UNITED STATES

NUCLEAR WASTE TECHNICAL REVIEW BOARD

WORKSHOP ON LOCALIZED CORROSION OF ALLOY 22 IN YUCCA MOUNTAIN ENVIRONMENTS

September 25, 2006

Las Vegas Marriott Suites
325 Convention Center Drive
Las Vegas, Nevada 89109

BOARD PARTICIPANTS

Dr. Thure Cerling
Dr. David Duquette
Dr. B. John Garrick, Chair, NWTRB
Dr. Ronald Latanision, Chair, Panel on the Engineered System

BOARD ATTENDEES

Dr. William Howard Arnold
Dr. George Hornberger
Dr. Andrew Kadak

WORKSHOP PARTICIPANTS

Tae Ahn, NRC
Randy Arthur, Monitor Scientific
Neil Brown, Bechtel SAIC Company
Charles Bryan, Sandia National Laboratories
Thure Cerling, University of Utah
David Duquette, Rensselaer Polytechnic Institute
John Garrick, NWTRB
Xihua He, CNWRA
Russ Jones, GT Engineering
Ron Latanision, Massachusetts Institute of Technology
Rob Kelly, University of Virginia
Fraser King, Integrity Consulting, Ltd.
Maury Morgenstein, GMII
Roberto Pabalan, CNWRA
Yi-Ming Pan, CNWRA
Joe Payer, Case Western Reserve University
Osvaldo Pensado, CNWRA
Raul Rebak, LLNL
Paige Russell, OCRWM
Don Shettel, GMII
John Walton, University of Texas El Paso
Lietai Yang, CNWRA

SENIOR PROFESSIONAL STAFF

Dr. Carlos A.W. Di Bella
Dr. David Diodato
Dr. Daniel Fehringer
Dr. Dan Metlay
Dr. John Pye

NWTRB STAFF

Dr. William D. Barnard, Executive Director
Joyce Dory, Director of Administration
Karyn Severson, Director External Affairs
Linda Coultry, Program Support Specialist
Davonya Barnes, Staff Assistant

I N D E X

Session on Environments on Waste Package Surfaces

PROCEEDINGS

1:00 p.m.

GARRICK: Good afternoon. My name is John Garrick, and I'm chairman of the Nuclear Waste Technical Review Board. This meeting is a little different from most of our meetings that at least I have presided over. It's a panel meeting, not a meeting of the full Board, and it's a workshop. Panel meetings are more narrowly focused than meetings of the full Board, and are, fortunately, less formal. Workshops are even less formal, in that there is more discussion and give and take among the participants. This is a workshop on localized corrosion, so, Ron Latanision and David Duquette are the Board members that are presiding, and they are the experts on corrosion.

I know most of you are familiar with the Board and how it works, so I'll be brief on those kinds of details. The Board, as you know, was created as a part of the Nuclear Waste Policy Amendments Act of 1987. We are eleven scientists and engineers appointed by the President from nominations--at least two per position--nominations made by the National Academies. Board members are part-timers, but fortunately, we do have a small, capable, and hard-working full-time staff to assist us and keep us honest. According to the Act, our job is very simple, very straightforward. It's to evaluate the technical and scientific validity of

DOE's actions regarding high-level waste and spent fuel management.

The issue for this day and a half workshop is localized corrosion of Alloy 22. The outer layer of the waste package is three-quarters inch thick Alloy 22. Once that layer is gone, DOE assumes--rather conservatively, I might add--that there are no more waste package barriers preventing water from contacting the spent fuel or solidified high-level waste. In a scoping-level peak-dose analysis DOE showed us earlier this year, waste package lifetimes, which were dependent only on general corrosion of Alloy 22 in that analysis, averaged well over half a million years, and the peak dose was found to depend strongly on the timing and rate of waste package failure. This result is not surprising. From a risk perspective, there is little doubt that the waste package is an important barrier whose performance greatly impacts the radionuclide source term and the magnitude and timing of the peak dose. In fact, waste package performance sets the stage for the response of the natural system, something I'll comment more on in just a moment.

The Board has had less than an hour in previous meetings to publicly explore localized corrosion of Alloy 22 at high temperatures and the technical basis for DOE's apparent decision to screen out localized corrosion caused by dust deliquescence from its performance assessment. I know the Board spent several hours in a meeting on a related topic before I became a Board member, but that meeting--in contrast to this workshop--was about deliquescent brines of much different composition and at significantly lower temperatures, and, very importantly, that meeting was before the court decision requiring a peak-dose performance assessment.

I am on the panel, but I think I will be reserving most of my questions and comments for tomorrow afternoon, when it appears we may be discussing, in part, the significance of screening in or screening out deliquescence-based localized corrosion. I am not an expert on corrosion. My interest is in the impact it has on the radiation dose. Would it decrease peak dose? Quite possibly. Would it increase peak dose? That's also possible, I suppose. Would any of these changes be significant? I don't know, but sure would like to.

Now, before I go any further, I need to make a blanket caveat about the workshop. Board meetings, including panel meetings and workshops, are open and spontaneous by design. Anything you hear from a Board member, including me, should not necessarily be construed as a Board position, or even the position of a Board minority greater than one. The Board comes to its positions deliberately and iteratively, and generally puts them in writing and posts them on our website.

The natural system provides an environment and a "home" for the waste packages. Even though it may take a very, very long time, eventually and inevitably the waste package will fail, and the capabilities of the natural system as a barrier will come into play. DOE chose to deemphasize the capabilities of the natural barrier back in the days of the 10,000-year dose standard. And, I think that that decision has come back to haunt them now that we are in a peak dose standard space. By deemphasis, I mean that they deliberately chose to model the behavior of the natural system very, very conservatively believing that doing so would make little difference for the 10,000-year case.

A key to the performance of the natural system is the source term--the complex mixture of solutes and colloids that the engineered barrier system delivers to the natural system. The source term is the product of interactions between waste forms, corrosion products, and rock and other materials in the engineered barrier system. It is an area where DOE has placed a lot of effort, but one that still is being modeled too conservatively and incorrectly, in my opinion. And, while this workshop is not explicitly addressing the source term, I am hopeful that it will make the linkage between localized corrosion and the source term more transparent.

So, having made my pitch once again for a more realistic source term for this project, I will now turn the meeting over to the experts, and in particular, to Ron Latanision. Thank you.

LATANISION: Good afternoon, everybody. Thanks for being here. I am Chair of the Board's Panel on the Engineered System, and together, Dave Duquette and I will moderate this workshop, as John has mentioned. What I'd like to do at this point is just give you some background that will hopefully orient the conversations we're going to have over the next day and a half, and give you a little bit of an introduction to each of the participants who are seated at the table.

At the Board meeting in Washington in May of 2004, we had a session which we gave the title "Corrosion During the Thermal Pulse." Many of you were there, and some of you actually gave presentations. The issue was pretty clear. DOE, as well as others, had much data showing crevice corrosion of Alloy 22 at elevated temperatures in brines containing high concentrations of calcium chloride. At the upper range of these data, in the range of 140 to 150 degrees centigrade and higher, nitrate, if present in the calcium chloride brine, seemed to lose most, if not all, of its capacity for mitigating localized corrosion.

After the meeting and based primarily on information presented at the meeting, the Board wrote to Dr. Chu, to Margaret Chu, then Director of OCRWM, that dusts that would accumulate on the waste package surfaces appeared unlikely to contain significant amounts of calcium chloride and, thus, the localized corrosion during these high-temperature periods of the thermal pulse seemed unlikely. We also expressed our surprise and dismay about the testing in calcium chloride, which at that point seemed to be an irrelevant environment.

The letter we wrote to Dr. Chu was on our website. We thought then that the issue of deliquescence-based corrosion of Alloy 22 had been put to rest. But, later that summer, we began to hear from DOE that certain salt mixtures had been determined to deliquesce at even higher temperatures than calcium chloride, and that these salts were virtually certain to exist in the dusts depositing on waste package surfaces. As part of the presentations at the May 2004 meeting, Tae Ahn and Bobby Pabalan, both of whom are here today, alerted us to the possibility that mixtures of salts containing sodium, potassium, chlorine and nitrate could deliquesce at very high temperatures. And, in a letter responding to our letter to Dr. Chu, confirmed that DOE had data in hand indicating that certain saturated brines containing these elements, sodium, potassium, chlorine, and the nitrate ion, could boil at maximum temperatures around

200 degrees centigrade. The letter also implied that experiments were underway or planned in order to obtain data at these higher temperatures in those brines.

Then, at our meeting last November here in Las Vegas, we heard about some of the corrosion data that had been generated in the interim from Gabriel Ilbevare, and we also heard that Alloy 22 specimens clamped between crevice formers showed crevice corrosion, but that the data were still being interpreted. A report on that data now exists, and is on the Lawrence Livermore website. I suspect we'll be hearing more about that from Raul Rebak tomorrow.

At the November meeting, we also heard DOE's technical basis for screening localized corrosion of Alloy 22 due to dust deliquescence out of the performance assessment. Frankly, we did not find that argument very compelling. It doesn't mean it's wrong. We just simply didn't agree with it, largely because of the absence of an experimental basis on which to provide support for that analytical proposal.

It was at that November meeting at which we decided that a workshop was needed to fully understand this new data, the interpretations of the data, and the basis for screening out localized corrosion at high temperatures. We had hoped to hold this meeting in February of this year, or March, perhaps, but that was too early for all the parties which were interested. We then targeted May and found that wasn't convenient, and, so, we're here today. At least it's in the same year. That's a good sign.

The objective of this workshop is to thoroughly air and discuss data, analyses, studies, and models of localized corrosion of Alloy 22 in aqueous environments that could exist in a repository at Yucca Mountain. This is a bit broader than the initial impetus for the meeting, but that is because it's not easy to draw the line between what is meant by high temperature and low temperatures, and because aqueous environments on waste packages can be influenced not only by dust deliquescence, but by seepage, dripping condensation, and cyclic or episodic events. From my own personal point of view, I want to know whether or not the "not compelling" label still applies. I want to know, in fact, whether there is a technical basis, and an experimental foundation on which to screen out localized corrosion from the assessment.

Now, the background. Let me introduce the panelists who are present today. They are listed in your agenda in alphabetical order, and, of course, I'm assuming we've aligned you in alphabetical order around the table. But, that's not true. I'm going to start with the Board, and as I call each name, if you would just raise your hand so people will know who you are?

I'm Ron Latanision. I'll raise my hand. I'm Professor Emeritus, recently Professor Emeritus, of Materials

Science and Engineering and of Nuclear Engineering at MIT, and I now practice as a Director of the Mechanics and Materials activity with the engineering consulting firm Exponent. I'm a metallurgist and a corrosion engineer, and I've had interest in the performance of materials and nuclear systems for a very long period of time.

John Garrick is our distinguished Chairman. He is a consultant, primarily in the application of risk sciences to a variety of industries, such as transportation, space, nuclear, chemical, and so on. His background and areas of interest are risk assessment and nuclear science and engineering. He holds degrees in physics, nuclear engineering and applied math and physics.

Dave Duquette is another of the Board members. He and I will share the duties of presiding over this workshop. Dave is Department Head and not quite ready for Emeritus status, Professor of Materials Engineering at RPI. Don't worry, I always do this. His areas of expertise include physical, chemical, and mechanical properties of metals and alloys, with special emphasis on environmental interactions. His current research includes studies of cyclic deformation behavior as affected by environmental conditions, stress-corrosion cracking. He has degrees in materials science and engineering.

Thure Cerling is a Distinguished Professor of

Geology and Geophysics as well as Biology at the University of Utah. He is a geochemist, with particular expertise in applying geochemistry to a wide range of geological, climatological and anthropological studies. His degrees are in chemistry and geology.

Also, on the panel at the invitation of the Board is Russ Jones. Russ is a materials scientist who recently retired from Pacific Northwest Labs after a long and distinguished career there. He is a senior materials scientist with GT Engineering. His degrees are in materials science and engineering.

There are also two Board members in the audience, and I expect there will be some others tomorrow. Howard Arnold is a consultant to the nuclear industry, having previously served in a number of senior management positions, including Vice-President of the Westinghouse Hanford Company, and President of Louisiana Energy Services. His degrees are in chemistry and physics.

George Hornberger is the Ernest H. Ern Professor of Environmental Sciences and Associate Dean for Sciences at the University of Virginia, also a Board member who is present today. His research interests include catchment hydrology, hydrochemistry, and transportation of colloids in geological media. He chairs the Board's Panel on the Natural System, holds degrees in civil engineering and hydrology.

Also in the audience are several members of the Board's staff: Bill Barnard right in front, Carl Di Bella, Dave Diodato, Dan Metlay, John Pye, Karyn Severson, Davonya Barnes, and Linda Coultry. If anyone wants to get a written comment or question to anyone on the panel, including whoever may be presiding, please give it to Davonya or to Linda. They will see that it is delivered to us.

Also, there is a special period for public comments at the end of the meeting tomorrow. If you want to speak during this period, please, again, register with Davonya or Linda.

Now, let me introduce the panelists. And, once again, if you would raise your hand? I'll start with those affiliated with DOE, that is, employees or contractors, or subcontractors. Paige Russell has a degree in Mechanical Engineering. Let's see, where is Paige. Oh, I'm sorry, there you are. She is general engineer in OCRWM here in Las Vegas.

Neil Brown. Neil has degrees in Mechanical Engineering. He is Manager in Engineered Systems, also in Las Vegas, for Bechtel SAIC.

Charles Bryan, Geochemist, Sandia National Labs, which will be taking over as lead lab next week. Charles has degrees in Geology and Geochemistry.

Raul Rebak is a senior scientist with Lawrence

Livermore National Lab, degrees in Materials Science and Engineering, and a corrosion engineer.

Joe Payer is not even close to being ready for Emeritus status, Professor at Case Western Reserve University in Cleveland. He also has the title of Director of DOE's Corrosion and Materials Performance Cooperative, and he is in charge of the Materials Performance Thrust in DOE's Science and Technology Program. He is a metallurgical engineer from Ohio State, as am I.

He and Rob Kelly, a Professor of Materials Science and Engineering at the University of Virginia, and Co-Director of the Center for Electrochemical Studies, will share a presentation as part of the agenda. Rob's degrees are in Materials Science and Engineering from Johns Hopkins.

From the Nuclear Regulatory Commission and its contractors, the Center for Nuclear Waste Regulatory Analyses at the Southwest Research Institute in San Antonio, Tae Ahn is a senior materials engineer in the Division of High-Level Waste Repository Safety. He has degrees in Metallurgy and Materials Science.

Xihua He is a Research Scientist in the Corrosion Science and Process Engineering Department of the Center. She has degrees in Electrochemistry and Corrosion Science.

Roberto Pabalan is the Institute Scientist at the Center, with degrees in Geochemistry and Mineralogy.

Yi-Ming Pan is a Principal Engineer at the Center, with degrees in Materials Science.

Osvaldo Pensado is a Senior Research Scientist at the Center, with degrees in Engineering Science.

Lietai Yang is a Senior Research Engineer at the Center, with degrees in Metallurgy and Chemical Engineering.

We have also two contractors from the State of Nevada. Maury Morgenstein and Don Shettel. Maury is president of Geosciences Management Institute and has degrees in Oceanography and Mineralogy. Don Shettel has degrees in Geochemistry.

From the Electric Power Research Institute, two contractors, Randy Arthur and Fraser King. Randy is with the Monitor Scientific Organization, has degrees in Geochemistry and Mineralogy. Fraser is with Integrity Consulting of Calgary, and has degrees in Materials Science.

Nye County in Nevada is represented by John Walton, who is Professor of Civil Engineering and Program Director of Environmental Science and Engineering at the University of Texas at El Paso, degrees in Chemical Engineering.

That identifies the people who are seated at the table. We put together four open-ended questions at the end of the agenda, which you all have. These are intended to help guide us during the workshop, and we'll be looking at them from time to time during our proceedings to see if we're addressing them.

Let me just take a minute to read them. First of all, and this is all in the context of the charge really to explore the issue of whether or not a technical and analytic basis for screening out localized corrosion can be supported. The first question is are data, understanding, and models sufficient to bound potential environments on waste packages in a repository at Yucca Mountain with reasonable confidence from a corrosion standpoint? If so, what do they show? If not, what needs to be done?

The second question. Are data, understanding, and models sufficient to assess with confidence whether localized corrosion of Alloy 22 outer surfaces of waste packages in a repository at Yucca Mountain is likely to occur? If sufficient, how likely is corrosion? If not sufficient, what needs to be done?

Third question. If localized corrosion of the outer surfaces of the waste package occurs, will it be deep and/or widespread? And, what is the basis for whatever response emerges?

Finally, what are the consequences of localized corrosion?

Now, Dave and I will take turns moderating the workshop. Our main job is to try to keep us on schedule, and at the same time, to allow a lot of time, as much time as possible, in fact, for questions and comments among the participants.

This is a workshop, and the agenda is designed to allow ample time for questions and comments and discussion. When making comments or questions, don't feel that you have to limit yourself to the presentation just made, but include questions and comments about any of the presentations, particularly, if you can integrate from one presentation to the next, questions that are of importance from your perspective.

Questions and comments from the audience, and by that, I mean the people not seated around the table, are certainly in order and welcomed at anytime during the periods for questions and discussion after each presentation. We will give priority to the people seated at the table, but everyone should feel comfortable asking questions and giving responses. The workshop will be recorded for transcription. There are microphones at the table, and microphones in the audience. So, we would ask you to identify yourself and to use a microphone each time you want to address a question or an issue.

So, with all that, let's now get started. The first speaker is Charles Bryan of Sandia. He will speak first, he spoke last November, and, Charles, it's good to see you again. Welcome.

BRYAN: Let me bring up the slides.

I'm going to talk about the environment on the surface of the waste package, and how it evolves through the history of the repository.

First slide. I'm going to talk about evolution of the environments on the surface of the waste package. We'll start out talking about the temperatures and humidity conditions, and how they evolve on the waste package surface, compare conditions for seepage and deliquescence, and then discuss the deliquescence environment, including the source and composition of the salts that will be present, how much salts accumulate, and how much brine will be generated, and then processes affecting the brine on the waste package surface.

Next slide. For the seepage environment, we'll talk about the water chemistry and how we estimate its composition and how it evolves over time, and finally, how it's represented in Total System Performance Assessment. And, finally, we will summarize the environments.

Next slide. These are the conditions on the waste package surface. Following emplacement, temperatures on the waste package will be fairly high. Once ventilation is implemented, the waste package temperatures drop to around ambient quite quickly. The RH goes up somewhat. Following closure at 50 years, the RH increases, and then over about 20 years, the waste packages heat to the maximum temperature. The hottest waste packages can reach over 200 degrees centigrade. Medium and cold waste packages can be as low as 110, 120 degrees centigrade initially. And, then, they cool over thousands of years back to ambient conditions.

Conditions for deliquescence. To the best of our understanding, currently deliquescence can occur at just about any temperature, all the way up to 200 degrees centigrade, and I'll discuss that in a minute. However, seepage can only occur once the drift wall gets below 100 degrees centigrade. The maximum temperature of the waste package surface at that time is about 105.

Next slide. Here are the two types of environments. Deliquescence forms because salts will be deposited on the waste package surface during the ventilation period. We think these salts will be approximately atmospheric, the composition of atmospheric salts. Following closure, there will be a drip shield on top of the waste packages. The drip shield is not displaced readily, and we do not expect there to be much accumulation of rock dust following closure, because the waste packages will be protected by the drip shields.

Multi-salt assemblages control deliquescence at higher temperatures. We think these are the assemblages that are characteristic of the atmospheric salts. The brine compositions, of course, will become more dilute as the relative humidity goes up and the temperature drops. Very small amounts of brine will be present on the waste package surface, and the brine will be suspended largely within the dust in an unsaturated state. So, there will be ready gas exchange with the environment.

Chemistry will be moderated on the waste package surface by interactions with rock-forming minerals and also will be modified by degassing and other effects.

With respect to seepage, it can only occur after the drift walls get below 100 degrees centigrade. That's conservative. The actual boiling point is 96 degrees centigrade, 94 degrees centigrade. The waste package outer barrier is generally protected by the drip shields in the nominal case. The drip shield last hundreds of thousands of years, after which the temperatures are so low that localized corrosion will not occur on Alloy 22.

The residence time, the degree of equilibration with temperature, the relative humidity at the waste package surface will control the chemistry of the fluids. The chemical conditions are generally most corrosive during the early cooldown, during the hot phase. And, finally, chemical fractionation may occur during transport. We include salt separation on the waste package surface in our model.

Next slide. Our current understanding of the dust environment is based upon two different sources of dust compositions. The first one analyzed Yucca Mountain tunnel dusts. These dusts were mostly rock forming minerals, with a small amount of salts. Zell Peterman of the USGS did these analyses. The most important deliquescent mineral assemblages in them are the ones shown here. Sodium, chloride, potassium nitrate, the same assemblage with sodium nitrate and, finally, four salt assemblage with calcium nitrate.

The atmospheric dust. Our current models are based upon this data. I'll present on the next slide some more current data, some new data. It's based on site specific data which suggests that there's about 10 percent soluble salts in the dust, and the compositions are based upon National Airfall Deposition Program regional data from the Red Rock area.

Here are the compositions of those salts. The important things are that the nitrate to chloride ratio is quite high, a factor of on the order of six to ten.

Next slide. The last time I presented this, there was some discussion of the use of site-specific data. We didn't have any at the time, and now we do. We've set up a cyclonic collector on the south pad. It's been operating for a year or so, and we've collected several samples. The collector cuts off during rainstorms and it collects both relatively coarse particles and finer particles.

The analyses that we have to date, we have analyzed five samples. Of those five samples, you can see that they do confirm our assumptions about the nitrate to chloride ratio. Nitrate and chloride ratios vary from about four to seven. However, there are a few differences from what we predicted. The ammonium concentrations are much lower than expected. We thought that would be one of the major cations in the dust, and apparently it isn't. And, also, the TDS are lower than expected. We had predicted about 10 percent. As you can see, it's as low as less than 1 percent, up to about 7 percent. It's possible we're losing some of the finest fraction, and we're exploring that.

Next slide. Conditions of deliquescence. Under what conditions can the minerals in the salt actually deliquesce and an aqueous phase form on the waste package surface? We've done a fair amount of experimental work on this, mostly at Lawrence Livermore, in fact, entirely at Lawrence Livermore. We have determined ammonium salts will thermally decompose. They are highly deliquescent, but they don't persist. Once they are heated up, they sublime away very rapidly. So, they won't contribute to deliquescent mineral assemblages on the waste package surface.

The three assemblages at interest are here. The two salt assemblage deliquescence is at fairly high temperatures, 134 degrees centigrade. The three salt assemblage with sodium nitrate doesn't ever dry out. It transitions from a brine to a hydrous melt at about 220 degrees C., and dries out at about 300 degrees centigrade. So, under the conditions expected in the repository, it would always be present as a brine.

The four salt assemblage has a boiling point of greater than 400 degrees centigrade. It would always again be present as a brine on the waste package surface. Again, the maximum waste package surface temperature is only, in our current model, is about 203 degrees centigrade.

Next slide. Once a brine forms in, our conclusion then is that there will be deliquescent brines on the waste package surface at just about any conditions, even the highest temperatures that will occur within the repository. Once these brines occur, will they persist on the waste package surface? Well, there are a variety of processes that will affect them. Acid-degassing will occur. Calcium chloride brines, we have experimental evidence that shows that these degas very readily, and they dry out. They form calcium oxide and chloride solids.

The multiple salt assemblages that we're interested in deliquesce at high temperatures. We've modelled these thermodynamically, but our model can't go to 200 degrees centigrade. It's only applicable to temperatures up to about

140 degrees centigrade. At those temperatures, we don't think the brines will degas sufficiently to dry out. This is a conservative assumption. We can't apply it to higher temperatures. But, we do know that the pH will go up. As degassing occurs, the pH goes up, and this has actually been observed experimentally at Oak Ridge.

The nitrate and chloride ratio also, the minimum nitrate to chloride ratio that can form by deliquescence increases as the temperature goes up. I think Raul will discuss this a little bit tomorrow. But, the minimum nitrate to chloride ratios get very high at temperatures above 150, as high as, oh, 60 or 80, or so. So, the brines that form will be very nitrate rich at high temperatures.

Reactions with silicate minerals in the dust can affect them. There will be some pH buffering that will occur. Calcium and magnesium will be removed from the brines if they're present in any significant amount as silicate phases. In general, these reactions can cause the RH to go up, and the brines might dry out if the reactions go to sufficient completion.

It's possible that chloride or other phases of the brine could be consumed by the formation of minerals. Some of these have been observed in the report on the autoclave experiments at Lawrence Livermore, for instance. They observed a phase they think was sodalite. So, it's possible then that silicate phases that consume chloride from the brines can form. And, again, with decreasing temperature and increasing relative humidity, the brines will become more and more dilute.

Next slide. The amount of brine that forms on the waste package surface has been estimated by the amount of dust that could be deposited. We know what the atmospheric dust concentrations are at the site, 22 micrograms per meter cubed of air. We know what the ventilation rate in the drift is. And, we can assume certain particle sizes and calculate the amount of deposition that could occur on the waste package surface using a dry particle deposition model.

Once we have the amount of dust present, we can calculate how much salt is present in it, because we have a site specific salt content, and, again, we're using our original value, not the data based upon the more recent cyclonic collector data. We haven't incorporated that in our models yet.

We assume the ammonium minerals volatilize. Again, our more current data suggested ammonium isn't as important as we thought it might be at the site. And, we do thermodynamic modeling to model how much brine would actually be present.

Next slide. These graphs just show deposition along the drift, and you can see that the highest deposition rates occur at the beginning of the drift, onto the first waste package. We chose the most conservative values for the size of the dust particles that were present, based upon our very limited amount of size information. And, we conservatively assumed then that the first waste package in the drift was the one of interest.

The upper bound then for the amount of dust deposited was only 26 milligrams per centimeter squared, fairly small amount. Of course, that's only 10 percent salt, so we're talking about 2.6 milligrams, approximately, of salts. This would be a very thin layer. I think it's 26 microns. Yes, if rock dust is deposited on the waste package surface, the rock dust, as analyzed by Zell Peterman, contains very small amounts of salts, less than 1 percent. So, any dilution by rock dust would increase the amount of dust present, but would not significantly add to the amount of salts present.

Using these values, we use our thermodynamic modeling to calculate the amount of brine present. At 120 degrees C, the maximum amount of brine present was about 1.8 microliters per centimeter squared. That assumes, again, that all of the salts within the dust are actually in contact. These salts will not deliquesce individually. They have to be a mixture. If there's a physical separation of the salt particles within the dust, then deliquescence would not occur. And, that corresponds to about 11 percent saturation within the dust. At 200 degrees centigrade, there's about an order of magnitude less brine present.

Next slide. So, we're dealing with extremely small amounts of brine that are present in a thin dust layer, and largely suspended in the dust. We looked at the dust, the physical characteristics of the dust, and determined that the capillary response is about 1 micron, which means that most of the brine will be retained within the dust, and very little of it will actually be contacting the waste package surface.

Because it's retained within the dust, it will be unsaturated. There's, as we said, about 10 percent saturation. There will be ready gas exchange between the atmosphere within the drift and the brine within the dust.

Also, because it's suspended within the dust, and because contact with the waste package will be very limited, we believe that scale limitations will limit the amount of compositional variation you can get within a single droplet of brine contacting the waste package surface. In other words, there will be hardly compositional gradients within a droplet of brine, only a few microns across.

Next slide. The seepage chemical environment is determined by the physical and chemical environment model, which basically dries out predicted seepage water compositions from the THC seepage model, the thermohydrologic chemical model, which calculates water/rock interactions around the drift, brings them in equilibrium, thermodynamic equilibrium on the waste package surface, okay, applying our Pitzer model for evaporative evolution of the brines, which we call the in-drift precipitive salts model.

What's provided to TSPA from the physical and chemical environment model is the parameters which are important for the localized corrosion model, the pH, ionic strength, chloride concentration, and the nitrate to chloride ratio. These are provided in look-up tables as a function of temperature, PCO2 and RH.

Next slide. The THC seepage model develops initial boundary conditions for the pore water reactions on the basis of available pore water analyses. We recently completed a re-evaluation of over 100 different pore waters that were collected from the repository unit. And, approximately 100 different pore waters, we analyzed. During this analysis, we realized that a large proportion of these, 60 to 70 percent of these, had actually been affected by microbial activity in the cores after collection. The effects of this, basically, the samples, the core samples were wrapped in plastic, placed inside sealed core tubes with packing on each end, and then the core tubes were wrapped in plastic.

Within the core tubes, conditions were anoxic, de-nitrification occurred, sulfate reduction occurred, organic acids build up, and approximately 60 to 70 percent of the pore water compositions were compromised. After throwing those out, we found out that nitrate chloride issues in the pore waters were actually much higher than we had originally estimated. Many of the values, over half of them, in fact, were greater than .5.

Based on the chemistry and based upon statistics, we have divided those into two to three different clusters of water compositions, which will now be input as feeds into the new simulations for the THC model.

Our current model simply examines conditions of the repository center. The new model, which we are developing right now, will have simulations at both the repository center and the repository edge. It will identify potential seepage water compositions which can enter the drift, and it will be validated using the drift scale test results. The output of it will be the compositions, but also the CO2 fugacity within the repository drifts.

Here is just a plot of the available water compositions. This plot includes the water that has since been screened out, which are basically all of the waters on this side of the plot, which are heavily super-saturated now with calcite because of microbial activity and the build-up of CO2 within the core tubes. And, this is the kind of output we get. This is the pH within the fractures above the drift over time, and from this, we have extracted data which is fed to the P&CE model.

Next slide. The physical and chemical environment model takes the waters from the P&CE model. It calculates the corrosion environment. It estimates the corrosion environment. It does this by assuming evaporative equilibrium with the RHs on the waste package surface at the temperatures on the waste package surface. It also incorporates salt separation. At any time if seepage contacts the waste package surface, and the relative humidity is below that of that of pure halite, of the deliquescence point of pure halite, it's assumed that halite will precipitate, the remaining brine will advect off of the waste package surface, and that pure halite will be left on the waste package surface. At some future point, this will deliquesce, and the waste package will corrode.

The way it's implemented in TSPA is if the relative humidity is such that halite is predicted to precipitate, localized corrosion is assumed to occur immediately.

In order to determine the composition on the waste package surface, the waters from the THC model were chemically binned and were grouped into similar chemical groups. And, then median water asserted for each group, and bin history amounts, which were ordered by mapping these bins back to the original THC runs. And, that's what these are. There were eleven bins in our previous model. And, this is how the water is mapped back to different time steps within our THC output. The most corrosive waters are the Bin 2 and 3 and 4 waters, and they occur only during the boiling period.

The outputs of the P&CE model are, again, nitrate to chloride, pH, ionic strength and the nitrate to chloride ratio, essentially. Uncertainty is propagated through the model based upon the uncertainty, the statistical uncertainty within the bins, and also the uncertainty from the IDPS model, the thermodynamic model for evaporative evolution of the waters.

Next slide. To summarize the seepage environment, seepage only occurs on the waste package composition, temperatures are below about 105. The RH varies. It can be as low as approximately 40 percent to as high as about 99 percent when seepage occurs.

Salt separation is implemented whenever the RH is less than 77 percent. Again, the deliquescence point for pure sodium chloride. This is a little conservative. The actual predicted RHs at which halite precipitates is actually between 73 and 68 or so percent for our current water compositions.

Nitrate to chloride ratio is controlled by the ambient water composition. In other words, the nitrate to chloride ratio, the THC model does not fractionate nitrate and chloride. So, whatever the initial compositions were that were fed into the THC model, that's what will come out on the other end. Okay? At least for input into the P&CE model, and then because we implement salt separation at 77 percent RH, this value does not change in our model. Below 77 percent RH, this value would change, but we implement salt separation and localized corrosion if we get below that value.

Calcium chloride brines are predicted during the peak thermal period. They can occur. The range of pHs that are possible is quite wide, 4.5 to 10.5, plus uncertainty, which is anywhere from 1 to 2 pH units. Generally, 1 pH unit or less, unless we have very concentrated brines. The pH increases as the repository cools, and after cool down, the pHs are generally much higher. They're on the order of 7 plus.

The corrosive seepage chemistry occurs mainly early in the cool down, between say 2 and 600 years in our current model. And, again, these system are open with respect to gases, particularly with respect to acid gases. Within the drift, the acid gas concentration is based upon the water compositions within the rock, are very low. 10^{-12}, 10^{-14}.

Next slide. Deliquescence environment. Brines can only form in very small amounts at elevated temperatures, a few microliters at most, per centimeter squared of the waste package surface. The conditions are unsaturated. The brine is suspended within the dust, and it's an open system with respect to gases. In other words, acid degassing could readily occur. CO2 diffusion and absorption by the brine could readily occur.

Capillary and adsorptive retention in the dust layer further decreases the amount of contact that can occur with the waste package surface.

The composition of the brines, as you can see, as we've discussed, there is basically sodium chloride, potassium nitrate brines, with some sodium nitrate and/or calcium nitrate present as well. They can deliquesce at very high temperatures. They are very nitrate rich, and at temperatures above 150 degrees C, especially the nitrate to chloride ratio can be as high as 60, or must be as high as 50, 60, 80, so, very nitrate rich.

Acid degassing will occur. As it occurs, the pH increases, and as the pH increases, the amount of acid degassing that occurs decreases. It is unlikely to result in dryout based upon our current models, which are only applicable at 240 degrees centigrade.

The background acid-gas pressures are very low, again, within the drift. So, we don't believe that the absorption of acid gasses is going to have any significant effect on the composition of the brines formed by deliquescence.

And, finally, again, the nitrate to chloride minimum ratio is controlled by the temperature. The higher the temperature, the higher the nitrate to chloride ratios.

Reaction with silicates. If it's sufficient, it will buffer the pH and it will remove the divalent cations.

LATANISION: Let's take some questions. The first question.

CERLING: Cerling, Board.

I'm just trying to understand Slides 6 and 7, and I'm just wondering if you can explain to me the units on six compared to seven.

BRYAN: Okay.

CERLING: They're vastly different.

BRYAN: Right, yes. In six, the units are milligrams per liter. That's rain out. So, it's the composition within the rain.

CERLING: Yes. And, seven?

BRYAN: Right. And, in seven, okay, actually I'm fairly certain that's incorrect. The units should be milligrams per gram of the total solids present.

CERLING: And, that's of the salts then? So, the salts have then been separated?

BRYAN: No, that's milligrams per gram of dust collected.

CERLING: Milligrams per gram of dust?

BRYAN: Yes.

HARDIN: This is Earnest Hardin. I'm with Sandia.

The gentleman next to me, Zell Peterman, tells me the units are milligrams per kilogram.

BRYAN: I'm sorry, milligrams per kilogram. I'm sorry, yes, my mistake. Micrograms per gram, yes. So, parts per million.

HARDIN: Okay.

MORGENSTEIN: Morgenstein, State.

I'm kind of worried about the THC seepage model, and how confident one can be relative to the chemistries. Could you speak to that a little bit more?

BRYAN: Relative to?

MORGENSTEIN: The actual chemistries, based on the fact that you see bacterial attack.

BRYAN: Right. Well, we spent all summer re-analyzing the water compositions. We're fairly confident, in fact, we're highly confident that most of the bacterial activity, perhaps all of it, or probably all of it, occurred after the cores reflected. The USGS did a good job of analyzing more samples. They showed that--well, let me describe what actually was--how the cores were collected and what we noticed.

The cores were collected. They were wrapped in Saran wrap. They were placed within core holders with packer to eliminate the head space, and then those were wrapped in another layer of plastic. Now, what we observed in these samples is that in some of the samples, there were high levels of organic acid, specific propionic acid. Propionic acid only forms under reducing conditions. In fact, oxygen, molecular oxygen inhibits the formation of propionic acid, the reaction of the first enzyme in the formation of propionic acid.

So, we know that conditions were anoxic when this stuff formed. We think it formed within the cores. If you calculate the equilibrium PCO2s with the water samples, they're as high as 3 to 10 percent. Okay? This is, again, far higher than anything that's ever been measured in situ in the rock, the highest values of which were .3 to .4 percent.

We see that de-nitrification apparently occurred. The higher levels of organic acids, which correspond to poor charge balance in the analyses, correspond to much lower concentrations of nitrate, and also lower concentrations of sulfate. Apparently, sulfate reduction also occurred.

Bryan Marshall of the USGS has also noticed that there are some trace element trends, which are directly linked to these things. He also, upon interviewing the people who were actually present when these cores were unwrapped for analysis, the cores were actually slimy to the touch. And Bryan has analyzed some additional cores and showed that only the cores that were wrapped in Saran wrap had high levels of organic acids. We're quite certain that conditions within some of the wrapped cores went anoxic, and that a lot of the compositional variation we see is due to this process.

As far as we can tell, essentially, most or all, of the microbial activity occurred within the cores. The most recent analyses that have been done, which were not wrapped, which were analyzed very quickly after collection, had much higher nitrate to chloride ratios, and had no evidence for organic acids, and are, in general, chemically quite distinct from the others.

Also, if you calculate the PCO2s in equilibrium with these waters, they are much closer to those that are expected at the repository level as opposed to being, you know, as high as 10 percent, which some of the others came out.

MORGENSTEIN: Two comments on that. One, might we take a look at that information relative to using the bacterial action there as an analog, or potential analog, for what might happen above the repository to vadose waters in a water system above the repository due to keting heating? We've been looking for something like that to analog, and this seems like an interesting way to go about it.

BRYAN: One comment there would be the amounts of organic acids that were actually measured were quite high. I mean, as high as a half a gram per liter. There is no source for that in the natural environment. You know, as you know, organic acids, propionic acid, acidic acid, these things are only one step removed from sugars. They are very rapidly metabolized under oxidizing conditions. They don't persist in unsaturated zones.

As far as we can tell, the source for those was breakdown of the Saran wrap that the cores were wrapped in. Within the natural environment, there is no source, you know, underneath a thousand feet of unsaturated zone, for this organic material, for food for the microbes. In the ambient system, we don't see these large changes in the nitrate to chloride ratio, and we don't believe that this process would be important, because there's simply no organic material present even should the heating generate steam and drive away most of the oxygen from the environment around the drift.

MORGENSTEIN: Okay. Understood. Thank you.

The second part of that, how confident are you in the analyses you actually do use, to the extent that these are pristine?

BRYAN: Well, we, in selecting the values that we are choosing to use, we've been conservative. We're trying to--we're probably not eliminating all effects of microbial activity. I would say that I think if we collect more analyses, we're not going to see any major changes in the range of values that we're using. This is based upon the results of our analyses. We actually ended up with a fairly, purely by chance, we ended up with--well, not exactly by chance--but, we ended up with a very consistent set of values, a very consistent trend when we applied our simple criteria for microbial activity.

I don't believe that will change much if we analyze more samples. What it might do would be to tighten down our criteria and allow us to eliminate some of the waters which were on the cusp of our selection criteria.

MORGENSTEIN: Thank you.

LATANISION: Dave Duquette?

DUQUETTE: Duquette, Board.

As you probably know, we've had questions before on whether or not bacterial action might deplete the nitrate, in this particular case, changing those ratios. Your data seemed to indicate that that happened very quickly in the Saran wrap situation. Of course, that will do two things, because Saran wrap is basically polyvinyl fluoride and polymeladine (phonetic) fluoride, so that could add to the fluoride loading, and change that ratio.

But, wouldn't you be concerned that if that happened that rapidly, with microbes that are present there, and there are nitrates which do act as food sources for bacteria, that over hundreds of years, that the nitrate to chloride ratios won't decrease considerably?

BRYAN: Well, two reasons why I don't think that's important. First, again, there's very little organic material in the natural system. Within the Saran wrap, the concentrations reached a half a gram per liter, but there's only 10 milliliters collected. So, you're talking about a few micrograms of organic material actually present. Within the natural system, you would have to have many, many kilograms of organic material within the molars. There's just no source for all that organic material.

Also, de-nitrification occurs much more rapidly under anoxic conditions. Even when there's steam build-up within the drift, even when it drives away and most of the atmospheric--in the drift and surrounding rock, conditions will not be anoxic. There will still be a significant amount of oxygen present. And, oxygen will inhibit microbial de-nitrification.

DUQUETTE: Right. Okay, thank you.

LATANISION: Russ Jones?

JONES: I have a question about your capillary retention of dust in the brine. It's mainly to do with the way that water would behave would be dependent on surface energies. The dust and the metal, I wonder where that data was acquired and how confident you are in some of those surface energies.

BRYAN: Well, that's a good question. Of course, we don't have any data for wetability of, you know, 60 molal brines on silicate minerals. So, that's an assumption-- neither for the silicate minerals, nor for the metal surface, so, that's an assumption that the wetting properties will not be so sufficiently different between the two that the brine will be drawn to metal surface.

MORGENSTEIN: Yes. Can we revisit the bacteria again? Much of the argument that you're making presupposes that the major mechanism for metabolism is organic, and that's an organic pathway. What if we're dealing with bacteria that doesn't focus in that direction, rather looks toward metals as a metabolitic pathway? Might this not still, even though we're dealing with a different metabolism, like say, for example, iron oxide, mechanism for metabolism, we're still going to get the use of nitrate in the environment during that process. To what extent can we totally rule this out?

BRYAN: That's a good question, and actually, there's currently a CR, a condition report, on that, and it will be evaluated in the next version of the physical and chemical environment. With respect to many of the metals present in the drift, soft steels will be gone long before seepage can enter, because they corrode very rapidly. But, there are stainless steel supports present in the drift, and those will survive for a long period of time. So, I'd have to say we're evaluating that in the next revision of the physical and chemical environment.

CERLING: Cerling, Board.

On Slide 11, I was just wondering about you have the upper and lower bounds for dust deposit and the brine volumes, and I was just wondering how you or what variabilities are counted in your modeling?

BRYAN: The amount of dust deposit?

CERLING: Yeah, like if we could go to Slide 11? I mean, is that an average of many runs, so your total, that total curve, that appears to be something with respect to--

BRYAN: No, again, that's based upon the limited amount of information we have on dust particle sizes. We have some information that states basically the distribution of dust is larger than and smaller than 10 microns. And, we have one number for that, essentially, where they call it the T-10, or whatever. We assumed that in order to get the maximum amount of dust deposited, we tried all different sizes of dust, and chose those, which fit the T-10 criteria. Russ, do you happen to remember how much?

JONES: Yeah, that's the less than 10 microns.

BRYAN: Yeah, so we had some fraction of dust that was less than 10 microns, and some fraction that was larger. We chose the size fraction that yielded the greatest deposition within that known distribution, which turned out to be using 10 microns for the less than 10 micron fraction, and using 30 microns for the greater than 10 micron fraction. And, then, we calculated for those two fractions, and the constraints that we knew how much was larger than and less than 10 microns.

CERLING: I guess my question had to do with, you know, is this a single idealized tunnel, or is this multiple tunnels that intersect?

BRYAN: This is a single idealized tunnel, with the typical turnout. Okay? Particles larger than 30 microns are deposited in the turnout limb. Particles that were too small would be largely transported throughout the entire tunnel, as shown right here. As you can see, the smaller particles end up being transported all the way through the tunnel instead of deposited. So, this would be for a single drift close to the inlet, essentially, assuming the entire loads of the inlet as being transported.

HARDIN: Now, this is a bounding calculation. It probably grossly over estimates the amount of soluble salt could be deposited on the first waste package in the ventilation stream.

MR. LATANISION: Identify yourself for the record.

HARDIN: Yes, it's Earnest Hardin, Sandia.

PABALAN: Pabalan, CNWRA.

On Slide 16, Bullet Number 6, you indicated calcium chloride brines are predicted during the peak thermal period. Do you expect these types of brines to occur in seepage waters? Because the previous DOE analysis indicates these waters have very low probability of occurring in seepage waters.

BRYAN: According to our analysis, you're right, calcium chloride brines occur primarily within the invert. They rarely occur within the crown. However, under some conditions, let me see, which slide is it. Go back to Slide 15. In some conditions, the Bin 4 brines and Bin 3 brines can evolve into calcium chloride brines, not under all conditions, but under some conditions, some of our conditions in some of our look-up tables.

PABALAN: So, this conclusion about calcium chloride brines are still based on a previous THC--

BRYAN: Yes, exactly. We haven't looked at the new data yet. We haven't run it with the new waters. Our new waters, it's been eliminated on largely the waters which are calcium carbonate rich, actually heavily super-saturated with respect to calcite, which tend to evolve towards the sodium potassium rich corner, as opposed to the calcium chloride corner. We do still have some waters without incorporating all of the

THC interactions, evolve to the calcium chloride corner. We haven't run the simulations yet to see whether that will be affected by the THC interactions.

LATANISION: Okay. Any questions from anyone in the room? Yes.

YANG: Lietai Yang from the Center.

On Page 9 of your presentation, acid degassing, you listed this reaction, hydrochloric acid, how about nitric acid?

BRYAN: Both will. Both, of course, will degas. Our original analysis in the dust report suggested that degassing of HCL would occur more rapidly than nitric acid. This was based upon our current thermodynamic database. At least two studies since then have suggested that perhaps nitric acid degasses more rapidly than HCL. We're, again, going to reevaluate that when we look at the dust, when we redo our analysis.

YANG: Because if hydrochloric acid degasses first, then you will deplete the chloride.

BRYAN: Right.

YANG: The other thing is--

HARDIN: This is Earnest Hardin. Dr. Yang, the other result that applies here is that you have, in order for there to be an aqueous space at an elevated temperature, you need to have a sufficiently high ratio of nitrate to chloride in solution. So, if you lose, let's say HNO_3 to the gas phase, then you essentially draw out the brine. Okay?

YANG: The other thing is that the pH of the salt mixture, you measure the sodium, potassium, chloride, nitrate.

BRYAN: Yes.

YANG: So, what is the range of pH? It goes high, then it actually stops?

BRYAN: Yes. Again, it doesn't even stop, but it gets very, very low, of course. Again, we can't model it above 140 degrees C. Our model is not applicable. At 140 degrees C, what we see as degassing occurs is the pH rises until a cognate phase precipitates out and buffers the pH, and then the pH is constant and the rate of acid--or, the composition, the P acid gas in the atmosphere becomes fixed.

For calcium chloride, this occurs at fairly--values because it's internally buffered. Basically, calcium, oxide, chloride precipitates out. For the monovalent salts, it doesn't happen until sodium carbonate or potassium carbonate precipitate out, or calcium carbonate. And, those don't occur, sodium and potassium carbonate don't precipitate out until the pH gets around 10 to 11 in our current, you know, again, at 140 degrees centigrade, or so. At that point, their composition becomes invariant, and has to be gassean contingent occurred at a very, very low rate.

YANG: Thank you.

LATANISION: Last question.

PAN: Yi-Ming Pan, CNWRA.

Back to your Slide 12, regarding the capillary retention effect. Can you give us a sense of what is the range of the dust and brine ratio in this assumption?

BRYAN: I'm not sure. We did the calculation earlier. There's about 10 percent saturation within the brine. Perhaps can you restate the question?

PAN: I'm not asking this assumption, the capillary retention effect is applicable to what range of dust and brine ratio? I notice it's a very low--

BRYAN: Yes, that's a good question. We've calculated about 10 percent saturation. In general, and in geologic materials, 10 percent saturation doesn't yield much in the way of movement. You get a lot of retention. I'm not sure at what point, it would depend upon the wetability, at what point the brine would become mobile within the dust.

Maybe, Ernie, do you have any estimate of how much saturation is usually required for transport?

HARDIN: Earnest Hardin, Sandia.

I don't have a characteristic curve for this dust. This work was done to show what the capillary response could be for dust. Let's look at dust. It's a fine grain material with incredibly high surface area. These aqueous brines do have affinity for silicate surfaces, so there will be wetting behavior. So, that's the essence of the argument. This is a qualitative argument that says there's no reason to believe that that tiny amount of brine that we calculated to exist has to be in contact with the metal surface. A lot of that brine is going to stay in contact with the dust particles themselves.

PAN: Thank you.

LATANISION: Ernie, I just want to understand something you said a moment ago. What I just heard was that both nitrate salts and chloride salts, they degas to produce hydrochloric and nitric acid. There's a possibility that nitric acid may be formed faster than nitrochloric acid; is that correct?

HARDIN: Yes.

LATANISION: Okay. But, you said something about it drying out because--what was the end point of that conversation?

HARDIN: Well, let me ask Raul. Are you going to show the slide?

REBAK: Yes.

HARDIN: Okay. And, I believe that someone like Joe Payer may have shown the slide previously. It shows experimentally what nitrate to chloride ratio you have to have in a--the experiments were done using equal molar combinations of sodium nitrate, sodium chloride.

LATANISION: I understand. The point being that we're interested in the nitrate/chloride ratio, and if both may acid degas, then the question is which degasses faster, and what's the consequence of that. So, we're going to hear some more about that tomorrow?

REBAK: Yes. I think Ernie--it would be that the nitric acid degasses, the amount of nitrate increases, so the brine may dry out because you need very high nitrate to keep the brine moisture.

LATANISION: All right. So, we'll hear more. All right. It's obviously important in terms of corrosion protection by the inhibition of the nitrates.

Roberto, you're up.

PABALAN: Good afternoon. My name is Roberto Pabalan from the Center for Nuclear Waste Regulatory Analysis in San Antonio. I'm here to talk to you about the studies that have been conducted by the Center for the NRC pertaining to the chemistry of water that may contact the engineered barriers, and hopefully, to give you a little bit of perspective with respect to the talks that my colleagues will be presenting tomorrow. Xihua He, Lietai Yang and Osvaldo Pensado will be talking to you about the corrosion experiments and the corrosion modeling that supports the NRC's performance assessment calculations. And, Tae Ahn from the NRC will provide tomorrow a summary of the work that's been done for the NRC, as well as some of the risk insights that have been gained from these experiments and modeling.

Next slide. This is the outline of my presentation. I will give a brief introduction, then go into the objectives of the Center studies pertaining to in-drift water chemistry. Then, I'll give you the key points that we would like to convey to you in this workshop, and then discuss the technical approach that may be used in our studies, give some of the results, and then provide a summary.

Next. As we all know, the mode and the rate of corrosion of engineered barriers will depend on a number of factors, and this includes water chemistry, and chemistry of the water will be altered by a number of coupled thermal-hydrological and chemical processes. Two of the thermal chemical processes that we think are important to waste isolation are deliquescence of inorganic salts that may be present with the dust that deposits on the engineered barrier surfaces, as well as the evaporation of initially dilute seepage waters. These two processes can form brines on the surfaces of the engineered barriers, and may initiate and propagate corrosion of those materials.

Next. Those two processes are relevant to the two environments that we considered in our performance assessment calculations. If the temperature is sufficiently high and seepage water is unable to enter the drift, there is a potential for elevated temperature corrosion that occurs from the presence of brines that form by deliquescence of inorganic salts.

When the temperature is low enough, wherein seepage water can enter the drift, but the temperature is still relatively high, such that you have evaporation of initially dilute seepage waters, then under this environment, there is a potential for localized corrosion. So, these are just schematic diagrams illustrating the periods of those two environments that we are concerned with. Shown here in this figure, of course, are the waste package temperature and also the relative humidity for a degraded drift scenario.

Next. The studies that we have been conducting with respect to water chemistry are designed to help us determine the range in the chemistry of waters that could contact the engineered barriers at the potential repository at Yucca Mountain. This information will be used to review the DOE technical bases for its Total System Performance Assessment abstractions. And, also, the information will be used to be abstracted into the NRC's Total System Performance Assessment code. This is something that Osvaldo Pensado will talk about tomorrow.

In addition, some of these studies on water chemistry helps us guide the laboratory studies that we are conducting. For example, we have been doing corrosion of Alloy 22 in salt environments at elevated temperatures, something that Lietai Yang will talk about tomorrow. Darrell Dunn from the Southwest Research Institute will talk about at the MRS meeting some of the results of our integrated tests on corrosion and the evolution of the near-field chemistry. We have presented some of the results for the deliquescence of Yucca Mountain dust salts at the Goldschmidt meeting I believe a couple weeks ago.

Next. So, the two key points that we would like to convey to you are these. Dust deliquescence appears unlikely to promote localized corrosion, at least up to a certain temperature. Based on our studies, this temperature, we have data to 110 degrees centigrade. We believe that dust deliquescence will be unlikely to promote localized corrosion because there is a high proportion of localized corrosion inhibitors in the dust samples that have been taken from the Yucca Mountain area and vicinity.

However, at more elevated temperatures, there is some uncertainty about the effects of these inhibitors. And, so, there is a potential for generalized corrosion and localized corrosion, which we're still studying. Some of the results will be presented tomorrow. And, also, we think that we need to do additional characterization of dust salt chemistry.

The second point that we would like to convey is that based on our studies, it looks like evaporation of seepage waters could form brines that support localized corrosion of Alloy 22. However, our studies need to be updated with new thermodynamic analyses to give more confidence in the results of our calculations.

Next. The approach that we have used in our studies comprise essentially thermodynamic modeling. Essentially, we have used modeling to look at the evaporation of initially dilute seepage waters, for example, to give us an idea of the ranges in the concentrations of corrosive species, as well as the ranges and concentrations of the corrosion inhibitors.

We have also done some thermodynamic modeling to give us a handle on the deliquescence behavior of salts and salt mixtures, specifically with respect to the effect of composition, because this, in turn, affects the time and the temperature of brine formation in the potential repository. This deliquescence modeling has been supported by some of our deliquescence measurements below 100 degrees centigrade.

In addition to the thermodynamic modeling, we have also done sampling and characterization of dusts at Yucca Mountain, so we can have an idea of what are the chemistries or compositions of brines that may form from these salts present at Yucca Mountain and vicinity.

Next. The thermodynamic modeling that we have conducted essentially has used the Environmental Simulation Program and StreamAnalyzer codes. These are steady-state process simulators for evaluating aqueous chemical processes in industrial and environmental applications. These codes have been developed at OLI Systems in New Jersey. The reason we selected this code is because it has a fairly large thermodynamic database. The temperature and pressure limits are 300 degrees centigrade and 1500 bars.

The concentration limits, at least for the standard electrolyte model, goes up to at least 30 molal, but there is a new model incorporated into these two codes, which is called the mixed-solvent electrolyte model, that allows calculations of the thermodynamic and transport properties from essentially dilute concentrations, and up to the pure or fused salt compositions.

Next. The thermodynamic modeling of the seepage water evaporation that we did essentially used the chemistry data on Yucca Mountain unsaturated zone porewaters published by the USGS. These data, for example, are shown by the process in this. We have selected some of these chemistry data and used those as input into our thermodynamic calculations. We have made simple assumptions in this kind of analysis. We have assumed that the seepage water is similar to the ambient Yucca Mountain porewaters that are, again, based on the chemistry data provided by the USGS. We have also neglected the interactions of these waters with the natural and in-drift engineered materials.

To help us in the abstraction process for our performance calculations, we have essentially supplemented this kind of thermodynamic modeling by using the chemical divide approach which allows us to group these water types into three groups, the calcium chloride, neutral, and alkaline water types.

Next. This allows us to group the numerous chemistry information on the porewaters and on the evaporated compositions into three. As indicated in these diagrams, these are box plots for the different brine types showing the pH and concentrations of the different cations and anions. These three different water types exhibit specific ranges in its pH or in its calcium concentration or chloride and magnesium and fluoride concentration. There's a little bit of overlap with respect to the nitrate concentration, but it's a convenient way for us to be able to abstract information from our thermodynamic simulations into our performance assessment calculations.

Next. Essentially, what results from this kind of analysis is that it shows that some brines that result from evaporation of initially dilute seepage waters can have elevated concentrations of chloride, and also fluoride. Fluoride wasn't a concern to us some time ago with respect to the generalized corrosion of titanium drip shield. But, for our discussion today and tomorrow, I think the important thing is the elevated concentrations of the chloride species after evaporation.

The figure on the right shows the ratio of the inhibitors, inhibitors that include nitrate, sulfate, bicarbonate and carbonate, the ratio of those inhibitors, the chloride, which is the corrosive species. And, here we plot for the three water types, the ranges in those inhibitor to chloride ratio.

Based on the results of the thermodynamic calculations, it appears that most of those waters that form by evaporation of those porewaters have high ratios of corrosive inhibitors to chloride. So, most of the compositions resulting from evaporation are outside the window of susceptibility to localized corrosion of Alloy 22.

This kind of information is abstracted into the TPA code, NRC's TPA code, as Osvaldo Pensado will be talking about tomorrow. But, there is, of course, some uncertainty here with respect to, for example, some of the thermodynamic data for calcium, nitrate, and sodium nitrate, the aqueous complexes, and also, of course, the threshold value for the inhibitor to chloride ratio that we use here of 0.1, as of course some temperature dependence also, hence, it also depends to some degree on whether the Alloy 22 is mill annealed or thermally aged.

Next. We go next to the thermodynamic modeling of the deliquescence behavior of salts. As we know, the DRH is a function of the salt composition and temperature. When we initiated this kind of modeling a couple of years ago, there was really very limited data for salt mixtures. There's some data perhaps up to about 100 degrees centigrade for single salts, but very limited data above 25 degrees centigrade, and especially above 80 degrees for mixtures of two or more salts. So, we had to rely on thermodynamic modeling to get at the DRH behavior and the different salt mixtures.

It's easy enough to calculate this if you have the thermodynamic data. The DRH can be calculated from the activity of water or from the partial pressure of water in a saturated zone solution versus the partial pressure of pure water. These numbers are calculated using the Environmental Simulation Program or the StreamAnalyzer code.

Essentially, the figure on the right shows the calculated deliquescence relative humidity as a function of temperature for salts in the system, sodium, potassium, chloride, nitrate, which are believed to be the likely dominant system in the Yucca Mountain in-drift environment.

The red curve is just the calculated curve for one atmospheric condition. Off to the right of that red curve, will be the inaccessible temperature and relative humidity because of boiling. What this figure is meant to show is that there is a significant decreasing trend of deliquescence relative humidity as a function of temperature. What's shown here, the calculated curves for, for example, for mixtures that contain sodium chloride, sodium nitrate, potassium nitrate. These can have very low deliquescence relative humidity, hence, brine formation can occur at times during which high temperatures can be present in the potential repository. Also shown as symbols in this figure are more recent experimental data from Joe Rard and others.

Next. So, if deliquescence relative humidity can be very low, and can occur at relatively high temperatures, then the question then is what are the compositions of the salts that may occur at the potential repository and deliquesce.

I believe I showed this to you about two years ago. These are literature data on chemistry of dusts collected in the vicinity of Yucca Mountain.. I think these samples are specifically from Death Valley, collected by Reheis. At the time, I indicated that it looks like the dominant anions are chloride, nitrate and sulfate. But, there are significant concentrations of the oxyanions, nitrate and sulfate, that potentially can mitigate localized corrosion of Alloy 22.

The ratio of nitrate to sulfate is highly variable, but mostly are greater than 0.1, the threshold value that we have used to indicate whether localized corrosion of Alloy 22 is possible or not. Since then, we have tried to collect additional samples from the Exploratory Studies Facility, both underground and also at the Yucca Mountain surface. These are just some pictures of the sampling stations that we have set up of a couple of days or maybe a week or so to collect those samples.

In addition, samples have been provided to us by the U.S. Geological Survey, specifically Zell Peterman. We have characterized the samples by a number of techniques, and some of the results are shown here. The results demonstrate that there's really a very low fraction of soluble salts present, less than 1 percent. Consistent with the data from Reheis, the nitrate and sulfate--the chloride ratios greater than 0.1, and, so, we think that localized corrosion of Alloy 22 could be mitigated in the presence of sufficient nitrate and sulfate indicated by the chemical data presented in this slide.

Next. Additional information from our sampling indicates that the dusts are mostly in soluble minerals, such as feldspars and silica phases. The presence of these relatively insoluble minerals has been used by the DOE, and Charles Bryan talked about this earlier, that likely could form brines to contact the waste packages, would be reduced because of the small volume of the brine that's mixed in with the rock dust. But, this is something that still we don't have a good handle on. I guess Charles has not been able to--as Charles indicated, these are based on qualitative arguments. So, what we have been doing is we have been doing experiments to evaluate the corrosion by a small amount of salts mixed in with rock dust. These experiments are still ongoing.

So, in summary, the chemistry of water that could contact the engineered barriers at the potential Yucca Mountain repository was evaluated, both evaporation of initially dilute seepage waters, as well as the deliquescence behavior of inorganic salts.

The evaporation of seepage waters looks like could form brines that support localized corrosion of the Alloy 22 waste package material. The studies that we have done have provided us ranges in the brine chemistry, which are proposed to support the NRC's Total System Performance Assessment calculations. However, our thermodynamic analysis needs to be updated based on ongoing simulations that incorporate coupled thermal, hydrological and chemical processes. We also need to look at the potential effect of drift degradation on water chemistry.

In addition, there are some salt mixtures that can deliquesce at elevated temperatures and form brines that could initiate and perhaps propagate corrosion of the Alloy 22. We have ongoing experiments to evaluate the potential corrosion at elevated temperatures in salts containing sodium, potassium, chloride, nitrate. Lietai Yang, again, is going to talk about that tomorrow.

There is still very limited data on the dust samples from the Yucca Mountain surface and the tunnels. However, current information indicates that the soluble salts in those dusts have significant concentrations of corrosion inhibitors, like nitrate and sulfate. So, at present, the proposed approach for the NRC performance assessment is to assume no localized corrosion due to salt deliquescence. However, I believe, we need to do further sampling and characterization of samples from Yucca Mountain, and these samples are still being planned, and we plan to--I believe we are still doing experiments to evaluate the potential corrosion by small volumes of brines mixed with rock dusts.

I think that's all I have.

LATANISION: Latanision, Board.

I'm going to take the opportunity to ask the first question. If we could go back to Number 11? The figure on the right showing the ratio of inhibitors and brine type. You've made it very clear that nitrate to chloride ratio of 1/10th looks to be very useful in terms of inhibiting localized corrosion. But, I guess the question is--well, there's two questions. One is how effective is it? I mean, does it limit it in the sense that it just doesn't occur, or does it occur less frequently? What is the metric you use to determine that line of separation?

And, then, secondly, this phenomenology is temperature dependent, as I understand it. So, what temperature does this refer to?

PABALAN: One of our corrosion guys can answer this better than I can, but let me try. The 0.1 ratio is based on experiments, I believe, at 80 or 85 degrees centigrade for mill annealed material. So, the ratio of inhibitor to chloride will be higher, required to mitigate--first, your question does it--it prevents the initiation of localized corrosion, but I believe we also have data that indicates it will stifle localized corrosion if the nitrate and chloride ratio is higher.

LATANISION: Are we going to see some of that tomorrow, or at some point?

PABALAN: Yes.

LATANISION: Okay.

PABALAN: So, it depends on whether it's mill annealed or thermally aged, higher nitrate to chloride is required for thermally aged material. Temperature dependence is also important, I believe experiments at 110 degrees, which Xihua

He might talk about tomorrow, indicates at, say, 110 degrees, you need .3 as the ratio of the inhibitor to chloride ratio.

LATANISION: Okay. Before I take your question, I'd like to, in the spirit of this workshop, get a sense of whether there's general agreement on that point. Does anyone have any difference with that? Maury?

MORGENSTEIN: Yes, I definitely have disagreement with that. As we raise temperatures, we don't see inhibitors being affected at all, as we get temperatures higher for just a simple chloride system of magnesium, calcium chloride, there's no indication that if we add nitrate to the system it affects the outer coating so that we get inhibition. We definitely get corrosion. So, we think that there's some serious problems with respect to temperature. We actually find that nitrate forms nitric acid at high temperatures, and is as effective a corrosive as HCL, or HL.

LATANISION: Let's get a project perspective. Raul?

REBAK: This is Raul Rebak from Livermore.

We find that Livermore is similar to what the Center found. We see inhibition to localized corrosion above a certain ratio of nitrate or chloride, even at high temperatures. I have some data to present, up to 150 degrees C showed a chemical test, and always showed the inhibition. But, also, we have data that is not part of the talk tomorrow. We have the immersion test in nitrate over chloride ratio, .5 for over two years, and we didn't see any localized corrosion under normal--conditions. So, the ratio of chloride over nitrate as an inhibitor works at high temperatures.

LATANISION: Joe Payer?

PAYER: Joe Payer, Case Western.

I think the point is, and we'll have to try to have the discipline here when we talk about higher temperature, you know, what temperature range are we really talking about. I think, Maury, I'm not sure, but you're talking about higher temperatures, ones above--

MORGENSTEIN: That's correct.

PAYER: And, the empirical evidence is quite strong that temperatures up to certainly 120, 130, and Raul will present some at 150, that the nitrate still is an effective inhibitor. So, I think we've got to be careful to try to narrow down some ranges we are talking about.

LATANISION: I agree. In fact, I'd like to think that by the end of the day tomorrow, we're going to have some convergence on this question. There were another couple of hands up. Where were they? Yes?

XIHUA HE: This is Xihua He from the Center.

I just want to clarify on the--on point one. The experiments were at a temperature of 80 degrees C, and 110 degrees C, in magnesium chloride, and magnesium nitrate solutions. And, the reason we show that we did observe corrosion at the ratio of .1 is based on electrochemical tests. We scanned the potential, and thermodynamic polarization, and we didn't observe any localized corrosion when the ratio was .1 for mill annealed--

LATANISION: Okay. Yes? Identify yourself, please.

WALTON: John Walton, Nye County.

Bobby, we just saw that DOE is now looking at close separation, observed the close separation of nitrate and chloride. So, to what extent are you looking at it? Is it in the TPA code? Should it be in the TPA Code?

PABALAN: That is something that I haven't looked at personally, but if DOE is considering including it into its abstractions, certainly that's something we will also take a look at.

BRYAN: This is Charles Bryan. I just wanted to say that it's already included in our TSPA abstractions. It's been in there since the last iteration. On the waste package surface, we incorporate salt separation.

LATANISION: Other questions or comments? Yes?

HARDIN: Earnest Hardin, Sandia.

I noticed from this slide, your comment on the right there about calcium and sodium complexes of nitrate. Do you think--this is kind of an open ended question--do you think that the question of nitrate inhibition, and at what ratio it becomes important to us, hinges on the actual concentration of free nitrate in solution? And, is there hope to that line of inquiry? And, can you calculate that above 140 degrees C, which is our limit of validation?

PABALAN: We can calculate it. It doesn't mean the calculation will give correct results. I haven't personally evaluated the thermodynamic data on which, you know, especially above 140 degrees centigrade, on which the calculations, the results rest. And, so, the window of susceptibility illustrated in this figure assumes that is the free nitrate that is causing the inhibition of localized corrosion. So, this window actually will become smaller if I assume that it's all nitrate bearing species that contributes to localized corrosion.

HARDIN: I see.

PABALAN: It will shrink.

HARDIN: Okay. Hardin again, Sandia.

So, let me put that back to you. It means that the point one threshold will be a higher threshold? So, our interpretation of point one is that that's--

PABALAN: Well, actually, it's not the window that will actually move. It's really the composition will move away from--the range, the calcium chloride brines, the lower, the left edge of that box will move essentially to a higher value if I include all nitrate bearing species into the numerator.

So, more of the waters that form evaporation will lie outside the window of susceptibility. The point one remains the same, except the compositions will kind of shift to the right.

LATANISION: Thure?

CERLING: Cerling, Board.

If we could just keep on this? What have you included in this for your calcium nitrate and sodium nitrate values? They are included in this figure; right?

PABALAN: Actually, no.

CERLING: So, this has no complexing of calcium and sodium?

PABALAN: That is correct. The numerator in that ratio only includes the free nitrate.

CERLING: Without those two complexes?

PABALAN: Without those two complexes. So, much of the nitrate is actually, at least based on the thermodynamic calculation, is tied up in the form of the aqueous complexes.

KELLY: Rob Kelly, Virginia.

On Page 16 where you have the characterization of the tunnel dust, do you have any idea that the water compositions are so different from the sample in the tunnel?

PABALAN: Yeah, essentially, the surface samples have been washed by precipitation.

LATANISION: Maury?

MORGENSTEIN: Back to 11. What if we took a look at this situation and we threw away the chlorides and just looked at, say, magnesium nitrate?

PABALAN: The pH would be lower.

MORGENSTEIN: I mean, this is an inhibitor, right, magnesium nitrate? So, you wouldn't expect to see any corrosion at all at any of our temperatures?

PABALAN: I don't know. Maybe one of our corrosion guys can answer that.

XIHUA HE: Xihua He from the Center. We have done some work, you know, where a high ratio of nitrate to chloride solution. We did the electrochemical test. We didn't observe any localized corrosion. So, based on this figure, what we can see is either the temperature, we start at 120 degrees C, with the ratio of nitrate to chloride is, I would say, at--we never have observed any corrosion in this kind of test condition.

MORGENSTEIN: These are saturated tests; correct? We would expect the same results with vapor?

XIHUA HE: Just in fully immersed conditions. The temperature--the solution, I would say that maybe it's not a saturated, it is still below the saturation limit.

DUQUETTE: In each case, would you identify yourself? Because the record needs to reflect who's speaking.

MORGENSTEIN: Morgenstein. Would you anticipate, based on your experience, that vapor phase would be similar to saturated tests that you're doing, or will it be different?

AHN: Tae Ahn. We will present that issue tomorrow.

REBAK: Raul Rebak from Livermore. I second what Xihua He said about the high nitrate. We never saw localized corrosion. We did also some tests in pure nitrate, sodium and potassium, and show it tomorrow, and also in a calcium nitrate, pure, and we never saw localized corrosion. You can see transpassivity, because you have very high potentials, but we were never able to initiate localized corrosion in pure nitrate solution, fully immersed again. Thank you.

DUQUETTE: Thank you. Any other questions from the Panel?

(No response.)

DUQUETTE: Any comments or questions from the floor?

(No response.)

DUQUETTE: If not, let's take a 15 minute break. There's some coffee, I think, outside in the corridor. And, we'll see you in just 15 minutes.

LATANISION: All right, let's come back to order.

We're continuing along in a theme of characterizing the environment that the waste package will see, or is anticipated to see, and, so, we'll next turn to John Walton.

John, welcome.

WALTON: Thank you. I'd like to thank Carl Di Bella for inspiring this great sounding title. I hope we can live up to it.

Next slide. I'm going to show you a bunch of results from the Multiflux Code that George Danko developed, and is applied for Nye County. I'm going to go pretty fast. But, basically, the vapor transport dominates the near field during the thermal period. Vapor in near field moves predominantly towards the drifts. What happens is you get evaporation in the middle of the drifts that transport out to the ends where it's cold, and you get condensation.

Three time periods we see. One is called drift attractor, where a lot of the vapor is being attracted and moved into the drifts. Follow that with the transition period, and finally, beyond the thermal period, we see very strong lateral diversion around the drift, the drift shadow effect.

Next slide. This is a picture of what George is doing. And, this is just a snapshot at 600 years for multiflux. There is the boiling front right here. There is the liquid flux, there is the vapor flux. Several things you'd want to look out. We still do see drainage through the pillars. We don't say that doesn't occur, but the big thing we see is you notice inside the boiling right here, the vapor is going very strongly towards the drift. And, furthermore, if you look even outside below it, the vapor is coming up and going into the drift very strongly.

Next slide. Here is just a snapshot of--not a snapshot, but here's a bunch of results that are kind of maybe hard to read. Here's the drift in this direction. The red part is the heated portion of the drift. The white part is the end of the drift with no waste containers. The top, we have condensation, and what happens is you get evaporation in the middle of the drifts, the temperature gradient drives the moisture out to the ends, where you get much condensation, so you get a big dryout along the drifts there.

Down below, we have something we call a water attraction ratio. The idea is to, rather than just putting numbers that don't mean much to people, put it in some kind of qualitative format. The attraction ratio is the ratio of the amount of vapor going into the drift, to the amount of water percolating over the drift footprint. And, what you see is, early on, this is the water that was already in the rock, and a lot of it's going into the drift.

The green line is the one to one ratio, where beyond this point, the drifts get less than their fair share of water, and you start to see capillary diversion, drift shadow effect beyond the thermal period. But, for a very long time, out to here, on the drift, it depends on what you assume for design and infiltration rates, the drifts get more than their fair share of water. I think that this ratio is greater than one.

At the bottom, what we do is we have approximate estimate of the salt accumulation. What happens is when you start putting the vapor towards the drifts, you get a larger accumulation of salt in the system. And, we don't have a fully coupled model, so this is just a simple bounding type calculation. But, what you see is over time, you get very large accumulations of chloride. This is chloride here, actually. And, you see this is like numbers like 15, 20 kilograms per meter of drift. This means you've got tons of salt, chloride, in the drifts along each drift in the rock.

Eventually what will happen is things will cool back down. The water will start to burn around here, and these salts will be washed out. We have modelled that. We just kind of show an arrow, just point out that it's going to happen.

Next slide. This is the historical perspective for about 20 years. We've seen simulations that showed the vapor behavior around the drift, and the arrows show the vapor going out where it condenses, and then this excess water goes down the pillars in a process some people refer to as thermal shedding.

What we have now is is that George Danko has shown for several years that, in fact, these arrows should be going into the drift. And, at this point in time, my understanding is the DOE models also show the vapor this close goes into the drift. So, I think that while we may fuss about the numbers, the qualitative direction I don't think is subject to debate anymore.

Next slide. You can see that was an old DOE graphic. This is my graphic. There's a little difference there. But, it's kind of a paradigm shift in how we view vapor transport in the near field. The old system is you had the vapor going out, condensing, it forms kind of a washing effect, it washes out the salt. Certainly, there's some salt accumulation in here, but it's a different flow system.

Now, what we see is the vapor is moving very strongly into the drifts, and what you get is very much accumulation of salt in the middle of the drifts in the rocks. Now, where is this at? We don't know exactly. Presumably, it would be where low and high permeability contrasts are along fractures, maybe where there's high permeability, next to low permeability, but, it's in the rocks somewhere around the drift. And, we refer to this as drift attractor behavior.

Next slide. So, to summarize what we're getting here, early time flow system. Water does flow through the columns between the drifts. We're not saying it doesn't. But, what we do say is the net flux, the dominant flux, tends to be towards the drifts and mostly as vapor. You can debate, you know, semantics, but I would say that thermal shedding doesn't occur, because the drifts get more than their fair share of the water, and you can't have it both ways. That is, if the drifts get more than their fair share, you can't also have the columns getting more than their fair share of water, which is what thermal shedding implies.

Accumulation of salts. The drift attractor period depends upon design, thermal loading, and it also depends on the infiltration history of water that we assume to occur in the future, because you have to assume something to model.

Next slide. Barometric pressure. The USGS has done a lot of work to look at barometric pressure and how it propagates into the rock. What they found is that, even predevelopment, that the pressure waves from barometric pressure would propagate down to repository level. When you talk about barometric pressure, you talk about a pressure wave, not amounts of air, that is, I stand up here and you can hear me speak, because my voice creates pressure waves, but probably you can't smell the onions that I had for breakfast, or anything. And, so, there's a difference, about a wave, and, so, the repository is more permeable than intact rock. So, we think there's every reason to believe that if barometric pressure got there before, it's going to get there more after the repository is built.

The important thing is that barometric pressure caused the change in vapor flux. That is, if all of a sudden the barometric pressure rises, and that comes down the fractures and into the drifts, what it's going to do is in the middle of the drifts, force a little bit of air into the rocks. And, when barometric pressure falls, what happens is more moisture comes out of the rock into the drift.

Now, normally what happens is the sooner the drifts get depleted of water because this temperature gradient causes the flux of vapor from the center to the edges, and then all of a sudden, when we get this resupply of moisture in the center, the relative humidity rises. And, so, what we're saying is barometric pressure fluctuations lead to fluctuations in relative humidity.

Next slide. Cycling of relative humidity leads to cycling of the corrosion environment. And, so, we believe that you get alternating deliquescence, efflorescence, wet/dry, wet/dry, under some sets of conditions. Other sets of conditions, you get alternations in ionic strength, changing solution composition, change in amount of adsorbed water.

Next slide. Here is some of George's early work on this, and I would stress that, you know, this is first of a kind work. We're trying to look at a process and say we think it's important. You know, we're not ready to stand behind and say these are the exact numbers that will finally be out there. But, it's important to see if this process is important or not.

What we have here is the drift along this way. We have different points in time. And, the green area is the range, actually, it's half the range of relative humidity caused by changes in barometric pressure. So, the barometric pressure drops, relative humidity rises. Barometric pressure goes up, relative humidity goes down. And, so, what we're really saying is is that we have cycles of a few days schedule going between these green lines here, and you can see it changes in time, and it has to do with temperature of the rock and the non-linearity of vapor pressure curve. And, you can see these are pretty significant, and we're talking about 20, 40 percent changes in relative humidity. And, again, this is not the full range even.

Next slide. So, what does this do to the corrosion environments? I apologize. My art work isn't the best. But, hopefully, it will do. These could be A, B, C, are kind of arbitrary places on the Alloy 22, or in time. You could place them a lot of ways. But, let's say we have some salts on the Alloy 22, and they dry out. Then, relative humidity increases. And, what happens is they take the moisture out of the air, and they deliquesce. And, so, now it's an aqueous solution. And, then, relative humidity goes back down again. They dry out.

Now, in a different location, maybe a different salt, maybe a different point in time, you could have a case where it doesn't dry out. What happens is relative humidity drops and the vapor pressure of water and the solution is higher, and so it starts drying out and becomes more concentrated. Then, relative humidity increases, and the moisture comes back into the salts, and it becomes more dilute, and then it becomes more concentrated.

Or, you might have a case where there's no salts, where it's really hot and you have adsorbed water, and you have certain underlayers of adsorbed water, then you have more, and you have less, and more, and less. So, a time scale of days.

What we're saying is the corrosion environment is cyclical, wet/dry, wet/dry, concentrated, dilute, composition changing.

Next slide. Now, let's look at repository scale type processes. There are a number of things going on in the repository with vapor transport that are likely to cause a lot of transient changes in the environment, and this is just a picture, let's talk about some of them. But, it's a very heterogeneous fractured system, permeability changes. Some parts of the repository will be warmer than others. Some colder. Some wetter, some dryer, and that leads to circulation systems within the repository.

We've also modelled in the past, and showed the Board how you'd get u-tube circulation, where you could have cold air coming down one fault system, warming up, and coming up a different fault system. So, we get u-tube circulation.

On top of it, you have this forcing functions, like barometric pressure, superimposed on top of it all. We kind of look at it as a complex large lung. I kind of think of it as my dad has emphysema, and look at it kind of like it's his lungs, you know, very complicated breathing pattern.

Next slide. Above boiling repository system dynamics. This is just kind of some relation in the last slide, but there's convection systems. One convection system is up and down fault systems. George Danko has modelled that, and it looks like it's quite plausible. Cold air comes down one fault system, warms up, goes up the other fault system, sends the circulation through the drifts.

Repository scale. The repository is interconnected, that is, drifts are interconnected. They have seals at the end, but I've never seen a demonstration of what the permeability is. I've never seen a demonstration of whether they'll corrode or not. And, so, we don't know what the air permeability of the seals are over time. And, furthermore, there's fractures through the repository, and there's different places. So, all of a sudden, you've got this barometric pressure changing. You get to this part of the repository and not that, you've got this funny circulation system going across the repository.

We also have drift scale from the center of the drifts, hot, out to the cold end. And, then, we've got circulations between hot and cold waste packages. And, all these are superimposed at once with different time constants, and the net result is we believe that the environment is like it would be fairly transient, that is, we're used to thinking that Yucca Mountain is it changes slowly over decades and centuries. Instead, we're saying now very rapidly changing.

Next slide. This is just a slide, you have to have George give a whole presentation to explain it, and, so, I said how can I explain a difficult concept in one slide, but what we have here is just a vapor pressure curve of water, different relative humidities. And, the point is is that the slope changes that you heat up. It's very, very non-linear. And, what happens is most transport phenomena move on total differences, they are arithmetic differences, not relative differences. And, so, what happens is we heat up the system, it becomes much more dynamic.

And, so, if you compare a hot repository with a cold one, you find that the cold repository has less of the transient phenomena we're talking about, tends to be much more stable and predictable than the hot repository, and it all gets back to this non-linearity in the vapor pressure water curve.

Next slide. Coupling of chemistry and hydrology is stronger. If you get more salts in the system, which is what we say this inward flow system does, then all of a sudden, you've got this difficulty that if you got enough salt in the rock above, then the salt starts affecting the flow system. And, that complicates things. We're not saying it fills up the pores. It may locally, but not in general. But, all of a sudden, you've got all this salt that can deliquesce, in response to relative humidity, and you've got a lot of things changing the flow system.

Cool down would lead to deliquescence and mobilization of these salts potentially. And, you have to realize that this is within a system where barometric pressure is changing, and relative humidity is changing. So, now, we've got a transient unsaturated system where these salts up on the roof can deliquesce and effervesce and move, or not, and we've got a very complicated transient system to try to model the chemistry.

There is a heavy reliance on drip shields, that is, when you've got so much salt in the ceiling up there, and then you've got your Alloy 22 down there, and what keeps them apart is the drip shields, and, so, there's particular reliance on the drip shields to protect the Alloy 22. And, we think there's a pretty heavy reliance on models.

Next slide. This I just--you've got to keep people interested. We keep talking about deliquescence. These are my Carlsbad rock samples that used to be beautiful. But, we had a--in El Paso this summer, and my rocks started melting away. And, so, this is just a picture of my living room, natural deliquescence of my once beautiful rock samples forming that little puddle of water down there.

Next slide. Flow separation. In Nye County, we tried to push flow separation for a number of years because when we started doing this work back in, like, 2001, it wasn't in the DOE's stuff, and we thought it should be. At this point, it's in the DOE model, and we applaud that very much. But, what it says is that depending on the flow system, you get flow and evaporation, then the different salts would precipitate at different locations, and that can separate your chlorides from your nitrate. And, so, you don't necessarily always get mixture of chloride and nitrate.

Down here, we talk about how you could model as a single cell, evaporates at one point all together, and then this multiple cells model, and different models to see how much the chloride will separate from the nitrate, and the salts.

Next slide. This is just a complicated one where we can walk through and say how flow separation occurs and what happens over time. I think in the interest of time, I'll just go ahead and pass through this slide, and we can come back to it if somebody is interested in it. We have a paper you can read on it if you're interested.

Nitrate reduction and uptake. I don't have a lot of new material to add on here, but I went and looked on the internet at what we could find, and I found this kind of generic statement in the DOE document about these microenvironments that could lead to nitrate reduction may exist in rock matrix. But, it's hard to capture by current analysis. Of course, what happens in the future is, and this is a direct quote in the future, as you heat things up, I don't mean above boiling, oxygen solubility depends very much on temperature, and it declines with temperature.

I think you can get anaerobic conditions along rock bolts adjacent to steel mesh, potential loss of inhibitory ions, and, so, just the question do current conditions really capture so much of the complex future?

Next slide. Drip shields. We said that drip shields are very important. It's important to protect the Alloy 22 from the salt on the roof. And, so, let's just do a little thought experiment. What happens is we put all the waste underground. We ventilate for 50 years, or whatever. And, meanwhile, a couple generations of people are being born. People have forgotten about Yucca Mountain. It's a footnote in the federal budget. And, then, all of a sudden, the Secretary of Energy comes over knocking on Congress and saying, you know, that war we had on Mars, or that, you know, bridge in Ketchecan over to the airport that just got, you know, Grandpa Ted's--we can't do it, you know.

And, so, I'd just like to point out there's a dichotomy between licensing and risk. Licensing has to do with regulatory rules. That is, the drip shields will be put in the license. And, so, they count the licensing. But, if you're going to do risk, one has to look at what actually will occur. And, if one doesn't believe that they'll likely ever be there, then independent analysts looking at risk reduction has to look at the probability of risk reduction, even if the drip shields are there, and the probability that the drip shields are actually going to be there.

And, so, we've got this kind of difficult situation where we have something that works for licensing, but it really doesn't address risk, at least in my personal view.

Next slide. Assumed percolation rate. What we do is if we're to model the future, we assume that the percolation rate coming down the reposition will increase over time. And, those numbers are reasonable. They're right here. We have to make some kind of assumptions, and, so, we do, plausible arbitrary. What I'm trying to say, though, is that these predictions are important to the corrosion environment, and I think that not all corrosion people understand that.

What happens is when infiltration increases over time, that tends to lead to higher relative humidity, tends to wash out the thermal period, to some extent. Past calculations have also underestimated drying processes, that is, axial transport in the drift, because of the stuff I showed you earlier.

Next slide. Alloy 22 corrosion issues are related mostly to concentrated solutions. That is, I've never heard anyone say that, well, a lot of--say we'll--the Alloy 22. And, that is what the issue of Alloy 22 is, it's very dry, hot environments that are crucial. And concentrated solutions are thermodynamically unstable at high relative humidity because they take on the water. And, so, high relative humidity protects against Alloy 22 corrosion.

So, models or assumptions that over estimate relative humidity under estimate the window of vulnerability for Alloy 22 corrosion. I think it's very important for us to cast a critical eye on anything that tends to increase the relative humidity in the repository.

Next slide. So, these are the conclusions. We studied the vapor for a very long time, and the last twenty years, what's happened is, at least close in, the direction of vapor transport has been reversed. I think I showed you the two pictures. I don't think this is really controversial. You may hear it presented different ways, but project lines are also showing that. And, most people would think that it's easier to model the vapor than it is to model the chemistry. And, so, if we're switching on the vapor after all these years, how well do we know the chemistry.

Corrosion environment is dynamic, periodic. It's not static. Coupling of chemistry and hydrology is stronger than previously anticipated. There's going to be a lot of-- but at least a high reliance on drip shields. And, I haven't seen a lot of corrosion testing under periodic conditions, cyclical conditions. And, so, I think we need to produce such data, or say that it won't be important, or show that George's predictions are wrong, the relative humidity won't cycle, the way we're doing it.

And, the other thing is, although I don't have time to show it, is if you cool down the repository, a lot of this cycling and difficult conditions tend to reduce the magnitude or vanish completely.

So, with that, there's one more slide. It's just a pretty picture. It's another one of my melting collections. You can see that it drips right here and down there. These are rock salt taken from mines in Carlsbad. So, I hate to see my collection go, but--

LATANISION: Okay, let's take some questions. Again, I think I'd like to begin the questions by asking the others who have spoken before, John and others in the room, you've introduced something I hadn't heard before in our conversation, and that's the concept of a cyclical corrosion environment. Let's see, Roberto, what's your comment on that? This is in the spirit of a workshop and dialogue, so I'm going to ask some pointed questions. Roberto, what do you think?

PABALAN: I'm going to have to pass at this point.

LATANISION: That's not an acceptable answer. Come on. We have to think about this. This is a workshop.

PABALAN: I guess my question is in your conclusion slide that after twenty years, the direction of flow of vapor has reversed. And, you claim this is not controversial, and I guess my question is what is the response to this? Is this really the new model that's being accepted, that the thermal barrier and the capillary barrier doesn't work?

WALTON: I'm not saying the capillary barrier doesn't work. The capillary barrier is very strong. That capillary barrier is very strong. What we're saying is early on during the thermal period, you saw that two years old Bob Andrews slide, it's been shown it heats up. I mean, now, it goes in, and I've been told that the DOE models are now at least qualitatively showing the same thing, although it makes sense with George about the magnitude. You'll have to have somebody from DOE really comment on it. I'm just saying from what I heard.

PABALAN: I want DOE to respond to that.

LATANISION: Let me just say before Ernie or Charles, whoever responds, I'm not trying to put people on the spot, but this is a workshop, and I really would like to have some conversation on issues that emerge. So, I would--Charles?

BRYAN: This is Charles Bryan.

I would respond a little bit on the amount of salt precipitated in the rocks. With respect to that aspect, our model predicts less. It predicts about 5 kilograms of salt precipitated over about 2,000 years. But, the amount of salt that's precipitated is neither--is small relative to the fracture volume in the dryout, around the repository. It won't be precipitated around the drift wall.

Also, with respect to that number, that 300 grams per liter of salt, regarding that, I want to say even at 20 or 30 kilograms of salt, is small relative to the fracture volume in the dryout zone around the repository. It won't be precipitated on the drift wall.

Also, with respect to that, remember that 300 grams per liter of salt would dissolve in water. So, it only takes 50 to 100 liters of water to wash away 20 kilograms of salt. It's a transient, the salt really is transient. Once rewetting occurs, the salt is removed quite rapidly.

Finally, under conditions when salt separation will occur in the rock, the temperature on the waste package surface is hotter and salt separate will occur on the waste package surface. It will tend to our model to that degree, that if it's going to occur in the rock, it will occur on the waste package surface, and we will predict that it occurs on the waste package surface, and implement localized corrosion.

LATANISION: Maury or Don, do you have a comment?

SHETTEL: Don Shettel. I'd like to know the basis for why you think the capillary barrier is strong.

WALTON: First of all, I'd like to say that the salt members that I showed were chloride, not total salts, chloride. So, that's the mass of chloride we're predicting. The total mass of salt is much greater. But, nonetheless, I do agree that it doesn't, in general, clog the pore space, locally, but not on the bulk. And, we also agree that once you get out there a few thousand years and start rewetting, you can just look at our figure, we kind of made the salts disappear. So, we agree that, you know, this is an issue where the window of--it's a few thousand year issue, and after that, they wash away. So, that we agree on, although our numbers are much higher because the numbers I showed you were just chloride only.

SHETTEL: My question was on the capillary barrier.

WALTON: Oh, the capillary barrier? Well, the capillary barrier, what happens is is that in George's model, what he shows is a very strong capillary barrier. Once you get out past the thermal period, the water tends to stay out of the drifts in his model, and he sees a drift shadow effect. And, so, why we haven't made a big deal of it, we think very strongly that that will be a long-term effect that will help performance of the repository.

SHETTEL: Doesn't the ground support affect the capillary barrier?

WALTON: I don't know. The capillary barrier, what I'm talking about is when you get capillary flow in the rocks, you've got the barrier when you hit the rock interface. That's different from this--

SHETTEL: There's ground support between the wall rock and the mined opening, and that ground support could affect the capillary barrier. Nobody seems to recognize that.

WALTON: We haven't looked at it. My sense is that it would not affect the capillary barrier. I don't see why it would. But, I haven't looked at it, frankly.

SHETTEL: Well, you have an impermeable sheet of metal with slots in it that's touching the rock. I don't see how that doesn't affect the capillary barrier.

WALTON: Well, because the capillary barrier has to do with what goes from small pores to large pores, tends to stay in the small pores.

SHETTEL: But, if the sheet of metal is touching the rock, you have a capillary contact there, and that compromises the barrier if it weren't there.

WALTON: I disagree.

LATANISION: Use the microphone, and state your name, please.

GOPAL DE: My name is Gopal De. I work for RPC on the project.

This capillarity, if dissolution has got too much salt absorbed in it, then the surface tension will increase, and surface tension will reduce the wettability. Consequently, the solution, even if the solution contacts the alloy. Still, there will be--because it is not wetting. The wettability is a very important parameter in the solution, and the metal has to come and interface, contacting, wetting.

WALTON: I couldn't make a lot of that out, but--

LATANISION: The first comment was the surface tension would increase and that would affect wettability. What I didn't hear was why would the surface tension change.

GOPAL DE: Because not too much salt concentration in the solution.

WALTON: In general, salt will increase surface tension, and helps keep things in the rock, but at the same time, increases density, and that would tend to make--the drift, and I think during this thermal period, that all this fluctuation relative humidity and the transient flow, once that's--with the deliquescence, would make dripping more likely. But, I think Don's comment was more, as I understood it, was more after the thermal period where we see this capillary effect. And, so, we see a very strong capillary effect after the thermal period. During the thermal period, I think it's extremely complicated, and no one really knows exactly what will happen.

SHETTEL: Don Shettel again. It certainly could affect after the thermal period, but if you have episodic flow of water before or during the thermal period, and the capillary barrier is compromised, then you could have dripping during the hot period.

WALTON: Yeah, I agree with that.

SHETTEL: Where does the salt go when you wash it away?

WALTON: Well, what happens is is that you've got all the salt up there, and then you've got this fluctuation to the relative humidity, and so deliquescent dryout, and you see the extremely complicated system that I don't think we have the capability to accurately model right now, so we don't really know. But, then what happens is is it cools off, the water percolating down comes in and starts to vary my capillary action, not my thermal process, capillary action around the drifts, and that water would pick up any dissolved salts and remove them, flush them out. And, so, in the long run, these salts would be flushed out. But, I think mostly, they're an issue for corrosion, and by then, the corrosion window is pretty--when it cools off.

SHETTEL: That depends on how good your capillary barrier is.

LATANISION: We had a hand up here, and then I'll come back.

KING: Fraser King, consultant to EPRI.

I have a couple questions or comments about the dynamic vapor with the variations in barometric pressure. This siting between the deliquescence and the efflorescence, that will only occur for a relatively short period of time, sort of a cusp of deliquescence, or as the temperature is dropping and the relative humidity is increasing. That's only going to take effect for a relatively short period of time.

WALTON: Well, Nye County is a small shop, so we haven't been able to try to evaluate that yet. If you look at some of those fluctuations, they're like 30, 40 percent relative humidity at some points in time. And, so, I think that condition could last, you know, a few hundred years in periods like that. But, it is a transient thing, and will go--you know, it gets wetter a little bit, it gets wet more and more and more, until it's completely wet, and just cycling the concentration.

KING: So, when do you get onto that period when you're cycling the concentration? If the parameter would concern the localized corrosion is the ratio of nitrate to chloride, cycling the volume of water isn't going to affect that ratio. So, that ratio will be relatively--so, the overall concentration will change. The ratio will be the same.

WALTON: The ratio will not necessarily be the same because what happens is is that the experiments then dries out, you could theoretically get flow separation of the nitrate and chloride. But, we really haven't processed that to see if it's likely to occur under those conditions or not. So, I would just have to say I don't know. I don't assume that it would stay mixed, but it may.

LATANISION: Let's see, we had two hands. Thure and then Howard. Go ahead.

CERLING: Yeah, I would still like to come back to the issue of vapor flowing into the drift versus the other direction, because I just find it hard to understand how we can have lower humidity if we have all the vapor flowing into the drift. So, there's an incompatibility with some of the presentations.

WALTON: Yeah, if you go back to that slide that showed the vapor pressing water towards the end, that's a good question. It takes a while to explain it properly. I'll try to give you the short answer, because it is quite confusing. What happens is if you look back, I guess, the one right after vapor--there, that one. What's real confusing is it's hotter in the middle of the drift than it is at the edges, and also, the relative humidity in the middle of the drift is drier, lower than it is at the edges. Okay? So, why doesn't water go from 100 percent relative humidity at the edges, into the lower relative humidity in the center? That's one way of stating the question. So, why is it not going the opposite direction?

So, what happens is is it has to do with the non-linearity and the vapor pressure curve, because it's hotter in the middle of the drifts, even though the relative humidity is lower, the humidity, the vapor pressure water is greater in the middle of the drifts than it is at the edges. And, that's what drives the transport along the drift, and it's quite confusing. Perhaps someone here can do a better job explaining than I can. George Hornberger would probably do a better job than I could explaining it. But, that's the essence of it. It has to do with the barometric pressure curve, in which you can have low relative humidity in the middle, and yet have a higher vapor pressure than you do at the edge because of the temperature gradient.

And, then, the permeability is so high in the drifts, you get very, very rapid transport. And, what's happened is early on when we modelled Yucca Mountain, we did these 2-D slice models, because that's all we had available, and we kind of like didn't let things run down the drift, and George had been very big about letting things move down the drift. So, I hope that helps.

LATANISION: Howard?

ARNOLD: Arnold, Board.

You caught my attention with the short times, the fluctuations.

WALTON: Sure.

ARNOLD: You're right in that some of the driving forces have short time periods. But, has anybody done an actual dynamic analysis that includes the equivalent of the inertia terms and the damping terms that you'd have to do to get a real answer on whether it fluctuates like that?

WALTON: Well, I don't have a real good answer for you because this, of course, George Danko has done this modeling. The USGS has definitely looked at the barometric pressure and has done the analysis and done some publications, which they could send you. But, look at this question, how long does the pressure take to get down there, what fraction of it makes it all the way down to particular millibars. What George Danko did to model this is said let's assume the pressure really gets down to the repository, he assumed a thousand millibar shift, 1 percent change, and then said okay, now we'll model this flow in and out of the rock and see what it does to relative humidity.

ARNOLD: The actual time constants involved?

WALTON: What George did was he assumed a--I think he did a heavy side step function, or something. I'd have to go back. He posted it on his model.

ARNOLD: I don't pretend to know the answer, but what I'm saying is if you take a series of steady states, you don't get the right answer.

WALTON: Well, no, we don't take a series of steady states. What he does is he runs his model transient in the drift, and he imposes an arbitrary change in barometric pressure and saw what that did to the relative humidity. I'd be quite up front. This is new material. George has been predicting this. I haven't seen anybody else predict it. I think it a really important question. That's why we present it, and I'd like to see answers.

ARNOLD: Yeah, me, too. Thank you.

LATANISION: We'll take a couple more. Ernie?

HARDIN: Yes, Hardin, Sandia.

I could try to answer that question. The modeling group at Livermore has coated up enough to run on a parallel super-computer, and has done some 50 year and 100 year simulations of the type of phenomenology you're talking about. However, the work they've done so far hasn't applied the barometric fluctuation at the ground surface. Now, there are analytical solutions for the attenuation of the amplitude of the periodic surface pressure signal at depth. However, you've got to go to a more impedance matching or finite discretization scheme in order to accommodate the effect of the large open void storage volume, which is the drift and its associated tunnels.

And, the other thing that the approaches that we're talking about here haven't taken into account yet is the attenuation of the pressure signal that you get when you try to move the gas phase total pressure front through a region where the gas phase is already at a state of condensing humidity. So, these are, I guess you could say these are research topics that, in sum total, I think tend to attenuate the phenomenology we're talking about.

LATANISION: Okay, last question?

YANG: Yang from the Center, CNWRA.

The first bullet in this, vapor transport driving force is the vapor pressure. Does that include or take account of the known thermal condition?

WALTON: Yes. If I understand your question right, what George does is he has enough embedded into his code, and so he has a full simulation of the temperature and vapor pressure in the rock, and then he applies this barometric pressure fluctuation on top of it, and sees what happens. So, it does consider what we think happens in the rock pretty completely.

LATANISION: I lied, I guess I'm going to ask the last question. There's clearly evidence of efflorescence and deliquescence. There's no question that they can occur under certain circumstances. But, is there physical evidence of the cyclic appearance of both phenomenon in such a short time constant in geological terms?

WALTON: Excellent question, and I don't know. I mean, George came up with these predictions, and it's the first I've heard of it. So, it's an excellent question, but I don't know.

LATANISION: Okay. I lied twice. Maury is going to have the last question.

MORGENSTEIN: I'd like to speak to that. My guess is there isn't on the basis that we currently don't have chronology that could take a look at short-term, we'd have to actually observe it.

LATANISION: Yeah, that's what I was asking.

WALTON: Well, the other thing I forgot to say, though, is is that if you look at the predictions, is what George says is this occurs at elevated temperatures. He doesn't predict it to occur at room temperature. It's predicted to occur in the hot repository. And, so, you have to have very special circumstances to see this.

LATANISION: Okay. All right, let's move on. Randy? We'll get an EP review at this point.

ARTHUR: Good afternoon. My name is Randy Arthur. I'm going to be discussing today some of the EPRI-sponsored studies on the evolution of environments at Yucca Mountain. I'd like to acknowledge my co-presenters and co-authors on this effort. Mike Stenhouse, Don Langmuir, Fraser King, Mick Apted, and John Kessler.

Next slide. What I'd like to do first of all is to add some focus, or to present some focus about what I'll be discussing this afternoon. And, the focus really has to do with the first of the panel discussion questions, and that is basically are the data, understanding and models sufficient to bound potential environments that will exist on waste package surfaces, and are they adequate from a corrosion standpoint. So, this is the first major thing in question that we'll be discussing, or focusing on today.

The second aspect, or the related aspect of that question is the possible dust deliquescence scenario, and what I'll be discussing in relation to that, in particular, is the soluble salts that are initially assumed to be present in repository dusts.

Next slide, please. These are the topics that I'll touch on briefly in the discussion. First of all, I'd like to discuss what about the importance of dust mineralogy, why is it important. Secondly, I'll discuss some of DOE's geochemical modeling approach that has been used to bound dust mineralogy. Third aspect or topic that I will discuss is in EPRI's alternative model. Also, the next point is I'll discuss some tests of model predictions, and then wind up the discussion with some concluding remarks.

So, the first topic then is why is dust mineralogy important? Why do we care about this?

Next slide. I believe that to put this in some sort of context, we need to go back to this decision tree that DOE has developed for FEP screening. That is portrayed schematically here. They consist of a series of questions. Can multi-salt deliquescent brines form at elevated temperature? If they form at elevated temperature, will they persist? If they persist, will they be corrosive? If the potentially corrosive brines form, will they initiate localized corrosion? And, once initiated, will localized corrosion penetrate the waste package outer barrier.

Now, each of the questions, or all of the questions have to be answered yes in order for a dust deliquescence scenario to be screened in to perform this assessment. If any one of the questions is answered no, then a dust deliquescence scenario can be screened out of Total System Performance Assessment.

Next slide. Now, with this background in mind, why is dust mineralogy important in this context? And, I think that the point that I'd like to make is that this screening actually starts with an assumption, and that assumption is that one of three possible salt assemblages will exist in the dust in the repository on waste package surfaces before the surfaces are actually heated up. So, the first aspect of this is that this assumption has to apply. We have three different salt assemblages, A, B and C. You can see what the salts are here. This assumption is made before the screening process is actually entered into. So, it's a top level initial assumption that underpins the entire FEP screening process. That's why it's important.

Can I have the next one, please. So, given the fact that the dust mineralogy is very important, then the question naturally arises are these initial salt assemblages, A, B, and C, reasonably bounding. Now, our position, EPRI's position is that the answer to this question is actually no, they're not reasonably bounding. The reasons for this is, first of all, that the point has to be made that there is, as far as we are aware, a complete lack of analytical data actually characterizing the soluble-salt mineralogy of repository dust.

In addition to that, these assemblages, A, B, and C, are actually inferred assemblages, based on geochemical modeling. So, we have no data characterizing the dust mineralogy. We have geochemical inferences. Now, our position is that the model appears to be unrealistic in the sense that with respect to the mass transfer of all relevant gases in the system. And, finally, we think that the more realistic assemblages would be much less deliquescent. So, this is basically what our conclusions are, and now what I'd like to discuss is the basis for these conclusions.

Next slide, please. The first aspect of this discussion then has to do with DOE's evaporation model. I'd like to spend a few minutes on this.

Next, please. An overview of the model is shown here. DOE starts with 54 leachates from dust samples that were collected at various locations in the Exploratory Studies Facility. The leachate from each of these samples was in--the evaporation of the leachate was simulated, at 25 degrees, one bar total pressure, and atmospheric PCO2 levels.

The simulations were carried out using DOE's in-drift precipitants and salt models. The model was evaluated using EQ3/6, Version Number 8, and a high-temperature Pitzer thermodynamic database that is shown here.

Next one, please. This is a conceptual model, as we understand it, of DOE's approach. Basically, you can imagine a glass of water continuing to leachate. The system is assumed to evaporate. That is, water and vapor is free to leave the liquid phase. The relative humidity is assumed to be low enough that it's an irreversible process, continuous evolution of water from the liquid to a gas. At the same time, carbon dioxide, the partial pressure of carbon dioxide is assumed to be fixed as an equilibrium constraint, the value is fixed at atmospheric values. As evaporation proceeds and continues, the solution becomes progressively more concentrated. Eventually, it reaches, the solution reaches saturation with respect to a number of salts, and the salts then precipitate. This is a conceptual model.

Now, there are a number of approximations that are made in this model. First of all, as DOE acknowledges, the ESF dusts may not be totally representative of dusts that will exist on waste package surfaces. These dusts are mostly crushed tuff with only a very small amount of soluble salts. In comparison, wind-blown dusts, which will be brought into the repository during the ventilation period, will have a higher soluble salt content, and they will also have a quite different composition.

And, in connection with this point up here is some recent data presented by DOE and as discussed earlier by Charles, suggesting that much of the nitrate in tunnel dust leachates is produced actually by the dissolution of ammonium salts. The point being that if ammonium salts initially exists in the repository dust, they will tend to decompose with increasing temperature, or sublimate and will effectively be lost from the dust at the time when they are exposed to high temperatures.

So, for that reason, DOE believes that these ESF dusts still represent a viable approach to bounding the mineralogy of dusts that will exist in the repository. Basically, any ammonium salts will be lost from the system as the temperature increases.

Another important point to make is that the model itself is based on equilibrium, and the equilibrium mineralogy is considered by DOE to be an end member case of what is probably actually in reality a mechanical mixture of dust from a variety of different sources.

Next one, please. These are the results of DOE's modeling. This is just a fairly simple histogram showing a number of salts that are considered in the models. There are numbers. The results of the modeling show that there is a distribution of salt and non-salt minerals that are produced by evaporation of the tunnel dust leachates. There are 17 unique assemblages of salts, each assemblage containing ten different minerals. And, you can see how these are distributed in the histogram.

Now, the main point is is a fairly complicated result is then abstracted by DOE based on groupings among the most deliquescent salts in those assemblages, and that is how these three different assemblages, A, B, and C, are identified and used.

Next slide, please. Now, what I'd like to discuss is EPRI's alternative approach, or alternative model, to DOE's model.

Next one. This is a schematic view or a conceptual view of what the differences are. Now, what we have done is to take our assumptions about what actually is in DOE's model, and try to develop a separate model called EPRI-1. The objective here is to confirm our own understanding about what DOE has done in their evaporation simulations.

Now, an alternative to this model is shown here with the EPRI-2 model. The key difference, the only difference in fact is in this model, the EPRI-2 model, we assumed that other acid gases are free to leave the liquid phase and enter the gas phase. The system is open with respect to all gases that can be adsolved from the liquid to the gas, not only with respect to carbon dioxide. That's the key difference.

Next one. This is a diagram showing the results of our model. I'd like to point out first of all that nitrate salts are not predicted in the EPRI-2 model, the one that is open with respect to all gases.

This is an example of our results for the so-called P07 leachates that were considered by DOE. These are the ones that produce Assemblage C in the DOE or EPRI-1 models. Assemblage C being the ones that contain most of the four-- it's the four salts system that contains three nitrate salts, very highly deliquescent.

Basically, this diagram shows, as represented by bars, if the mineral is present, it's represented by a bar, if it's absent, there is no representation of that. The main point to take away from this is that the DOE and EPRI-1 models agree exactly. All of the minerals predicted in DOE's model are also predicted in our assumption of what that model is.

The EPRI-2 model, on the other hand, predicts a quite different salt assemblage. Some of the minerals are the same, for example, calcite, sepiolite and amorbasilica (phonetic). Others are very different. In our model, the EPRI-2 model, glauberite and arcanite are predicted precipitate, as well as syngenite and thenardite. These are sulfate minerals, and carbonate minerals. They are not nitrate minerals. The EPRI-2 model does not predict that any nitrate minerals would form as a result of evaporation.

Next slide, please. The next slide is exactly--it's a different example focusing on the so-called P14 leachates, which are important because they produce Assemblage B in the DOE and EPRI-1 models. It's the same kind of a diagram, the same conclusion applies. Nitrate salts are not predicted in the EPRI-2 model. The ones that are predicted in the EPRI-2 model are sulfate salts and carbonate salts.

Next slide, please. Now, the key point of the differences, I think, in these two modeling approaches are two different conceptual models, the consequences on the relative humidities predicted at the eutectic, or so-called dryout point, after all the liquid phase is gone. This is a comparison of the two models, looking at the relative humidity for a variety of leachate categories. P07, as we discussed, is the most highly deliquescent one. P14, P22 and S82c produce the Assemblage B salts.

Now, the DOE and EPRI-1 models predict very strongly deliquescent solutions, very low relative humidities. The EPRI-2 model, in contrast, predicts much higher relative humidities, indicating that the salts predicted in this model are much less deliquescent.

Now, the relative humidities here would translate into lower temperatures, as the salts are heated up on the surface of the waste package. So, for example, if we have deliquescence of these kinds of salts at temperatures exceeding, say, 190 degrees celsius, the corresponding temperature for the EPRI-2 salts would only be slightly above boiling. It would be on the order of 100 to 105 degrees celsius. So, the consequences are very important. They predict much lower temperatures in this model as compared to that model.

Next slide. So, just a summary of what I just said. We believe that equilibrium constraints on gas partial pressures will have a very strong effect on the mineralogy that is predicted for these evaporated dust leachates.

There are significant mineralogical differences that are predicted by these two different assumptions. Nitrate salts are predicted to precipitate in the DOE and EPRI-1 models. The nitrate salts do not precipitate in the EPRI-2 model. And, as a consequence, the EPRI-2 models would be much less deliquescent. We believe that the EPRI-2 model is more realistic. It makes sense to us that consistent with respect to all gases, not just with respect to CO2, it's difficult to imagine any kind of physical or chemical system that would be selective with respect to the open or closed system nature of acid gas volatilization.

Next slide. Now, what we'd like to do at this point is make some tests. We have a test, I think, of these various modeling approaches, so, I'd like to discuss that now.

Next slide. This test is based on a USGS study on evaporation of tunnel-dust leachates. This study has been presented to the Board before in the 2004 meetings. It's also described in Appendix E of this new report. It provides, this study that I'll discuss now, provides a basis for an evaluation of the evaporation model predictions. However, the study itself is not a natural characterization of dust that actually exists in the dust. However, it is a model that we can use to test these model predictions.

Now, just briefly, what is involved in this study, five different dust samples were obtained by vacuum sampling of dust at various locations in the ESF. The dust samples were immersed in deionized water for about an hour. The leachates were separated from the remaining solids, and the samples were analyzed for major cations and anions.

The leachates were then evaporated to dryness at room temperature. The minerals that were precipitated as a result of evaporation were then identified by x-ray diffraction.

Next slide. This is the result of a study. The main point to be taken away from this result I think is the fact that no nitrate minerals are detected in this XRD study. What are observed, actually, chloride salts, halite and sal ammoniac, and ammonium salt, sulfate, a variety of sulfate minerals, and a phosphate. But, we don't see in this study any evidence for the existence of these nitrate salts, which are the real drivers for these very low deliquescent systems.

Next slide, please. Now, there's a number of discrepancies in both of the models that I discussed, the EPRI-1 model, as well as the EPR-2 model, and the DOE models. There is a number of them that I point out here. But, neither of these models compare exactly with the USGS results. A very important, I think, point to make is that neither model predicts what is observed experimentally.

Ammonium salts are not present in these models, and the reason for that is quite obvious. Ammonium as well as total carbonate and pH were not included in the original leachate analyses. So, it's a fairly simple explanation for the discrepancy.

On the other hand, there are some other discrepancies that are much more difficult to explain. Two of the ones that are most important I think to mention is the fact that nitrate salts that are predicted in the DOE and EPRI-1 models, but not in the EPRI-2 assemblages, and are not detected by x-ray diffraction.

On the other hand, halite is not predicted in the EPRI-2 assemblages, but it is predicted in DOE and EPRI-1 assemblages, however, it is detected in all of the XRD analyses. So, there are some very fundamental differences between the model predictions and what is actually observed.

Could I have the next slide, please? So, those are the differences. What I'd like to focus on here just briefly is make some comments about this apparent absence of nitrate salts in the USGS assemblages.

It could be argued, for example, that the nitrate salts were present, but that they were below the detection limit of XRD, which is on the order of 1 to 5 volume percent.

We believe this is not the case, however, because if you look at the modeling results, niter and soda niter, the nitrate minerals, are predicted to be present in abundances that are comparable to halite. Halite was detected by XRD. The nitrate salts should have been detected by XRD if they were present in these kinds of concentrations.

The second point I'd like to make in regard to this question about the nitrate salts and their absence is if we look at the dehydration equilibria involving the minerals gypsum and anhydrite, for gypsum to be found, or to be stable, the relative humidity would have to be greater than about 79 percent. Now, this relative humidity is much higher than the relative humidities that are required to stabilize the nitrate salts. And, so, this is further evidence that the nitrate salts were not present in the experimentally evaporated mineral assemblages. Two points indicating, again, that there is very little--that there is no evidence for nitrate salts being present in these experiments.

Next slide, please. So, a summary then of this test of comparisons between the model predictions and experimental results, the first point I'll make is that the relevant experimental data are very limited. And, so, any conclusions that I am making today are very provisional. But, what I think we can say at this point is that there are very important discrepancies between the experimental observations and both of the evaporation models that we have evaluated, both the DOE/EPRI-1 and EPRI-2 models.

Some of the discrepancies are fairly easy to explain. The lack of ammonium in leachate analyses clearly is a reason why we don't predict any kind of ammonium salts. Other discrepancies are much more difficult to explain. The chief one being that assemblages, the nitrate salts, and assemblages A, B, and C are not observed in these experiments, although they are predicted by DOE, but not by the EPRI-2 model.

Next slide, please. So, this is my last slide. This is a summary and concluding remarks about what I have just discussed. The points are basically that DOE is using a geochemical model to infer the existence of these key salt assemblages that are driving the entire FEP screening process. These are inferences. They are good inferences in one sense because they are used by DOE to conservatively over estimate the maximum temperature at which a deliquescent brine could possibly form on waste package surfaces. So, it's a conservative inference.

It's EPRI's position, however, that these assemblages are probably, or may be unnecessarily conservative because the evaporation model that is used to define them is based on a model that appears to be overly simplified with respect to acid-gas degassing.

In addition to this sort of modeling discussion, there are two important points I think that should be made. First of all, nitrate salts have not been detected in the experimentally evaporated leachates. This appears to contradict the results of DOE's model, suggesting that these nitrate salts are key assemblages comprising A, B, and C. A further point that is very important I think is the fact that as far as we are aware, there has been no direct determination of the soluble salt and mineralogy in repository dusts.

And, finally, I think it's important also to state that EPRI concurs with DOE that other factors, which are not addressed here, but will be discussed by Fraser King tomorrow, would mitigate the persistence and the corrosivity of any deliquescent brines that might be assumed to form in the in-drift environment.

That's my presentation. Thank you.

LATANISION: Okay, let's take some questions. Again, I'm going to ask the first one, seeing no hands up. I did give you a chance to raise your hands. That's the reality.

That seems to be a very important conclusion, the nitrate conclusion. They have not been detected, which appears to contradict DOE's inference. So, what is that saying about the inhibiting behavior of nitrates in this circumstance?

ARTHUR: That's the key question, I think. I think that there are two basic sort of countervailing portions. If you have no nitrate present in the salts, then the assemblages will be much less deliquescent, that is, they would deliquesce at a much lower temperature.

LATANISION: Yes.

ARTHUR: So, they would tend to inhibit the initiation of localized corrosion from a temperature point.

LATANISION: Right.

ARTHUR: On the other hand, if the nitrate salts were present, that would cause the temperature at which deliquescence could occur to be much higher. But, then, nitrates are present, which would tend to inhibit corrosion.

LATANISION: I see where you're going. Dave Duquette?

DUQUETTE: Duquette, Board.

Go back to Slide 7, please. I think that answer of "no" is an interesting conclusion that you arrived at, given the fact that your first sub-bullet says that you don't have enough analytical data to characterize the soluble-salt mineralogy of plausible repository dusts. I'm not sure how those two tie with each other. If you're going to say that answer is no with a big capital "no" in red, and, then, indicate you don't know what the dust is, I'm not sure how you can make that conclusion. That's the first comment.

ARTHUR: I think that the question addresses whether or not these salts are reasonably bounding, and our answer to that question is no. And, the reason we say that is because these models that have been used to predict the salt assemblages are not realistic, in our view. The earliest models will predict salt assemblages that are less deliquescent, and, so, for that reason, they are not reasonably bounded. They are certainly bounding in the sense that you could have very high temperatures. But, if you have a more realistic model of evaporation, we think that a reasonable bound would be assemblages that are much less deliquescent.

LATANISION: Charles?

BRYAN: Can we turn to Slide 10, please?

Let me see if I can clarify the conceptual model here. What this is based upon are less leachate compositions. In other words, a fraction of the dust, a gram, whatever, was taken and is dissolved in water, reacted with water. The soluble materials were drawn off. And, that was what we had to start with, was dust leachate compositions. Now, there is nitrate present in the leachate compositions, which presumably came from the dust that was leached. The presence of nitrate in the liquid shows that nitrate was present in the dust. Now, there is no doubt that nitrate salts were present.

Now, what we did here with this particular model was we took the leachate and we attempted to derive what the salts were that were actually present in the dust by drying it out, because we didn't have bicarbonate data or pH data, we assumed equilibrium and CO_2 in the atmosphere, $10^{-3.5}$. We dried it out, and we ended up with a set of chloride and nitrate minerals which were the eutectic composition. We assumed that those were then the deliquescent minerals that are present.

Now, nitrate minerals had to be present, because there was nitrate present in the leachate. Now, your analysis in which you allow acid gassing to occur is more relevant with respect to what would happen if a brine formed on the surface and it completely degassed and equilibrium--and the degassing was fast enough for equilibrium to be constantly maintained. In that case, eventually all of the anionic species would degas and you would end up with nothing but a carbonate brine, or if you didn't allow a sulfuric acid to degas, then a carbonate sulfate would form.

So, that's kind of what your model predicts would be the end case, if complete degassing occurred, and there was no background concentration, and no minerals precipitated which buffered the composition of the brine at some point.

But, with respect to the salt minerals that are initially present in the dust, you wouldn't want degassing to occur because all you're doing is trying to dry out, to concentrate what's in that leachate to the initial eutectic mineral assemblage. There is no opportunity to absorb acid degasses when that leaching process occurred. So, allowing acid degassing to occur when you reverse that process would be incorrect.

ARTHUR: Well, I'm not quite sure I understand your question. But, I think that what we're trying to show here is the fact that--it has nothing really to do with whether or not degassing occurs in the repository. This is a conceptual model that is used to define these three key salt assemblages.

Now, the model is based on a series of assumptions. The assumptions, as far as we can tell, allow for CO2 to equilibrate with a liquid phase, and not with respect to the gases. Now, these other gases, if they are allowed in the model to degas, to be open with respect to those gases, then we see a different mineral assemblage.

And, so, the question, what's realistic for the repository, is what mineral assemblages are actually used in this FEP screening procedure.

BRYAN: Again, the process of evaporating the leachate is merely intended to concentrate the leachate back to the initial precipitated salts. The final salt assemblage must reflect the composition, the entire composition of the leachate.

ARTHUR: Yes, I agree with what you saw. And, where I differ with you, however, is whether or not these three salt or four salt systems are actually represented at the site. There's no doubt that there's nitrate in the salts, in the dust, but the question is not whether or not there's nitrate there, but what is the actual mineral assemblage, is very important, and that's what drives the deliquescence.

BRYAN: And, again, I didn't make this point in my presentation. Our mineral assemblages are based upon the tunnel dust samples and leachates. However, the same mineral assemblages control the eutectic and the atmospheric samples. Those mineral assemblages are very robust. It has to do with the relative solubilities of those different salts. So, there's not much doubt that if we're dealing with potassium, sodium, calcium, nitrate, chloride systems, those will be the important mineral assemblages.

LATANISION: Maury?

MORGENSTEIN: Morgenstein, State.

We went through the same process of dissolving a variety, actually a large variety of dusts, and our results were that everything that DOE has done, we totally agree. We see the same mineral results. I know this is shocking. So, we have to concur and stick with that one.

PABALAN: Pabalan, Center for Nuclear Waste.

I'm trying to understand your EPRI one and two models. You used the same geochemical code as DOE did?

ARTHUR: Yes, I did. I'm sorry, I forgot to mention that.

PABALAN: What temperature?

ARTHUR: 25 degrees.

PABALAN: 25 degrees? And, the only difference, at least in the EPRI-2 case, is you considered the partitioning of HCL, nitric acid, you know, bromic acid, and hydrochloric. What constraints did you apply to the activities of these species?

ARTHUR: The partial pressures of those gases were fixed in simulations based on the initial equilibration of that liquid. So, the initial calculated partial pressures of 25 degrees C for a given leachate composition was used for defining the partial pressures of those gases before the evaporation took place.

PABALAN: We did some calculations, looking at nitric acid and HCL degassing I'd say two years ago, or something, we did not observe such acid gas formation until you get to relatively high temperatures, you know, above, say, 110, 120, even 130 degrees. I'm quite surprised by this result that you got.

ARTHUR: I think that the point needs to be made again that this model is used to define these three salt assemblages. It's strictly a model calculation that is used to refer to the existence of those salts.

Now, the assumption is that CO2, the system is open with respect to CO2, and in our EPRI-2 model, it's simply assumed that the model is open with respect to those other acid gases. The model is strictly equilibrium based. The key difference between the models is whether or not they're open or closed with respect to all or just one of the gases. And, because it's strictly a modeling approach based on these reasonable assumptions, we don't take into account the fact that the partial pressures may be exceedingly low, at 25 degrees.

LATANISION: Other questions or comments?

(No response.)

LATANISION: Okay. Well, we're right on schedule then. Let's move on. Thanks, Randy. Maury?

MORGENSTEIN: I'd like to start out by saying that we're probably not going to come to any conclusions or major statements in this talk. My main purpose is to let you know of some of the considerations that we have that are coming up with respect to the environment, and how we're coming around to dealing with some of those.

The characterization of existing conditions, as we were just discussing, what happens when we dissolve some dust and pull salts off, we take a look at what we have, addresses the conditions that we have in the environment presently, the dusts that we find now. For example, it is obvious that the major particle of dust that we have is ground rock flower in the environment, that that is essentially a silicate or an aluminum silicate, and that it's fairly rare, maybe 1 to 10 percent, depending upon where you are in the repository, whether you're going to see any salts at all. And, when you start seeing salts, the most common salt that you're going to see is calcite. And, the next most common salt you're going to see is selenite.

Next, please. But, in reality, once we load the repository and we start moving the system, to the extent where we heat up, where we have water as vapor moving through the system, we assume that we're going to see an increase in salts. That assumption fits fairly well with John's presentation earlier. And, we are going to make the assumption that we see more salt eventually, or more salt surface eventually, than we're going to see rock surface.

And, the reason we say this is as follows. We believe that salts themselves will contribute to dust as they break from surfaces where they're deposited. And, we believe that present rock flower will be coated with vapors that will precipitate salt crystals.

So, we see two things happening as time goes on. We see an increase of salt coating existing rock, which is rock flower for the most part, and rock surfaces. This is supported, in essence, by what we see in nature when we're looking at evaporative systems. And, we'll take a look at that in a little bit later in this talk.

A small fracture of these salts have the capability to deliquesce. A small fraction of those have the ability to form acid solutions that could address an attack on metal surfaces such as Alloy C-22.

Next slide. We have looked at dust collected in the repository tunnels in a host of locations. For each sample that we looked at, or took, we analyzed 1,000 dust particles through EDS, SEM. We did an autosystem. And, so, we have a fair--of each particle in size and composition. I'm showing you a few of those that are representative of essentially the things we've been talking about today, so you can actually see what the particles look like that we've been talking about.

It's rare, for example, to see a particle that is only calcite. It's rare to see just a gypsum particle. These are complex particles. They have a variety of sizes. Size does not necessarily conform to mineralogy. Mineralogy does not conform to size or shape. There is no uniformity to the system. This here is a mixture of sodium, potassium, calcium, chloride and sulfate. We have no ability to look at nitrates this way, so we don't do it. So, I can't really speak to nitrates through this process.

Next slide. When we looked at nitrates, what we did was, just as DOE has done, and others, we took for each of these samples, as much as we could, about 10 grams of dissolved and analyzed, and our results are the same as DOE's results. So, we see nitrates and we see sulfates and we see all the things that we formed in salts. I'm just showing you pictures here of some of the salts that we would see and how they formed on these particles so you get a sense of how these things really look. What are we really speaking about?

Here's a mixture of calcium, magnesium, chlorides, some sulfate salts, and this is sitting, of course, on rock flower. This is a coating. So, this is a coating on rock flower, something that we probably would see a lot of, and actually, we do see a lot of.

Next slide, please. This one is calcite, chlorides and sulfates. Again, this is a lot of stuff being deposited in a very small sample. These are very small samples broken off from a larger sample.

Next slide, please. The calcites in that last sample were fairly well crystallized. Mixed with magnesium, calcium, potassium, carbonate, sulfate, phosphates in this case, on rock flower. Again, notice almost every situation, we have a substrate of either aluminum silicate or silicate.

Next slide, please. This is a feldspar. All these are rock flower. And, actually, what we're looking at right now is the predominant analysis that we would see, either pure silicate, sodium silicate, calcium silicate or potassium silicate or aluminum silicate. So, most of the particles that we see are actually just rock flower, with no coatings, no salts at all. And, if we saw a pure salt as a dust particle, it was extremely rare. It would be ridiculous to even try to calculate the percentage.

Next slide, please. So, in this list of service environmental parameters, some service environmental parameters that we're concerned about, mobile surfaces or dust, are pretty complex units. They're complex items. We're unable to summarize our study of samples to tell you that there were so many calcite or we can't really do that effectively, because if I did, it would be meaningless. It wouldn't have any value. It's probably better to just dissolve things and look at them from the point of view of what basic ions we have present.

With respect to fixed surfaces, we see mostly the fixed surfaces that will be present in the repository are going to be surfaces that are man made. If we have a surface coating around the walls, we start out with, of steel and we have a drip shield and an invert, our largest two surfaces are the floor and the invert that were exposed natural materials. So, that's dominantly where the first silicates are.

Dripping water coming through the roof in the early sequences is probably going to have to come through rock bolts that tie everything to the ceiling. And, if that's the case, then we'd better be really concerned about iron in our chemical modeling. And, so far today, no one spoke of. And, if we were concerned about dust in those early, early times, we'd better be concerned with iron oxyhydroxides as well. And, these are sorbers for a host of elements, and we can count salts on them, and it's a whole different environment than we have talked about at all today. But, yet it's probably the most likely environment that we're going to see.

So, if I come back to our first question, are we really addressing the environment, or the service environment, we have certainly missed the step in the early days of repository closure.

I'm going to skip the rest of the list. Most of those items are self-explanatory. We'll save time.

We just had a discussion about which salts we might see. Next slide, please. If I can side-step for a moment and look at an analogue, there's a publication out by the European Commission dealing with museum studies essentially, salts in museums in archeological materials and other materials are a big problem. You get efflorescence. It's a huge problem in preservation. And, so, a large effort went in from the European community to take a look at how they could model what might happen behind glass cage in the museum at STV conditions.

And, what's really interesting about their list, and that's what I'm presenting here, their list of salts, is their list of salts, for the most part, looks pretty close to our list of salts for Yucca Mountain. Their list of salts is a little bit more comprehensive.

Next slide, please. So, that our list of salts is not necessarily unique. In our list, I have to say this again, is that DOE's list, and the State's list, we may in the State have a few more salts added to that as we're finding some other things that are out there that are in the DOE list.

Next slide, please. I'm just showing you single--next slide please--and double salts. We can get real complex. Now, based on those earlier slides that I showed you, you know and I know now that we're not going to see--any one of these items in a single particle. It's going to be a combination of these items in dust particles, or on surfaces. And, these are the babies that we have to worry about. In particular, there's some in here that are more problematic than others.

For example, tachyhydrite, we have put a lot of time and effort into it at the State. Just in simple salt systems, magnesium nitrate, we showed you in much earlier times in presentations that we could take a beaker with just magnesium nitrate solution, boil it down to where we have almost complete dryness, drop in C-22, cover it and let it stand at atmospheric conditions and cool down--we cover it because we want to maintain some humidity in the beaker, so we essentially approximate humidity that we might see in the repository environment.

And, what happens is C-22 is attacked. We see corrosion. In this case, nitrate is not an inhibitor. The concept that nitrate is an inhibitor fits very nicely in solutions at low temperature. It does not fit in vapor phase conditions. Nitric acid that does vaporize is caustic.

Next slide, please. I'd like to take another side-step and take a look at what happens in natural environments, say, for the last 2,000, 3,500 years, because we're having to look at time as an element in this situation. What happens to open systems, open being somebody excavated something, and you have a hole or a mine or a burial chamber? What happens to these things in desert environments that actually are much dryer than Yucca Mountain in those periods of time?

And, so, I'm able to show you two situations in Egypt, in the Eastern Desert in a place called El Hibeh, which is three hours south of Cairo. I'm not going to give you a map. And, just about an hour south of a city called Bettiswait (phonetic). And, can we use some of this information as analog? We see two situations.

Go to the next slide. We didn't quite get that last slide, but that's okay. There's a mud brick wall that you see. At the base of that wall, there's an oven. The oven is lined with a double lining of mud, built in mud brick. So, mud brick being very porous. We're in the desert system, and this system has a vadose zone that is a sulfate based chemistry. So, there's anhydrite and gypsum, mostly anhydrite at the surface. When it does rain, which is rare, or when we get dew drop, which is not rare, we dissolve some of that anhydrite, we move it down the system a little bit, and precipitate it out as gypsum.

Next slide, please. This is the inside of that oven. That even surface that you see is composed of selenite crystals that are coated with a clay dust, and actually a gypsum dust as well, selenite being calcium sulfate, hydrate. This is a very common feature in the desert environment. This oven is 2,000 years old. There's no evidence that we see--we don't see any other chemistries, salt chemistries, going on here. It's solely a gypsum system.

Next slide, please. This is a burial chamber and shaft located in the Eastern Desert. You can see what it looks like. There isn't much in the way of vegetation, essentially nil. It's extremely dry. It's at the same site, instead of looking in--I'm actually standing on the city wall on the first picture here to the left, looking out to the desert. And, in the desert there, what you see is little potholes, and those potholes are actually shafts, they're burial chambers, they have burial chambers. And, the two shots on the side that were taken this season, this past summer, show you before and after clearing the shaft so that we can go into the chamber.

Approximately 20 centimeters, or so, before we get to the bottom of the shaft, it took a pick and ax to clear it. It took a pick and ax to clear it because when they dug the shaft, they left some debris on the bottom. It's a limestone environment. And, that debris is about hand size to larger, made out of limestone particles, for the most part, with large void spaces. The voids were all coated with selenite. The contact points were cemented together so that we started to fill in the end of that void with evaporate minerals, in this case, gypsum again, because we're in a sulfate system. That occurred, the age of this feature is about 3,500 years old, so that occurred within the last 3,500 years.

So, the tendency for voids to fill by evaporite precip is common in at least desert regions. If we had more water in this system, where we had some flux that was worthwhile, we would see probably a lot more salt deposition because we'd see a lot more salt mobility. There's a tremendous amount of evaporation that obviously goes on here, and we see, actually when we get out into the Nile system, which has the same environment, other than the salt environment is going to be different, it's a salt environment that is sodium chloride, and what we see there is we can see 200 centimeters worth of suction up from the ground water table to the surface, and we get salt crusts on the surface. So, evaporation is a huge precipitator in this environment.

In those cases where we're in the Nile system, salts are quite complex, quite numerous. But, that is not an analogue to Yucca. This is closer, but it's certainly much, much dryer. So, we could assume on this basis as an analogue discussion that surfaces in the tunnel environment are going to be coated. They're going to be coated with whatever common salts we have in our system, and those common salts are going to be calcite carbonates, at least, and sulfates, or at least dominated by carbonates and sulfates. Nitrates, phosphates, chlorides will probably be less common. But, that will certainly depend upon where we are in the repository, and what the chemistry is of the various fluids coming in.

If, for example, above the repository, we see a high bacteria, because this is an incubator zone, and that bacteria chews up first the nitrate, then we're not going to see a lot of nitrate coming down through the system. If that doesn't occur in some areas and we get nitrate through the system with chlorides, and nitrates and chlorides dominate the chemistry, then obviously calcite and selenite are not going to be the dominate salts.

At no point in time am I going to come out here and tell you where I anticipate seeing, because I have no idea at this point. We don't have any analysis in the field, sample taking, sample collection, that will allow us to make decent predictions. All Zell's mineralogy that he's presented and he did, and we totally concur with, don't tell us really anything about what we're going to see in salt precip dust particles in the future, unless we know something about a vadose chemistry and how we got it.

As far as I can tell, we don't know that. If we're going out and squeezing some samples that we're not totally sure about, we don't have a good list of what are the parameters going into the system from an aqueous point of view that could address our geochemical salt precip.

So, I don't think we're handling far enough to dry the models, other than having the models tell us what to look for. I think models are a great tool right now for us to use to be able to go into the field and collect sufficient data so that we could actually make predictions. I think if we tried to model based on the information we have, what we have is garbage going in. I'm sorry. And, garbage coming out.

Not that the information we've taken is bad, but it is insufficient, I think, in its scope.

I think the question of what the dust looks like now is not the right question. I think the question really is what the dust will look like in the future. And, I think if we're going to ask the questions about what is happening in the repository, we need to start looking at things like that.

Thank you.

LATANISION: Questions? Joe?

PAYER: Joe Payer, Case.

Maury, a clarification. On your SED EDEX results that you showed several of, and you listed what these chemicals are, the EDEX analysis only gives us elemental analysis.

MORGENSTEIN: That's correct.

PAYER: So, then, you had to surmise what those were. But, you don't get any direct evidence of what they are.

MORGENSTEIN: No, you don't know for sure.

PAYER: Just a clarification.

MORGENSTEIN: Yeah, definitely. And, you also miss things like nitrate. We could take a guess at it, but it would be stupid, so, we don't.

LATANISION: Other questions? Thure?

CERLING: Cerling, Board.

So, Maury, it seems to me that you're point would be that these analogues would be good before closure, but then after closure when you've got a new temperature and moisture regime, you'd have a different situation. So, what it seems to me you might have been saying is you could have a period where salts would migrate towards the opening, and then, after you close the tunnel, you'd no longer have that migration, but then, you would have concentrate salts closer to the site where they could be important in later dust deliquescence. Is that right?

MORGENSTEIN: Yeah, you hit it on the head. What you're really doing is after closure, you have a new start point, and we haven't started to look at that start point. That's my point.

LATANISION: Yes?

YANG: Lietai Yang, from the CNWRA.

Just a clarification. The magnesium or nitrate test of the corroded Alloy 22 specimen, you were mentioning a vapor phase, also a molecular phase?

MORGENSTEIN: That was hydroscopic liquid. But, actually, most of the corrosion took place at the air/liquid interface, not in the liquid. In fact, I don't remember corrosion in the liquid at all in any of those experiments. And, I could be wrong.

YANG: Okay.

MORGENSTEIN: But, I think not.

YANG: Nitrate would be, for corrosion inhibition, nitrate would be in the liquid? So, if you didn't observe corrosion in the liquid--

MORGENSTEIN: What apparently happens is when you're looking at nitric acid as a vapor, coming off of that, and it's nitric acid concentrated, and when that coalesces on the C-22 surface above the liquid, it corrodes, and that's probably what's going to happen in the repository.

YANG: Thank you.

LATANISION: Joe?

PAYER: Joe Payer, Case.

Again, I think it's important to separate the two time periods. The seepage period, and I think there, it's not dust that we're talking about accumulates, but, it's evaporated minerals, is different than the dust that's ingested during the ventilation period, and occurs, and I think is the topic, primary topic, of this workshop, and that is high temperature dust deliquescence, and, it's my understanding that that dust is ingested during the ventilation period, builds up, and then you seal the repository. And, once you do that, I don't think there's another continuing source of that dust. You can have seepage, but in order to get the seepage, you've got to go through the thermal barrier and the capillary barrier. Am I missing something, or are we talking about just two different time periods here again?

The other part is is the limitation of the thickness of the dust that can be adjusted during that 50 year, whatever time period, of ventilation.

MORGENSTEIN: Charles, what's your answer to that?

BRYAN: I'm not quite sure what the question was there. I guess I'd say that he's right. We're assuming that most of the dust deposited on the package occurs during ventilation. After ventilation, the drip shield is in place, any dust that is generated on the walls of the repository would be deposited on the drip shield, not on the waste package.

As Joe pointed out, I think that, you know, evaporation of seepage water requires that the waters reach the repository wall, and isn't going to occur before the wall cools to less than 100 degrees centigrade. At that point, if the capillary barrier fails, or if evaporation occurs on the surface of the wall, then salts could build up. But, at that point, the RH is pretty high along the drift wall. I don't think salt precipitation occurs.

LATANISION: Ernie, do you have any comments on that?

HARDIN: Sure. This is Hardin, Sandia.

My take on it is that the soluble salt load deposited on the waste package during preclosure ventilation is the limit. There will also be soluble salts deposited on the invert during that same period of time. Once we put the drip shield in place, what you've done is you've limited the velocity of air currents that could mobilize dust. And, so, the size of particles that could fly around in the air space under the drip shield is going to be very small. The net result of that would be redistribute the soluble load, make it even more homogeneously distributed. So, I don't see that as being a hole in the argument. I hope that helps.

BRYAN: I was thinking more if you could comment on the RH at the drift wall at the time at which it reaches boiling.

HARDIN: Well, yeah, there's something very basic here that I was going to offer anyway, and that is that the drip shield is there because it is a design feature intended to address an uncertainty in the evolution of the system. And, it is there because of the uncertainty that attends to the composition of seepage that might occur in the thermal or post-thermal period. It's there because of the possibility of efflorescence that might occur if you had a transient pulse of water that caused the salts to reach the drift wall and then evaporate, leaving behind crystals of salt. Now, that's why the drip shield was originally put into the design. After the system cools back down, that function of the drip shield may no longer be needed.

LATANISION: If the drip shield were replaced by bentonite, or some such material, that would change that picture pretty dramatically, wouldn't it.

HARDIN: Oh, sure, yeah. We've contemplated alternatives to the drip shield we have now.

LATANISION: It's about 5 o'clock. We have a few more minutes, and I will take some more comments. But, I just want to make a couple of observations before we go on.

This session was constructed with a view of getting some sense of this community's views on the environment that might generate in the repository and which could be of importance from the point of view of localized corrosion. I told you at the outset what our goals were. I didn't tell you what our goals are not.

And, I do want to say that one of our goals is not to identify new science projects. And, I'm quite serious. At this stage, we're looking at an engineering project. We've got to make sure the engineering is right if this is going to go forward, and we've got to make sure that the engineering is doable. If it's neither right nor doable, then I think it presents a big problem. But, I really don't--the consensus of our meeting is not going to be the evolution of a lot of new science projects, because, frankly, I don't think that's in anybody's interest right now.

Having said that, we heard two observations today that I think we have to consider. One of them was the observation from Randy that contradicts the opinions or views or perhaps even data of others, and that is the issue of whether nitrates are present or not. That's a pretty important point.

And, Randy, I'm going to ask you and Charles and Ernie and anybody who else is interested, to talk somewhere off-line over this next day, and maybe we'll get a short summary of your opinions at the end of that period. I really wouldn't like to leave this meeting with that dangling out there, because I think it's an important issue, and it either needs to be addressed, or we need to come to the conclusion that perhaps there's some mollifying phenomenology that we're missing.

The same is true of the cyclic corrosion environment, the efflorescence, deliquescence argument that John made. You know, this is a new observation. I hadn't heard that before. I don't know whether it's a first order of concern or a fourth order of concern. But, I think we need to have some clarity on that, and I think this room includes as much of the intellectual horsepower on this project as we're going to find anywhere.

So, John, I'd like to suggest that you and Roberto and anyone else who is interested, find some time over the next day to talk a little bit more about this, because I think it's an important issue.

The one other thing I'd like to do, and if I could turn to Randy's presentation, and to Slide--I don't know whether it's 5 or 6, it looks like it's 5 in this outline, but it may be 6 in the--the decision tree.

I would like to take a poll. This is not a binding referendum. It's just a poll. But, I would like to ask the five organizational entities that are here as stakeholders in this process--as I say, this is not binding. I just want to get your sense at this point of the first two items on this decision tree.

Can multi-salt deliquescent brines form at elevated temperature? And, then, secondly, if they form, will they persist? I think the other questions we'll come to. I'm going to come back to this over the next day, because I think it's a particularly nice way of looking at this problem.

When I first saw this I think in 2004, I think all the answers were no. I want to find out right now from this group whether the answers are still no, or whether there's some ambivalence, or some other opinion. So, I'm going to keep score here as you give me your answers.

From the project's point of view, Charles, what do you think? Multi-salt deliquescent brines form at elevated temperatures?

BRYAN: Yes.

LATANISION: How about from the NRC's point of view, Roberto? Okay, Tae?

AHN: We continue to study.

LATANISION: Tae is becoming much too political. I want a yes or no. I'm going to be like an attorney in a courtroom. Yes or no?

AHN: I don't think we have enough information to say yes or no at this point.

LATANISION: That's not acceptable. I've got to get-- I'm not trying to put anyone into a box. I want to get a sense of this--this is the intellectual strength of this whole discussion. We really do need to get some opinions out here, even if it's a reserved yes or no, just give me an answer.

PABALAN: Well, I can answer for the Center for Nuclear Waste Regulatory Analysis, and I will say yes. But, that's not going to be an NRC--

LATANISION: I'll put a small "r" next to it. How about from Nye County's point of view. John?

WALTON: Yes.

LATANISION: How about from the State's point of view?

MORGENSTEIN: Yes.

LATANISION: Randy, I guess I don't need to ask you.

ARTHUR: The answer is a definite yes. But, the question actually is qualified. The question really is are these salts that form, are they nitrate salts?

LATANISION: Okay. I think I have two qualified yeses and three yeses; is that right?

APTED: Define elevated temperature.

LATANISION: We'll come to that. We'll come to that tomorrow. Yes, use the microphone. Otherwise, we lose this conversation, and I don't want to do that.

APTED: Mick Apted with Monitor Scientific. Again, we don't need all no's. We just need one no type of thing, and then we can all go home and save a lot of money, and stuff. Multi-salt, so even some of the salts that we saw that deliquesce at temperatures, like at 140 or 130, okay, and that's elevated temperature, and so on, so, our view is if you mean elevated temperature to 200 degrees, 190 degrees, then the answer is clearly no, is our opinion.

LATANISION: What about at 160?

APTED: Tell me the system. Again, tell me the multi-salt system you're suggesting at 160.

LATANISION: All right, no, I take your point. The only reason I'm asking this is when I first saw this in 2004, I think it was at the May meeting of 2004, the answer was definitively no. And, I sense there's a little bit of a change in attitude at this point. How about the second question?

ARTHUR: Let's go back. The answer was definitively no in that case because we're dealing then with a calcium chloride, pure calcium chloride.

LATANISION: No, no, I'll buy that. I agree. I understand. That's exactly right. That's more than a friendly addition. You're absolutely right. So, let's look at the second question. If brines form, will they persist?

Charles?

BRYAN: Well, by default, because we can't model what happens at really high temperatures above 140, or so, the answer is yes, they will persist. Certainly they will persist for some length of time. Our assumption is they will persist long enough to cause corrosion.

LATANISION: I'll buy that. Roberto?

PABALAN: I'd have to say a qualified yes also along the same reasons that Charles said.

LATANISION: Okay. John, Nye County?

WALTON: Yes.

LATANISION: Maury?

MORGENSTEIN: Yes, but I'd like to extend that to low temperatures.

LATANISION: I'm sorry?

MORGENSTEIN: Yes, and I'd like to extend both of those quests to low temperatures as well.

LATANISION: Okay.

MORGENSTEIN: I'm not satisfied with high temperatures.

LATANISION: And, then, from Randy?

ARTHUR: The answer to that is no. If the pH is buffered (inaudible) by reaction to the dusts.

THE COURT: Okay. I'll buy that. All right, that's helpful. Let's see, yes? Sure.

PETERS: Mark Peters, Argonne National Laboratory.

I was to second what you said. I consider myself an informed observer sitting here listening, and I didn't hear any discussion of how likely anything was or what the consequences were. And, so, I don't know what to take away from this entire discussion. So, when you go home and sleep tonight, the panel needs to come back tomorrow ready to talk about service life and the environment in the context of how likely something is, and what the consequences are, because I don't know what the--I'm not going to walk away with anything meaningful if I don't hear that.

LATANISION: I agree with that, Mark. I think that's part of what our goal is. You know, I'm not of the opinion that we're going to reach 100 percent consensus. But, I'd at least like to have a sense on issues like these, because I think this decision tree is really the crux of the whole issue.

If, at the end of the day, we get down to the bottom and we've got a no somewhere along this line that we can really defend, then I think that answers a very important question. And, you know, that's part of what we're aiming at.

Dr. Payer?

PAYER: Joe Payer, Case.

I think the first two questions are legitimate questions, but they don't address the issue of is a dust layer a corrosive environment. And, we're going to focus on that quite a bit tomorrow in some of the talks, and that is the volume of water that you generate. So, can deliquescent brines form at elevated temperatures? Yeah, if the salts are close enough together and we can't rule that out. Will those brines persist? Maybe. But, if you distribute that small amount of brine in a dust layer, will it act as an effective electrolyte, and will it act as an effective crevice to prevent corrosion? And, that's sort of in between there. So, you know, it's a very important point that's not recognized in the straight question.

BRYAN: Charles Bryan. That's actually question Number 4, which is if you do have the brine, if it's corrosive, can it still result in corrosion.

PAYER: I think it's before 4, but anyway, it's--

BRYAN: Yeah. All right, thank you, Joe.

APTED: Mick Apted, Monitor.

Picking up on Mark's point here, this is truncated, this is very much sort of the science fair part of the decision tree. There was a very key one on the bottom that's not listed, and I saw it's sort of Question 4 on the back of the agenda here. And, that is, in a sense, does it matter? Is it going to affect some sort of peak dose standard compliance.

And, if you remember from the May 2004 meeting on this, when we were looking just at the calcium chloride situation, it doesn't matter whether it's got some chloride early penetrations, or penetrations by these, and so on, the answer that was at that meeting still stands in for the general case, is that we don't see any consequence, even of early penetrations in terms of meeting the NRC dose compliance.

And, I think if you recall back to, I think, the February meeting this year, Tim McCartin got up and he showed some of the early TPA results that was like a 4 millirem per year peak dose, and that was based like on a 10,000 year mean canister failure, or something, or 50,000 year, and the TRB members, I asked, well, what happens if it's longer or shorter mean time of failure, how does that peak dose change. And, Tim's answer was it moves it in time, but it doesn't change the peak.

And, I think that's really the answer you're going to find, is that we're straining at a question here that overall really is not going to, at the end of the day, strongly affect compliance.

LATANISION: Nick, I think you're right. I think that really is the ultimate question, does it really matter? What's the upshot, even if we think there is penetration?

So, yes, that should be on the agenda for our conversation. Dave?

DUQUETTE: Duquette, Board.

Just to address that comment, one of the reasons for having this meeting is as late as last year, I saw a defense for FEP-ing some of this stuff out, based on that decision tree, or fault tree, call it whatever you want, where the first two were no. And, now we've come to not a consensus, but at least a possibility that those two could be yes.

The Board questioned FEP-ing out on the basis of each of these, and now we find that at least in the first two, there may be some question. I agree with the last comment that Nick made, that in the final analysis it's going to be does it matter. But, that's different from putting together a document that says you can eliminate these things because they don't exist. And, I think that was one of the reasons for holding this meeting at all.

So, I just want to close my comments with that.

LATANISION: Yes.

BRYAN: And, I would just like to comment on that, that actually for the last year and about a half--

LATANISION: Identify yourself, and then use the microphone so we can capture this.

BRYAN: This is Charles Bryan, Sandia.

Actually, for the last year and a half, or so, we have been saying that the answers to the first two are yes. It's been a while since we felt that the answers were no to those questions.

LATANISION: Okay. All right, any other comments? Well, we're off schedule. We're about ten minutes off, but close enough, don't you think? In the Abkowitz tradition, I think we're right on target.

All right, we'll adjourn and meet again tomorrow morning at 8 o'clock. Thank you very much.

(Whereupon, the meeting was adjourned, to be resumed at 8:00 a.m. on September 26, 2006.)