UNITED STATES
NUCLEAR WASTE TECHNICAL REVIEW BOARD

Hyatt Regency - Denver
Anaconda Tower - Room 210A-B
1750 Welton Street
Denver, Colorado

December 12, 1989

BOARD MEMBERS PRESENT

Don U. Deere, Chairman
Melvin W Carter
Donald Langmuir
Ellis D. Verink
Dennis L. Price
John E. Cantlon
D. Warner North

William W. Coons, Executive Director

INDEX

PROCEEDINGS

MR. BLANCHARD: If everyone will come up and take their chairs, sitting up toward the forward so they can see the screen.

Last night when we closed the session, Don had mentioned that we were going to pull a switch and take the overview effects of repository development session that was original scheduled for 10:45 and move it up to 8:30, and then spend the first hour talking about these two. And the basic reasoning for that was that the radionuclide behavior at elevated temperatures, was an ideal precursor to introduce the talks about the geochemistry laboratory experiments. So, we thought there was a phasing there that was reasonable, and so we did that.

Now, the first speaker is Bill Glassley from Lawrence Livermore. Bill are you ready?

DR. GLASSLEY: In this overview of the effects of repository development, I will be highlighting work that has been going on for quite some time. I'll emphasize highlighting. Much of the material that will be discussed, will be presented in much more detail in the January meeting with the NWTRB.

The effects of repository development, at least as far as we are concerned deals primarily with issues concerning waste package performance and development of a source trend can be passed onto those doing work in a far field. The focus of this work is primarily on the response of the near field environment or the environmental system to changes in temperature that will be experienced. We know that there will be a very rapid thermal pulse or a thermal spike that will last for a short period of time, followed by a protracted cool down period, extending for thousands of years. That complex thermal behavior has a lot of implications for both chemical and mechanical properties, and it's those properties and processes we want to understand.

One of the things I want to emphasize though in this presentation, is that the near field is not considered in terms of a specific distance away from the waste package, but instead it is defined in terms of processes. We want to know what the chemical environment is that the waste package will experience and what its mechanical environment will be. Those processes can extend for some distance away from the waste package. They can extend beyond the EBS and beyond the disturbed zone, and therefore, we are interested in how those environments, or that extent of the system will influence the particular properties we are interested in. It means that we are going to overlap to some extent with those people doing far field work. But, in fact that overlap could be advantageous and in fact should be, primarily because it will provide us with a way of checking our numbers that we pass onto them when they do their travel time calculations and radionuclide migration studies. And, it will also provide us with a means of making sure that the numbers we pass to them are consistent with their concept of the way things should be. In other words, we are generating in essence an internal check.

The emphasis of this particular presentation is going to be on the following. First, I want to describe some of the physical effects in the waste package environment as a result of waste package and placement on the environment. I will describe primarily work that we are doing in G-Tunnel, or work that has been done relatively recently. And, then I'll describe some of the laboratory work that we have accomplished, highlighting things more than getting into detail.

Radionuclide behavior at elevated temperature will be described by those who will be speaking after me. Some of that has also been described by Rich Van Konynenburg and Ben Ross yesterday in what they were talking about, so I will not be describing source term in this particular presentation. Some of those issues, however, will be discussed in the January meeting, as well.

As to the physical effects of the waste package and placement are concerned, there are four things we are particularly concerned with, the thermal response of the environment, and here I'm going to be talking about some of the modeling work we've been doing, and how that modeling work has been evaluated in terms of field tests at G-Tunnel. I'm going to be describing some of the radiation work, but only in a very cursory way, describing the results of some experiments we have be doing in dry and moist atmospheres in high radiation fields.

I will talk a little bit about some of the excavation studies that we are planning. We are particularly concerned with the effects of the thermal pulse on borehole stability and how changes in the rock stress system can affect fracture development and how those ultimately may affect fluid flow of the hydrology and water chemistry.

Finally, I'll describe some of the work we plan on doing on the emplacement of man-made materials and how those can affect the near field environment. We have initiated some modeling work in the high temperature behavior of rock-water-concrete systems, but it's very preliminary. That will be described in some detail in January. Also, be conducting or planning work to evaluate other materials, as well. I'll talk about that in a little bit more detail.

Now, as far as the physical effects in the thermal processes, I want to summarize very briefly some of the work that's been done at G-Tunnel. This figure represents a cross section through the G-Tunnel facility, a drift represented here and a horizontal emplacement hold there (indicating), and the dark area represents a heater that we have emplaced.

This test was conducted to determine how--what the thermal field and hydrological response would be if a simulated waste package were emplaced, in this case, in a horizontal configuration. We were planning to conduct vertical tests as well.

Now, before the tests were run, the response of the system was predicted using the TOUGH code as modified at Livermore, and what I want to show you is the predicted response and what was actually observed, and some of the other characteristics of the system.

Before I get into that though, simply to summarize what the thermal cycle was, a heat load was imposed on the rock by a heater, a resistance heater, in which the heat load approximated 1.0 to 1.2 kilowatts per meter of heater. A boiling region or vaporization region was predicted using the TOUGH code, that would not exceed 1.4 meters away from the center line of the heater. The heater, heating history was 128 days full power, and then it was ramp-down at power for 67 days, and one day with the power off. If you add those up, you get 196 days, not 195, but there was an extra day where we didn't have the heater on, so the numbers are where we can add most of the time.

One important point about this particular study is the fact that the cool down period was highly accelerated. It does not mimic the way a real system would behave. It does, however, give us a handle on, or give us an opportunity to challenge the code and see what to expect. We obviously need to conduct in the future much, much longer term tests to be able to compare our code predictions to what in fact happens.

This represents the results that were obtained on three thermocouples that were in the system. Horizontal axis is time and days, vertical axis is temperature and degrees C. Borehole wall thermocouple, the predicted response is indicated by the solid lines. The predicted response at .55 meters away from the heater and at 2.4 meters away from the heater. The correspondence between observed and predicted is exceptional, and we are quite happy with that. Notice, in fact, that even the shoulder to these curves where vaporization was predicted to occur, and in fact was observed, matched very nicely. So the response, at least for these particular thermocouples was quite nice, but things were not perfect.

And, this cartoon, which is more or less accurate provides a way of discussing some of the things that did not turn out quite as expected or predicted. What is shown here is a cross-section through the heater hole. The heater is represented by this shaded region; the borehole wall by the circle around it. The unornamented area is the zone in which--in essence all fluid was vaporized and the rock was dry. There was a zone that developed around this, essentially a halo of saturation above ambient saturation, and then the ambient wall out here.

A couple of important features, there were two fractures noted that ran through the system. One was here and the other was here (indicating). Now, in previous runs of the code, it was evident that fractures could provide pathways for vapor migration, and in fact, the consequence of that is something that's observed here. You can see that the dry out zone and the region of increased saturation extends much farther away from the heater both here and here (indicating), along the fracture than anywhere else in the region. And, what we think we are seeing is the effects of vapor migration along the fractures, essentially enhancing removal of water. As the water moves out, it cools down, condenses and we end up with the zone of increased saturation extending further away from the container.

That's an interesting behavior and it needs to be looked at in much more detail, but something else that's important is the asymmetry vertically of the width of the saturation and dry zones. You can see that both are relatively narrow above the borehole, but are much thicker below the borehole. What we are seeing is the consequence of gravity, obviously, it's going to play a role. But, because gravity was not a component included in TOUGH at this point, the prediction of the form of this dry out zone and the saturation zone within this region, was not consistent with what was observed. It provides us with a means of evaluating the magnitude of the gravitational effects and a means of going back and incorporating that into the code in a vigorous way.

The results from G-Tunnel will be described in much more detail at the January meeting, and it's something to look forward to, I assure you.

The other effects as far as waste package emplacement are concerned, radiation effects are very important. We need to understand the radiolysis process as it affects the dry air and the most air system. And we have initiated experiments in that field. Don Reed at Argon National Laboratory in collaboration with Rich Van Konynenburg have been conducting those experiments.

The experiments that have been conducted so far, have been on relatively simple vessels, no tuff has been present. Ultimately, we want to look at how tuff interacts with this system. The experiments that have been conducted so far, have been in dry air and with moist air Whitey cells at radiation levels of about .1 megarads. And, the effects that have been noted in particular in the dry air system, the principal radiolysis products are N_2O and NO_2. In a moist air system, the principal radiolysis products are N_2O and NO_3 minus, the radical, presumably is reflecting generation of nitric acid. Clearly those compounds are important for the corrosion processes that can affect container materials and we want to evaluate that in substantial detail, and that work is going on.

We need to understand, though, how that kind of radiolysis environment, that chemical system, will respond if tuff is present, because tuff has the potential for buffering or neutralizing acids or other constituents that are present within this radiolytic environment. So, we plan on conducting experiments with tuff present in that same system.

The role of excavation will be described by Steve Blair in the January meeting, but in summary, the kinds of things we are concerned with are primarily stress in the rock that's due to the excavation process, how the stresses change, and the effect of the thermal perturbation on the system and how that will influence the stress fields.

The work that has been done so far has been primarily key block analysis, trying to understand the influence of block geometry on borehole stability. That work was carried out by Jesse Yow and is in the process of being put together in a report right now. What we want to focus on in the future are much more dynamic processes. The effect of stress, temperature and moisture on the mechanical properties, the effect of long-term "creep" and to what extent does it occur, and what will its consequences be. And, also, which subcritical crack growth of phenomenon that could be extremely important in influencing the hydrological environment immediately around the borehole, and potentially as a result, could also influence water chemistry. Subcritical crack growth refers to crack migration at a very slow rate that often occurs in response to a thermoperturbation. Critical crack growth is when the rock reaches a critical stress and the crack explosively evolves.

We are interested in those primarily because of their implications for the spalling of the borehole wall and block stability, and how those could affect the retrievability of the waste package.

Finally, as far as the emplacement of man-made materials are concerned, we know that a wide range of materials will be used in developing the repository. Paints will be present, concrete, rubber, grease, potato chips, peanut butter sandwiches, you name it, it's going to be there. All of those things have the potential to affect the chemistry of the environment, and we need to understand how all of those things will behave over a long period of time at elevated temperatures in a moist atmosphere.

We have designed or are in the process of designing, laboratory modeling and field studies that will focus first on identifying those materials that could have adverse consequences for the chemical environment. And, then once we've identified those, obtaining thermodynamic and kinetic information about those substances so that we can then undertake experimental studies and modeling studies, to evaluate the consequences of those materials in the environment.

We are particularly concerned about coupled processes such as the interaction of epoxy-concrete-rock-water-metal, what kind of chemical environment will that generate. And, ultimately being able to develop long-term model predictions for the behavior of this environment. To accomplish this, we are also going to have to look at man-made materials that have been around for thousands of years, and those will provide us with the means for validating to the extent possible our models for the effects of man-made materials and their behavior in this environment.

That's essentially a summary of some of the physical processes. I want to talk now about the laboratory and field evidence we have been generating. I'm going to talk about laboratory tests that have looked at one particular process, although, we have looked at a number of them. I've described some of the field tests that have been conducted. The geochemical work that I will be describing will be rock-water interaction work and the thermodynamic and kinetic data for geochemical models of waste form dissolution work, and source term for far field studies. Some of that was described by Rich Van Konynenburg and Ben Ross. More of it will be described at the January meeting, and some of it will be talked about later on after this presentation.

As far as the thermohydrological results are concerned, the one thing--there's an important result that we have that I think should be emphasized, and that is the fact that laboratory results from wetting and drying experiments have demonstrated that fractures do not be behave in a reversible way. And, I'll describe what I mean in just a moment.

What we see in some of the experiments that I'll describe are that asperities change form along fracture surfaces, and that minerals dissolve and precipitate in those fracture surfaces and they result in a radically, modified hydrological regime and chemical regime.

The experiments that we have performed have taken pieces of core that have natural fractures in them, placed them in pressure vessels where we can control the temperature and the vapor pressure or water pressure. We can also dry or hydrate the sample. We can measure permeability in this apparatus. One of the experiments that was conducted with a piece of coal with the natural fractures was the following. The fracture was first opened and we examined the fracture surface and that's what the figure here represents.

The important things to note here are the presence of these little tiny balls scattered along the surface. They are balls of cristobalite, S_iO_2. Something that occurs quite commonly in the tuff. Also note the roughness of this surface. There is a bar scale here of 100 microns, a lot of small, sharp asperities along the fracture surface. That sample was placed in the pressure vessel, its permeability was measured. It's permeability at the beginning of the experiment was about 1,000 microdarcies, somewhat higher than that. The vertical axis, by the way, is permeability and microdarcies horizontal axis is time.

The sample was then dehydrated and the permeability radically dropped to values below 100 microdarcies. And, during the course of saturation, it eventually stabilized more or less in this range. The sample was then dehydrated again at 90 degrees C and that's what this second drop in permeability represents.

The final values of permeability were essentially those of the intact, unfractured tuff, a few microdarcies. This is not reversible. If you rehydrate the sample, you cannot get back to the original permeability--the original effective permeability of the sample.

Once you take that sample out and try to open it, usually it's extremely difficult to pull the two pieces apart and what you find once you are ultimately able to do that, is a fractured surface that looks like this (indicating), same scale as the other figure. Minerals are deposited on the surface. You can't see it in the xerox copy that you have, but in the SCM photo, obvious deposition of minerals along the surface, primarily cristobalite, but it appears as though there may be clays as well. Clays or zeolites. Also, the surface has changed its roughness substantially. We no longer have the small asperities, we have much larger ones. This combined process of mineral deposition, dissolution and changing asperity form must be the reason why the permeability, or the hydrological processes change.

Now, in this environment, clearly there are a lot of chemical processes that take place. The chemical processes have important implications and we are trying to understand those to the extent we can. What I want to summarize now are some of the experiments that have been conducted to understand this chemical environment.

Many of these experiments have been run in which Dixon rocking autoclaves have been used. They are systems where you have a pressure vessel, a large volume one, approximately a liter of volume. A rock sample is placed in there, in this case, tuff along with fluid, J-13 water. The sample is taken to the temperature and pressure of interest and then you can extract fluid during the course of the experiment and monitor reaction progress, and that's what this particular graph represents, one of those experiments. It ran for a little bit more than--about 70 days. We have experiments that have gone for over 300, so time is on the horizontal axis.

Vertical axis is concentration and the points represent compositions of the solution extracted from the pressure vessel as a function of time. Calcium, potassium by the pluses, aluminum by the diamonds and magnesium by the little crosses along the bottom axis. The lines represent the modeling of this experiment by using the code EQ3/6. And the important results are first of all, calcium and magnesium fit relatively well, the actual observed concentrations. And, their behavior reflects the behavior of carbonates in the system, primarily calcium carbonate and calcium magnesium carbonate.

Potassium and aluminum on the other hand don't fit the stated points nearly as well as the others--as well as the calcium and magnesium. The reason is that, the potassium and aluminum go into clays that develop in the reactions. The thermodynamic and kinetic properties of the precipitation and dissolution kinetics of those phases are not well known. Therefore, given the data base that existed at the time, this was the best we could do. Clearly, we have a data deficiency and what we need to do is generate data on the dissolution and precipitation kinetics of those phases and their thermodynamic properties in order to come up with appropriate information so we can do the modeling and have confidence in it.

Some of the work we have initiated in that realm, trying to understand the properties of the phases, is summarized in the next figure.

MR. CANTLON: These were done on intact cores or on crushed material?

DR. GLASSLEY: Both. In this particular sample, you are looking at a wafer--a core wafer.

The kinetic studies, what we have been trying to establish, the dissolution and precipitation rates of the phases that we are concerned with. In this case, this is just one example. We have been looking at the dissolution kinetics of heulandite, which is a zeolite.

The horizontal axis represents time, the vertical axis is log ion, the concentration is in essence, but I should note, the numbers are reversed, this should be 3, 4, 5, 6, rather than 6, 5, 4, 3. That was my mistake. The solid lines represent the changing composition of the solution that was actually measured. I should note also, the potassium lines should not fall over, it reached steady state.

Had the heulandite dissolved stoichiometrically, the composition of the solution would have been indicated for potassium, sodium and calcium and aluminum as is shown here. Clearly, this mineral is not dissolving stoichiometrically. It's extremely important, because it means that the surface of that mineral is forming either a gel layer or a variety of other mineral phases whose chemistry is not the same as the zeolite. That's important because the zeolites are the most sorptive phases that occur within the environment.

Because this surface is going to participate in the sorption process, we need to understand what that surface is and how it's affected by changes in the chemical environment or the thermal environment. And, so we are initiating work now to try to characterize that surface layer that results from these dissolution experiments. I should note also, these experiments are being conducted over a wide range of pH's and a wide range of solution ionic strengths and a wide range of temperatures.

In summary, what we have been able to demonstrate so far is that our modeling activities successful reproduce what is observed both in the field and in the laboratory for a certain range of conditions. However, there are conflicts that exist between what is predicted and what we actually observe. That's particularly true in the hydrological regime where we need to deal with the gravity component. It's also true in the chemical regime where we need to generate a much more substantial data base, particularly in terms of thermodynamic properties and dissolution and precipitation kinetics, and, in terms of the effects of man-made materials in the environment.

Future work will concentrate on dealing with these data needs, and also on the validation of our models. We want to emphasize in their validation, work in natural systems. We have to be able to demonstrate that our codes can predict the behavior of systems that have been around for thousands, or tens of thousands or hundreds of thousands of years, in order to have confidence in our predictions. That work is going to be difficult and time consuming, but it's clearly some of the most important stuff we have to accomplish in this effort.

Thank you.

MR. LANGMUIR: Bill?

DR. GLASSLEY: Yes.

MR. LANGMUIR: Are you comfortable with the thermodynamic data you've got for the zeolites that you are trying to model at this point?

DR. GLASSLEY: Not with the data that exists right now. There's a lot that we have to do. There are a couple of things that we need to do where we have significant problems. One is in the activity composition in relationships. It's clear that the zeolites that occur in the Echo Mountain site, their compositions are somehow related to the ground water chemistry or vice versa. The activity composition relationships for those solid solutions need to be defined in substantial detail. We've done that for clinoptilolite and we have a model that we feel good about. But all of the other zeolites are virtual unknowns at this point and we need to generate those models.

The basic thermodynamic properties of free energies and enthalpies, etc., for a few zeolites, we feel pretty good about. For maybe three or four. But, for most of them, we have a long way to go before we feel good about that data.

MR. LANGMUIR: Have you looked at the papers by Holland, an american mineralogist, early this last year on estimating entropies and enthalpies and a paper by Rimstead in a co-author where he's looked at free energies?

DR. GLASSLEY: Yes.

MR. LANGMUIR: It's as if they have got some good approaches to getting fairly decent numbers for zeolites as well as phyllosilicates by estimation methods.

DR. GLASSLEY: We are in the process of evaluating or comparing the different estimation methods that have been presented to see which ones are consistent with data that currently exists and we have confidence in, and which things appear to be problems.

That's an substantial effort. And, we are in the process of doing it, but we don't have any results at this point that would allow us to choose between the various estimation techniques that have been proposed.

MR. DEERE: Have you been able to identify any of the clay minerals yet that you feel may have precipitated on that fracture?

DR. GLASSLEY: No. We are--it's extremely difficult because the phases are very, very small. And, so, we have started an effort using the high voltage electron microscope the LBL to look at the structure of those phases, essentially looking at electron defraction.

And, the problem with that, although it looks as though we are going to be able to do it, the problem with that is that the energy of the electrons is such that it can modify the structure simply in the analytical process. And, so, we are trying to come up with techniques where we can actually measure the structure before this sample disintegrates.

It looks like we are going to be able to do it, but it is going to be pretty touchy. We don't know what the phases are right now. We suspect they are smectites, but we don't know to what extent they are interlayered and what kind of interlayers there are. That needs to be established.

We have done preliminary work with bentonites and well-characterized ones before, using that technique. And using the techniques developed there, it looks as though we will be able to look at the stuff we've seen on the fractured surfaces as well.

MR. DEERE: About 20 years ago, in the N-Tunnel, where the tunnel crossed a synclinal axes, there was water, the first water they had hit was flowing down along the axes and that was a zone where the rails in the tunnel gradually were being raised. And, I think over a period of months they took a total of two to three feet of excavated material out and then set the rails back down again.

Well the studies that were made--I believe at that time it was USGS, somebody here probably knows better than I. Dr. Corning, perhaps will remember. But, what they found adjacent to the syncline we had zeolites and in the axes that were swelling we were dealing with smectite. At that time we called it montmorillonite.

DR. GLASSLEY: Yes, that makes a lot of sense. That kind of behavior is something we will have to be concerned with during the excavation process. If you change the hydrological regime or you get into a region where you a dealing with relatively smectite rich environments, a lot of unusual processes are going to occur, including the swelling process and we need to understand that in substantial detail and particularly the chemistry of it as well.

MR. BLANCHARD: Our next speaker will be Dave Hobart.

DR. HOBART: Good morning, gentlemen. I will be talking about two topics today, radionuclide behavior at elevated temperatures as well as colloid characterization stability.

I'm the principal investigator on the solubility task at Los Alamos for the Yucca Mountain project. I'll be presenting data from my colleagues at Los Alamos as well as some data from Dr. Heino Nitsche at Lawrence Berkley laboratory who was under contract to take some solubility studies for us.

Solubility studies have provided solubility or concentration limits for dissolved species of several key radionuclides under expected conditions at Yucca Mountain. And studies at these various laboratories indicate that this migration may be controlled by a number of factors, including dissolution of the waste form, whatever that may be. We can make assumptions about what the waste form is a the present time. Precipitation of solubility controlling solids, there are the thermodynamically stable solids, and of course, the formation of soluble species and one minimum analysis or speciation of this would be oxidation states, and the formation of colloids, which I'll discuss in detail in a few moments.

My graphs might vary somewhat different from your packages, because I rearranged them slightly for logic. The nature of the compounds and solution species depends on several parameters. I indicated oxidation state earlier, and the nature in concentration depends on which ions are precipitating and what complexing ligands are present. Now, the main complexing ligand for actinides at Yucca Mountain is carbonate ion at the present time and I'll discuss that in detail to some extent. We also have to worry about what is the hydrogen ion concentration, pH of ambient conditions in the ground water as well as the redox potential, the E_h and of course the temperature which is the topic of my discussion this morning.

Let's talk about how we determine solubility, just the nuts and bolts type approach. Let me talk about these in reverse order right now, because it will match up with the graph I had. I'd like to talk about supersaturation first, or what we call oversaturation. Supersaturation is a specific term where we add an excess amount of some compound, in an acid, perhaps to a near neutral solution. And what happens is you have precipitation of insoluable material, and you monitor the supernatant as a function of time.

The other approach is from undersaturation. It's where you take a well-characterized solid, you contact it with your ground water solution and you watch it redissolve according to equilibrium and thermodynamics and kinetics. And, both methods should reach the same answer, and I've shown that graphically on the next overhead here, where again I like to use the term oversaturation rather than of supersaturation, where we put in a high concentration and watch it with time. And, what happens is we reach some kind of steady state which may or may not be equilibrium and indeed, from the undersaturation direction by dissolution of a well-characterized solid, we should wind up at the same point somewhere out here in time.

The reason we may not reach equilibrium for--particularly for plutonium 239 is we are talking about radiation damage, the radiolysis of oxidation products, so on and so forth, and we may not reach equilibrium but simply bracket it. In fact nature may never reach equilibrium under these conditions.

This solubility information is used to obtain good estimates on the upper limits of radionuclide concentration and is a source term for solubility studies. We can also use it to validate models, and that is the chemical component of transport model and for data base validation for things like EQ3/6 that they are using at Lawrence Livermore.

So, essentially, we are assessing the potential of radionuclide release, from a high level waste repository to the accessible environment.

Okay, let's look at some more nuts and bolts for some specific soluble experiments done by Dr. Nitsche. He used filtered ground water to extremes at the site J-13 and UE-25p#1. They have a broad range of concentration of carbonate. J-13 is assumed to be what we would expect in the vados zone, that's 10^{-3} molar carbonate ion concentration, slightly oxidizing conditions, a couple of millivolts. And low ionic strength as compared to UE-25p#1, which is from the carbonate aquifer, underlying the potential repository horizon. It is 10^{-2} molar in carbonates, substantial carbonate ion concentration slightly reducing in high ionic strength.

We are looking at supersaturated conditions for the three bad actors at the present time. That's neptunium, plutonium and americium. They have the longest half lives and will be around for many hundreds and thousands of years. We are looking at pH's ranging and bracketing the pH regions at Yucca Mounting, 6, 7 and 8.5. And we are looking at temperatures from room temperature, ambient temperature, up to 90 degrees celsius. At 95 degrees celsius, we expect the boiling point of water at the Yucca Mountain site. And, I won't go into details right now on the carbonate for the interest of time.

DR. LANGMUIR: Dave, has Heino done any research or has anybody done any research on possible reactions of the nuclides with the true vados zone kind of water, which is more saturated and more concentrated in salt species than either of these examples?

DR. HOBART: If you can provide me with a gallon of vados water, we would be glad to do some experiments.

DR. LANGMUIR: Well, I can give you an average analysis. You can create it yourself, we've done that. That's available.

DR. HOBART: Some experiments have been done at Oak Ridge with artificial waters, but right now we'd like to look at the two regions and extremes that are naturally occurring waters. And, I'd like to show you that it doesn't make a whole lot of difference whether we are using one water or the other the solubility--

DR. LANGMUIR: I guess what I'm saying is these extremes aren't extremes.

DR. HOBART: They are not extremes--

DR. LANGMUIR: They are not as concentrated as vados water tends to be.

DR. HOBART: We have no data a the present time on exactly what's available.

DR. LANGMUIR: On what's available. I can get it to you.

DR. HOBART: Here is a typical example of americium solubility experiment, and I think the first thing we want to do--well, this is a concentration versus equilibrium time in days. And, the first thing you want to notice is you don't go into the laboratory, throw your stuff in the beaker and wait three hours and get a solubility, which some people are doing and publishing. You can't even wait 40 days because different solids are forming, or solubility limiting, and this may not be a good number either, but it might be an upper limit, because we don't have infinite amount of time to watch these solutions. So, this gives you a typical value and a range for americium is around 8.7 times 10^{-9} molar, which is fairly low concentration.

Let's look at some raw data from Dr. Nitsche's laboratories in Berkley. Again we are plotting concentration, and this time we are looking at neptunium V, neptunyl montivalent ion at J-13 water at various temperatures. Now, there is a trend for pH here and not for temperature. And this is pH at 25, 60, and 90 degrees, and most of these will be the same slide so I have to go over the details.

Why we have a trend for pH is the following. The solubility living cells that are forming are these double salts of carbonate, sodium neptunyl carbonate. And, of course, as you go to the higher pH's, you get more carbonate ion available to precipitate these materials. So, that's the case with J-13. Again, I apologize these are not exactly in the same order as in your packet. But that was the neptunium data.

For plutonium (VI) now, a different oxidation state with different behavior, we have J-13 water at various temperatures and pH's. There is no apparent variation for pH, but there certainly is for temperature. And, the reason again is that we are forming a plutonium for a polymer or colloid, if you will and some carbonate species.

And, the reason we are doing this is we get the solid form in which is not a function of pH, but rather we are annealing crystallite structures and I'll talk about colloids in a few minutes and making it more likely that they'll precipitate.

Now, let's look at the oxidation state distributions of plutonium and this is at pH 8.5 J-13 water at three temperatures. This is a surprise which is no longer a surprise and indeed plutonium (V) seems to be the most stable oxidation state under environmental conditions, which would surprise most academicians who say plutonium (IV) is the most stale state. And, you can see here that the most predominant species at all the temperatures is indeed plutonium (V). Plutonium (V) normally disproportionates. It's like copper (I). It's these two plutoniums that react together makes (VI) and (V) and goes off about its business. But, here at such low concentrations, the kinetics are such that the plutonium (V) ions are separated or carbonate complex that they can't get together and react.

Let's compare two waters for plutonium oxidation state distribution and of course Dr. Nitsche is collecting data at the present time as we spea, essentially, except he's sitting in the aududience right now.. This is J-13 and UE-25 comparisons at pH7 at 25 degrees. Not a whole lot of difference. Again plutonium (V) is a predominant oxidation state under these conditions. Again we are looking at 10^{-2} molar carbonate versus 10^{-3} molar carbonate.

Quickly, here's americium (III) and J-13 ground water. I don't see any particular trends with either pH or temperature. And, one reason might be that sometimes with americium we are dealing with solid materials, americium colloid and a lot of unusual and strange behavior. The solids that are forming, however are hydroxycarbonados as indicated on the overhead, both the hexagonal and orthorhombic forms.

Let's talk about colloids. We are primarily interested again in the bad actors and the first most insidious colloid is plutonium (IV) and that's the one we are studying intensely. And, certainly colloids may contribute to radionuclide migration. What am I talking about? What are colloids?

The Betty Crocker cook book of definitions, colloid is a small particle which remains suspended indefinitely assuming you don't centrifuge it a number of gravities. And, we can further break it down to different kinds of colloids. Radiocolloids are indeed those colloids formed from radionuclides such as plutonium, americium and neptunium. And, I'd like to further define a natural colloid as essentially a small piece of dirt, if you will. I would like to at this present time change the term from pseudo colloid, because I don't think it's an accurate term, I think it's a misnomer, and call these other things complex colloids, because, indeed, that's what they are. That is a colloid resulting from a combination of natural colloid and radiocolloid.

While the study of colloid is just another level of speciation studies, and let me demonstrate what I mean by speciation. This is plutonium (IV) all in the same oxidation state, but different speciation. The one on the left is the chloride complex. If the lights were a little lower, you could see this better, but I think you can see it just fine here. This reddish color is the hexa-chloro complex of plutonium (IV). This is what plutonium (IV) really looks like when it's uncomplexed and that's in perchloric acid medium, which is a non-complexing ion for actinides in general.

Here's the nitrato complex. This looks like a solution but is indeed the sol. It's plutonium for colloid, this green color, highly recognizable because it usually winds up in all your solutions no matter what you are doing, with time. Again, you can see the colors with your eye, so you know we can get spectral information from this.

While this is not particularly important for this audience, but I want to briefly go over the formation of sol. And that is the first stage is hydrolysis. We have plutonium, a very happy plutonium (IV), which finds itself in the middle of a near neutral solution. Hydroxide ions start attaching to it, and you form oligamers and so on and so forth, and then this hydrolysis is then followed by colloidal polymerization. And this is the agglomeration of bigger and bigger pieces of these hydroxy things, making oxygen bridges and aggregates are formed. They do not get big enough to fully precipitate under certain conditions and fall out of your solution.

But, we can precipitate them by a number of methods, including in the sol gel process which is used at Oak Ridge to make fuel elements. By much in spectral characterization, and you looked at the various species of plutonium in solution with your eye, I'd like to remind you if everybody has got this in their wallet, I'm sure this is the plutonium (IV), (V) and (III) spectral region invisible. This is a visible region from about 300 to 800 nanometers. That's the other oxidation states.

What I'd like to point out here is this dotted spectrum here is indeed the uncomplex plutonium (IV), with this main peak about 4,600 angstroms or 460 nanometers. Overlaying, on this darker one is indeed a colloid spectrum. I would like you to pay particular attention at this 6,300 angstrom peak for the colloid plutonium (IV). That's a fingerprint that we can identify plutonium with. It looks quite a bit different from the aquospecies.

Well, what we did is we took the reflectant spectrum, a slightly different approach, but we get the same electronic information of high-fired plutonium dioxide. This is a fuel element crushed and light reflected off of it. Now, you can see, by comparing straight up and down, that each one of these peaks lines up quite well with what we get for the plutonium sol in the (IV) state. So, this means it has the same electronic environment.

What that means, is that indeed plutonium colloid sol is very similar to this material with a few water slapped around it. We've taken reflectant spectra of other plutonium (IV) compounds. They do not look like this. They look more like the aquospecies, with that main peak around 460 nanometers.

While we further investigated colloid with the electrochemistry, we can find out chemical information, electron transfer rates and read-out potentials, of course, whether we can oxidize or reduce colloid from the (IV) state to the even (V) or (VI) or (III) states.

Furthermore, we have studied the physical properties. We are collaborating with Bob Rundberg using an autocorrelator spectrometer to determine particle size. And, we are investigating particle charge also by electrochemical methods.

This is what you have in your packet, but it's kind of hard to see what's going on here, so I wanted to throw the raw data up. And, this is a spectral results of the reaction of plutonium (IV) colloid in this case zinc amalgamate. Again, it doesn't matter where the electrons are coming from . It could be an electra amd HBL with what's happening here is we see the spectrum--our old friend, again I cleverly put it in green. This is the colloid. And, as we reduce with zinc amalgam, you see this bluish spectrum forming which indeed is the same color of plutonium (III) in solution, which is a blue color. And the fact that we have a number of isospestics point here mean that we have a simple reaction from A to B. And, so we don't expect conditions at Yucca Mountain to be as strongly reducing as zinc amalgam, but certainly we can reduce the colloid. It's more reactive than most people might think under extreme conditions.

This is simply a plot of what we just saw, except this time by electrochemistry. This shows the rate of reaction versus applied potential. And you have to get pretty healthy--you have to get down her about minus one volt or so. That's a battery for all practical purposes, which you will not find in the environment. So, reduction of plutonium (IV) by this mechanism, will not happen.

Let me summarize the results from the solubility experiments first and then I'll talk about the colloid. We have identified controlling solids, in fact Dr. Nitsche has published some new solids which had formed the hydroxy carbonate forms in some of his solutions. And, they have not been identified previously by x-ray methods. We have looked into solubility behavior of plutonium and we notice it does not vary as a function of different ground waters, either J-13 or U-25 which goes back to your question. If the vados water is quite different, it may not make a hill of beans as far as it goes. We might look at this range of waters here. And, one thing we can do is look at concentrated dilute perchloric acid solutions, which we are also doing.

DR. LANGMUIR: The only important difference is going to be higher alkalinities in the vados water.

DR. HOBART: Yes. Well, again we have a baseline here, a bracket. And, if you give me a different water, I can do a couple of quick experiments and say, yeah this fits the trend, or we need to go back in the lab and do some more experiments with this particular water.

DR. CARTER: Dave, could I ask you a question?

DR. HOBART: Yes, sir.

DR. CARTER: What have done to characterize the chemical composition of the vados water once it may be able to interact with the radionuclides? I'm thinking particularly of vados water that's reactive with a container for example, may contain iron, chromium, nickel and this sort of thing. Has any work been done on that, or do you anticipate doing it? That to me would be the real water that you are interested in.

DR. HOBART: Yes, if we had some vados water to that. We are equilibrating, of course, our water with the containers and in fact we've found that teflon is not a suitable container in some instances. And, I have to defer any further elaboration on that question to Dr. Nitsche who's in the audience, doing this work, if you'd like after I finish here.

Plutonium (IV) solubility decreases as a function of increasing temperature, because we are getting colloidal salt formation where essentially annealing the crystals and they are forming a colloid. Np(V) solubility decreases without any increasing pH. We see no temperature dependence. Again this is because of the double carbonates which are formed. And, we see no general trend at the present time for americium which is still somewhat of a mystery. It's very difficult to americium chemistry. You have to do it in a glove box. At least at Los Alamos, we can work with plutonium and neptunium without using a glove box, if we are extremely careful.

We have shown spectrally and have published this indeed, that plutonium (IV) colloid is similar to high-fired PuO_2. The colloid is observed in ground waters. It will form in near neutral solutions. It's important to both sorption and transport studies. In time Pu(IV)-Colloid more stabilized to PuO_2 and completely dehydrate, and this is important in assessing radionuclide migration and talking about dynamic transport. And, of course the colloid is obviously stable under the expected conditions for the potential waste depository.

I mentioned dynamic transport, that's Bob Rundberg's task. I would also like to emphasize something that I didn't emphasize which I should have at the beginning of this talk, is that this data also feeds the sorption test which I think was on one of the slides and I didn't elaborate enough. Let me elaborate slightly on that.

In order to make a meaningful sorption test, you have to be below the solubility limit. If you are above the solubility limit, Arend Meijer's test, you will find that you are seeing not only sorption, but precipitation, and you can't differentiate between the two.

We want to extend the work to other radionuclides which have not been studied in near neutral solutions. These are all very common or most of them are most common metals.

You say, why haven't these been studied in near neutral solution, because the people that are interested are miners or they are corrosion chemists and they've got extremely basic or extremely acid, and there's also a lot of good analytical techniques you can use in both extremes, but there's very low concentrations of these materials at near neutral pH's, so we want to look at these.

We want to extend our colloid work, which we know we are getting. We are getting some americium colloid and we want to investigate these. And, other ligands which may be predominant in ground water including organic things like humic acids.

And, with that gentleman, I close and invite your questions.

DR. LANGMUIR: Dave, one of the things I didn't get from your presentation was what is the affected temperature, assuming the colloids are stable thermonamically in the environment of a canister in your field, what's the thermal stability of those colloids? Do they become less stable with increasing temperature or more stable with increasing temperature.

DR. HOBART: I showed one of my overheads, it shows with the higher temperatures, we get a decrease in concentration with plutonium.

DR. LANGMUIR: Okay, but then you have americium also decreasing but neptunium and plutonium (V) not.

DR. HOBART: Well plutonium (V) now is not going to be in the colloid form. See that's the soluble species. But, if it does form the colloid by disproportion over a long period of time, higher temperatures will anneal this colloid material much as you use any old a crystal will form bigger aggregates which may filter out through geologic medium. I believe that answers your question.

We are dealing with two faces of plutonium the (V) state and of course, the (IV) colloid.

DR. CANTLON: Based on what you've learned now, would you expect there to be greater or less or no different migration of these materials than you had thought before you started?

DR. HOBART: Well, we were surprised. I'm sure everybody in the room was surprised about plutonium (V) being the most stable state. Yes, we were surprised about that. We expected the normal behavior from neptunium (V) and certainly americium that will stand in the three valence state. No, there are not too many surprises here. And the concentration limits are reasonably low, like we might expect. But, you can sit around and guess all you want to until you actually go into the lab and measure it, nobody is going to be convinced.

DR. CARTER: Max, before you go on, I would be interested if somebody would like to comment on the possible characterization of the water layers in container--the real water you are interested in.

MR. BLANCHARD: Sure, as you may not immediately recognize right now our geochemistry program is divided into two components. One is done by Los Alamos which is the far field radionuclide transport. The other is a near field which is conducted by Lawrence Livermore, the rock-water-waste and waste package interaction. And I think Bill Glassley would be glad to address that.

Bill, would you care to make some comments on that? Please come up here and use this microphone or that one over there.

When you all go out in January to Lawrence Livermore, I think you'll find out a lot more detail about this particular subject.

DR. GLASSLEY: If I understood your question, you are particularly concerned with the composition of water as it might be influenced by container materials. One of the efforts we have underway now is to understand first the composition of water that could get to the container than what the composition of that water would be when it interacts with the container. What that water would be once it interacted with waste and was inside the container. And, then as it comes back out again, how will it interact with corrosion products, and how will that fluid then, when it gets into the environment interact with the rock system?

We are trying to understand that entire complex. The work that has gone so far has identified primarily the corrosion products that exist on various container materials. Work that is planned will look at the water that comes from interaction with those corrosion products, with the waste form, and then the kind of--once that product is established, how that will interact with the TOUGH system. So, it's kind of a sequence of steps in understanding the evolution of this thing, but it's very much a part of the project that we are undertaking as far as geochemistry is concerned.

DR. CARTER: And, I presume you are fairly early into it on comparisons?

DR. GLASSLEY: That's correct. One of the biggest problems is knowing which metals to use and then such a wide range of corrosion products.

MR. BLANCHARD: Dave, before you leave, would you see the court reporter, Scott, today, he needs to have some clarifications.

Okay, now, we are ready to go onto the next component, and it's the applicability of the geochemistry laboratory experiments to field conditions. There are two speakers from Los Alamos. One is Arend Meijer and the other one is Bob Rundberg. They share this about equal, except they were going to divide the topics approximately in half, their factors for controlling sorptive behavior is kind of a phase in, phase out.

I suggest that we take a break right about the time we switch from Arend to Bob Rundberg if that's all right with you Don. And, we will start now with Arend.

DR. MEIJER: As Max said, Bob and I are going to tag team this morning, and talk a little about the applicability of laboratory experiments to the migration of radionuclides in the unsaturated zone in Yucca Mountain.

I'll be talking primarily about static experiments. In fact, static batch experiments, and Bob will be talking more about dynamic experiments, column experiments.

Now, this is an overview of what both Bob and I are going to be talking about this morning. First of all, we'll talk about the physical and chemical processes that determine radionuclide mobility in the unsaturated-zone at Yucca Mountain and then separate from that grouping the main factors that control sorption behavior. And then, talk a little bit about how we determine sorption coefficients or how we investigate this behavior and then talk about the experimental determination of some other transport parameters in the dynamic experiments. And then, finally talk about how we might apply these things to the unsaturated-zone at Yucca Mountain.

These are the list of some of the physical and chemical processes that might determine radionuclide mobility in any ground water system actually including that associated with Yucca Mountain. First of all, there are the ground water parameters that have been discussed yesterday in some detail. So, that's the base line case. And then, in addition to the ground water flow parameters, we've got the parameters that are determined by the radionuclides themselves including the solubility that Dave Hobart just talked about and potential colloid formation and the transport of colloid. We also are concerned with diffusion rate and osmotic potential. The diffusion rate relates to things like the ^{14}carbon discussion that you heard yesterday, as well as the radionuclides that might be dissolved in ground water. We won't spend a lot of time talking about this in this or Bob's presentation. And then, finally, we've got the question of the interaction of the radionuclide with the host rocks and any fracture linings that might be in the system. And, this interaction could take a number of forms. Bob will discuss some work on anion exclusion and colloid filtration and I'll concentrate on the sorption reactions. Co-precipitation is also a possible mechanism, but we won't spend much time talking about that today. So, this is where Bob and I part the plays and I'm going to talk about the sorption part of it and then Bob will carry on with his dynamic experiments.

These are some of the main factors that control sorption behavior. First of all, the primary factor is the type and the adsorption capacity of the mineral phases or any phase that might be in the rock system including fracture linings and such. The kinds of reactions that can take place will control the behavior of different radionuclides for things like the alkalies and alkaline earths. Ion exchange in zeolites and clays would be very important and that would include things like cesium and ^{90}strontium, et cetera. For actinides and some of the other fission products, surface adsorption may be more important and surface adsorption, in particular, on things like iron and manganese oxide and oxyhydroxide phases, as well as some of the major mineral phases that are in the rock including feldspar and various silica phases and the volcanic glass, anything else that might be there. However, zeolites and clays and these sort of phases will likely dominate adsorption behavior. So, those are the ones that we're going to concentrate on.

This is a rather complicated slide and it's, in fact, towards the end of your collection of view graphs. It may, in fact, be the last view graph. I put it up here to present a summary of my discussion and a little bit of the logic of how we go about this before getting into the actual experimental data. The idea is that we'd like to obtain some measure of the adsorption coefficient for a given radionuclide in either a part of Yucca Mountain or a certain mineral phase, et cetera. In order to do that, we can take a number of different approaches. First of all, we have to make sure, as Dave Hobart emphasized, that the solutions that we work with are under-saturated with respect to any solid compound of the radionuclide that we're working with and we can test that in various ways and I'll talk about that in a bit. And then, you decide on which sort of approach to use.

The approach that's generally been used at Los Alamos over the years is the one furthest to the left here, the green color. Basically, an empirical approach in which a rock sample from Yucca Mountain is reacted with a ground water composition from Yucca Mountain which has been spiked with radionuclides of interest and then these two are reacted for some period of time, subsequently separated, the concentration in the solution phase is measured, and in many cases the concentration of the solid phase is measured and then an adsorption coefficient, an R_d, is calculated for that rock and water composition at some concentration of the radionuclide used in the experiment. If a number of different concentrations are used, then you may be able to define some isotherm parameters for that rock and that ground water composition.

MR. WILLIAMS: Is the rock ground up or is it core?

DR. MEIJER: These experiments have mostly been done with ground-up rock, but I'll get to some specifics on that in a bit.

This approach is fine as long as you are familiar with the variation in rock composition and water composition within Yucca Mountain at the present time and are able to predict what might happen to these compositions in the future. So, ideally, you'd like a more general approach than that. One way to go is to start taking the rocks apart and looking at the individual mineral phases in the rock and the adsorption behavior for the various radionuclides on these individual mineral phases. And, that's this approach outlined in orange here.

In this approach, you'd select the mineral phases that dominate the adsorption behavior and, as I mentioned, zeolite and clays are one group and then iron and manganese oxyhydroxides are likely another group. So, you'd concentrate on those and obtain isotherms for each of the major or important radionuclides on these mineral phases. So, you end up with the ability to predict adsorption behavior on that mineral phase under a range of conditions depending on how you set up these experiments. Now, ideally, you'd like then to combine the results on individual mineral phases into some set of predictor equations, you might say, to come out with an adsorption coefficient for a reconstituted rock, if you like, which then is a function only of the water composition, but you can vary the mineralogy and the radionuclide concentration in the predictor equations and predict this R_d. At the present time, we don't have the capability to do this, but it isn't necessarily an impossible task and we are working towards being able to reach this point.

Finally, you'd like to ultimately have some sort of theoretical means of predicting the adsorption coefficients and that's the far right hand part of this slide. The theoretical means that I've put on the slide here basically involve things like ion exchange models or ion exchange reactions in zeolites and clays and these reactions are fairly well defined. Surface complexation models for the iron and manganese oxides and oxyhydroxides, as well as the silica minerals and framework aluminosilicates. And then, in addition to data on speciation, which Dave Hobart talked about, as well as data on the models for the minerals surfaces that are actually going to be present in Yucca Mountain, one might then be able to hopefully put all this together into some geochemical code such as EQ3/6 and calculate adsorption coefficients based on a more theoretical approach and thereby be able to calculate these things on the basis of ground water composition, mineralogy of the whole rock, and concentration of the radionuclide. I doubt that we'll be able to reach this level of understanding within the time frame of this project, but the way that we're going about it is we're pushing in this direction and any distance that we get in this direction will allow us to investigate and, to some degree, validate the results that were obtained by this simpler approach. So, that's really the value in this at the moment.

DR. LANGMUIR: All right. Have you tried this with any of the simpler adsorping species, the species such as radium or strontium which have the simplest behavior, this mix across these different approaches?

DR. MEIJER: Yeah. That's a good question. We have data for cesium and strontium and for different rocks that have different mineralogic compositions. Adsorption coefficients for these radionuclides can generally be deconvolved, if you like, into the mineralogy or correlated with the mineralogy of the rock. So that a rock with 80% clinoptilolite or some zeolite will have adsorption coefficient which is some factor of 5 or 10 larger than a rock that only has 20% zeolite. So, in that simplistic way, we have done that sort of analysis, but it's not really based on pure mineral data. It's just based on a series of rocks that were analyzed that had different amounts of these phases and thereby -- and also different values for adsorption coefficients and you're able to correlate one with the other.

DR. LANGMUIR: You should be able to do all of these things now, I would think, or come close to it with respect to the simple radionuclides, the radium and the strontium and the cesium, all three.

DR. MEIJER: You mean do up to this point?

DR. LANGMUIR: All three?

DR. MEIJER: Well, perhaps and --

DR. LANGMUIR: If it's going to work at all. If you can, in fact, combine the effects of individual minerals in the total rock, which no one has yet proven to me you can. We're trying it, too. But, going beyond two adsorping minerals, it seems very difficult to make it work, so far, even for the simpler ions.

DR. MEIJER: No, I grant you, I think that this is going to be a difficult thing to achieve within the time frame of the experiment, but at the -- are you saying that we can now take one of the rocks at Yucca Mountain and predict what the strontium adsorption coefficient is going to be based on pure mineral data? Is that --

DR. LANGMUIR: I didn't put Yucca Mountain in this yet.

DR. MEIJER: Okay.

DR. LANGMUIR: But, just conceptionally, this approach being applied to a rock in which you have perhaps two adsorping phases, it should be something we could do or come close to doing now. Maybe not with Yucca Mountain rock at this point. Coming across from these several approaches.

DR. MEIJER: Okay. Yeah, I would agree with you. I think that -- and then I would imagine in the next year somebody is going to write a paper to doing just that. But, I think you realize that this is pretty much the state of the art stuff over on this side and we're concerned primarily with the Yucca Mountain end of the story and our papers likely will reflect that. Okay.

MR. WILLIAMS: Have you looked at the impact of grind on R_d?

DR. MEIJER: The impact of grinding?

MR. WILLIAMS: The impact of grind -- the grain size distribution that you end up with in the grinding process on R_d?

DR. MEIJER: Yes, we have.

MR. WILLIAMS: What is it?

DR. MEIJER: Well, we've ground the -- up to various size fractions, all the way down to something like 30 microns. I mean, we've taken and ground these things up and then separated out sized fractions and looked at the adsorption behavior of each sized fraction for a given element, such as strontium or cesium, and it turns out that below about, oh, I'd say, 70 microns, the adsorption coefficient starts to deviate from the adsorption coefficient you get at sizes greater than 70 microns. From 70 to 500 microns, we don't see any effect of grain size. From 70 on down, you start to get some. It's not clear that the effect is due to the grain size. It may also be due to enrichment of the finer grain material in clays or, you know, some of the strongly sorbing phases. So, what we do in our experiments is we restrict the grain size we use to that between 100 and 500 microns to get away from this problem. I also ought to explain why we think that the 100 to 500 micron fraction shows little effective grain size and that is the minerals that are in these rocks are very fine grain. They're on the order of 10 microns, you know, 5, 10, 20 micron size grains. So, when you take a grain size fraction that's 100 microns, you already have multi-mineral aggregates in each one of the grains that you're using in the experiment. So, you're not crushing individual grains, if you like; you're crushing aggregate. You still end up with an aggregate of mineral phases. And, that's likely the reason we don't see variation in sorption coefficient with size above 100 microns.

DR. LANGMUIR: But, there's another side to the whole problem of grinding, of course, too, which you know and that is that when you grind, you're exposing mineral surfaces to solution which will not be exposed in the rock in situ. When the flow is dominately in fractures, you're not going to be getting this kind of exposure to those particular minerals, and when it's in matrix, you may not either. So, whether or not it's a representation of the two rock behaviors, it's debatable.

DR. MEIJER: Well, I have some slides that will address that for you. This was only intended as a summary, but I think we may have overdone that summary.

What I'd like to do now is get into some of the experimental work on sorption coefficients and I should explain that I use the designator R_d instead of K_d as a personal preference since the R_d's reflect the experiment and aren't necessarily equalibrium numbers, whereas the K_d I normally try to associate with an equilibrium situation. I'm not saying these experiments aren't under equilibrium conditions, it's just that we'd like to prove that before we actually say that they are. Okay.

So, what we're going to do now is talk about batched crushed rock experiments, some experiments on solid rock wafers, and I'm going to throw in an experiment on one crushed rock column to anticipate some stuff that Bob is going to talk about. We're going to obtain the adsorption coefficient for each of the important radionuclides under actually the range of anticipated conditions, whatever that range may be, including ground waters from the unsaturated-zone. And then, at some later date, we're going to investigate the sorption kinetics for each of the radionuclides for the actinides that may become a factor. And, after I've discussed the experimental results, I'm going to talk a little about how we might go about validating and extrapolating some of the data that we've obtained experimentally. Part of that will involve discussion of how we deal with experimental artifacts and then the other part is the discussion of this more theoretical approach that I discussed in the summary. So, I'll go ahead and get on with the experiments, the R_d experiments.

Just so that we're all talking about the same thing, I want to discuss in the next couple of slides how these batch R_d experiments are actually done because these are the numbers or the results that are reported in the SCP and in the EA. There are tables in both of these publications for each of the important radionuclides in contact with each of the rocks and those numbers were done using this approach.

Okay. First of all, we choose some appropriate rock sample and ground water composition. For the most part, this work has been done with J-13 ground water. A number of experiments have also been done using other ground waters from Yucca Mountain including the ground water from the paleozoic aquifer and I think it's Well H-3. We also have done some experiments involving artificial waters that we have put together so that we end up with a range of ionic strengths that may be appropriate to the unsaturated-zone. And then, we decide what radionuclides you want to stick in this experiment and the concentrations, of course, are going to be determined by the solubility constraints.

Then, we have to decide on appropriate atmosphere. For most of the elements of interest, the atmosphere, it's just ambient atmosphere. For some of the elements that are sensitive to redox properties or pH properties, we have to constrain the atmosphere during the experiment.

Then, we have to decide on a water/rock ratio and this is somewhat a difficult question because in Yucca Mountain the water/rock ratio may be quite -- let's see, have I got that right? Yeah, the water/rock ratio may be quite low in the unsaturated-zone, for instance. Well, in order to do these experiments, we need enough solution in order to analyze the concentration of the radionuclide in the solution. So, chances are, the experiments that we have done have been done at higher water/rock ratios than might apply directly to Yucca Mountain. So, we have to come up with some understanding of the effect of water/rock ratios on the sorption coefficient.

And then, finally, we have to decide how long to do these experiments so that we achieve what we believe to be some metastable state and perhaps an equilibrium sorption state. Okay.

So, once we've done all of that, then we develop an experimental technique and this is not trivial because there are a number of potential artifacts that come into this and that I'll talk about. And, you obtain the sorption ratios and if you do these experiments in a number of different concentrations, you may be able to derive sorption isotherms or obtain sorption isotherms. And, from this sort of information, then at some point we're going to be able to put together a coefficient of -- a matrix of sorption coefficients for the various hydrologic units within Yucca Mountain and the conditions anticipated for the site. And, we may be able to come up with some predictive equations for fracture surfaces, sorption on fracture surfaces, by the work or through the work on pure mineral phases.

What I'd like to show you now is some examples of the kinds of experimental data that we've obtained. Here's an example of some data on a zeolitic tuff involving the sorption of technetium and this was done in J-13 water, by the way. It's not on this log, but it perhaps should be. It turns out that technetium doesn't sorb very much to Yucca Mountain zeolitic tuffs. In fact, the R_d -- and in here it's a K_d -- but perhaps this should be R_d is .2 ml/g, a very small number. But, it does offer you some positive number to retard the movement of technetium. What we're plotting here, by the way, is the concentration of technetium in the solid versus the concentration of technetium in the solution that's in contact with that solid, the tuff. We did this at several different concentrations, as you can see here with these experimental points, and it turns out that these sorption -- or the isotherm or technetium on this tuff is linear up to this concentration which is good to know.

DR. LANGMUIR: Is pertechnitate unaffected by competition with other anions, for example, the effects of pH, changes in -- you've done this also with different water/rock ratios? I mean, there's another 20 variables.

DR. MEIJER: Oh, I grant you that.

DR. LANGMUIR: It -- to draw a line.

DR. MEIJER: No, no question about that, at all. The problem is that you could do 10,000 experiments in this game of -- and still not answer all the questions. So, we concentrate on trying to understand a limited number of systems that we had in the past first and then, as we get some sensitivity to what the controlling parameters are, then we'll investigate those parameters. And then, we're in the process of doing that now.

DR. LANGMUIR: Because the danger that someone is going to take .2 ml/g and throw it in a transport code and assume that's it for technetium and we're done.

DR. MEIJER: Um-hum. Yeah, oh, you're right.

DR. LANGMUIR: And, that's the big, big danger.

DR. MEIJER: Well, all you can do is write this stuff into the results and say this is where this rock under these conditions, and if the transport modelers choose to ignore that, then there's not too much I can do.

DR. LANGMUIR: Which they will unless you tell them otherwise.

DR. MEIJER: Well, but -- now, presumably, they can read, but we'll -- I really do like transport modelers.

Okay. Here's another one that shows a little different effect. In this case we have the sorption of strontium onto a devitrified tuff, again in contact with J-13 water, ambient temperature in air and here we have a larger number of data points. Again, we're plotting the concentration in the solid logrithmetically against the concentration in the solution. This particular tuff is made up of dominantly of alkali feldspar and quartz. It has a little bit of mica, a trace of smectite, and a trace of hematite. For strontium, these are likely not to impart, but at the moment we can't really judge that.

All right. What we see then is that over a considerable range the isotherm for strontium is linear and near linear, but as we get to higher concentrations, it falls off the linear curve and, in fact, can be fit fairly well with a Langmuir isotherm. The last data pointed out here clearly falls off that Langmuir isotherm and likely reflects precipitation. We're getting into the range here at which strontium carbonate likely will precipitate. Be aware that this is a concentration in the solution of moles per milliliter, not moles per liter. Okay? So, in terms of mole per liter, this would be more like 10^{-3}. So, this then gives us the ability at least to interpolate the sorption coefficient over this range of concentrations for this particular rock/water system.

And, I probably should talk to you, Don, before I put this next one up, but this is the sorption of neptunium on zeolitic tuff and again here's the mineralogic composition of the tuff. It's largely clinoptilolite with a fair amount of opal-CT, some smectite, alkali feldspar, quartz, and a relatively -- well, a very small amount of geothite which I believe is going to turn out to be a very important amount. Same coordinates. What we've done is a number of experiments at different solution computations, as you can see here. We were able to fit this with a 6 parameter Langmuir isotherm -- just kidding. See what your response to that was there. Anyway, we had a little trouble with the graphics here. We probably could do well by overlaying -- I don't know if this will work or not, but this is the kind of curve that we would fit to this. Okay? Maybe, this confuses the issue more than I should confuse it. But, at any rate, you've got a fairly good Langmuir fit on the neptunium, as well. And, again you have a data point up here that's well off of this Langmuir isotherm fit.

DR. LANGMUIR: I'm not sure what you're isotherm fits accomplish in so far as the isotherm is basically going to be an empirical equation with fits and points and it doesn't tell you what the processes are for the -- on the serving surface which you almost have to know to be able to predict things effectively. You have to know what the processes are.

DR. MEIJER: I fully agree with you and we're going to get to that in a bit. But, the isotherm basically gives you a few parameters you can use; in fact, basically two independent parameters or a constant so that you can fit this curve and predict the R_d in this system with a limited number of parameters, if you like.

DR. LANGMUIR: Until you change the pH and a few other things?

DR. MEIJER: Right. No, I agree with you and that's a problem that I'll be getting into in a minute. Anyway, this one point up here that's off of this curve turns out to correspond almost precisely to the solubility limit that Hieno Nitche has determined for the solubility controlling neptunium compound which I've written here as $Na_3NpO_2(CO_3)_2$. Okay. So, it looks as though at this point our experiments are over-saturated and -- well, we've defined that in this and corroborated his solubility measurement.

Okay. So, what I'd like to do now is get on with discussion of the validation and extrapolation of experimental R_d data and at first I'd like to talk about potential experimental artifacts. It's not that we're the only ones that have these sorts of problems; everyone who does sorption experiments is subject to these kinds of artifacts and presumably the better results reflect more intensive consideration of these artifacts. There's controversy in the literature over various kinds of data and a lot of that controversy revolves around these artifacts.

Here's an example of a potential artifact. It involves the adsorption of americium to the walls of the container in which we do these experiments and in this particular case it was a teflon bottle. So, what we did is we, in this simple experiment, just took some J-13 ground water, spiked it with ^{241}americium and put it in a teflon container, shook it for a while, and then measured the concentration of ^{241}americium in this container at different time intervals. Initially, the concentration in the container was 7.1×10^{-12} molar. After one day, this had gone down slightly, 6.7×10^{-12} and then after three weeks, it's down to 4.5×10^{-12} molar. I.D. here refers to the isotope dilution technique which is the best technique for the analysis of ^{241}americium and, fortunately, Los Alamos has got a history of analysis of actinides by those techniques. So, we can get very accurate data.

Well, the bottom line here is that in three weeks we lost on the order of 35% of the americium to the walls of the container. The implication is that if you do a sorption experiment and you only measure the concentration of the radionuclide of interest in the solution that you take out of this container assuming that the rest of the radionuclide is on the solid, you may be off because in this case 35% of it was on the walls in three weeks. So, you have to take this into consideration. Alternatively, you can measure the concentration in the solid, of course.

Here's another set of americium experiments and this one relates to the question of over-saturation that Dave Hobart referred to earlier. What we've done here or what I've done is I've assembled a number of earlier experiments involving the adsorption of americium onto a number of different tuff samples from Yucca Mountain and that's what these numbers relate to here. This is the well number, G-1, and this is depth in G-1 in feet that the sample was obtained. And then, we have a set of sorption coefficients in milliliters per gram and desorption coefficients and the concentration of the americium solution when the experiment was initiated.

Well, the earlier experiments, as you can see, have adsorption coefficients that are quite variable. They go all the way from 79 to 14,000 and, although these are all large numbers and suggest that americium is not going to be a problem, we'd like to know why on the same rock type -- and these, by the way, are all devitrified tuffs -- why do we have that sort of range of sorption coefficients? Well, part of the problem relates to the concentration or the solubility of the americium in this system. Just recently, we -- well, in fact, Dave Hobart talked about the americium solubility and it turns out the solubility of the americium controlling solid is on the order of 10^{-9} or 10^{-10} molar in this sort of system. That is J-13 water at pH -- I think this one's 8 -- most of these are 8.5, but anyway between 8 and 8.5. That indicates that most of these experiments were over-saturating with this particular solid and that may explain why, you know, some of these numbers are lower than they might be. The experiment we did was at 10^{-12} molar which is well below the solubility of americium. And, in that case, we end up with a sorption coefficient of 14,000 which fortuitously happens to be the same as the largest coefficient obtained in these earlier experiments.

At any rate, we're comfortable now that americium is not a problem in terms of adsorption or sorption potential in Yucca Mountain. It's going to stick like crazy. The remaining question is how might americium be adsorped to colloids that might be transported in Yucca Mountain. If it sticks this strongly to the rock, it's obviously going to stick to natural colloids, as well. And, that's an issue that remains to be investigated.

DR. DOMENICO: Have you tried -- based on those numbers, I agree. But, have you tried these experiments on zeolites that have had water knocked out of them, dehydrated, albeit under the temperature effects?

DR. MEIJER: We haven't tried them with dehydrated zeolites. We have tried other experiments with dehydrated zeolites and I'm glad you asked that question. There's another group in Los Alamos that's investigating the effects of dehydration on the structural properties of zeolites and clays and probably iron oxides, as well. And, what they're finding on their dehydration/rehydration experiments is that there really isn't that much of an effect. And, they've also done -- or actually, we've done some sorption experiments on zeolites that they had dehydrated which we then rehydrate and do a sorption experiment and these experiments are done with strontium, cesium, and barium, not americium. And, the effect is almost unnoticeable.

DR. LANGMUIR: Arend, how high a temperature have they gone on the dehydration?

DR. MEIJER: Well, that's probably a question for someone else to answer, but it seems to me they've gone up to a couple of hundred degrees anyway and in some cases they've gone up to 500 degrees. So, they've really beat them up, no question about that. And, the effect seems to be minimal. So, this obviously -- the stuff is not written up yet and it's in progress, but the preliminary conclusions are that that's not a significant factor.

DR. DOMENICO: That's based on the fact that they were rehydrated?

DR. MEIJER: Yeah, and you have to rehydrate them in order to do the sorption experiment.

DR. DOMENICO: That's what I mean.

DR. MEIJER: Yeah, yeah. But, I mean, they were dehydrated. The x-ray defraction was done on the dehydrated sample and then they were rehydrated and they were re-analyzed and they came back to -- I mean, they lost some volume on hydration, but then on rehydration, the volume came back and they had the same -- essentially, the same x-ray pattern. Dave Bish is the person at Los Alamos that's primarily responsible for those dehydration/hydration experiments and I'm sure he'd be glad to talk to you about that.

Then, we get into this question of the effect of rock crushing on the experimentally measured sorption coefficients. What we have here is a set of data that was obtained on two different types of samples and actually there are three different rock samples in two different forms and the experiments were done with three different radionuclides; barium, cesium, and strontium in at least two of these and in this third one we only get cesium and strontium. The set of experiments was done involving a solid wafer of each one of these rocks -- well, pillbox shaped wafer, if you like. And, the sorption coefficients were obtained on these wafers, each of these wafers, for each of the radionuclides. And then, this same rock was crushed and sorption coefficients were obtained on the crushed material. And, as you can see in this case, in most of these instances the differences are not that substantial. And, the main one here is this cesium difference and if you're familiar with these kinds of experiments, you'll realize that the difference between 2400 and 14,900 is not difficult to explain since this number represents a very small amount of material in the solution phase. And, if you have a little bit of colloid involved in the experiment or that stays with the solution phase, then you can explain this difference here.

DR. DOMENICO: How do you get away from the pure strontium or pure cesium in terms of your initial starting material?

DR. MEIJER: These were done with all three of these at the same time.

DR. DOMENICO: Together? Simultaneously?

DR. MEIJER: Right, right. So, for these particular elements then or radionuclides, the crushing doesn't have a substantial impact; however, I should add that the crushed material is pre-treated with the ground water that's going to be contacted with it, the spiked ground water that's going to be contacted with it. So, it has some chance to react with that crushed material before we then add another aliquot of ground water that has this spiked material. So, in a sense, we're -- well, preequilibration is not the term that we like to use, but for pre-reacting the rock, if you like.

DR. LANGMUIR: One has to assume then that the crushed material is going to expose the same minerals to adsorption that would occur by diffusion through the wafer?

DR. MEIJER: Um-hum.

DR. LANGMUIR: Which infers matrix type transport in the system.

DR. MEIJER: Yeah.

DR. LANGMUIR: It still doesn't explain what's going to happen in the fracture yet, though.

DR. MEIJER: Oh, no, I grant you -- we're not even sure what all the mineralogy of the fracture is going to be and the way that we're approaching that, as I mentioned earlier, is to study the mineral phases that we believe are going to be on the fractures individually and then at some point try and put the sorption coefficients together for whatever proportion of each of the minerals around in a given fracture filling.

Okay. In addition to this wafer work versus crushed work, we've got a result on crushed rock columns for strontium that's also of interest. In this case, a crushed tuff was packed in a column and J-13 water spiked with strontium was eluted through the column and this is the elution curve for that strontium in the column. And, basically, you can model this elution curve -- in fact, this curve is based on a batch sorption coefficient obtained for this sample and the elution of tritiated water in this particular column. So, the fact that that curve fits the data very well indicates that the batch sorption coefficient is giving you a number at least that's appropriate to the flow regime that you see in this particular column.

DR. DOMENICO: How many milliliters in a pore volume?

DR. MEIJER: I think in this case there was five -- on the order of five milliliters for the common volume. A small column.

DR. DOMENICO: How long did you have to wait for that breakthrough?

DR. MEIJER: A long time. Yeah, it was a long time. That's one of the problems of this kind of work is that these experiments take a long time when you're dealing with an element such as strontium that adsorbs onto the sample. In this particular case, the sorption coefficient was on the order of 50, I think. If the sorption coefficient is 1400 or 20,000, then you have to wait for the next 10 years or longer for this thing to break through and it's just not an experiment that's do-able.

Okay. So, the bottom line then is --

DR. DOMENICO: Is that C over C_0 or C over C max on that left axis?

DR. MEIJER: C over C_0. It's C over C_0, but it was normalized. Okay.

All right. I probably ought to move on a little more quickly here. Another experimental artifact I mentioned earlier on is the question of water/rock ratios, and early on, on a set of experiments that is six years, seven years ago, a set of experiments was done to evaluate the impact of water/rock ratios, variations of water/rock ratios on sorption coefficients that were measured and two different samples were analyzed. One was a divitrified tuff and one was a zeolitic tuff. For the divitrified tuff, the data could be modeled with a Langmuir isotherm. That is, the different water/rock basically reflected different masses of the radionuclide that are able to contact the solid and you could model those variations with a Langmuir isotherm. Basically, you're dealing with different solution concentrations, if you like, or you can look at it from that point of view.

However, for zeolitic tuffs, the situation was quite different. For zeolitic tuffs, the sorption coefficients actually went up with water/rock ratio. It increased with water/rock ratio and this was not what you would expect theoretically. So, there's obviously a problem here. So, we re-did these experiments on a zeolitic tuff from G-4 from the Callico Hills unit and first we did some ultracentrifugation experiments thinking that we could take out whatever colloid or whatever might be in the solution phase that could be causing this increase with water/rock ratio, but we were unsuccessful. As you can see, the sorption ratio for barium, for instance, at 5/1 -- that is, 5 milliliters to 1 gram of rock -- is quite a lot smaller than it is for in the case in which we have 30 millimeters to 1 gram of rock. Well, my suspicion was and other people have said this, as well, that likely we have colloids resulting from the actual agitation of the sample during experiment and we know that zeolites are soluble and so are the silica phases that are in the zeolitic rock. So, we end up with very find grain colloids that we simply can't centrifuge out. With sorption coefficients this high, it doesn't take very much of that colloidal material to influence adsorption coefficients.

So, we decided to do ultrafiltration experiments thinking that if we got a small enough pore size in the filter, we might be able to filter these colloids out. Well, we did somewhat better. I mean, now the ratios simply have stepped up to even larger values, but we still see a range and the suspicion is that we need to use a yet smaller pore size in our filters and if we do that presumably at some point we're going to be able to separate out this, what I believe to be, a colloidal component. But, we're working on this and the story is not yet complete.

Well, now, I'd like to get on to the mechanistic studies or what I call mechanistic studies. Mechanistic studies refer to the idea that we're going to study the way that a given radionuclide sorps onto mineral phases that might be in tuffs at Yucca Mountain, look at the mechanism. Well, first of all, we can't study all the mineral phases right off the bat. So, we want to concentrate on those phases that have the greatest potential for sorbing the radionuclides of interest. So, we select key minerals and I'll tell you in a minute how we do that. And, we characterize those key minerals, characterize their surface properties, and a whole set of other properties in the case of things like iron oxides and we -- and we need a whole bunch of other parameters. We obtain isotherms for each of the important radionuclides on each one of these key minerals and, in addition, we'd like to investigate the actual structure of the species as its adsorbed to the mineral. That is look at the experiment that we're doing, take a mineral phase, adsorb the radionuclide to it, and then take that and investigate it spectroscopically somehow to see what the nature of the complex is that's actually adsorbed to the surface because that's important for modeling purposes. And then with all this sort of information at some point we'll be able to develop models for sorption behavior. Okay.

With these sorts of models then, we can start to re-evaluate the existing data base on this whole rock sorption coefficient data that's in the SCP and in the EA and that we're still obtaining. And, we may be able to develop predictive capabilities which then will give us some idea of what the sorption coefficient is going to be under a range of conditions that we may not have covered in our experiments.

Okay. Let me show you one example of this kind of state and that example is going to involve neptunium adsorption. We've chosen neptunium because it's fairly soluble. It's one of the more soluble actinides and so it's easier to work with from an analytical point of view, but it's also an important radionuclide. So, first thing then is to choose these key minerals. So, what we did initially is we obtained or formed, made a series of pure mineral separates and that included hematite and iron oxide, geothite. We made the geothite. The hematite was obtained from a vendor. We obtained some pure hollandite from a mine and this was measured with XRD, x-ray defraction analysis, and it turns out to be essentially pure hollandite. Romanechite, another manganese oxide. And then, some calcites, both natural and synthetic. A montmorillonite from Cheto, Arizona. Actually, it's from Chambers, Arizona, and the Cheto Mine at Chambers, Arizona. And then, finally, a clinoptilolite. We did these experiments in a buffered solution, buffered at a pH of 8.5 with a sodium carbonate/bicarbonate buffer. It was in J-13 water. We have not corrected any of these for differences in surface areas, but this is a first cut and based on the appearance of each of these separates under the microscope the surface areas are in the same ballpark. We have now measured these and they turn out to be in the same ballpark.

Okay. The bottom line here is that the iron oxides and oxyhydroxide have very high affinities for neptunium, the manganese oxide somewhat less, and then the calcite and montmorillonite, and clinoptilolite considerably less. So, from our point of view then the key minerals in this case would be the iron and manganese oxides and oxyhydroxides.

The values for clinoptilolite and montmorillonite need to be investigated further because if it turns out clinoptilolite does indeed have a K_d or an R_d of 30 when it's in contact with Yucca Mountain that is J-13 and other Yucca Mountain ground water, then that will be a substantial sorption coefficient and we probably don't need to investigate this element in detail, but we need to look at that in more detail.

What I'm going to do now is look at the nature of the complex of neptunium that might be on the geothite surface. We did a set of experiments involving geothite and neptunium in anticipation of an EXAFS experiment and I'll be talking about that here.

First of all the EXAFS experiments and EXAFS experiments basically refer to the spectroscopic characterization of a complex on the surface of a mineral using a monochromatic x-ray beam which is scanned over a range of energies and we look at the absorption of that beam by the element of interest. In this case, it's neptunium. In order to get any signal out of this above noise, you need to have enough neptunium on this geothite to, you know, be able to get a decent signal. The first thing we had to do is figure out how we could maximize the top surface coverage of neptunium on geothite in order to optimize the conditions for this experiment. So, this then is a pH edge or adsorption edge, you might call it, and what's plotted here is the sorption of neptunium on geothite at different pH's, the percent of neptunium in solution adsorbed onto the geothite. As you can see, once you get up above, oh, 7.5 or so, most of the neptunium is on the geothite. So, for EXAFS' experiments, we chose a pH somewhere around 7.8 -- between 7.8 and 8, obtained a pure geothite sample, contacted it with a buffered solution with a pH of 7.8, spiked with the neptunium. The neptunium then sorbed onto that geothite. The geothite was separated from the solution. A slurry of that geothite was put into a cell, taken over to the Stanford linear accelerator, to the synchrotron facility, and the EXAFS work was done there.

Okay. So, I'll show you a little of that EXAFS work. The title on this slide is NEXAFS and what that basically refers to is the near edge x-ray absorption fine structure. Okay? EXAFS actually refers to something a little different. It refers to -- EXAFS refers to extended x-ray absorption fine structure. So, NEXAFS is the near edge stuff and EXAFS is a little further out. Okay.

What we have here then is the absorption spectrum for neptunium on this geothite surface. That is the degree to which this monochromatic beam over a range of energies was absorbed by the neptunium on the geothite surface. First, we have a reference material. This is the NpO_2 solid, a crystalline NpO_2. Then, here's NpO_2^+/Solution, the neptunium in solution. Here is neptunium adsorbed onto the geothite. The first thing you notice is that the NpO_2 solid and these other two spectra are quite different and I'll get into that in more detail in a minute. The second thing you notice is that the solution spectrum and the geothite -- the NpO_2 on geothite spectrum are very similar. What that suggests is that, first of all, in this case the NpO_2 on the geothite is not simply crystallized. The NpO_2 didn't precipitate on the surface of the geothite. We can rule that out. Okay. Then, the question is what is the nature of the complex that's on that surface and probably a question before that is -- well, a corollary -- a related question is what's the NpO_2 in solution? So, if we can get Dave Hobart or Hieno Nitche to tell us what's in solution, then we know more -- then, we have a better idea of what's on that surface. But, I'll get into some more details of what we think to be the case -- what we think is on the surface.

Well, you can do a Fourier transform on those very spectra that I showed you on the previous slide. And, what you get when you do that is a structural distribution function. So, you have -- it's a radial structural function, I think, instead of the radial distribution function. At least, that's the way the EXAFS people like to refer to it. We have radius on the ordinate and then some sort of value for this transform. The different components of that transform on the abscissa. Or, have I got those backwards? Anyway, the key point here is that you see a number of different peaks in this transform. At the low end down here below 2 angstroms, the peaks you see are largely a result of the data reduction technique. It turns out that you've got a normalize things. You have to take care of some interference effects that occur during the EXAFS experiment and some other things. So, we will talk about this part of it. We will talk about these peaks here.

This first peak here basically relates to the oxygen neptunium distance that you see in NpO_2 and there's crystallographic information available on that and this is the kind of distance you see -- bond distance you see -- bond length you see for that. Next, you see another peak and this peak relates to the distance between neptunium ions and NpO_2 to neptunium closest neighbors, if you like, in NpO_2 solid.

In the case of the solution, you get a quite different set of peaks. Again, the low energy -- or this step at the low end, we'll ignore for the moment and concentrate on these two peaks. In this particular case, you again get this neptunium/oxygen peak and now you get a peak that's closer than the neptunium/neptunium peak that would be out here somewhere and that neptunium/neptunium peak isn't obvious. So, the initial indication is that you don't have a close clustering of this NpO_2 on the solid and we already said that based on what I've shown you in the last slide.

The question then is what's the origin of this peak? And, the preliminary interpretation is that that peak results from a series of oxygens that are distributed around this NpO_2 molecule here. Here's the NpO_2 and these then are additional oxygens around it and the interpretation is that we've got a pentagonal bypyramid complex, if you like, in the solution and on the surface of the geothite. The possibility exists, of course, that these are oxygens from the water molecule. It's the water molecules that are bound to this thing in some way. But, in any rate, the EXAFS data gives you this kind of structure. So, this is the kind of thing that we can obtain for practically any of the radionuclides given that they have a sufficient coverage to be sensitive to the EXAFS technique.

Okay. Let's get on to a similar set of data. I'm just going to put up this slide for this case because it is some recent work that resolves a long-standing controversy. What we've done here is we've adsorbed ^{6}uranium onto the surface of geothite under these conditions. Okay? So, this is the background electrolyte, this is uranium concentration, and the geothite is one gram of geothite per liter of solution. What we have is the amount of ^{6}uranium adsorbed on the geothite at a range of pH's. We have several sets of data on this line. First of all, we have a set from a PhD dissertation by V.J. Tripathi and this dissertation was done at Stanford University essentially under the same conditions of this experiment, the experiment we did. Then, we have another set of data over here -- or actually two sets of data over here. One set is from Hsi & Langmuir, is it Don Langmuir, and another set is from the stuff that we've done. And, the bottom line is that the work that we've done -- in fact, I should say that Jim Leckie -- Jim Leckie's group at Stanford has done this work for us on contract with us and they're continuing this work. Basically, Leckie's results and the Hsi & Langmuir results are coincident. The Tripathi results are substantially different from both of those other groups. So, our conclusion or at least our preliminary conclusion is that this is the set of data that will work with.

So, that will end the discussion of the mechanistic approach. What I'd like to do now is just briefly summarize what we've done. You've seen this slide before. Colors aren't here. Again, most of the work that's been done so far has been done along this path. We've obtained individual adsorbtion coefficients, as well as some isotherms for particular whole rocks under -- in contact with given ground water compositions from Yucca Mountain. So, those data are appropriate to Yucca Mountain in given situations, but they reflect only the material that was used in the experiment. Okay. Then, we've done some work on individual minerals, both to get at the question of fracture sorption potential, as well as the question of how these important radionuclides may be sorbing to the various phases. And, that last question then will entail doing a whole series of additional detailed experiments on the factors that are listed here that I mentioned earlier and which then give us some basis for validation, as well as some basis for extrapolation.

Thank you.

DR. LANGMUIR: Just one quick question, Arend?

DR. MEIJER: Sure.

DR. LANGMUIR: Don't you currently have the data in hand from your experiments which would allow you to use EQ3/6 loop on that project -- on that exercise and compare what you'd predict that way or is there insufficient experimental data from the runs?

DR. MEIJER: Well, there are two problems with that. First of all, EQ3/6 doesn't have surface complexation --

DR. LANGMUIR: Okay. That's the first problem.

DR. MEIJER: That's the first problem. And then, the second problem is that we don't really have all the data we need in order to model the system.

DR. LANGMUIR: But, MINTEC does have those models.

DR. MEIJER: That's right. That's right.

DR. LANGMUIR: So, you could test it that way, couldn't you?

DR. MEIJER: That's right. In fact, last week, we got together and we're going to bring up MINQL or MINTEC -- MINQL, I guess, is the one that's available to us and we will do our modeling with MINQL.

DR. LANGMUIR: You can do that now?

DR. MEIJER: Yeah. See, the problem, Don, is that we are constrained by a quality assurance program and before we can do this sort of thing that MINTEC has to be quality assured or -- yeah, I mean, somebody has to go through the quality assurance procedure for that program before we publish --

DR. LANGMUIR: Are you sure that hasn't been done because that's now an EPA official program which they're selling or teaching in workshops.

DR. MEIJER: Um-hum. Okay.

DR. LANGMUIR: EPA is using it. So, I think you'll find it's going to --

DR. MEIJER: Sure, sure. But, we're looking into that right now and I'm glad you brought up the EPA line and then we'll follow that one up. In fact, I'll get together with you and see who it is at EPA we might talk to.

DR: CARTER: Let me ask you a question. Do you expect to eventually concentrate primarily on the long lived radionuclides that are a regulatory concern in meeting the requirements of 40 CFR 191?

DR. MEIJER: I think that's a fair evaluation. I mean, we want to do the simple strontium and the simple elements first in order to learn the mechanism and get the procedure, and then once we've got that down, we'll go to more neptunium work and more americium work and more plutonium work, in particular.

MR. BLANCHARD: Are there any other questions?

(No response.)

MR. BLANCHARD: Don, I think now would be a good time to take a break. It's a natural on this topic between Arend and the next speaker. So, if we took at 10 or a 15 minute break, that would be just fine.

(Whereupon, a brief recess was taken.)

MR. BLANCHARD: Before we start back with the next presentation by Bob Rundberg, some people have come in today and later yesterday afternoon, who have not yet been introduced. I know from the department standpoint, Carl Gertz, my boss, the project manager for the Yucca Mountain project is here. He's in the back of the room for those of you who would like to discuss things with him. And, I know some members of the Board came in and Don, would you like to introduce them.

DR. LANGMUIR: I'll let Bill.

MR. COONS: We have two additional NWTRB Board members who now are present, and if you would stand. Dr. Clarence Allen is here, and Dr. Warner North is here. And, we also have a consultant, Dr. Ed Cording, there he is way in the back. There he is, way back there (indicating). Ed is assisting the NWTRB in the geotechnical area. So, I guess we have a full Board right now except for three people.

MR. BLANCHARD: Also, I wanted to pick up on a question that you asked, Pat, that we weren't answering at the time before the break, and that was a question about the test program that we've had where we have been looking at zeolites and other minerals that sorb radionuclides as a function of temperature, and their ability to sorb radionuclides as they dry out and then re-wet. We did have some viewgraphs and a presentation by the group from Bish, Bennam & Broxman prepared, but we didn't have enough time available to make a cohesive presentation on that topic. However, we did bring the viewgraphs that were in the last dry run package on that subject, and I'm sure Julie Kanipa and Dave Dobson will be glad to discuss at a break or later on with you about this. And, we'll look forward to providing that information to you later.

DR. DOMINIC: The reason I brought that up is a publication by Smith in 1982, and Smith did these experiments for Sandia, I believe. And he made some very strong statements about what the temperature rise can be, 30 meters from a repository in order to keep those zeolites stable. And it was a very small temperature rise could actually start a dehydration process on them, and I was just concerned about not only the affect of the zeolites, but the modeling affect on the temperature distribution in far field and what goes into those models because that will be the critical parameter that determines whether or not they remain stable.

MR. BLANCHARD: Well, I'd like to ask Julie and Dave to meet with you after the session is over with.

Okay, the next speaker, keeping in tune with the same subject, geochemistry laboratory experiments, is Bob Rundberg.

DR. RUNDBERG: I'll just be picking up where Arend left off, and be talking in a little more detail on the column experiments. We've got quite a few experiments and in order to not make this a confusing talk, I have focused it on some of the conclusions that I used in interpreting some of our intact tuff column experiments from the crushed tuff column experiments, and also one of our success stories, the anion exclusion of volume, I'll be talking about.

But, before I get into that, I'll talk about the general purpose of the task. The primary purpose of the task that I've been PI'd for is of course the test of validity of

K_ds from the batch measurements calculating the retardation of radionuclides by adsorption on minerals. And, in the case of the simple cations, we get good agreement and I'll give you some data that really proves that. In the case of the actinides, of course, we haven't had the same success, and we are starting to get a handle on the understanding of that with Arend's work as he showed you neptunium is primarily adsorbing on metal oxides and is probably not in ion exchange mechanisms surface complexation.

The next role that this task plays is to measure the effects of diffusion and dispersion on the transport of radionuclides. We have a number of diffusion experiments which I won't be talking about, because I have focused on the column experiments, but in support of the project, I have been measuring the diffusion in intact tuff using breakthrough diffusion slabs, and in an effort to see if dead end pores are going to hamper diffusion. And, in general, we have seen good agreement between those measurements and what the apparent diffusivity we have seen in saturated fracture flow experiments. So, at present, we haven't seen any strong evidence for dead ending in the pores as far as diffusion is concerned.

We are also providing experimental evidence for speciation and/or colloid formation. That's one way one could interpret the anomalies that we've seen in some of the actinide column experiments.

Colloid filtration coefficients we have begun to measure. I had intended to give you a copy of my Focus '89 paper, but I think they've all been scarfed up, I have only one copy left. In that paper, we summarized the few measurements we had made on colloid filtration in fractured tuff. Perhaps, somehow we can get you copies after the fact.

And, finally, we are at least in the planning stages studying radionuclide migration in unsaturated tuff. We have it subcontracted out to PNL to do this, but at present I believe that contract has not gone through.

Arend referred to determination of other transport parameters that are involved in predicting transport. And, the ones that I'm focusing on are anion exclusion volumes and dispersion parameters from solid rock columns.

And, then I'll try to demonstrate the problems that occur in trying to infer an R_d from a column experiment that's caused by dispersion. And, that's the third issue here, and I believe that relates to some of the early work I did with the transport of radionuclides in saturated fractured tuff, I believe is related to that. I called it channeling, but it's the same phenomena I think that I'm seeing, and I hope I'll be able to show why the dispersion gives some ambiguity in the interpretation of those experiments.

The scope of the experiment originally planned in the SCP, involves crushed tuff columns, which we felt was a minimal change from the batch adsorption experiment. We felt we don't want to change too many parameters at once. We wanted to only change--the only parameter here we are changing, is now that the fluid is moving, at least that's what we thought in our concept to this, as opposed to a static system which is tied back to the speciation argument. For example, if you had two species that for some reason kinetically didn't exchange, they would separate out in a crushed tuff column, whereas in the batch, you would just see an average K_d.

DR. CARTER: What's the size range of the crushed material?

DR. RUNDBERG: The crushed material? I'll get into that. In the early experiments we used everything below 500, but then we ran it through a column that inherently has a sieve, so it would be 38 microns, which is the sieve at the bottom of the column to 500. Now, our standard is 100 to 500. All of the newer experiments are sieved to that size range.

We also have a point of measuring adsorption kinetics and we get at that in several ways. This part of the SCP refers to running some of the crushed tuff columns at high velocities, so that you can see broadening due to mass transfer or kinetics. We would have no way in that experiment for differentiating between mass transfer in kinetics, other than you should be able to calculate mass transfer from the particle size.

And, unsaturated tuff columns is the title of that sub-task in the SCP, but that also includes the saturated intact tuff columns that I'll be describing later in the talk.

Fractured tuff columns, as I stated, had been run in the past. And, we did see some behavior that seemed to be anomalous. We saw earlier arrivals of some of the sorbing tracers than we expected. I think this is related to the dispersion problems that I'll be talking about later on in the talk.

Colloid filtration, the only experiments we have run at the present, that we have data available, hasn't been published other than in the Focus '89 paper, is from a fracture experiment. And in that experiment, we saw the kind of size dependence that is expected from the engineering literature, where if you model it as having a diffusion limited part, and then a sedimentation part, you get--you tend to get a maximum filtration at about one micron over a rather broad range of velocities, grain sizes and conditions.

We have seen effects that couldn't be described by that model. I haven't published that anywhere and we are developing a new model with UNM using an electrokinetic model, so that we should be able to have desorption of colloids. Some of our experiments that are very preliminary, I don't even have data to display with intact tuff, are showing definite evidence of desorption colloids.

Diffusion cells, I mentioned earlier are being run in sort of a static fashion.

And, then sorption kinetics with intact tuff includes a set of experiments that are related to questions that Arend mentioned. Looking at the kinetics of adsorption of the actinides, we felt that with some of the artifacts that one has with the actinides having them stick to walls and other materials, that we best do these experiments with rock beakers. And, right now we have the intact tuff beakers, and these experiments are actually in progress, and are measuring the removal from solution of the actinides with time. We are going to model them in a diffusion model and see if we see a more rapid loss than you'd expect from diffusion, or a slower loss than you'd expect from diffusion.

We also section them after a long period of time, we intend to cut those rock beakers up and see the depth of penetration of the actinides.

DR. LANGMUIR: Bob, this is strictly matrix type movement?

DR. RUNDBERG: Strictly matrix.

DR. LANGMUIR: You don't have any intact fractures you are looking at at this point?

DR. RUNDBERG: Not--

DR. LANGMUIR: Do you intend to do that?

DR. RUNDBERG: We've entertained the idea. Right now at present we don't have any intact fractures that haven't been used in other experiments. And, there's nothing available from the core library any longer. So, that's on hold. But that is a useful thing to do particularly in view of what we are learning about the adsorption mechanisms.

And, then finally, unsaturated diffusion cells. We have a few of those running, where we've equilibrated some blocks of tuff with a small hole drilled through them. We have equilibrated them in an unsaturated condition now for more than two years in an attempt to get steady, and even distribution of the saturation through the rock and we will be placing a small volume of tracer so that the imbibition will be minimal, and then monitor those after a long period of time and we'll be cutting those up and seeing what the diffusion in the unsaturated condition is. A very long-term experiment.

So, with actual data, I'm going to start with a summary of some of our older crushed tuff columns, and I see this is a G-1 core. In the old days when holes were drilled on the test site, they were given a different name. I think these are Ue-25A the YM series if I remember correctly. We also didn't number them by depth. This is run number. You'd have to go to one of our summary tables to find out what depth that is.

This corresponds to the Topopah Springs member of tuff, however. This is a devitrified tuff from lower down. I believe it's the Bullfrog, but at any rate, the point here is that we get fairly good agreement. Now, we see differences, and I'll interpret that difference in a bit. But, you can see based on the batch K_d we can calculate what the retardation factor is. The measured retardation factor seems to agree in general within a factor of two or three, which you'd think we could do better than that, but when you look at the bottom experiment, I think we will be able to explain why the agreement isn't that good.

This bottom experiment now is different from these in that these were all sieve materials in the batch measurements. The batch measurements were sieved between, I think 75 and 500 microns. These batch numbers were not sieved. They were the fraction that went from 0 to 500. They were sieved on the upper end at 500.

DR. CARTER: What units are these numbers?

DR. RUNDBERG: In the batch K_d? We always report them in milliliters per gram. Our european colleagues like liter. What is it cubic meters per kilogram, I think.

And, if you calculate the retardation factor when you use the tuffs that have no lower limit on the particle size, we get enormous retardation factors, especially compared to what we observe in the column experiment. And, we've done a bit of work to prove it but we've found that this is due to mineral fractionation. In the fines, we tend to concentrate the clays, particularly montmorillonite clay. And, of course, zeolites are generally also one to three micron size crystals, so you would tend to enrich in the small particle size fraction, those minerals that have the highest K_ds, and the column can't be run without a cutoff. The column has a 30 day micron frit at the bottom, so that you will be continually flushing out these fines. And, that--I think this illustrates that problem, but along with that, as a corollary, it's almost impossible to ensure that the batch measurement and the crushed tuff column have exactly the same mineralology. And I believe that that's the reason that we get a spread of about a factor of 2 to 3 in here.

DR. LANGMUIR: Bob, are these just essentially J-13 water, pH around 8 with all these constituents in them?

DR. RUNDBERG: Yes, this is--our old philosophy of trying to do everything with a standard water the same way.

DR. LANGMUIR: And these have all been run through the computer and they are undersaturated with respect to solids?

DR. RUNDBERG: Right.

DR. LANGMUIR: Before you put them in.

DR. RUNDBERG: That's right. The barium might be close to saturation, but it's undersaturated.

Well, maybe before I leave that, I guess there's another point that I want to make here and, I don't know if it's appropriate here--but before I get to the intact tuff columns, I might review a little bit. Arend showed some isotherms for strontium in particularly, which were linear over very wide range of concentrations. It wasn't until you got to very high concentrations, near the solubility limit of the strontium that you really got a non-linear adsorption isotherm. So, what I want to say here, is that for strontium we can predict in a uniform column with reasonable accuracy, what retardation factor we ought to see. The isotherms are essentially linear, and I'm not sure if I have any viewgraphs, we've also looked at the kinetics in a number of these columns and found that the kinetics were diffusion limited for strontium, cesium and barium.

As far as the anion exclusion effect goes, I'm going to refer this back to a field test, but I'll give you a little more detail later when I get back to the dispersion problem. This field test is, and I think the first day somebody asked about how we tie into the weapons program. This is tied into the weapons program. We are looking at--we have been pumping at this well for 16 years now, and we have been looking at the migration of tritium from the cambric test that's in Frenchman Flat. This is not 25, it should be 2S for the satellite well.

And, we've measured recently chlorine 36 using the same technique that Ted Norris used in his chlorine 36 work, accelerator based mass spectrometry at Rochester. And, we've observed the chlorine 36 profile. And, what you see, and this is documented in the literature, is that the chlorine leads the tritiated water. And, we had read about this effect, and it's been known and most people called this the anion exclusion effect. So, I've done a number of crushed tuff columns to verify that this effect can be explained by exclusion from the pores inside crystals.

I'll show you some of the minerals that I have good crystallographic data for that were present in the tuff samples that we used in this set of studies. And, we have three zeolites. We have analcime, clinoptilolite and mordenite in varying amounts. We have one tuff that essentially has only analcime as a sorbing component. And then we have various mixtures of clinoptilolite and mordenite.

With respect to this anion exclusion effect, the data I used from the crystallographic data base, and this is also the kinetic diameter is determined independently by using molecular sieving. What I have is a channel aperture. Now, if you will remember zeolites are frame work structures that have openings running through them in either a three dimensional or two dimensional structure. Most of these are two dimensional.

This is the amount volume inside the crystal structure. You see it's like an 18 percent porosity in the crystal, in these channels. But in order for an ion to migrate into those channels, it would have to have a diameter at least less than 2.6 angstroms. Clinoptilolite is about 30 percent porous, has a larger channel size than analcime and here the kinetic diameter is 3.5 angstroms. And, mordenite has an intermediate porosity. It has two distinctly different channels, one very large and one very small, and the average kinetic diameter is from molecular sieve studies is 3.9 angstroms.

Well, what about anions, why would anion be excluded? Well, I went and found some measurements of ion size and also calculated some using standard methods of calculating ion size. And, what we find is that fluoride is the only ion that would fit into those channels readily. It's diameter would be 2.7 angstroms. And chloride is 3.6 and they all get larger up to pertechnetate, which of course is the one that's really relevant to nuclear waste. We have a 6.3, nearly, angstrom diameter molecules, so it's quite a large species. And based on the observed anion exclusion, with pertechnetate. I have a set of measured and calculated exclusion volumes. I have a spread in the calculated exclusion volumes, because there's dependence on the density used for the zeolites and the exact composition of the cations in our zeolites wasn't known and they weren't always reported in the crystallographic literature, so depending on whose data I used, I had different--I came up with different specific anion exclusion volumes. But in general they agree.

And analcime, which doesn't vary so much in terms of its cation composition, because only the smallest cations can fit in it, you see it agrees quite well with the crystallographic data. These three tuffs have varying amounts of clinoptilolite and mordenite and using the weighted average from them I had good agreement with this tuff, which I believe was mainly clinoptilolite. Then I had good agreement in this case within--it's within the span of the independent crystallographic measurements. And, then this one I had a little poor agreement, but if you take this span to represent some sort of error, you might be able to say that it probably was within the range of variability.

This tuff did not contain any zeolites, it contained smectite clay. That was interesting, because my calculated anion exclusion volume was based on a monolayer of water in the interstitial space. And you see it came out to be about one half the measured anion exclusion volume. So, you could simply say, well, if you had a double layer of water, it would be in good agreement, which would be consistent with a calcium loaded smectite.

So, I think we have a good understanding of this anion exclusion effect. And, I may make another point here in terms of colloid behavior. The anion exclusion really--I really should call this size exclusion. A neptunyl cation, I would expect to be large enough that that also would be excluded. Most colloids--all the colloids that we've looked at would be excluded, so this also applies to more than just anions. The anions, I guess, caught the attention of a lot of people, because they weren't quite expected to behave that way.

And, that brings me to the business of dispersion. And, that's what I think I'm really concerned with in going to the intact tuff. I feel confident from the wafer experiments that the K_d for an intact tuff ought to be a reasonable value. The velocity range that I found from the crushed tuff columns before you really saw any kind of mass transfer problems, was large enough in the experiments we have run that I don't expect kinetics to occur. But, I know nothing about the dispersion in the intact tuff until I ran these experiments and then I'll show you what I inferred from that.

Basically, the first thing I want to say is to talk about how dispersion affects the migration of contaminates. The breakthrough, if you look at contaminate moving as a front, the step function and a front moving through, depending on what the dispersion is, that front will tend to broaden out and become a rather smooth, is rather than a sharp increase in concentration, you have this rather gradual increase in concentration. And, in chemical engineering, we referred to this by a lot of things. We referred to it as mass transfer units. You read a lot of terminology, but all refer to the same thing, and in analytical chemistry, we talk about theoretical plates and the height of the theoretical plate. And in the hydrological literature, you'll find dispersivity and you will also find the clay numbers. They are all related. There are sometimes some minor difference betweem the factor of 2 difference in the way they are defined.

A broadened breakthrough curve results in the early arrival of a fraction of the total contaminate. In the next viewgraph, I'm going to illustrate what that can mean in terms of the interpretation of an observed breakthrough. If the dispersivity is large, and you have a pulse, as my experiments are run, because they run over such a long period of time, there is no way I could deliver a constant--I'd have to have a lot of radioactivity sitting around in my syringe. So, I run them as a pulse.

Then the peak concentration will arrive earlier. And that also applies to a conservative tracer as well as a sorbing tracer.

DR. DOMINIC: Why didn't you run your experiments with conservative tracers?

DR. RUNDBERG: I did.

DR. DOMINIC: Oh, then you don't have to wait so long.

DR. RUNDBERG: Well, but that wasn't what I was after. I was after the sorbing tracer. But, I did run them with tritium and pertechnetate.

DR. DOMINIC: Well dispersivity is supposed to be ion independent, presumably.

DR. RUNDBERG: Yes, I'll get to that. There is some flies in that ointment. If we--and this thing might be confusing. I was thinking of dropping this viewgraph, because I thought it might cause more confusion than clarification. I'm not talking about the average movement of a tracer which would be when C over C_0 is a half, because there's no dispersion dependence on that. The mean behavior is independent of dispersion. But, let's say we were looking at a tenth of the concentration and let's say that broke through at some time, and I think when I did this calculation the scales here are really arbitrary. I just said suppose we saw ten percent at one free column volume. You could explain that either for adsorbing tracer by changing the retardation factor, or the K_d or the dispersion coefficient. Either one would give you a solution. So, there is a definite relationship. And, this applies as well to conservative tracers in respect to velocity in the field.

This one isn't in your packet and I think this one makes what I'm saying a little clearer. The viewgraph isn't clear, but hopefully the concept is clear. If we have a very low dispersion and you have a narrow pulse coming through, you get just a slight broadening in the arrival of the peak. As you increase the dispersion, at first you just--apparently you have very little shift in the position of the peak. You just get a broadening. I've re-normalized this to the maximum, it says C over C_0 and C over C_{max}, just like we had in the previous viewgraph.

But as you get to very large dispersion, then you tend to shift the peak. Now, the center of mass hasn't really moved in these, yet a long tail containing a lot of the mass, but that's hard for me to measure. So, that what I'll actually see, is where the peak is, so this is a point of confusion in terms of interpreting the data and you'll see what kind of problems it's caused me and the intact tuff columns.

And, these have all be renormalized to the peak. In actuality if had this in C over C_0, this would be an extremely small concentration. But, the peak would be arriving much earlier than you expected from the free column volume.

Well, as Pat pointed out, that shouldn't be a problem, because we can use conservative tracers to get our dispersion. We should be able to model everything the same. Well, I make some assumptions and that's what the rest of this talk is going to be about, how good are those assumptions. And, the first assumption is we've assumed that in that solution that I've shown you, I assume that this equation applies, which means that this looks just like diffusion with a moving boundary. That dispersion is just a diffusive process.

And, also it assumes that you can treat heterogeneous aquifer if you apply this to a large volume as a homogeneous porous medium. Normally, that's not what is done. The normal assumption is that we assume that there is what we call a representative of elementary volume. And, that is that only on a small scale do you have fluctuations and things like velocity or porosity, on a scale of a pore. And, as you take a volume where you've averaged enough pores and enough grains, you can get an average that's representative and only until you get to a very large scale to a field scale, do you have to consider the heterogeneity.

And, that was the philosophy I had when I first entered these experiments. I thought that I had an experiment that was rather small scale, but quite a bit larger than the pore size, and that I should be in this region.

Another assumption is, which is essentially assuming that you can use this representation, is that dispersion can always be treated as Fickian. It either takes this form where you assume that if you went to a large enough scale, it could be treated as Fickian. There are a number of ways that you can make that--you can attempt to make that assumption. And, of course, the assumption that we always apply, that I've applied all throughout here, is that we can--the migration can be predicted using this retardation factor, which in this equation would just occur in front of a derivative of the concentration with time.

This derivation has inherently a number of assumptions. One is that you are dealing with an equilibrium process at least on a microscopic scale, that the isotherm is linear and as I showed you the isotherm for strontium at least is linear. And the equilibrium assumes that the kinetics are fast, and as I stated for the column experiments we ran as a function of velocity, we found that over a very wide range of velocity, that was true.

And, also, another assumption in the derivation that was made was that they have, by Heister and Vermeulen was that you had a constant pattern. And, that's essentially assuming these assumptions, that the medium is homogeneous. And, one of the ways that I have viewed the observations that I'm going to be showing you, is in this context. And, that's in the context of stochastic models. And, I have this just to kind of explain where I'm coming from here.

This gives you a different view of the dispersion problem. Basically, if you look at Lynn Gelhar's model, or de Marsily's model, de Marsily published, I think a year later, than Lynn Gelhar, essentially the same treatise on how to develop a stochastic model for describing advection dispersion.

They made some very simple transformations. What was done is they said well, Kolmogorov has shown in the 40's that diffusion could be represented by stochastic equations. That you could have a Brownian walk that described diffusion. So, you can rewrite that equation in terms of these two stochastic equations. This is a random Gaussian variable, and then this is a velocity term that depends on where you are in a strata, the transverse dispersion and is treated as a Gaussian random variable.

If you take that approach, you get a diffusion coefficient that has this longitudinal diffusion that is essentially Fickian which corresponds to this Gaussian variable and then you have this integral where the covariance function determines whether or not this apparent diffusion coefficient changes in time, because it's integrated over time in the outer variables. And, you are left with some functional dependence on time.

And, without going into the details, it can be shown that the only time that dispersion is strictly Fickian over all times, is when the covariance function is equal to the first derivative of the delta function. Well that's an impossible covariance function. It's not a valid covariance function.

So, you come close to that function in the sense that if you look at the pore structure that's used as a basis for the REV principle, is you'd have within a pore, you'd have a covariance being 1 and as soon as you went into the grain it would go negative and anti-correlate with the grain in terms of velocity over a very small scale. So, that comes close to this requirement.

However, when you have very large scale variations in the fluid velocity, that is not true and you get a linear increase in the dispersion at the early stages. And, awhile back I had looked at something that Ben Ross had proposed many years ago. I think around--I've forgotten exactly when, but it was few years after the Lynn Gelhar paper had been published. He said, well you could look at this as a fractional Brownian motion. So, in that case, only when you have a very rough conductivity distribution, would this thing become asymptotically Fickian.

I've got another viewgraph that might make this a little clearer because it's visual, but it's colored so it wouldn't reproduce for the book, so you don't have it in the book. And what basically that equation is saying is that if you have two wells and you have inserted some contaminate in this well and you are pumping at this well, is that the velocity is going to move in different layers. So, if you wanted a single dispersion coefficient for that, it would not be diffusive unless you could mix all these layers. This very fast layer obviously, if it's moving at a high enough velocity that the transverse dispersion can't mix the volume with the slower moving nearby layers, you will never achieve the average flow. So, it's dependent very strongly on this covariance function and the covariance functions that are the most anomalous are the ones that have let's say a fracture in it. You know so you correlate poorly over space. I'll show the first evidence that I had of this was from the Cambric test. So, I'm going to give you the details, in my experience of the first evidence I saw for this kind of behavior was from Cambric.

Cambric was a test that was done in Frenchman Flat in the mid-60's, and many years after it had been sitting there in the early '70's, Los Alamos, Livermore and the USGS in a joint effort, went back to make this a field test, and RNM-1 was drilled to sample the radionuclide concentrations in the cavity water. This is where the detonation point was. And, then a satellite well, RNM-2S was drilled and you can see there is a gravel pack in here, so it's sampling water, like I had in my diagram over a wide range, of a large volume of the alluvium and perforations down here within this gravel pack along the side of the well.

And, what was observed is a tritium elution, that I tried to fit to some type curves. And very early on, I found before we had very much data, when we were about here. Many years ago, I took one of these type curves just to see if I could calculate a dispersivity and predict the rest of the arrival, and I wound up using fairly short dispersivity, about nine meters or so. And, then as time went--so the earliest fit to this data, that fit the leading edge, dropped off fairly rapidly. It was a sharp peak. And, as time went on, it wasn't really very satisfying, because, if I integrated my curve there, I wouldn't fit the source term, and we knew the source term or the tritium pretty well. We knew how much tritium was in the device, how much was burned.

We knew pretty much what we should see, and I was fitting it abysmally, so I knew there was a problem. Then, as time went on, it got broader and broader and I wound up increasing dispersivity with time. And, this is exactly what the de Marsily had told us. And, an unsaturated zone working group in around 1984, when he came to visit us from France, he told us that's what we should see in a field test. He said that if you take any portion of this curve and try to fit it to a dispersion coefficient, you'll find as time goes on the dispersion coefficient will get larger and larger and larger and I'm up to about 16 meters now, and I'm still--my latest curve with 16 meters still doesn't fit the tail.

DR. DOMINIC: You get the very same result if you fit a three dimensional phenomena to a one dimensional model, which truly migration is. That has to increase. If you use a one dimensional model to analyze that data and it's behaving three dimensionally, then it has to increase.

DR. RUNDBERG: Oh, no, I didn't use a one dimensional model, I used a two dimensional conversion flow--

DR. DOMINIC: Well, if you use a two dimensional model for three dimensional data, you get the same thing.

DR. RUNDBERG: Actually, to support my point of few, the DRI group had calculated the tritium elution and what they used was inferred conductivities in the layers from grain sizes--I think way back when Larry Ramspott was involved in this thing, they had looked at the cuttings and had gotten grain sizes from the drilling of RMN-2S, I think or at least a nearby hole. And, they calculated permeabilities from that, and it gave them sort kind of structure like I drew in my diagram, and they actually fit the data correctly. If that's what you mean, then I guess we agree.

DR. DOMINIC: If you did a broadening, then you are going to have asymptotic product dispersivity for many, many reasons.

DR. RUNDBERG: That's probably true. And, then that brings me to my lab experiments. And, the lab experiments are fairly simply apparatus we ran through. We ran tracers including tritiated water through a solid rock column. We were concerned about fluid movement around the edge, being in effect an uncontrolled fracture, so we used an epoxy that's used for thin sections, making some thin sections. It penetrates into the poor structure within a thin layer on the outside to ensure there was no fluid movement around the fracture and, that we used inside of our confinement curve.

If I used the Fickian dispersion--now, this one I would have thought was a one dimensional flow problem, so I wouldn't have the objection that Pat just raised, because of the way we confined it.

If we tried to fit it to a Fickian dispersion curve, we didn't get a very good fit. If I got the concentration down low enough, then I didn't really fit the shape of the curve very well. So, I went back to de Marsily's treatment and said, well suppose I used a linear increasing dispersion with time and then the fit got much better. So, in this curve I've actually plotted two independent runs with the same tuff core, the circles and "X's" being the two independent runs, and it all agrees rather well.

So, I think the way I interpret this is that there is heterogony in 80 and the fluid movement of tritiated water. Now, there are a number of ways of interpreting that statement. I tend to leave it in that general fashion. You could say that the tritium is diffusing into dead-end pores or into crystals or any number of ways of looking at that, but I think it amounts to the same thing.

Predicting pertechnetate, I had a little bit less success. If I predicted the pertechnetate using the tritium curve, which I expected because pertechnetate has a very, very small K_d in this tuff, what I got is a rather poor fit here, but I've also done something here to confuse everybody. I've re-scaled the data. I re-scaled this curve--well I guess I multiplied by a factor of 2 to recover the loss of tritium I observed. About half the tritium in this run didn't appear when I integrated all of the pertechnetate up to this point. So, I multiplied by a factor of 2 just to see if the shape fit the tritium, well, it didn't fit all that well. You can see that there's quite a bet of tailing indicating to me at least, that part of the pertechnetate has been retarded. And, I believe, this is belief now, I have no way of proving this, I believe that there are probably some iron oxide minerals responsible, or manganese oxide minerals responsible for the adsorption and retardation of pertechnetate, but it's not uniformly distributed enough for all the water to contact it. So, some of the pertechnetate is going through without seeing enough of the mineral to be retarded and some of it's not. I think this is further evidence of heterogeneity in that tuff.

And, this is another problem, and there are a lot of ways of interpreting this, as well, except I've ruled out most of the standard problems. This is my strontium run. When I started this experiment with strontium and cesium and barium, my technicians were arguing with me. I said use strontium 90, it's going to be a long-term experiment. They said we hate counting beta emitters. We want gamma emitters. So, I said, okay, but you've got to start out with a fairly high specific activity in the initial pulse, so we put in a fair amount of tracer in the initial pulse with the assumption that we weren't going to see much strontium until a year and a half down the road. This is in days here and I expected the peak to be about 400 years.

What I observed instead was in the very first sample after one week, significant strontium. And, it peaked in about four weeks. So, back to the argument, what's the problem here? Is it the K_ds are wrong, or is it the dispersion? And, where I'm coming from is I think it's probably the dispersion.

You can see that there's a long tail on here, unfortunately, we can't monitor this for the next four years, because it was decaying too rapidly, so we'll never find the center mass of this curve, but I suspect that the center of mass of this curve is probably close to where it should come for the given K_d. Because, we did measure for the same tuff, the K_d for that.

So, I played a different game. I said, what happens if I take that tritium run with the linear increase in dispersion and apply that? And that was my better fit. And, that had an interesting effect. It actually was a little bit conservative. If I took the time dependent dispersion, I get a peak here with a low tail that goes on essentially forever. It doesn't fit the data all that well, but it predicted that I should have seen the peak arrive actually earlier than I expected using the batch-sorption K_d. If I fooled around with it a little bit and changed the time dependents, I could improve the fit without adjusting the K_d.

What I had done--the tritium belongs here (indicating) and the strontium belongs (there). What I had done was I had fit the tritium to this curve. I had a Fickian component with linearly increasing component, but when I readjusted that--now, if I just extended that, I got the prediction that I showed for the strontium that was a little bit too conservative. It indicated that the strontium should have actually peaked a lot earlier than it did.

If I adjusted the dispersion time dependents a bit, then I got this curve. What that means is not at all clear to me. What I think I'm saying in playing this game, is that the rock is heterogenous. There are probably micro-fractures, and Topopah Spring member tuff is extremely impermeable. There are probably micro-fractures running through it that are dominating the flow path, so that the fluid is not mixing very well throughout the column. So that hydraulically, I have a heterogeneity problem. You can call it dead-end pores if you want, but I have--I have a heterogeneity problem for the hydraulics. I may also have heterogeneity for the sorbing minerals. It's not obvious to me that the sorbing minerals should be distributed evenly, and the flow paths unevenly. So, the fact that I have a different dispersion for the sorbing material maybe due, at least in part, to the heterogeneity in the distribution of sorbing minerals.

And, this gives us--this philosophically is very difficult to deal with, because you'd like to do exactly as Pat suggested, which was to use the dispersivity from the tritiated water to predict the behavior of the sorbing tracer. And, if that's not the case, if they are not the same, what then do you use?

So, the conclusion of this experiment, is that the dispersivities are large and appeared time dependent. I mean very large. The length of that core was five centimeters. In order to fit that strontium curve, I had to use between 10 and 30 centimeters. Longer than the core.

DR. DOMINIC: That's impossible.

DR. RUNDBERG: So, obviously, I can't be contacting the whole core.

DR. DOMINIC: The logical conclusion is that your batch-sorption K_ds are too large. That would give the same result.

DR. RUNDBERG: It really wouldn't--

DR. DOMINIC: Based on your second conclusion.

DR. RUNDBERG: I should have done that. It wouldn't have fit the shape of the curve either. I mean, I still would not have gotten that curve's shape fit correctly, even if I had lowered the K_d. I should have made that graph.

DR. DOMINIC: But, the arrival times would have been closer together.

DR. RUNDBERG: But I can't--see, I can't think of any reason that the K_ds should be lowered. The wafer studies that we did agreed. That would be very special to this particular tuff sample. And, I've seen it in the fracture flow experiments as well, so whatever the problem I'm seeing, it's universal. It's not--

DR. DOMINIC: Well, dispersivity is a mixing length and it's impossible to have a mixing length larger than the length larger than the length of the sample. Right?

DR. RUNDBERG: Well, if it's not mixed. The peak arrivals for the sorbing trace appear much earlier than expected from the batch-sorption. And, the alternate explanation would be that for some reason, K_ds weren't correct.

The other thing is the radioassays of the column sections, which I have a view graph of the supplementary stuff, shows that it is very unevenly distributed. That the sorption of the radionuclides for the ones that are remaining, we did not see elution of the cesium and barium. And, those remained in the column and they were distributed unevenly through the column.

The pertechnetate retains the same dispersion as tritiated water, but there is a loss of the tracer in the Fran Ridge outcrop column.

I also ran a sample of the zeolitic tuff from the Calico Hills. In that case, I saw a different dispersion in the tritiated water, but no loss of the pertechnetate. I think that the movement of the radionuclide is a complex phenomena. I think that in this case, anion exclusion probably changed the mixing through the flow paths, because some--the transverse dispersivity must have been different for the pertechnetate than for the tritiated water.

My conclusion is that heterogeneity is an important factor to deal with. And, I think the talks that I heard on Monday would support that notion, that you can have a small amount of a tracer arriving extremely early, even though you'd expect, let's say you'd expect an average flow velocity to be--the average travel time to be very, very long, there can be a small amount that arrives very, very early.

DR. LANGMUIR: All of these tests are saturated columns, right?

DR. RUNDBERG: We don't know what will happen in the unsaturated.

DR. LANGMUIR: That's the crux of my question.

DR. RUNDBERG: And, that is a good question. We have been taking our time at seeing which technology was the best for doing those experiments, and we had decided that centrifugation was probably the way to run those experiments. But, that was to be subcontracted out in this fiscal year, and I don't think that's going out.

DR. LANGMUIR: Have you considered Van Genutchen type columns and the approach that he uses in soil tests?

DR. RUNDBERG: We could do crushed-tuff columns would be doable, but I thought the real crux of the question was the intact tuff where the you have the real heterogeneity, and those are hard to do.

DR. LANGMUIR: But, you can also--you can improvise and this is an approximation, of course, but you can--with the knowledge of what the mineralogy in the fractures is, you can crated a crushed-tuff column out of fracture minerals in the same area proportions as the fracture would expose. We have done this.

DR. RUNDBERG: You mean make a physical model, yes.

MR. LANGMUIR: Create a column in which you have the same areas of exposed sorbing minerals as you would have in a fracture. It doesn't duplicate the hydraulics, but it does at least address the geochemistry adsorption.

DR. RUNDBERG: And, actually the guy at PNL we were going to have take this contract, he actually had done some preliminary experiments with total parts pre-membered tuff. And he did find that the fluid--the dye in the fluid was confined to micro-fractures. Not all the micro-fractures, but some of the micro-fractures did conduct the fluid. We are probably seeing in this intact tuff of fracture flow scenario, which I think is what you are saying, Pat. I think that our dimensionality of the model is too low, but I don't know what the real dimensionality is.

So, my conclusion is that the batch R_d measurements augmented by isotherm and mechanistic studies should yield a defensible database for us in performance assessment. But, larger sorption coefficients may be required to mitigate the effects of dispersion in the geochemical barriers. But, it's my own personal conclusion.

Am I done? I'll welcome any questions.

DR. LANGMUIR: We have probably been asking them all the way along.

DR. RUNDBERG: Yes, have we covered them all?

MR. BLANCHARD: I would like to just take a minute in closing to make a few closing remarks. First, obviously, we are looking forward to your feedback from this day and a half of presentations on technical topics that are different from our July meeting where we are going into the in depth discussions on topics in the science disciplines like hydrology and geology and so forth. And that feedback will help us better prepare for future meetings, we think.

Second, I'd like to just reiterate a moment, the preliminary nature of the results presented by the speakers. It's in advance of them having their own internal technical review process. Much of the data except for what was presented by Dwight Hoxie, as you can tell is information that was obtained by our ongoing program that's not yet been published by the speaker in journals or from his own organization.

And, that as we mentioned in the beginning, the topics we selected were things that we thought were going to be interesting to you and topics that you also requested, and one doesn't necessarily get the comprehensive picture of the geohydrology program or the geochemistry program, so we look forward to future interactions to bring that together.

Third, that the ongoing studies that we have, I believe personally, are very useful. For this phase of the program they are what we would normally be doing. The technical program is not experiencing--we are not doing mate work. We are actually doing things that we would normally be doing at this phase of the program in the absence of land access has not caused us to do things that we would not normally do in this part of the hydrology and the geochemistry program.

However, as you can tell from each of the speaker's presentations, there's a significant need for more data. There's a sparsity of information about our knowledge and understanding from the processes operating in the rock units beneath the surface at Yucca Mountain. And, we are looking forward to the opportunity to conduct the test we want to and do the drilling programs and the trenching programs that need to be conducted, in order to have more data and improve our understanding of the processes and shed more light on the models that might be operating at Yucca Mountain.

Fourth, proximity to the test site, I think is proving to be very, very beneficial to the program, in that some of the presentations discussing radionuclide migration, especially tritium, and the chlorine 36 measurements are giving us information about the processes that operate at the site, that we wouldn't otherwise get if the site was a long ways away from the Nevada test site. And, of course we are seeing tritium and other things that are migrating from the surface. Given our state of understanding of infiltration processes and the debate about fracture versus matrix flow that's ongoing in the program, we can't answer with any degree of certainty of how they got there and even whether or not it's our own contamination from the surface activities in the drilling fluid that were used in the past.

So, that's a question that I think having these tracers there will help us go along ways towards understanding the processes operating.

DR. DOMINIC: Are you saying that the reports on tritium and chlorine 36, that there could be alternate explanations other than meteoric water? Is that what you just said?

MR. BLANCHARD: Well, I don't want to take words out of the PI's mouths. I think that they should say what they think are the processes that are operating there. All I'm observing is that we don't have reports that are prepared now that have gone through a technical pre-review process that identify with some degree of certainty or confidence, all the processes that are operating that can get the material down to different depth.

It's pretty clear that some are migrating in fracture flow--

DR. DOMINIC: But, I'm leaving here with the impression that the tritium is due to meteoric new water. If I am wrong, I wish someone would correct me.

MR. BLANCHARD: I wouldn't try to change that impression.

DR. DOMINIC: And, the chloride too, I think.

MR. BLANCHARD: My main point was, we learn things from the process by being close to the test site.

The fifth point is that the discussion yesterday that was somewhat generic on concepts from model validation and verification, is a programmatic strategy that the project office and headquarters have been working together with the project participants, trying to develop what the commonality is in moving forward with that from a management and a technical standpoint. And, that has not yet been implemented in the program. And, we were in the process of translating that strategy into implementation from a management and a technical task standpoint. And, so that's why that presentation appeared the way it did.

Sixth, the roles and responsibilities within the project activities may still be causing some confusion, and it came to mind by nature of the way we handled the presentation and the discussions, where Lawrence Livermore is doing near field waste package and Los Alamos is doing far field geochemistry, those two have to gum together and overlap to build confidence and there are other areas in the program where that also occurs. And, we will be glad to work with you to improve your perception and understanding. It may also be helpful to us to improve our linkage in those programs.

Seventh, We invite suggestions you may have to introduce regulatory aspects into these technical topics. We felt that for quite some time there was a need for us to focus with you on the technical aspects, and I'm sure you'll continue to do that for quite some time, but eventually you are going to want to translate the technical results into a manner in which we would go about demonstrating compliance with provisions in 10 C.F.R. 60. We are not sure how best to do that. We certainly don't want to waste your time by bringing it in prematurely and I'm not sure our strategies are all that final, although we have prepared licensing strategies in the SVP, as you know, but we welcome some interaction with you on that.

Well, what I just talked with were basically things that those of us who organized through dry runs of the presentation, Jean Younker, Dave Dobson and myself. What I would like to do is give the people I work for and work with an opportunity to add anything that they may care to add. Carl?

MR. GERTZ: Max, it's all in your hands. I'm sure you've done well.

MR. BLANCHARD: Okay. Dick, would you like to add something? Steve? Okay. All right, I thank you very much for the opportunity and we look forward for the opportunity to do it again.

DR. LANGMUIR: Max, I'd like to thank you very much, and the rest of the DOE staff for an outstanding job of putting this program together, and the scientists and engineers who worked for you and with you for a great job of presentations in the last day and a half. And, I guess with that, we close the meeting.

(Whereupon, the meeting was concluded.)