids calcium hydroxide yet still has the properties you need to develop strength and bonding with aggregates and other properties that you would like.

Another issue is that by reducing the calcium to silica ratio, I think we're -- anyway, this is the dehydration. Obviously, when you heat up cement to about 200 to 300 degrees, which is about the estimated heat pulse that you would get at Yucca

Mountain, you dewater the CSH. And you have to go all the way out here to 5-, 600 degrees before you actually decompose the calcium hydroxide.

Well, we're eliminating the calcium hydroxide, but the other aspect we're looking at is controlling the low density CSH and the high density CSH. Fred refers to this I think as microcrystalline CSH, but it doesn't matter, CSH forms with two packing densities. And I think a lot of the work out of NIST points to this as well. In fact, this is data from a NIST-based work that shows the distributions.

And so by adjusting the formulation, what we're hoping to do is reducing the fraction of low density CSH, which is responsible for shrinkage, both from dehydration and from curing, because what happens then with aging is that the low density CSH redistributes and repacks itself into dense CSH, which -- so if you can slow down the formation of low CSH, extend the curing so that when it forms in its early stage you get the high density CSH, then it is less prone to shrinkage on curing, it's less -- it won't shrink on aging, and it's more resistant to dehydration.

And, again, this talks about the two packing densities of high density and low density CSH.

And they really don't change much below 250 degrees, so that gives us some indication that the wasteforms will be resistant or the structural materials that we choose for the repository couldn't be expected to be reasonably resistant -- in other words, maintain its physical integrity over the thermal pulse.

Now, that's not related to time, but Fred has talked about the time, in that if you do form this high density CSH, the reactions that redistribute the materials are slowed down because they're now solid diffusion limited. So if you create the micro-nanostructured CSH or the high density CSH, you've essentially increased the diffusion barrier or the rate at which they recrystallize with aging or aging under thermal conditions.

Now, there's really no -- there's no modeling at this point. Maybe if I have time at the end I'll talk about some of our methods of modeling. Certainly, Ed is following on with the NIST, but the other aspect of lowering, as Fred alluded to, is if you reduce the calcium to silica ratio to -- you know, from 1-1/2 down to 1, you -- the soluble silica that's available in leaching, either for healing microcracks and later wetting episodes, or forcing the geochemistry of the system in insoluble components is improved by lowering the calcium to silica ratio. And, again, it's a balance between early strength and this calcium to silica ratio.

So what we're really doing, then, is that if we raise the silica counts -- and that's -- some of the earlier discussions talked about the carbonate and the pH. They left out the part about the silicates, because when you add aluminum silicates then you force these insoluble compounds, and even then those initial insoluble compounds which precipitate on the surface of the fuel or on the surface of the cement, which shuts down diffusion, shuts down oxygen transport, may perhaps at this point not -- we don't know how to quantify those or model those kinetically, but we certainly have a good intuition that these things form and that they are very, very effective at reducing the mobility and solubility.

And even then, more complex than that is that it's really a sequence. We talked about kinetically we get soddyite and urethane forming, but then over time they alter themselves into even more stable compounds of haywetite and ursalite. So, unfortunately, nothing in this system is simple. Nothing comes out of the solution directly in forms. It comes out as an intermediate and slowly undergoes a transition.

So even phosphates or carbonates are silicates all come out in a very complex sequence. And we're just starting to unravel that. We're just starting to get the tools to get -- to start to get a handle on that. But it -- as Fred points out, we're in the infancy of identifying precisely which compounds and the sequence of which they form.

The other issue it talked about is we talked about stress cracking and load. Certainly in the -- we have a great predilection for using steel fibers for two reasons. One, they increase the area under this curve, so they increase the fracture toughness by sometimes 10-fold. And if you really go out, maybe 20- or 30-fold. This does several things.

First, the metal adds a reducing quality to the mix. And, second, it increases the flexibility, the flex strength, and its ability to absorb energy. And it's quite critical from the standpoint of using silos for hardening against missiles and things like that.

So there's a tremendous body of knowledge on how to harden facilities and how to harden materials that at some point or another will be germane to waste disposal.

Okay. And this is the one we've all seen before. I've used this slide a dozen times. But the point is is that when you try to accelerate the tests for temperature, as we pointed out nothing is that -- nothing is in a nice linear simple step. And that as I said -- others have said before is that when you change the temperature you change the reaction path of the system. And so you have to be very skeptical about what you see in an accelerated test.

So is there a way around that? Hopefully, I'll talk about that. So what's missing, then, is a mass transfer, coupled thermodynamic model, a deterministic model. And NIST has part of that, and unlike Fred I -- as a physical chemist, I'm not so uncomfortable with stochastic methods. But I think we're just now starting to really get a serious handle, and NIST has led the way.

The team at Lawrence Berkeley -- John Epps and Carl Stieffle -- have been working with Tough React, which is another variation of a coupled thermodynamic and kinetic model. And we're trying to come to grips first with just getting the literature data in it.

And, again, I -- my experience with culling the literature is the literature was taken for another purpose. And we'd go back and look at that data, and there's such a range of experimental conditions and these measurements are so sensitive to your choices of those conditions that it's really hard many times to just gather this up and put it in a coherent database. But it's something that needs to be addressed, and, skeptical or not, it needs to be tried.

So then it gets to the issue of anthropogenic and natural analogs. I found it curious, I was looking at some background material, and there are guidelines from the IAEA, what constitutes a good analog and not. And Pettit has worked in this area also.

What I found curious was that in the German waste disposal program they chose that the most important thing, number one on the list to be solved, is looking at anthropogenic and natural analogs, which my reaction was that somebody was smart enough to pick out the fuzziest, most unreliable, and most difficult task and put that as number one to disposal.

But it's very difficult, and it can't be done independent. There has to be an organized approach to your laboratory work and you analyze these materials and you are constantly looking at the information. You're not going to see validation from this.

You're going to get ideas about what to look for and what not to look for or find things that you found in the laboratory, you didn't see in natural materials, and try to resolve the differences. But you're never going to converge on the answer with this system, but you need to do it to at least find bounds, to get some sense of where the systems go and -- with these very long times, even though it's very difficult.

Now, we've located -- most people are familiar with the Gallo-Roman. Naboseans are kind of unique, but we found in the U.S. we have a formation in Marble Canyon, Texas, there's the Hatrium formation in Israel, and the Scawt Hill in Northern Ireland that are fairly well documented areas where you could find materials that -- where through heat events, whether it was magma or an underground fire, that you baked the formation into a cement clinker, it hydrated naturally, and you can go back and then try to unravel what happened to these systems over the last million or so years.

So it at least gives you some sort of benchmark, but that benchmark alone only works if you have a concomitant or a parallel study in the laboratory to take a look. And I'll talk a little about the link -- mass transfer.

What may save us is that besides the better models that are evolving is that we also have much better microtechniques where we can start to look at modifications to crystalline layers, almost a molecular layer at a time.

And so if we have these extraordinary methodologies that gives us -- so we don't have to wait 10 years to see an effect, we can wait maybe one, two, three years and we can start to look at the direction in which the surface of the crystals are starting to evolve. That gives us an early indication of where the system is going to go in longer time.

So somewhere between the natural analogs and applying these extraordinary analytical techniques we might be able to start to link up the thermodynamic and kinetic deterministic models and then link it. And also, with the help of the NIST in their stochastic modeling, at least come up with a better picture of what's going to happen.

So we can't do it now. Just the elements necessary to do it better are just now starting to come out, and no one is putting them all together in a coherent way at the moment.

I didn't talk much about leaching. But think about leaching two ways. If you disrupt cement-making -- we usually look at leaching from the standpoint of trying to keep some nuclide or some bad guy in the mass. But the other turned that around and said if you have an aggressive agent in the environment, and it wants to -- in other words, for cement to degrade, some environmental element has to diffuse into it.

So the same mechanisms perhaps that control the release of things also control the ingress of things, like diffusion, effective diffusion coefficients, porosity, permeability. And so some of the leaching approaches may or may not be as successful.

The problem of -- okay, let's take the issue of permeability. What do you really expect? All you really need from permeability from a wasteform is it has to be 100 times less than the permeability of the adjacent formation. And if there's any advective scenario, then a particle of water goes around rather than through. So most times we're looking at soil permeabilities of 10^{-5}, and we can generally -- we can make wasteforms at 10^{-7}, 10^{-10}

microdarcies.

So we know how to make impermeable wasteforms. We use the pozzolans so they cure very slowly. The plastic state is extended over long periods of time. Ed will talk about, you know, the creation of internal tension or stresses that cause microcracking. It relates to the placidity of the mix and the time at which it sets.

So if you extend the placidity of the mix way into the setting process, you relax all those interior stresses. You allow those interior stresses that cause microcracking to relax, and it reduces it, and that's another virtue of choosing cements with low C3A or C3S and the use of pozzolans.

Okay. Diffusion -- again, as David pointed out, using a single diffusion coefficient to describe the complex sequence of chemical events is pretty imaginary. I mean, the term "effective diffusion coefficients" is one I use a lot, because it's something we measure in the laboratory, and it reflects many processes, not simply -- it's not a simple diffusion coefficient.

It's a coefficient that may at one point in time in the life of a wasteform reflect the sequence of events that controls the release at that point in time. Now, that changes with time. And as David pointed out, if you pick a diffusion coefficient early in the age of a wasteform, it's generally very, very conservative. And you're right. If it -- if it overestimates the release by two orders of magnitude it's the wrong answer.

And so we've looked at that. It gets back to the use of static KDs and static leach tests. It goes back to exactly what Fred was talking about is that the results reflect the experimental design. So that the time is really driven by the solid surface to liquid ratio.

And so, again, Fred wants to go back and look at the literature, but very seldom if you compare these either -- either from leach data or partition data can compare those unless they are taken under similar experimental conditions, similar experimental configurations. So it's very difficult to interpret those results.

It's good news and bad news. The bad news is that when you use static KDs and static leach tests and effective diffusion coefficients, you get the wrong answer. It's there any good news in there, generally it overestimates the release.

And if you can accept that, then it's

fine. But if you can't, then you have to go back into the more deterministic models like David was talking about and that we're trying to develop with Tough React and some of the other geochemical models where it's a sequence of geochemical processes that ultimately determine the release. And it's not a -- it's never going to be very simple.

Okay. So we do have a lot of experience, and we've taken these data. And we have a good sense that they are fairly conservative, but we also know they're the wrong answer.

I think I'll leave it go at that. Again, we're beginning to use Tough React and build more geochemistry into our model. Our particular modeling is looking at the near field of the repository, the impact of the cement and the cement chemistry on the immediate contact with the formation. NIST is working at looking at the inside of the cement fabric and its effect. And eventually hopefully we'll meet. It's our intention to do that.

Questions?

VICE CHAIRMAN CROFF: At this point, as before, I think we'll defer the questions to the panel discussion. And we're doing reasonably well here, but I think it's time we took a short break. That's what we've got scheduled. So let's come back about five minutes after 3:00 if we could.

(Whereupon, the proceedings in the foregoing matter went off the record at 2:52 p.m. and went back on the record at 3:07 p.m.)

VICE-CHAIRMAN CROFF: Last leg of the race. At this point, I'd like to introduce our final speaker who is Dr. Ed Garboczi from NIST. Dr. Garboczi is a physicist and leader of the Inorganic Materials Group in the Building and Fire Research Laboratory. This group carries out a combination of experimental and computational materials science on cement and concrete to supply measurement and prediction technology to industry and helps support the development of science and performance-based standards. It's this group that developed the Virtual Cement and Concrete Testing Laboratory software which is a tool for predicting the performance of concrete from fundamental materials science.

With that, please.

DR. GARBOCZI: Is this coming through all right?

Okay, so I was here last year, I remember, at a similar meeting. This year is much more focused on concrete science and I'm in a very distinguished crowd of speakers here, so I feel honored to pick up the end here.

I'm glad we had a break because it woke you up a little bit, I hope. I hope you had some coffee and it's been a long day.

I just use the title that Allen said, the last two talks before Dr. Glasser and Dr. Dole had the same title, but they focused on other aspects of it. I'm going to focus on the computation aspect of it. And just to give you a little bit of background, I think some of my introduction will seem a little familiar to you by now, but I was talking to Dr. Glasser the other day. I said I think a lot of these talks overlap each other. He said oh, that's good to see the same thing with different points of view. So he said it must be okay, so --

(Laughter.)

For a long time we've been providing scientific and technical foundations with performance-based selection use of concrete. The whole -- try and drive the whole world to performance-based specifications. We do that through material science, trying to give a better material science basis for tests, performance-based standards, etcetera.

Part of our -- fairly unique to us, at least a while ago it was the use of computational materials science. We have always felt that the complexity of concrete demands computational materials science along with experimental materials science to back it up. Jeff Frohnsdorff, my former boss who passed away this year, was really the driving force behind that for many years. In fact, in the '60s, he helped write the first computer-based model. So it's a little testimony to him. He passed away in March of this year.

We look at the length of scales of concrete from meters down to nanometers. Our main work has been in the micrometer and millimeter scale. Some early stage work on the nanometer scale and some of the prediction tools we'll talk about today generally fall in this area.

We have a structural group which concentrates more in this area as well.

I'm going to set up, trying to find the problems we're looking at in terms of time scales and structural complexity. It's just my point of view. I remind you that's my point of view and if I say something, it's kind of runs counter to the current norms in this whole area, please excuse me, because of my ignorance.

So for me, when we talk about prediction, we're looking first at shorter time scales. Shorter, I mean that 100 to 200 years type scale. And that region there's two kinds of problem. There's the high structural complexity problems like new nuclear power powers, for example. There's a lower structural complexity, things like low-level reactive waste -- vaults kind of thing. They're much less structurally complex than say new nuclear power plants.

I don't really mean crack free. That was sort of stupid to put it there. I mean sort of control crack or not too many cracks or doing the best you can with cracks. But for this kind of concrete, like the usual construction industry concrete which we really serve the construction industry, so that's my point of view, just like Rachel was saying earlier today.

The use of degradation processes, you should remain pretty immune to them for 100 to 300 years and that will make your barrier work right. It will make your concrete in your nuclear power plant work right.

There's also an additional problem though. It's not just the usual processes like Rachel talked about, but also the other chemicals that could be there like the waste, stuff in spent fuel pools or some WR problems. There's other chemicals too. There's other chemistry involved as well.

And for all of this, as you've gathered today, I think, prediction is not so easy. Then there's the other point of view which I'm not so familiar with, even though we worked at NRC for the last 15 years or so, it's not -- it's a little bit far for me is the longer time spans, the thousand years, the 2 thousand, 10 thousand year time spans. We talk about thermodynamics.

That time span, the concrete must continue to function in its physical and functional containment. The degradation processes are a little bit different. You have to avoid the usual shorter-term degradation processes. If you want something to last 10 thousand years, you can't have it fall apart by alkaline silica reaction in 50 years.

I think there's some ways to make progress on this and we've heard some today as well. I'll talk more about it later. And if anything, prediction is probably even harder for this time scale than the shorter time scale which is no surprise to anybody.

Was it Yogi Berra who said about the hard thing about prediction is it's about the future?

(Laughter.)

Why is prediction difficult? I mean the time scale gives difficulty as well, but I'd argue for this material, it's even more difficult. I would say the reason is anything you're going to predict about the concrete, how it's formed, what its properties are, how it degrades, interaction of chemistry, microstructure, micromechanics. It's not just things reacting, look at the reaction product. See if they look at the mechanics and they interact with each other. I'll show you some examples of this.

Of course, you can't ignore cracks. That's part of the micro mechanics as well and the micro structure, and sometimes the chemistry.

Let me give you some examples of what it means, how closely these things interact. Just plain hydrating cement. Cement, paste mixed up or you have a concrete mixed up, if you have a lower water to cement ratio, probably around .4 or lower, or any hydration involves chemical shrinkage. The products take up less space than reactants, volume-wise.

If not enough water comes in from outside, you tend to start using up the water inside the mix and you end up with air/water menisci. Menisci have forces in them which induce tensile stresses. Tensile stresses can induce cracking. That's the autogenous shrinkage cracking that was mentioned a couple of times. So that's chemistry and mechanics missed up together. Chemistry induces mechanics which can affect the material. Every cement has that. It's just a lower ratio, tends to be a bigger problem.

Degradation is -- one example of degradation. Alkaline silica attack and alkaline pore solution reacts to the morphosilica and the aggregates. This is a gel. The gel can swell and cause induced tensile stresses, cause cracking.

Carla Ostertag at Berkeley has introduced fibers and tried to control the fibers going in near the aggregate paste interfaces. It turned out the ASR was controlled a lot, but it's merely mechanical means. There is the chemo-mechanical problem. Usually people do a chemistry to alleviate ASR. She did fibers, so she controlled the swelling. The chemistry changed. So into the mix of chemistry mechanics, this is one example of that.

I'll say a word about cracking, another difficulty in this material. If you have a block of concrete and you wonder what the transfer properties are, if you can spatially and topologically characterize the cracks, there are ways to predict transfer properties. You do 3-D calculations, find out whatever. And you can predict transfer properties. If you can do this, this is probably the harder job, characterizing spatially and topologically in the cracks.

It's a lot better to, of course, predicting the occurrence of cracking is a lot hard to do. It's much better to -- much easier to prevent it in the first place. The ways you do that structural design, you know, obviously good constructional design means you don't have settlement cracking, that kind of thing. That's beyond my field of expertise.

You mix designs, ways to look at mix design and proper curing. And this was mentioned. I'm going to try to mention a few things that weren't talked about earlier. One way to alleviate cracking which can alleviate cracking sometimes, is curing, but internal curing. Instead of applying water from the outside, especially high density concrete, high performance concretes, high strength concretes which might be used a lot in say nuclear power plants or some places it may be in waste disposal. It's so dense that you can't really pour in water from the outside. The transfer rate is so slow the water can't get in, so you can run that water inside through this cell desiccation I talked about before.

So one way is to try supply water reservoirs inside the concrete. This thing can be drawn on as the emergency supply of water when the regular water, mixing water runs out. Well, there's many ways to do that. One way is if you replace some of the fine aggregates with porous fine aggregates, quite porous, they have water tied up in them. You mix it in and then water can be pulled out of the fine aggregates when the water is needed in hydration process to alleviate some of the cell desiccation. And that's been shown to work well.

Dale Bentz in my group did an x-ray tomographic study where these are the porous fine aggregates. The blue is showing where water has left the aggregate. So as curing went on water is pulled out of the aggregates into the space where the water is needed in curing. So he can definitely show that this water was being used as a water reservoir for internal curing. In fact, it could be very helpful. There's other ways to do it, first kind of polymers, you can use that too. But that can alleviate cracking and it's shown to alleviate cell desiccation shrinkage quite a bit.

That's a fairly new technique that's out there, but something that could be very useful for any time you're going to use high density concretes.

I'll say one word about mineral admixtures before I get on to more prediction stuff. I'll say it's a monkey wrench. You know, it's very common to use mineral admixtures today. Pore cement chemistry is hard enough, chemistry mixed in with dirty water type stuff, is even harder. You mix in some of these other things, you get problems even harder. I would say that chemical interactions are not well known.

For instance, you can pretty well measure the amount of cement that's hydrated versus time. The reaction of cement versus time. When you have cement mixed up with flyash or silica fume or blast furnace slag you can make a measurement of the reaction of the flyash versus time. That's not that much data on that. There's some, but you have to work very hard at it.

So I would say when you're mixing this stuff, your durability predictions are probably even less steady than before. We saw before that just the durability predictions for Portland cement and concrete are not that great.

These mineral admixtures are often used to

-- if you can avoid cracking -- to get low permeability, low hydration. You also tend to ameliorate the usual degradation stuff. This was mentioned -- I think you mentioned that. You also tend to lower the pH of pore solutions, so you have a trade off of lower permeability with low pH.

Also, chemical shrinkage involved with these kind of admixtures are more than Portland cement so even the higher tendency toward cell desiccation shrinkage cracking with mineral admixtures than you do with just plain Portland cement.

And so internal curing is probably even more important when you use those materials than just plain cement. And the whole world is using these mineral admixtures right today. Anything new built with these materials, built with this cement, it's going to have mineral admixtures in them.

Okay, let me get to prediction now. Predicting durability failure for first principles, that's sort of a grandiose title to the slide. We'll just pass on by that title and I'll give some details for it. But you need to correctly predict transporting reaction mechanisms, ions moving through cement paste pore solution, how they move, how they react.

As they move and react, how they change the material micro structure, cause cracking or close cracks or fill up the pore space or open up the pore space, how that changed material microstructure changes the properties, mechanical properties and the transfer properties which then change how the ions transport and react and change into a micro structure and so forth and so on, how everything changes with time.

You expect the surface environment is not so easy. That's beyond my research, my level of expertise, but that's a key thing to characterize how something is going to react over even 100 years. And of course, the relevant thermodynamics which is not totally well known for all these materials.

And any predictions you make must be accompanied by the results of valid -- I say auxiliary tests for valid experiments, accelerated or not. And the point Fred made is well taken that the models and the verification need to go together.

Actually, I'm not going to talk about this very much today, but just to mention in passing that to kind of highlight for my group for our current abilities and prediction, the Virtual Cement and Concrete Testing Laboratory, we're trying to build up a software laboratory, just like a physical testing laboratory, but only on the computer so you build concrete on the computer, test it on the computer, etcetera.

Try to make it as fundamental as possible. It's not empirical at all. And we have an industrial consortium we're working with and they're focused on producing concrete and selling concrete. So it's mainly focused on predicting current properties of concrete, short-term properties. Eventually, we'd like to be able to use it for durability in the industrial construction 50 to 100 year time frame. In fact, Rachel and I didn't talk together, but 50 to 100 seems what she said. Fifty now, 100 hopefully next decade or something.

So that's what the focus is on now. There's pieces of it though which can be used for the kind of prediction more interesting to nuclear industry. I'll get to that in a second.

That's the people we're working with and I need to put them up because they do supply funding and research over the last six years. So it's important to mention them.

Software base tool. It just looks like a web page and you just pick various things. Just like you go into a laboratory and pick various instruments to measure. It works the same way.

Okay, the rest of the talk now, I want to go through and just highlight some topics of things we can currently predict or hope to predict, things we're working on which could be relevant to the topic of today.

We'll look at hydration, micro structure formation and chemical interactions, rheology of cements and concrete, micro mechanics, transfer properties of ions and pore solution, thermodynamics, a little bit and a little bit about soil durability tests.

Fred pretty much trashed them, but I'll try to trash them a little further.

(Laughter.)

Now cement hydration. There's been models of cement hydration for a long time. Like I said, Jeff Frohnsdorff passed away recently. His 1960s model was a computer model of hydration and solved for differential equations and that's been carried on a lot around the world. In the '80s, there was work at NIST led by Jeff Frohnsdorff to develop a microstructure model, how a 3-D microstructure form for hydration. Unfortunately, it didn't have any of the fancy chemical kinetics. It was more kind of empirical, but more of a structural model.

We've improved on that with our current model. But still, it doesn't have the kinetics in. It forms a nice microstructure, it has sort of pseudo kinetics in, but doesn't have what you really want in a model.

What we're working on now is we're trying to marry the two and have a real model that gets you a real three-dimensional micro structure that does real chemical kinetics, real chemistry and physics of the cement reacting. That's the way forward to clean water cement and for dirty water cement.

The way we do it is to break up particles into rock seals and do a three-dimensional digital model where you actually represent the cement particles and the formation of products and get a three-dimensional microstructure.

You have to start with a -- with the real cement. If you just start with idealized cement you get the wrong properties, so we characterize the cement very well with SEM and backscattered electron imaging. You get the atomic elements, mix them all together and come up with a three-dimensional version of the real shapes, the real sizes and the realistic distribution of clinker phases among the cement particles. And that, we found is crucial to start out with -- if you don't start with that, the model is not going to be very good. It might not be very good anyway, but it sure won't be any good with - -if you start with that.

Our current cement hydration model is rule based. The rules are based on chemistry, real chemistry and there's various chemical phases in there, but there's no true kinetics. We're now working on, Jeff Bord in my group is working on HydratiCA which is a chemi-physical model which hopes to marry all this stuff together. I'll tell you a little bit about that soon.

I should note that working with mineral admixture companies in our consortium, they have lots of experience with mixing organic and inorganic chemicals, effecting cement hydration. It's possible that we could learn from their experience to help us with their -- work with dirty water cement and the various stuff that occurs in the nuclear waste containment.

HydratiCA, what we're working on now is object-oriented code. And you don't really know what that is, just a new way of computer program which is very adaptable.

Algorithms designed the model that's reaction and transfer equations of the ions dissolving, reacting, foreign product, it's all in there. It's real kinetics. If you run the model for an hour, you can tell exactly how many hours, minutes, days it was in real life. There's an exact relationship between the kinetics.

All that stuff is just to impress you. I don't really want to talk about it, but just lots of stuff there and it goes in the model. Jeff has done a very nice job with it.

Let me just mention before I leave that because there's real kinetics in there, because the model is set up to easily add new materials, for us it's been adding new cements or adding flyash or something, but it works for any materials. So if you want to start reacting, some uranium complex, if you know what the ionic species is, you know how it reacts with stuff, you can put it in this model and let it react. It will react to full microstructure. If you know the laws, if you know the various coefficients needed, that will work. So it's very easy to add new materials in, any materials at all, as long as you know some basic information about them.

We'll switch to rheology. Rheology is important for construction issues, obviously, for placing concrete. We talked about the tank problem, filling in the grout and i guess Barry mentioned all the rods and stuff in there. Rheology is going to be a big -- it's going to play an important role for that as well, to get the concrete, the grout to flow into all the interstices and fill up without voiding, large voids, filling up the tank. So rheology is important for both problems.

We can quantify roughly the rheology of any suspension by viscosity and seal stress. What we're working on is measuring experimentally, predicting computationally and I'll tell you something about both. The modern drive for rheological research has really taken off in the last 10 years or so and it's been self-consolidating concrete. That's the thing that came out of Japan, I guess Japan about 15 years ago or so, where you make concretes with very low yield stress.

So typical concrete, you are trying to pour it into a heavily reinforced region. It has to flow between the small holes and reinforcements. It gets stuck. If it has a non-zero yield stress, it gets stuck. You have to kind of stick in vibrators or push it along or guys with shovels and boots slam it along. But self-consolidating concrete has been lowering the yield stress, keeping the viscosity high so the rocks don't just drop right out in the bottom of the form and self-consolidating means that it can flow anywhere, sort of go in and fill up and you're done. You get rid of voids. You get rid of the need for guys in boots with shovels and vibrators pushing concrete around.

And so the usual way of looking at how concrete flows is some tests are not good enough for self-consolidating concrete, hence, the drive toward a more sophisticated rheological measurements for concrete.

All right, so rheology applies right from the mixing stage through the mixing of truck stage through the flowing and placing. We measured in the lab at the mortar scale. Also measure in the lab the concrete scale and then we simulate it using real shapes of rocks, shapes of rocks that are scanned from x-ray tomography and put into the models and we have code to let the matrix flow and the rocks spin and tumble and bump into each other.

And then the results from these experiments, preliminary results compare to the experimental data and then we can tell, basically we can tell where the data is wrong or we need to do better experiments. Because the theory is always right, but the experiments are wrong sometimes. It works both ways.

Although I must say in my experience, it's been a little easier to get the modeling right than to get the measurements right because spinning a suspension around and you get rocks in the fly out to the outside, it's hard to keep suspension uniform and measure at the same time. So there's difficulties in both, but I think we're overcoming them.

So we have some -- I think we can do a decent job of predicting rheological parameters. We're starting to do any way.

Let's look at micro displacements in concrete, I mean micro mechanics. We're real good at compression strength measurements. We put a block something and smash it. That's sort of macro. But if we really want to look at degradation you have chemistry happening at the pore level. You have growth of cracks and growth of phases. It shrinks in phrases. You have micro mechanics. You have stress at the local level and that's really what I'm talking about. That's a hard problem to get at. I think we had some of the pieces for it, but it's a particular problem.

So several different mechanisms of degradation involve some kind of localized displacement. Aggregates expand or shrinks, various things. They all set up stresses in the micro structure. Tensile stresses drive cracks to form.

So this is a piece of real concrete that actually was cracked and just some mechanism. We cut out a piece of it computationally. This is in 2D. We can do this in 3D. It's just a lot more visual in 2D, obviously. You take this and put it in the computer, specific elastic properties for each phase, realistic properties and then you can test various mechanisms. You can say well, was this cracking caused by all the aggregate expanded? Let's try and see what happens. So we did that hypotheses and said let all the aggregate expand a little bit. That's going to drive stresses in the cement base matrix which didn't expand, just gets squeezed. So where would the cracks go?

So you saw the fine element problem. Saw stresses everywhere. Find principal stresses everywhere. Map of tensile stresses. And then this shows where the cracks would be. This is the probable crack directions that is based on the tensile stress is up by that mechanism of having aggregate expand. And so you can go back and then compare this to the real one and say well, was this how the cracks actually went? If it didn't, then that mechanism was wrong. You go back and try another one.

This is a 2D simple way of looking at micro mechanics. We have three dimensional models. We can look at stresses in 3D and hopefully coupling that into the models of HydratiCA with degradation reactions going on and start coupling this together.

It's really what our kind of window of work is, trying to couple the microstructure and the chemistry and the properties together via the micro structure. We're not real great at any one of them, but all together, we kind of do I think fairly unique, in trying to couple together those things into one kind of model.

Let's look at transport and reaction degradation. This is a piece of cement paste matrix. We have unhydrated cement particles. You have all kinds of hydration products. You have cracks and you want to know as you flow in ions, ions react and what's going to happen to them as they go through the pore solution.

You want to calculate transporting the concrete pore solution. It's a pretty nasty problem. The reason is several times today we mentioned effective diffusion coefficient. The pore solution in cement paste is very high ionic strength, much higher than -- if you look in the handbooks for transport properties versus pH or versus ionic strength, usually they run out before they get to cement paste. So Ken Snyder has worked on this a lot and has had to go beyond that and look up in the literature to get how the transport rates depend on ionic strength.

So that's hard. High pH is hard and the many chemical species involved, even in clean water cement is pretty hard too. And so if you want to look at the ionic species going through the pore solution, you have a couple of problems because you have reactions going on as you have transport. You have degradation happening and then the degradation changes transfer properties, so the code that he's worked on for a long time is called 4SIGHT and that's been worked on at the NRC for many years.

We're trying to handle it, those things, those complications that set about at a continuum level. I don't actually have a picture of the microstructure in the code, but it's more of a continuum level where you know how much of each of the things you have there.

The model tries hard to avoid empiricism. I don't think there's anything empirical in it. It's basic physics and chemistry. The fundamental treatment of a concentrated ionic solution is probably the hardest part of it. We encountered many ionic species. We can predict the onset of severe degradations. It's not a model of mechanical failure though. It doesn't have mechanics in it. Right now it can be extended. It doesn't have radionuclide chemistry in it right now. It can be extended to that so the prediction capability as a model could be extended to radionuclides.

Other species like boric acid things like that could be put in as well with surface complexation which you probably have to have if that could be put in as well.

And those you have printouts that you can look up those references.

I'm going to briefly say something about thermodynamics. Looking back at my graduate education, I think the weakest part of it was thermodynamics, so I'm not going to say very much at all.

But looking at longer term problems, these thousands of years problems, one thing you worry about is what C-S-H forms do we have for a long time? Dr. Glasser said that C-S-H is only meta stable. It's going to change. What's it going to change into? What are the properties that those things are going to change into over many years?

One thing you might try is if you can get an idea of what it will change into, you can synthesize those forms in the laboratory and it measures properties like do radionuclides bind to them for instance. Right now, we're synthesizing some of these minerals for different projects. We're not measuring binding on radionuclides on them, but you can't synthesize as minerals and that might be a way to get at that long-term problem.

And I think Dr. Glasser mentioned, this was -- if you go to high temperatures and pressures, like an autoclave or the oil well cementing people, they pump cement down two miles so you have high temperature and pressure down there, you get crystalline phases of a set of meta stable amorphous C-S-H. Maybe we can make use of some of their experience in our sorts of problems. The same C-S-H, some of the same crystalline forms it's transforming into.

Okay, here's my opportunity to trash these more. Current durability tests we have and quote unquote accelerated and I don't have to re-explain that to you, but it's pretty much empirical. I'm probably less kind than Dr. Glasser is to them, but you make a bar. You drop it in a bucket of bad stuff. You measure length change ever so often and hope for the best and repeat it again as many times as you need to because the first six months don't tell you anything. I was probably being a little severe on that, but I'm a physicist. I'm allowed to be severe on that stuff.

We're trying to get ahead of that. We're trying to get a different kind of test and this is just the beginning. This is not the problem solved, but looking at a sulphate attack, we've done some collaboration with the Portland Cement Association where we don't - -we still don't know how to really accelerate it. It's still empirically accelerated, but we can at least improve it somewhat.

We don't really need a one foot long mortar bar and dump it in a bucket. You can do better than that. You understand microstructure. You understand what the aggregates do. You don't really need to do that. So going on to smaller cement paste samples, it turns out it's faster than the old method, but also coupled with the SCN investigation of the mechanisms of attack, what forms in the space, how does attack happen and that can be used to help us understand the results of the test.

So I worked with Paul Stutzman in that group, worked on this and by looking at that, the damage on the surface of these big mortar bars found that most of the damage, even after many weeks was confined to the first quarter millimeter or so. So we thought well, why have an inch-wide, 11 inch long bar and have the quarter millimeter, you might as well have a small sample. That's all the degradation you're going to have in the typical time of the test.

So we're able to change a foot long mortar bar to about a four centimeter long cement paste sample. It's much more controlled, better temperature control, better statistics because it's a small sample and you get better results much quicker. Still empirical, but it's a lot better than empirical and I think it's the way to go for these tests.

Again, repeating -- we're going to do other things besides sulphate attack the same way. Enumerate possible reactions. Use SEM to quantify microstructural effects. We understand the chemistry of a lot of these, but we don't understand the microstructural effects with the binding chemistry, learn how to correctly accelerate degradation mechanism and that's the hard one right there. I don't know how to do that right now. We need to learn how to do that.

And then we have small samples and do high through put and if you need good statistics, you need to do 200 samples. We'll do a small sample, high through put measurement. You can do it a lot faster, a lot quicker and get the results out. Now do it just as good as before. If you can do it faster, it's going to help industry a lot more. I hope we can do it better as well.

Let me finish up with some thoughts of research needs and then a summary. I think you've seen a lot of research needs today. This is my personal opinion for something else that's needed worked on. This is my area.

Need to develop HydratiCA better and if we're going to apply it to nuclear waste type simulations, we're going to need aggregate information on ionic species of interest to reactive waste containment problems. We need to develop 4SIGHT more, looking at a continuous scale, but hopefully link up 4SIGHT and HydratiCA together so we have a microstructural at a continuum level married together. I think it would be a very powerful combination tool.

I should note here as well that in the Virtual Cement and Concrete Testing Laboratory, you're given a microstrucure and it predicts properties. It doesn't care where the microstructure came from. So if we modify HydratiCA and be able to get new microstructures that are based on reactor waste problems, we can use the tools already existing to calculate things like lasting modulus and tensile strength and tensile properties, etcetera. So I think we can start attacking the problem of linking microstructure mechanics, chemistry and transport together into one model. I think we have the pieces to do that. It's going to be hard, but I think the way is there.

We certainly need fundamental research on property accelerating degradation mechanisms. Properly accelerating correct degradation mechanisms. I'd like to see a lot of research done on that. That's something that we can do. We can do some of that, but other people have much more expertise than we do on that. And it would be nice to have more research in the chemistry of this kind of applications to build into these models. And I'd like to see experimental measurements on the crystalline endpoints, thermodynamic endpoints to C-S-H because you need that kind of information to do computational modeling as well at the Thomas scale or the continuum scale.

Then the idea of the talk is then the prediction tools must be based on carefully characterized materials and fundamental physics and chemistry, thermodynamics. It is nice to have good, materials science-based standard experiments, crystalline C-H-S, controlled environment, etcetera, you need to have that to get prediction to be anything worthwhile at all.

If we combined those kind of computations and experiments, we should be able to make better predictions, I won't say accurate, better predictions of the durability of cementitious materials whether used in a construction industry or used in a nuclear waste, reactive waste type of application.

We're primarily focused on the concrete industry. That's our goal, 1600-year durability. But overall we're still interested in NRC, because we're a government agency and want to help the country. So

I think the same kind of tools can apply to this long term globular prediction that NRC cares about.

Okay, so that's all. Thanks.

VICE-CHAIRMAN CROFF: Thank you very much. Thank you for some very interesting talks. I think at this point we'll move into the Q&A. I'd like to take the first little while to just focus on the last three speakers and then we'll have sort of another session where we broaden out maybe the considerations and the victims, I guess.

So with that, Bill?

MEMBER HINZE: Sorry. Very interesting talks and particularly interested in hearing about the various research lines depending on the areas of expertise. There were a couple of questions that came out of your presentation, Fred, that I'd like to ask.

You criticized a couple of things and one was the QA problem in the production of cement. I wondered if you could expand on that a bit in terms of what are the causes. Are we lacking in protocols? Should we have protocols for waste types of -- for concretes used in nuclear waste problems? Are we just not adequately enforcing QA standards? Could you expand on that a bit?

DR. GLASSER: I don't consider myself an

expert on QA so I would have difficulty in giving you a prescriptive answer. But I what I pick up from reports that I assess are descriptions of how grouts and concretes are in place. I don't find any evidence that the people who did the work knew what the objectives were, what quality was expected, and how it could be measured, and it doesn't seem at intermediate stages where process was stopped and started to have been any checks in quality.

So really what I'm talking about I think is sort of a common sense approach to it. I think if you want anything fancier than that, you'll have to go to a genuine QA expert.

MEMBER HINZE: Okay, fine. Let me ask another question to you. You criticized, and rightly so from what you said the standard test. I had the question immediately to my mind of what do you have as an alternative? And you actually had a slide which you kind of approached the alternatives and one of the things was the tests should be better focused. Standard tests have a great place in all of this, I believe, and we can't just completely eliminate them. But can you give us better insight into how we could improve those? We heard a little bit of this from Ed in his presentation.

DR. GLASSER: Yes, I don't want to totally preempt what we're going to say in Quebec in September, but I think I can tell -- and some of things we're going to recommend are quite complicated. But one is quite simple and let me deal with just that one alone.

Now you, Ed has said you take a piece of concrete and you put it in a bucket. Well, it turns out that depending on the concentration of the bad stuff in the bucket, that how big the bucket is has the important role to play in what you get out of the test.

So we're going to recommend that if you use the ASTM standard of sodium sulfate, which I think from memory is 32 grams per liter, but I might be wrong on that. Don't put it down in the minutes without checking. You need to --

MEMBER HINZE: It's already in there.

(Laughter.)

DR. GLASSER: You need to use a mass ratio of at least 10. That is the mass of the aqueous solution has to be at least 10 times greater than the mass of cement. I don't mean the mass of concrete. If it's concrete you're using you're allowed credit for the aggregate is being inert, 10 times greater than the mass of cement. Otherwise, you run the risk of serious depletion of sulfate in the solution.

And we will also be making recommendations about how you control the change in pH.

MEMBER HINZE: One of your alternatives related to the need for supplemental calculations, and if you start putting caveats on these results of standards tests, I wonder how really standard they become because people will use different calculations and some will consider them, some will not. Is this really an alternative to this?

DR. GLASSER: I think what we're trying to do is make the test more reproducible, which is in the spirit of things. Not to complicate it or put non-standard features into the test. But I mean, I can't change what ASTM have in their test specification.

MEMBER HINZE: Let me ask one more question if I might, and this is to Ed. When you talked about small sample sized testing as a geo-scientist, that immediately raised red signal flags because there is always a problem of representative sample. In fact, Fred and some of us at lunch were discussing the size factor in some of these determinations.

Can you give us a better insight into how you can justify using the small sample and what kind of restrictions should be placed upon the results?

DR. GARBOCZI: The reason you can do that is in the -- I'll just say sulfate attack only. You're not really testing a structure at all, you're testing the cement. That's really all you're doing is testing the cement. Is the cement conducive to sulfate attack? How susceptible is it to sulfate attack? So the things that you worry about is the length scale of cement piece micro-structure. So you can probably get away with three millimeter samples because that's big enough to be representative of a cement paste micro structure. The four centimeters may even too big, because you're trying to test the concrete then you have to go to a bunch of bigger sample, concrete size sample. But the current tests the mortar. You don't build things out of mortar anyway. You're really only testing the cement.

So it's very similar. There's an ASTM strength test for cement strength. You make a two inch mortar cube and break it and that gives you a feel for the cement strength. So it's really the same kind of thing. If you're only testing the cement, then why not use a cement paste size sample. That was our point of view. So you know, structure of concrete is different. But cement only you can stay with a small sample.

DR. DETWILER: I'd like to add a comment here related to that and that is there may actually be some things that would be somewhat different depending on exactly how you mixed it for example, because the mixing can effect the rate of hydration at the beginning. You know, so there are certain things that might affect.

And also I supposed in the size sample you're talking about, bleeding is not really an issue. But it's conceivable that it might be in that also and could open up some things. So there are some possibilities there and same with if you had the presence of sand in there, you would have those transition zones and that would have more to say about the rate. Although I don't know that is such an issue if you're comparing apples with apples. But certainly the mixing would have an effect.

DR. GARBOCZI: Right, you wouldn't get -- your small space samples wouldn't necessarily give the exact same results as the big mortar samples, but you don't care so much because you're just testing the cement. Yes, I agree with you.

DR. SCHEETZ: The other thing is that I

guess I was talking to him, I guess, offline is that he's doing more samples so he's getting a bigger body of statistics to work with. So part of that is compensated. But certainly the mixing effect and the energy that a mixer puts into the mortar or into the concrete is a very, very significant concern.

I mean, when we do our developmental samples at the laboratory, we have a one-third yard mixer, but when we get the data, when the rubber hits the road, when we get that data for PennDOT, we have contracted with the ready-mix companies to bring it in and mix it in their truck, drive it into our laboratory and dump the truck to do the measurements on. So those scale problems are real.

VICE-CHAIRMAN CROFF: Mike.

CHAIR RYAN: The last two presentations were interesting from several points of view. Professor Glasser, I was taken by your comment that there really isn't a good compendium of all this information. That's striking to me and that's probably part of the problem that we struggle with. The second part is kind of a synthesis from all three talks and that is that I think it is troublesome to me that we rely on tests where it's clear as a bell to everybody at the table that the models are wrong.

That really creates a ripple into performance assessment for which there's probably a high penalty being paid, that if we're overpredicting failure or underpredicting success of behavior, that's a bad thing in performance assessment. And the third gets to the statistics issue, the uncertainty analysis issue that we're kind of it sounds like we don't have a very good rudder on where we are relative to the center line of what we think is the best answer.

And without a real serious and comprehensive treatment of uncertainty and probability of one answer over another being right, we really need to think about how to work on that. Of course I would jump on Dr. Garrick's risk triplet and try to catalogue them by some ranking of how important they are to overall importance or risk assessment or whatever it might be. But I think we need a thoughtful review of what would be a really good approach to do a systematic approach of these uncertainties.

It's interesting that when we've asked you to do this, though it's not really a bad thing, but you've compartmentalized into your own areas of specialty the risks and the uncertainties. And while I appreciate the fact that this is certainly valid based on how all of you work on different aspects of this area, it doesn't facilitate the bringing together all the information or the systematic analysis of uncertainty which then could flow into a performance assessment.

I guess the one question I ask is do you think I'm making any sense or is this crazy? I mean, am I on the right track of maybe how to move ahead here a bit or not?

DR. GLASSER: No, I agree with what you said. I think that's a very good synthesis from the standpoint of regulator and overseer. You have a different role to play than many of the other participants in this process. I think anything that we can do to assist in the discharge of those obligations, it is our duty to do it and I think that's a very clear statement of what you need to do.

CHAIR RYAN: I came at it from perhaps that perspective but also as a former applicant and licensee, I think it's helpful from that side of the fence too because then you know what the expectations are and you don't have to worry if the two order of magnitude difference between a test and your answer is going to be good, recognized as reasonable, or recognized as wrong.

You know, again I want to give credit to Tony Malinoskos who worked at ORNL because he's the fellow that I quoted when I said if it is off by two orders of magnitude, it's not conservative it's just wrong. So but it really helps both sides of the fence, whether it is the applicant who is trying to describe reality or the regulator who is trying to evaluate that assessment of a reality.

DR. GLASSER: These two order of magnitude differences that we were looking at and I think you're probably referring to the, what was it Professor Kosson showed earlier this morning. I think there the prediction was based on a rate model for the prolongation of a particular process that was effectively using fixed laws of diffusion and applying them to a situation. So you've got a profile which was a constant times the square root of time, that governed the slope. But then Professor Kosson's own data showed that in many cases you didn't get a Fickian profile of diffusion, you got steps.

So even without the mathematical analysis, you can tell there's a serious divergence. There are processes occurring within the cement that have not yet been built in to the model. So it's not that the model is wrong so much as the model is inappropriate, which is the way I would put it.

CHAIR RYAN: That would be close enough to wrong. I would say it is wrong.

(Laughter.)

CHAIR RYAN: But I appreciate your point.

DR. KOSSON: If I can comment on that a little bit further, I just wanted to point out the divergence between what is currently being assumed in performance assessments versus what we recognize to be the phenomena. And to go a little bit further on something you said a little bit earlier, Mike, is that I think what is really needed is a concerted effort over a committed period of time. Not six months, not tomorrow, hurry up and get it done today, but to develop an integrated research development program that feeds into incrementally into performance assessments and other applications so that you take advantage of data that evolves as Jim mentioned from field monitoring and the like and you really put it on a continuous improvement basis.

CHAIR RYAN: Absolutely. I couldn't agree with you more.

DR. KOSSON: That's not what is happening now.

CHAIR RYAN: I couldn't agree with you

more. I think that is well said. There's one other aspect to all this that I just think to add as a comment is that I'm always nervous when people are satisfied with deterministic overestimates of failure. Well, it is conservative so we feel pretty good about the number, we're okay. Conservative and ultra-conservative estimates mask the true uncertainty. They ask for phenomenology and all sorts of other things, so I think there's a real tendency to rely on that perhaps and I challenge that as being a little risky.

DR. GLASSER: They also end up with a situation that you can never contain radioactive waste.

CHAIR RYAN: Right.

DR. GLASSER: It's like trying to put gas into a sieve. No barriers really work.

DR. KOSSON: I contend even further as if you mask the phenomena and your assessment protocol is misleading in terms of phenomena and the results, then you are missing the incentive to improve and the opportunities to improve what you're doing and the insights to lead to improvements for a much better performing system itself.

CHAIR RYAN: Well said. I think that kind of captures the essence of it.

DR. DOLE: There's a push-me, pull-me. Certainly the EPA regulations sort of prescribe a methodology for assessing the transport and we know from our experience that the essence of that, the heart of that is based on phenomena that we observe.

Okay, so the question is we have so many different conflicting observations. Are we confident enough to tip over the current methodology. I don't think we're ready for that when we know, in fact, that is the Agency ready to accept that they based all these assessment on the wrong basis.

CHAIR RYAN: Then again, maybe somewhere and I'm not trying to exactly be the champion for oh, let's just turn on the PRA switch and go all wild with that. But there is a way to get at your question I think, Les, and I think that is to systematically assess these uncertainties. Which ones are important to performance, which ones are less important to performance, and somehow line them up in a way where I think we can attack the tough ones that need to be answered first and maybe order them in someway after that.

If a phenomenon is interesting but not important to outcome of issues related to performance assessment, it's kind of a secondary thing.

DR. KOSSON: I think it's important to recognize that you have to make the best decision based on the information that you have and understanding that you have available at the time. However, a lot of what we were seeing and what things propagate right have an appearance of being stuck in time. That not taking the last decade of understanding of computational advances, of analytical advances, and incorporating them into the next generation.

Inherently, there's a lag time in these things, but also there's got to be a commitment to incorporate them. Not just maintain the status quo.

CHAIR RYAN: I have one final question and sort of off this topic, but we've talked about concrete in terms of small, medium, large, and really, really large constructions. And with the issue of seismic, it's a very specific point but why do we build such big structures if we're interested for waste disposal, if we're interested in seismic control? I know very little about seismic analysis, but I know one big block is not as good as five little ones.

DR. DETWILER: I'm not sure how important seismic activity is in some of these things. I realize that the Hanford site, for example, does have some, you know, is subject to seismic activity and I would assume that the Idaho one is too just from having grown up in that area. But I think actually for underground structures, I don't think it really matters all that much.

By the time it is actually underground, if you're talking about underground tanks and that sort of thing, I'm not sure that the stresses transmitted are really all that big a deal. So something we make an issue of, but I'm not sure that it really matters.

I would assume that the really big problems with what might happen underground would have more to do with soil settlement, differential settlement and that kind of thing.

CHAIR RYAN: Okay, thanks for the clarification.

DR. GLASSER: I'm not like Rachel. I'm not an expert on it, but from the work that we've done on cements intended to be used in seismic areas, what the geophysicists tell me is that what's much more important than size is coupling. Not to leave void spaces, not to leave gaps, but to ensure that concrete is in contact with -- well, I've only worked over hard rock mines in this context, but the contact is good.

And that's more important than the actual size of the structure, because the structures that I have experienced with gold mines have miles of large diameter tunnel and very large underground crushing plants. So scale is large.

CHAIR RYAN: Okay, thanks. That helps.

Ruth?

MEMBER WEINER: We all come at these questions from our own backgrounds, and I've just learned more about cement than I ever thought I would know and I sure can't remember it all.

(Laughter.

MEMBER WEINER: But this is fascinating. It seems to me that this is for the physical chemists. It seems to me that the concrete has a lot of surface area. Does it act ever as an absorbent? Can you absorb and desorb water contaminants from concrete? Could it ever act like an absorption column or an ion exchange column or something like that?

DR. GLASSER: I think the answer to that is yes.

MEMBER WEINER: Well, could we then use that property to isolate, sequester if you will, radionuclides in these tanks?

DR. GLASSER: I think cement will have a

response for almost all nuclides where at low concentrations there will be absorption is what you refer to. But then depending on the particular species, you shift into a regime of precipitation where they form some solubility limiting phase with the cement.

Now there is a huge spread of concentrations over which that occurs. For example, for cesium, you never really attain the point where you get a precipitate phase. There's not solubility control. But for most di- and trivalent radionuclides and possibly for some anionic species, you will have a boundary somewhere and it's not been found possible to predict where that boundary is. But especially if you don't have to do the experiment with the radioactive species, if you do it with an active stimulant, nickel or chromium or something like that.

We have seen examples today where the precipitation phase was noted, but the concentration is lower than that. Yes, you will get absorption.

MEMBER WEINER: Well, since radionuclides that have stable analogs behave chemically and physically, according to what they are chemically and physically and not what they are radiologically,. would this be a fruitful area to examine for sequestering radionuclides?

DR. GLASSER: Well, there's two comments that I would make. First of all, the worry always is in the minds of people that what you absorb can easily be desorbed. That tends to be an element of reversibility about many of these processes. So the worry is that while there might be binding by absorption, if conditions were changed you would get desorption. Nonetheless, there's a hold up in the transport process.

Secondly, at the -- I'm surprised nobody mentioned the natural analog site at Makaren in Jordan, because there has been a lot of work done on the absorptive potential of the calcium silicate hydrate for various species. Now obviously you can't do it on everything. You have to do it on what nature has provided you with. But there are quite a bit of data in that area as a result of the joint Swiss-Swedish-British initiative to study the area. And I have been onsite and it is fascinating.

It's on a huge scale and you can actually see if you go during the rainy season, you can see springs coming out at the base of information, stick a piece of pH paper in and bingo, you get pH 13. And it's wonderful, all these predictions that you made you can see them happening.

DR. DOLE: You know, the idea that -- certainly the work at NIST can talk about the fabric of the C-S-H is simulated by discrete granular entities. And then there is the surface of the cement and I don't know whether it was a miscommunication is that cement as a fabric of a mass may be granular and have internally have very high ionic exchange capacity or capacity to promote insolubles, but as an exchange media to outside flowing water, there's not ready transport within the mass of the cement, because the apparent diffusion coefficient is the best thing we can use to describe are exceeding low. Ten to the minus twelve, 10^{-16}, almost imaginary numbers for actinides and many of the materials.

So the effective transport within the small masses, now you could postulate that you could have little balls, you know, through which you could percolate like backfill or something like that. And then they would be very effective.

MEMBER WEINER: Thank you, that's very clarifying.

Another question I had and I think this is for more than the last three speakers. Is clearly, in looking at the tanks using as cement to stabilize the underground tanks at Savannah River and Hanford, you're not looking at structural strength. You're looking at the ability of cement to hold back the radionuclides. Do you design the composition?

What processes go into that design? Is there some overriding formula that you use or is it empirical, you try it out?

DR. LANGTON: Well, at Savannah River, the tank fill material, there's multiple layers. And the layer in contact with the waste was actually designed on a concept that the concept was cement hydrates to C-S-H, the more C-S-H, the better the sorption.

That lower layer also contained slag cement to achieve reducing properties. And silica fume to control microstructure to act as a pozzolan. So yes, there was a thought process that went into that. Actually, Rachel is the one that came up with it.

MEMBER WEINER: So it's basically a designer cement, if you will, for the particular purpose.

DR. LANGTON: A blended cement and there were some leaching tests performed.

Now unfortunately for the contaminants of most concern which are the long-lived anionic species for technotate, the neptunium, iodine sorption in cementitious materials, whether they're -- I won't say they're reducing, nonreducing, just ordinary cementitious concrete mortar materials is 50 percent at the most or less. Fifty percent or less.

So that would be a KD absorption coefficient of between 1 and zero. Now if you add a reducing agent, I can't say that you're having sorption by a different mechanism by precipitation, by chemical reduction and subsequent precipitation. You're lowering the source term in solution by precipitating it rather than absorbing it.

So the effective KD when there's a reducing agent present would be lower. And I measure values like 6,000, 5,000, 6,000, that range.

But absorption is the wrong mechanism.

MEMBER WEINER: I wasn't suggesting either a single mechanism or that sorption would be -- I thought there might be. But you're quite right that what you're looking at is the effective case D. And that's -- so you design your -- the question is you design your cements -- you design the system to provide you with the effective case of D. Is that correct?

DR. LANGTON: Yes, the two knobs that are tweaked right now are ph and KD. Oxidizing, oxygen potential and --

MEMBER WEINER: And KD.

DR. LANGTON: Well, I'm sorry, pH and EH are the two knobs that are tweaked. Now other things can be done. Additives, getters could be added for cesium, add a zeolite for cesium or for strontium. So there are other knobs that could be tweaked, but we're not doing that at the moment.

DR. DETWILER: We also have some other considerations that when we were formulating that particular route and some of them just had to do with can we pump it into place, will it flow? Because we knew we were going to be placing it at very limited number of entry points. And so we had to make sure that it could be placed there and that it would flow to the edges of the tank and still retain its integrity as grout.

So that was one reason why the silica fume was in there. Had it done nothing else, it was doing something very important in maintaining the integrity of the liquid grout to get all the way out to the edges of the tank and not have segregated into its separate components.

So there were some engineering aspects of it as well and we did mock ups. there were a number of mock ups that were done that tested that ability for the grout to be mixed and trimmed into place and that it would flow out. It would flow over obstacles. All that sort of stuff was part of the testing. And that's really more of an engineering concern and just constructability.

MEMBER WEINER: That's a very good point, by the way.

DR. KOSSON: If I could just comment also, when -- getting back to Mike's comment about wrong models and your comment about KDs, when the mechanism of retention in the cement matrix or cement paste is one of precipitation/dissolution, modeling it as an absorption process, as a KD approach which I've seen frequently done is just plain wrong.

Or as an effective diffusion coefficient. You need to couple dissolution --

DR. SCHEETZ: What you have to look at when you're doing your designer concrete is you have to look at the different mechanisms by which the radionuclides are sequestered.

You have sorption. You have precipitation. You have a raisin bread model where it's -- where the waste is a raisin in a raisin bread model and it's just physically encapsulated.

So what you need to do is you need to look at all of the potential ways in which the waste is going to be sequestered. Not all components will be sequestered in the same manner.

Chris was talking about the anions. Anion hydroxy anions like selenite, arsenate, chromate, protectnate, they tend not to be tied up very readily and they -- and we see this in other environmental fields.

This is why we go to the use of slag, so it reduces those down from an anion to a chadian and chadians are retained. So you need to look at the big picture. You need to look at what mechanisms are available. You will need to look at what elements are -- you're trying to tie up and which ones are going to best suited to which mechanism and then you try and integrate all of those mechanisms into your grout.

And you have the other thing to do and what we've been hitting upon here, we've been bouncing back and forth, but nobody has enumerated it. We have grout people. We have structural engineers. What sets in between is material scientists. These are materials problems. They're not -- and that materials chemist has to have his foot in engineering as well.

So we have to balance the mechanical and the engineering constraints with the fundamental materials properties of what you're trying to do. And that's what Chris does.

MEMBER WEINER: Thank you.

DR. LANGTON: Designing waste forms to past tests at 28 days to demonstrate that contaminants have been stabilized is straight forward. The contaminate chemistry of the various species that we're interested in is well known.

Designing waste forms for placement. It's another set of tools, another set of techniques and strategies. That's well known. And can be worked around. Can be engineered around.

What's missing is long-term performance predictions. For cement waste forms, the long-term issues depend on migration or movement of water and air. And the air contains two constituents of concern: oxygen and CO2. That's what it gets down to.

How do you predict how the transport of water and air in the environment in the land fill, in the waste form, through the containment, what conditions that containment or waste form are going to be in, what conditions the cap, the cover are going to be in; how it's shedding water, how is it transmitting water. And how do you do that for 10,000 years? Or for 1,000 years?

DR. DOLE: Yes, just to pick up on a small, delicate thread that she touched on is that, was that designing a waste form to pass the test, and take you down the wrong path, specifically the TCLP, comes with a chealating agent, acetic acid, so if I design a waste form that blinds the acetic acid, and I apparently pass the test, I had generally made a waste form that's very geochemically unstable. That's a caveat you have to look at. If you specify a test, it can sometimes push, have unintended consequences of driving you to waste forms that --

MEMBER WEINER: Yes.

DR. DOLE: -- less desirable.

DR. LANGTON: The chemistry is known for people that want to look into it.

DR. DOLE: Yes.

MEMBER WEINER: Could you talk into the microphone? We'd hate to miss any of this.

DR. LANGTON: Oh sure. But the chemistry in the qualification, we call it the qualification testing, the chemistry that needs to be adjusted or that shouldn't be adjusted, is well known for the contaminants that we're interested in.

MEMBER WEINER: I have a final question for Dr. Garboczi. And that is, in your model, how do you model your chemical reactions? Do you model an equilibrium? Is it based on minimizing the Gibbs free energy? What's the overriding way that you do that?

DR. GARBOCZI: That might be a detail beyond me. This is for Jeff Bord. All the chemistry takes place in a node. I will ask him to email you the answer to that.

MEMBER WEINER: Thank you.

DR. GARBOCZI: It's better than me trying to wing one.

MEMBER WEINER: Thank you.

VICE-CHAIRMAN CROFF: Thanks. I think that before going to Jim, we seem to have merged out of the, to the questioning the entire group here. So I think we should assume with it at that point.

MEMBER CLARKE: I ask permission to officially begin the round table.

VICE-CHAIRMAN CROFF: Yes, I think we're in the round table.

MEMBER CLARKE: And the rule that he or she speaks last is also applicable to he or she questions last. So, a lot of the things that I wanted to ask have already been asked.

But, picking up on the recipe, one of the things I heard from all of you was that these processes may be important, this may be important, that may be important. What I took away from that was this is very waste-specific and this is very site-specific, and so the value of having a recipe that addresses as many things as you can with that knowledge is very important and that, I think, gives us what we need for the QA, because we need to tailor the QA obviously to the recipe and, you know, what performance we're looking to.

And I think, Christine, you do this, I'm sorry, do you not? You don't, you know, you mix your cake and apply it and you can control the things you need to control. Is that a fair statement?

DR. LANGTON: Yes. A problem with the Q. We do. And the QA, we have as good a QA for concrete vaults or for waste forms as any construction job has. The problem with QA is that, for concrete, for concrete, in general, compared to a product coming out of a factory. The factory process is over in a short time. The raw material, temperature, particle size features can be adjusted to meet any specifications that are required by the process.

To a large extent, the reactions that take place for the cement materials and for the waste forms, the cementitious materials like concrete in waste forms, take place in ambient conditions. And the placements are done under outdoor ambient conditions, which are variable.

So, the QA that's done is to get a certain placement property, a certain flow or a slump or some placement at whatever conditions exist outdoors. And they'll be a range on the amount of water that can be added, the amount of admixture, the need for admixture, and that takes care of the placement.

But the curing, and so ambient conditions over the range of ambient, of normal ambient conditions, makes a big difference. And there are adjustments made, just like routinely they're make on the fly for concrete. The curing process also takes place over a range of ambient conditions, and the curing period is not like a product in a factory where it's a few hours. It's weeks, months, or longer.

So, the QA problem is a lot bigger. And it's a lot different than what a construction job would experience. Construction jobs can test the 28-day strength, if that's what it's designed for, and if it passes, they're finished.

For our QA, for waste form QA, do we test at five years, and then take the waste form out if it didn't meet the specification? When people are talking about QA, they're trying to mix concrete and disposal and they don't mix.

MEMBER CLARKE: So you test as you go. That's the best you can do, I guess.

DR. LANGTON: You test as you go and I would say that the requirements are met, the specifications for placement are met. But there's a lot that happens after placement and things need to happen in order to achieve placement. As I said, more water, admixtures, more vibration necessary, and that's how concrete jobs work also.

DR. SCHEETZ: Let me add a cautionary note here. A lot of what we talked about when we criticized QA was done on, you know, on engineering structures and we're having just fits with this right now building Interstate 99 out through central Pennsylvania, where we're placing a ternary mix of flyash and slag concrete on a bridge deck and it comes out and the people who are placing it judge it to be sticky. So, not knowing, and this is back to what Fred's point is, not knowing that this was an experimental design, not knowing the properties of it, not knowing the objective of it, not knowing its performance, they arbitrarily decide to mist it. So they've changed the water to cement ratio. And the concrete is not what was intended to go down. And I'm sure that Rachel, with her vast experience, probably can enumerate dozens of these types of cases.

You have the situation where, on the fly, this is out in industry, where you have on the fly people making decisions without the full background and scope of what the consequences of those decisions are. And you know, if you're the PennDOT inspector standing there, what do you say? They may or may not see it. They may or may not, you know, have anything that they can do about it at the time, because he's already added the moisture.

So it's those types of QA concerns are less manageable in the real world than in, under a controlled condition where, you know, everybody, if you're going to pour a tank, you're going to stand around and look it, look at it. And I would think that, under those circumstances, your ability to control the QA is better than it is a three o'clock in the morning in central Pennsylvania.

DR. DETWILER: I would like to add to that, though. I now work for a company that does construction testing, you know, for more routine things than what we're talking about here. But, we have tried to position ourselves in the market as a company that really cares, that always provides a qualified technician and all that. And I can tell you that a lot of that has to do with providing good training for all of your people.

And we have one of the issues that we have is that every summer we hire a lot of student interns to come in, and so we'll increase our number of personnel from 400 and some to 500 and some over the summer.

So, we have a big training program that goes on where we teach everybody and we make sure that they all get certified by, in our case ACI, but, you know, you would have your own program whatever that was. And then, every one of those junior people is assigned to a senior person. And that senior person is also on-site with them. So that every junior technician has a senior technician that he can go to if he doesn't understand something and who is watching over him. And that senior technician reports to a project manager and I serve as a resource to these people.

A lot of the senior technicians have my

number programmed into their cell phones so they can call me from the site, and I can provide them with any kind of information or anything else if there's any question.

So that, these things have to do with, you know they're not really technical issues any more. They're management issues. They have to do with how you organize it, how you support people, how you train them, how you communicate, make sure that they know where to go if they have a question, that you have somebody there who's willing to answer the question without biting their heads off. You know, all of that sort of thing goes into that and I think that it may not be done perfectly every time.

It certainly is not as easy as in a factory because, for example, we can't control the weather. But, certainly, you know, we can tell our technicians if we are trying to design and often it is more of a prescriptive specification. In our case you have to meet a certain mix proportion. That batch ticket will tell you what went into that particular batch. If they ask you whether you can add water and you see that there's already all the water they're allowed, you say no, it's not allowed.

MEMBER CLARKE: Reminding me that there is a distinction between QA and QC and we started out talking about QC and you're talking about QA so I think we're covering it. It, also this need for a site-specific, waste-specific recipe impresses me that there's a need for a site-specific, waste-specific leeching test as well. And so we've talked about the TCP and how the TCP doesn't do any of this. The other standard tests are probably appropriate. I mean I don't know of impressibility and things like that. But maybe they're just fine. But if we're looking at the potential for leeching under certain conditions, I would think that would be --

DR. KOSSON: Jim, I couldn't disagree with you more.

(Laughter.)

MEMBER CLARKE: I set you up as best as I could.

(Laugher.)

DR. KOSSON: Rather than a site-specific leeching test which I think would be an unmitigated disaster, because of all the different permutations and the like, you want to have leeching tests that have net measure intrinsic parameters, properties of the material and you want a closely couple of both the laboratory measurement as Fred inferred, the interpretation of the data and the data reduction as well.

It seems a bit crazy that we can use computational models and simulation in a host of different ways, but if you want to take a test result from a laboratory that you have to interpret it by hand, but I think there are appropriate algorithms for interpreting tests and that the rigor that goes into a design basis for a building or for anything else also has to go into the design basis for a test.

Both how you're going to use with the output is, all the parameters being modeled and then verified for the test itself so that you can appropriately get the parameter estimates out of the test that you want and then use it in a feed-forward way and to either as quality control or in your performance assessments models.

MEMBER CLARKE: And the other thing I would just throw out to all of you -- by the way, one other thing let me throw out. I enjoyed the exchange on deterministic versus probabilistic. I think that's an interesting area to look at and what I took out of that maybe I didn't take out what I should have, but for certain valuations, where we're looking at a process and maybe we can control it fairly well, we want to really understand the underlying science deterministically.

It would make a whole lot of sense, when we're scaling out to a facility where we have variability and uncertainty of large proportion and then maybe a probabilistic route is the way to go. So I throw that out to see what you think of it, if we need to talk about it.

And the last thing I would throw out would be how do we put all this together? I mean we have heard so many different things, so many processes that may be important under some conditions, maybe less important under other conditions. To use a word that's a little overworked, you know, how do we have a road map that takes us to what we need to do? I'll say it again, for a specific waste type and a specific environment?

And do this in a risk-informed way so that we know what's important, what is less important. What's the best way. We've all agreed that predicting -- we're driving way beyond our headlights and our ability to predict much beyond our experience, it's questionable, way beyond our experiences, very questionable. So how do we deal with all of this?

I just throw that out to all of you.

DR. SCHEETZ: With an integrated program, with an integrated program that's got some foresight to longevity, you can't work on a six-month contract on a six-month basis and do it hodge podge and willy-nilly.

We've all worked at this and all of us at this table at various times and in various conditions for various periods of time. And I don't see the integrated program that needs to be -- somebody has got to do it and unfortunately that takes the crinkly green lubricant and the commitment to stand behind it.

But what we need to do here is look at Yucca Mountain as an example. I mean look at all of the vast diversity of backgrounds and fields and models and everything that went into coming up with the performance assessment for Yucca Mountain, effectively we've got to do that here, but not necessarily on such a grand scale.

But we have to make a commitment to bring the material scientists together, bring the civil engineers together, bring the people who are doing the thermodynamic modeling, bring the people together who are doing the computational modeling and integrate them into a program that the output of which will -- we need to get them to talk together and the outcome of that program then can be used for the ultimate performance assessment.

CHAIR RYAN: And again, I'd offer my friendly amendment to your summary that that has to be structured so that we're touching on the things that are important to risk in the context of performance assessment.

DR. SCHEETZ: Absolutely.

CHAIR RYAN: As a priority from the top down.

DR. GLASSER: I think you might have to face some hard choices, for example, I am not optimistic that we can cope with conditions which are fluctuating, wet one moment and dry the next.

It might be necessary to come back and say well, in the sort of time scale that you envisage, even allowing for a substantial component of additional research, we're not going to be able to cope with fluctuating conditions. You must choose a repository siting which is going to be permanently dry or permanently wet or whatever, but not fluctuate back and forth between states. This is one of the things I was referring to earlier when I said there needs to be a more holistic dialogue.

Cements are not like a bandage to cover up other deficiencies and inadequacies . It's not true just for cements. It's true for any barrier material that you're going to use. You have to have a fairly particular and relatively constant set of conditions if you really want to know what the future performance is going to be. You can't deal with too much fluctuation, too much erratic, unpredictable behavior.

MEMBER WEINER: I could make a comment. We have an example in this country where we actually did it, did a performance assessment and acted on it and are putting wastes into a repository which in theory is going to sequester it for 10,000 years and that's the Waste Isolation Pilot Plant in New Mexico. And it does exactly what Dr. Scheetz said. It took 28 years and a great deal of money and an integrated performance assessment with a huge variety of disciplines and the license application fills several miles of library shelves, and that's it.

CHAIR RYAN: I think that's an interesting example. You know, I really grudge that folks think about what is in the waste before you decide that's the model to follow. There's a lot of actinides and lots of long-lived materials. Those time horizons are meaningful, but if you look at say pretty much the commercial low-level waste, with the exception of source material uranium, the show is over in 300 years pretty much.

MEMBER CLARKE: Also, I think we're talking primarily today for the waste determinations applications about near surface disposals.

CHAIR RYAN: Right. So it's a whole different kind of setting and I think the point is that, and I take the point clearly that the setting, you know, very much can drive the bus. Whether it's the fluctuations of, you know, is the water table going up and down through your waste zone? I mean, that's always fun to figure out. Or is it static either in the saturated or unsaturated zone and so forth.

I mean those things all help shape the framework in what you're going to, I think, be well served by trying to assess uncertainty. And then the waste forum and all the rest of the things that have been talked about today. Again, I see a framework shaping up here as kind of the way to think about.

And again Jim, along the lines that you said that I think you can -- I very strongly believe that a waste site is qualified in the first phase of its life through licensing or permitting, whatever it might be. But I think there's a tremendous opportunity that is often not taken advantage of when people do monitoring.

Monitoring is done for two reasons: compliance demonstration with something, a concentration at a location or a concentration you plug into a dose calculation or something of that sort. But if you take the second step and monitor for modeling confidence building, you know you can do a lot to say well, we were on the right track or we can make a course adjustment and may get on a better track, or whatever it might be with regard to performance.

I use the example in my own class where are the most stream samples taken in a large facility? Well, on the bridge where it crosses the road because it is the easiest place to get to it. So often the sampling that's done for compliance, that might be perfectly fine. But is that the best place in the surface seismologic system to get a system so that you can do other things to understand the model? Perhaps yes, perhaps not. So I think that second step can help break the conundrum that we're stuck with and we really don't know enough.

I mean, there are ways to get at it. It might be incremental. I think that word was used before but it's a way to proceed. Again, if anyone thinks I'm crazy just pour a little cold water on me. It seems like a good idea to me.

MEMBER CLARKE: Well, yes, and you know how I feel about that as well. But I wanted to see if this is going on. Is there an integration effect? How do we sort all of this out? Do the best thing for the best situation and the best location.

VICE-CHAIRMAN CROFF: Are you done?

(Laughter.)

DR. GLASSER: A further example is integrated approach. It's for a repository which is in clay and the clay is pyritic and then the operational phase, well the testing in pilot plants has been going on since 1974 or 1975 and the repository will shortly become operational in three, four years, something like that. So it's going to have -- and then it will be another 30 years before it's closed. A long life.

And it turns out that in the performance assessment that the serious worry is that pyrite in the clay will oxidize by leakage of oxygen through tunnel linings.

We know that this result in production of thiosulfate and the impact of thiosulfate on canister corrosion and concrete durabilities, we're not very certain about it. So at quite an early stage it was decided that what should be done was to simply limit oxygen leakage into the repository surroundings. Now all sorts of things were considered including way out things like people going around in space suits because the whole tunnel was filled with argon or something.

But in the end it came down just to common sense because the measured leakage of oxygen through the tunnel lining was extremely low. So it was decided to leave the tunnel in air or fresh air, but simply to make sure that there were no unsealed access ports where the tunnel atmosphere could come into direct contact with clay. And that is working very well.

So sometimes if you deal with these problems on a one-off basis, but if you deal with them in good time and integrated into the overall operational plan, testing plan and the operational plan for the repository itself, you avoid problems.

DR. KOSSON: Let me jump in also. If somebody could put back up slide 18 that I used, because I think that that in turn serves as a framework for looking at an integrated approach for this that you might want to be thinking about as you go forward in terms of coupling mechanics with chemistry and the various aspects.

(Pause.)

DR. KOSSON: No, the Power Point, please. Lower right. Slide 18, I believe. But I think you want to be in the Power Point one because Adobe -- there you go. If you go to 18 and go to the slide.

Basically, integrating the various conceptual models of testing in the simulation, I would suggest that this an approach to think about how you might want to tie it all together.

CHAIR RYAN: Yes, and I would add a couple of steps. I think lots of folks, and I don't mean this as a criticism specifically, but tag and sensitivity in certainty analysis boxes at the end is part of it. The other part of it is figuring out what is sensitive and what isn't, what is certain and what isn't, and one of those things is important to whatever your measure of risk is through the system.

DR. KOSSON: I agree completely.

VICE-CHAIRMAN CROFF: I think at this point, if it would be good, there are a few other people we need to get questions from. I'm going to try one and I'd like to try to follow on something that Dr. Langton said a little bit earlier in response to some question. And that was concerning the, you know, basically there's two materials coming at this cement that can affect it. There's the water and the air with the two components of the air.

And I was thinking with an analogy, about analogies, with the Yucca Mountain Project, where of course corrosion of metals and the waste package is a great concern and an equally problem and maybe a greater problem is predicting the chemistry or the atmosphere, if you will, inside that repository over long times. And I'm wondering is it possible that the greater issue for cements is predicting the environment that it is in as opposed to its behavior given that you know the environment?

DR. LANGTON: The environment to a large effect determines the condition that the cement waste form of the concrete will be in. If there is no water coming into the system, none of these degradation processes are going to take place. They all require the presence of water. Chemical durability of a contaminate that's chemically reduced, like protectnetate going to technetium sulfite, technetium hydroxide, is dependent on whether or not oxygen gets to it, is transported to it.

And then the contaminants need to be

transported out through the fluid phase, an interconnected fluid phase in the pore structure of the waste form of concrete and soil.

VICE-CHAIRMAN CROFF: At this point, what would you say is our predictive capability for the I'll call it the environment that's coming at the cement waste form? Is it mostly assumptions or do we have some, are we actually able to get at it from some predictive capability?

DR. LANGTON: There are sensitivity studies, uncertainty studies, but the sensitivity studies I think are covering a larger range. And no, that's really the big problem. We have a lot of information to design for situations that we know about. The problem is that movement of air and water into and through the system control the performance and we don't, that's unknown.

One of my questions was if you have a waste form that you were happy with, was performing right on target, right just the way you wanted it to, improving for 100 years, do we have a way of saying it is going to be okay in a thousand or five thousand or ten thousand years? So I personally would look at, I'd reevaluate the risks. How bad is it if technetium leaches out faster than what is acceptable by current calculations? Exactly what is that, not exactly but how much do we want to pay for mitigating that risk?

And it's really the long-lived isotopes that we're concerned about. Long-lived isotopes and stable isotopes, I supposed.

VICE-CHAIRMAN CROFF: Okay, thank you. I think at this point, do any of the speakers have anything that they want to follow up on or a question they would like to pose to another speaker?

Okay, seeing none there, NRC staff questions?

Pete?

MR. HAMDAN: Just one question or comment and they are to many of us we've got a good education on cement here, me included. Thank you very much. Because of the time frames we are talking about, it seems to me that the solution may lie in us having to change our approach to performance assessment. And by that I mean instead of doing it as a one time shot, uncertainties and all, and come up with results that probably we cannot defend, and assumptions we don't know enough about, it seems to me if we follow an approach like what David Kosson hinted on earlier, a PA, a performance assessment, that's carried over many years, let me call it -- I'll give it a name "a High

Maintenance PA". And that would allow you to give you a framework to work on and evaluate, to systematically evaluate your uncertainties over time as you go along.

It will allow you to make more use of your monitoring data. It allows you perhaps to even take advantage of new PA technologies and you don't have to defend it so much at the very beginning. And you know, we can choose to go and do that approach ourselves or I think ultimately we'll be forced to do that. And I would love to hear your comments.

VICE-CHAIRMAN CROFF: Anybody going to leap into that one?

DR. KOSSON: Well, I'll leap into it. I think you do performance assessment, you ought to revisit to see how well your predicting even the near term and updating it on a regular basis. I wouldn't say continuously, because that would be a nightmare, but at regular intervals and take the short term monitoring data that Jim was referring to and update your models based on the science, will certainly help you understand that site and the next one you have to do. Because we're going to be doing these for a long time when you look across the complex.

DR. SCHEETZ: I think what we have to do is we have to take it and look at a paradigm fit, and

I think Chris was the one who brought this up. I mean, what we've been looking at now is the situation where we're going got close it and we're going to walk away from it and we have to be able to leave it without looking at it.

And that's not going to happen. If you're going to look at, if you're going to take and use advantages of evolving skills and evolving knowledge, as Mike said, you can monitor for two reasons. You can monitor for compliance or you can monitor for knowledge. And you can use the long-term monitoring that you're doing and apply it to evolving knowledge. I mean, let's not be conceited that what we know today is going to be valid 50 years from now.

So that within our discipline, we have to look at the potential that we need to change the way we're going to look at this. We have this problem of stewardship and legacy wastes out there. These things, we would like to get it out of DOE's hands into someone else's hands. But the reality of the matter is it's going to be there, somebody is going to have to maintain it, somebody is going to have to look at it.

And what we have to do is decide we need to look at this. We need to be able to look at it and see how it is changing with time. If it breaks, we need to fix it. That's maintenance. But there's going to be the evolution of understanding. There's going to be evolution of models. Our science is going to get a hell of a lot better than it is now. And we have to have a mindset that we're going to go back and we're going to adapt to the new changing, evolving technologies. So I think it is a fundamental mindset that's going to have to change.

CHAIR RYAN: I guess that I would offer that one very important part to this is the John Garrick so what question. There's lots and lots of work that gets done and that's specifically in the waste area, but it really doesn't get at this idea we're managing risk, we're managing some endpoint of impact hypothesized down the line.

There's lots of "ology" work that gets down to get to that endpoint, but it's got to be focused on what it is contributing to our understanding of whatever the risk endpoints are that we want to measure. We can't lose sight of that strike zone, because without that we're just --

DR. SCHEETZ: But that's all part of it. If you understand what's going on, you can calculate the risk from it.

CHAIR RYAN: But I just want to keep driving that point because I think often we lose track of the fact that we're doing this for that endpoint, not for the, not alone for the intrinsic value of whatever the research project might be.

MEMBER CLARKE: I would just like to add to that. I've used the term monitoring a lot. I've used it and I've heard what comes back from that I've been reminded that it's one of those words that you can throw out and everybody might have a different understanding of what you mean by that.

I'm talking about monitoring not necessarily groundwater, although clearly we want to do that and that at least tells us that something has gone wrong. But it tells us something has gone wrong too late.

So we want to look at monitoring that can help us with our monitoring so we can cycle through that from time to time whatever is appropriate. But the monitoring and the re-upping the performance assessment need to be based on consequences I think and I think risk. Is this something that's going to be a serious problem if it fails and we have exposure, is this something where failure may not be as serious. In other words, I would suggest that the monitoring need to be risk-informed.

DR. SCHEETZ: But the monitoring also it's not that it has failed. The monitoring can alert to an impending failure, if you know the system and the --

VICE-CHAIRMAN CROFF: Right, the precursor. That's the precursor. Because what should we be tracking that tells us that things aren't going exactly as planned and we don't really, I don't know what those are yet. We know water is a big component. I mean in this kind of a waste world there are probably other things that we should be looking at as well. But in a land fill, we know infiltrating water is something we don't necessarily want. So what are precursors?

The other thing that hasn't been mentioned, I'll just throw it out, is that the institutional controls that are needed need to be monitored as well and they need to be evaluated for their performance. But all of this is as Mike has articulated very well, needs to be risked-informed. That's so hard.

CHAIR RYAN: Dr. Langton, go ahead.

DR. LANGTON: We do have a, DOE does support a PA monitoring plan, just to use monitoring one more time. But for example, Saltstone had a 1991 performance assessment and we're getting around to a 2006 update. In the interim, we've had special analyses performed, but every year there is a plan for work that will be done to support the performance assessments at the Savannah River site.

Now right now it is a year-to-year plan. Our funding comes year to year. Some items have carryover into subsequent years, but probably a longer term performance assessment updating plan would be very useful. Performance assessment roadmap to updating performance assessments over a longer time period to allow us to quality work, not on the yearly annual budget schedule. But we're all faced with those problems so I don't know how much hope there is for that.

DR. SCHEETZ: It's a crinkly green lubricant.

DR. LANGTON: Over more than a year.

VICE-CHAIRMAN CROFF: Anymore from NRC staff?

MR. LESLIE: Yes, this is Bret Leslie from the NRC staff. I appreciate Mike's focus to going back to risk informed. But I also want to remind folks of the regulatory constraints in which the process is working.

You know, we're in terms of Savannah River and Idaho, we're governed by the Nuclear Defense Authorization Act which specifies certain things. We have been conducting and using independent performance assessments in conducting our reviews of the waste determinations.

In fact, if you look at the standard review plan, there's a portion on monitoring. And what goes into those factors that we think are important is based upon our risk-informed review using our analyses. And so part of this generic, there is site specificity associated with it. The cementitious barriers are not treated monolithically across the DOE sites.

Savannah River takes a very different approach than Idaho, okay? Consistent with the NRC approach where the applicant decides what its safety case is, we, the staff, are forced to review how much credit they will take for concrete. We can't give them more credit than they're willing to take.

So part of this is that for a particular site, Idaho, where they might not be taking any credit at all, a hundred years performance for concrete.

We might not have any monitoring because they have decided that they're not going to take any credit. Whereas if you go to Savannah River, they might be taking a lot of credit. So to understand what needs to be focused on, what the focus of the monitoring should be or the support for long-term performance, you have to look at what is the outcome of those factors from our review.

So for instance, we've looked at based upon our reviews to date, we think the long-term chemical and physical stability of concrete is one of the things that has very little support for. The effect pH diffusivity and hydraulic conductivity of these monoliths over long periods of time is something that needs to be evaluated.

So I wanted to bring in that perspective that it is risk informed but it also is a factor of two regulatory aspects -- the law and the NRC's perception and policy. The applicant decides what kind of credit they want to take. We can research and can inform and suggest and identify that they might not be taking as much credit as they could, but ultimately it's DOE and its particular sites that determine how they want to make their safety case.

CHAIR RYAN: And I think Bret, just so I'm clear, you identified two things that have fallen out of that as being important -- diffusivity and the block behavior and some of those things. But I think that observation where you are right now is dependent on those choices that the applicant made. So if the applicant went back and made different choices, for example, or another applicant made different choices, you may end up in a different place.

The point is is that it's a case. I think it's a case where there's in a way a partnership in my view for what's in the application and what you have to do in the regulatory constraint that you mentioned. That's a good point, because it is a world we got to live in.

But the science case you develop in your assessment is strongly dependent on what the applicant gives you. So if they go through the process of saying we're going to take credit for concrete in a different way, in an extended period of time, for these reasons with this information to justify that, and you satisfied, you can end up with a whole bunch of different things that are important versus where you are at the moment with the current cases.

I think in a way that's not exactly completely risk informed, but it's risk informed based on what choices you're presented with. I think that's maybe a view that what we're getting at and that's part of my comment of I think it is risky to just assume the bounding cases. But we're only going take credit for concrete for the 100 years, for the 50 years, which is what construction people do.

Well, you've shut off a whole world of things you might better understand that could give you margin or confidence. I just wonder, you know, how to get at that. So it is a very flexible exercise of trying to nail pieces of Jello to the wall, but I think it's been a real informative discussion and thanks for that Bret. That was a good comment.

VICE-CHAIRMAN CROFF: I think at this point, does the Center have any questions? I think they've been on all day.

MR. HOWARD: Yes, we have and that's very much appreciated. But no questions other than what has been asked.

VICE-CHAIRMAN CROFF: Okay, thanks. I think with that we're at the end of it. I'd like to thank the speakers for much. You've given us a wealth of information to consider and we will consider it going forward.

As you know, our products are letters and I feel fairly certain we're going to see a letter out of this and we'll talk just a little bit about that right now. But, you know, it's been like drinking from a fire hose is all I can tell you. There's a lot of information to digest. I'm sure Latif is going to have great entertainment while going through the transcript. I think most of you know, this is recorded and there will be a full transcript like a legal transcript and it will have all the view graphs in it some place at the back of it. So that will be out in a month or two, I think, in complete form, on ADDAMS, the NRC Information Management System.

And my thanks to Latif for helping to organize this and I think with that again, my sincere thanks and the working group meeting I think will close and I guess talk just momentarily about a letter?

CHAIR RYAN: Sure and I want to add my thanks on behalf of the entire Committee for your generous time and talent that you presented to us today and also to Latif and the other staff and to Allen for putting together this fabulous working group that's covered an awful lot of ground in a short period of time. And again, I sincerely thank you on behalf of the Committee. So we'll leave this in a letter discussion?

VICE-CHAIRMAN CROFF: Yes, and it's going to be fairly short. It's late in the day. Is there any disagreement that we need a letter?

CHAIR RYAN: None.

(Laughter.)

VICE-CHAIRMAN CROFF: At this point -- what I'd like is something like middle of next week. If you'd email observations and any recommendations that you think are important or any other thoughts.

CHAIR RYAN: I think for the benefit of our panel members, I think in the last half hour or so or maybe in the last couple of hours of summary comments and points by you all and by us will be organized into the body of our letter. I don't think there is any real need to rehash all those over again, but we will be mining the transcript with a little bit more detail to get the good words down.

VICE-CHAIRMAN CROFF: Definitely. We'll be mining the transcript, and just the big points or distillation or integration of things or this kind of thing is what I want from you.

And I'll try to prepare a letter and we'll try to bring it into the August meeting which is where we're going.

CHAIR RYAN: Our subcommittee meeting.

All right, with that no other business before the Committee. We'll adjourn the record and adjourn the meeting. Thank you all very much.

(Whereupon, at 5:10 p.m., the meeting was concluded.)