UNITED STATES
NUCLEAR WASTE TECHNICAL REVIEW BOARD

FULL BOARD MEETING

October 14, 1992
Plaza Suite Hotel
Las Vegas, Nevada

BOARD MEMBERS PRESENT

Dr. John E. Cantlon, Chairman, NWTRB
Dr. Ellis Verink, Co-Chair, Morning Session
Dr. Donald Langmuir, Co-Chair, Afternoon Session
Dr. Patrick Domenico, Member
Dr. Clarence Allen, Member
Dr. John J. McKetta, Member
Dr. Edward Cording, Member
Dr. Dennis Price, Member
Dr. Garry Brewer, Member
Dr. Warner North, Member

ALSO PRESENT

Dr. William Barnard, Executive Director, NWTRB
Dr. Leon Reiter, Senior Professional Staff
Dr. Sherwood Chu, Senior Professional Staff
Dr. Robert Luce, Senior Professional Staff
Dr. Carl DiBella, Senior Professional Staff
Russell K. McFarland, Senior Professional Staff
Dr. Nava Garisto, Consultant
Dr. Michael Apted, Consultant
Ms. Paula Alford, Director, External Affairs
Frank Randall, Assistant, External Affairs
Ms. Vicki Reich, Librarian
Ms. Helen Einersen, Executive Assistant
Ms. Linda Hiatt, Management Assistant
Ms. Nancy Derr, Director, Publications

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P R O C E E D I N G S

(8:30 a.m.)

DR. CANTLON: Welcome to the Nuclear Waste Technical Review Board's fall meeting. My name is John Cantlon. I am Chairman of the Board, Vice President Emeritus for Research and Graduate studies at Michigan State University. My professional field is environmental biology.

Let me briefly introduce our other Board members here today:

Dr. Clarence Allen, Professor Emeritus of Geology and Geophysics at the California Institute of Technology.

Number 2, Patrick Domenico, who is the David B. Harris Professor of Geology at Texas A&M.

Dr. Donald Langmuir, Professor of Geochemistry, Colorado School of Mines.

Warner North, Consulting Professor in Engineering and Economic Systems at Stanford University and a principal with Decision Focus, a consulting firm.

Dennis Price, Professor of Industrial and Systems Engineering and Director of the Safety Projects Office at Virginia Polytechnic Institute and State University.

Ellis Verink, Distinguished Service Professor of Metallurgy, Metallurgical Engineering Emeritus at the University of Florida.

John McKetta, the Joe C. Walter Professor of

Chemical Engineering at the University of Texas, Austin.

Garry Brewer, Professor of Resource Policy and Management and Dean of the School of Natural Resources and Environment at the University of Michigan.

Ed Cording, Professor of Civil Engineering at the University of Illinois.

We have asked three consultants to join us for this meeting. Unfortunately, Professor Thomas Pickford, Professor of Nuclear Engineering at the University of California, Berkeley will be unable to attend because of illness in his family. However, Dr. Nava Garisto, with Beak Consultants, Ltd., of Brampton, Ontario, and Dr. Mick Apted with Intera Information Technologies, Inc., of Denver are with us today.

Also in attendance today are our technical staff. Most of you know that the Nuclear Waste Technical Review Board was created by Congress in the 1987 amendments to the Nuclear Waste Policy Act of 1982. The Board is charged with providing an unbiased source of expert advise on the technical and scientific validity of the DOE's work in high-level nuclear waste management.

The topic that the Board will be hearing about during the next three half-day sessions is the characterization of the source term for the performance assessment of the Yucca Mountain site. This is a complex topic that involves the calculation of the concentration of radionuclides released under various failure scenarios from the engineered barrier system. This is a very broad topic that cuts across scientific and engineering disciplines. To reflect this, our three sessions will be chaired by three other of our Board members. Ellis Verink will chair this morning's session in which the waste package effects on the source term are discussed; Don Langmuir will chair this afternoon's session in which the geochemical effects on the source term are presented. Tomorrow morning, Pat Domenico will chair the session in which we will hear how the source term is being handled currently in performance assessment and how it might be handled in the future.

Following the three sessions on the source term, we will hear a presentation on the recent detailed mapping of the Ghost Dance Fault at Yucca Mountain. Then, after introductory remarks by John Bartlett, there will be a talk by Carl Gertz of the Yucca Mountain Project Office on his organization's fiscal 1993 budget.

To stay within our tight schedule, questions will be accepted during each presentation only from members of the Board and its professional staff. During discussion periods following presentations, an opportunity will be provided for questions from others. Since the Board has a formal transcript of our public sessions, each speaker should identify his or her name and affiliation.

Just one logistics announcement. The hotel has set up a buffet for speedily getting lunch to this group so we can get back for our afternoon session. This will be in the regular restaurant here for $5.95, rather than the usual higher-priced hotel meals.

Now, I'd like to turn the morning session over to Ellis Verink, who will chair our opening session on source term.

Ellis?

DR. VERINK: Thank you, John.

As John indicated, I am the Chair of the Board's Panel on the Engineered Barrier System.

We have a suite of very interesting presentations scheduled for this morning. With only one or two exceptions, the presentations all will deal with what goes on at or inside the waste package wall. That is, of course, the very heart of the source term.

For example, Dave Stahl, of Babcock & Wilcox, will start the technical presentations by describing the concept and the definition of the source term. Following Dave will be Rich Van Konynenburg of Lawrence Livermore, to refresh our memories on what appears to be the only potential gaseous release of possible regulatory significance, Carbon-14. He will bring us up-to-date on its current status.

The innermost part of the spent fuel source term is the spent fuel itself, and Ray Stout from Livermore will give us an overview of the spent fuel area before the morning break. After a short break, we will then hear from Bob Einziger of Pacific Northwest Laboratories, about his ongoing experimental studies regarding what happens when the waste package filler and cladding are all eventually breached and oxygen comes in contact with the spent fuel.

Walt Gray, also of PNL, will then talk about his laboratory work on the leaching that occurs when water eventually penetrates the protective layers and contacts the spent fuel.

Steve Steward of Livermore will cap off the morning session by discussing his experimental efforts on what happens when water comes in contact with unirradiated uranium oxide.

When I looked at the agenda, I noticed that there were some rather key source term topics which are missing from the entire two-day session. For example, there apparently will be no discussion of experimental work on spent fuel characterization or cladding corrosion or waste package corrosion.

At the end of the day, Diane Harrison, of DOE's Yucca Mountain Site Characterization Project Office here in Las Vegas, will talk about plans for future work, and Carl Gertz will talk about the fiscal '93 budget tomorrow afternoon.

I hope either or both will address something with regard to plans for experimental work to gather long-term data on the performance of waste package materials.

We have two really very full days ahead of us. Therefore, we will have to adhere to the schedule very rigidly. And I want to repeat Dr. Cantlon's comment, the ground rules for this morning are very simple. The speakers all know that they must time their presentations to allow for questions. As time permits, at the end of each talk, we will have questions first from the Board and its staff, then from the audience. Questions that can't fit in will just have to wait until the end of the day tomorrow.

I'd like to mention one last item for your possible interest. Three members of the Engineered Barrier System Panel, Drs. Langmuir, Price and I, have just returned three weeks ago from a brief visit to Japan. In terms of nuclear electric generation, the Japanese nuclear program is second only to the programs of the United States and France, and the Japanese have made a very strong commitment to expanding the role of nuclear energy. We met with officials and researchers of the PNC, which is the Japanese government-owned organization, and which has a leading role in the nuclear waste disposal research. We will be reporting formally about it in upcoming reports to Congress and to the

Secretary, but I want to mention one thing we learned on our trip, which I believe is instructive.

Despite the fact that the Japanese do not intend to start repository operations until some 2030 or later, or at the very latest, 2040, perhaps the mid-'40s; in other words, some 20 to 35 years after the target of 2010, the operational proposed date for the U.S. repository, the Japanese, nonetheless, have an extremely strong experimental program in the area of the Engineered Barrier Design. They are looking at a multi-barrier concept, with a massive, robust Engineered Barrier System.

It is now my particular pleasure to call for Carl Gertz, who will get us started with some comments from DOE.

Carl?

MR. GERTZ: I just have a very few comments. I would like to welcome the Board to this full Board Meeting. I am pleased that on Friday you are going to be going out to the site. I have distributed an updated agenda to Bill about the things we are going to do and see and who you are going to talk to at the site. If you all have any comments for additions, if you can get them to me by the end of the day or tomorrow, we will try to incorporate that into Friday's agenda, but we have not only a full two days of presentations, a day and a half certainly on the source term, we're eager to talk to you about the mapping at Ghost Dance

Fault, and I am also very eager to talk to you about the '93 budget and explain to you how we are going present our program in progress in '93. But I will save that all until tomorrow.

Once again, welcome, Dr. Cantlon and your Board. We are glad to have you, and we're looking forward to a fruitful interaction with you these next three days.

With that, I guess Dave, you are going to start the technical session.

DR. STAHL: Good morning, members of the Board, ladies and gentlemen.

I am David Stahl from the M&O, B&W Fuel Company, and it's my pleasure this morning to kick off the technical sessions here on source term concept and definition.

Just a brief outline of the things that I'll address this morning: These will be a very high level, with a great deal of detail on these areas as we progress through the technical presentations.

I'll start off with source term definition and the major interfaces. As you can see, a very succinct definition: radionuclide release from the Engineered Barrier System into the host rock, and this is the definition that we're working with now and it's conceivable that it could change slightly over time, depending on definition of the near versus the far field, for example.

These are the three major interfaces: containment performance, EBS release, and near-field flow and transport, and you'll see that as I get into the model hierarchy and the interaction between those different functions.

The next area is the model hierarchy, and I didn't intend for you to study this diagram, just to show basically its pedigree. This is the model hierarchy from the SCP on how we are to reach resolution on these upper level issues.

On the next chart, what I've done is to focus on this upper portion of the diagram specifically dealing with the waste form and the source term.

These are the issues that we are addressing: overall system performance, and the release from the EBS, and the waste package itself, waste package containment. You can see here the interaction between containment performance, EBS release and the source term, and today you'll be hearing presentations in regard to waste form release, a little bit about waste package environment as it affects flow and transport, and performance assessment.

We specifically will not be addressing waste package corrosion in this session. That will be the subject of another Board meeting, but we will address briefly cladding corrosion work, and Ray Stout will cover that.

As far as the EBS components, I think that many of the Board have heard my presentation in regard to some of the concepts that we've been considering in addition to the SCP design, which focuses on a thin-walled single, metal barrier, vertical borehole-emplaced package.

Here is another concept that we've been considering. This is a multi-walled, multi-barrier container, we believe a robust container, and this shows a concept of drift emplacement where you have an engineered invert, have an opportunity for engineering the packing material as well as the backfill material. And this just shows here the various components that we'll have to consider in the analysis of the source term. You can see here we have groundwater entering and eventually we will have groundwater exiting the EBS. And we have some possible materials, not, certainly, exhaustive nor meant to say these are the ones that we have chosen, but this is one concept that we have been considering.

You can see here for the backfill we have crushed tuff, perhaps in different diameters, to allow us to be able to shed water away from the package. In this particular case, we have an outer containment barrier which is a weathering steel, it could be another steel. We're looking at, as I've explained in other presentations, corrosion allowance materials for this thick wall overpack.

We have a separator. It could be stainless steel shot, some other high conductivity material such that we can have room for the space here between the inner and the outer containers, so they can be made up separately. This is the inner containment barrier, most likely Alloy 825 or some other high nickel corrosion-resistant material, which you've heard about, and Lawrence Livermore has done some extensive work in evaluating this particular alloy.

Within that barrier, you have the spent fuel basket assembly, probably some kind of borated material for criticality control. More than likely, if we have an opportunity, we will have some buffer or filler materials that we can control the geochemistry; also have a mechanical restraint for the spent fuel assemblies that will be emplaced inside. That could be an iron oxide powder or some other material. And, as I indicate here on the bottom, the engineered inverse could be a coarse tuff, but it could also contain zeolites or other materials for radionuclide absorption and retardation.

On the next chart, I've indicated some of the processes, I hope I have them all, that we might see as we go down through the various barriers that I show here.

As I mentioned, water enters the EBS, we are going to have some water backfill interactions, and eventually the water and waste package will interact. We will then have a container degradation. Hopefully, failure will be extended in time. We will then have Carbon-14 release, because

Carbon-14, as you know, and you will see in the presentation following by Rich Van Konynenburg, there is Carbon-14 on the surface of the cladding and that could be released when you have the barriers failing.

Then you will have some water filler interactions and water and water vapor can then interact and contact the waste form, leading to leaching and corrosion and we'll deal with those issues in presentations by Ray Stout. Also at the same time, oxidation will be going on, and Bob Einziger will talk about some of the work that we're doing there. Leaching and corrosion has been the subject of work at PNL and to some degree at Argonne, and Walt Gray and Steve Steward will talk about the work that we're doing there.

Then we have the potential for radionuclide release from the package. As I mentioned, we could have some zeolitic or other materials in the invert, in the backfill, so that there could be some radionuclide backfill and invert interactions, and eventually, a release from the EBS.

Now this is a subset of the model hierarchy that I've shown earlier. It shows releases for the waste form, aqueous releases in carbon and gaseous releases, mostly Carbon-14, although there are some noble gases that will be released when the cladding fails.

We have glass and spent fuel releases and you'll hear a little bit about the glass work as well that's ongoing at Argonne National Laboratory. Hardware release, we had planned some work on that, but it is not currently funded. As far as spent fuel, we have the outset matrix itself and the cladding, and of course the gap and grain boundary, and you'll hear about those activities.

Just a few words about waste acceptance. I think you've seen this slide before from another TRB presentation. Basically, we are going to accept spent fuel and high-level waste into the waste management system. The acceptance of spent fuel and high-level waste is based on 10 CFR Part 961, the standard contract. There have been suggested modifications to that contract, and DOE is currently negotiating with the utilities on the acceptance criteria.

As far as high-level waste glass, you've heard discussions in the past about the waste acceptance criteria. These are currently being emplaced in a new waste acceptance system requirements document, and the objective there is to provide a high confidence that the product falls within a range, an acceptable range of chemical and physical properties. And we are using, as we've discussed previously, the product consistency test that was developed by Savannah River Laboratory. And later, of course, we will be testing and modeling those glasses to confirm the compliance with the NRC and the EPA regulations.

As you know, we have about 24,000 metric tons of inventory currently. By the year 2000, we'll have over 40,000 metric tons, and as you can see, that's growing at a roughly linear rate of about 2,000 metric ton per year based on the no new order case of existing reactors.

This is shown in this bar chart here as a comparison between the current inventory--and, unfortunately, this is an older chart, but it hasn't changed much as far as the distribution--shows the PWR and the BWR component and you can see that the peak burnup here is in the range of 25-30,000 metric day per ton. The utilities are expanding the burnup ranges of their fuel, and as you can see, as the inventory builds for the repository the average is going to be higher than 35,000 to 40,000 metric tons, 40,000 gigawatt days per metric ton, and as you can see, the outer edge is pushing up to 55,000 to 60,000.

So that's a slightly different inventory that we have presently and have studied presently than will exist, and Ray Stout will address this issue about the need to get new, what we call ATMs, approved test materials.

I want to address the issue briefly of our approach to model development, and again set the stage for some of the things that you'll hear later on. We'd like to bound the performance of spent fuel using the ASTMC 1174 procedure, and I'll show you in the next chart a schematic of that procedure. Basically, it focuses on mechanistic understanding. If you don't achieve fully mechanistic understanding, what you shoot for then is partial mechanistic understanding.

We need to perform saturated and unsaturated testing of both unaltered and altered waste forms, and you'll hear about that, as I mentioned.

We have and will continue to use EQ3/6 simulations to aid the modeling process. We'll also have to evaluate natural analogues as a means to partially validate performance models. There is no way we can fully validate them, but with natural analogues, we hope that we can at least partially validate those models. And last, we have to define and perform integrated tests to confirm in-repository interactions.

This chart basically shows the parallelism between the model development side and the material testing side. See, you start with identifying the credible conditions, identifying alteration modes, developing conceptual models, eventually come down to be able to validate or partially validate your model.

Over here on the material side, the testing side, you see we do the same kinds of things; identify the concepts, evaluate data, develop plans, conduct tests, and at each stage here we have some interactions between the testing and the modeling activities. And as they indicate, eventually we'll have these natural analogues against which we can compare long-term performance and prediction of the code. And eventually we can go into our PA and our total system performance.

I should indicate also, and it's not shown in the graph that there are feeds to performance from the concept models and the full bore models. So, hopefully, there will be some interaction there as well.

With regard to information needs, for spent-fuel we need to understand the Carbon-14 release mechanisms. We know the inventory and we've done some scoping tests to evaluate Carbon-14 release, but we don't fully understand the mechanism, and Rich is going to bring us up-to-date on that. Spent-fuel oxidation kinetics, again, it's an area that we've done considerable testing. More needs to be done.

We're just beginning to understand where technetium is and how it's released, as well as the other soluble species. As far as colloid formation, again, that's an area we've done some work, but much more is needed.

As far as cladding and hardware release, we have just done some preliminary tests, scoping tests on cladding, and have done essentially no work on hardware.

Now for high-level waste glass, basically two areas: the reaction hydration kinetics--and you'll hear a little bit about that today--and the release from the reacted glass; again, some experimental work, but much more needs to be done.

And the last subject of my presentation is just to touch briefly on our near-term activities, and you'll hear about them during the other subsequent presentations.

We do need to characterize appropriate approved testing materials, as I mentioned, because of this shift in the spectrum of available spent-fuel and its characteristics. We have to define a thermodynamic data base because there are some holes in our ability to model using EQ 3/6, so this activity will fill those holes.

One of the things you will hear about later is the oxidation threshold. UO_2 or spent fuel can convert to higher oxide forms, and there is a threshold over which, a temperature threshold over which the fuel will go to U_3O_8, which creates a lot more surface area and then, as a result, can lead to much higher radionuclide releases. So we need to understand that oxidation threshold.

We need to continue our spent-fuel and UO_2 dissolution test matrix, try to understand those processes and be able to better model them. We need to reinstate our glass testing and modeling effort. That's been in hiatus as far as the project is concerned. And lastly, we need to perform tests on altered waste forms.

Are there questions from the Board? I'd be happy to try to answer them, but I know that the details will be presented by subsequent presenters.

DR. LANGMUIR: Dave, Don Langmuir, Board. The implication I get from how you are presenting all of this is that the M&O is assuming a certain thermal loading strategy at this point. At least you are considering a strategy which will have saturated conditions in it at some time.

DR. STAHL: That's always true. What we've looked at as far as thermal loading strategy is to examine both cold and hot, or, let's say, a spectrum of thermal loading. And what we'd like to do is focus on a particular area, and right now we've chosen to study the higher loading area because we feel from an engineering sense that makes the most sense. But at the same time, we will be bringing along some of the other scenarios that we will study. Does that answer your question?

DR. NORTH: Could you tell us a little bit more about the research that was contemplated on hardware releases--this is going back about halfway through your slide package--and what the schedule is for getting that research done under the plans for future funds?

DR. STAHL: Yes, certainly. You will see in Ray Stout's presentation a schedule for the activities within the spent fuel area, and I believe we show some work starting in FY94; is that correct, Ray?

DR. STOUT: Commission 2001 planning says it will start FY94.

DR. STAHL: Basically what we were looking at is the hardware within the assembly--the end fittings, for example, any zircaloy that's in there--as well as other components. And they are a source of fission products. We don't feel that it's a major source as far as release is concerned, but we do need to do those tests, and we haven't done them yet.

DR. GARISTO: Nava Garisto from Beak. In your modeling approach, there were some geochemical details and I wonder if there is any plan for integrating the specific geochemical source term work with hydrogeology and mass transport, because the two actually are a specific part of--

DR. STAHL: Yes, absolutely. That is not the subject for this meeting, but I'm not sure if there is anyone here that could adequately cover it. But one of the things that we're planning to do in the near term is to couple the V-TOUGH, for example, to a geochemical code so that we'll have an understanding of the processes that are going on simultaneously. So that's something that's planned, and there's been some effort started this past year to couple those codes, but it's a minor effort. I don't know if there is anyone in the audience that can respond to that.

Tom?

MR. BUSCHECK: Tom Buscheck from Lawrence Livermore.

I'm test leader of hydrology. Just a very preliminary sort of uncharted effort right now. We have been looking at pathways through the system and we are producing temperature pressure saturation histories along these pathways, and this will be used to drive EQ 6 calculations. The initial calculations would assume no back-coupling into the hydrological properties, but just to look at the hydrothermal conditions that a packet of fluid moving through the system would be subjected to. So this--we already have a prototype for this.

DR. VERINK: Dr. Cantlon?

DR. CANTLON: Yes. Do you see any changes in the way you approach source term emanating from the new change in the standard for licensing Yucca Mountain?

DR. STAHL: I suspect there will be some changes, but we haven't taken a hard look at that yet. That basic approach will not change.

DR. CORDING: Just a brief question that goes, I know goes beyond the detail, the topic of the source term, but the engineered barrier you show for the canister, the drift emplacement, shows the tuff surrounding it and it looks like a very interesting concept. Are there groups presently working on that part of the barrier as well, and are they considering the effect of some sort of fault displacements on that combination of that tuff surrounding the containment vessel?

DR. STAHL: To answer the first part of your question first, B&W Fuel Company, as part of the M&O, is responsible for the design of the waste package and the engineered barrier system. And we have developed, as a first step in the process of design, seven or eight concepts that we're taking into our advanced conceptual design phase, which has just started October 1st. So we will be evaluating those designs. That is, the one that's in the package is just one design of those.

As far as the second question, we do have a small effort looking at mechanical stability of the openings. I'm not sure if that fully addresses your concern, but that's part of the work that we will be doing.

DR. APTED: Mick Apted with Intera. In the next two days, are we going to hear someone actually derive from some sort of modeling approach these data needs, or did they spring sort of full-grown from someone's head?

DR. STAHL: No. You'll hear them again as each presenter speaks on his technical area. This is just a roll up, at least my view of all the activity.

DR. APTED: But is someone going to present some sort of systematic use of performance assessment or source term modeling to show how these data, out of the tremendous range of data that could be collected, are the ones that represent sort of key performance?

DR. STAHL: You'll hear some of that when we get to the system performance papers, but not a lot. I agree it's not as fully integrated as you're suggesting.

DR. APTED: All right. The second question I had, your definition that you start with says for source term, it is radionuclide release from the EBS, and then a couple of pages later--and I'm just trying to understand the differences--when you had that sort of simplified hierarchy, you had EBS release and then you have something separate called source term. And that seems to be, the difference seems to be some sort of near-field flow and transport.

DR. STAHL: That's correct.

DR. APTED: So is someone going to be talking about that sort of coupling between the near-field and the far-field as part of source term?

DR. STAHl: You'll hear those in the performance assessment papers.

DR. APTED: Thank you.

DR. VERINK: Are there other questions from the Board or the consultants; the staff? We would have time for perhaps one, maybe two questions from the audience, if there are any.

MR. WILDER: Dale Wilder, Lawrence Livermore Lab. I want to just follow up a little bit on the questions asked about coupling, and this isn't so much a question as a comment.

Bill Glassley has been doing some work, looking at numbers to look at when kinetics versus equilibrium takes place relative to the rapidity with which the moisture is moving. The work is very preliminary, but that is some of the kinds couplings that we are currently doing. That not only will tell us where we can use equilibrium codes versus kinetic codes, but it also tells us where we can expect geochemical reactions to have gone to completion so that we will have rock water interaction.

DR. VERINK: Thank you, Dale. Is there perhaps one more question?

If not, Rich, I guess you are next. We have a little extra leeway here.

DR. VAN KONYNENBURG: Good morning. It is a pleasure for me to be able to talk to you about Carbon-14 today. A lot of the information that I'll be discussing has been developed over the past few years. We first became interested in this problem about nine years ago.

I thought it might be helpful to start from the cradle, essentially, and figure out where the Carbon-14 really originates. As you can see here, there are three reactions that I have listed, and in the case of light-water reactors, the first reaction predominates in the fuel and in the cladding and in the structural materials because of impurity nitrogen. It's important to notice that nitrogen here is an impurity at a parts per million level.

Then we have another reaction here on Oxygen-17, which is a naturally occurring oxygen isotope at low abundance, and as I am sure everybody is aware, oxygen is a necessary constituent of water and the cooling of water, and also of UO_2. So we've got some of that present. And that second reaction predominates then in the cooling water.

The third reaction is not really important in light-water reactors because of this extremely low cross-section. However, it is important in graphite reactors.

So what's the fate of the Carbon-14 that's produced? Well, the fraction that is produced in the cooling water mostly leaves the reactor out the stack, and that's permitted under regulations and it amounts to about 10 curies per year for 1000 megawatt plant. A small fraction of that is extracted into the ion exchange resins and ends up in low-level waste burial, but most of it goes out.

The amount that's produced in the fuel, the spent fuel, more or less stays there. A small amount is lost and is being lost as we speak while this spent fuel is stored in water storage by exchange with dissolved carbon in the water, eventually going to CO_2 out the ventilation system and again out the stack.

The structural material could end up either as low level waste or as greater than Class C, which is currently destined for a repository. And that depends on levels of certain radionuclides that are there.

Now, in order to get an idea of how much we're dealing with, I'd like to look back at what was done in the past first and then talk about more recent estimates. As with most things, there are two ways to get at this. One is by calculating; another is by measuring. To do a good calculation, you have to know the nitrogen impurity levels in these materials. That's the most difficult problem. The most recent or most comprehensive work was done by Wally Davis at Oak Ridge and the subsequent documents that have been put out on the spent fuel inventory for this program have been based on that work.

Now, when I say the value for UO_2, what I mean here is the value of the nitrogen impurity content in UO_2. That's what I'm talking about. That was determined by looking at measured data from reactor fuel manufacturers. That's what Wally and others did.

And then the values that they used for nitrogen content of the other things were estimated. And these estimates were done using ASTM standards for those metals where they exist, and also ASME standards. This has a result of giving high estimates because the standards are made in a conservative way so the producers can meet those impurity levels. So that tends to give you high numbers.

Well, anyway, using these assumptions, they ended up with a value of about 1.50 curies per metric ton with that burnup. And I have to emphasize here that this is always proportional to burnup. So the higher the burnup, the higher the number of curies per metric ton you're going to have.

Then I made some revisions to these calculated numbers and I have to make a correction here. This is not megagrams, this is micrograms per gram of uranium. Essentially, a weighed part per million number here, 25 parts per million; not megagrams.

And we did retain that number because it was the only one that was based on actual measurements. The values of nitrogen impurities for the other parts, we adjusted. And you can see these were the original values. These are the new values we've come to, and you can see some significant changes, particularly in the nickel alloys that are part of the hardware on the fuel assemblies. It's over a factor of 10 reduction.

These were based on discussions with producers, and these are two of the gentlemen that I talked to. This is from a reference in the Aerospace Metals Handbook, and we believe that these numbers are closer to the actual production values average in the inventory.

So then by using these new numbers and

recalculating and adjusting, and also taking account of the work of a gentleman named Luksic at PNL, who looked at how the neutron flux and the spectrum varied over the reactor core, taking account of where these various parts were located in the core, we ended up with a new number on the same basis as that one and a half. It's down to 1.00 curie per metric ton; so essentially, two-thirds of the old number.

Now, as I said, the other approach is to try to do measurements, and measurements have been done, particularly by the Materials Characterization Center at Pacific Northwest's Lab. They've looked at a lot of samples. The samples, however, are from only a few fuel assemblies, and I think you're aware that it's not an easy or an inexpensive thing to get a hold of a lot of different fuel assemblies. We'll be talking about doing some more of that, but that's a rather laborious and expensive process.

Now, in only two fuel assemblies do we have measurements on all the components; that is, the UO_2, the cladding, the various kinds of hardware, and the gas inside the fuel rod plenum. The Carbon-14 has been measured on all those components for two fuel assemblies, and in the cases that we were then able to compare with the calculations, believe it or not, one of them came out 25 per cent higher and the other 27 per cent lower. Now that's not a lot of statistics, but that's what we have, and I think it tells us that our calculations are somewhere in the ball park. Naturally, it would be nice to have a lot more data, but as I say, there is a certain amount of cost involved and we have to look at balancing this against a lot of other things.

So to do a more precise value, we'd have to look at a lot more fuel assemblies, and there is always this problem, as Dave showed in his view graph, that two-thirds of it doesn't exist yet. It is pretty hard to analyze things that don't exist yet, so we really are stymied by that. The result of all that is, I think, that this calculated number is the best value we have at present.

Okay, now to take that number that we have just used and put it on an entire repository basis, we have to look at the mix of fuel in there. We have this capacity and some of that is defense waste. The defense waste has already lost its Carbon-14 to the atmosphere during dissolving in the acid in the reprocessing plant. So the Carbon-14 from that part is already out there.

I've taken these burnups, and I think as Dave indicated, burnups are going up. There is some PWR fuel, I'm told now, that's licensed at 60,000 megawatt days per metric ton, and there's some BWR fuel with a peak pellet burnup again of 60,000, and some people are estimating that within ten years it could go to 75,000. Now, of course, we're averaging over what's already in the inventory and the amount that the burnup is as we grow. So, the overall burnup is not going to get to values that high for the repository, but it will go up. So that needs to be kept in mind. These numbers might be low.

And then there is some fraction, BWR and PWR, and the result of this kind of calculation is an inventory of about 70 kilocuries in the entire repository, with the caveat that burnup affects that in a direct relationship.

So we know, we have an idea how much is in there. What form is it in, and where is it? Well, in the various components, again taking this example of the PWR with 33,000 burnup, you can see the distribution of where it's located. Most of it is in the UO_2, about a fifth is in the zircaloy, and the rest is in the hardware, and the gas has essentially nine orders of magnitude less. I think the reasons for that are clear chemically; that the zircaloy and the UO_2 are effective getters for carbon gases, and so if they were in the gas they would be gettered back out. So that makes sense.

Two per cent of the overall Carbon-14 inventory is located in an accessible location on the outside surface of the cladding, and these numbers come from Harry Smith and Dave Baldwin at PNL. This number here is an estimate and this data from Chuck Wilson is actually leaching in water and what he found is that the short time release into water, amounts to about half a per cent from the UO_2. So I'm just roughly estimating that if we had gas present and we were able to oxidize, that is roughly the amount that's accessible in a short time to the gap. I'm not saying that that's in the gap as gas. It's located either on the UO_2 or on the zircaloy, but it's accessible rapidly. So, roughly, we're talking about 2.5% that's available if the clad fails; from the outside of the clad, plus what's right inside the clad.

Now, chemically we are not in as good a shape. We don't really know the chemical form. It's been inferred that at least part of the Carbon-14 exists as elemental carbon in the UO_2 and the rest is probably as carbide or oxy-carbide. At these levels, in highly radioactive material, it's difficult to get a direct analytical technique to work on that. So the kind of thing that's been done is to look at how the chemical activity behaves as the concentration of carbon is reduced. And this was done some years ago at GE by Martin Adamson. That's where this inference that some of it, at least, is elemental carbon comes from.

In the metals, it's probably dissolved carbon at the levels we're talking about, maybe it is carbides, and the oxide layer, we really don't know. Now, as I said, in 1983, we first observed that Carbon-14 could come off of the outside of the cladding if it was heated in air. This was done in conjunction with dry fuel storage work by

Westinghouse and PNL that was carried out here in Nevada at the test site. We analyzed gas samples in support of that project and found Carbon-14 dioxide in the gas.

Then we followed up with some work by Harry and Dave at PNL, and, again, that's where that 2% number comes from, and that's from an experiment at the highest temperature they ran, 350 C, for eight hours. The time dependents of the release they observed is consistent with diffusion from a finite thickness layer; in other words, not from a semi-infinite medium, but from just a thin layer. And from that, I infer that it's coming from the oxide layer.

Now, we also have evidence that at these temperatures, the diffusion coefficient of carbon in zirconium, in zircaloy, is small enough that it shouldn't have released much from the bulk of the metal. So putting those two together, we're inferring that that release is from the oxide layer. Temperature dependence was roughly Arrhenius, with an 18 kcal/mole flow.

Then with that kind of Arrhenius dependence as a function of temperature the release in a 8-hour time period drops off by these factors at those temperatures. Now this was also done in commercial-grade argon, and one of the things we've kicked around, for the package in the repository, is to backfill with argon. Commercial-grade argon, of course, is not ultra high purity, it has some oxygen in there. But the release of carbon dioxide, Carbon-14 dioxide was a factor of ten lower. Now, subsequent to that there's been some German work by these gentlemen that indicates that when they went to ultra high purity argon; that is, they passed it over hot zirconium burning to really take out essentially all the oxygen and water vapor, then they were able to stop the release of CO_2. So, what it looks like is that oxygen is necessary to oxidize carbon off of the clad.

Now we also know that there's gamma radiation and betas and other things present there, and we know that when air is irradiated, we get a much more active form of oxygen, and either ozone, oxygen atoms, or free radicals, and we've found that even at low temperatures you can get oxidation of carbon off of surfaces. So, simply going to times where the temperature is very low isn't sufficient. We have to also take account of the radiation component and how that will lead to release of Carbon-14.

Now what I just talked about was from the cladding. Now I'm moving on to the UO_2 itself. We have not in this project, at this point, done measurements of that, but what I have here is an old data point from Stacy & Goode on the old oxidation program, and the idea there was it was a method of treating UO_2 spent fuel. The real intention was to remove tritium from it, and so the way they did that was by roasting in air and tumbling UO_2, until it oxidized and was in powder form. So it's a rather severe experiment in comparison to what we anticipate would happen in the reactor. The temperature is much higher and we've got this agitation and air blowing through there. But in that case, they found that 50 per cent was released, meaning that fifty per cent was still in the uranium oxide, even in the higher oxidation state. So that is an interesting point. This bears on the issue of how much of the Carbon-14 inventory in the UO_2 is really available for release? Will some of it be tied up as, for example, some kind of a stable carbide, or oxy-carbide that won't be released?

Again, bear in mind that this is a four-hour test, and extrapolating that to 10,000 with other kinds of conditions is problematical, but I thought I'd put it up because it's the one data point we have on that subject.

Now these are probably obvious, but I think they bear mentioning. You can't get Carbon-14 dioxide out of the package unless the container is breached. We're not worried here about solid state diffusion. And you can't get it from inside of the fuel rods unless the cladding breaches.

Now, the significance of these releases in terms of what the picture has been in terms of regulations, the DOE in the site characterization plan had a trial, let's say a trial interpretation of the term "substantially complete containment," which has never been officially defined. But they, in the case of Carbon-14, took that to be one part in a million per year, which would be an order of magnitude better than the NRC one part in 10^5 per year over the ten thousand year period.

Well, anyway, with that interpretation, breach of only one container in 20,000 of those in the repository, coupled with that 2 per cent loss that we are getting from the work of Smith and Baldwin, would cause this interpretation to be exceeded. So that would require an extremely high reliability of containers. Then looking at the NRC release rate limit, it's an order of magnitude down; one in two thousand would violate that.

We have had analysis by groups from the Lawrence Berkeley lab and from Brookhaven on the passage of CO_2 through small perforations, looking at effects of perforation size. These have been calculational efforts.

I was also asked to comment on what would be the consequences of total release, and now I'm moving from observations of what we see happening and what's there, to what would happen hypothetically if all of the Carbon-14 inventory from the repository were released.

Well, first of all, there's a comparison here with the global Carbon-14 inventory. As you know, it's produced naturally by cosmic rays and the repository inventory is less than 1/3000 of the global Carbon-14 inventory naturally. In three years, the cosmic rays can overwhelm the total repository inventory just by production in the upper atmosphere, and that's put right into the atmosphere.

If we somehow produced instantaneous total release of the entire repository, and then mixed the winds and mixed the atmosphere up, the maximum increase in the Carbon-14 concentration would be two per cent by doing that. That's mixing both northern and southern hemispheres' atmosphere together. If we released over a time longer than a few hundred years; in other words, rather than instantaneously, but let it go for a few centuries coming out, total inventory, then we only raise the concentration in the atmosphere by about a tenth of a per cent or less. Now, the reason is now that we can exchange with the ocean and with other reservoirs on the earth for carbon, like the organic material, plant life and so on.

And just for comparison, not that I am advocating this or anything like that, but this is an observed point. The atmospheric nuclear weapons tests did raise the concentration by 84 per cent. And by the way, the air that we're breathing right now is still coming down from that peak of 84 per cent. It still has not reached background levels from the weapons testing which ended in 1963 with the treaty that stopped testing, and it just takes that long to exchange with the oceans and so on.

And then there had been modeling by a group at the University of Glasgow to see what will happen in the future to the Carbon-14 specific activity in the atmosphere. And the important thing here is that if you burn fossil fuels, they're too old to have Carbon-14, so they dilute with Carbon-12. The same thing is true of roasting carbonate minerals to make Portland cement. Those release a lot of Carbon-12 O_2 to the atmosphere.

Well, if you model those--and, of course, you have to make some assumptions about fossil fuel use and so on, but the general result is that out to 2050 there is no substantial increase in Carbon-14, because the two essentially balance each other. Now, of course, that's going to depend on what people really do. Are we going to take the global warming theory seriously, or are we going to really cut down a lot of fossil fuels? What will happen to the growth of nuclear power or so on? There are a lot of uncertainties there. Out to 2050, though, the assumptions aren't too bad, because it takes a long time to build a new nuclear reactor and we know how many we have already.

How about the dose to individuals? On the average, the release of the entire inventory, again, would be less than one microrem per year as compared with the background of 300 millirems, so that's 300,000 times as large, and that includes the radon that's partly the result of house construction.

Now, the maximum dose to individuals gets to be a little more controversial. You'll see different models for this, and I have made a judgment here when I say "for reasonable assumptions." Someone else might not think these are reasonable. This should be Daer, by the way, D-A-E-R, no "g" there.

It comes out less than a tenth of a millirem per year. Now the big issue there is where is the food grown? And we have seen models where a person builds a greenhouse on top of Yucca Mountain and lives inside of it and grows all his food there. We have even seen models that, although they don't say so, it would require a large herd of Maxwell demons to sit inside the greenhouse and emit Carbon-14 dioxide molecules into this greenhouse but nothing else to collect them all, but not build up a back pressure due to other gases. Well, that is what I'm talking about when I say reasonable. Again, that's somewhat controversial. You might make that number go up a little bit, but it's still in that ball park.

Now, the average fatal cancer risk lifetime to individuals, using these values here, would be less than 1 in 100 million, and these kind of levels are well below what are controlled in other regulations for chemical toxins.

Now this here has been the big bugaboo with the existing EPA regulations. As you know, they were derived on the basis of population dose to the entire world population over 10,000 years; real population assumed at about 10 billion. If you do that, integrate these extremely small doses over everybody in the world, you can end up calculating an average of something like one death per year over 10,000 years. So this has been the regulatory issue. Do you look at on a viewpoint of population dose, like this, or do you look at it from the basis of an individual? And I think people are aware of what occurred in the Congress last week. There was a shift in the paradigm from going from the population dose to the individual. We don't know what all the ramifications of that are going to be yet. Will the President sign it? Will the National Academy agree with these recommendations? Will they set the level at something comparable to other risks? What will happen? I can't tell you that. But I can tell you what I hope will happen, maybe over coffee.

All right, information needs. And I phrased these from the standpoint of improving our ability to model the source term. Now whether we need to model the source term a lot better is, I think, something that needs to be discussed. But if we do, then these are the things we need. This gets to the point you were mentioning a little earlier.

Time-to-failure for the containers and the zircaloy cladding. Again, if they don't fail, we don't release Carbon-14.

Better estimates of what happens when they do fail. What size hole do we have? How many holes? When do they happen? What's the temperature at the time they do happen?

More data on release from zircaloy in air. We do have some data here. It would be nice to have some more.

What is the chemical form in UO_2? We have some inferences about that. Maybe we could do better on figuring out what that really is quantitatively.

How about the release from the UO_2 in air? As I say, in this project, so far we have not measured any data in that regard.

What about quantifying the effect of radiation on release of Carbon-14 from both of those components?

How about the long-term oxidation rates of these metals? You can see that stainless steel had a pretty good inventory, the hardware there. At what rate is that released as the materials oxidize?

And then, what really is the fate of the carbon during the oxidation of the UO_2 in metals? Can you assume as the oxidation front for these materials moves into the material, that all the carbon there goes off as CO_2, or is some of it going to be retained as a carbide or oxy-carbide or what? We really don't have a lot of information on that.

So then finally to summarize, first of all, in my opinion at least, the inventory is fairly well established. Now, again, two-thirds of the fuel hasn't been produced yet, so it's hard to argue with that statement.

There are many uncertainties, though, when we go from what the actual inventory value is to producing a source term for calculation of release. And that's where all these other mechanisms come in.

Now, the consequences of releasing all of it are very small from the standpoint of the individual. However, if you look at it from the standpoint of a population, you can calculate a significant number of cases.

The source term uncertainties do need to be reduced further. How much we need to reduce them is going to depend on what the new regulations are. We won't know that for quite awhile. And the feasibility of actually significantly releasing them needs to be taken into account when we set out to do it. Some of these things are very hard to put a number on, and I think we ought to take a look at the big picture before we launch into it, so that's the conclusion.

Are there any comments or questions?

DR. VERINK: Any questions from the Board?

DR. CANTLON: Cantlon; Board. As we shift to dry storage, as seems to be the case with the delay in MRS, things like that coming up, is there any thought about possibilities of extracting some of the $^{14}CO_2$ from the dry storage casks before they get into the repository?

DR. VAN KONYNENBURG: I don't know whether there is or not. I do know that in the course of working on dry storage we have done an analysis of gas inside the casks and seen what sort of levels are there. And we do observe some Carbon-14 there. I can't say whether there is a plan to do that. That's an interesting point.

DR. VERINK: Any other questions--yes, Dr. Apted.

DR. APTED: Rich, one of your slides, I guess, implied that with burnup, this Carbon-14 would increase linearly, is that what you are saying?

DR. VAN KONYNENBURG: Yes.

DR. APTED: Even though there are two separate reactions that are leading to Carbon-14?

DR. VAN KONYNENBURG: Yes. They're not coupled reactions, they're in parallel. Yeah. The point is, if you take the five sigma product, even at extremely high burnup, it's still far less than one, so you haven't exhausted the nitrogen that's there.

DR. APTED: So if you wanted to make an extrapolation, then, the 60,000 megawatt day burnup fuel would have a linear increase in the Carbon-14?

DR. VAN KONYNENBURG: Yes. As long as the new reactor designs don't change the neutron spectrum or something like that, but if you have essentially the same thermal neutron spectrum, yeah, it would just go directly.

DR. APTED: The second question is just sort of more as a favor. I applaud you including the references, it really helps, but since they're not a specific reference, is there some way you can supply that in terms of the specific references that are cited?

DR. VAN KONYNENBURG: Yes. Earlier, I guess it's been a couple of years, the Board requested my full draft report. It has all the references in it. I guess you probably weren't here then, but maybe I can get you a copy of that one.

DR. VERINK: Dr. Garisto.

DR. GARISTO: You described some maximum dose calculations that included food chains, and I wonder if you also considered operational phase source terms and could they be higher in the long term?

DR. VAN KONYNENBURG: I'm sorry, if we considered the what?

DR. GARISTO: Operational phase source terms, like X points during the--

DR. VAN KONYNENBURG: Oh, during the operation of the repository.

DR. VERINK: Can you repeat the question? I don't think it was very well heard.

DR. VAN KONYNENBURG: Okay. What Nava is asking is, I presented some doses to people based on eating food. What she is wondering about is during the operational phase of the repository, I presume you are talking about releases into the atmosphere from the ventilation system and so on.

DR. GARISTO: The effects to the workers.

DR. VAN KONYNENBURG: Oh, occupational doses you're talking about, okay.

I haven't done any of that work. Assuming the waste packages are able to survive for 50 years, which, you know, they sure should, we shouldn't have Carbon-14 releases during the operational phase. Now, no doubt there'll be some failures and we have to take those into account. But I would think the Carbon-14 releases during that time should be extremely small. I can't do much better than that.

DR. VERINK: Any other questions from the Board or the staff? There would be time for--pardon me, Leon.

DR. REITER: Leon Reiter, Technical Review Board Staff.

Rich, you were a member of the SAB subcommittee of the EPA which looked at Carbon-14, and according to at least the trade press, the committee is recommending--and let's assume we're not in an individual release mode--aggressive investigation of multiple barriers for this problem. Could you comment on that?

DR. VAN KONYNENBURG: Well, the deliberations of that subcommittee are still underway, and I don't think I had better pre-judge what the outcome of that's going to be. As of the day before yesterday, we're still not in agreement. Whether we will be able to reach consensus wording remains to be seen, and I've given them my local phone number, so we're still at it. But there is something like 13 or 14 people on that subcommittee from a wide variety of backgrounds and opinions and it's very difficult in that environment to reach a consensus on anything, but we're working on it.

DR. VERINK: There would be time for one from the audience. Please give your name and association.

MR. CURTIS: My name is David Curtis. I am from Los Alamos.

Could you reiterate the argument for ignoring diffusional losses?

DR. VAN KONYNENBURG: Solid state diffusion?

MR. CURTIS: Yes.

DR. VAN KONYNENBURG: Well, the diffusion coefficients coupled with the thickness of the wall make the releases very small. First of all, you've got to get oxygen in. There's some oxygen in at the beginning, but you've got to get oxygen in to form the carbon dioxide for the bulk of it, and then you've got to get the carbon dioxide back out. So it just doesn't look like it's something to worry about.

MR. RAMSPOTT: Larry Ramspott from Livermore Lab. Rich, that was a really good, concise presentation, but you left the impression that we really have a good handle on the inventory of Carbon-14, and I think that's true for PWR and BWR. Would you care to comment about a lot of the other types of fuels that might go into the reactor, HTGR, some of the experimental reactor fuels, naval fuels, things like that that might possibly be going in?

DR. VAN KONYNENBURG: It's true that we haven't quantified the amounts of Carbon-14 in some of these other ones. What we have to look at is the quantity of that relative to the overall inventory of fuel in the repository. Now, if a big change in policy is made and we go to, let's say, a lot of naval fuel or something like that, then I think that'll make an impact. But I did look at, for example, the Fort St. Vrain fuel sometime back, which has a lot of carbon in there, and it still wasn't a very significant change just because the total inventory of that fuel was small relative to the whole repository inventory.

MR. SHAW: I am Bob Shaw from EPRI. I have two questions. The first has to do with that 2 per cent quick release that's from the surface of the zircaloy, and you made reference to that being released from the zirconium oxide, and I'm wondering if there's any justification for saying that in contrast to the corrosion products, commonly referred to as crud, that's in the fuel and how the inventory might be distributed between those two?

DR. VAN KONYNENBURG: The only piece of data that I can cite in regard to that is that Harry Smith and Dave Baldwin took some cladding that had an oxide layer and some crud, and they did an acid rinse to remove what was easily removable and then looked at it again and they got essentially the same release in both cases. So that's the only piece of data I have. It's possible that there's some in the crud, also, but that's all we have to go on.

MR. SHAW: You have touched on a point I wanted to make, and that is that we have done some testing on the decontamination of fuel and been able to very successfully remove corrosion products, not the zirc oxide, but corrosion products from the surface of fuel that was used in the Dresden Plant and we didn't make any Carbon-14 measurements, naturally, but it does provide a technique if there is much Carbon-14 tied up in the crud to remove that before the fuel would actually be put in the repository.

I have a second question. The measurement that you made reference to for the amount of Carbon-14 in the uranium dioxide was referred to in 1977, and I presume that was on spent fuel that had already been irradiated. Consequently, it must have been manufactured either in the late sixties or the early seventies to have reached that point. That was about the time when there were significant fuel failures, and as a result of that, a lot of changes took place in the way that fuel was manufactured. A lot of that change I know had to do with zircaloy, but I would expect that some of that had to do with UO_2. And I am wondering, I have a real idea about this, but I'm wondering if there are significant effects in the way the UO_2 is now processed compared to the ways it was then, which might have influenced the amount of nitrogen impurities that would be in that system? And a follow-up question to that is, is there any reason why we don't, since it's 60 per cent of the total Carbon-14 inventory, make more current measurements of Carbon-14 in UO_2?

DR. VAN KONYNENBURG: Okay. I'm in favor of more measurements. The point you made earlier, though, about that these measurements in '77 were probably on spent fuel, that was not exactly what happened. Wally Davis and the earlier work was actually made at the fuel plants. There were five different fuel plants, and analyses were done of nitrogen in the UO_2 before it went into the reactor. So these were not spent fuel measurements, and the fuel was early seventies-type fuel that the 25 parts per million was on.

MR. SHAW: So there were no Carbon-14 measurements made from UO_2?

DR. VAN KONYNENBURG: Okay. The Carbon-14 measurements that were made were made by the Materials Characterization Center on fuel that was taken out of, for example, Turkey

Point reactor and some of the others, H.B. Robinson, and there was both BWR and PWR. So that was done by MCC later on. But the nitrogen contents that are used in the calculations, those were measured on virgin UO_2.

MR. SHAW: And was it those--the calculation that led you to the 60 per cent or the .6 curies in the UO_2, did that come from the nitrogen content?

DR. VAN KONYNENBURG: Yes.

MR. SHAW: Thank you.

DR. VAN KONYNENBURG: Now, getting to your other point, you know, what the manufacturers do, in a lot of cases it's hard to find that information out. They view the process for making fuel as proprietary. They're in competition with others, and it's been an area that's gotten a lot of work because of the economic incentive for going for higher burnup. So, fuel development, you know, continues, each company doing the best thing it can to get the longest life out of the fuel. And there were some manufacturers who, for example, when they put helium gas in just before welding the rods shut, didn't evacuate in the past; left air in there. So there's nitrogen from that source and they put the helium in on top of it. I think that practice has stopped. There are also more than one practice for converting UF_6 to UO_2 and for governing the stoichiometry of the UO_2 during the centering of the pellet. If you use ammonia in those processes, there's a nitrogen source. If you don't, you know, then there isn't. So there are some variables there, but it's very hard in discussions with manufacturers to get all that pinned down.

Maybe there's some potential there for reducing this, but bear in mind, we're talking at part per million levels now in a commercial manufacturing process and I think it's a real challenge to try to reduce that much further. Even if you do reduce nitrogen, you're stuck with the Oxygen-17 which is a natural isotope and starts to be significant once you've got the nitrogen down, starts to be a significant source. Unless you want to do isotope separation of the oxygen before you make the UO_2, I mean, this can go on and on, but the costs would really go up.

DR. VERINK: Dr. Apted.

DR. APTED: Just a point of information, that throughout you've been presenting most of your results in percentage released, so you must have been assuming the one curie per metric ton.

DR. VAN KONYNENBURG: Adjusted for burnup. Every time you do it on a real element, you've got to adjust for burnup, but, yeah, it's basically that number.

DR. APTED: Okay, so if we wanted to actually get an estimate of what the actual measured value was it would be hard from the data because it's some sort of sliding normalization method.

DR. VAN KONYNENBURG: Right, and you have to--see, all of the numbers I've quoted here are on the basis of total inventory of a spent fuel element, okay. When people do cladding work, they talk about per cent release of the cladding inventory. If they say it's 10 per cent, well, that's only one-fifth of the total so you're down to two per cent on the total basis, okay? I quote all my numbers on the total basis because that's what the regulation said.

DR. VERINK: Thank you very much, Rich. I think we'll try to pick up a few minutes on the schedule, and Dr. Ray Stout.

DR. STOUT: Good morning. My name is Ray Stout. I'm going to be talking about spent fuel modeling concepts. This is an overview. As you recall from courses in college, when you take these introductory courses, they always bring in the experts later, and so I'm going to tell you the experts will be coming later when we talk about oxidation and dissolution. These are the two main topics that we have activities in now.

What I'm going to give you first is the objective in spent fuel characterization activities and to point out how we are going to roll up things, and how we are rolling up things, but this is what we have as a charter. We're to gather data, we're to do testing, and develop models. And our interests are the physical properties, the degradation responses, and the radioactive release responses of spent fuel waste forms. This information then is to be used in waste package as well as system performance assessments in the Yucca Mountain Project.

This kind of information we are rolling up into a document. It's the Waste Form Characteristics Report. It's now got the term preliminary on, because when we started gathering information from the literature, we took what we considered readily available.   The physical property data comes from a variety of sources, Oak Ridge, Savannah River. We have in it both the spent fuel waste form--there should be a map--and the defense high-level waste inventories. This is like geometry. What kind of materials? What kind of dimensions? You'll need this when you start sizing containers and talking about material response and handling the various waste forms.

Radionuclide data for existing and projected, again, this should be--that was my mistake on the original slide. This kind of data you'll need when you talk about thermal loads, heat response because that's a decay heat as well as a release. You'll need know all the species that are in the waste forms.

The main thing that we are doing to add to this report rather than gathering things out of literature, although some of this data certainly comes from the MCC of PNL, who do work on ATMs, detailed work and reinforces what's in the literature, and will be added to this, is test data and models for the potential release rates from spent fuel and the glass. Now, the subsequent talks this morning, they will be talking about spent fuel. In the afternoon, there will be talks on glass waste forms.

What I hope to do is to show you how we have set up test matrices, how we're rolling up the experiments and developing models based on these tests, and how we'll roll that up for a performance assessment kind of model and perhaps get at some of the issues, but hopefully not get sufficient detail that we spend all day talking on this topic.

This is an overview, so this is the outline. There will be several subtopics, so I'll try to keep you more or less in tune with where I am. Essentially, we'll spend a little bit of time on spent fuel characteristics. Some of this is feedback to what Rich was saying, maybe make some of the terms he was using clearer. We'll talk about release modes; there are two, the gaseous and aqueous. And then we'll get down to kind of the work we're now doing. We have five main sources or topics here and potentially modes of release, and finally, I'll summarize and tell you what we plan to do in the future based on Mission 2001 budgeting.

Now, this view graph isn't in your handout. It would only show up as a black page. Some of you have seen it before, but one of the things that's been mentioned is PWR. That's a pressurized water reactor. It means that there's a pressure in the core. This is core, showing you cells where assemblies go. There is a couple hundred cells, typically 170. This is a typical assembly in the core. These are--this is probably, I think, a 16 X 16 and that's a PWR. That means it's only got 16 this way, 16 this way. They are probably three, four--well, four or five meters long and each one of the rods is about a centimeter in diameter.

The things that you see are spacer grids. This is considered part of the hardware. This stuff on top and bottom is part of the hardware.

The next view graph is also colored. It shows a BWR. This is a boiling water reactor. They typically have fewer rods per assembly. I think this is either 7 X 7 or 8 X 8, but we also see in this cutaway that there are pellets and plenum region. What I've introduced, then, is an attribute that there's two kinds of reactors out there. We have it in the core. The length of time that's spent in the core will give you an attribute called burnup. That's essentially a measure of the fissions per unit volume. That's the number of Uranium-235 atoms you split plus, if you get into the plutonium, where you create plutonium, we will be splitting those. These will create fission products, so burnup gives you a measure of what's in the fuel in terms of its radioactivity in all the species.

In the operation of the reactor at high temperatures, some of these fission products are gaseous. They will be released. This is called fission gas release. This pressurizes rods. That's important when you talk about failure of cladding, so that will happen.

During the fission gas release, you sometimes have volatiles which come out of the pellets and they get into the pellet gap region, and so that gives us a source term for rapid release. So these are little things that you heard some from Rich, and this is where they're coming from.

So this is, to summarize, reactor types, burnup, fission gas release.

This is a typical size of a pellet. Westinghouse sent out a little brochure. They are really very small. They're about a centimeter in diameter. The Swedes say about five or six of these UO_2 pellets will heat your house in a reactor and power it for one year. So we're talking about literally millions of these. And what we have as a problem is a link scale problem when we go to addressing performance assessment. So this is all introductory kind of comments and when we get going, we'll get into some details. But essentially, all I'm trying to tell you is that for a repository, these are meters, hundreds of meters, kilometers kinds of measures. What is here--and this is the SCP look--is a container with assemblies in it, PWR, perhaps BWR, and you come down from this size, which is meter by four or five meters, to assemblies with its hardware, individual rods, and go over to where we do tests and our main modeling is on small pieces, small samples out of a piece of rod.

Now I have a blowup of this, but the main idea is if we do testing and modeling on this, we have to have the right kinds of units and dimensions to integrate back up to rods, to full assemblies, to container packages, and finally get you information that is useful for the performance assessment.

This blowup gives us most of the terms that you will hear throughout today and sort of a definition. I've already given you some of them. We've heard about fuel cladding. On the outside is the oxide film, which you've heard Rich talk about Carbon-14 being in and being releasable from that. You have a pellet interfacial gap that's this domain in here, which I have mentioned fission gases, and there are products coming out during reactor operation. These are soluble species mainly, we think of them; cesium, iodine, perhaps technetium. Inside the fuel pellet during reactor operation, you start out with a nice cylinder, but when you go up in temperature, thermal strains occur because of the free surfaces. These pellets fragment; they crack both radially and sometimes cross-horizontally. So this means an increase in surface area which we have to take account of. If we are doing dissolution studies, we talk about what I call intrinsic or specific, in the sense we're talking about per unit area. Anything you do to increase the area will increase the release rate, but the basic intrinsic dissolution rate will be perhaps very similar, independent of that, and we'll talk about that more.

The thing that happens, though, these grain boundaries also can load up in fission products because of diffusion out during reactor operation. So there is a grain boundary inventory. Again, these we think of--and we do not have a lot of information; Walt has done just a preliminary test. He'll maybe address some of this--so there's a grain boundary inventory. Then inside an individual grain is what we call the actinide species. Most of them are tied up in here and to get them out you have to do grain volume dissolution and grain volume processes. By far, the curies involved in spent fuel are the actinides, particularly after a long period of time. The thousand-year inventory is essentially actinides.

Well, let's go on after that to release modes. I have a few view graphs here to kind of set the stage on what we're going to be talking about. The two modes are gaseous and aqueous. This is more of, I would say, a logic kind of diagram. We'll talk about a potential time sequence in the next one. This introduces some notation which you will be hearing in my talk. It's certainly not uniform, but it only tells you that we're trying to tie down what we want to measure and how we're going to roll that up into performance assessment models.

Basically, this says that we have inventories in a waste package which we have to know fairly well, otherwise we cannot even talk about release. These are gaseous, fuel, and I have put glass in parentheses here, and metal, and by this, I mean the hardware.

A container is surrounded by air at all times and temperatures of the repository, so there will be some temperature history which will eventually be defined, based on thermal loading. We think water potentially will come back or can potentially come back. That would be less than 95 degrees, so this sets temperature ranges that we should be addressing based on what people think that max temperature thermal history will be. But you can have container failures. You should know something about this response in time. What we try to do is always talk about response rates, rate of response, rate of processes. From that, we can always integrate up one time to get what actually is occurring, or how many containers have failed at some period of time.

If you do have that, you'll have rods and hardware exposed. All this means is that you then have the capability of releasing gases, as Rich has talked about. This is Carbon-14. And you also have, if you have water, a potential of metal. This is essentially a corrosion process on hardware. We do not have any information on D_m. We can probably pick out a lot of that from the literature. And then these delta D_m's and delta G's are what we call the instantaneous response, which means that that will come out in a period essentially less than a year. And so the instantaneous response is sort of a direct delta function for a period of time represented which is long, perhaps, for us, but for a repository it's short.

After this is exposed, then you can talk about rod failure response. We need the time response for this. If a rod fails, there can be a gaseous release from inside the rod. We don't think this is going to be much. As Rich mentioned in the plenum region, Carbon-14 is nano curies compared to micro curies elsewhere, based on data that the MCC had measured. But if a rod fails, now you're over and exposing fuel and here you have the main source that we are studying, the dissolution response. Of course, you have gaseous dissolution perhaps or release some fuel, but this requires water contact. So when we'd go through the processes we have talked about here, dissolution requires water contact, air contact, may degrade the fuel and also degrade the clad, but other than gas, we don't get a release from it.

These are responses which we are looking for rate processes for, and essentially what I think of is we have a potential event sequence in time. If this is a package which already has failed, then rods are exposed, have gaseous release, we need data on what is sort of the release rate over long periods and the instantaneous. If it's exposed, then you can also have the cladding failure response. In actual fact, of course, clads can fail even though the container hasn't failed because it is a pressurized tube, and so it has a driving force for failure. We'll talk about that.

This is a time response. You'll see the symbol R, R_f, R. That just tries to tell you the number of rods which have failed per assembly per unit of time.

Going down in time, if this fails, exposes fuel, the first thing it probably sees is air, so there's a UO_2 oxidation response. There's two things that are important here. There is basically the rate at which it is oxidizing and picking up oxygen, and there is also the phase change kinetics. Bob Einziger will tell you more about this, but basically you start out with a lattice structure of UO_2 and the first phase that is seen in spent fuel is U_4O_9. That's a lattice structure. This is not exactly stoichiometric and there are some experimental details that we still need to do to understand what's going on when we get to U_4O_9. The next phase up is U_3O_8 and this phase transition here, we've done essentially very little detailed work. We hope to get started on this somewhat this year.

After the oxygen--now, the reason we study oxygen is that, as I mentioned, there is so much area here because of fragments, but if you go up to U_3O_8, this is a significant volume increase, and so the area increase because of the volume increase, it kind of forms flakes and spalls off as several orders of magnitude. So even if you have very little difference in terms of basic dissolution rate, the increased area will significantly increase your release rate.

The water, if it contacts, you have the dissolution response. Here we have D, D, which we talk about this, which should be per year here. Delta D, the instantaneous. The D comes from what's going when you dissolve a fragment that includes both grain volume and grain boundary. Delta D is the gap surface off of it, instantaneous release.

What we do, or what our thinking is that we will try to do tests which aggressively test, put the stuff in the water, put the species in the water, do a subsequent step in which we talk about solubility limits and colloidal response.

There will be some subsequent talks which talk about where we are in this and what needs to be done. But, essentially, the domain that we're studying up here--and this for preliminary design--is what's worst case in terms of oxidation response; what's the worst case in dissolution response?

Well, I believe Dave showed a view graph and this gets us into how we sort of do things. When we started, much of this started before I was on the program, but we have these main topics in spent fuel. You go into problem definition, planning, reporting, how you're going to interface. Where we are is in this box, now, we are getting quality affecting--have quality affecting experiments on oxidation response and dissolution response, and what we do is we essentially have to look at experiments. They have to be done. Then we conceptualize models, go back, say, can we do additional experiments, do better experiments, and update the models, update the experiments? This is the kind of information we're putting in this Preliminary Waste Form Characteristic Report. It is for conceptual design and assessments.

In the future, we hope to get down into here where we actually do replication experiments, validation checks for models, and finally come out the end with what we call a knowledge and data base complete for the license application design.

To do this kind of work, one of the first things you have to do is talk about what are the attributes of the spent fuel and what do we need to study and so, we'll talk about setting up a test matrix design, spent fuel, and then we'll go down and talk about where we are in these subtopics, and finally, the summary.

I keep repeating that. I think I'll be eating up too much time. You have seen this view graph before, but the important thing for us is burnup. It's certainly an attribute. It's spread out. There is a distribution of spent fuels out there, but how is this going to influence, say, oxidation? How is it going to influence dissolution? Is it a significant parameter, and how do we bring it in? So this attribute is there. The other attribute I mentioned early on is PWR versus BWR. These break down into big clumps in terms of metric tons. There is the GE reactors, the BWRs, and then there is this set of rods which are pressurized reactors, so it is kind of, if these two look alike, it's really nice. And there is evidence that there's similarities in terms of some of the preliminary results we have, but in the PWRs in the future they have a fuel which is a burnable poison fuel. It has a lot of gadolinia in it, and we do not have any information except just bits and pieces on how that's going to respond. So there is work that needs to be done there.

The other parameter is fission gas release. This is the way people at MCC have--it's certainly not objective--feel that it's probably going to be distributed. There's a large number of rods with very low fission gas release; there are some out here with high fission gas release. This is important, this distribution is important because it drives rod failure, and also because of gap/grain boundary inventory, perhaps, correlation. This is certainly uncertain, but we do feel that the higher the fission gas release, probably the more cesium iodine you are going to have in the gap/grain boundary. To get at this is going to be very difficult. We are probably going to suggest a vendor meeting and try to come at some kind of best consensus for it.

The conclusion view graph here is that if you're going to look at spent fuel, you want to set up a design and you want to include what's important. There's reactor types. I have included AECL. We have an international agreement under which we're going to share data and some testing with the Atomic Energy of Canada, Limited people and this will give us another sort of point on this plot. Most of our ATMs, which is the approved testing materials, at MCC come from a domain here, and burnup 26 to 48 low fission gas release. There is one out here which is being tested. There is UO_2 unirradiated. This gives us a zero point in burnup and fission space and, of course, reactor type. What we'd like to do is procure something, low fission gas, low burnup; low fission gas, high burnup, and similar out here, high fission gas, low burnup and high burnup. This will give us enough that when we design a test matrix, we feel that if everything is fairly smooth that this will look fairly smooth in terms of a response surface that comes about primarily by testing materials.

A gaseous release, Rich has done an excellent job on this. I will only present one view graph which shows how we plan to roll up the information once we get it and get at people's feeling that we are going to come to closure. Essentially, all this says is if you're going to release some gas, you must know how much you've exposed and you must know the rate that it's releasing. If you are exposing it at some rate, though, and this is container failure rate, you've exposed this surface, then this is the instantaneous coming off of, say, rod surfaces. And similarly with the fuel, you have container failures. You have this potentially gradual release. We know practically nothing about this, and then each rod that fails will give you perhaps an instantaneous release. And these are convolution integrals which take care of history effects. But this rolls it up for performance assessment. Our problem is then to talk about rod failure response, what are these in terms of experimental data and what are these rapid releases?

Cladding, that's the next topic. I have few view graphs on cladding. We currently have no activities in cladding so this is a repeat from the previous TRB meeting. It's done a little differently and there's only a few, but there are three sort of modes we think are regimes in terms of temperature that will have cladding failures. At this period of time, when we think of high temperature and probably the high pressure rods, we're going to cause creep deformation and perhaps even split the rod. This can happen whether or not the container has failed, but the model that we're thinking about is to take advantage of the oxide film. Zirc oxide forms with a significant volume increase. That means that this will be compressive. If we can maintain a compressive non-crack film, then those rods should survive this period so we need to do tests to look into that and we can develop analytical models to address the stress and deformation analysis.

The second period is when temperature starts coming down. I should mention that if we find cracks in this, then this is a stress riser and so it impacts during this period, because when temperature comes down there is hydrogen in the zirc, it comes about because when you oxidize zirc in a reactor it picks up a hydrogen atom now and then as an oxide atom comes in to oxidize zirc. And that goes into the zirc and it will come out as platelets as you come down in temperature.

If these platelets are circumferential, then there is no problem. However, if they form radially, then there is a problem. Their orientation is stress dependent, so we need to do some tests on that. But if you crack the oxide film, this hydrogen also will diffuse down a stress gradient and it'll probably drive a crack through that. So we would worry about throwing and probably just throw that clad away, too, in terms of a model.

The last response we worry about is after water comes back. This is low temperature. What has been seen in really preliminary tests is kind of a real wormy cylindrical pitting corrosion. We think that this may, in time, promulgate through if there's enough fluoride in the water, but there's very little data. But this won't hurt us because we're going to be low in temperature so the oxidation response will be down and these little holes will be essentially, you won't see a lot of water on the inside. So that's not a mode which we are really aggressively worried about; we are worried about these two.

What would we expect to get when we get to testing? It's important to realize that we cannot set just a limit, say, on temperature. It's really time-to-failure function and we expect to get some kind of failure surface where we talk about the time it takes. In other words, if you are very high temperature you can oxide the zirc and it'll fail very quickly. This is probably 400 to 450☜ C. You don't have much time.

The same way with the stress axis. If you're at high stress, you precipitate these. All these are going to fail, so this gives us some domain down in here to worry about time-to-failure, and we have done some work on creep-deformation fracture-map failure. This is very difficult because we need to get experimental data. I talked about oxide film, hydride crack growth rate. That probably lays in this region.

The region that we feel that we're going to be comfortable in is this elastic response region. There will be BWR rods in this region, we're pretty sure, because they have low initial pressurization, they have low fission gas. There will be extremely low pressure, so there will be, I think, a substantial number of those. If we get good information on PWRs, then I think some of them will lay in that domain, also.

This next view graph, I'm not going to go through it. It just tells you what kind of tests we are going to do. We have developed a pressurized tube testing system at PNL. It looks like it can do the job once we get started.

A summary view graph on zircaloy, this is what we would expect to furnish performance assessment. You have failure rates, high temperature, high pressure, time, and so this is the number of rods failed, say, per assembly or per container, and then you have hydride stress. Some of those may fail and you may have some zircaloy fluoride corrosion failures. Remember, there are initial numbers which may come in as failed rods or defective rods and there is some statistics on that out there which we factored into our report.

So we have no numbers on this. This is the kind of information you get. If you take a derivative, then you get these distribution functions to give you these little S-curves. And that's the kind of information you need for performance assessment if you're going to include rod response.

Oxidation response, this is the UO_2 oxidation. I have already told you why we feel it's important in terms of performance assessment and also potentially for dissolution, because the oxidation state will perhaps depend or influence the dissolution rate, although preliminary data says at the first stages it's not too significant.

What happens here is you have a breach in the clad; expose fragments. The way we're looking at this is essentially we need the experimental data. Once we see experimental data, we can create a way of putting this together in a model. Right now, if you take a fragment, what is seen in the next view graph--and it's not universally seen--is an oxidation front propagate in where the grains are being oxidized out here. There's a zone of grain, grain boundary oxidation and UO_2 in the center. Now this zone, as we'll see in the next view graph, is of interest, but essentially what we can say is if we break up space into pyramids for each fragment, we can do that, but when we look at the next one, we can get an upper bound model by breaking up space of grains into pyramids.

Now, Bob is going to give you more details on this, so this is an overview. But these, you can see that without experimental data, I don't think you're going to start modeling this kind of response at all. This is the oxidized. This is only up to U_4O_9. These dark spots are remnants or the remaining sections of UO_2. So up to here you can see that this is all U_4O_9. We have this zone where grain boundaries are opening up and then oxidation front is going into individual grains and this is UO_2.

Now in some more recent results--and it may be just a different fuel--but it seems like the whole fragment rapidly has opened up the grain boundaries, and so all you see is grain volume oxidation. On an upper bound response, if you say, let's just consider the grain volume oxidation and you split up this space in terms of pyramids and talk about how fast this front propagates in, it's a simple geometric model. Most of the data has to come from this model from doing experiments. This just illustrates, though, analytically how you get at it. You have a planar surface on a piece of the grain volume. If the front propagates in at U_4O_9, it propagates in at some velocity. So you can write this kind of formula where this is the weight of oxygen you pick up at the front as it propagates in, so this is a weight gain as it propagates. You'd get a dependence here because this area decreases as you go into the point and you do that for every grain.

Experimentally, what are we doing? We're measuring, we have measured this rate C dot and we also mainly measure the total weight pickup. Test matrix says, let's worry about fission gas release. Is it a problem in terms of these parameters; different reactors, is that a problem? Burnup, and so you can think of this as an empirical response surface. It's a model, it's a statistical regression model. But we need to look at these kinds of fuels. We need to look at oxidation phase. As you go through different phases, the rates change. Temperature is probably the primary coordinate we look at because we will be coming down in temperature in repository and we have some information on air moisture.

So that's the way we're thinking of setting up. That's the kind of work we're doing, and Bob will give you some details on some of the interesting things we're seeing during the phase change kinetics. This view graph tells you then to get time response, the subdomains we have to look at. This is a time axis and this a grain size. Essentially, there is a time for UO_2 space time. You have to get enough oxygen diffused then at the surface of the grain to get you to a state where you can create UO_2 or U_4O_9. It turns out the weight gain is $U0_{2.4}$. If you had U_4O_9 stoichiometric, it would be $UO_{2.25}$. So there is this interesting fact that it takes more oxygen to get the phase to propagate.

Once you propagate in, you create then a space of U_4O_9. After you have created that, Bob will show you data that looks like it sets there again and waits until they can get enough oxygen to get to--this is U_3O_8. We think it may be 2.66, but this time domain may well be very big in here, and certainly at low temperatures this is good news for a repository because these oxidation states back in here do not degrade the basic structural integrity of fragments. Out here you'd get problems because this increases the surface area.

The topic on dissolution, this is certainly the hardest but most important topic we have because this then is the heart of release rate. The oxidation is an important topic because the release rate can go--significantly increase if you have U_3O_8. Most of the work is experimental data. We'll talk about, though, how we're going to roll up if we have the experimental data to get at something for performance assessment from our experiments. In fact, we need this kind of model if we're going to do a simple analysis of experimental resolve, but it's so simple that it's really straightforward.

What we say, though, is essentially that if you have a fragment and it's dissolving, this is sort of a front that moves in. There may be a zone where you have both grain boundary and grain volume dissolution and we'll see in the next picture from Chuck Wilson's work that this is indeed true, and I think Walt will show some, but this disappears, and so you have a front propagating in to the center of the fragment.

This is a geometric response kind of model. The basic data comes from experiments which talk about how fast that front moves in.

This view graph shows some dissolution work that Chuck Wilson did at PNL and it was deionized water for a year. But initially, if you looked at this there would be no opening up of these grain boundaries. So what happens is you have a front dissolving off the grain surfaces, plus you have dissolution of these grain boundaries. So this gives us two pieces of, or a complication in the simple model that we have to worry about. The Canadians have set up what they call a schematic view and feel that this is the way it's going to go. I have mentioned gap, which is instantaneous, shorter than a year. Grain boundary may be longer than a year and it's additive to this basic dissolution front going into the grains.

Now, Walt has broken this down and been able to separate out the grain volume dissolution rate and we are getting ready to set up to do some grains plus grain boundary dissolution rate work on fragments. But this kind of gives you a feel then whether it's the subtle complexities these problems are in dissolution and the other problem, of course, is the inventory which is distributed there.

Basically, though, we have an experimental program which addresses, again, analogous to oxidation, this kind of plane where we talk about what is our response variables we worry about. This is attributes of spent fuel, and this is certainly an illustration. It's hard to plot this many dimensions and make sense. But there is an oxidation phase which you have to worry about of the spent fuel. It may have differences in its dissolution rate, D, that we've talked about. There's a temperature dependence that occurs. We're getting at some of that data. And the big one is solution chemistry. Here we took aggressive waters. We're trying to nail down what happens in aggressive waters. This will be what you will use in preliminary design in performance assessment.

But we have a few cases where we have nominal data and that would be more of a silicate water. This is Chuck Wilson's early data. And what we did, we looked at, from an ATM report, some fragment statistics, which gave size classes and their volume weight fraction. From this we got area and what we need, then, is a dimension to get at geometric effects.

What this shows you is if you put in this distribution of fragments, this is time normalized to essentially the total time for that last little speck to dissolve. In other words, you have a big fragment that starts dissolving down to its little speck, and this is essentially surface area response on the release rate.

Now this time goes to one, but if you look at this for a silicate water for this size, you are talking about something like 55,000 years. But if you do a kind of a linear extrapolation down to here, this time response where most of it is actually going to be gone is something like 8,000 years and that higher temperature is going to be about 2,000 years. So this is the kind of information we are building up a data base on for performance assessment. We're certainly not done. We don't have all the fuels that are out there. We don't have all the water chemistries, and we don't have all the oxidation states.

This view graph, though, will perhaps address some question that Mick has brought up. How are we rolling this up? Essentially, the release rate for, say, an ensemble of containers, rods, area exposed, area wetted, and volume of water--these are the things we're measuring--you must have container failure; you must have rods failed. This gives you an exposed area of spent fuel. How much is exposed depends on the oxidation state; how much is wetted depends on this. This is hydrology and this dissolution rate is what we're providing.

This is the instantaneous part and it's essentially the rates of things that happen here. Now, this--you may quibble on what--how to do this. There may be another A dot on this, which means a rate, but essentially all we're saying is, this is what's exposed at any time. If you want instantaneous, then you have to take the rate that new stuff is exposed and multiply it by the instantaneous.

This is the most you can get in solution because we do not, from our data--we're doing what we call forward reaction rates. This will be clearer when Walt and Steve talk. We have, in a sense, all I am trying to say is there are no solubility constraints on our tests because of the way we do them. So there's no precipitation.

To get actual solution out the door for performance assessment, you need to know solubility limits and you need to know colloidal response restraints. These are necessary. This would be worst case kind of data, so for preliminary assessments, that would perhaps be appropriate.

Someone mentioned hardware. We have not touched hardware except to take a look at inventory. Again, this is PNL. Andy Luksic did that and several reports for DOE. One of the things that we know the way we want to look at it is to talk about a dissolution rate per unit area, so we have come up with some areas estimated and Andy estimated these. The inventory is fairly well tied down by Andy's work. These are the kind of numbers we are looking at in terms of area. We need this corrosion rate, this dissolution rate, but essentially, there's acres of material out there to be exposed with water. Whether or not the rate is so small that you'll have any significant release, we don't know yet.

In terms of summary, what I hope you have gotten out of this is that we have a test program. We are worried about modeling. We do not feel that you can do a priori theory and get to the answers. You're going to need the test data. You're going to have to represent that, perhaps extend it with a model to extrapolate. But what I've gone through is there is spent fuel attributes we worry about. These are initial conditions. This is what people give us. We can't change this. There are some significants still to be addressed in terms of our procurement at MCC program, the program for procurement and future ATMs. There is repository environment for us. It's air contact, water contact, and temperature histories, what kind of water is it. These are certainly uncertain and there is stuff to be characterized and decisions to be made there.

Where we are is in this area. We are doing knowledge base models. This is multi-laboratory, so we feel we have some checks and balances. This is concrete work. We have a test matrix to try to cover spent fuel attributes and what we sort of see is a nominal, and also a worst case repository environment. This has kind of come to closure on test matrix and the knowledge based development. The modeling is an interface. We cannot do this blue sky without test data, so this gives us these checks and balances on both modeling and also on testing, and do we understand the testing.

Everything's rolled up into a report. This report was put out last fall. It's been reviewed. The issue resolution stage is now in progress and we hope to get that out this fall.

Just flash this. This is too much information. But essentially what we have is information primarily from the literature on data, that's Chapter 2. And over here is where we're requiring more detailed experimental information on mechanistic model development and trying to put together the models which would go into performance assessment. And this is true for both spent fuel and glass.

The final view graph shows activity that we have put together and hope to do for Mission 2001. It tells you where we are now. The Waste Form Characteristic Report has been ongoing for essentially two years. We have oven oxidation tests. These are the dry bath tests which Bob will be talking about. We hope to start up TGA oxidation. This is important if we're going to understand some phase change kinetics. We essentially will not start oxidation modeling until '94. The dissolution effort, this FT, is flow-through testing. We essentially flow fast enough that we don't get to precipitation.

We have needs to do dissolution on saturated conditions, unsaturated conditions. Chuck Wilson did some of these several years ago. They need--we need to revisit that. We need to revisit this. This may be some alteration modes. Actinide solubility, this needs to be addressed. Of course, the modeling, you are not going to do any modeling, significantly, until you get the data. Gaseous tasks--and this should have been tests instead of tasks--we hope to start those up. The modeling and cladding tests we hope to start up.

The thing down here is assembly hardware. Of course, we will probably start up if we get the funding. The MCC has sort have been placed on hold these past two years. It has gotten funding, but it is only a maintenance funding. If we're going to get the new ATMs, we need to start procuring those, setting up, shipping, and all of the things that have to be settled before--well, we'd like to do that in '93, but it has to be done in '94; otherwise, we will not have samples to go forward in the test matrix.

And that's probably more than you needed, but that's all I have to say, and thank you very much.

DR. VERINK: Any questions from the members of the Board? Dr. North?

DR. NORTH: Let me ask you to go back to your Slide No. 12.

DR. STOUT: You'll have to tell me which one it is.

DR. NORTH: It is called, "Illustrative Rod Population Distribution of Gap and Grain Boundary Inventory." It's a graph showing the fission gas release and the gap and grain boundary distribution function.

DR. STOUT: Yes.

DR. NORTH: I think the point that you were making there, at least what I got out of it--and I seek illumination by trying to form this restatement--is that there is wide variation in the gap and grain inventory for radionuclides we care about, like iodine, cesium, technetium, and that the failure of the cladding may, in fact, be correlated with extreme values in these inventories. I'm not sure I understand the problems in inhomogeneities in the fuel or problems in the fabrication of the fuel elements that might lead to this relationship. But what strikes me is when you do performance assessment, you'd be making potentially an important error if you assumed that we can Monte Carlo the boundary inventories as independent from fuel element failures; that it might be that the elements that are going to fail are going to be the ones that are going to give us the biggest releases. And I'd like you to comment, " Did I get that right?", and then ask, what is being done in the performance assessment to make sure that this issue is appropriately covered?

DR. STOUT: I can't address the performance question. I think there will be talks on that. I think you have said very nicely that if you do worst case analysis, you should worry about worst case distribution of these products in this gap region. That's paraphrasing, I think, what you said, and I certainly agree with that.

The inventory, the industrial inventory techniques they call LIFO, FIFO. I call this WIFO; worst in, first out. It is kind of performance for worst case. Now if you do Monte Carlo, you might feel that you should worry about, is there a bias such as this, and I would agree with you.

What my point is, though, that right now, in terms of getting data, this fission gas release population is extremely difficult. We are going to have to go to vendors, people like EPRI, and get some data on this. We simply will not be able to address this very well and get some kind of consensus. So that will require a special proprietary agreement which we have asked for, but since--it has not come forth yet. But your correlation there, I think, is right on.

DR. NORTH: As long as I have the microphone, I'd like to make one more generalized comment, and this really goes at your last slide and is directed not so much at you, but at all of the presenters in this meeting.

I found your talk gave me a lot of additional conceptual insight as to how these problems work. You had excellent diagrams and I felt I understood better than I ever have in previous meetings just exactly how some of these phenomena interact. However, I didn't see much in the way of analytical results. It was, indeed, a conceptual overview.

As we go later on, we're going to hear a little more about the source term calculations in the performance assessment. But when I look at your last slide, the one called, "Activity Plans, Mission 2001," I'm concerned about how fast we are going to get this conceptual overview translated into additional analytical modules so we can see how the numbers change. And this gets to the point that Mick Apted raised with the last speaker. What are the priorities on acquiring the critical data elements? Does the chart, "Activity Plans, Mission 2001" make any sense in terms of are we getting the critical data elements early enough? And I don't see that in the plans so far, and I think that it's really critical for the Department of Energy to be able to set forth those insights. Based on the analysis that you have done, what are the critical data elements that emerge, and now, how have you factored that back into your program plans such as you have illustrated on this chart, such that, indeed, the long lead time critical tests are going to be done in time to give us the improvement in the analysis that we need?

DR. STOUT: I think this is outside of my--

MR. GERTZ: As you look at me for that answer, Warner, let me point out that what you saw was a small part of what we call Mission 2001, which made an attempt to set priorities, set schedules of 6,000 activities, and assure they were all tied together and would produce a license application in 2001. Some assumptions go with that, appropriate funding and things like that, I'll talk about tomorrow. But certainly, we made an attempt by talking to the scientists, getting our schedulers together, doing the interactive networks and assuring that the data would be ready for the model in time for SAR and a license application or site suitability. And we've come to the conclusion that we've got a good shot at it, given sufficient funding in 2001.

But this Mission 2001 is a exercise based upon a 6,000 network, six-month activity just asking those questions: Are you getting the data in time?

DR. LANGMUIR: Question going to your Overhead No. 18 as a starting point. That's the one called, "Zircaloy Cladding Failure Modes." We've been wrestling as a Board and you as DOE, DOE and contractors, with the issue of what thermal loading strategy to select for the repository, and there are various arguments one can go with in terms of what this might mean to the near-field geologic environment and the performance in that area. But you've got some information here for us on the waste package which is maybe not going to say the same kinds of things.

There's a zone in that figure called elastic response, and if I remember correctly, you suggested that was where you'd like to be with regard to cladding. What kind of a thermal loading, what kind of a temperature are we--this is schematic, I appreciate, but roughly, what kind of a loading? Is this a high thermal loading system that you're dealing with, or a low, or what? And let me extend that to the other behavior aspects of the waste package and other features such as the stability of the waste itself, and so on, and the corrosion features. Can you give us a gut feeling of where you think you are now in terms of what you'd recommend for the best performance of the waste package?

DR. STOUT: Let me say, I'm going to be stuttering here a minute. Let me put it this way: Total performance assessment has to factor in a temperature domain, a temperature history. Now, my feeling is if you go to an environment, and if we got back to the last view graph where I rolled up what the release rate is, and you have very few container failures, you would not have this mode. You would not have zircaloy oxidation, because there's no oxidation inside.

If you were there a long time, though, you may have a lot of failures of the rods because of this domain, because they're going to be creeping very slowly and you may have this hydride response causing you grief. But if you don't have container failures, you don't have much exposed.

Now, the other thing is in that equation on what is a release rate, there is the hydrology. So you have to worry, am I trading things off? And so this is where it gets interesting. If you do a cold repository, you better hope or establish, I think, that you have a lot of rods down in this regime, because you're going to have a lot exposed. This elastic response domain becomes very important.

Up in a regime where you have extended dry repository, we can get this information very quick, because at 400☜, it's very rapid. This information will take us longer because this is a very difficult experiment. It involves some rates that are hard to measure. But I think you would say that you might forego some of these studies if you knew that. But you have to do the performance assessment and do these tradeoffs, and that's the key in the repository.

I look at it as you now have sort of two limit points. The optimum for thermal loading may be somewhere in between. You're going to have to know some of these things if you attain that optimum, but the optimum could be the end points, more or less a cold, wet repository versus a dry, extended dry repository, and that's about all I can say because we don't have any numbers on these things.

DR. LANGMUIR: Let me follow up. In a discussion of thermal loading, we addressed the issue of what the very high loadings might mean and comments were made that this would represent a range of temperatures in which you'd get significant failures and that was, perhaps, a reason for not going up there. I presume that somewhere on that right axis you've got to measure failure in terms of, perhaps a thermal loading you could identify, or at least a temperature.

DR. STOUT: Here? If you have container failures and you have high temperatures, then this is like 350. Zircaloy itself will oxidize quite rapidly. When it oxidizes, it has a significant volume increase. So as you go through the thin wall, you're going to rip apart and probably have a breach. Now, that won't hurt you if you don't have any water. It will mean, though, if you remain in high temperatures that your spent fuel will probably oxidize up to U_3O_8, but again, that won't hurt you if you don't have water.

So you have to do these--I mean, these symbols for these integrals are retarded integrals or time convolution integrals, and one can't do these in his head, but you can see that you're trading off these things and that's the reason, though, performance assessment is important, but this kind of data to feed performance assessment and have them do a good job is also very important. Otherwise, you know, they're putting in sort of numbers but they may not be as good as they need to be even to do a worse case. And certainly, when you start nominal design, you want to be fairly sure about those.

I don't know whether that answers your question, but--it's partly philosophy, but partly that's where we are.

DR. GARISTO: Source terms, the way Dave Stahl defined this morning, are a release from the engineered barriers, and in order to calculate them you have to understand the mass transport properties and the hydrogeological properties of the surrounding media, and I haven't seen too much of it here. I can give you an example of how, if you include it, it will completely--it will change what you are talking about.

The example that I am familiar with is obviously the Canadian program. You have shown the figure and shown relatively similar contribution from gap, grain and grain boundaries and grain in the long term, but if you include mass transport in the calculation, you will get something completely different.

This is not for the American program, this is for the Canadian program. We have seen earlier a plot of instant release as a function of time, and grain boundary release as a fraction of time without taking mass transport or hydrogeology into account. And in the figure that we saw earlier, the contributions from all of them seemed quite similar. But if you include mass transport in the calculations, at least in the Canadian program, you see that the instant release dominates for a very long time; it doesn't finish in a year. It dominates for very long times and its difference compared to the grain boundary release is what? Seven or eight orders of magnitude.

So I'm not saying that the same results will exist in the American program where the conditions may be more oxidizing. But this kind of a analyses can help you after with feedback, you know, when you calculate your budgets and allocate things, and you can set priorities right there.

DR. CANTLON: Since oxidation clearly is a problem, I notice that in Dave Stahl's presentation he had the casks with a buffer filler material, iron material. What kind of delay do you get in the oxidation if you have an appropriate iron sump or oxygen sump material surrounding the cladding and the rods? What kind of delays are we looking at; tens of years, hundreds of years, thousands of years?

DR. STAHL: We haven't done the analysis. This is a case for near-term performance assessment. We will be analyzing this very shortly. We have done some theoretical determinations using EQ 3/6 that indicate that it does reduce the oxidation state and does prevent a release, for example, of Technetium-99, which is an important radionuclide.

DR. APTED: Mick Apted. Ray, just to maybe get your feeling, as far as I know, the U.S. program is the only program that's looking at fuel that is looking to take any credit from the cladding. The Finns don't, the Canadians don't, the Swedes don't, as far as I know the Germans don't. Would you care to contrast your philosophy on that with theirs? Why are we deciding to take credit from the cladding when they seem to be not going after that?

DR. STOUT: I have not been on the program for a large number of years. I think historically the SCP design said that we're going to look at all the potential barriers. And out of that, then, cladding became a material, a barrier. And in a dry repository it does not look like to me that, I mean, that looks like a good decision. If you have low pressurization, zircaloy is an excellent material, particularly at moderate temperatures. And, in fact, I had heard that--and this was before I got on the program--they would have made containers out of zircaloy, except zircaloy is one expensive material to look at for container design. So that would seem to me to be a logical thing to take advantage of. You have to trade off, of course, what your cost is and, of course, what your other designs are. If you get another design out there that says you don't need to take advantage of it, then you trade that on.

But I think that's what they have. They have a design which they don't want to put the money in. They have a design in which they feel it would be a small part.

DR. VERINK: Thank you very much. Carl wanted to make an announcement before we take our break.

MR. GERTZ: I just want to make, in fact, two very brief announcements. First of all, I'd like to introduce Steve Goldberg with the Office of Management and Budget. He is not only our budget examiner, but he's your budget examiner, too, I think. But Steve went through an extensive review of our program the other day for seven hours with us so I'm still a little punchy from that and that's why I forgot to introduce him earlier today. He will be here for both days and will go on the tour Friday with us. So when we talk about priorities, he's one of the men we need to talk about because priorities revolve around dollars, Warner, so I appreciate you being here.

MR. GOLDBERG: I'd like to ask one question, if I could. Hi again.

This is a question addressed, I guess, both to the Board, as well as to DOE. We may be in a situation ten years from now that the inventory that will be used to burn the fuel will be different than we think it is today. What I'm talking about is blending down high admixed uranium, and already I've been told that the high admixed uranium may have unique characteristics such as concentrations, Uranium-232, 234 and 236, as well as elevated concentrations of Technetium-99. How is this being factored into the program?

DR. STAHL: This is David Stahl from the M&O, B&W Fuel Company. The basis for a design currently is the spent fuel that is in current inventory that we discussed, plus high-level waste glass. The naval fuels are a new add-on that we're going to have to consider later on. It's not part of the current design basis or license application, and I think these new blended fuels will fall in that same category.

MR. GERTZ: In summary, we don't have programs that are characterizing that type of fuel now. We are looking at strictly light water reactor spent fuel and the glass logs from the defense program and the fuel at West Valley. We just haven't started looking at that, nor do we know that that's going to be our mission at the first repository yet.

DR. VERINK: Do you have an announcement or what?

MR. GERTZ: Yes, one more announcement. I'm sorry. Also, tomorrow, of course, Dr. Bartlett will be here and also, we'll be honored to have the new Undersecretary of Energy, Hugo Pomrehn will be here for tomorrow afternoon's presentation and he will be going on the tour; he's just recently been confirmed the Undersecretary of Energy. So there is lots of activity and lots of people here and I just wanted to make sure you are aware of that.

DR. VERINK: Let's take a quick break and we will reconvene at 11:10 a.m.

(Whereupon, a recess was had off the record.)

DR. VERINK: The next speaker is Bob Einziger of PNL.

DR. EINZIGER: I'm Bob Einziger. I'm from PNL. I've been studying or attempting to study spent fuel oxidation since around 1982. I'm only the PI for this particular program. I want to acknowledge the contributions of Larry Thomas, who generated a lot of this data, and also, really, the person who is responsible for making this go, our technician, Craig Buchanan.

Let's get started by looking at what happens when things oxidize, and here's a progression of oxidation, and this is taken from some work that we did in about 1983 for EPRI. Here's a rod, and if you look closely, there's a hole drilled in it. It's immaterial that it's a drilled hole. This could have been a breach of only five micrometers, you'd get the same results. This was done at 360☜ and it was for about 15 hours. We took a rod like this and, lo and behold, this is what we got. Why did that happen? It happened because air got into the rod and it oxidized the fuel. Let's take a little closer look at what happens when we oxidize fuel.

Here's some pellets. These are pellets that were just dropped out of a very similar rod just like this. Oh, we had maybe about 20 of them that represented the fragments from about six or seven pellets. We oxidize it, and if it's spent fuel, the next state it'll go to is U_4O_9, where it penetrates down the grain boundaries, and the light-colored areas is the oxidation. If it's unirradiated fuel, you won't go to U_4O_9, you'll go directly to the state of U_3O_7.

Now, the thing about both of these states is the density is pretty much the same as UO_2 and you won't disturb the fuel matrix. But let's say we go beyond U_3O_7 or U_4O_9 and we go to the next step, which is U_3O_8. Well, we have a decrease in density of about 35 per cent, which expands the fuel, tears the matrix apart, and, lo and behold, this becomes that, and that's essentially a powder grain-sized material. If you want to continue it on in your high moisture content, you can actually get to the point where you start disrupting the grains.

So why do we want to study spent fuel? Well, there's going to be a small fraction of the rods that are going to enter the repository breached. It's going to be somewhere less than one per cent, and most of those breaches are older fuel. The utilities have been doing a fabulous job in cutting down the rate of fuel failures by controlling the water chemistry. The rates now are well below .01 per cent of the new fuel coming out. But there will be failed rods that go into the repository. In addition, during the handling process, you may fail some more. So there's going to be failed rods.

Also, from this higher temperature data, which may be above what you are going to be at in a repository, we know if we oxidize the fuel we're going to disrupt those failed rods. So we have a number of effects we want to look for. We want to see what the changes in the phases of the fuel are because that may change the leaching response. We also want to see whether we opened additional internal fuel surface areas to leachant because the material you're going to release is going to be dependent on the surface area. If we oxidize the fuel, we may release a lot of trapped fission gas and in addition, we get cladding splitting which, of course, changes the path for radioisotope release. It's going to be a lot different if a rod like this gets in contact with a leaking solution as opposed to a rod like this. And this is only part of it. This was ten hours. If we had let that go, that would have unzipped the whole rod.

So we started an oxidation program, and what was the basis of this? Well, from the literature, we knew that temperature was an important variable. We did not know the effect of atmospheric moisture, nor what the effects of burnup were. At the start of this program in '82, they took oxidation all to the high burnup of .02 per cent burnup, not very high compared to today's standards. There were no low temperature oxidation data available, especially on irradiated material. People went down to about 250 and then it dropped off. Everybody assumed that oxidation wouldn't occur. There were some studies, like people in--Watson in England--who took some powder, calcine powder of fuel that was a couple of microns in diameter and very quickly at room temperature oxidized it to U_3O_8. And he said, "Geez, we can get this thing oxidized in no time," but, in fact, all he was doing was surface oxidation and if you looked at the effects on a rod, it was virtually negligible.

We also made a very poor assumption, as it turns out to be. We assumed that the UO_2 and spent fuel had similar oxidation behavior, and it took us approximately five years to unlearn that assumption.

We had two types of tests. One was a dry-bath test, which I'm going to talk about a little later, where we did long-term oxidation. Another type of test was a thermogravimetric analysis test where we could use small samples. We could work at higher temperatures and we monitored the oxidation continuously.

One of the things--some of the things we found from the TGA study, one is that there was a different oxidation behavior between spent fuel and unirradiated UO_2. Spent fuel oxidized in a two-step process. Basically, we were going down the grain boundaries, then into the grains, as opposed to unirradiated material, which oxidized from the outside of the pellet in.

There was a Arrhenius type dependence on temperature, and this was consistent with the diffusion of oxygen in UO_2. Activation energy was in the neighborhood of 27-28 kilocals per mole, which is just about what you'd expect. We didn't see much effect of moisture level. Oxidation was more rapid at the pellet surface, but it still went down the grain boundaries. And also, the majority of the mechanistic data that we were able to get doesn't come from the weight change information, it comes from examining the fuel pieces, taking them out of the tests, putting them under the microscope, looking at them, seeing how the phases have changed, and seeing how the microstructure is changing.

Here's a picture that shows you some of the oxidation. As we saw before, here is the oxidation down the grain boundary. Now let's look at a grain boundary itself. Well, here we are. This is the oxidized region. This is the unoxidized region. There's a very distinct boundary. And just, once again, to compare what we're looking at when we're comparing spent fuel and unirradiated UO_2, here's unirradiated UO_2. We see a U_3O_7 boundary on the outside of the fragment. We don't see much penetration down the grain boundaries. Here is the spent fuel and this is in the neighborhood of about 30 gigawatt days per metric ton, pretty much average for what you have nowadays. It's a BWR fuel, and we see the grain boundaries and we see the U_4O_9 around the core of UO_2, illustrating the difference in the behavior.

Well, we had a dry-bath program and we used this to provide rate data for an oxidation model, which is handing it over to Ray for his modeling. We wanted to determine some long-term oxidation behavior. We could use many samples in this test. In fact, this test was set up to handle about 190 samples. Also, it provided the source of fuel for leach testing. So when we oxidized this stuff, we weren't sitting with 20 milligrams of fuel. We actually got it in ten and twenty-gram batches. There were also repetitive samples.

Here is a quick picture of one of the dry-baths we used that uses Ni-Chrome crucible. It's about ten grams of fuel that sits into a dry-bath hole. There's a cover on the top so that we don't contaminate fuel samples as we move them. There's a moisture inlet, and each of these sections has an individual temperature monitoring.

We covered a range of temperatures between 110 and 195☜ C. Some of the earlier data on the unirradiated material indicated that we might be able to get something in the 130-110☜ range. Subsequently, that's proven not to be quite accurate.

We covered two dew points: -55☜ C and +80☜ C, and to orient you, -55☜ C is about 3 ppm of moisture; +80☜ C is one out of every three molecules floating around is a water molecule. We used two types of samples. One is the fragments as we dropped them out of the cladding. We took the cladding, cut it, tossed the fragments out and we used it. In other cases, we took the stuff and we ground it up to various sizes to look and see what size effects we might have. We used a number of different fuels. There was Robinson fuel, Turkey Point, Cooper and Calvert Cliffs. These covered a range of burnups. They covered a range of gas releases and grain sizes.

In terms of grain sizes, it went from 5 to 30 microns, and that pretty well covers the grain size that you would expect to see in the spent fuels that are being produced from the earliest times up to what we have now. The burnup range was 25 to 48 GWd/MTU. Now 48 isn't up to where we expect to be. Eventually, we expect to be up to 60, so we might have to get a little bit higher, but we didn't want to go a little bit higher in testing just for the hell of saying you're going have some fuel up there. We do think there may be some materialistic changes in the fuel that warrant looking at higher burnup fuels. Also, there are some things that were seen, which was there's a difference in the unirradiated material and the irradiated material that indicates that there's a transition zone at the lower burnups and we want to look at some of that material.

Fission gas release, we've looked all the way from .1 per cent fission gas release, up to 18 per cent fission gas release. That's a pretty wide range. The current times of the tests are about 40,000 hours, and that's about equivalent to five years of running time.

Let's give the punch line before we start. What we seem to be seeing based on this range of tests--and it's by no means complete, but it does represent more than one sample. There's a number of different fuels, burnups, et cetera--is that we seem to see similar oxidation behavior in all the fuels, which has a significant result and we may be able to reduce this population down to a manageable size so we don't have to test everything. We just have to test a number of fuels. Also, it appears that there may be a limiting oxidation state of U_4O_9 structure that has a O/M of 2.4.

Here's some oxidation O/M data for LWR fuel at 195☜ C and 175☜ C. It covers a number of different types of fuel; ATM-105 which is a BWR, and ATM-104 which is a PWR fuel. Both of them seem to have a weight gain and then level off at an O/M of about 2.4. If we look closer, and this is a test at 195☜ C, this is a number of fuels all oxidized at the same time. We notice that some level off at 2.4, some 2.35; there seems to be a difference in initial behavior, and we wanted to take a look and see are these things really oxidizing differently or is there some commonality between them. So we looked at how the O/M was changing with time, and this is what we found.

Most of the change that was fuel dependent occurred in a very short period of time, in the first thousand hours. And, in fact, as you go to lower temperatures, we're seeing the same sort of thing. Here it is at 175☜ C. Out at 25,000 hours, you can see that the O/M or the oxidation rate's pretty much changing consistently from fuel to fuel.

Let's look at a test where we looked at different types of fuel and moisture content. Well, the solid points are 80☜ C dew point. The open points are -55☜ C dew point. We don't see much difference in the behavior of the fuel due to moisture content. That seems to be good.

So what's the progression look like? Here is a progression at 195☜ C starting from an O/M of 2.5 up to an O/M of 2.31, and we do have further pictures going on up to 2.4. You can see how there's a little bit of oxidation along the grain boundary. It's getting larger, larger, and by the way, these are unetched pictures. Normally, in unoxidized spent fuel, you get out of a reactor, you can't see the grain boundaries. And eventually, we get to the point where it's essentially almost all oxidized. There's one or two main cores, and you get out to 2.4 and there's no cores there.

We did some XRD measurements on this, and the difference between UO_2 and U_4O_9 is basically a small splitting and shifting of the peaks. And you can see that all we're seeing is the U_4O_9 and the UO_2. We took one of the samples and we decided, let's raise the temperature and oxidize it to where we do get U_3O_8 just to make sure we're not getting any peaks in here we're not recognizing. In fact, here's the spectrum for U_3O_8 and you don't see any of the commonality among these other diffraction patterns.

An additional result is we looked at the lattice parameters. Excuse me, this is an electron diffraction and we took electron diffraction in this area and this area, and we looked at the lattice parameters as a function of the bulk O/M as the mass was oxidizing. What we found is that the lattice parameters did not seem to change with the bulk O/M. What that's telling us is whatever this layer is that's forming and oxidizing, it's the final oxidation state at that point. It's not that the thing is going up to U_4O_9 and then additional oxygen is going in. The final state's already there, and that makes it nice because it means we don't have to oxidize this stuff all the way up to its final oxidation state before we can do leach testing on it.

So, being an experimentalist, we tried to put together some simplified look at this whole thing, and this is what we came up with. We see that the fuel is oxidizing. It's sitting, going up to some O/M of about 2.4--maybe it's 2.42, maybe it's 2.38. It's sitting there for some length of time and eventually, based on some high temperature data we have, we expect it to eventually oxidize to a higher oxidation state. It leaves us with a few questions. How long does it take to reach this state as a function of temperature? Along here you have a mixture of states, UO_2 and U_4O_9. How does the fuel leach as a variation of that mixture? In other words, we have to have some leaching data. If, a big if, the UO_2 leaches the same as U_4O_9 or the $UO_{2.4}$, then maybe we don't need to know anything about this region, just how long it takes us to get up here, because both constituents are leaching the same.

We'd also like to know how long it takes before we get to this additional state, this U_3O_8 because, remember, at this point we haven't disturbed the lattice. It still essentially looks like a piece of spent fuel. The fragments are intact. At this point we start tearing the thing apart, both the cladding and the pellet.

Well, we went back to some old data that we did back in about '85 for EPRI. It was data intended for a different aspect of the program, so it's not what we would do if we were doing the experiment again. But basically, we looked at various temperatures and we looked at the O/M ratio as a function of time and, once again, we're seeing a plateau here at about 250, and at the temperatures above that, it seems to not have a plateau and go right through pretty quick, through this 2.4 pretty quickly. Some subsequent short, very short-term tests on small samples indicate as you get to higher temperatures, in fact, what you're doing is you're getting a mixing of the processes that are going on, that the oxidation up to this state and the oxidation off the plateau, this has been condensed so small that they're starting to compete with one another. And as you get to lower temperatures things seem to be spreading out. So we decided, let's see what this may tell us.

And we said, let's assume that this generalized curve applied to this data and let's say there was a plateau at 2.4 and let's plot the time it takes to get that plateau versus the temperature, and that's what we got, these data points. We go to some of the lower temperature data which we'll be doing in the current set of tests at 195☜ C and 175☜ C, and this is the data that we're getting. It may be fortuitous. It's pretty good Arrhenius behavior and we can do a few predictions based on this. And, in fact, if you take this line and you predict what would be the time it takes to get up onto this plateau at about 95☜ C, you're in the neighborhood of about 2,000 years, just to get up on that plateau.

The question is, how long, once we're up there, does it take to get off of it where we rarely do damage? We went back to this same data and this is a plot of the time it takes one of those little breaches in the cladding to start opening up as a function of temperature. The solid points are failures; in other words, times when we actually got the splitting to occur. The open points, no splitting occurred.

This bottom line is the line you saw on the previous graph. This upper line goes through the failure points. There was some data from Turkey Point, which was about 30 gigawatt days per metric ton, and that's about up in here, about two orders of magnitude difference in time. So it says, geez, maybe we could, if this is true, the time to get off the plateau may be as much as two orders of magnitude higher than it takes to get on it. And you're going to look at this and say, hey, wait a second. Here are some failure points right down here, and that's true. The thing is, these points were from rods that had burnup of about 12 gigawatt days per metric ton. Remember, I told you before, unirradiated stuff doesn't oxidize the same as irradiated stuff. Maybe we're fooling ourselves. Maybe it's not the high burnup stuff that's going to give us trouble. Maybe it's the low burnup stuff that's going to be our limiting oxidation case, but you've got to tie this into the whole performance assessment thing and say, geez, the stuff that's low burnup may be so cold that you're getting a temperature effect and it really doesn't matter anyway. But it does indicate to us that there is a gap in the knowledge down at the low burnups where we're going to have to fill in.

What kind of preliminary conclusions did we get? Well, the spent fuel oxidizes differently from unirradiated UO_2. The fuel variability may be a transitory effect, and after the transients, all the fuels appear to be oxidizing in a similar matter. It does not appear to be an effect of atmospheric moisture; also, that the test temperatures, and that's up to 195, may be too low to get us off this plateau and get into the next phase. Also, in an O/M less than 2.4, the only phases we're finding is UO_2 and U_4O_9. We're not finding any of the disruptive U_3O_8 phase. Also, at temperatures around 95☜C, it should take approximately greater than 2,000 years, if you believe this projection, to reach that plateau. Well, we haven't finished and packed the hole, by the way. We do have some information needs.

There have been no conclusive tests on high-burnup fuel and it's going to be very important to pick the right high-burnup fuel, because why are we interested in it? Not only for the reason that it's part of the inventory, because people have seen what they call the rim effect at higher burnup. But you can't just go and get any high-burnup fuel you want, because it may well be what you're looking for is the high-burnup fuel that was very cool, so you didn't release the gas and that may be what's pulverizing the fuel.

In a nutshell, what the rim effect does is it takes a grain that may be 10 microns across and it pulverizes it down to a lot of little grains that may be one micron across, and imagine the difference if I'm leaching a fuel that's got one micron grains or ten micron grains.

We need to know the oxidation kinetics beyond $UO_{2.4}$; in other words, what's the kinetics of getting up off that plateau? We also need to have low burnup fuel tests. We need to do tests on gad bearing fuel. As Ray mentioned earlier, there's a number of fuels being manufactured with burnable poison up to 8 per cent gadolinium. What effect is that going to have on the oxidation behavior?

Also, we need to have leaching studies from oxidized and non-oxidized fuel. It's really imperative that we find out in a convincing manner that we're down in this region, that we're not dependent on that mix of oxidation states to predict the leaching.

We did do some scoping tests in the last year. These are very inconclusive results. There's only been a few samples, but it sort of provides a guideway. One of them is gadolinium additions appear to improve the oxidation resistance. We did some work with unirradiated fuel that had gad that was at 4 per cent and 8 per cent, and the stuff with 8 per cent seemed to oxidize a little bit slower than with 4 per cent. Interestingly enough, when we took this unirradiated material and we put gadolinium in it, the oxidation behavior we saw was not what you would expect from unirradiated fuel coming in from the outer surface. The grain boundaries started to oxidize, just like in spent fuel. So it may be that the fission products are what's responsible for this difference in behavior.

Some niobium additions were used. They did not have the same effect as the gadolinium effect. They didn't have any effect at all on the oxidation. Also, from some of these higher temperature effects, it seems that this does not go up continuously, but it appears to be leveling off in another plateau at about $UO_{2.66}$, which is U_3O_8.

Thank you.

DR. VERINK: Thank you very much, Bob. I think we'll have to go on directly to the next speaker and reserve any questions until the end.

The next speaker is Walter Gray of PNL. Walt?

DR. GRAY: I'm going to talk about some of the leach testing, dissolution testing that Bob has alluded to. I'm going to try to summarize the results of a number of different tests that have been performed in the last few years at Pacific Northwest Laboratory. Most of these are one of a kind or one of two or three kinds of tests, which have led to some interesting and important results, but I'd like to emphasize that these are a limited number of test conditions and so just what it's done at this point, it has given us, I think, a good feel for where this program needs to go. but we're not at all done, by any means.

Well, the overall objective is to provide experimental data for our modeling people, as it says here. What I'd like to do is to give a little bit of background of what spent fuel is like.

Spent fuel is a heterogeneous material in a couple of senses. It contains soluble materials and insoluble materials, radionuclides, and the locations of these radionuclides differ depending upon the type of material. It turns out that most of the activity is actinides, particularly americium and plutonium, and the release of those will be controlled by solubility, providing we don't have a problem with colloids, which has really not been addressed. There's been some work done on colloids. I don't mean or want to say that it's been totally ignored, but there's not been much done on it.

The release of soluble radionuclides, such as the one listed here, will be controlled by a couple of mechanisms. One, rapid release from gap and grain boundaries somewhere, we think, in the neighborhood of a few tenths of a per cent up to 20 per cent of the inventory, and then a potential long-term release of these soluble radionuclides that's governed by the kinetics of dissolution of the UO_2 matrix in the fuel.

This next chart just gives you more detail about what the activities are in fuel after 1,000 years, and the reason that 1,000 years is used is because of the criteria for essentially complete containment for 300 to 1,000 years, so we listed it in that manner.

This chart was put out by Ray, I think, which shows three different modes of release from the fuel; one from the gap. This was borrowed from our Canadian colleagues, this graph. We get a very rapid release of things like cesium from the gap upon contact by water, then a slower, but still relatively rapid release from the grain boundaries, and finally, some release rate that's controlled by the dissolution kinetics of the UO_2 matrix.

Now, in a lot of spent fuel dissolution testing, you put spent fuel in water and you get contributions from all three of those sources at the same time. It's difficult to tell what's coming from where. One of the things that I will show you is a method that we've developed for dividing these into individual components so that we can better evaluate them.

Now, I want to put up this chart, which shows some of the things that we need in the assessment of fuel as a waste form, and the reason for why we need that data. Obviously, we need thermodynamic data, basically solubility data for low solubility radionuclides, because these are the ones with most of the activity in the fuel, as I just showed you. We need experiments to determine the nature and importance of actinide-bearing colloids to determine whether that's an important thing so that they might have some control on the release, rather than the solubility, which is what you would get from the thermodynamic data. We need to measure inventories of gaps and separate inventories of grain boundaries of the soluble radionuclides, because the Yucca

Mountain Site Characterization Plan assumes and, in fact, it's common worldwide to assume immediate dissolution of gap and grain boundary inventories upon contact by water.

If you're going to make that assumption, then we need to know what these inventories are. And in the case of the U.S. fuel, there's been almost nothing done on that. The Canadians have done quite a lot of work on looking at gap inventories, and more recently on grain boundary inventories, but the U.S. situation is very much in poorer shape than that.

Additional needs. Another assumption that's made is that the UO_2 matrix dissolves congruently, and that it will control the rate of release of cesium and other soluble radionuclides from the matrix. But that assumption needs to be demonstrated experimentally and, in fact, we have done some of that lately and I'll show you some data on that. We need to find out the kinetics of spent fuel dissolution as a function of water chemistry. We don't know much about the spent fuel oxidation/dissolution mechanism. We don't know what the effect of oxidation on dissolution is, and we need to understand these if we're going to be able to predict, in a performance assessment sense, the long-term performance of fuel in a repository condition.

Well, the next few view graphs summarize some of the accomplishments in the last few years. Earlier, Chuck Wilson of PNL completed three series of semi-static tests; one in deionized water, the second and third in J-13 well water from the Yucca Mountain site. These results are documented and I will show just one or two slides from it. More recently, we've developed a method for preparing separated fuel-grain specimens, and I'll show you a picture of that and describe a little bit more why that's important when we develop a method for conducting flow-through dissolution rate measurements which gives us the kinetics, the true kinetics of dissolution of the matrix. We have measured gap inventories and separate measurements of grain boundary inventories for a couple of different fuels. That's all that's been done in the U.S. to date, and we have shown that in the cases tested--there's only been three of them--that the grains do dissolve congruently, as we expected they would. And I'll show you some data that shows some of the importance of some of the water chemistry constituents that are common in groundwater.

I'm going to skip over this next slide and show you one here. This is derived from some of the semi-static data that Chuck Wilson generated a few years ago. It gives you some annual release rates at 25☜ C in the J-13 water as a fraction of the 1,000-year inventories, assuming 20 liters per year per waste package, and a certain inventory in the fuel. These release rates are relatively low compared to the 10^{-5} per year criteria of the 10 CFR 60. So from a solubility standpoint, which is what these basically are, this looks relatively good. It's based on one or two fuels and one condition, and it doesn't tell you much about colloids. There are some data that's pertinent to colloids--

DR. LANGMUIR: Walt, Don Langmuir. Is that fluid oxidized or reduced? It's very different, what you have there. Can you tell us?

DR. GRAY: This is an "as-received fuel," just pushed out of the cladding.

DR. LANGMUIR: But the release rate is a function of the--it's the water chemistry that you're looking at here. Is the water oxidized or not?

DR. GRAY: Oh, it's air-saturated water.

DR. LANGMUIR: Okay.

DR. GRAY: I'm sorry.

I mentioned that we had developed a method for generating individual grain specimens of spent fuel. Basically, we just crushed the fuel and it tends to fracture along the grain boundaries. We can screen it to get rid of the larger particles and we can wash it with water to get rid of the fine particles. This allows us to do two things. Because all of these grain boundaries are exposed, we can do some very short term dissolution tests on that kind of a fuel in a matter of minutes or hours and analyze the solutions generated and measure the grain boundary inventories. This is something that had not been done until this kind of fuel was generated. Some of our Canadian colleagues are using a similar method to measure grain boundary inventories in their fuel. So we're both aiming in the same direction there.

The other thing this does is it allows you to put a sample like this in a column and continuously flow water across it and measure the kinetics of dissolution of the matrix after the gap inventory and the grain boundary inventories have already been washed away and thereby separate out the different components of dissolution that I mentioned earlier.

A few results of gap and grain boundary inventories. This is results for cesium that covers fission gas releases from very small values up to about 18 per cent, but I want to emphasize that all these fuels are a single fuel, just different rods within the same fuel. It happens to be a Calvert Cliffs fuel, ATM-106 we call it. It has a burnup of about 48 megawatt days per kilogram of metal. But, as I said, different rods have different fission gas releases. This is a different fuel with a very much lower fission gas release.

Here, what we find is that the gap inventory of the cesium, which is represented by this regression line, is about a fourth of the fission gas release. The projections, the assumption that had been made is that they would be equal. This limited data suggests, at least for this fuel, it's a little bit less than the fission gas release. And the grain boundary inventories are, in general, quite low, less than one per cent.

We have similar data for technetium and strontium. We don't have iodine yet, because at the time these data were generated we didn't have an analytical technique for measuring iodine concentrations as low as they were in these solutions. We think we're getting a technique to do that now. The point of this data is that the strontium and, in particular, the technetium gap and grain boundary inventories are basically too small to measure. These numbers, they're just scattered around zero; a very small amount of the technetium is found either in the gap or in the grain boundaries. Again, this is--now, this is the same fuel. This is all the same fuel just like the last one was, so it's basically a single fuel.

Now, those individual grains that I showed you a few minutes ago, after we wash off the grain boundary inventories we can put into an apparatus like this, our so-called flow-through dissolution testing method. We put a small amount of grains in this column, pump a feed water through the column continuously. Periodically, we can intercept the waste stream with a sample vial and collect the material for radiochemical analysis. The gas bottle here is used to sparge the supply water to control our oxygen concentrations and the CO_2, which tends to stabilize the pH. Most of our work has been done under air-saturated conditions. Only recently have we begun to sparge the water with gas that contains smaller amounts of oxygen.

This is an example of the congruent dissolution that we have recently measured for about three different fuels; that is, the uranium, cesium, technetium, strontium are all dissolving at about the same fractional rate. This is in one of these flow-through tests. We get a little bit of a transient period, then we come down to something more like a steady state later on. These data, all of these data can be read on the fraction per day side of the graph on the left side. Only the uranium data applies to the right side.

As I said, we have data on about three different fuels that suggests that we do, in fact, get congruent dissolution if you wash away the grain boundary inventories first.

I mentioned another one of the things that we had done--this was a couple of years ago--we looked at some effects of water chemistry on dissolution rates in one of these flow-through systems. We started off with some J-13 water. Our purpose at the time was to try to go to elevated temperatures. We wanted to get rid of the components in J-13 water, like calcium sulphate, that would precipitate at higher temperature and clog up the frits on the end of our flow-through column. And we assumed that sodium carbonate was the active ingredient in the J-13 water. So we said, well, let's just take sodium carbonate at the same concentration as we had here, change from this water to this water, and we ought to get the same dissolution rate. Well, we didn't by something over an order of magnitude, almost two orders of magnitude increase when we changed from the J-13 water back up to the sodium bicarbonate solution.

Then we began to add back some of the components that were in the J-13 water. We added the calcium in the same concentration as it was in the J-13 water and we got a small drop in the dissolution rate, and then we added both the calcium and the silicon at the same concentrations we had here and dropped down to something like we had in the J-13 water to begin with. So the purpose of this is to just show that there are a number of important constituents in that J-13 water and it's an experimental space that we need to cover in more detail, and we have just barely started down that path.

One of the other things that we've started here a year or more ago--and I'm not going to say anything more about this because Steve Steward will talk about the work that's being done both at Livermore and at PNL--looking at these four different variables on the dissolution kinetics of both unirradiated UO_2 and spent fuel.

I think I put something out of order here compared to what's in your handout. Let me show you this because this tells you what I'm going to show you next.

For a limited number of conditions, we have found that unirradiated UO_2 and spent fuel up to about 50 megawatt days per kilogram are about the same. Now this is based upon two or three different fuels in the range of burnup of about 30 to 50 and unirradiated UO_2, and there's a limited number of test conditions.

I'm going to show you that for one fuel that we tested, one test condition, that spent fuel oxidized to U_4O_9+x, the kind of stuff that Bob was talking about, and dissolves at about the same rate as unoxidized fuel. I'm going to show you one test condition where unirradiated UO_2 and unirradiated U_3O_7 dissolve at about the same rate. I will show you some results for unirradiated U_3O_8. I'm going to show you a test where we compared static dissolution rates to the dynamic dissolution rates that we measure in these flow-through tests.

The first case here is spent fuel compared to UO_2. This just happens to be about a 3 megawatt-day per kilogram of spent fuel. Under these kind of test conditions, again, this is--unless I say otherwise, these are air-saturated solutions and this happens to be 25☜. That somehow got left off of there.

We get, after some period of time, a UO_2 rate that may be a little bit smaller than the spent fuel rate, but the difference is a factor of 2 or 3. It's not a great difference and the differences that we see in the spent fuel as we go all the way up to 50 megawatt-days per ton fall within that kind of a range. Again, let me emphasize that it's just two or three fuels and basically one or two test conditions within this regime.

Here is the data that I promised on unoxidized versus oxidized fuel. This legend applies to both drafts. The upper chart shows spent fuel grains, the individual grains that I showed in this former SEM photo, and for both cesium and uranium the dissolution rate is essentially identical. Now, we took a different sample of spent fuel, same oxidized fuel, but one that had not been pulverized up into grains, but yet was rather coarse powder, about a millimeter in size. And there is a couple of differences between this that I call particles, these one millimeter particles, compared to the grains.

One is that we do now see a small difference between the oxidized and the unoxidized sample. There is not quite a factor of two difference for the uranium; slightly over a factor of two difference with the cesium results. And what this apparently tells us is that the oxidation slightly opened up the grain boundaries to the point where you get a little bit greater grain boundary attack for the oxidized fuel compared to the unoxidized fuel. But the difference is relatively small. It's a factor of two, about. The other thing that you get out of this is a difference between the rates here for the grains versus particles. Here the rate is 8 or so. Down here the rate is 30 or so for the uranium. The surface areas that we used here are probably pretty good numbers.

We did a particle size distribution, calculated the surface area, assuming that the particles were grains, multiplying by a surface roughness factor. We happened to use 3. Down here we did essentially the same thing for the particles, but we assumed that the grain boundaries were tight; that is, that they were totally non-accessible to the water. This factor of 5 or so difference suggests that the grain boundaries are not entirely tight. And this difference, factor of 5 or so difference could be accounted for if just the top layer of grains on each particle were available in the water.

If the grains were cubes, the surface area of the top of the cube compared to the top plus the four sides would be just about a factor of 5, which is what we have here. So this suggests that about the top layer of grains from these particles have their grain boundaries open to the water, both for the oxidized and unoxidized; not a lot of difference between those. We also have some microscopic evidence that supports that, but in the interest of time, I didn't bring that along to show.

Here's some data for unirradiated materials. Again, this is air-saturated solutions. The bottom chart shows unirradiated U_3O_7 compared to UO_2. You remember the graph that Bob showed with the oxidized rim of U_3O_7 around the particle. That's the material that we used for these tests. There is not very much difference between these materials. We took some of it, then, and oxidized it all the way up to U_3O_8.

Now if you look at the left-hand scale, which is a surface-normalized dissolution rate--and the surface areas used for both this and this were B.E.T. surface areas--there's not a lot of difference, a factor of maybe 3 or so, 3 to 5 between UO_2 and U_3O_8 when you normalize it on the basis of surface area. But, as Bob said, you get a big increase in surface area when you go to U_3O_8. So if you look at a fractional basis, now the U_3O_8 numbers are more than a factor of 100 greater than the UO_2, and so it's mostly based on the increase in the surface area.

One further experiment that we did comparing U_3O_7

to UO_2, we did some dissolution rate measurements in water that have been sparged with oxygen containing only .2 per cent of oxygen. That is 100 times less than in air. Now we see a small difference between the UO_2 and the U_3O_7. There's a factor of 3 or 5, depending upon where you want to make the comparison. We have a gradual increase in time here. If you compare it back in this area, there's a factor of about 3 to 4 difference between the two. So there is some difference that starts to show up based upon this one test, if you look at less oxygenated water between the oxidized form of the unirradiated material and the unoxidized form.

The final piece of data that I want to show is a comparison of dissolution rates from semi-static tests to these flow-through tests. This chart requires a little bit of explanation, so you need to bear with me for a minute.

These numbers were derived from semi-static tests done a few years ago by Chuck Wilson. In those tests, the uranium concentrations quickly saturate. But if you look at the concentrations of cesium, technetium and strontium, they continue to increase with time. And after quite a long period of time, Chuck took the slope of those curves and calculated a dissolution rate for these soluble nuclides from these semi-static tests. And these are the numbers that he got in units of fraction per day, same unit as this.

That fuel then was set aside as an archive and we more recently then took that same sample of fuel, so it's exactly the same fuel sample that had been in the these semi-static tests for four or five years, took it out and put it in these flow-through columns and performed these dynamic dissolution measurements on it.

Well, here, of course, the uranium doesn't saturate. These are done under conditions where the uranium concentrations remain well below saturation. And here you get a little bit of incongruent dissolution because these are fragments that are three or four millimeters in size and you get some preferential dissolution of cesium and technetium from the grain boundaries. But if you look at the rates for the technetium and the cesium here, the numbers are four or five times, 6×10^{-6}, about a factor of 10 higher than we had here in the semi-static tests.

Some people think that there will be orders of magnitude difference between this very non-repository relevant kind of flow-through test that's done for measuring dissolution kinetics, compared to something that's a little more repository relevant, and which is representative of the semi-static tests. This data shows that the difference is a manageable factor of 10; one test, one condition again.

The next couple of slides that are in your handout just summarize these results. I don't think we need to summarize those again. They are there for your perusal. Let me just put up my ideas of the things that are needed. These are not immediate plans. These are just things that the U.S. program, in my view, needs to address in the years to come.

We need to generate a larger data base of thermodynamic data. That'll be talked about, I think, later today by Livermore. They're working on this to some extent now. We need to work to identify solid phases that control the solubilities. These two kind of go hand-in-hand, but some of this kind of work needs to be derived from actual spent fuel studies, and some of this kind of thing was done in the past by Chuck Wilson in his semi-static tests where he did identify some of the solid phases in these tests. There's a lot more that needs to be done along that line. And we need to develop some way of getting a handle on whether or not colloids are important.

Gap and grain boundary inventory measurements. I mentioned that there is only two or three of these in the whole U.S. White Water Fuel Program. That needs to be extended to a variety of fuels in both BWR and PWR, and over a variety of fission gas releases for different fuels, not just within a single fuel, which is where we have the data.

With regard to our flow-through dissolution rate measurements, Bob mentioned that we need to figure out what happens to spent fuel if you oxidize it beyond this $UO_{2.4}$ state. What kind of time/temperature regime is needed to do that? And we, then, need to take whatever the result of that is and make measurements of the dissolution rates. We also need to expand our work to additional oxidized fuels. We've only done it for one fuel. We need to look at other water chemistry conditions. In particular, we ought to look at less oxygenated conditions. Although Yucca Mountain is an oxidizing environment, there may be things in the waste package that would make it less oxidizing, and so we need to know how that might affect the dissolution rates of oxidized fuels.

Steve Steward will talk about our current test matrix for UO_2 in spent fuel. We need to complete the work we've done on that, which includes four variables. The only water chemistry variable, really, is the carbonate concentration--well, pH as well. We need to add these kind of things to it. I showed some data which says that those are important constituents in the water. And we need to extend our measurements to gadolinia fuels--Bob mentioned this--fuels with very high burnup, and it may be that we need to look at low burnup oxidized fuels if it turns out that those act in the near and immediate fashion between UO_2 and spent fuel.

The data that we have now suggests that oxidized fuels and unoxidized fuels may behave the same and different burnups are not important. It may be that the low burnups could be just as important as the high burnups here.

In the handout, I have put on a number of publications that we've come up with over the last few years. I won't put those up, and so that completes my talk.

DR. VERINK: Thank you very much, Walt. I think we'll go right on ahead into Steve's presentation to preserve our schedule.

For those of you who are concerned about the discussion possibilities, we'll defer any discussion on these two papers until the end of the session this afternoon. We're going to have a little time at the end.

DR. STEWARD: Some of the material I'll cover will be a little bit like Walt has talked about but I'll try to de-emphasize some of the things in my talk to avoid any redundancy. I'll already make a change when I first get started. Within the topic, I'm going to emphasize more the UO_2 results that we've been getting, but at the same time I will look at some analytical work, some data analysis of the spent fuel work that Walt's done to show you some modeling to start getting towards what we call our source term or our intrinsic dissolution models. And then I'll talk a bit about the experimental design work that we've been doing to give you a sense of why we're doing the experiments that we are doing.

Now, there's a little background. One of the reasons for doing these results in the first place is that the complexity of the spent fuel dissolution requires a fairly controlled approach.

Anyway, the complexity of the dissolution problem requires a controlled approach. There are a large number of variables that can come into play in the dissolution problem, as you've seen already, and the results of the previous data show there's quite a wide range of results from earlier studies where the data or variables were not controlled as well, up to a million-fold. That presented a problem we needed to look at.

The semi-static tests that were conducted at PNL, and some in other places, allow precipitation. Although it's more indicative of perhaps the kind of environment that might be true in a repository, if we're really wanting to understand the intrinsic dissolution we need not to have those. So the flow-through method, then, which has been used in other areas was brought into this problem to look at that.

Then we wanted to compare studies of just UO_2 by itself with spent fuel to look at the differences between those two areas, see if there is an effect in components of spent fuel, the radiation, the other radionuclides that might affect that matrix dissolution, and also to see if the studies with UO_2 by itself might lend--be easier to do and give useful information without all of the difficulties involved in looking at spent fuel.

So the way we decided to look at this, then, is use a statistical experimental design as really the only way to approach this multi-variant problem with a sensible number of experiments so one can get to a modeling phase. That's really what statistical experimental design is for, is to eventually allow you to model the problem you have. And, in a sense, that's how I got into this program a couple of years ago. Even before I was working with it, I helped Herman Leider and Ray Stout with an experimental design area which I know quite a bit about.

I think it's important to point out the advantage of experimental design, besides the fact it allows you to get to a nice model with data spread out in your multi-dimensional experimental phase, is that very often, and in most cases, you can get a design that limits you to only about 32 experiments or so. Rarely do you need to do more experiments than that unless you have an unusual situation where you have very many variables that turn out to be important. And, normally, Mother Nature is not that cruel, and you can eventually, through a series of screening designs and modeling designs, get down to a small set that allows you to model.

And that modeling effort can either be empirical or mechanistic. The experimental design itself doesn't care about the character of the model you use, only really about the number of terms involved, which drives the number of experiments you're going to have to do.

All right. Again, if we look at Grambow's paper from 1989, the data plotted in a variety of different ways in there, both by the oxygen content, test methods, different kinds of fuels. In any case, you've got a fairly broad range of data plotted in those particular manners, and so it emphasizes in this business with controls. As Walt pointed out, the UO_2 itself, the fuel matrix dissolution, governs, really, the long-term soluble radionuclide release and the bulk, then, of the fission product and actinide release is controlled by that dissolution rate. The total fraction isn't determined, I understand, but I think a good guess is approximately 80 per cent of the radionuclide release is governed by the matrix dissolution, and approximately 20 per cent or so is probably at the gap and grain boundaries. So it's important, obviously, then, to look at these matrix dissolution studies.

A quick statement about the flow-through method. Again, the reason that was used is if we go at high enough flow rates--and high flow rates are still are not very high. I mean, it's not a waterfall by any means. We're talking about 100 cc's a day through these small multi-gram samples that we're using, so these are drip tests by our definitions, but it's a much higher flow rate than a semi-static test over a number of months.

This technique has been around in the literature for many years, used in geochemistry and so on, but a first use was by Knause at LLNL in 1986 on glass. I think that was kind of the first instance where it really started being used in the waste form area, and then over those few years it's been refined both at LLL and at PNL for both use in the waste form problem, the glass form and the spent fuel problem. And Bill Bourcier, I think, will talk this afternoon about his studies with glass and using that same technique.

The measurements, then, on UO_2 dissolution, as I've pointed out, are really important to modeling, because once you get the UO_2 dissolution term, you can put that into your --you can define the matrix dissolution and with UO_2 itself, which is the work we're doing at Livermore, versus the spent fuel, then you can compare that to the spent fuel results such as what Walt's doing at PNL, and look at such things as the chemical effects of fission products on the matrix behavior, chemical effects of high radiation levels that you don't see with UO_2 by itself. And then, again, grain boundary dissolution of some of the fission products may affect the spent fuel results differently than UO_2 by itself.

I think one of the themes I'm probably going to point out in this talk--and Walt alluded to it in his talk as well--is that what the early data we're seeing in this test matrix that we developed using experimental design with some of the ancillary experiments that he's been doing, I think one theme starts to come into play. In fact, when we're starting to control the variables that we think are important to dissolution, we're starting to see dissolution rates that are forming a much narrower range than one saw in the historical data, you know, probably a factor of, within a factor of 10 in this data, maybe a little larger than that, but certainly much less than two orders of magnitude.

And I think this is encouraging because it shows that we're really starting to get down to the actual effects of the individual variables, and not a lot of other effects which may be more based on surface area problems in the samples than actually on the effect of the variables themselves.

This was some of the first data we took last fall. This is one part of the data. These are the results at 20 per cent oxygen that we picked out of the test matrix. The test matrix that we're doing both at PNL and at Livermore, just using UO_2 at Livermore in spent fuel is a 19-run test matrix that looks at the variation in carbonates, oxygen, pH and temperature. So this is one group at 20 per cent oxygen and 25 per cent--20☜C and 20 per cent oxygen. These are different carbonates and pH's. There was some oxygen loss from our experiments through the tubing we were using, but I think one thing that's useful just in these experiments, we see that even under a variety of carbonate and pH conditions, we see a relatively small range as a whole of dissolution rates in these units, milligrams per meter squared per day over a period of a month or so, and some of this data went out further. We're staying down. All of these are in factors of 2 to 4 of each other, so they're not large. That's not to say, however, there's no effect of the variables. That's just to say that they're not large effects.

After that particular set of runs, we thought it'd be useful to compare, since there's a little variation in results between the two laboratories, compare powders which came from PNL and their crushing method, using both techniques at the laboratory. We have similar techniques, but they're are different. We had plastic cells and they had metal systems. We had different kinds of pumps, and so on, so we thought it was important to kind of calibrate between the two laboratories, and I think that's what we did in this series of runs. These two here are two cells of our style and design with our particular peristaltic pumps that we used. And this was a cell that Walt sent down, his metal cell with high pressure liquid chromatographic-type pump, the piston pump that he used.

I think the main thing from this result, then, even at different laboratories and different altitudes, latitudes, whatever, we're starting to see similar results and this kind of brings things together again, that with the same samples that we are, indeed, getting good results between the laboratories.

Now, there was one particular result we had, I think, is important to look at. It was a little bit of a negative result that turned out to kind of be a positive result in the end. It's come up in a number of these talks, and I think we actually had a real-life expression of this in our laboratories, that in the end, in a performance assessment model, one of the big unknowns is going to be and one that's going to have to be addressed is what is the surface area that you can assume in a scenario where water gets to the spent fuel? Is it the pellets themselves, or large fragments, smaller grains? And I think this particular experiment we did points this out.

This was the same type of experiment we did. We initially have been using pellets, UO_2 pellets, to do these experiments. We did that because we thought this would give us a nice geometrical surface area. It'd be easy to know the surface area of that. We assumed the dissolution liquid would not penetrate into these pellets, only see the outer surface and only protect--in the outside grains, be able to get into the first layer, so we could define that surface area better.

Well, these are similar experiments that we'd done before at 20 per cent oxygen and room temperature, similar to the first slide. We got much higher dissolution rates in these experiments. When we took those cells apart, it worried us at first. We studied the chemistry. We looked to make sure that something hadn't gone wrong in the way we had done our experiments, there were some contaminants we didn't catch, analyzed it, didn't see anything wrong with any of the buffer solutions we used. But we got this high dissolution rate.

When we took it apart, we found that there was a significant amount of powder inside those cells, that the outside of the pellets had disintegrated a bit and provided particulate matter in there that provided a large surface area, and then it had provided this large dissolution rate. So I think we still don't understand that entirely. There is a suspicion these pellets may have a slightly different oxidation state than UO_2, and I mean slightly, 2.01. Our Canadian colleagues indicate that a slight difference like that may make a difference in the dissolution rate. So I think it does point out the importance of keeping track of these surface areas and trying to understand some of the subtleties that may have some effect on the final dissolution rate in the repository. The intrinsic dissolution rate of the pellets didn't change once we took the surface area, but certainly, the surface area affected it.

Now I want to look at some analysis we've done with Walt's data. This work is being published in the Journal of Nuclear Materials in a joint paper between us. The capabilities of the experimental design software that we have, besides help us design different types of designs, is to just have analysis capabilities built in. In this case, we used its regression capability.

Now, again, I want to point out this is just part of the data of the test matrix. This does not represent all of the test matrix that we've done, which looks at a wide range of conditions of oxygen, carbonate, pH. These are just conditions at 20 per cent oxygen and varying the pH/carbonate compositions, and these are at room temperature as well, so--or, excuse me, not at room temperature. These are over a variety of temperatures, but at 20 per cent oxygen. So oxygen is not a variable in these particular fits.

What I think is important to point out, though not definitive yet, that with that data--which represents nine runs in our test matrix--that the best fit actually came from the simplest model, a very simple empirical model that's linear in logarithm of the carbonate concentration and linear in the temperature.

Now, these are correlation coefficients. They're adjusted correlation coefficients, and as the footnote states, that means it takes into account how many terms you have in your equation. If you look at a full six-term quadratic--and it's actually seven terms, including the constant, where you look at all the square terms and linear terms--you get a very good fit because you've got seven terms and nine pieces of data. But when you take into account you have only two degrees of freedom, its fit isn't nearly as good as a simpler model which has six degrees of freedom and provides a very high correlation coefficient.

So there are some things that come out. A fairly simply model can explain our data best. We look at the hypothetical mechanistic model, which we'd all like. We feel better if we have a mechanistic model if we need to extrapolate our data to other conditions. This is just a simple kinetic equation with the concentrations of hydrogen ion, carbonate, and an Arrhenius-type temperature fit. We get the worst type of fit.

Now, that doesn't mean we shouldn't pursue the mechanism. Perhaps as more data becomes available here in the test matrix and others, it may improve. But yet, it also tells us that the pH has very little effect. We can look at this particular equation which is the same as No. 2.

Equation 1 has pH in it; Equation 2 does not. There's a very similar fit, measure of fit between the two, almost identical, and you can see that the coefficient for the pH is very small. So we have already seen, based on this test matrix, it doesn't look like pH is going be a strong effect.

So I think this gives a sense of the power of the experimental design approach. With the 19 experiments we're going to do, nine so far with the spent fuel, we can start getting a very good sense of the dependencies between the various variables. We don't see any interaction effects that are significant between any of the variables of pH on carbonate or temperature on carbonate. These don't seem to be important.

I put up this view graph, and it's a little controversial to some people, so I want to make sure I say what the view graph says and not what, and don't read anything else into it.

What we've done here is plot, again, the data that we have available with spent fuel at PNL, some UO_2 work at PNL on powder, from both polycrystalline material at Livermore, and some powder work that we did at Livermore. I think--I get the feeling a view graph got left out here. Let me take this one off a minute and just point this out.

Some of the results I just mentioned we're going to show in that table include some results we did after the problem we had with powder coming off the pellets. What we did then was shift to a different type of sample where we had polycrystalline pellets. It was close to single crystals. They had just a few large crystallites in them, a millimeter in size, so the surface area could be much more easily defined than they were in the pellet studies.

So we did those results sort of mid-summer and came up, again, I think the important part is these are room temperature and 20 per cent oxygen. We're just now starting our lower concentration oxygen runs as part of the test matrix.

Again, we get back to the kinds of results and kinds of dissolution rates from one to ten milligrams per meters squared per day that we had seen last fall, that Walt's seen with his spent fuel and that we both have seen with the UO_2 powder. So once we get rid of this confusion of what the surface area is with these samples and go back to nicer samples that have a better-defined surface area, we come back down to the general range again where we've been before with the dissolution rates.

Now, sorry I left that slide out. I hope it didn't confuse you.

Finally, we're back to this table. Again, the only thing this is supposed to do is look at the two variables so far that we've seen to be important; that is, the temperature and carbonate, the most important two variables. We're taking a slice in our four-dimensional space, a slice of the data, carbonate and temperature, and just over the full range of pH and oxygen concentration. Now, I just want to point out this is 2 x 10^{-3} atmosphere is oxygen. In our test matrix, we're trying to do 2 x 10^{-2} atmospheres. That represents some of the data we did last fall when we lost oxygen out of the system, so we did some subsequent tests with some oxygen probes and saw we were losing about a factor of 10 of oxygen and diffusing out through tubing. So this lower limit is somewhat of an estimate, but I don't think it changes what we're trying to say here.

We're just saying that with both spent fuel and UO_2 in both powder, pellet, polycrystalline forms, that we're getting a fairly narrow range of data compared to historical data. That's really the point I want to make. Despite what the variables are, whether it's different carbonate, temperature, oxygen, pH, the actual intrinsic dissolution of these, of the spent fuel and the UO_2, at a variety of conditions -- are in a fairly narrow range, one order of magnitude. From the lowest dissolution rate of all the samples we saw at this concentration up to the highest, we see a factor of 55.

It points out--it doesn't mean those variables aren't important, oxygen or carbonate, it's just saying that

that range is much smaller once we've started to control the variables that we wanted to do in the experiment.

All right, now, I just want to look at--I'm showing you the data we have at the present time and I just want to look at near-term plans. I'm about finished here. Before I forget, I want to point out in the package you have, I did not include any copies of these test matrices or experimental designs that we're working from. I have copies of those. They're tables, so they're not very pretty to put up on the screen. But if you have an interest in those, anyone on the Board, I'd be happy to give those to you so you could see in detail what experiments we're doing.

The near-term plans. First of all, when we finish the current test matrix, the four variables test matrix, which should be done in the next few months, and once we've finished it, we've done the modeling effort, further analysis to try to determine the intrinsic dissolution rate, we want to expand that then to, as Walt had mentioned, to a broader water chemistry and other fuel attributes which will add up in a design we currently have, to about ten variables. Those ten variables include the existing test matrix, the four variables we have, using only carbonate as the really reactive ion. The carbonate, as Walt pointed out, has been done because it's been shown to be one of the more aggressive ions with uranium and kind of a worst case sort of ion.

The major components in J-13 water that we want to look at that we anticipate will have an effect--again, using the result of the PNL studies--looking at the four variables, silicate, calcium, sulfates in a fairly high concentration, so we want to look at that, and then a halide. It's not clear yet whether fluoride or chloride or, if it matters, which one might be useful that we can look at.

And then looking at the reactor-type fuel burnup level we can also explore, and I think we're also talking about considering the oxidation level of the fuels, too, which we may or may not set up as a separate variable or include in these variables.

And then, that same matrix, then, we can do with UO_2 to compare again, for the same reasons as before, the effect of UO_2 by itself on these different fuels using the same water chemistry.

Now, to do the ten-variable study, I want to point out the power of experimental design. Ten variables are a lot of experiments and a lot of variables to look at, and I hope all ten of them won't turn out to be important. But the reason for doing that is, particularly in a program like this, where you really need very solid justification in experimental data and otherwise for the actions you've taken, the experimental design gives you the ability to look at a broad range of variables and study them experimentally and determine: A, whether those variables are important; and B, once you've determined they're important, you can do the right set of experiments to get a model.

So, what we're going to do with those ten variables, we're not going to do a modeling design initially. We'll do a simple screening, what's called a screening design in the parlance of experimental design, which determines simply whether each of those variables are important. Then when you're done with the screening design, you can take the variables that are determined to be important and do further studies, building on the screening design. The screening design results can actually be a very strong part of your modeling effort at that point. The variables that aren't important just act as constants in the problem. So, we'll do this design.

For those ten variables, we only need to do 32 experiments by using a fractional-factorial screening design, and that will test the importance of each variable. And then as I said, once that's done, say five variables turn out to be important, you can still do another design. It may have 32 or less experiments that you can build on that, but you'll still be using your screening results to add to that data which will actually enhance the quality of your fitting effort later because your model itself could have 15 to 20 terms, and you'll have quite adequate data after that effort to have a nice model of your system.

The screening design simply tests variables at two ranges as far apart as you can in size within the constraints of your experimental problem.

All right. That's the last view graph I have.

DR. VERINK: Thank you very much, Steve.

Just by way of giving the potential question askers a better chance to deal with the questions they had this morning while they're still fresh in their minds, we've decided to start the afternoon session at the time shown on the schedule, but reserve the first ten to fifteen minutes for a few of the questions that refer to this morning's session. So would the speakers and those interested in asking such questions try to be very prompt about their lunch arrangements, and we will get on that before we start on the afternoon session.

Okay. We're dismissed for lunch, then.

(Whereupon, a lunch recess was had off the record.)

AFTERNOON SESSION

(1:45 p.m.)

DR. LANGMUIR: I'm Don Langmuir, Co-Chairman of the Hydrology and Geochemistry Panel. I'll be convening the afternoon session. We'll start with about 15 or 20 minutes of questions which we had no opportunity to ask this morning of our speakers after the break.

First, if I might ask Dr. Einziger to come on up front so--if we have questions. I think we're going to need overheads, though, so questions from the Board?

(No audible response.)

DR. LANGMUIR: I guess I have one.

You talked about the oxidation of UO_2 and pointed out that you discovered that the rate of dissolution of UO_2 as spent fuel was not the same as UO_2, natural UO_2 material.

DR. EINZIGER: Actually, Walt talked about the dissolution rate.

DR. LANGMUIR: But your discussion was somewhat similar to that, and my question relates to if you add water to the system--you looked at two different moisture contents--does the rate pick up for the complete oxidation to UO_3 or UO_3 hydrate?

DR. EINZIGER: The Canadians have done some work where they've essentially done the system in steam so that they were able to form a water film on the surface of the fuel and they've gotten some preliminary data that gives an indication there might be some U_3O_8 forming. There are questions, though, whether that's applicable to our particular systems, inasmuch as where it's forming is in the fuel that's run at very high powers, not typical of the kinds of fuel we've seen, and it's also much of a surface effect. It's not a bulk effect. So there are some indications if you get enough moisture that you're putting a water film in there, that you may have some slightly different performance.

DR. LANGMUIR: I'm trying to recall the overhead. You had one which showed the rates as a function of temperature for the breakup of the fuel. You had two rate plots, two Arrhenius plots. I can't seem to recall the overhead number.

DR. EINZIGER: Is that the one?

DR. LANGMUIR: Exactly.

Your 200☜ point up there is beyond the data, and I guess that's what a lot of us are worried about or wondering about in terms of what's proposed for the repository at the waste package. And I'm just wondering what your thoughts are on the rates of survival of the fuel as UO_2 or U_4O_9 under proposed repository conditions at high temperatures.

DR. EINZIGER: Well, this program was first set up to look at what happens after the time that the canister breaches, and we were looking basically at the 300 to 1,000 year period, so it was looking at lower temperatures.

DR. LANGMUIR: What about the fraction of a per cent that are failed when they are put in the repository?

DR. EINZIGER: If you have a rod that is failed and in day one, when it goes in the repository, and the temperature --and the canister breaches, if you happen to have a canister that has a birth defect in it and it's breached, so that fuel is exposed to air, then this curve is pretty well going to tell you the time when you can expect that rod to start having appreciable U_3O_8, and it's saying that at 200☜, you could expect it at maybe 2×10^5 hours to have taken that rod and appreciably--and started to open it up.

If you want to go--this was a rod at 350. In about 60 hours, the thing was opening up. People talk about what's the temperature limit. The temperature limit is anything you want it to be, depending upon how long you want it to be. If you only want the thing like the Canadians have it, for handling purposes, when they did their programs and they only needed a couple hundred hours, they could put it into air at a much higher temperature than we wanted, in order to last

10,000 years. And the temperature limit would be different for the guy who wants to put it in an MRS for 100 years or wants to put it in a transportation cask for a couple days. You pick your time and we'll give you a different temperature. There's no such thing as a temperature limit. It's a time/temperature dependency.

But if you're going to put something in the repository at 350☜C, and that's the number I keep hearing bandied around, and it's going to be exposed to air at that temperature, you're going to unzip that rod and you're going to have U_3O_8 powder.

DR. LANGMUIR: Any more questions from the Board? Mick Apted?

DR. APTED: Bob, one of your questions you said you thought was key was how long does it take to reach this O/M ratio of 2.4 as a function of temperature. Given what Walt said subsequently, which is that the U_3O_7 and UO_2 phases seem to be dissolving pretty much identically, it seems to me that the question really becomes far less important. I mean, we can just assume it's there. Why bother trying to do up an elaborate theory for that when it has no real consequence on performance?

DR. EINZIGER: The only reason it's important to know when it gets up there is, so far, that's the only thing we've had to be able to extrapolate. If you remember the curve when it starts--I'll get the curve. (Pause.) If everything is leaching at the same rate here--and remember, Walt's data was only one fuel and he has to test a lot more things--if everything is leaching the same then it really isn't important to know when we get up here other than the fact that so far this is the time we've been able to get some data and make some extrapolations on. Once we get experiments where we have confidence and we can extrapolate this number, you'll probably get a lot longer times and, by far, this is the number we want. So far, though, other than this curve giving us some indication of where we're going, we have no data.

We would much rather generate this curve than this curve. It gives you better characteristics. And yeah, once we start generating this point, the time to get up here becomes far less significant.

DR. LANGMUIR: Further questions from the Board? Board staff? Audience for perhaps one question? If not, let's go ahead and ask questions for Walt Gray.

Thank you, Bob.

DR. EINZIGER: You're welcome.

DR. LANGMUIR: Walt, I have a question for you. I wondered if you or Steve Steward--and you can't speak for him, perhaps, or maybe you can--had speciated your solutions. I saw a lot of data on kinetics and questions about process, but I never saw an analysis of the kinds of complexes and aqueous species that would be in your solutions and which might control the rates you were looking at. It would seem to me that something like EQ3/6, for example, to pick a code, since it's relevant today, or some other geochemical code could be used to speciate and get you at the fundamental processes that control the rates. Having given you a speech, I'll let you answer.

DR. GRAY: No, there's been no work done to try to look at the speciation. I think that's probably true in the Livermore program as well. Is that true, Steve?

DR. STEWARD: I could address that a little bit.

DR. GRAY: Okay. There's been no work within PNL to look at speciation at all.

Now there was in the data in the semi-static tests, where, you know, but that's a different issue.

DR. LANGMUIR: One more from me. You mentioned the need for thermodynamic data, and I wondered what thermodynamic data you thought you needed. There's an awful lot that's been done in recent years to fill that gap.

DR. GRAY: Oh, that's true, and I didn't mean to imply that there is none. There is a lot of thermodynamic data available, but there are some gaps in it and I am not prepared to say specifically what they are right now, but there are some important actinides that we need to look at.

And I think there is some potential solid solution specie data that's still not been generated yet. And I think, more importantly, we need to make comparisons between the kinds of concentrations that are seen in spent fuel experiments and compare this to what EQ3/6 predicts.

For example, there was some rather poor agreement between the codes and the concentrations that we're seeing in the semi-static tests that had been done earlier by Chuck, which suggest that the right numbers aren't in the code, I think.

DR. LANGMUIR: One last comment from me. I think you might be able to explain the suppression rates that you observed with calcium and silica by using a speciation code. My sense is it's an incongruent adsorption phenomena you're looking at, with perhaps a mineral called uranophane, a calcium silicate, or coffinite, the uranium silicate that you're looking at in your experiments.

DR. GRAY: Well, those tests were done under conditions where we believed that the species remained far below saturation. So we're not looking at solid solution-type equilibrium sort of things at all. It may be that what you say is true, but what you need to look at is solution species, not solid species, we believe. We did do some looking at the surfaces of the UO_2 particles following these tests--this was all done with unirradiated material--to see if we could see with auger spectroscopy--that's the only technique we used--things on the surface like you see silicon and calcium on the surface, for example.

You do see it, or we did see it, but only after a couple of months of testing. And yet, the technique ought to see fractions of monolayers. Granted, we're looking at relatively small spots, but we basically saw very little or essentially none on the surface until after long periods of time, yet the effect is rather instantaneous.

We also know that it tends to be irreversible, as though you may be forming some kind of a protective layer. That's why we're looking for these things on the surface, but didn't see them except after long periods of time. So there's a lot about--we know very little, nothing, I should better say, about the mechanism of the effect. So that's something that we'd like to explore further with a variety of techniques.

DR. LANGMUIR: More Board questions?

Nava?

DR. GARISTO: Do you think that there is a need for work on radiolysis to complement your kind of experiments?

DR. GRAY: The work of who? I'm sorry.

DR. GARISTO: On groundwater radiolysis, alpha radiolysis, things like that?

DR. GRAY: Well, there is always the potential that radiolysis, either gamma or alpha, will have some effect on the work, and that's one of the reasons for trying to compare spent fuel and unirradiated UO_2 data.

You know, some of the Canadian electrochemical work, for example, suggests very strong effects of radiolysis, and yet, so far, we haven't seen any real differences of spent fuel compared to UO_2, which would suggest that maybe radiolysis isn't very important.

On the other hand, the regime where radiolysis is likely to be important, I think, is in very low oxygen concentration solutions where the radiolysis would produce the oxidizing species. If you're already in an oxidizing environment--which most of our tests are; well, all of them are, even the relatively low oxygen concentrations--they're still fairly oxidizing compared to the kind of conditions that Dave Shoesmith works with, for example.

So to say that we see no effect--no difference between spent fuel and UO_2 and, therefore, there may not be an effect of radiolysis, that's probably true only in the oxidizing regime. It might become much more important in low oxygen situations.

DR. LANGMUIR: More questions from the Board? Mick Apted?

DR. APTED: Walt, did you bring your view graphs?

DR. GRAY: Yes.

DR. APTED: Do you have the one on the spent fuel dissolution rates where you had the grains and the particles?

DR. GRAY: That one?

DR. APTED: Yes. You explained--

DR. GRAY: Can you see it clear over there, or should I put it on this one?

DR. APTED: No, that's fine. I think you explained it, but I just want to be sure because I'd like to compare it with the one following on just UO_2. Your reason for the particle spread there, you're saying, is that you actually didn't have a correct surface area normalization, that new surface area formed and it's not accounted for, and that's why the--

DR. GRAY: You mean the difference between particles and grains?

DR. APTED: Yeah, exactly.

DR. GRAY: Okay. That's exactly right. The surface area that was used to generate this number was more or less a geometric surface area of the particles multiplied by a roughness factor, but specifically not taking into account any grain boundary surfaces. And so the implication is that the surface areas are wrong, and they're wrong by a factor of maybe about 5 because of the grain boundaries from the top layer or two or three of grains really are being attacked by the water, rather than totally unattacked, which is what this surface area assumption value assumes. Now, does that answer the question?

DR. APTED: Well, I guess you were here for Steve's talk that followed yours. He, also, in the UO_2--and he can, I guess, comment on this, too--showed some different tests which also showed even a bigger sort of a range of normalized release rates. And I guess--would you be expecting the same thing, that perhaps even for UO_2 it's a question of these pellets opening up and that the surface area is actually increased over what the initial surface area was?

DR. GRAY: Well, I'm not sure if I'm understanding your question.

DR. APTED: Steve had a figure that looked a lot--

DR. GRAY: Yeah, in his case--I don't want to necessarily speak for him, but he had some powder that was generated that was not accounted for.

DR. APTED: Right.

DR. GRAY: Now, the UO_2 data that I have like, for example, on the next slide here, as far as we know, we don't have powder generated beyond what we started with. Now, this is for particles that are, oh, in the neighborhood of 50 microns in size. And the surface area that we used is a B.E.T. surface area, and we don't have any indication that there was finer powder generated so that the surface areas are higher than we think they are. This looks like the right kind of a number, and we don't have anything yet really to compare what you might call grains of unirradiated UO_2 with multi-grained particles of UO_2. But everything we've seen suggests that the grain boundaries in UO_2 is not very important, like it is in spent fuel.

We're basing that on saying that the rates for the UO_2 and the spent fuel look pretty comparable when we look at grains of fuel, where we have, we think, a good handle on the surface area, and the rates look comparable. We've looked at different--we have looked at this kind of UO_2 powder compared to the pellets and the single crystals-type material that was done at Livermore, and you get comparable numbers. So we think we have--we know the surface areas reasonably well.

DR. LANGMUIR: I think we need to go on. Walt, thanks very much.

We now have Steve Steward for questions, please.

Steve, while you're getting organized, a question for you. You mentioned that most of the radionuclides, 80 per cent of the releases came from dissolution of the matrix and maybe 20 per cent came from gap and grain boundaries. If one oxidizes the fuel and heats it and it breaks up, decrepitates, do those figures change? Are we then looking at much more releases, not congruent, perhaps, if the waste is hit by ground water?

DR. STEWARD: I hadn't really thought about that problem, but I would suspect that if the grain boundary or the fission products are trapped inside those grain boundaries and once the pellets start breaking up, they're going to be certainly available to any dissolution process that goes on. So they become more available than they were before the pellet broke up, sure.

DR. LANGMUIR: So what you're saying is radionuclide releases could be incongruent. That might be quite significant from a waste that had been broken up into fragments from heating.

DR. STEWARD: I think so. Do you disagree with that, Walt? If you get fragmentation of the pellets, you're going to get a lot more release.

DR. GRAY: Well, we showed some data on oxidized particles--I call them particles. They're about one millimeter in size--of spent fuel, and we did see incongruent dissolution, the difference between the cesium and the uranium, for example, was a factor of 2 or so. And, in addition, the difference between oxidized and unoxidized fuel was roughly a factor of 2. So there is some small increase in the incongruency, if you will, as a result of oxidation for that kind of--for U_4O_9 for that fuel. Now, what happens when you go all the way to U_3O_8, for example, when you totally fragment the thing and create a subgrain powder, we don't have any data on that yet, but that's something that would be of interest to study.

I guess when you form U_3O_8, the surface area is so big that you already have a big effect, and if you further impact it by releasing fission products at a much higher rate than you do the uranium, that would be a secondary effect. It's something that we need to look at, I guess.

DR. STEWARD: May I address the first question you had, I think, with Walt with regard to EQ3/6 and whether--I think there are two issues there that we've looked at at Livermore, and Bill Bourcier has helped us with this. He is a kind of a guru on operating EQ3/6.

The first thing we use the program for is when we calculate, when we make up these buffers for these various pH's and carbonate concentration, clearly, the carbonate concentration affects the pH, and so on. We use EQ3/6 at the different temperatures we want to make the runs to actually calculate what those buffer compositions should be. So we use it in that regard to do those calculations. And then, secondly, we have, oh, it's been within the last month, Bill and I, when we were looking at sort of what we were going to do in the future and what chemical species and what water chemistries, we took a run of sort of J-13 water compositions and calculated what uranium species would come out in solutions. And we've done that, and we've got a fairly long list of rather, as a chemist, I'm not used to all these geological terms for minerals, so we had a long list of these minerals to look at. We haven't done anything further with that yet, because of all the other pressures, but that's certainly something that we're doing.

DR. LANGMUIR: My key question has to do with the application of those models to your data for kinetics.

You stated this morning that you could not fit a simple kinetic model for dissolution, and my sense was that if you were to take the same lab data you have and put it in the code and speciate the system, you might find you could, once you know the complexes and the system involved in the kinetics process. It might make simple sense, and I'd sure feel better about it starting there than adding more uncertainties with additional variables to a large matrix of experiments if I knew the beginning and what I had going on fundamentally for the simple experiments to begin with, where you certainly have carbonate complexing and other things going on which you can define.

DR. STEWARD: Well, I think we can do that. I think Bill and I can look at that probably even further. Does EQ3/6 deal with complexes in solution as well as precipitates, too? So, you know, we can look at all those things.

DR. LANGMUIR: More questions from the Board?

Warner North.

DR. NORTH: I'd like to ask you some questions, really following up on Dr. Langmuir, relating to your second slide and your final slide. This is No. 2 and No. 13.

In No. 2, you talk about "previous data show greater than a million-fold variation in dissolution rate under various conditions," and then you have highlighted, "controls are needed." And then at the end you talk about the statistical experimental design and the 32 experiments in the various cells. Well, I come at this whole problem from the point of view of performance assessment and priority setting, as opposed to the details of the chemistry and the problems of doing a good experiment that you have to be so close to in order to do your work.

And it seems to me what we're really interested in doing is exploring why the large variation either has occurred in previous data, or might occur under some conditions that possibly might be present in the repository. So I'm very concerned about issues such as the formation of colloids, or the presence of complexing agents--and I'll use organics as an example--which perhaps might be present as a result of human activities within the repository as opposed to something that's present there naturally, and I ask the question: Are there some conceivable conditions that could give us much more rapid dissolution than the scenarios you've been exploring among your 32 experimental cases?

So I wonder if: one, you could comment on what I've just stated; and two, you could explain to me what plans you have for communicating with those that are doing performance assessment so as to set some priorities for your future experimental work?

DR. STEWARD: All right. I think first I would say the previous data, as I said, did spread over a fairly wide range. What we think went on there, in fact, was probably--I'd have to look at the individual reports rather than the summary report of Grambow. What I think probably went on there is just, again, the kind of thing we've been talking about, is the lack of control of surface areas. One of the things we tried to address in our studies was that very likely these samples had a fairly wide range of surface areas to start with, or either evolved during our experimentation that led to this large variation. I suspect the dissolution rate did not vary over that wide range simply because of differences in individual variables like oxygen concentration or species in the water chemistry.

Secondly, I think what we're trying to address in these studies right now is simply to come up with an intrinsic dissolution for the fuel itself, as well as the UO_2 under fairly controlled conditions, looking at what we would generally expect in somewhat of a pristine environment with J-13 water, and as I understand, I haven't been to the site, even the J-13 well, which is sort of the definitive water that we look at is fairly far removed from the mountain itself, because no one wants to drill in the mountain, so we're not even really certain, I suppose, whether that chemistry would represent what the chemistry would be if the water did come into the repository itself from other parts of the mountain. So that's certainly a question.

We haven't done anything directly with any of the people in the performance assessment to address the kinds of issues you bring up, like the results from human activity and the repository area or other issues beyond just the simple water chemistry that we know, but we're certainly not adverse to doing that, and Bill Halsey and his group at Livermore, we certainly talk to and see at lunch all the time, so we can do those things if it's the sense that those are issues that should be pursued, and we can use some of these techniques that I've talked about to look at those if we can come to some sensible agreement to what they are. Does that answer you at all? It doesn't come up with an answer. We just haven't looked at those broad range of things.

DR. NORTH: Well, I'll be putting this question to people later in this meeting who are doing the performance assessment, and ask if they've been talking to you. And I would hope that you do more than pleasantries over lunch.

DR. STEWARD: Well, maybe Ray can answer this.

DR. LANGMUIR: We've got to make it pretty short here. We're going to be rather far behind schedule.

DR. STOUT: I have just a few words.

I think when we started this series of tests, we wanted, as I thought I said, an aggressive water chemistry to see how fast we would get rid of these particles. And this is a kinetic forward solution without any precipitation. You know, there may be some surface effects when we go back to silicate waters and calcium waters. But this will be, we think, the fastest you're going to get it into the stream.

Now, the second stage would be the solubility limits, and also colloids to worry about that. But if you get it in the water, even with colloids, then there won't be any more than that in the water. So this is kind of a worst case experiment that we tried to address with this first set of--or test matrix to get at that problem.

DR. NORTH: Well, one way this might come out is that a relatively simple worst case calculation might be all you need. You don't need to go to a great deal of effort gathering more data for the purposes of this program. Maybe it's scientifically interesting and for some other reasons having to do with fuel rod performance and the like, it would be useful to go get this data, but for the purposes of assuring that the repository will perform acceptably, you don't need it. And if that's the answer, maybe it's disappointing in terms of your ability to run or to get the funding to do additional experiments, but I think it's very important that the program have a way of determining which data are critical and which data really are of lesser importance, scientifically interesting, perhaps, but not critical in terms of issues having to do with the repository design or whether the site is suitable.

And what I keep asking for--and I'm going to continue--is let's see the details of that priority setting so that we can be assured that something is happening that's a little bit more responsive to present information than taking study plans that were written five or more years ago and simply implementing them without any thought of what's being learned from these performance assessment exercises.

DR. LANGMUIR: I'm going to be unfair at this point and let Warner have the last word so we can start the afternoon session.

This session is concerned with some geochemical aspects of the source term. Following the potential failure of nuclear waste canisters, radionuclides may be released from spent fuel in defense waste glass to the near-field environment. This afternoon's presentations will consider glass dissolution, radionuclide thermodynamic data, and geochemical computer modeling. Then we will hear what plans the Department of Energy has for filling in the gaps in our knowledge.

John Bates, of Argonne National Laboratory, will start off by describing tests that have been conducted on simulated weathering of high-level nuclear waste glass. He will bring us up to date on his research on the formation and fate of colloids of the actinides.

John. You get your full 30 minutes, starting now.

DR. BATES: Well, before I start my formal presentation, I thought I'd ask a rhetorical question. That is, to confirm the subject of the talk, you'd like me to discuss source term information with regard to glass, which is a waste form that has not yet been produced, that will go in a waste package that has not yet been designed, that will go into a repository that has not yet been completely evaluated.

My response is, let me make sure you can read the caption, but it says: "What fools we mortals be." In reality, though, it's a very good question, because without information regarding the source term, regarding the source of radionuclides, myself, I don't see how you can do credible waste package design or realistic risk assessment. So it's a good question. It's not an easy question to answer.

So I'm going to talk about glass testing and colloid evaluations that we've done over the last two years. Since I made a presentation to the Board, we've done quite a lot of work, and I can only give you an overview. We'll start off with a background.

You've been to Savannah River, Hanford, and Idaho, so you know the waste producers have a problem. They've got high-level radioactive waste sludge in tanks. They'd like to get them out of those tanks into something more stable. So at Savannah River and West Valley, they're going to mix them with borosilicate gas frit, produce high-level waste glass, put it in a metal canister, and that will be the first step in the process. The second step in the process is geologic disposal. So what's the objective, then, of the work?

The objective is, in a joint testing and modeling program, to evaluate glass reaction under a range of conditions that can be used, in part, for design and risk assessment activities, but there are really two purposes. One is to support start-up of the vitrification facilities by demonstrating that we know a little bit about how glass is going to perform, and, hopefully, to provide information that will be useful to repository licensing.

Okay, now, what is the approach that we've used? Well, you heard Dave Stahl earlier on talk a little bit about the ASTM approach. I spent four years on this committee, together with some people from the NRC, the waste producers for the repository, putting together what is really a common sense approach to predicting long-term material performance. The first two boxes--they're very important boxes--are identify the materials and identify the credible conditions.

In the case of glass, we're going to have glasses of varying composition. That creates a problem. We've got glass from the Defense Waste Processing Facility, glass from West Valley, and as of right now, those glasses are still being refined. Those compositions are still undergoing changes. So we have to incorporate that into our program.

Then we have to deal with the credible conditions for the unsaturated environment at the Yucca Mountain site. That's where we're focusing, although from the standpoint of the waste producers, we want to look at a range of conditions because it isn't at all obvious that the Yucca Mountain site will be the site where the high-level waste is buried. So from a waste producer's standpoint, we want to know how glass is going to behave under a range of conditions. But for the Yucca Mountain site, we want to identify credible conditions. We believe it's unsaturated, and from a glass standpoint, we really have to re-think some of the basic premises that we've got in glass reaction models and mechanisms because we don't have very much water. And so, as I go through my talk, you will see what the ramifications of that are.

Okay, more with the approach. The ASTM approach requires the joint modeling and testing program. On the modeling side--and Bill Bourcier is going to say a little bit more about that--it has to be a mechanistically-based model because you can't do empirical extrapolation. And modeling and testing have to go hand-in-hand, because you learn from each as to how to interpret and proceed.

On the testing side, I've listed a variety of tests here that are necessary to get the information that you want to be able to predict the long-term performance in material.

You start off with, perhaps, response tests. Response tests are those types of tests that allow you to identify important parameters that affect the way the material reacts. You want to do accelerated tests so that you can be sure that the mechanisms that you're observing in your response tests are actually the mechanisms that are controlling the long-term reaction of the material. Very importantly, you have to do service condition tests. After all, you don't want to go through a lot of modeling, a lot of response tests, a lot of accelerated tests if you're not getting information that's relevant to the repository. And that might be, in part, an answer to Warner's question about the performance of fuel. You want to make sure that--and you want to do the same thing for glass--you want to make sure that you've got your response and accelerated tests done in a way that's going to be together with your service conditions.

Then if you do your accelerated and your service condition testing cleverly, they can turn into confirmation and validation tests, which are necessary to convince yourself that your model's going to work. In other words, if you can't do extrapolations, you have to have some way of judging whether your model is a valid model or not and you do that with longer term testing and comparison.

Okay. What are the conditions we are looking at for the unsaturated site? Well, the variability, indeed, does cause problems. We're looking at three conditions. One is humid air, the other is dripping water with intermittent flow, and the third is small amounts of standing water with very slow exchange. You might consider that as a static condition.

Now, very importantly--and I'll come back to this view graph several times--what you want to do in the ASTM approach is take a look at your materials, take a look at your conditions, and try to decide before you start what type of modes of reaction you're going to come up with or that you anticipate. And when you do that for glass, you can put together a plot that looks like this, where this is the amount that's reacted, versus the reaction progress, and you'll see that initially the glass reacts fairly rapidly, and I call that the initial stage.

It then goes into a stage where it slows down, and that makes sense because glass, after all, is made of silica. As you dissolve silica into the water, you start to concentrate the silica in the water, the affinity for the reaction is reduced, and you approach a steady state. However, once you start nucleating secondary phases, the affinity to react increases, and you'll see a final reaction rate which is going to be more rapid than the interim rate.

Now, you've listened to the waste producers, and they have described PCT tests and MCC-1 tests. Those are tests that are designed not to predict durability, but to show that the waste form is consistent. Those tests fall right down here during the initial stage of reaction. In order to get to the interim or the final stage, you need to do either long term and/or accelerated-type tests.

The type of information you get out of these are source term information which would include the reaction rate, depending on where you are on the curve, together with the radionuclide release and distribution information. It must be evaluated at each stage because under unsaturated conditions, you might be in any one of these stages.

Now let's take a look at some results. One of the things that we've done just recently is to go through a worldwide review of information available on glass. And we've put out a document called: "The High-Level Nuclear Waste Borosilicate Glass: A Compendium of Characteristics." This is undergoing formal review right now. It's going to be a considerable review process. I believe it'll be published in the spring, but what we're looking at is production, transportation, durability from a testing standpoint, modeling and analogues, and we're looking at natural, historical, commercial analogues. The use of analogues isn't to say, oh, look, glass has lasted well in the environment. In the case of historical and commercial analogues, where a historical analogue might be a stained glass window, and a commercial analogue might be a plate glass window, those types of glasses have been exposed to unsaturated conditions.

If we can look at how those glasses have reacted, come up with test methods that can reproduce the type of reaction that's occurred under those conditions, we have confidence that the test methods that we're using in our tests to evaluate high-level waste glasses have some validity. So that's one of the reasons for looking at analogues. At any rate, this compendium will be out in several months, hopefully.

Now, what I want to do is go through briefly the results for the three conditions that I described. Humid air, I described in detail the results a couple of years ago in my presentation, so I'm not going to go over that again. I'll just give you the highlights. Essentially, when you react glass and humid air, it's not a reaction between water vapor and glass. It's a reaction between a thin film of water that sorbs to the glass surface in the glass. The water becomes rapidly saturated with respect to glass components, and you form those secondary phases which allow you to get to the final reaction state on the graph that I showed previously.

Temperature, relative humidity, glass composition are important variables. Another important factor is as the reaction occurs, the glass ages, it reacts, such that when you eventually contact that glass with liquid water, it's not the same as contacting fresh glass or as-cast glass with liquid water. You're contacting aged glass with liquid water, and I'll show you later on what some of those results are.

Another interesting factor is that when the glass ages, it sorbs water onto the surface and it can sorb enough water such that you can actually get water dripping off of the glass, even though you don't have anything but a humid air environment.

And then finally, and I mentioned this, eventual contact of aged glass with water can provide additional source term input.

Now, very briefly, to show you pictorially what I just described in the previous view graph, here is a cross-section, a color-enhanced cross-section of a reacted piece of glass. These are the secondary phases that form on the surface in a thin film of water. This is the reacted glass and we've color-coded the radionuclides. And the important point here is that the radionuclides start off homogeneously dispersed throughout the glass, but now you can see that they have been sequestered into discrete phases that form on the surface of the glass, and within the reactive layer of the glass. This type of information is important from the standpoint of if you're doing risk assessment and you're looking at speciation, you're going to get different speciation and you're going to get different solubilities if it's glass that is in equilibrium with the solution, or whether it's the secondary phases that are in equilibrium with the solution.

We can go through and now tell you exactly which phases are contained in the radionuclides so that you can hopefully go back and do a better job with your thermodynamics and your calculations.

Okay. With regard to intermittent and dripping water, again, I have described these tests previously so I'm not going to go over those in great detail other than the fact we drip water on glass at a rate of about one drop every three and a half days, trying to generate what I consider one type of service condition test, and what we're looking at here is simply the glass in the canister. After all, from the waste package standpoint, that's all we know for sure that's going to be in there.

We've looked at as-cast glass, we've looked at aged glass, we've looked at actinide-doped glass, and we've looked at fully radioactive glass. When you were up at Hanford, you asked the question, has anybody done tests on fully radioactive glass. Well, the answer is yes. Savannah River did tests on fully radioactive glass in the early eighties. We took over the results that they had, decided that the tests hadn't gone for long enough and they weren't really very relevant to the Yucca Mountain environment, so for the last three years we've got a whole slew of tests going on with fully radioactive glass to provide confidence that the fully radioactive glass and simulated glasses are going to give you the same types of results.

We use varying flow rates. We use sensitized stainless steel, because the pour canister is likely to be sensitized. An important point is the tests have been ongoing for now eight years, and results of actinide release look something like this. This test is done on as-cast actinide-doped glass. It's a drip test. And what we see is over a five-year period--I've only got five years of data plotted here, but the next three years are continuing the trend. We see a fairly continuous release. I'd say there's really no evidence of the release slowing down as you would expect if you got to that interim portion or interim stage of reaction that I showed on the reaction progress plot.

Yes, we see some bumps and I can show you later on exactly why those bumps occur. These tests have been done in triplicate; pretty reasonable agreement between the results. The important point, though, here for these results is for the actinides that are in solution, we find that plutonium and Americium are actually suspended in solution. They're suspended in solution as colloidal or particulate material, and after five years they haven't settled out. In the case of neptunium, it's actually dissolved in solution.

Now, what if you do the same type of test on aged glass? And here we've got the results for fully radioactive glass made from sludge taken from Savannah River, and these are the results of drip tests. And in this column, I've got concentration in parts per million for as-cast glass, and in this column I've got concentrations for aged glass.

You see the as-cast glass concentrations are pretty benign. They look pretty much like drinking water. The aged glass concentrations look an awful lot like sea water. They've got 8,000 parts per million sulfate. If you look at the composition of the Savannah River glass, sulfur is not one of the elements that's even supposed to be in the glass, yet you've got 8,000 parts per million. What's the effect of that? The effect is that the actinides--Americium, plutonium, and curium--are no longer suspended in the solution as colloids. Even though the pH is 12, very basic, they should be very insoluble, they're not. They're quite soluble and they go through the smallest filter that we've been able to filter. So we have a real change in the way the actinides are released from the glass depending upon how we've treated the glass prior to contact with water.

Now, I wanted to show you for the drip tests on as-cast glass, why we're getting material actually suspended in solution. Well, it's very clear when you look at not only the solution, but you look at the glass. These are micrographs, TEM micrographs of reacted glass in cross-section, and what you see after 56 days is a reacted layer that looks fairly homogeneous, and it's attached to the glass. After 280 days, the reactor layer has changed significantly. It's now crystalline. Americium and plutonium remain in the reacted layer, but the striking thing is it's no longer attached to the glass; such that if you get wet/dry cycling, or get small intermittent flow, these layers are washed right off the glass and they're suspended in solution. So that corresponds very well with the results that I showed you for the as-cast glass; where the americium and plutonium are actually suspended in solution. They're suspended in solution because these layers are coming right off the glass.

Okay, the third scenario that we wanted to look at were static tests. Static tests are done essentially to represent a filled canister. They're done in a batch mode, which means for each time period we do a separate test, duplicate test, triplicate test. We use varying surface area to volume ratio. And this is a very important parameter for an unsaturated site. Surface area is the surface area of the glass. Volume is the volume of the liquid. And it ranges between 3040 and 20,000 inverse meters. To give you an idea, 3040 inverse meters would be four half nickels covered with two milliliters of water. 20,000 inverse meters is 5 grams of crushed glass covered with five milliliters of water.

In each case, there's plenty of water to go around and contact the glass. The 20,000 inverse meters is simply a higher surface area to volume because the glass is crushed. 90☜C groundwater from the site; long-term tests--and you'll see the importance of doing long-term tests in one of the upcoming view graphs--and do a full suite of analyses, including solution, colloids, and layers, so that we can get a complete picture of how the glass is reacting, so that we can feed that into Bill Bourcier's modeling, and also into any risk assessments that would be done.

Okay. On the next view graph, I've got the results from a set of static tests done at 20,000 inverse meters, high surface area to volume. A long period of time, go back to the initial view graph that I showed you of the three reaction stages, they're all here. What you see on this plot is a variety of elements ranging from boron down to sodium, lithium, uranium, silica, different components of the glass over a period of two years. And you can see for the first half a year, geez, not very much happens. But for the next period of time, you get a final reaction rate which appears to be fairly linear which is quite a bit more rapid than the interim rate that you see here.

If you blow up this portion of the curve, which is what I've done over here, you will see that, indeed, we do have the initial and the interim portion of the curve--here's the initial portion of the curve, here's the interim portion of the curve, and here is the final portion of the curve. So the three stages of reaction that I described in the reaction progress plot, indeed, is exactly what we see in the testing that we do. But we've got to do the tests for long periods of time and we have to use accelerated conditions, high surface area to volume ratios, to get there.

Now, the interesting thing is that the final rate can be greater than the forward rate, and within the envelope of glass compositions to be produced by Savannah River, we see final rates ranging from 0.04 to 1 gram per meter squared per day. Now 1 gram per meter squared per day are the units: grams per meter squared per day is a rather esoteric set of units. You may want to do a back of the envelope calculation, convert that into something more meaningful. I'd be glad to go over the results of your calculations with my calculations to show you how fast the glass is reacting.

Why is the glass reacting in the final rate the way it is? Well, essentially, as I described earlier, the solution is controlling the reaction. And when you get to a high pH, you start nucleating and precipitating a different set of secondary phases than you did during the initial and the interim part of the reaction. And here I've got plotted, or here I show another TEM micrograph in cross-section. If you look out here, you will see that the layer looks very much like it did in the drip tests. In the drip tests, that layer spalls off and reforms. In the static tests, once you get to the final reaction rate, the initial layer stays there, the glass reacts rapidly inward such that all of this area is now reacted glass.

We identify all the secondary phases. Interestingly, one of the phases we see is amorphous silica. That can help you understand why the final rate has increased. It decreases the concentration of silica in solution, such that the glass can now continue to react.

Okay, that gives you a quick overview of the type of information that we've been able to collect from the three types of scenarios that we've studied that we consider to be "in service" condition-type studies.

Let's take a look now, again, pretty briefly, at some work we've done over, again, the last two years to look at colloids. Again, to fully evaluate source term data, the distribution of radionuclides in solution has to be known. They can either be dissolved in solution or they can be in solution as colloidal material.

Just as a little bit of background, the types of colloids that can exist are radiocolloids, which are essentially hydrolysis products of actinide elements; pseudocolloids, which are actinide elements that have sorbed onto colloids that already exist; and something that we found, which I call primary colloids or real colloids, they come directly from the waste.

Now, in the case of a unsaturated repository, you would think since the solubility of Americium and plutonium is quite low in the groundwater, these types of colloids which are dependent upon the elements going into solution and then forming the colloids, may not be of primary concern. However, if you look at what happens to the waste, and recognize the fact that you're not going to have very much water present, the importance of primary colloids becomes a little more evident.

Okay, what were the objectives of what we were doing? Well, we first of all wanted to determine whether radionuclide colloids are formed or not. Can we look at the solutions that are generated in these tests and find any colloids? If we do, can we then characterize the colloidal material that we observed? We want to characterize it in terms of what is it, what's its radionuclide content, what is its electrical properties? Is it going to sorb back onto the glass or is it going to stay suspended in solution? And then, eventually, it's important to characterize the transport behavior. I would say in order to characterize transport behavior, you have somehow got to connect your waste form evaluations if your primary colloids are the important colloids, together with your transport studies so that you're looking at the transport of the right colloids.

Okay, what have we actually seen? Well, what we find in the case of glass is that the nature and size distribution of the actinide-bearing phases is dependent upon the glass, and it's dependent upon the test conditions. What I show you here are two micrographs, TEM images of colloids that have been trapped on substrates with holes in them. These are the holes in the substrate, and the dark specks are the colloids. And these colloids have formed by precipitating from solution. You can see that they're on the order of a tenth of a micron or smaller, little round things.

Over here, this colloid looks an awful lot like one of those reacted layers that I showed you in a previous view graph in cross-section. If you envision that reacted layer looking down from the surface, it looks exactly something like that and that's exactly what this is. It's a colloid that's been spalled off of the glass in one of the drip tests, collected on the substrate, and that's what it looks like. So we see different types of colloids forming, depending upon what the test conditions are, and also depending upon what the glass composition is.

Now, one of the things we want to look at is to be able to isolate and identify the actinide-bearing phases. So what we've done is develop a technique by which we can actually isolate individual colloidal particles, and I've got two of them here. Again, this is transmission electron microscopy. Here we've got a relatively large one, and if the contrast was as good as it could be, you would see that this is actually a rather light-appearing colloid. This is a smaller one, and it's quite dark, which simply means the darker it is, the heavier the elements, heavier the phases are that are in the colloid. We then took these exact particles and did alpha radiography on them, because we wanted to know did they contain actinide elements.

Well, indeed, colloid number two, which was the small one, contained a lot of actinide elements or gave a lot of alpha tracks. Colloid number one, which was the larger one, gave very few. We then went and, in detail, looked at the dark specks which make up this colloid and we were able to identify exactly what the actinide-bearing phase is. In this case, it's a calcium phosphate phase called brockite;

not too surprising. Calcium phosphate phases in nature are known to incorporate rare earths and actinide elements.

Where do the colloids come from that spall off of the glass? I showed you in cross-section previously. Here is what they look like forming face down on the surface of the glass. Here is the layer as it starts to spall off, and here is the layer after it's spalled off and is reformed. And so what actually happens is, as the glass reacts, the layer spalls off, forms the small colloids that are suspended in solution, the layer reforms, spalls off again, and so, if you recall the plot that I showed you, the five-year data plot that essentially looked like continuing increase of Americium, plutonium and neptunium, that's because the layer forms and reforms and continually spalls off and goes into solution and that's why you get that type of result.

Okay, for a summary of what we know with regard to colloids then, as the waste form reacts, it strongly influences the distribution of radionuclides in solution. It's possible, using the techniques we've developed, to identify what these colloid species are. We can give you the size distribution of the species. We can give you the radionuclide content. I think we can give you all the information you need to know to characterize the colloid.

What we found is primary colloids that come directly from the waste form are due to spallation of material from the waste form under service conditions. We can see concentrated Americium and plutonium phases. They remain suspended in solution. We also see in the batch tests--and I didn't have a chance to describe this, but we see pseudocolloids that form as the glass dissolves. The glass dissolution products nucleate on colloids that are already in existence in J-13 water. We see more colloids in J-13 water than we do in deionized water.

Distribution of solution depends on the ionic strength of the solution. Colloids aren't very stable when you have a high ionic strength solution, so what we see is a lot of colloids forming when the glass initially reacts; very few colloids remain in solution in a batch test after you get to the final reaction stage.

So that's a very brief summary of what we've been able to develop with regard to analysis of colloids and some of the colloids we've been able to observe.

Now, I want to make a few concluding remarks with regard to the presentation, and that is in terms of the reaction progress diagram. I keep going back to the diagram, but it's a very important diagram. Depending upon the conditions that you have in the repository, you can be anywhere on this plot. You tell me what the conditions are, and I can tell you pretty much where you're going to be. And if we've done the right tests, I can probably tell you the reaction rate and distribution of radionuclides to solution.

For humid air, we get to the final reaction state very rapidly, because based on what I said previously, you concentrate the solution and you form the secondary phases and the glass goes ahead and reacts.

Okay, that, then, is going to affect the subsequent radionuclide release. Subsequent radionuclide release from an aged glass is going to be way over here in the initial stage.

When we do intermittent contact, we get constant release of Americium and plutonium suspended in solution when we do as-cast glass, and I would say that that puts us somewhere right around in here. We haven't gotten to the interim stage of reaction where the silica concentration is saturating and slowing down the reaction because what we're forming are these layers that continually spall off the glass. So in that case, we're somewhere right around here.

Now, in the case of when we do these tests with aged glass, the radionuclides are actually dissolved in solution. So we're seeing two types of behavior of radionuclides in the same test depending upon the condition of the glass.

And then, finally, for the static tests, you end up with a final reaction rate, if you do the tests for a long enough period of time; in other words, you've got to do extended tests. The key here, though, is that the actinide elements are going to be retained in the glass either because, as I showed you, as the reaction occurs the glass reacts from outward, inward, the actinides don't have a chance to get out; and those that do get out tend to form colloidal species which don't remain suspended in solution.

Okay. So this is a quick overview of the testing we've been able to do with regard to glass. Bill Bourcier in the next talk is going to give you the complimentary information with regard to how do we fit this information together into a modeling approach.

DR. LANGMUIR: Thank you, John.

We're a little bit over the 30 minutes, so if we may, let's hold questions and go right on to Bill Bourcier and his modeling of glass dissolution.

MR. BOURCIER: Thank you.

Two years ago, we presented an overview of the status of the glass modeling task. Today, I'd like to report mainly and dwell on work we've done in the last two years to enhance and update that model, but I thought I should start in this talk by giving you a brief overview in three or four view graphs of the status of the task two years ago and briefly outline what that model is, how it's incorporated in EQ3/6, and exactly what it is so you have a framework to think about in the rest of this talk.

Basically, in that presentation two years ago, we showed how the glass dissolution rate is primarily controlled by solution composition, the so-called affinity effect, as glass is dissolved and released components in solution, these components built up in concentration. The primary control and the rate that glass dissolves in a repository or anywhere else is how concentrated that solution is. The more concentrated it is in glass components, the slower the rate at which glass dissolves.

This contrasts with other models of dissolution rates in glasses which called on some sort of diffusion or transport control. It's sort of the general consensus of people internationally working on glass waste form testing and modeling that is this affinity effect/solution chemical control that limits the rate of glass dissolution. So knowing that, we've incorporated a simple mathematical model of that process into EQ3/6, and at that time I showed you how that model could be applied to experiments of glass waste form dissolution.

We showed at that time that the glass itself was not the thermodynamic material that controlled the long-term dissolution rate. It was some other more stable phase, probably an alteration layer that formed on the glass surface, and we presented data to support that conclusion. And finally, we pointed out the need for an experimental program to provide model parameters independent of the site-specific tests that we used to regress model parameters for in our model results.

So over the last two years, we've undertaken a program to do those experiments, to provide parameters for our model, and also to do more modeling of experimental results. Conceptually, this glass dissolution model that we have incorporated in EQ3/6 has three components to it, three mechanisms that take place simultaneously and are coupled during the glass dissolution process.

The first essentially is an ion exchange process; whereas, when you put glass into water, ions in solution go into the glass and extract alkalis from the glass. This causes the pH of the solution in contact with the glass to rise. You form these alteration layers as a consequence of the depletion of the glass surface, and you have, basically, as a simultaneous process, bulk dissolution of the glass; the glass components going into the solution.

And finally, when those components in solution, like silica, released alumina, iron, other components build up in concentration in the solution, they re-precipitate at secondary phases. So you have these three processes: ion exchange, bulk glass dissolution, precipitation of secondary phases that are all accounted for in the EQ3/6 model we use to simulate the glass performance.

There are additional processes we need to incorporate, in the future, but these are the main ones that control the release of components of the glass, such as actinides into solution, and also, the rate at which glass dissolves.

In mathematical terms, the rate of glass dissolution, this is a rate expression that comes from the field of irreversible thermodynamics. Basically, the rate of dissolution of a glass when it's affinity-controlled is proportional to the surface area of the glass; a rate constant, which is a function of temperature and pH and other solution parameters, concentrations of different dissolved species in solution; and the so-called affinity term, which accounts for the fact that as glass approaches some sort of saturation in solution, the rate of dissolution slows down.

The affinity term itself has this form of (1-(Q/K), and to get back to one of Warner North's questions about doing these flow-through tests to get at absolute maximum possible dissolution rates of glass, according to this theory based on thermodynamics, under the conditions where Q, which is the concentration of dissolved species in solution are very low, this affinity term in the rate equation has a value of about one; and, therefore, the rate we measure when the affinity term is about one, which is the case in these flow-through tests, we have what we think is a maximum possible rate of dissolution of this solid. This applies to glasses, to UO_2, to spent fuel and any other solid that behaves according to this rate equation.

One of the consequences--and I want to kind of take a brief digression right now and refer back to something John Bates discussed--is that if a glass, in fact, dissolves at a rate that is affected by the concentrations of dissolved species, what happens in long time frames in a repository when you have different types of secondary phases forming that sequester glass components, such as silica and iron, and precipitate them out of solution? And what I present here is a simulation of a SRL-165 glass dissolving. The Y axis, which is boron, and the fluid in parts per million is simply an indicator of how fast the glass is reacting.

What I've done is perform the simulation for this glass reacting, but at the same time, incorporated into the model what's called the Ostwald ripening sequence; whereas, we start with--I should say in background to this, when you do a glass dissolution experiment, you tend to form secondary phases. But what you see in experiments are usually metastable, thermodynamically unstable phases that with time transform into thermodynamically more stable phases. As consequence of this, because the more stable phases are less soluble, this tends to reduce the concentrations of dissolved species.

So in the simulation, I've incorporated both our model of glass, ion exchange, reaction kinetics, and secondary phase precipitation, along with allowing the secondary phases to age and become more stable with time. So, I don't know if you remember John's view graph where he showed an initial fast rate slowing down with time, this is due to the affinity effect. But now, because these phases are transforming into more stable thermodynamic counterparts and pushing down silica concentration, the rate takes off and gets faster with time. This has obvious implications for repository performance. Ordinarily, we don't see this part of the reaction path, we only see the initial fast rate and the slowdown due to this affinity effect. So it's something we have to watch out for, something that our model results told us, and something that was possible to see in experiments and, in fact, we've seen it and they're pursuing it at the experimental program at Argonne.

So what are the important problems and limitations of our current modeling approach? The most important one is the first bullet on this view graph. It's that in essentially all the modeling done to date by ourselves, and people in other countries, when we apply a model to a glass dissolution experiment we use the results of the experiment to regress model parameters. So what that tells us, basically, is not that the model is correct, but it is consistent with the experimental results.

People do this sort of modeling and the fact that the model can predict the experimental results, but based on a regression of the experimental results does not necessarily diagnostically indicate that that mechanism is correct, and to show you an example of this, how this is a bad assumption, is that if we look at experimental data from, again, for Savannah River 165 glass, these data points are concentrations of silica as a function of time as this glass is dissolving in J-13 water, and we have fit to this data two completely different mechanistic models.

The first is where the rate of dissolution of the glass is controlled by diffusion of ions through an alteration layer of the glass, and this is given by the dotted curve on this diagram. And the other model, a totally different mechanism is the affinity-controlled dissolution rate model, and that is the solid line on this curve. We see that both models successfully fit the experimental data in a condition where we actual use the experimental data to regress model parameters.

So that, in and of itself, if you propose a model and fit experimental data with it, it supports and it's a good first step in indicating that that model is correct or validating that model, but it is not in itself indicating that the model is correct.

So what we basically need to do to get around that problem is to come up with a mechanistic model, perform experiments independent of the experiments we use to so-called validate the model, determine the values of the parameters in the model independent of these experiments, and then, from first principles, apply the models to the experimental results and hopefully predict accurately the release rate of glass components into solution.

Some other limitations currently that need to be taken into account in our modeling, is that, first of all, we don't have in our models accounting--experiments done in the last few years, that, if you dope the solution with various components, such as iron or calcium or magnesium, they can affect the glass dissolution rate, presumably due to a surface chemical effect. We haven't yet incorporated that sort of knowledge into our models. We haven't either qualitatively or quantitatively done that. We don't currently exclusively account for glass composition in the models, and at this point, we do not account for glass water interface surface chemistry, which we know from workers in other fields, is very important in understanding mineral dissolution kinetics.

So over the last two years, we have undertaken an experimental program to try to provide these parameters independent of our experimental test results. These are experiments designed specifically to get parameters for our dissolution model, not to simulate repository performance. And what we've done in the last two years is essentially a matrix of flow-through tests, flow-through tests that are very similar in nature to what you saw this morning presented for spent fuel and UO_2 dissolution tests, where we take a glass and flow a solution by it with some composition, at some fixed pH, and measure the steady state dissolution rates of the glass.

These are our so-called most rapid glass dissolution rates, and we do these tests at varied temperatures and pH's, and as a result of those, we get information such as this, where now for SRL-165 glass, we have--they didn't put the axes on this diagram. Let's see, the z axis essentially is the rate of dissolution of the glass. This axis is pH; this axis is temperature. So with increasing temperature, the rate increases. At neutral pH's, the rate is slowest. It increases at both lower pH's and higher pH's, and we fit a mathematical function to the surface and put it in the EQ3/6 code, and when you do reaction path calculations, when you're doing, for example, performance assessment calculations or something where the temperature is changing and the pH is changing, the code knows exactly what that intrinsic rate of dissolution is as a function of those parameters. So that provides us now with parameters in our model that are not a function of them being fit to experimental data, but are derived from experiments independent of the experimental data.

Just one point I want to make before I move on to some applications of EQ3/6 to doing modeling of glass dissolution experiments, is something we found in doing these matrix of tests. As you know, real radioactive waste glasses are very complex solids. There may be 20 or 25 components in them. If you want to do an experimental investigation of the effects of glass composition on durability, you've got 20 or 25 parameters to vary. We thought, based on our understanding of glass structure, acquired mainly through nuclear magnetic resonance studies of glasses, that we can make simple analogs of these real waste glasses that have the same structure, same type of structure and bonding as the real waste glasses, but with a reduced number of components.

So we did this. For example, for an SRL-165 glass, we wanted to come up with an analogue and, say, put sodium in that simple glass in the same proportion as all the old fractions, a summation of all those fractions of ions that structurally are identical with sodium in a real waste glass, but form non-ridging oxygen sites or a charge compensation that--where aluminum substitutes for silica in the glass. So we did this. We made a simple analogue of all the waste glasses in terms of just sodium, calcium, aluminum, silica and then boron in the same amount that's in the real waste glass, and looked at and compared the performance of these glasses versus real waste glasses in our flow-through tests. And this is a result of one of those comparisons where we look at log dissolution rate versus pH. This is at 70☜C. The CSG glass is a simple analogue glass of the SRL-165 glass. The filled in circles and triangles are results from experiments using the real uranium SRL-165 glass.

Essentially, we see very similar behavior between the glasses. This is to give an idea of how good the reproducibility of the experiment is. These were experiments done when we changed laboratories from one building to another to see if we could reproduce the original set of data. We see basically good agreement between the two, the same pH at the minimum dissolution rate.

So this allows us now to do a lot of work using simple glasses with a fewer number of components to get at these fundamental questions of glass durability versus composition where we now only have to vary five components in our matrix of tests designed to look at the effects of glass composition.

So instead of having 20 to 25 components, where it would be physically impossible or intrinsically impossible to do all the tests necessary to get down to the data you need, you need to only vary five and you would only be limited by your current funding level.

I have to present here two examples of using the EQ3/6 code to model glass dissolution behavior. The first is an application to look at the effects of surface area to volume times time scaling on glass dissolution rates. This is an area--people have tried to find out ways, discover ways to accelerate test results so that we can look supposedly at experiments that would faithfully mimic long-term behavior, but do it in a matter of a few years in the laboratory.

I wanted to look at an analysis of this with the EQ3/6 code to see just how good an assumption that is; and second of all, look at some experiments designed to get at the nature of this affinity control on glass dissolution rates, which is, again, the rate that limits overall glass dissolution rates in the long term.

Basically, it's been proposed that if you look at glass dissolution tests at a variety of surface area to volume ratios, given our knowledge that glass dissolution rates are proportional to surface area and that the glass dissolution rate is limited by this affinity term, it follows from a simple conceptual model of that process that if you take experiments and scale them according to surface area over volume times time, all these experiments should fall on a single plot when they're scaled this way. And, in fact, for some experimental data, this seems to be true; in others, it's not true. So what can modeling tell us about this problem? Should it be true, or is it not true, or what's the deal here?

So what we've done is simulated some experiments using our model now that incorporates ion exchange and precipitation kinetics and secondary phases and all that, over a range of surface area to volume ratios and looked at the results when these models were done and normalized to surface area to volume over time.

But first, look at some experimental data we want to do in the simulations. This was collected by Bill Ebert and co-workers at Argonne, which shows essentially the rate of dissolution in terms of log boron released from the glass. Boron is a glass constituent that doesn't get incorporated in the secondary phases, so it's a good indicator of overall release rates, and the experimental data scaled over surface area of volume times time for three different SA/V ratios. And we see, first of all, that it doesn't scale according to surface area or volume times time. If that were the case, all the data would fall along a single line or curve.

In fact, at some point in SA/V times time scale, we see that different SA/V experimental data fall on different parts of the curve.

What is the reason for this? These experiments were done for SRL-131 glass. We've got great data for that glass now from our tests that I described a moment ago. Let's plug all that into the model and see what kind of results we get. So again, we are accounting for ion exchange, for bulk glass dissolution, and formation of secondary phases. So these are rigorous calculations.

Again, the data is plotted, but in this time we have three curves generated. These are a result of EQ3/6 simulations of these experiments.

These simulations show that, in fact, you don't expect to see SA/V times T scaling when these three processes operate during glass dissolution kinetics. That's the first point I want to make.

The reason for this is basically because when you first put a glass into water it undergoes this ion exchange process. This affects the pH of the solution in which the glass is in contact. Although the amount of ion exchange is proportional to the surface area, it is not proportional to time. So, essentially, what you're doing when you do test at different SA/V ratios, is starting out at different pH's, so you have different trajectories and reaction path space that give rise to this fact that at higher surface SA/V ratios, the glasses, because of ion exchange go to higher pH's, and because, as you saw on the previous diagram, the rate of glass dissolution increases with pH, and the in the outcome regime you get scaling where the higher SA/V tests dissolve at faster rates than the low ones.

At very low SA/V ratios, you'll see a curve here for one inverse meter and 10 inverse meters. Because there is so little glass surface area, the pH effect isn't large, you do get good scaling in that regime.

In this regime, of course, you don't. And then, eventually, when the amount of mass transferred in the process of this ion exchange zone on the glass surface is small relative to the amount of glass dissolved, whether it's high surface area tests or long time durations, the curves once again come together. So you have this regime in the middle where the SA/V ratio does make an effect on your reaction path; whereas, at low values of SA/V times t and very high, the curves come together.

So what's important here is if you want to use the high SA/V test to get at--to use it as an acceleration phenomena, there are essentially two things you can do. One, it might be a good idea to put the glass in some solution for a few days and then take them out, discard that solution and put fresh solution in, so you'd start all the tests at the same pH and avoid that pH effect of the initial ion exchange.

And another thing to remember is if you do use high SA/V tests to try to get at repository performance, you have to account for this early pH effect due to this ion exchange effect. So you need to be aware of it, and need to take it into account. It doesn't preclude the use of these high SA/V tests to accelerate reaction rates, but you just need to be aware of what it is a consequence of.

That's just a view graph to summarize what I just said. Okay, the second example is an example of using a glass dissolution test we did for the specific purpose of trying to get at this affinity term in the rate equation. I don't think I mentioned it when I first showed this view graph, is that the affinity term has this form of 1-(Q/K), where, again, Q is the concentration product of dissolved species. K is an equilibrium constant for the dissolving solid which controls the rate of dissolution, and M and N are exponents that must be determined experimentally.

The kinetic theory that gives us this sort of affinity relationship is not so well developed that we know from theoretical insight what these values should be. In fact, in most cases, we assume they're equal to one. But the idea here is to do experiments, that show us how the rate of glass dissolution slows as species build up in solution and regress from that data, essentially better define this term, what is the value of K for the dissolving solid; what are the values of M and N; essentially get at that term, because we don't have a theoretical way to do that. And, of course, even if we did, we wouldn't trust it.

So what we want to do with this model simulation is what is the functional form of the affinity term and what is the solid controlling dissolution rate? If you remember two years ago, we showed that it was not glass controlling the glass dissolution rates. It was probably the surface alteration layer. Glass is too thermodynamically unstable to do that. So we both want to find out what is the form of the equation and what is the solid controlling the dissolution rate.

We want to do some well-characterized experiments on a simple glass, and then perform simulations where we try different approaches to finding out what the form of this equation is and what solid is actually controlling the rate.

The data we used to do this we obtained from, again, from our simple analogue of SRL-165 glass. And using this analogue glass, we don't have problems with redox, any sort of redox kinetics. All the components of this simple glass are redox independent. We don't have the problems with formation of protective layers that we might have with a real SRL glass. It's better, more better-behaved data in order to try to regress these parameters from, which we still think we can relate back to the actual waste glass based on our flow-through test results.

So what I show here are normalized concentrations of releases of ions from the glass versus time for silica, boron, aluminum, and calcium, normalized. By normalized, I mean they are normalized to their concentrations in the glass. So if glass dissolution were completely stoichiometric or congruent, all these curves would form, all these elemental release data would fall under one curve. Essentially, in the area of our analyses, these three do. Essentially, silica, boron, and aluminum relate pretty close to the same rate.

When we do an EQ6 simulation of this experiment, we find at about this point in reaction progress, calcium, the two phases become super-saturated, calcite and a calcium-enriched clinoptilolite zeolite. So it's probably very likely that we're just seeing a drop-off in calcium due to precipitation of a secondary phase, either calcite or clinoptilolite, but there's such a small amount of it precipitated we haven't identified it in x-raying the samples.

Okay, now what we want to do with this data is that the rate of dissolution starts out fast and slows down with time. We just pull the silica data off this view graph. Since this is concentration of silica over time, essentially, the slope along this curve gives you the rate of glass dissolution as a function of time. So we take the derivative of this curve and get this curve. So if you remember from the rate equation, the rate of dissolution is proportional to the surface area, which is constant here, the rate constant, which is changing a little bit because of the change in pH but not too much in this duration, and that affinity term. So essentially we have two constants during the duration of this experiment times the affinity term.

So basically, what this curve is, is the affinity term in the rate equation. And that's what we want information on, and that's is how we're going to use--that's what we're trying to do here is get information on what kind of solid is dissolving and the buildup of solution species gives rise to this curve in this view graph. So what we can do with EQ6 now is do a bunch of different simulations, assuming different values for M and N and the affinity term in the rate equation, different solids controlling the rate of dissolution of the glass.

So, as we've said before, the most likely candidate is this layer that forms on the glass surface, this hydrated gel layer. So what we've started out, here again is our measured data with circles indicating the data points. The surface layer of the glass, once the calcium is depleted from it, and the boron as well, is essentially a silica and aluminum-enriched layer. So let's approximate the thermodynamic properties of that hydrated layer as a solid solution of cristobalite, which is a silica oxide, and gibbsite, which is aluminum oxide. So as a first guess, let's say maybe it is the surface layer controlling the rate. If we do that, we get this dotted curve. In other words, if we use this phase to control the solution, the affinity to dissolve, assume M and N in this case are both equal to one, we get this curve, which does not reproduce our experimental curve. We need something that's steeper, a steeper curve in this region and gets a lower value.

So I'll skip the middle one and get back to the final one that best fits for this reduced set of simulation results.

If we assume that it's a cristobalite plus gibbsite solid solution, use those thermodynamic properties to calculate the K in the affinity term--and Q is, of course, the silica and aluminum concentrations--we get this dashed curve.

So essentially, in order to mimic the behavior of the slow down dissolution rate of the glass, we need to call on this thermodynamic model where the thermodynamic properties of the surface layer, which we're assuming controls dissolution rate, can be approximated as a solid solution of cristobalite and gibbsite, where the end value in that rate equation then is about two.

So this serves as kind of an ad hoc model. It fits this data. Will it fit other data? And that's sort of the status of what we are investigating, this phenomenon. We need to do other tests where the surface layers have different compositions, apply the same sort of model analysis to those results, and see if this does fit a wide variety of glass compositions determined in glass dissolution experiments.

Of course, this is really critical for determining long-term glass performance because it is this near saturation of the glass that slows down this rate. This is likely to be the condition of a repository, where glass is bathed with water in some sort of bathtub scenario, glass starts to dissolve, things build up in solution, and the glass dissolution rate slows down as a consequence of that. How close we are to glass saturation determines the glass dissolution rate. So we really need--this is a very critical part of the model to predict long-term glass waste form performance. And that's--we've got some experiments underway right now to try to investigate whether this sort of ad hoc model at this point will fit other sets of glass dissolution experimental results.

I guess I forgot to make this point. Basically, if you use bulk glass, anhydrous, and you estimate the thermodynamic properties of glass with any variety of methods from actual calorimetric analyses of glass thermodynamic properties to the hydration theory that's been used to estimate glass thermodynamic properties, et cetera, you find that you do not build up species in solution to the--because glass is so unstable, you never approach saturation with glass. Glass itself cannot be the solid that's controlling its own dissolution rate if this idea of affinity control is correct. The glass dissolution rate is consistent with these surface layers that have thermodynamic properties, in the right ball park for slowing down the rate of dissolution, and then we need to do more tests to evaluate our current model.

Okay. In conclusion, basically, we feel we're at a state where we have a mechanistic understanding of how glass dissolves, but have not yet quantified critical parts of it. I mentioned a few of those. Our glass dissolution model, I didn't mention this, is generic. It's not specific to the Yucca Mountain site. What we have here is a model that if you give it a solution composition, it returns to you the rate at which the glass is dissolving for those conditions. So this is a model that can easily be coupled with other mechanistically-based repository performance models, such as those for metal barriers or for manmade materials or minerals present, rocks and minerals present at the waste site.

Glass dissolves, it affects the solution chemistry, as do other species interacting with the glass. For any sort of scenario, we're trying to build a model that would stand on its own and say, you give me the pH, the temperature, and the solution composition, this model will return to you the rate that glass is dissolving for those circumstances. So it's designed to be interfaced to other mechanistic models for other submodels for repository materials.

And, of course, in our understanding of glass, we work hand-in-hand with the people at Livermore and other places doing spent fuel and UO_2 dissolution kinetics. This whole field of understanding what controls mineral dissolution rates is a very active one, a very contentious one among geochemists and chemists right now working on these problems, and that everything we learn from doing glass work is applicable to spent fuel and vice versa, and other repository material. So there's still a lot to be learned, but we're making some progress, and that's the status.

Thank you.

DR. LANGMUIR: Thank you, Bill.

Don Langmuir; question to start. I'll try and make you to think generically about Yucca Mountain, not generically, but about Yucca Mountain. You're going to be looking presumably at water in tuff. There are glasses there. There is cristobalite there. They will probably be near saturation or at, especially at elevated temperatures. Does that slow down the dissolution and release of radionuclides from spent fuel glass?

MR. BOURCIER: Yes, it does. Well, other--

DR. LANGMUIR: Have you modeled that? Have you tried to shoot at that one in terms of putting the data in EQ3/6 and seeing what its effect is on the rates?

MR. BOURCIER: One thing I didn't mention, we've done tests where we've doped the composition of these buffer solutions in the flow-through tests with silica and looked at the decreasing rate as a consequence of that. I don't think we're at a point with the model that we can accurately predict those things. Qualitatively, we know it's going to decrease the rate. There's been experiments done at PNL, Battelle, that show the effect of silica, but that's something we'd like to apply the model towards, but haven't yet.

But it will, based on our experimental data that we have, it will drastically slow down the rate versus the rates we see in the flow-through tests, when we've got 40 to 50 ppm Si in the solution.

DR. LANGMUIR: We have time for maybe one more question. Someone from the Board? Dennis Price?

DR. PRICE: Can I ask Dr. Bates, do we know, or do you know with a reasonable--

DR. McKETTA: What's your name?

DR. PRICE: Pardon?

DR. McKETTA: What's your name?

DR. PRICE: Dennis Price, Board.

DR. McKETTA: Thank you.

DR. PRICE: That was Mr. McKetta who asked what's my name.

(Laughter.)

DR. PRICE: Do you know with a reasonable degree of certainty that the J-13 water is representative of the water at the repository at the waste package?

DR. BATES: Livermore did an extensive survey of well waters from the repository site, around the repository site, around the test site. The conclusion of that evaluation was that, and somebody else may be able to correct me, but the J-13 water was very typical of water from that region. So is J-13 water representative of what will be contacting the waste after it's gone through the waste package? I don't know what the waste package is, so I can't answer that question. Is J-13 water representative of water that's found in the Nevada Test Site area? I think it is. Isn't that the conclusion of the report?

DR. LANGMUIR: No, it's not. It's not what you're finding in the unsat zone at all. Yang's work shows that that's several times as concentrated in most constituents as you find in J-13, which is not representative of what's likely to be at the repository.

DR. BATES: Right, the report I was referring to was looking at--

MR. GERTZ: It's representative of saturated zones. The question is, what is the water tied up in the matrix or wherever at the repository level.

DR. PRICE: So if it is not representative or if you do not have that reasonable degree of certainty, what does that say about the generality of your presentation to the Yucca Mountain history?

DR. BATES: Well, I believe that the conditions and the results that I showed, I only showed results for J-13 water. We've done tests in deionized water which don't have any silica in there to begin with, and we've done tests with higher concentrations of silica in the water. And the general trend and the stages that I described are going to occur regardless of what the starting concentration of the water is. The displacement of where they may occur could exist, but the fact that the three-stage approach is going to describe glass reaction, I think, is universal.

DR. LANGMUIR: We need to go on.

Our third speaker is Cynthia Palmer, also of Livermore. She will report on the current status and future plans for the thermodynamic data base used in source term calculations.

DR. PALMER: Good afternoon.

As was indicated, I'm going to talk this afternoon about the status of the thermodynamic data base, specifically with respect to the actinides.

Robert Silva is the task leader in this area and due to his extended illness, I am here on his behalf, but he sends his regards.

The objective of this project is to be able to model released nuclides in groundwater under proposed repository conditions; that is to say, we'd like to be able to evaluate the speciation, which is an indicator of migration fate, and the solubility, which is an upper bound of the bulk solution concentration of, in this case; plutonium, americium, neptunium, or uranium under proposed groundwater conditions.

Today I'm going to describe a three-phase process that we are undertaking to get us to that point; that is, first I will discuss data review and data evaluation phases at 25☜C, and then discuss what we'd do to get to repository conditions.

First, I found it useful to review the difference between solubility and speciation. The upper expression here is an expression for the solubility of this uranium species in acid solution. This thermodynamic value expresses how much of this uranium is soluble under those conditions; that is, how much uranium will be in solution, not what is the oxidation state of the uranium, or with what anions is it combined.

Those types of questions can be answered by these expressions on the lower half of the page, which describe specific speciation issues with regard to that uranium species. The equilibrium constants for all of these expressions are tied up in this value. If you want to understand what is the speciation of the uranium in solution, and have some indicator of its migration fate, you need to understand the thermodynamic values for each of these expressions. You would have to solve all of these expressions simultaneously with this data to get that information if you do not make the experimental measurements separately.

That is further exacerbated in the presence of other anions. For example, here I show it with carbonate, where you'd have a series of uranium carbonate species also competing for uranium in solution and able to bind it as well.

Here I show a prioritized list of the waste nuclides that we're proposing to study as a function here of curie limits and the NRC and the EPA release limits.

Today, as I mentioned, I'm going to focus on Americium, plutonium, neptunium, and uranium. Of these, based on the per cent in the inventory, we expect that Americium and plutonium will be the most significant players.

The studies I'm going to discuss will focus on the complexation of those four actinides with anions found in J-13 well water. Those are hydroxides, carbonates, silicates, fluorides, sulfates, phosphates, chlorides, and nitrates. As a function of these important parameters, as are present in most thermodynamic studies, pH, Eh, temperature, ionic strength, and the composition of the water; that is to say, the anion concentration.

We've taken an integrated approach in our data evaluation and data determination teams, working side-by-side rather than in parallel. The data evaluation portion of this task is what I'm describing today, and we work in concert with the Nuclear Energy Agency's international collaborative effort of critical reviews of thermodynamic data.

They have recently released their critical review of uranium thermodynamic data. The americium one is expected sometime in 1993, and the neptunium and the plutonium reviews will follow shortly thereafter. Several of the data that I will report later were, in fact, measured by our data determination group.

After these have worked in parallel to develop what we can feel to be an internally consistent thermodynamic data base, we will then be able to model the waste nuclide behavior in groundwater and validate our model by performing certain experiments which I'll be able to show you later on.

The first phase of the project which I'm going to describe really answers, "what do we know now?" We started with reviewing the available literature and we used, as a start, the NEA data compilations which were available to us.

To bound the first phase of this project, we're going to look at only speciation, not solubility, start only with 25°C, looking at only J-13 groundwater anions, americium, plutonium, neptunium and uranium, as I described in the oxidation states, +3, +4, +5, and +6.

As I mentioned, we used the NEA data compilations as a starting point. We went through their compilations, we verified the experimental conditions for each of the experiments they described against the original literature whenever possible.

We omitted any thermodynamic data that was based on estimates only, and kept only, in fact, data that had been actually determined. And without further interpretation, we took the uranium data base provided by the Nuclear Energy Agency in its entirety, without editing.

Based on the report and the site characterization plan, we felt confident in using these concentrations of the anions in J-13 well water, and we feel confident in bounding the actinide concentration in these studies at 10^{-5} molar, which is about the solubility limit of actinides in near neutral water solutions.

So what we end up with is a tabulation for each oxidation state of each metal for each anion as a function of the number of ligands. What is shown in the box under each intersection are the formation constants for that complex.

And, in fact, some of those values represent an ensemble average of multiple independent experimental determinations of those values. And, as I mentioned--it's not shown on this particular one--the Plutonium-5 carbonate and the hydrolysis numbers were numbers that were measured in our laboratory as part of our data determination task with our photoacoustic spectrometer.

You also have in your packets that for the +4. I won't go over it, but we have a table for +4, +5, +6, and some for multi-metal nuclear species.

So what are our conclusions after collecting all that data? We think that we're in relatively good shape for solution species, with the exceptions of silicates for which there is virtually no thermodynamic data that has been experimentally determined in the literature. There is slightly more for the phosphates and we can see, to proceed, that we'll need more data in those areas.

If we were to have considered solubilities and made the same type of matrix for solubility data, we'd see that we'd be in much worse shape than we are for speciation data.

Experimental efforts continue in the United States and internationally on both of these fronts in solubility and speciation data, so more data we expect to be forthcoming, and as I said, the NEA Critical Reviews are in process. They are very helpful to this end. However, they are not guaranteed to be complete, although they are guaranteed to be internally consistent. What that means is if there are species that they cannot, in their minds, justify or understand from the literature presentation of the experiment, or if there's only estimated data for those thermodynamic functions, those species may not be included in the NEA review. That doesn't mean that they don't exist.

The second phase of this work was to answer questions, such as, "how sensitive is the speciation of these waste actinides in groundwater to the thermodynamic constants?" such as "--and the anion concentration?" Also, how well do we need to know these thermodynamic values or is just merely an upper or a lower bound "okay" to satisfy our objective of being able to model their behavior? And finally, what are the most important species, and do we--are we confident of the data that we have for those species?

So what we did is take the data base that we had so far and evaluate it with respect to internal consistency with respect to ionic charge and ionic radius. And then we estimated data that was missing using the same criteria. So we have now generated our own, what we consider to be complete internally consistent, thermodynamic data base which we are going to test.

Here's a copy of what we now have in our data base for +3 oxidation state of americium, plutonium, neptunium and uranium with these groundwater anions. And as you can see, that we now have a much more completely filled in table than previously.

Now how are we going to test this data base to see if it has any merit? What we did was take this as our input to EQ3/6. We set the ingoing anion concentration or that of the J-13 groundwater and sequentially stepped it over several orders of magnitude in concentration. We fixed the Eh of the solution and the redox values to those that are currently in EQ3/6. We calculated the speciation for each of these metal ions in solution at 4 pH's. That affords us our variation in hydroxide concentration.

The result is a series of plots for each metal with each anion at each of four pH's. We present it in two different formats. Here we see the per cent of total metal versus the concentration of the anion concentration starting down in the ball park of J-13 well water and sequentially increasing it several orders of magnitude. And here we show it as the log of the absolute concentration of the metal, again, versus the log of the concentration of the anion.

From these plots, we can determine what are the most important oxidation states for each of these metals, which are the most important species that these metals will be combined in, and get some feel for how well we think we need to know the thermodynamic data associated with the formation of each of those complexes.

For example, here you can see that Americium carbonate is a major player. We feel relatively confident that we have that in hand. The formation constant for this species was experimentally determined by multiple experimenters throughout the world, and so we feel that we're justified in assuring that as a major species.

We can also see down here, for example, that the sulfate is not a major player and, in fact, it's of declining importance as we step up the concentration of carbonate. I didn't point it out before, but, for example, the sulfate is one of the formation constants which we had estimated in our work. We feel confident that our estimate is certainly realistic and the fact that sulfate is not even close to being concentration-wise to that of the carbonate, even if our estimate is not extremely good, then we don't need to worry about that any longer.

I would point out here that any vertical line across this plot describes an experiment that we can conduct in our laboratory. We can put in the right amount of J-13 well water, adjust the anion concentration to be what the X axis is, and then verify the speciation to see that it is, indeed, what is suggested by this modeling effort.

So what are our conclusions from the second phase of this work? Remembering, again, that we only looked at speciation only at 25☜, we see that carbonate formation and hydrolysis dominate the chemistry under J-13 well water conditions. This was not a big surprise to most people, I don't believe. And most of the thermodynamic data that was used in calculating the speciations of these complexes has been experimentally determined. The phosphate and the hydrogen/phosphate, although it didn't show on the single plot that I chose to show you, in others we see that it apparently competes with carbonate formation and hydrolysis. As I had pointed out earlier, the experimental data for phosphate and hydrogen phosphate systems is lacking and we strongly recommend that more experimental work be done to understand whether the phosphates really will compete with carbonate and hydrolysis formation.

The silicates were virtually not addressed in this work because there was so little experimental data in the literature that we were even uncomfortable trying to estimate what those values might be. I think we all expect that silicates will be a major player, given the bulk concentration of silica in J-13 groundwater, which I think is about 30 milligrams per liter, and certainly, experimental work is indicated in that area.

Chloride, fluoride, sulfate, nitrate do not appear to be significant species even at anion concentrations much greater than those found in J-13 well water. We feel that our estimates provide adequate information about these species, and consequently, we don't recommend any further experimental work be done on those complexation studies.

What we recommend finally is that you repeat the first two phases that I have just described, evaluating the data that's available, making estimates where appropriate to include solid phases.

Finally, the third phase is what would we expect under repository conditions. To understand the speciation and solubilities near the waste package, we need to have the same study done at elevated temperatures. And we would suggest that we'd use the same process that I have just described for 25☜C. Unfortunately, we can see right off the bat that very little experimentally determined thermodynamic data exists at elevated temperatures.

Our recommendations on how to proceed at this point would be to begin some measurements at elevated temperatures, initially focusing on carbonate and the hydrolysis formation. Those were the two important players at the lower temperatures. They seem likely candidates at the elevated temperature.

We in Livermore have the capability of doing this using our photoacoustic spectrometer, and we were able to do it at 60 and 90☜ in a glove box where we were able to control the oxygen and the CO_2 atmosphere above our sample.

We also recommend initiating some solubility measurements at elevated temperatures, using J-13 well water, in which we could modify the anion concentration. We recommend coordinating with Heino Nitsche at the Lawrence Berkeley lab, who has started to investigate some of these solid phases. Heino's work is focused largely on looking at the bulk metal concentration in the solution, not necessarily the speciation, which is something that we feel we could contribute to his work. One kind of interesting note to what Heino has already found, is some of the solid phases that he's identifying in his experiments and trying to identify don't appear to have been previously identified in the literature; that is to say, he's having an extremely difficult time matching his x-ray data to any other x-ray data he's seen on the solid phases of these actinides with these anions.

And that's all I have to say.

DR. LANGMUIR: Thank you, Cynthia.

You ran a sensitivity analysis--this is Overhead No. 14--which I wonder how you can run a sensitivity analysis when most of the constants in the analysis are estimates. If you look at the ligand constants, you'll have to persuade me that you can guess they're all the same. I mean, they're going to be related, but, for example, the carbonate constants with the trivalent actinides--

DR. PALMER: Is this the one you're talking about?

DR. LANGMUIR: Yes.

DR. PALMER: Okay.

DR. LANGMUIR: You can see there's a lot of numbers that are obviously estimates.

DR. PALMER: There are a lot of numbers that are the same, that is correct. I think when you go--I think what we're saying is that we expect their behavior to be similar. In the lack of any other information, we're going to say they're the same. We really have no way to move an estimate higher or lower.

DR. LANGMUIR: Actually, presuming you're basing that on at least one measured constant in that set, and there's almost always--

DR. PALMER: Let me go back to the other one.

DR. LANGMUIR: There's almost always a systematic trend of those constants with size or ionic potential or something similar.

DR. PALMER: I'll put over here the known ones. It gets to be more ambiguous as you go to increasing the ligand number. You see that they are not the same up here for the first complexation. And it gets harder and harder to predict what's going to happen to those values as you put more ligands on there.

And I guess it's comforting, then, to see that we don't see very many of the multiply complex species ever show up in solution. So, you know, here we have the americium numbers and it was americium ones which we knew didn't show up.

DR. LANGMUIR: I have a suggestion, and then I'll request other questions. But to make this really focus on Yucca Mountain, a perfect marriage would be to take EQ3/6--and I think this has already been done--and you run solution chemistries in the pours anticipated at repository temperatures in the presence of Yucca Mountain tuff, and that's the chemistry you put in your model to predict radionuclide transport, because that's the kind of water you're going to have. You're not going to have J-13. You're going to have water which has been equilibrated with a rock present next to the waste. And that fluid is the one that you're going to have transport in if there is any. And that's something you can easily do.

Any more questions from the Board? Mick Apted?

DR. APTED: Yeah, just sort of a couple of points, and I don't mean to come off as a curmudgeon on it, but I guess I've never seen the, sort of the total system performance analysis where Americium isotopes show up as particularly key, and with all deference to Don Langmuir, I'd rate them the same way. It's a curious emphasis. I guess, to me, the great yawning uncertainties are the things that appeared in your second priority list, the fission products, what's known about tin and technetium and selenium are really, yeah, I mean, are particularly poorly known. It would seem like we're, you know, Americium is a particularly sexy nuclide and it's well-behaved, it's not redox sensitive, but again, is it a symptom of where we're looking where the light is good rather than where really the great uncertainties are?

DR. PALMER: Well, I guess I can answer that by saying this priority list was put together as part of this effort, and there is a document that describes how this priority list was generated. The whole task that we are on is thermodynamic data evaluation, and the directions were to focus first on Americium, plutonium, neptunium and uranium.

DR. APTED: I guess my point is it seems to be a list that's put together by people who like to--who are experts in collecting the data, and that's fine, but I would think a list of people actually engaged in performance assessment would probably come up with a slightly different priority ranking.

DR. NORTH: Warner North, and we can refer to this as Warner North's standard question at source term meetings, number one, because I think I've asked it at all the previous meetings and it's not on your slides yet, and this is the issue that we have a construction site here. If we're going to build a repository, we're going to bring in a lot of human beings and we're going to bring in some machinery. So we don't have a pristine site. And one of the things that will be introduced in that site, perhaps, if we're very careful, in small quantities, is organic material. And from what little I know about the geochemistry of the actinides, I am told that organics can be quite important. They can complex these materials such that they migrate. And I would like to see that start entering at least in your lists of future work to be done, that we ought to understand that issue. You ought not to be surprised from it some years from now when somebody brings in a little bit of data. Oh, if we add the equivalent of, let's say, one several-year-old decayed sandwich, we can make kilograms of Americium migrate.

DR. LANGMUIR: In defense of Cynthia, what's your level of funding to work on these activities for the DOE right now?

DR. PALMER: Does someone else want to answer that?

DR. LANGMUIR: Well, you can--I don't believe you're getting anything, are you?

DR. PALMER: That's correct.

DR. LANGMUIR: So we're asking, we're suggesting things that we'd like to see done, but you're not being supported to do them.

DR. PALMER: Bill Clarke has volunteered to--

MR. CLARKE: Bill Clarke, Livermore. Cynthia was not on the program last year. She is reporting this because Bob

Silva, as you know, had a serious surgery and was not able to attend. Cynthia graciously consented to come down and make the presentation.

There was $100,000 put into this last year, largely through Carl coming up with it through the NEA, and right now there is $100,000 put into it for fiscal year '93.

Also, as a result of discussions that were held as recent as a few days ago with Livermore and the M&O, we talked about and have continuously talked about several years, the manmade materials and importance of it, and we felt that it was important enough to adjust some of the monies in the program and to get the manmade materials effort started this year, so we have put $100,000 into that effort and to at least begin with what is going on at the site in terms of drilling and whatever in support of the ESF, looking at those types of materials that could be brought in in the near term, and then to get that activity started because we recognize it as a very, very important activity for the future.

DR. NORTH: Please reassure me that you're not going to forget about organics.

MR. CLARKE: Well, I was going to tell you a story, but I won't. We're not going to forget about organics.

DR. LANGMUIR: Further questions, Board or Board staff? Any further questions from the floor, from the audience, or comments?

DR. CANTLON: Let's take a coffee break, then, and we will try and come back in ten minutes, which is three minutes before the hour.

(Whereupon, a recess was had off the record.)

DR. LANGMUIR: Our next speaker is Tom Wolery of Lawrence Livermore Laboratory. He will present an overview of the geochemical code EQ3/6, the chief chemical code in the DOE program which he was in the middle of developing and has been leading the development on for something like a good ten years now, I believe.

Tom?

DR. WOLERY: I'm going to be talking about the geochemical modeling code, EQ3/6, which I have been involved in writing with a number of other people of Livermore in the past several years. I'll mention some of their names in various places during the talk.

The first point is, what is EQ3/6? And the answer is that it's a software package for modeling the geochemistry of water, rock, and waste systems, and it treats the overall water/rock/waste interaction as the sum of many simpler processes, such as the dissolution of an individual mineral or the formation of an individual aqueous complex and simply considers the sum total of these things.

It links complex applications to fundamental data.

One example which I could give on that would be modeling experiments on UO_2 and spent fuel dissolution, much in the line as suggested by Don Langmuir. This approach has been used more extensively in recent years on the glass waste form, as people have pointed out. Another example which I'll get to later in the talk concerns models of experiments on hydrothermal tuff/J-13 water interaction, and these models incorporate data for the solubility and the dissolution and growth kinetics of individual minerals. So we have a link, in terms of understanding something complex, basically; we try to cast it in terms of things which are fundamental.

The software makes two distinctly different kinds of calculations. One, it makes calculations of an analytical nature using the EQ3NR code. One inputs groundwater composition or the composition of some water sampled during an experiment, and what one gets out of that is the chemical form of the dissolved components, and also a set of values for saturation indices and affinities which tell us where various reactions in the system are with respect to thermodynamic equilibrium.

EQ3/6 also makes simulation calculations using the EQ6 code. This code also incorporates models for aqueous complexation, and so forth, into it, but it operates in a fundamentally different manner. It can be used to calculate reaction paths in which a set of primary minerals dissolve, water chemistry changes, and secondary minerals form. And it can do simpler types of calculations, such as calculating the equilibrium state of a system initially out of equilibrium. It can also simulate titrations and groundwater mixing processes.

Again, what goes into and comes out of this type of simulation includes mineral growth and dissolution, changes in the water chemistry, including Eh and pH, and formation of, of course, the secondary solids. Individual reactions can be basically dealt with in one of three ways. One is by means of a rate law using kinetics. One can specify an equilibrium constants for an individual reaction, or one can treat an individual reaction as being locked.

An example of a locked reaction would be one in which we have a solution which is supersaturated with respect to a certain mineral, and we simply do not allow the mineral to precipitate; or, perhaps, also, the reduction of sulfate in certain systems may also be blocked basically as a means of simulating slow kinetics.

EQ3/6 has been applied to a variety of problems involving water/rock and water/rock/waste interactions. It was originally developed to model seawater/basalt interactions in mid-ocean ridge hydrothermal systems. It was later developed for applications related to geologic repositories for high-level nuclear waste, primarily under the auspices of the Salt Repository Project and the Yucca Mountain Project.

It has also found usage outside these projects in such areas of application as geothermal fields and hydrothermal systems, in general, studies of ore deposition, mineralogical evolution and petroleum reservoirs, processes in landfill geochemistry, and in some aspects of DOE site cleanup.

Some of the current and planned applications of EQ3/6 within the Yucca Mountain Project can be summarized as follows, and some of these have been illustrated in the previous talks:

At LLNL, the software has been used for analysis and simulation of water/rock and water/rock/waste interactions experiments primarily pertinent to the near-field environment. The code has also been used in the design of some experiments and is planned to be used in some natural analogue studies. The code will also be used to predict near-field interactions and to support prediction of the source term.

The USGS also plans to use this software to analyze the ambient groundwater chemistry at Yucca Mountain.

Los Alamos plans to use EQ3/6 for analysis and simulation of water/rock/waste interactions experiments pertinent to far-field radionuclide migration, and EQ3/6 has a supporting role there for prediction of the far-field migration process.

PNL is also using EQ3/6 for use in performance assessment.

A little bit about the recent history of EQ3/6. The most recent version of the software is Version 7.0, which was originally put out in November of 1990. The previous major release was Version 6.0, in February of 1988. We have recently released a Version 7.1, which basically contains a number of fixes to Version 7.0.

Version 7.0 has been distributed to LANL, PNL, NAGRA, the Center for Nuclear Waste Regulatory Analysis, and the NWTRB, among others. There was no development of a new version of this software during FY91 or '92. If DOE provides the funding, we will start work on Version 8.0 in FY93.

I want to briefly summarize the quality assurance status of Version 7.0 of EQ3/6. Version 7.0 has not yet been certified as qualified for use in quality-affecting work on the Yucca Mountain project. In terms of getting it qualified, four manuals, totaling over 720 pages, have been written to meet the NUREG-0856 code documentation requirements, and these manuals are about to be published.

Also, there is a large library of test cases for this software, many allowing comparison with other codes, particularly PHREEQE and PHRQPITZ.

And an independent qualification effort was started in late FY92. In this context, independent means independent of the code author, so that is the responsibility of someone other than myself.

A little bit about the software characteristics. The software is written in FORTRAN. Version 7 export package contains about 7.5 megabytes of material, and there are over 62,000 lines of source code. The largest executable code has the size of about one megabyte, and the largest data file has the size of about 2 megabytes.

The host platform is a Sun SPARCstation, which is a type of UNIX workstation. The software also runs on other types of UNIX workstations, including the Silicon Graphics and the IBM RS6000 series, and it's also easily ported to a VAX or a 486 PC.

A code such as EQ3/6 requires a supporting data file of thermodynamic data, and what we actually have for Version 7 is a set of five such files from which the user must choose the one which best meets the needs of the application. These files are known by three-letter designators, such as com, sup, nea, hmw, and pit, and come from different sources. The largest of these data files is the com data file, where com stands for composite, and this basically is our largest collection of data and probably has everything in it which is most pertinent to Yucca Mountain applications.

Three of the data files, including the com file are specific to an extended Debye-Huckel formalism for treating the activity coefficients of the aqueous species, and because of that, they can only be applied in dilute solutions, but this will probably be adequate for most if not all YMP-related needs.

We also have two data files, hmw and pit, which operate with the Pitzer equation formalism. These can only be applied to a relatively smaller set of components, but they can be applied to very concentrated solutions.

The data files at LLNL are created and maintained using a relational data base system which is called GEMBOCHS, which stands for Geologic and Engineering Materials: Bibliography of Chemical Species. This is basically the brainchild of Jim Johnson and Suzanne Lundeen of LLNL.

This contains thermodynamic data for over 2,000 chemical species. It contains two types of thermodynamic data: First, standard state thermodynamic data, which consists of things like equilibrium constants and standard modal, Gibbs free energies of formation and such, which are what we normally think of as thermodynamic data, but also contains parameters for the various activity coefficient models, such as Debye-Huckel parameters, hard-core diameters, and interaction coefficients.

This relational data base allows us to control mixing of data from various supersets, such as the SUPCRT92 set or the NEA92 compilation.

EQ3/6 data files were actually created from GEMBOCHS, using a code called D0OUT, which accesses GEMBOCHS for the various types of data stored in it, converts data into the appropriate form, which in our case is basically equilibrium constants for the standard state data, uses various temperature extrapolation algorithms to get data on a grid as a function of temperature, so that we can make high temperature calculations, and then writes these data files.

Some features of Version 7 are listed on this slide. There are three options for treating activity coefficients of aqueous species; the B-dot equation, Davies' equation, and Pitzer's equations. The first two have very small data needs and suffice for dilute solutions. Pitzer's equations can be applied to very concentrated solutions, but have rather extensive data needs.

Version 7 includes a limited range of solid solution models, and these solid solution models are important because we have to deal with solid solution phases including clays, zeolites, feldspars, and carbonates in an analyses of what is going to happen in the interactions at Yucca Mountain.

This software has the ability to model over a temperature range of 0 to 300☜ Celsius, but is restricted to a standard pressure curve in which the pressure is treated as a function of the temperature. And up to 100 Celsius, the pressure is set at one atmosphere or 1.013 bar. At higher temperatures, the pressure follows the liquid/vapor equilibrium curve for pure water. This is a limitation which we propose to remove in future development.

Version 7.0 also allows control of mineral dissolution growth via simple rate law expressions. We can also fix gas fugacities along reaction paths, for example, to simulate the effects of an experiment being open to the atmosphere, and although the software is probably mostly used to model the chemistry in a box, it also contains an option for modeling a pseudo-1-dimensional fluid-centered flow-through system, which essentially models what happens to the first pocket of water to start moving down a column of rock or other reactive material. I call it pseudo-1-dimensional because basically it does not tell you what happens with subsequent pockets of water.

Version 7 is probably adequate to meet at least some of the technical needs of the Yucca Mountain Project. There are some particular needs, however, which go beyond what we have now and one of these, which other speakers have touched on, is the need for more thermodynamic data, especially for radionuclide elements. There is also a need for continuing development of models for dealing with phenomena such as sorption and waste-form leaching, and we think there is also a need for some new versions of EQ3/6, or perhaps something else with additional capabilities to address needs in the areas of near-field environment, waste-form release, source term, and far-field migration.

Basically, on the next three slides I'm going to tell you what some of these anticipated additional capabilities deal with. This first slide is devoted entirely to what I call "sorption", in quote marks. This basically encompasses several processes which are not all of the same type, but which perhaps all contribute to what one might call an accrued sense of sorption.

One thing which has been worked on at Livermore in a prototype version of the software is a simple ion exchange model, which Brian Viani and Carol Bruton have worked on. This is a very simple model. It deals with the generalized substrate, which has an exchange capacity that is not necessarily either two-dimensional in the sense of taking place on a area, or three-dimensional in the sense of taking place through the volume of a crystal. In fact, it could be applied equally well to try to model some processes in which the exchange occurs either on a surface or through the volume, and some success has been achieved with this which I will show later in the talk.

There is also a need to look at incorporating the surface chemistry models, dealing both with the generalized substrate, with multiple substrates, and taking another step, looking at specific solids and substrates. These particular types of models have been incorporated into a number of other codes, particularly in a series sort of originating with the code, MINEQL, but they basically tend to deal with essentially sort of a generalized substrate whose surface area tends to remain constant during the calculations. So there are a number of features that it is difficult to deal with in the codes that have been developed thus far. But there has been a lot of progress outside of work done on EQ3/6 toward developing these kinds of models.

Another aspect of sorption is for a more expanded range of solid solution models, and people who have been working on these sorts of things at Livermore have included Brian Viani, Carol Bruton, and Bill Bourcier. The types of models that we have now are basically restricted to substitutions on one site, and one of the things that we need are models which deal with substitutions on more than one site in the same crystal lattice.

Another aspect of sorption concerns zoning of solid solutions, which would be appropriate for feldspars and carbonates, but not clays or zeolites. With clays and zeolites, it is very easy for the interior of the crystal to re-equilibrate with an outside aqueous solution. But in phases such as feldspars and carbonates, you can develop layers with different compositions present.

One thing which has come up as a problem in several applications areas is a need to be able to deal with aqueous redox disequilibrium in reaction path modeling. This is a capability that we would like to develop for Version 8. It would allow us to deal with things like metastable persistence of things like sulfate and nitrate at the experimental modeling level. If we were able to deal with aqueous redox disequilibrium, it would be very easy to deal with it in a kinetic manner, also, if that is required.

We are also very much interested in adding pressure corrections to allow calculations off this standard pressure curve. The main thing that we would need to be able to do, that would be to add partial molar volume data to EQ3/6 data files and, actually, a lot of such data is presently available in the SUPCRT92 subset.

We could use the same data to do a better job in dealing with volumetric properties, including conversions of solution concentrations between milligrams per liter and molality. It would also allow us to calculate the solution density and porosity changes.

Another thing we think that we should look at, particularly for near-field modeling, is to look at heat balance and look at the production or consumption of heat by chemical reactions and phase changes. And to do that, we would need partial molar enthalpy data in these data files, and again, we can get a lot of that data from the SUPCRT92 subset.

This is basically the third slide listing additional capabilities anticipated to be needed. One of these is a model for a gas phase. Basically, EQ6 does not now allow one to do a reaction path model in which a gas phase is formed or which is initially present. One can fix gas fugacities, but this is only useful if you consider the system to be in equilibrium with a large external reservoir of gas, with very easy communication to your reacting system. We need something more sophisticated than that.

Another thing which follows, what is being done in the outside world of aqueous geochemistry is to go beyond the simple rate law expressions that we now have for mineral dissolution and precipitation and develop models with explicit links to mineral surface chemistry. This is essentially where things are going in the outside world and we need to be able to follow that.

We have also talked about the development of a pseudo-1 dimensional rock-centered flow-through system. This also would model the physical system that one has in a leaching cell, where one has the volume in which a solid is placed and an aqueous fluid flows in and then flows out with all solid dissolution and precipitation taking place within this one fixed volume.

Some thought has been given to coupled 1-D transport modeling, whether we would do that or not, or whether it would be done in the context of EQ3/6. We presently have no firm plans. There is also a possibility of adding stable isotope mass transfer calculations into this. A similar thing has been done in some other codes and, in fact, some people have added this capability to EQ3/6 in the universities.

I wanted to say a little bit about other geochemical modeling codes because there are quite a few of these things. Various other codes such as MINTEQAQ2, MICROQL, PHREEQE, PHRQPITZ, CHILLER, Gt/React are out there and they can also be used to model rock/water and rock/water/waste systems.

One thing about these codes is that every code tends to have its own strengths and weaknesses, those things which it covers and those things which it ignores. And no code now in existence covers everything that we could anticipate might be needed for Yucca Mountain Project applications, and no other codes are currently being developed for this purpose by the Yucca Mountain Projects.

We think that other codes may be useful for some purposes on the YMP, including activities of submodel evaluation, for example, evaluating specific surface chemistry models for code-to-code verification activities, and perhaps actual applications if the technical capabilities match up to what is required and if QA requirements can be met.

I want to add two slides of propaganda here.

DR. LANGMUIR: This has all been propaganda, Tom.

(Laughter.)

DR. WOLERY: Well, yes. You're very astute, Don, but don't tell anybody else, please.

Basically, why is geochemical modeling important to this project? Well, if you look at how are we going to figure out what water/rock/waste interactions in a repository are going to do, what's our prime means of figuring this out? Well, we do short-term experiments, primarily lab, or it could be field. You've seen some experiments today, which if you looked at the time scales, you've seen a few things which have gone on for several years, which is really quite long for a laboratory experiment. We can't do a large matrix of experiments like that. It's too costly. And even if we could, would we get the entire story, because we have to predict things over much longer time scales? And this is basically where the need comes in, because we have to be able to make--we have to go from this to this, to the long-term projections.

Well, there is evidence which suggests that extrapolating short-term results to make long-term predictions is possible, but it requires considerations of certain factors which may not manifest themselves in the short-term experiments. I like to call these non-linearities, and if you took a simple engineering approach and extrapolating the short-term results, you would miss these things.

Well, why do we believe that that is the case? Well, from other experience in aqueous geochemistry, we know that short-term experiments have a tendency to give results that tend to be at least partially inconsistent with what we see in natural systems. And the natural systems, basically, that we're talking about have evolved over long time periods. One example of such an inconsistency is that hydrothermal seawater/basalt experiments yield mineral assemblages that are dominated by a clay, smectite. But if you go out to see what the process has done in nature, you see rock assemblages or mineral assemblages that are dominated by chlorite or mixed chlorite/epidote.

Another thing which we may consider is that tuff/J-13 water, hydrothermal experiments run up to times of about three months and give water chemistries that appear to reach a steady state or a near steady state. Yet if we analyze these results with thermodynamic calculations, we see that these water compositions are supersaturated with respect to a variety of minerals, and that tells us that these systems are metastable.

So, basically, the role of modeling in this is to account for differences between short-term and long-term results, and long-term results tend to adhere more closely to what one would predict using thermodynamic equilibrium. And basically, thermodynamic equilibrium is what most of these geochemical modeling codes were originally designed to do.

I'm going to do basically a little summary of LLNL applications, then I'm going to talk about two of these in some more detail. One particular set of applications concerns the tuff/J-13 water hydrothermal interactions experiments, and this work was done by Joan Delaney, Kevin Knauss, and others, and basically what it did was to use kinetics to try to model actual rock/water interactions experiments, and I think it was the first time that had ever been done.

Another usage, which is kind of mundane sounding, but basically you've also heard about earlier, was using the software to calculate pH buffer compositions for things like single mineral dissolution kinetics experiments. And people like Kevin Knauss and myself have done that type of work, and then more recently, the same type of usage has been done to design pH buffers for other types of experiments.

The software has been applied in glass waste form dissolution modeling, as you were told about earlier by Bill Bourcier. There was some early work on spent fuel dissolution modeling done back about '87, I think, by Carol Bruton and Henry Shaw. Basically, they didn't attempt to really model any specific experiments, but simply said, okay, if we take the code and say, here is some spent fuel, there is J-13 water, go to it, assume lots of chemical equilibriums as the spent fuel dissolves, what kinds of secondary minerals would form?

And one of the interesting things that came out of that study, which was very preliminary in nature, was an understanding that uranyl silicate minerals may form in these kinds of systems and may end up being very important syncs for uranium immediately about a waste package. These particular minerals include soddyite and haiwiite, and at the time the calculations were made, the thermodynamic data actually had been estimated by a fellow at the USGS, and then some work was later done to confirm the importance of these things.

Another application more recently is the development of ion exchange models for clinoptilolite and smectite in Yucca Mountain tuffs, work done by Brian Viani and Carol Bruton.

What I'm going to talk about, sort of to close out the talk here, are some of the results from the tuff/J-13 water experiments and the ion exchange modeling.

The tuff/J-13 water hydrothermal experiments were primarily done in the period of about '85 through '89, and the experiments themselves were done in Dickson rocking autoclaves. And in the first set of experiments, we utilized Topopah Springs tuff, which is a thoroughly devitrified tuff which consists of cristobalite, quartz, an Na-K feldspar, and small amount of plagioclase. Some similar studies were done later with glassy tuffs.

The modeling approach basically was fairly simple: Take rate laws and rate constants for the dissolution of the tuff-bearing minerals from the literature, extrapolating and estimating as necessary.

Then partition the measured surface area of the tuff among the individual minerals, because we need the individual surface areas to plug into the rate laws.

And then run the model, allowing secondary minerals to form according to equilibrium constraints. So as soon as the water would saturate a particular secondary mineral, that mineral would immediately start forming. And this is basically treated in kind of an iterative process in which we would lock reactions for specific secondary minerals until a reasonable fit was obtained. And this was, in part, guided by results of the experiments themselves. These Dickson bonds could be opened and you could basically determine what had formed and what had not. And, basically, by not allowing a number of things to form, such as quartz, we would get a reasonable fit.

I might say something about the importance of this business of quartz not being in equilibrium. Both quartz and cristobalite are present in the tuff to begin with. They're both SiO_2 minerals. Cristobalite is less stable and, hence, more soluble, and you can't have an equilibrium mineral assemblage with both of these things present. So in the presence of water, what tends to happen is that cristobalite dissolves and quartz grows, and eventually all the cristobalite should be converted to quartz. One sees, however, essentially no formation of quartz in these particular experiments.

Basically, we got reasonable results for 150☜C experiments, and this was done with little or no adjustment of any of the rate constant values. And one thing which was somewhat surprising is that it was not necessary to invoke secondary mineral growth kinetics. Essentially, secondary mineral formation in these systems seemed to be either very rapid so we could treat it by equilibrium, or very slow so that we could consider the reaction formation to be locked.

Experiments at higher temperatures, 250☜C, could not be modeled due to precipitation of the zeolite dachiardite, and the zeolite was not in the EQ3/6 data base. So we had no luck with those experiments.

The final state in the experiments appears to be near steady-state, but again, thermodynamic analysis shows this to be a metastable situation.

I sort of illustrate some of the results that were obtained with the Topopah Springs tuff. This figure was actually taken from one of Joan Delaney's reports. Basically, the concentrations are given in parts per million. What you see is a rapid rise in the silica concentration, which then levels off. The reason that it levels off, essentially, is that we're approaching near equilibrium with cristobalite. Now, if quartz were forming as rapidly as cristobalite is dissolving, the silica level would be much lower. So essentially, one of the key features of obtaining this is that one has to suppress the formation of quartz.

Basically, then, the model also gives reasonably good results for some of the other aqueous solution components; sodium, calcium, potassium, aluminum and magnesium. And basically, we have a fair amount of comfort with this model in terms of what it does in modeling the experiment. One of the big questions, though, is what happens at longer time scales, because at some point the quartz has got to start to grow, and eventually the silica level would have to come down.

Move on to cation-exchange modeling. There are two ideas in ion exchange modeling concerning ideality. There is something called an Ideal Vanselow Model, in which the activity of a component is taken to be equal to the mole fraction of the exchange cation. And there's also something called the Ideal Gapon Model, in which the activity of the component is taken as equal to the charge equivalent fraction of the exchange cation. This leads to slightly different formulations in terms of what the equilibrium should look like.

This particular set of studies that I'm going to talk about used only the Vanselow Model. The exchange is assumed to take place on one site, and in this particular work, which was done by Brian Viani and Carol Bruton, what they did was to go to the literature and get published energies of exchange for the major cations, strontium and cesium; on the phases, clinoptilolite and smectite. Now these phases are present in Yucca Mountain tuffs, and so what they then tried to do was to say, okay, can we use this simple ion exchange model incorporating these published exchange energies and model experimental results obtained for Yucca Mountain tuffs?

Now, in order to do these models, they needed to know the mineralogical composition of the tuff and its total exchange capacity. They also needed to know what exchange cations were initially present, both on the tuff sample and in the aqueous phase.

The first test of this was to see if they could model isotherm data reported by Los Alamos. And essentially, this gives results for one particular tuff sample, and, again, the isotherm is obtained by spiking the system of rock/water with different amounts of either strontium or cesium. The experimental points are shown here. The line in each case is the prediction. Now, this is in no way a fit. Basically, this line was obtained purely by prediction, and it seems to work very well for both strontium and cesium.

This work was further extended to see if you looked at large number of different tuffs, could you predict reported Kd values? And basically, these results are summarized here. This is a plot of predicted Kd versus observed Kd. If you look in the case of strontium, with the exception of two or three outliers, this seems to work quite well.

If you look at cesium, it doesn't work quite so well. What's happening here is that the model is under-predicting the actual amount of sorption. And that's thought to be, in this case, because the model only accounts for sorption on smectite and clinoptilolite, and there may also be present in these tuff samples a third mineral acting as an exchanger, namely, a mica or illite phase to which cesium has a very high affinity. But perhaps if that were also accounted for, we could get results as good as those obtained for strontium.

My last slide was not actually intended as something I wanted to talk about, but basically I said before that we have produced 720 pages of code documentation for this software. This is it. If you have an interest in this, please let me know or write to me at Livermore.

DR. LANGMUIR: Thank you, Tom. I think many of us in the geochemistry community feel that you have the premier program out there. The code does most of the things you want it to do.

One of my problems, though, is that I'm concerned, as you know, and you discussed it--in fact, there's an overhead which is No. 15, I believe, in which you list the other codes and acknowledge some of their abilities.

I've always felt that it would be really nice if the DOE could accept some of these other codes for what they can do, and instead of having to further enlarge EQ3/6 as the only program that can do anything. Adopt, for example, MINTEQAQ2 as the code or the routine that does the sorption part of things, and perhaps couple that with yours, rather than having to start all over again and build a larger and larger program.

DR. WOLERY: Well, one of the things, as you know, in geochemical systems, you have various processes going on and these things are linked. So if you have, say, a solid solution in EQ3/6 and sorption on mineral surfaces in MINTEQAQ2, and you have a system that has both solid solutions and sorption on surfaces going on in it, and both must be accounted for, you have to have one code that deals with both at the same time because the processes are linked.

What we would hope to do is something like the following, and that is to look at what has been done in these other codes. I mean, we certainly wouldn't be starting out in a vacuum in this to look to see what has been developed and used in other codes in terms of the specific submodels and the data, and basically use that as a basis for what we would put into EQ3/6.

DR. LANGMUIR: I guess another thought is that there are so many obvious uses to EQ3/6, or to any geochemical code throughout this program, so many experimental studies being done, field studies being done, that my sense is that frequently all that's needed is a smaller code, an equilibrium code or a pathway code that is very simple PC-oriented, although I know yours can now do that. And maybe we don't always have to go to the master of all codes for some of the simpler problem solving. It would be nice if they were within the program and accepted for use in the program.

DR. WOLERY: Well, one of the problems in terms of actually using other codes is going to be the quality assurance issue.

DR. LANGMUIR: I gather that's the thing you have to, line-by-line, go through the code, QA requires you to QA each line in the code to get acceptance?

DR. WOLERY: Well, one problem concerns the documentation requirements. If you look at most of the other codes, there was some kind of manual available, but, in general, it was never written to satisfy the NUREG documentation requirements. So somebody on this project would have to take what there is and add to it in order to bring it up to speed for the NUREG requirements. There would probably also have to be a process somewhat like this independent qualification process which is now going on for EQ3/6. If we have one code which reaches this qualified status, it may be easier than to bring in some other codes as well, by saying that we can do code comparison studies, for example.

DR. LANGMUIR: Well, I'm thinking particularly of MINTEQAQ2, which is QA-approved by the EPA and taught by the EPA as their code.

DR. WOLERY: Well, I met some of those people about a year ago at a Pittsburgh conference, and in talking to them, the impression that I had was that within the EPA they sort of consider it to be their code, but it apparently has no QA status analogous to what would be required for use on this project.

DR. LANGMUIR: That seems bizarre insofar as their staff teach the use of that code all over the country. But--

DR. WOLERY: Well, that may be, but, you know, the EPA operates one way and the DOE operates another.

DR. LANGMUIR: Let me ask you one last, then I'll stop hogging.

If you had your druthers on funding, how would you prioritize the top things in order that you would propose to accomplish in the further development of EQ3/6 to satisfy the needs of this program?

DR. WOLERY: Well, I'm flexible in one regard, and that is basically I'm looking for the people who are doing the applications to define the priorities. In terms of where I would have to perhaps lend my guidance or even put my foot down, it would come in with regard to the fact that sometimes what--if someone wants something, and something else is a prerequisite for it. But, you know, apart from that, basically, I'm looking for support from whatever direction that I can get.

DR. LANGMUIR: I'm trying to ask you to sell what you can do for the program, though, as a basis for support. What can you offer that's needed that currently doesn't exist in the program that you consider very important to it, to the licensing, to the performance assessment approval of the site? Have you thought that one through?

DR. WOLERY: Well, I think one of the particular, the particular strength of this software is that it enables you to study a process in terms of something which is mechanistic, maybe not at a very deep level, but something which connects into what are considered to be well accepted, physical principles.

In terms of the actual applications, I think perhaps the greatest need is in the area of the near-field environment where we're going to be creating an artificial hydrothermal system. And we can go and we can look at natural analogues, but there are not perfect natural analogues for Yucca Mountain repository. There are some analogues where we can see some features which are similar or which may allow us to test some of the predictive capabilities, but, you know, we're not going to be able to like directly take data from a natural analogue and plug it into the Yucca Mountain analysis.

So, basically, I think I would emphasize the connection with fundamentals and the applicability to the near-field environment.

DR. LANGMUIR: Other questions from Board members?

Mick Apted.

DR. APTED: Tom, I guess two questions, one following on from your near-field environment statement. Have you looked at including radiolysis in here as a sort of a separate set of reactions to--I mean, the way radiolysis often works is through the chemistry of the solution, so why not consider that?

And then, secondly, in your reaction modeling with precipitates, don't you need a model for the surface area of these growing precipitates, and isn't that perhaps a more likely explanation for--

DR. WOLERY: To answer your second question first, yes, you need to know something about--have some kind of model for the surface areas of growing precipitates, particularly if you talk about a system in which the substrate in which you're going to grow either is not present initially or it's present initially in a very small amount. So that kind of thing is needed. There are some fairly simple geometric rate laws that could be used to account for some of that.

Jumping back to your first question, what about radiolysis? So far, nobody on the project has really pushed that as something which is needed in EQ3/6 applications in the project. I think where it would perhaps tend to be more significant would be in the area of waste form dissolution or in processes right around the originally emplaced waste form.

And a lot of the application of the code, of course, would take place farther away. But it's the type of thing which we have considered in the past and if someone wants us to do it, we could do it.

DR. APTED: So, conceptually, there's no problem in implementing such reactions into the--

DR. WOLERY: I don't think so, although I think what one would probably try to do would be to look at some of the models which are incorporated in the current radiolysis codes and then try to make some simplifications of that for use in EQ3/6.

DR. LANGMUIR: Further questions, Board staff?

From the audience?

I promised and I failed. I forgot. Ardyth Simmons wanted to say something at the end of the previous session. She would like to now make a comment regarding, I believe, the thermodynamic data base discussion we had prior to the break.

MS. SIMMONS: Yes. I wanted to make a comment as the DOE geochemistry manager of the program. First, in regard to the question that Dr. North asked about the importance of organics and the influence that they have on complexing with the radionuclides, and I wanted to point out that DOE, indeed, does have a concern about the influence of organic materials and the way in which they would be important as colloidal transport of the actinides. And we are looking now at studies that will adequately characterize the potential of transport of the actinides by colloidal materials, both those that complex with organics, and those that exist as natural colloids, like plutonium. We are going to be having a workshop in the spring of next year that deals with colloidal transport.

The second point that I wanted to make was that the thermodynamic data work that's done by Livermore, and which you heard about today, is integrated with work that Los Alamos Laboratory is doing. Cindy Palmer mentioned the work that Heino Nitsche has been doing, and this is experimental work on the solubility of actinides, particularly looking in detail at plutonium and neptunium. So the other side of some of the speciation discussions that you heard Cindy mention has to do with experimental work that's been going on now for quite some time at Lawrence Berkeley, and also speciation experiments involving the PAS that Cindy talked about as part of the speciation studies at Los Alamos. And those are being integrated together.

DR. LANGMUIR: Thank you, Ardyth.

MR. GERTZ: Don, I need to comment, if you don't mind. This is Carl Gertz. To take Tom off the hook a little bit, when we talk about qualification, QA of codes, et cetera, we are working now, I think, with a fairly reasonable QA qualification procedure within the project. We've gone maybe from something that was too rigorous to now something that we think meets all requirements, and I think we're moving in the right direction. The scientists and the modelers are getting together with the QA professionals and we're working on procedures that are necessary to document. So we hope it's not as rigorous as it has been in the past.

But, I do need to point out EPA, in their accomplishment of activities, is not required to achieve an NRC license. They don't have to have the documentation. So it's perfectly appropriate for them to have models and teach them across the country and not have to go through a rigorous procedure that other people do if they license something.

DR. LANGMUIR: You have gotten to the point now where you can conceivably accomplish that QA approval of some outside programs that are being used in a reasonable length of time so it doesn't discourage people who might do it?

MR. GERTZ: We hope so. Let me just tell you, one of my biggest frustrations when I first came on the project--and I'm a civil engineer--is we couldn't do cut and fill codes because--which were off the shelf and the guys were doing it by hand because they couldn't get QA procedures. Certainly, that's an extreme that I hope we've turned around, but it still it is cumbersome. It's more cumbersome than not doing it, but it's necessary to meet regulatory requirements, and we're trying to streamline it, and it's only a matter of the --we constantly hear of it between the professionals and the QA and software quality assurance people and the modelers working on it.

DR. LANGMUIR: Thank you, Carl.

Okay. A question from Larry Ramspott? I'm told I should remind him.

MR. RAMSPOTT: I thought you'd forgotten. Basically, I wanted to ask this of Tom.

Five years ago, Tom, one of the priorities I was trying to urge on you was an organic data base for EQ3/6, and in light of what Warner North was saying, you know, at that time I understood it was possible to put that in there.

DR. WOLERY: I'll try to respond to that, Larry.

Well, there actually is some representation of organics in the present EQ3/6 data base, most of it coming from the SUPCRT92 superset. However, most of the data concern is your basic garden variety species of low carbon number, things like acetic acid, propanoic acid, alcohols, et cetera, and very little in the line of metal-organic complexing, which I think goes directly to the heart of what people have on their minds right now.

There is a problem, I think, in terms of developing all of these data. One problem, I think, is that if you look at who would use these data, that it goes beyond the bounds of the Yucca Mountain Project and I think immediately comes to mind that the same kind of stuff is needed in dealing with things like low-level radioactive waste dumps; site problems at the various DOE labs and facilities. And one question, then, is who's going to pay for it if all these people can use it? And the usual response is, is to sit back and say, well, I'll wait for awhile and see if the other guy funds it. And I think that's where this is at right now.

DR. LANGMUIR: Thank you, Tom.

Diane has been waiting very patiently here. Our final presentation is Diane Harrison of the DOE, who will summarize the day and DOE's plans for future work on source term.

MS. HARRISON: Okay. Yes, I'd like to discuss a bit about the plans for future work, specifically relevant to the source term. I don't like to talk quite as much as all these scientists, so I only have a few view graphs.

Really, in order to have this discussion, I need to preface it with what were our priorities for the following year, the year coming up?

First and foremost, we are to support the activities necessary to get an ESF, the exploratory study facility underground this year. So any activities in the waste package program that will support that, that's our number one priority.

And secondly, of course, to support the site suitability testing program.

Our third priority is those activities that are necessary to evaluate the repository thermal load. We're well aware of the importance of this issue throughout the program. It's important to repository design, waste package design, system level implications, so it's a very high priority.

And then, of course, we wanted to support activities that were necessary to accomplish the license application in 2001.

In the area of waste package environment, a big item that has started this year, hopefully, is to activate a large block laboratory heater test. And it is a laboratory test taking 27 meter cubed blocks, putting them together under pressures, under a load, and conducting a heater test and evaluating models. Some of the results we are hoping to get would be models validated to help us better understand the processes of rehydration, dehydration of the rock, what is the repository response to the heat. There are a number of activities that we would get from this large block experiment. This would be done at Lawrence Livermore.

We're going to issue a near-field environment report.

As Tom Buscheck said, we'll initiate the coupling of geochemistry and hydrology codes, determine rate constants for zeolite interactions, conduct geochemical simulations for specific analogue sites that we've been looking at, and then verify the baseline V-TOUGH hydrology code for a suite of test problems.

Additional waste package environment work: improving the hydrology code to support radionuclide transport; initiate studies of heated-drift stability. This is part--very important information for helping to evaluate the thermal load issue.

If we're going to get underground sooner, we should be at the ESF test level sooner, so we need to be initiating planning for that testing we need to be doing, and then continue participation in the international efforts to characterize the effects of man-made materials, and since these view graphs were made, we had decided, as was discussed earlier, that we would also initiate some of our own work in the area of man-made materials to support the ESF program. There'll be operations going on and we need to better understand any implications of materials that might be input into the environment as a result of ESF operations.

In the area of waste form characterization, as Ray mentioned, we are planning on issuing the Waste Form Characteristics Report. We're going to continue the long-term spent fuel oxidation and dissolution testing, continue the spent fuel and glass dissolution model development.

In the area of integrated testing, continue the core-flow experiments at elevated temperatures, plan some core-flow experiments to address colloid transport, continue the experiments to determine adsorption of radionuclides in oxide minerals, continue, again, participation in international efforts, looking at existing thermodynamic data for actinides and technetium.

Lastly, I did these view graphs and things were taken off and put back on. We really didn't address waste package materials corrosion in this meeting today, largely, in part, because we haven't done a lot of work in that area that you all haven't already heard. What we're planning, however, is to initiate that program again, get it started again. We're planning on looking at starting some corrosion tests, particularly humidity temperature-type corrosion tests in the upcoming year, and that's really it.

DR. LANGMUIR: Thank you, Diane. That's a very exciting list of things to be doing, but I wonder what funding levels we are talking about?

MR. GERTZ: That comes tomorrow at 2:55 p.m, and we will tell you what funding there is at that point.

DR. LANGMUIR: I'll hold my breath. Thank you.

Questions of Diane from the Board?

DR. PRICE: Dennis Price.

So far, I don't see anything in there to verify J-13 water and the question I brought up earlier, and Don Langmuir's suggestion as a way, maybe, to generate something that you could argue in some of these things we've been hearing about all afternoon, that there is some generalized ability to do the experiments and the models and the rest of it. Is there any effort going to be planned to do something about the dilemma about J-13 water?

MS. HARRISON: I really can't answer that. I know that it's going to be a matter of acquiring the core, and if you're talking about water at the waste package near-field environment, we need to get rock from that horizon and do whatever processes it takes to extract the water and I know that's a difficult issue. I don't know, and I don't know if anybody is here that can really address that.

DR. LANGMUIR: I can. I worked with Al Yang before I joined the Board on the analyses of those waters in the unsat zone, which really are the ones we're talking about. And so, Al Yang has published, a lot of data, as the DOE folks, many folks know, on the chemistry of the moisture in the unsat zone that's currently there now. The experiments at Livermore were done on determining what the chemistry would become in the presence of moisture in that tuff under heated conditions. So there's a fair amount of data on what kind of waters one should prefer to use in the studies of waste package performance and corrosion, and so on, which relate directly to what you'd expect in a repository.

It's already out there. I think we have to keep talking about: "Don't use J-13!" It's just--people are so used to doing it. It's an easy way to say they're working on Yucca Mountain, but, in my view, they should throw away the analysis and start over again with what is more pertinent, as we know.

MS. HARRISON: Dale, did you want to add something to that, my near-field environment person?

MR. WILDER: Dale Wilder, Livermore.

We have looked at the problem of what water chemistry to use in our calculations, and our approach--which we have not done yet, but which we intend to do--is to take the EQ3/6 code, as has been suggested, looking at condensate water, because our feeling is that it's not the water that's in the pours that's going to contact the waste package. That water is pretty much immobile. The water that's going to contact the waste package in the most likely scenario would be condensate that gathers somewhere away from the waste package, and which sometime in the future is able to drain down the fracture system. It's probably, when I say sometime in the future, 10,000 years or whatever, so we'll certainly be under equilibrium conditions. Therefore, the use of the EQ3/6 code is justified, and also, some work that Bill

Glassley has been doing would indicate that anywhere out beyond 400 years, and certainly out in the temporal, as well as spatial scales that we're talking about, will be adequately addressed by EQ3/6. We really don't think the J-13 or the vadose water chemistry is the chemistry of concern.

DR. LANGMUIR: More questions or comments from the floor or from the Board?

DR. NORTH: I'll put in the request that's obvious, following the questions I've been asking earlier. I'd like to see more detail on how priorities are being set. A number of the items in your view graphs are fairly general descriptions of continue this effort or continue this modeling activity. And yet, if I look ahead to the presentation we're going to hear from Dr. Michael Wilson tomorrow, his conclusion slide says: "Detailed source term may not be necessary for initial total systems performance assessments", which I think is an interesting hypothesis.

The issue becomes, how much detail is enough? What data elements are critical? And I hope that if not now, then soon you could share with us a document which represents discussion between Russ Dyer and the performance assessment community and all the people working for you as to how one can use the information from both sides to set those priorities.

MS. HARRISON: Yeah, there are a lot of issues. You need to have, I think, for performance assessment, you need to have some basic assumptions up front. You need to have a waste package design or a repository design or a thermal load. You need to start somewhere, and we're so early in the program that we're in that mode of trying to get things connected up to get that plan detailed and laid out.

DR. NORTH: Well, the other issue is the timing question. Some of these experiments take a long time. I mean, we heard about one, eight years taking data on something. And from now to 2001 is about eight years, so I think it becomes very important to try to think out what are the long lead time items, the experiments that are hard to do and take a lot of time, and get those things started.

MS. HARRISON: Well, what we've done as part of our Mission 2001 exercise is look at all of those activities, look at the long lead time, testing programs, to make certain that we're getting the data when it's needed by the end user. And, if we've had--if we come to a point where we've got to reduce that time period, we have to evaluate that, is there an acceptable risk associated with doing a six-year test versus an eight-year test, or can we do--work around--can we start a test in the laboratory and get data that we need if we can't get underground or whatever. So we are certainly, and we have certainly looked and prioritized.

DR. NORTH: We'd be very interested in seeing that next level, either in terms of documents or a future presentation.

MR. GERTZ: The process, Dr. North, has been part of what we call our Mission 2001. In other words, Diane's people have been working with Russ's people and saying, is this the right sequence of activities and network, can we get the answer to do a PA? But we hear your request and I'm sure we'll respond.

DR. NORTH: Good.

DR. LANGMUIR: Further questions or comments?

DR. APTED: Diane, on your integrated testing, it's very interesting, but could you explain a little bit more what you mean by integrated core-flow experiments? I mean, not today and not tomorrow, I don't think anybody's actually going to speak on flow or transport, so this is a big open question. What are these things, because there is an awful lot of very bad science masquerading as integrated systems tests.

MS. HARRISON: If I could actually pass that on to Dave? Can you elaborate, or--hi, Bill. Could you please address this for me?

MR. HALSEY: Bill Halsey from Lawrence Livermore. That particular nomenclature at the moment refers to preliminary sets of tests looking at aqueous transport through tuff core, core samples. It's the first step in a series of tests to integrate the processes between the EBS and the natural system, looking at both saturated and unsaturated transport processes. The easiest thing to do first is to take rock, flow water through it, look at the distribution of radionuclides or surrogates for radionuclides, a transfer function. You can put in colloids or pseudocolloids and look at their transport, and then from there you go on to some more complex transport processes in the near-field environment.

DR. APTED: In the first year, Bill, these will be saturated tests, cores with sort of saturated flow, either through porous or fractured tuff cores; is that right?

MR. HALSEY: Both, yes.

DR. APTED: But not unsaturated, just saturated flow?

MR. HALSEY: The first experiments are saturated because they are easier to get data more quickly.

DR. APTED: It's where the light is. Okay.

MR. HALSEY: That's right. But you also use it as a baseline, and in those performance assessment scenarios where you have episodic flow, some of the release modes are saturated flow or advective flow release modes.

DR. APTED: Through the fracture?

MR. HALSEY: And the data is directly appropriate to those, when water comes through a fracture, interacts with the waste, carries in a flow regime, radionuclides into the rock.

DR. LANGMUIR: More questions or comments? I think we've had quite a full day here. I'd like to thank all the speakers for what's been a very valuable day, very stimulating discussion. We start tomorrow at 8:00 sharp in the same room, I believe. See you then.

(Whereupon, the meeting was adjourned at 5:20 p.m, October 14, 1992, to reconvene at 8:00 a.m. on October 15, 1992.)