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TRANSCRIPT
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480 Columbia Point Drive
Richland, WA 99352

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PROCEEDINGS

BAHR: Okay. Well good morning and welcome to the U.S. Nuclear Waste Technical Review Board's meeting on the Department of Energy's search and development activities on corrosion of high-level radioactive waste borosilicate glass, and that's a mouthful, but we'll all be able to say it in unison at the end of the day.

I'm Jean Bahr. I'm the chair of the Board. I'm going to introduce the other Board members in a moment, but first I want to tell you a little bit about the Board and why we're holding this meeting and what we plan to accomplish. As many of you know, the Board is an independent federal agency in the Executive Branch. I want to emphasize that the Board is not part of the Department of Energy or any other federal organization, such as the Nuclear Regulatory Commission.

The Board was created in 1987 by amendments to the Nuclear Waste Policy Act to perform objective ongoing evaluations of the technical and the scientific validity of DOE activities related to implementing the Nuclear Waste Policy Act. The 11

Board members are appointed by the President from a list of nominees submitted by the National Academy of Science, and we are mandated to report Board findings, conclusions, and recommendations to Congress and to the Secretary of Energy. And copies of all the Board's reports are available on the Board's website at www.nwtrb.gov, and so I invite you to that website. It's going to be updated sometime in the next couple of months, hopefully with a new modern view, but still the same information, and we hope, in fact, in ways that are easier to find.

Today's presentations and discussions will focus on the long-term durability of borosilicate high-level radioactive waste glass and the research activities the Department of Energy has done to improve our understanding of the rates at which this type of glass will corrode, or dissolve is another word for that, in a repository environment. A lot of effort and planning for this meeting and arranging the presentations went into this.

I'd like to thank the Department of Energy for making staff members from the National Laboratories available to make presentations at our meeting today. And I particularly want to thank Sue Brantley, the Board member who acted as the lead and coordinated the Board's staff, and Bobby Pabalan who put this meeting together. And Allen Croff, another Board member, also participated in a fact-finding meeting on this topic and in developing questions for the speakers.

So now I'm going to introduce the Board members and tell you a little bit about the schedule for the meeting. First, for the introductions, I'm going to say the names of the members of the Board and just ask that they raise their hands to be identified. To begin with, I'm Jean Bahr. I'm the Board Chair. All the Board members serve part time, so we have other jobs. In my case I'm a professor of hydrogeology in the Department of Geoscience at the University of Wisconsin. Madison.

Dr. Susan Brantley, there -- got her hand up -- is Distinguished Professor of Geoscience and director of the Earth and Environmental Systems Institute at Pennsylvania State University. Steve Becker, who likes to sit with the staff, is professor of Community and Environmental Health at the College of Health Sciences at Old Dominion University in Virginia. Mr. Allen Croff is a nuclear engineer and an adjunct professor in the Department of Civil and Environmental Engineering at Vanderbilt University. Dr. Tissa Illangasekare, who is our newest Board member, was appointed in January this year. He holds the AMAX Endowed Distinguished Chair of Civil and Environmental Engineering position at the Colorado School of Mines and is the director of the Center for the Experimental Study of Subsurface Environmental Processes at that institution. Dr. Lee Peddicord is director of the Nuclear Power Institute and professor of Nuclear Engineering at Texas A&M University. Dr. Paul Turinsky is professor of Nuclear Engineering at North Carolina State University. And Dr. Mary Lou Zoback is a consulting professor in the Department of Geophysics at Stanford University.

So, I've just introduced seven Board members, plus myself. Our normal full complement is 11 Board members. Due to other commitments, Dr. Linda Nozick, a professor in the School of Civil and Environmental Engineering at Cornell University, and Dr. Efi Foufoula-Georgiou, a distinguished professor in the Department of Civil and Environmental Engineering at the Henry Samueli School of Engineering at the University of California, Irvine, were unable to join us today, and the Board currently has one vacant position. As we usually do at the Board meeting, I want to make clear that the views expressed by the Board members are not necessarily Board positions. Our official positions can be found in our reports, letters, and testimony available on the Board's website.

If you would like to know a bit more about the Board, there is a one-page handout summarizing the Board's mission, and presenting a list of Board members and their areas of expertise, and that can be found at the documents table at the entrance to this room. And more information about the Board and its activities is available on the Board's website. Again, that's www.nwtrb.gov. All the Board reports, correspondence, testimony, and meeting materials can also be found on that website.

During this meeting, there will be two opportunities for members of the public to make comment. One of those will be before the lunchbreak, and the other will be at the end of the day. We've asked that if you'd like to make a comment, you add your name to the signup sheet that's at the registration table outdoors so that we know how many comments we need to accommodate. Written comments and other written materials may also be submitted after the meeting by providing material to one of our staff members today, sending the material by mail, or e-mail to the points of contact that are noted in the press release for this meeting, and the press release is also posted on the website.

Documents submitted by the public will become part of the meeting record and they will be posted on the Board's website, along with the transcript of the meetings and the presentation. If you're going to make a comment during the meeting, please state your name and affiliation first, and make sure to speak directly into one of the microphones so that you'll be identified correctly in the meeting transcript. And I will just remind Board and staff members who have microphones in front of them that if you're going to ask a question, please move your microphone close to you so that we have a clear record of that for the transcript.

We also want you to be aware that the meeting is being webcast live, so you'll see cameras in the room, and depending on where you're sitting, you might be part of the webcast. I'd also request that presenters speak loudly enough so that those at the back of the room can hear, and it would be helpful to those who are watching on the webcast if the presenters will summarize questions before they answer them. The webcast will be archived after a few days, and then will be available on our website. And to assist those watching the live webcast, the meeting agenda and presentations have been posted on the Board's website and can be downloaded, and they will also be part of the webcast.

Before I get to today's agenda, just one more note for the speakers, Debra Dickson, who is sitting in the back of the room there, is going to be giving you a three-minute warning when your speaking time is up, and then Steve has the hook to pull you off the stage. We don't want to cut short discussions, but we do want to try to keep things on time, so we will be giving you those warning, so look for Debra.

Okay. So now I'll outline today's agenda, which is also on the document table in the back of the room or outside, I guess, the door here. This morning, after some welcoming remarks from Dr. Jud Virden, the Associate Director for the Energy and Environment Directorate at Pacific Northwest National Laboratory, we've invited Dr. Bernd Grambow of SUBATECH, in France, to give us an international perspective on modeling of glass performance in repository environments.

Next, Dr. Carol Jantzen of Savannah River National Laboratory will give a description of the DOE approach to glass waste form acceptance for geological disposal. And then in the final presentation of the morning, we'll hear from Dr. Stéphane Gin of the French Atomic Energy and Alternative Energies Commission, who will tell us about the current understanding and many challenges in measuring and modeling the long-term performance of borosilicate nuclear waste glass.

After the lunchbreak, Dr. Ian Pegg of Catholic University of America will tell us about glass formulation and durability studies that have been conducted at the Vitreous State Laboratory. He'll be followed by Dr. Joe Ryan of Pacific Northwest National Laboratory, who will discuss DOE studies to improve understanding of rate-limiting mechanisms for corrosion under varying conditions. Then Dr. Bill Ebert of Argonne National Laboratory will give us a presentation on the DOE high-level radioactive waste glass corrosion model and its implementation and safety analysis.

Finally, Dr. Aurélie Verney-Carron of the University Paris-Est Créteil, will tell us about what we have learned, as well as what more we can learn about long-term high-level radioactive waste glass corrosion from studies on natural and archaeological glasses. And after all these presentations, we will get a short introduction to the papers that will be presented during the poster session. That's scheduled right after the public meeting. The poster session presenters will have two minutes each to give us a brief summary to whet our appetite for their posters, and then I hope we will have a lively discussion around the posters prior to people heading off to dinner.

So, now please mute your cell phones and let's begin with what I'm sure will be an interesting and productive meeting. And it is my pleasure to turn the podium over to Dr. Jud Virden, who will get the meeting started.

VIRDEN: Well thank you, and good morning. I'm just here to officially welcome each of you to Richland, Washington. Thank you for being here. I'd like to thank each of you for taking the time to -- personally take the time to commit to this really important function of independent assessment. I think it's absolutely critical to our scientific endeavors throughout the national laboratory system and independent assessments of the national labs, by the way, have said the national labs should be focused on long-term multidisciplinary high-risk research. I think this qualifies, at least for the long-term part of that. So thank you for taking that time, the time today, and thank you for being here.

I'd like to also thank our DOE colleagues, because many of you yesterday got to see some of the capabilities at Pacific Northwest National Lab. We steward those capabilities for the country to ensure that we have the people, the equipment, and the facilities to meet the long-term needs of the country, so thank you to the DOE colleagues who steward those capabilities for us over years and decades to ensure we have them now and in the future.

It looks like you have just a fantastic agenda. You're going to hear from some of the leading experts in each of the areas. Again, welcome, and I hope you have a really productive day, and I'm very much looking forward to the output of this meeting, so have a good day. Thank you.

BAHR: So our first speaker is Dr. Bernd Grambow, director of SUBATECH, which is the Joint Research Unit with Ecole des Mines, University de Nantes and IN2P3/CNRS, and he's going to give us an international perspective on high-level waste glass and its performance in a repository.

GRAMBOW: Thank you very much for this nice introduction. I don't know what I should -- I need to wait for my presentation, otherwise it will be difficult on this one. No problem. So, just to recall, SUBATECH is a French laboratory of nuclear physics and nuclear chemistry somehow, and so we're working on many areas in nuclear waste disposal, not only on glass but also on the other barriers. So, you will see, also, in my presentation not only the vision from glass performance but also on repository environment. Both of the things are linked. Glass properties are not an intrinsic property of glass but depends also on the environment. And now I need to learn how this goes to the next. Okay.

So, first, a general slide, just showing what are the controls -- it's a little bit busy, but what are the controls of glass dissolution, and what's a control somehow of radionuclide release. We're interested in glass because we want fixed radionuclides. Now radionuclides can be linked -- controlled by the glass dissolution, by the kinetics, but they can also be absorbed on solid reaction products. There can be solubility controls for them, which mechanisms then dominate will depend on the radionuclide itself and the environmental condition on some of them are solubility controlled or kinetically control and so on, and solubility control is sometimes difficult to assess because the pure phases are typically not formed but mixed solid solutions and things like that. However, often simple solid alteration products can describe solution behavior. There's some examples, like cesium typically can be rather soluble during dissolution of glass while actinides are rather insoluble. They will be blocked.

I will just recall a statement, which was made in one of the U.S. reports on glass dissolution, in which case there was a statement saying that essentially the release rate of radionuclides can be calculated by multiplying the glass dissolution rate to surface area and the inventory of the radionuclides. And I would somewhat oppose this type of view, because radionuclide solubility is a very important issue, and the release from the glass is much, much lower than calculated only by the rate of glass dissolution. This is not a defense in depth. I will come to this question rather later.

Now here I show you some slides, for example, plutonium release from borosilicate glass with some work, which we did some years ago with Dhan Rai here from PNL, I think as well PNNL. And what you do see is, for example, areas in which kinetic controls of plutonium released by glass corrosion, maybe even here. This is very, very low, very small areas. Most of the parts, plutonium is controlled by solubility either here in the oxidizing environment, like you would expect in Yucca Mountain, or a relatively high solubility or in reducing conditions, like in more European repository concepts with very, very low concentration. But this difference has nothing to do with the stability or not of the glass, it is just solubility of plutonium, which makes the difference.

Now there's also other barriers, as I said before, the glass itself will be surrounded by different types of barriers. This depends, of course, on the repository concept. I took here, as an example, a glass with bentonite environment around, and so the ground water would come to the glass through this barrier, and radionuclide will release across this barrier as well.

And now I have here in this diagram the release of fraction of inventory per year release from the glass through this overall barrier and finding out what is there, the controlling mechanism. It depends of course, a little bit on the thickness of the bentonite. But what you do realize is that for actinides like americium or plutonium doesn't really matter how fast the glass dissolves. The release is always controlled by the transport and the absorption on the clay, and there will be decay of americium and plutonium a few centimeters close to the glass. It is essentially a very strong barrier.

And on the opposite you find iodine, cesium and other types of elements quite depending on glass dissolution rates. So the boundary of bentonite is not sufficient to fix it, and, indeed, we have a glass dissolution rate as an important parameter.

This is also some Japanese study, which has coupled the two things together experimentally. We have the glass and around you have the bentonite environment, and then you just measure as a function of distance the plutonium release coming out from the glass. You have the bentonite barrier around, you cut it in slices, and you look just for the plutonium concentration. And you can see that here, one in case, this is for cesium, this is for plutonium. The release can be very nicely described and predicted also using KD concept for release for absorption inside of the clay barrier. The clay barrier is a key barrier in this release, and I think we need to look for a coupled understanding of glass dissolution and its environment, looking radionuclide by radionuclide to have a vision of what's ongoing.

So just coming back to the word defense in depth, in many performance assessment concepts, glass dissolution rates control only very few, if any, radionuclides. In many cases for those contributions of other nuclides, it sometimes suggests that it's okay, but we still have defense in depth. The glass will still dissolve somehow very slowly, so plutonium should get an additional barrier by glass dissolution. My point, it doesn't.

My point is that control, like solubility, are, first, very strong concepts. If you abandon them and look for a second barrier, more stronger than this, then the burden which you put on the glass is too high. The glass would dissolve too fast, and plutonium would be released too much. Here is an example. What would happen if all radionuclides would behave like iodine in the glass, controlled by -- release controlled by the glass?

This is an ANDRA calculation, in which case ANDRA is a waste management agent in France, in which case the dose is calculated. Considering all the barriers in the repository you would see that the nuclear waste glass is effectively controlling iodine and so on at a very low level. Here is a dose threshold, so we have about three orders of magnitude lower than a dose threshold. So we're relatively happy with the situation, even considering that only 1% of the iodine is in the glass, the rest, 99%, is in the ocean.

And then we have here another situation, and that is if we assume now that plutonium and so on -- or neptunium would be released like iodine, then I just take the toxicity --

inventory of toxicity here as a function of time. This is the yellow curve. It's an iodine curve. And now the neptunium curve would be this one here, and which is much higher than the iodine curve and so on. So, putting just the neptunium on and just having the same ratio as you have here and considering that there's 100% of neptunium in the glass and only 1% of iodine, you get such a curve, so you have bypassed the dose threshold. And I think for the safety case it is important, that the weak contribution of actinides to disposal risk is linked to weak solubility and strong retention and filtration of colloids and the actinides and technetium would be very close to release limits if they would behave like iodine. And I think the defense in depth concept is not sufficient.

So now we come back to some questions, which you have seen also in the agenda, I think, which I should respond. What are the various approaches modeling of glass corrosion in the repository environments, and how do the different countries take account of glass corrosion and release and so on? So, to address the first one, what are the various approaches to glass dissolution modeling, and just a general scheme, which has been many, many times developed with an initial interdiffusion, hydrolysis, and then slow down of reaction rate by either diffusion and by affinity controlled processes then a residual rate, and then maybe alteration renewal after some long period.

If you look for the knowledge in this area, I think this very early process, there's very strong knowledge available of course, everything can increase, but I think that it's not critical for glass dissolution, but I think there's very strong knowledge available.

On this question of release decreasing rate, there was a strong dispute the beginning of the century, but right now I think this has been somewhat settled, find out that both diffusion and affinity together control the decreasing rate. Then, still, and the residual rate, I would still think that there's still only empirical knowledge with some qualified explanation. I would still think that we are not yet at the position to really describe the full mechanistic model here, and then for the long-term part, there exists also some ideas, and I think it's not yet entirely understood now for this renewal.

Now the environment, and, again, quite different in the different steps. In the beginning, the initial rate may be only depend on pH, temperatures, glass composition, while later on, for example, the decreasing term will also depend on the volume of the water, the flow rate of water, of other materials present, like iron and clay. So this would be very complicated function depending on many, many parameters in the repository. The residual rate on the other hand, again, on much less parameters, and this decreasing function. There is this whole coupling with environment and with the near field and is essentially in this decreasing term included.

Now, the first part, this is a very old diagram already. I just put it back in again to say where this affinity concept comes from. You see the [inaudible] relation, which is also described in the U.S. report, and where you see affinity-derived to glass solution. Affinity does not mean affinity with respect to between the solution and the glass, but the glass hydrolyzed and hydrated and is essentially affinity between this hydrated glass and the solution and not between the pristine glass, and so on.

We developed, in time, some additional parameters to this type of model including mass transfer resistance for silica in the gel, absorption of silica in the gel, diffusion of water, variation of pH, and many other things which I'm involved.

Just an example of very old data, so this started in the end of the '80s, and there was 14 years of leaching data, and they were all plotted in a single diagram, normalized time multiplied by surface to volume, so some kind of simplification of normalized concentration in solution. All data fell somehow on a single line; therefore, leaching of a French reference glass. And what you can see is here that you could have done in 14, in 35 days about the same. You could have got the same result in 35 days than you could get in 14 years, which means that you are able to predict things, and so on. You could distinguish this whole process from this initial maybe protective gel, at the beginning maybe not protective, whatever, the affinity term and the other diffusion part, different mechanisms. So, I think this early part here is relatively well-understood, and this long-term part, we still have here some more empirical approaches, even if we give it now here a diffusion coefficient of water, I think there's still a lot to learn.

This is taken from a PhD thesis of Diane Rebiscoul, showing how the glass during different steps of this process somehow becomes densified, the layers which form become densified and so on. You see here that the density changes with the degree of alteration and so on. However, there's also some other data which shows that even in the absence of -- that without the gel layer, that the de-alkalized layer will have about a very, very high density.

Modeling of glass corrosion can also be done by Monte Carlo calculation, so we see here some data from Ecole Polytechnique in France, and there you see how the gel somehow gets larger and thicker and thicker with time, and it gets more dense here with time. So, between here and here, there's only very slow variation of thickness. Even so, the time increases by a factor of five and so on. So there you see the slowdown of reaction rate predicted by some kind of calculation special and so on.

However, this alone cannot explain all the data. It is quite often observed that even without a gel, without all of these layers, the glass corrosion rate would slow down as well. And it's a dissolving phase stabilized by recondensation of silica and not the secondary phase, which the gel would be a secondary phase. The affinity concept still has a role, and so we have a key role of this reacting interface between the glass and the gel somehow. This interface, the gel is interfaced with a solution, but it's a reaction product. It's not a dissolving phase. The pristine glass is modified by hydration water and by alkali exchange, so it is not directly in contact with the water either. So the interface between the two is what is sometimes called passive reacting layer, the PRI, or the interface diffusion barrier, and there are many names, but essentially, I think it's still the hydrated layer between the two, which makes a difference.

We have, then, these GM models, which somehow presented the different steps in glass solution, from the initial dissolution from silica retention, saturation processes, and advection in the aquifer around water diffusion in some kind of diagram of capacitors and resistors in some way, the different versions of these things. I will not go into detail, sometime just to show that if two processes are here in line, two resistors in line, the rate would decrease, and if they are in parallel the rate would increase and this would have competition in here and this type of thing.

The grand model, developed essentially by the French group, and maybe Stéphane will tell you a little bit more about it. There's water diffusion in this interface layer, this hydrated layer, and then you do have dissolution of this layer from the outset, formation of secondary phases, and then moving of this layer into the pristine glass. Mathematically, from my point of view, it's rather similar to the GM model that more -- the terms are interpreted a little bit different, but I think mathematically it's about -- from my point of view, it's about the same.

There's a fresh -- we can have a fresh look at glass dissolution modeling. By paper just printed getting out this year here from Chinese colleagues. They did a detailed analysis of all these models, of the GRAAL model, which I described briefly, the GM model, and so on. And they said that somehow we all agree on it, that diffusion and affinity are not contradicting. Controlling different reactions are taking place concurrently as if together somehow. Water diffusion controls reactions that occur rapidly, such as ion exchange and reactive diffusion, chemical affinity controls the distribution of silica among the different alteration phases, and the two mechanisms not only control different types of reaction but affect each other also.

This model somehow defines different steps, somehow different modes of operation of glasses which could be first order dissolution rate, controlled secondary phase control for final rates or final rate controlled by the diffusion in the interfacial diffusion barrier or complex behavior coupling all of this. I thought it was a very nice and interesting concept. There is one problem of this. Here you see this more detailed diagram of the pristine glass, the diffusion and so on, the hydrated and interfacial boundary, and then precipitated minerals and the solutions. I thought it was a very good understanding of the current discussion in the area of nuclear waste dissolution modeling; however, there is a small problem. Now I went the wrong way. Okay.

There's a risk of over interpretation of data. This model gets very complicated. There are very, very many parameters. We had had a project about ten years ago. It's, of course, called Glamor, financed by the European Commission, showing some of the difference. The same data could be explained equally well by different types of models. And the parameters in the model may have different significance. The question is how to treat model uncertainty if it is coupled to data uncertainties. Both things are interlinked. Waste management organizations choose, typically, a model without looking for all the other models. So they are just choosing, say, the Department of Energy working on this -- this laboratory works for the Department of Energy, so everybody would use this model, the French would use another model and so on. And so you try to optimize this, and but the question of parameter uncertainty and model uncertainty, to me, they are interdependent, they are not alone.

This is now just to show an example. This was a previous version of a CA model. It's not a recent one. But I just took it out of the shelf in some way. You have the time here, and you have concentrations. You have two interpretations of the same experimental data by two models. Okay, you can say this one looks better, or it's this one. It's not the point really, which looks better. The point is that the parameters describes the one or the other entirely different. Here you have, for example, no water diffusion taken into account. Here water and diffusion is integrated. Here the silica diffusion coefficient is 10 to the minus 21. Here's 10 to the minus 13. That means the same processes somehow are explained entirely different. And the reason is not that the diffusion coefficient of silica varies by all the uncertainties, but it varies by a factor of eight orders of magnitude. The difference is only that by integrating this silica diffusion coefficient in an overall model, you attribute, it functions somehow to describe experimental data, and then it's just a fit. So I think it's really an important point of this type of data.

Another challenge is interdependency of parameters. Here we had two examples using essentially the same model but using just different data. I wouldn't say which one is better of the two, and in one case you had a silica saturation concentration of 300, and one case was 1,100, and you could see here a curve of silica saturation concentration as a function of diffusion coefficient of water, quite strong dependency of the two though. And I think there's very little work done in this community on interdependency of parameters and so on, and, really, so I think there needs to be more work done.

The second question now, how different countries take into account glass corrosion and radionuclide release. You see here Germany, for example, takes about this GM approach with different -- described it somehow briefly before already with -- this would be the saturation part, and some other long-term rate slows down with the square root of time, and then the final rate somehow being dominated in the long term. Here you see the reaction rate. I will just go to the next step.

And the UK, on the other hand, they have about 2,000 tons of glass to be considered by NDA. The statement I think is important here. There's sufficient good understanding of glass dissolution mechanism to allow the dissolution rate over long-time scales to be predictive.

Now they used a model which is just a linear model with LogTri probability density function somehow to describe the behavior in a statistical manner, with an average value of about 7 times 10 to the minus 6 as a fraction of inventory per year to be released, so the glass would be dissolving about in some 100,000 years completely if this would be the average value.

They are not dissolution rates as defined by experimentalists. They are derived from parameters that include information about particular waste form, disposal concept, and scenarios to be modeled. They ignore that glass dissolution rates are a function of time. They ignore the influence in environment, and so on. And the hypothesis is that after container breaching, somehow everything would change only very little.

The dissolution rates of HLW glass are largely based on French and Belgium programs, and to a lesser degree on the UK program. The two dissolution rates are higher for the UK glass, which is magnesium rich, about by a factor of 10 than the French glass. For one thing they may have to consider in the future is the behavior of the glass in the environment, alkaline environment because they may think codisposal of intermediate-level waste and high-level waste, and if they do this they may have an alkaline plume to take into account. Also important is the cracking factor of the glass.

In France we have a model more -- just a schematic model, which I think is quite interesting. We don't only have the dissolution of the glass, we have of glass hydration. In France we put the glass in a clay environment, so this takes about 1,000 years or more until the water really comes to the glass and so on. So there may be a large time period of some thousand years in which the glass is just exposed to vapor. And so this first phase will, of course, hydrate the glass and this rate, which decreases with time. At some moment, liquid water would come in contact with the glass, and so you would dissolve this initially hydrated glass, which is not dissolved, it's just hydrated, would dissolve in a single glass, and then you would have release to continue.

But even there, I think in France, impact of environment, we've just discussed the -- I just mentioned the GRAAL model. It would not be able to describe all the complicated interactions of environment, which includes container corrosion, the initial part, which is hydrated part, resaturation and so on. And there's lots of what-if scenarios to take into account of container corrosion, silica forming because silica has been absorbed. So all of this is rather complicated to be included.

In Switzerland we have essentially, as I have mentioned already in the UK case, a study based on long-term dissolution rate of glass, either of the French or the UK glass, of the two, they get dissolution rates for the UK glass about one order of magnitude higher than for the French the glass. They also consider the sorption of silica in the clay as a potential retention barrier. And temperatures were not considered in the case -- in the study. Cracking factor is considered equal to a factor of 12.

In Belgium, there are two cases which are interesting to compare to each other. One case before 2000, they had the four source term models with fracture factors between 5 and 27. Reference dissolution rate of 0.002, and then the worst case, the solution leads to dissolution in about 20,000 years, and the reference case would be 72,000 years of complete dissolution. And when they saw all of this, sensitivity analysis had shown that the glass had only very limited impact on the system, so this was very intriguing to them, and they made an engineering solution. They said, okay, if it's like that, forget about the glass. Forget about the glass entirely. We'll build a super container around it, which is essentially a container filled with cement. So there's cement environment around the glass. The cement will stabilize the container for corrosion or low corrosion rate, and then the glass may dissolve fast, leading to faster dissolution rate. But since it's anyhow too fast, no problem. This was somehow the -- so I think it was very important.

And then there was a study of glass stability after 2000 in concrete environment, where you see that the corrosion rates could be quite high in this type of environment. If you'd still consider the cracking factor, it will be important. Very important here is, really, to understand in detail how the corrosion occurs in each of the cracks. So there's lots of work to be done, and I think this is, for the overall community, important to have this really module metric description also of corrosion, how it is ongoing.

In Japan we do have more generics. I don't have yet a repository concept. It's a more generic concept there. This concept considered cracking factor of about five. The glass is surrounded by bentonite and the dissolution rate is about one milligram per square meters per day for, 60 degrees.

In the U.S., the cracking factor included was for -- 15 was included. Maybe now more recent data is I think probably -- Carol will say this better than me and so on. And then an increase cracking factor of about 600 was used for 1% of the container due to the possibility of accidents in handling the waste, there may be even cracking during handling and so on.

If I am just making a summary of this data, it's not my summary, it's a summary from the OECD in here, which looked at the different barriers concept, glass as a key uncertainty in the engineer barrier system and glass as a key parameter for the engineered barrier system. And a key uncertainty is that none of the countries it is considered a key uncertainty, while for the engineered barrier system, as a key parameter it's considered important in France and Japan and in Switzerland, and not necessarily in the other countries.

The second question, what are the remaining technical gaps or uncertainties in understanding and modeling of long-term glass performance in repository, how important is the glass performance in the overall safety in different repository concepts. So I will just record to you, or I will inform you probably even that the European Commission is ongoing to making a new European joint program starting in 2019, and with a budget of about 30 or 40 million Euros, not only in or not even largely in the area of glass, in many other areas and so on. So we had already a two-years preparation phase, which was called JOPRAD, we had a strategic Research agenda in the JOPRAD Program developed, which will be the base of the joint European programming, in which case the glass was taken into both for intermediate-level waste and high-level waste.

The key research items in the Strategic Research Agenda was the impact of fracturing, hydration under unsaturated conditions, interaction with surrounding materials like carbon steel, corrosion products, concrete, resumption of alteration rate, the influence of irradiation on the residual rate, the mechanisms governing the residual rate, the influence of composition congruency between glass alteration and radionuclide release, and improved understanding of coupled interaction between reactive transport and corrosion of glass in the near-field environment. I think that's a very large program now. This program is heading for about the next ten years at least, so we will just start and suggest in the process of building. I think also foreign partners can participate, on own cost of course, in such a program.

For the GM model, which I described, I think that many things are also necessary to include. I will probably not do it, but I think it's important to mention the GLASTAB project has, for example, shown that gel can be simulated as a solid solution. It's not yet included. The description of absorption of silica in the gel is in this type of model is still too simple. The evolution of passive properties, diffusion of silica are not taken into account as a function of structural evolution of this gel, and absorption of radionuclide is not taken into account. So there's quite a number of things which could be improved.

The one thing which I would draw a little bit of attention to is to model evolution of the morphology and the overall glass dissolution of the fractured glass. The glass is, as we have learned from all these previous modeling exercises from the different countries, at least a factor of ten higher is the total surface area than the geometric one. And just taking, for example, some calculations, it's about 110% increase in aperture due to dissolution result in an estimated permeability, that this would result in a 100% increase in apertures of certain parameters would result of the void space, which results in an increase to about 500% of difference for Peclet numbers and so on. So, I think it's very important that this -- the mass transfer resistance, a cross section barrier and the corrosion rates inside of this barrier needs to be better calculated. So there is some data on Lattice Boltzmann calculations that suggest that there's a coupling between transport and morphology and so on. But I think this should be done for glasses, was for rock, this should be done for glasses and so on.

Glass hydration is important. As we said, seen in France, it is at least for 1,000 years just vapor phase present. If you have Yucca Mountains, there's a long time of vapor phase presence, so the transition between vapor phase and liquid dissolution is very important to calculate. So you see here some data showing that also in case of vapor phase hydration the hydration rate he described by the silica absorbancy, analyzing by infrared spectroscopy, would somehow slow down with time, and the rate would decrease and so on.

We need to have an overall mechanistic view on worldwide data generated since '35. This was a slide, which I had adjusted this slide after discussing with Jim on this question. There's so much data generated all over, since at least 35 years, and I think the people even from your own laboratory, like in PNNL laboratory, you don't have access to all the data which your own laboratory has been generated in the past. And that's the same in other countries. And I think then a newcomer starts glass dissolution models from scratch and doing again new data, which are not necessarily better. They may be, in some cases, more fancier techniques and so on, but there's no link to the previous data.

When I talked to Jim, I said have you looked at this 11 component study from [inaudible] about 30 years ago? He doesn't even know it, which is normal for him, yeah. But I think there are so much studies which have been done. Okay, I see I should stop, and I will just continue. Just we have, then, quantification of pumping effects to be considered. That means that near-field materials would increase the dissolution rate with time and so on, and this could be bentonite, magnetite, and so on. This would be -- this pumping effect needs to be more systematicized.

Other subjects would be the critical release of anions from the glass. There's very little studies on anion release from glass as many is on cations-- the belief is always that cations like boron, things like that, would be somehow a summary of the rest. I'm not sure. I have not seen a single study on iodine release from glass. Even so, iodine is a key radionuclide, at least in France. I have not seen a single study on selenium release from glass and so on, even at other key points.

Then 3D modeling of fractured glass, I mentioned already somehow, and the future challenge of the computational molecular modeling on glass dissolution. So that's all. Thank you.

BAHR: Well, thank you. Do we have some questions from the Board? Paul.

TURINSKY: Lifting weights.

BAHR: Okay.

TURINSKY: Turinsky from the Board. One is to confirm what I think you said, and that is this issue of time scaling from experiments to repository times. I get a sense that that is not a major issue; that you feel confident that those time scalings?

GRAMBOW: No. I think it is a major issue, and I think we tried to do this with the surface-to-volume change and then to simulate long times by very high surface -- by surface to volume ratios higher than [inaudible]. But I still think we should be doing more work also on coupling this type of laboratory work. I didn't mention this, and so you're right, I should have maybe, with analog studies which would cover somehow the range all the way to a hundred thousand millions in years. And in particular, not only to show that these things exist, but also to apply the same mechanistic models, which we do apply on the laboratory glasses to this type of long-term data. So, Stéphane did some work in CEA on this. We did this about 30 years ago, I think, already been brought in some areas.

But also, there I think one should take into account all the data which has already been generated by the community. There was some old reports from Rod, for example, in this area, maybe 40 years ago right now, and in 2000 -- in 1979, a PNNL report on national analogs of glasses, and it's not even quoted in the more recent publication of the same laboratory. So I think there's many of these things which could be done and which could be improved, and I think my point is this overall vision needs to be generated if you want to have credibility. If you have confidence always generating a new data point, it does not need -- without really taking reference to the overall picture, I think that's a key message.

TURINSKY: Okay. And a second question. This community doesn't use Bayesian inference techniques, which is, you know, a systematic mathematical approach to incorporate new data? But your description of how these parameters, some of them can be so unrealistic, that would also reveal through their uncertainties and their covariances the linkages and the uncertainties, which would basically disqualify a model if you soar basically very, very large covariances between various parameters.

GRAMBOW: Yes, you're right. You're right.

TURINSKY: So does this community use this?

GRAMBOW: Very little. Very little, I would think. And I would also think that -- so I'm heading a laboratory with nuclear physics, so we're looking for the data of sound and we're trying to find the boson of Higgs and this type of things. So, yeah, you have millions of data and you have procedures how to really get the important data out of a lake of unknown, yeah.

And I think this is something which one needs to develop. And I think it's not good just to take -- I don't know --

some new logic and just having fussing around with our result in a big box and trying -- so we still need better mechanistic understanding. We can maybe have a good model describing data existing. If we have not the confidence that they are also relevant, not only for three, four years of laboratory work but also for 300,000 years, and so on, in the field, in that case the only link to this is understanding. So, having just big data approach to this type of thing would somehow fail as well. So I think we need some kind of coupling of such a big-data approach with some kind of mechanistic understanding and guiding these key mechanisms through this, maybe. But also, I think this is very important.

TURINSKY: Yeah. But many times we get that understanding by more by single effect sort of experiments.

GRAMBOW: You're right. You're right. So we have this -- we need to combine both. We need to combine the single effect approach with the overall system. And sometimes, lots of time, we have single effects which contradict these, where author doesn't know the other data and so they have -- for the publication it's sufficient because the author doesn't know it, so it's sufficient just to get things publish, but it would not really, I think, get confidence.

BAHR: Other questions from the Board? Sue.

BRANTLEY: Sue Brantley, the Board. Thank you for that talk. It was great.

BAHR: You want to pull your mic.

BRANTLEY: I'll try. I guess I would like to return to the natural glasses and this problem that you were talking with Paul about with the interdependence of parameters and not knowing which model was correct. One thing you could do is take your different models and make prediction for natural glasses and see how well they predict, because over the long time frame the different models will, you know, predict different discrepant time durations that a glass might remain in an environment. So has that been done?

GRAMBOW: Well we have done a little bit, but now I'm coming to 1985, and so on, in which case we had used, for example with Rod in Albuquerque at the time, some natural glasses from ocean-dredged sample and so on, some of them covered with sediments, others not covered with sediments, and you can also the age know relatively well, and they were all covered with water, so the conditions were relatively simple. We could see that these affinity types of approach with an initial rate in an open ocean environment to the more saturation approaches in a sedimentary environment and so on could be somehow be described. Now I think this has never been done in a very systematic way to really cover our complex understanding which we have today, which is not just saturation and so on, but also the whole fracture network, and I think Stéphane has done some work, and maybe he later on can comment on this, in which you have ancient glasses and looking inside of fractures how the corrosion is ongoing with respect to outer surfaces and so on. So, I think there's a couple of work in which some confirms the approaches taken, but they are not necessarily to the level that you can really confirm long-term rates and things like that, which are the key parameters in this area.

BRANTLEY: I mean, I think it's interesting, the natural analog approach is interesting because it allows you to tweak one variable over a large scale, mainly time, which you can't do in the laboratory. Is there some reason why the natural analog experiments haven't been followed up as much as the laboratory experiments?

GRAMBOW: I think it was always individual initiatives of individual people, and it was never really a national program in none of the countries, neither in France nor in – Stéphane did this on his own interest. We did it on our own interest. Rod did it on his own interest. But there was never some kind of systematic approach from a national program on this.

And it was recently, we had -- in 2013, the European Commission had this [inaudible]-based conference describing all the different things. And so the commission is funding the last five years and so on. There was a clear message that national analogs should be studied more deeply. However, in this JOPRAD exercise of European joint program I would describe by the different countries, the national analog thing was included but rated rather low. That means the rating was done by asking the different countries how do you want to participate in this. Tell me what you want to do and things like that. Natural analogs did not get a high rating.

BRANTLEY: So, on a different tack but somewhat similar, obviously there's been a huge amount of data collected, and you were mentioning this yourself, just the need for sort of meta-analysis of data that exists, and Carol Jantzen has talked to us about that. I think, you know, when you think about putting glass into a nuclear waste repository, what you might worry about is why would the rate get faster? I mean, because normally we take a lab rate and you compare it to a field rate, the field rate is slower, and that's reassuring, so it's going to dissolve even slower than you might predict. But I think there are some cases where the rate could actually increase. I mean, certainly there's the Stage III or stage four, you know, where something else precipitates and it starts dissolving faster. Can you just talk about the different mechanisms that you know about that might make the rates be faster in a field system than in a given lab experiment and, you know, what do we need to do to understand why it might become faster?

GRAMBOW: We had published already some first work in this area in 1988, with Pierre Van Iseghem from Belgium, in which case this type of rate increase was explained by formation of zeolites, which somehow eat up the silica, which you would need for slowing down the reaction rates. Now this, I think there's a systematic study in Marcoule Laboratory on this, showing that the link between this speed up of reaction rates on the one hand and existence of either CSH phases or zeolites. So I think this link is important.

Now, I saw I think one important thing also from the U.S. glasses, all of this related to alkaline conditions. Now in European glasses the pH is about 9 or 8, or something like that, even for the very long-term, and I think this effect would not exist. But if you put -- now Europeans, this is French conditions. Now, put this to Belgium conditions, you have pH of 13. There you are in the range where exactly these processes occur, where they are important. You have some of the U.S. glasses which have sodium alkali ratios, sodium boron ratios somehow, with more sodium less boron, and in a certain way, some of these glasses would go to very high alkaline condition, and you may find the same things as well. So I don't know how -- this was my understanding now ten years ago. Maybe things have changed quite a bit. I don't know the actual situation in the U.S. on this area.

But I think the glass composition itself has a pretty key role in whether the pH keeps in the pH 9 range of lower, or whether it drives to pH 11 and 12. And I think there is a difference also between this resumption of rates when you go to the pH. So I have never seen -- maybe I'm ignorant, but I have never seen a rate -- resumption of glass dissolution if you had pH 6, pH 9 range.

BRANTLEY: So I was asking what might make the rate faster in the field, and you talked about precipitation, so the precipitates.

GRAMBOW: Yeah.

BRANTLEY: Are there other mechanisms that could make the rate faster in the field that you've thought about or that we need to be thinking about?

GRAMBOW: I don't think so. Maybe fracturing, but I don't think so. I think the fracturing, what I've seen some people talking mechanical effect makes this -- fractures the glass more. I think what we have studied in this area, this may occur, but it is rather low, a low effect. I wouldn't consider this important. Now, other effects would be chemistry. But the chemistry in such a geological environment is rather well constrained, so I don't see it neither. Now what is relatively little understood right now is the vapor phase hydration phase. This part, I think, I would -- we see zeolites and things on the surface of such glasses, and so there may be an effect.

BRANTLEY: And what about biological effects?

GRAMBOW: There were some studies done by, for example, in the University of Strasburg in France on this, on the effect of microorganisms. To my feeling, when I have seen these effects, but they are local. They are not global effects, and also the glass is very, very radioactive typically, so you need some very radiation stable glasses, microbes being present and so on. So microbes could play a role, but I think probably not a dominant one.

BRANTLEY: Thank you.

BAHR: Other questions from the Board? I'll ask when you, in comparing the different modeling approaches that different countries are using, some of them -- it sounded like most of them are using either a single rate model that's based on residual rate that you get after the initial one.

GRAMBOW: Yes.

BAHR: Or in some cases they're using a two-phase, two-time period where you have a fast initial rate and then it slows down. It looks like none of them are incorporating that resumption at Stage III that you characterized as a poorly understood process to begin with. How important do you think it is to understand that Stage III and --

GRAMBOW: I think it is important, and it's one of my key arguments also, when discussing with waste management organizations like ANDRA. But it's not related only to glass. It's a general question. That means safety analysis today -- maybe in the U.S. it's different, I don't know -- does not include or rarely includes chemistry. So that means even sorption is studied by a KD, that's all. Solubility is look-up table. It's not really chemical evolution. So, in such an environment, in which case you have just key parameters from look-up tables put together in very complicated transport models, I think you cannot do other things.

What I'm looking for is a fully-coupled chemical model which includes the chemistry of transport, the chemistry of sorption, and the chemistry and double layers and surface complexation, whatever, depending on different parameters. All of these things are not yet included, I think, worldwide in safety analysis, and so I think Yucca Mountain was -- no, in the WIPP site, there was some inclusion or at least of the thermodynamics of -- for actinides and so on, with the saline solution the question of Pitzer model and so on. So, I think there's, probably in this area, the most advanced type of chemistry inclusion in types of safety analysis. Normally it's not done.

BAHR: What's your guess as to how that would change the conclusion of a safety analysis? Would it change --

GRAMBOW: I think it would change quite a bit. But I think it's now -- I was just discussing with Carol, I am getting old, and she didn't even recognize me. So that means I'm working since about 35 years on this area, and my critics about 30 years ago was already, why do you do look-up tables? Shouldn't you really include chemistry as a functional dependence on pH, on carbonate pressure and whatever? You should have this functional dependency integrate. Now we are 30 years later, it's still done. It's still not changed. So my feeling is -- but now there's also another question of time, is that the repository will not be built tomorrow. The repository, even in France, where we think 2025 we will have our first repository, we will have the first glass to be put in the French repository in 2075.

So it is about 50 years later, after opening the repository. So the models, which we have here we have described and discussed, needs to be developed for the next 50 years.

So, 35 years ago we worked on this already with glasses. I did my PhD thesis on glasses and so on. This was simple polynomic description and so on in the beginning, which described predicting things. Today we have mechanistic models, but maybe in another 50 years we need to have molecular models and so on. So I think we need to inscribe all of this in time, and evolution of time on knowledge to get credibility and so on.

BAHR: Thank you. Other question from the Board? Tissa.

Illangasekare: So the models you presented are based on individual processes understanding of dissolution. But when you go to the field you are looking at large systems where the effective dissolution behavior can be quite different. So is there any work going on primarily it’s more an upscaling problem, any work going on when you understand the process at the smaller scale to larger systems and all these others parts come together? And you sort of mentioned indirectly that the interdependence of parameters. Interdependence of parameters, in my view, is because when you go to larger systems they sort of -- they are related by the large-scale behaviors. So any work done in sort of upscaling this understanding from a smaller scale processes to the larger modeling scale?

GRAMBOW: I think there's done a couple of work in this area. Also, experimentally effects of having full-scale glass block or having one centimeter square glass chip, there's already quite a tremendous difference. In CEA, there was done some work on this large-scale experimental approaches to this. Now, there were also coupled approaches, in which case you have a mockup somehow between the glass inside of a clay environment and some iron present, and so then you understand the different interfaces and analyzing these modern techniques like EXAFS and with -- I don't know -- with electron microscopy and whatever, yeah. So, I think at that level, some of the work is done, which could probably be much more.

What is more difficult is this complex systems behavior to do this on a one-to-one scale, because then the time is too slow. Essentially nothing should happen for the first thousand years, and you don't have -- you work only two or three years. So I think there needs to be more modern techniques developed to have at least doing this upscaling in a step-by-step approach, and verifying each of the steps, that the steps are taken correctly and so on. So there's still lots of work to be done. And upscaling is one of the key points also in this European joint programming I just called.

BAHR: Do we have any questions from the staff? Bobby.

Pabalan: Roberto Pabalan, Board staff. Bernd, you pointed out a number of studies that would help improve our understanding of glass corrosion rates and mechanisms. I know you mentioned we can spend the next 50 years improving these models. But you also pointed out early in your presentation that, you know, glass corrosion is not the only factor important to radionuclide release. You can have solubility limits and sorption processes. So, given that, especially in a reducing environment for clay repositories do you think we still need to do these additional studies, or do we have sufficient and technically defensible basis to do performance and safety assessments?

GRAMBOW: I think we have good technical basis to do performance assessment using the data which we have. I would not discredibilize the approach ongoing right now. Yet, I would think the word sufficient is not correct, because sufficient relates that we don't need to do more. I think we need to do more, because the knowledge is increasing; that even if we show today that we can somehow predict glass behavior over time, there are many uncertainties still involved. You need to present this in front of public and so on. People may not believe you, or you may involve experts on glasses, which tells you, yeah, this process has not been taken into account. And so if we do not continue developing our understanding in this area, we would somehow lose credibility and even at the end it may be safe, we need to show that it is safe, I think that needs to be -- the demonstration part. And the demonstration part of safety, somehow by models and by performance assessments, is evolving with time, and this is because knowledge evolves with time. What's credible today will not be credible tomorrow.

Pabalan: Thank you.

BAHR: Any other questions? We're just right at 9:15, which is when we're scheduled for a break. So we'll start again at 9:30. Thank you.

BAHR: Okay. Well welcome back. It's my pleasure to introduce our second speaker for the morning, Dr. Carol Jantzen from Savannah River National Laboratory, where she's a consulting scientist. Dr. Jantzen has a PhD in material science and engineering, with a specialization in glass chemistry and has 37 years of experience working on glass waste forms. She's a past president and distinguished life member of the American Ceramic Society, and she's also a member of the National Academy of Sciences Nuclear and Radiation Studies Board, and she's going to tell us about DOE's strategy for Glass Waste Form Acceptance for Geologic Disposal.

CAROL JANTZEN: Well, good morning. I feel like this is the second part of the history review, because Bernd and I have been in this field for 35 to 40 years, each of us, and so I'm going to try and relate some of that history to you, at the same time, trying to answer the questions that the Board has asked. And I will say to the Board that you have asked some very thoughtful and thorough questions.

I was asked to speak about four things. I'm going to try and take these two at a time, because the first two are actually intimately related. The first one has to do with standards that we've developed, test methods, databases, and models. The second one is what is the technical basis for applying the results of short-term tests on reference glasses, or glasses with simplified compositions to assessments of long-term performance on more chemically complicated high-level waste glasses in repository environments.

So, as a preview to what I'm going to tell you, I would like to give you the short answer to question number two. The waste form producers use short-term tests because if we're testing a glass that we're making during production, we can't wait a month or three months or three years to get an answer, so we use short-term tests. While the repository people, whose technical basis for the repository modeling uses a combination of both long-term and short-term modeling.

Now it just so happens, around the year 2000, that the people who were doing the repository modeling demonstrated that the short-term PCT-A test for the environmental assessment glass standard actually was an upper bound for their repository modeling. So I think there's been some confusion that these short-term tests form the basis for the repository modeling, when they do not. The repository modeling uses a plethora of different kinds of test responses. And you'll hear more about that from Bill Ebert and some other speakers this afternoon. But I just wanted to set that straight, because I'm going to talk about it, and then they're going to talk about it later this afternoon.

It's kind of the same thing with the simplified compositions. Our standards are actually 15 or 20 component glasses. The only thing that we've really simplified is to take the radionuclides out of some of them so that it's easier to do the experiments. But you can't take the radionuclides out of them unless you've done the studies to show that taking the radionuclides out doesn't alter the mechanism or alter the response that you're looking at. So they really are not simplified compositions, and I was going to actually cross that out, but I didn't on this final version of my slides, so we'll talk about that some more. But three quarters of my talk is actually about the testing and the standards and the databases, and then we'll very quickly get on to the issues to do with crystalline precipitates and archeological natural analogs. There we go.

So I wanted to start with a little bit of history. In 1957 the National Academy of Sciences recommended deep geologic disposal of high-level waste once it was made into a solid form, and this is the cover page of that 1957 report. I don't know if you can read that. It cost a dollar if you wanted to buy it at the time. In the late 1970s, DOE began evaluation of the waste forms. In 1982, there was a record of decision issued, selecting borosilicate glass. This was endorsed by the EPA and by several different independent review groups. The NRC had no objection, which basically was "no comment."

In 1982, the Nuclear Waste Policy Act mandated that high-level waste be sent to a federal repository. This was based on the 1957 National Academy recommendation. In 1985, the President ratified the DOE decision to send high-level waste to a civilian repository. This organization was called the Office of Civilian Radioactive Waste Management. Sorry, I've got the R and the W transposed. The short name was known as "RW" at the time.

In the early 1990s, the Waste Acceptance Systems Requirements Document, the WASRD, required that DOE EM develop waste product specifications. Whoops, one too far. And for any of you who were here in April of 2014, when I last spoke to the Board, these were some of the last slides I used, so this is a mashup of the first slides that I've used, so it's kind of like a continuation.

I put this together because I think the business of the governance and the regulatory -- who has regulatory authority and what kind of models are used by whom, I think, is very important. So the Nuclear Regulatory Commission is licensee or regulator of the repository. The Office of Civilian Radioactive Waste Management, RW, was the developer and operator licensee. The EPA set the standards, the regulatory standards.

So I put a dash red line through the repository, because this is, as I said, a regulatory governance-type boundary between these three organizations and the Department of -- the DOE Office of Environmental Management to whom the waste form producers, DWPF, West Valley, and Waste Treatment Plant, all are responsible.

Not only is it a regulatory interface, but it is a different type of modeling approach. As I said earlier, the waste form producers use short-term testing, short-term models to tell us what the composition of the glass is doing, whereas the repository people use many, many different types of testing and different kinds of models. We work together; okay, but the modeling and the objectives have different end points.

So we were sitting around in 1982, which is about the time I hired into Savannah River National Lab, and these nuclear waste policies decisions had come out. We were looking at multiple repositories. We were looking at, of course, the Yucca Mountain in Nevada. We were looking at several different salt deposits. We were looking, actually, at some granites up in here. And we were looking at the basalt lava flows up in here, in Hanford. So we actually had to come up with -- I'm going to call it a reasonable strategy that would fit a generic repository, because we are making canisters and waste forms now. We are half done with our sludge mission already at Savannah River. And we didn't know in 1982 if a repository would even be chosen by the end of the century. And we are still in that same position. We don't know what repository or what kind of geology we are ultimately going to go to.

So this is a pretty big job to sit around and think how are we going to, you know, guarantee that this is going to be okay in 35 to 50 years from now. And so we said how can the waste form producers comply; all right? And there were options. We could take a glass-dominated short-term durability test and eventually think that when there was a repository, the repository would have their own repository relevant test, and then we would have to relate the responses of our short-term tests to whatever this repository relevant test was. That was one option.

The other was to still to develop a short-term durability test, because we needed that in either case A or case B, that meets the repository requirements defined by geochemical and HLW performance modeling. That modeling I'm going to describe on the next slide had been done by ONWI in the late 1950s -- oh, sorry, I guess it was in the late 1970s. And then if we developed a standard glass that met those modeling requirements, then we could say that all production high-level waste glasses must be more durable than the standard glass. So this would at least help the waste form producers have some confidence in what they were making and that it was going to be acceptable in 35 or 50 years.

The technical justification for doing this were all the other testing that we did, and that other laboratories around the country did. We performed long-term tests, high-level waste glass burial glasses, natural analog testing. We performed repository relevant tests. We made rock cups out of basalt and tuff and granite and salt. We used various ground waters. I developed a technique to do low Eh experiments for the basalt repository test. We performed in situ tests. This was work of George Wick's in WIPP, in STRIPA, and in Ballidon, and I'm happy to say that some of those samples are still in Ballidon. I just talked to Claire Corkhill and we're trying to see if we can get together and figure out a way to use all of this data, because I still have all of these samples at Savannah River.

We've performed materials interactions tests where we not only have the rock tuffs, but we also glass and we had the metal, the kind of metal that you would expect with the canister, with and without crushed rock, with or without low Eh, high Eh, ground water, whatever ground water was required. We also performed accelerated short-term tests without changing the durability mechanism, and with high-level waste glass and analogs. And we related long-term and short-term testing, both radioactive and nonradioactive to have the confidence that we could take the radionuclides out of most of these glasses and still get the same kind of glass response. And I'll go into that in a little bit more depth in a few slides.

So this comes from the Waste Form Technology and Performance final report of the National Academy in 2011, which Rod Ewing and I both sat on. And so, in the early '80s, an acceptable waste form durability was derived by ONWI from geochemical modeling based on high-level waste performance modeling. What that modeling showed was that a fractional dissolution rate somewhere between 10 to the minus 4 and 10 to the minus 6 parts per year would take 10,000 to a million years to totally dissolve. This would be a block of glass without a can around it, and without a geologic repository around it. So this is just what the glass waste form, their glass waste form, would do in a repository.

This is in the middle, so the 10 to the 5 was in the middle of the 10 to the 4 to the 10 to the 6, so it finally wound up the 10 to the minus 5 parts per year was adopted as the waste form specification by ONWI, and that is what wound up in the early versions of 10 CFR Part 60.113. If the long-term fractional dissolution rate was less than that value, most of the soluble and long-lived radionuclides then borosilicate glass would provide acceptable performance for any kind of repository.

From about, actually, the late 1970s, the Materials Characterization Center, MCC, started to develop a host of tests, and the MCC, because of funding issues, was eventually disbanded, and a lot of those standards have now become ASTM standards. And these standards, whether they were in the MCC or the ASTM, provided an understanding of the glass durability mechanisms from a combination of test protocols.

Now you heard from Bernd in the talk before mine that dissolution is very complicated. In the very early stages you have ion exchange and some other things going on. You have this affinity going on. In the very long-term you have this resumption of dissolution, so you need different tests to test those different mechanistic regimes. And so there was ASTM 1220, leaching of monolithic waste forms; ASTM

1285, the product consistency test. Product consistency test, the short term covers stages one and two that he talked about. I'll have a slide about that in a minute. And the long-term PCTs cover Stage III. The single fast flow through covers Stage I of dissolution. ASTM 1663 covers Stage III. The pressurized unsaturated flow test has not been made into an ASTM procedure, but it's used for repository relevant or disposal relevant conditions. And ASTM 1308, which is the accelerated leach test for diffusive releases from solidified waste forms, mostly from monoliths. And these are the references.

So I broke this into testing up here, and then into standards down here, so they're not exactly in numerical order. From 1987 to present, we have all, in this country and abroad, been developing data to model the maximum release of, rates of, borosilicates, and we did that because we had done experiments to show that technetium 99, the various iodine isotopes and cesium, all relate to or come out as fast as sodium, lithium, and boron, the soluble species in these leach tests. They all come out congruently. So we could use boron, lithium, and sodium to basically monitor what the maximum rate of radionuclide release, because nothing comes out any faster than these, and that includes molybdenum, because we've actually done some tests recently on molybdenum.

The approach with references a part of the ASTM 1285 PCT procedure is about 12 of them, I think. So we continue to develop short-term tests and process control strategy, because don't forget we're the waste form producers for ensuring that every glass product had a dissolution rate less than this standard glass -- which I'm going to talk about the standard glass in a little bit -- at the lower 95% confidence level, based on sodium, lithium, and boron. This ensures acceptable performance, which is the waste acceptance product specifications that we have to qualify to.

From 1996 to present, we continue to test and qualify the radionuclide response of the production glasses. Remember, the radioactive melter at Savannah River started up in 1996, and in a few slides I'm going to show you the little sampler gadget that fits into the throat of the canister that we actually sample and pull out and continue to do short-term PCTs on it.

And the standard itself that was developed was the borosilicate glass. It was the environmental assessment glass that had been used to qualify the EIS and the EA for the actual groundbreaking of the Defense Waste Processing Facility in Savannah River. And this was found to bound the upper release rate, found to be acceptable again in 10 CFR 60, part 60-113.

Now, when you're developing tests -- and I showed this back in April of 2014 when I was here -- it's very important that you simulate the correct long-term mechanisms. And so you know if you want to get a chick out an egg, okay, you need the mother hen, or you need some kind of conditions that are like a mother hen; all right? And if you just do time, you know, at whatever temperature the mother hen produces, and you don't have the mother hen, you're going to get some rotten eggs. And if you decide, okay, I need some temperature to simulate the temperature of the hen's body, you know, and you go a little bit too high, you're going to get hard-boiled eggs, so you're not going to get a chick. So whichever one of those mechanisms, whether you're in Stage I, Stage II, Stage III, whichever one of those mechanisms you're in, you have to have a test that simulates the correct long-term mechanism that you're looking for. That's my famous chicken slide.

So these are the stages that we talked about in the previous talk, the Stage I, the Stage II, and the Stage III that I have alluded to. So, as I showed you in the chicken slide, different times, temperatures, different pH range all simulate different mechanisms. So glass corrosion is more complex than most people would like to think; okay, and involves a variety of mechanisms, as you can see by this slide here. There's diffusion, affinity, hydrolysis, aging, resumption, and so on. And so different tests, as I said, are needed to study those different mechanistic regimes.

The MCC tests were developed actually from the late 1970s, early 1980s, and the ones that got developed were MCC-1, 2, 3, and 4. 5 is the Soxhlet test that's used quite a bit over in Europe. The ones in red never even got written, okay, before the MCC was defunded. Some of them were about canister corrosion resistance that got written. The ones in black got written. The ones in red did not get written.

These were supposed to be repository interaction tests, and, for example, MCC-105 and 14 were supposed to be divided into site-specific subcategories, so there would be a 105 for basalt. There would be a 105 for salt. There would be a 105 for tuff. Well, those never got written either. So, when the ASTM took over revising the MCC tests, MCC 1 and 2 got joined together into ASTM 1225, which is a monolith test, and the monolith sits in a little Teflon basket in hot water for however, or in ground water for however long you want it. Before they had the Teflon baskets, we used to have to tie Teflon fishing line around these without ever touching it to your fingers. So the Teflon baskets were wonderful things.

The vapor hydration test, you hang a coupon, very much like you would have done before these baskets were available, in steam, and this tells you -- this actually accelerates things at about 200 degrees centigrade. This accelerates things greatly and gets you almost immediately to Stage III so that you know what kind of phases are going to form. The single pass flow through, which was MCC 4, you have a sequence of leachates that flow through and get collected over here. That actually tests Stage I and gives you a forward rate of dissolution.

And the PCT is a crushed glass test so that you get maximum information about the glass composition out of this. This is the modification of MCC 3. We also looked at a whole host of other EPA tests, and took some the best parameters from all the different tests and put them together in ASTM 1285 or the PCT. There was a PCT-A, which is a short-term seven day, and a PCT-B, which I'll talk about in a few minutes.

So the first couple bullets up here are why did we have to do this. The next is what were the criteria. So we needed to ensure the acceptability of the high-level waste glass being made for the repository by doing some testing, and then the producers needed to define the durability before and during production for the waste acceptance product specifications, which said demonstrate control of radionuclide release properties of the waste form and determine the release properties of crystallized glasses, which I will get to at the back end of the talk.

The producers needed a test that was sensitive to glass composition and glass homogeneity. So, if you only want glass composition to be your major factor, then you want to hold everything else very, very, very constant and very rigorously. So there are controls on the surface area. There are controls on the amount of glass to the volume of solution. There are controls on how long you can run it to get good precision and reproducibility, and the standardized test temperature, which is 93, to simulate the heat of radioactive decay.

You wanted a simple sample preparation because you had to run this remotely once you were making radioactive glasses in the glass plant. And it had to be accepted by the waste form developers and the repository. So we tested one-day test durations. We tested three-day, five-day, seven-day, fourteen-day, and twenty-eight day, and finally decided that seven day got us right up here on top of this plateau. We didn't want to go too long. If we did the one, three, five, we were down here, and we didn't get as good precision and reproducibility, so we finally keyed in on the seven-day PCT as the production test.

So PCT was shown to be more sensitive to glass composition and homogeneity than any other durability test out there. We developed -- this part of this piece of apparatus sits in the neck of the canister, of the high-level waste canisters that are produced at the vitrification facility, and this little gadget here is pushed in remotely to catch part of the waste glass pour stream right there, pull back out. The sample can be extracted and sent up to the lab to run the durability test on it.

This is the test durations of seven -- equal to seven days were shown to be adequate, as I showed you on the previous slide. The test response has been related to other ASTM and other high-level waste glass test responses, and this particular committee, which I sat on from 1987 to present -- we had a meeting yesterday -- was composed of waste form developers, repository representatives, and the Nuclear

Regulatory Commission sat on this committee. We peer reviewed the test from 1987 to present. There was independent confirmation of the test, discrimination testing at PNNL.

This is the significance and use statement right out of the PCT, and it says that both of these tests can provide useful data for evaluating the chemical durability of waste forms, as measured by elemental release. The short-term test is the one that we use during production and evaluates the chemical durability; that they have been controlled during production. That means we know that the glass that we're making today is as good as the glass that was made 21 years ago when the glass plant started up, or vice versa, that that glass is as good as the glass that we make today.

PCT-B allows you to use various test conditions, various test temperatures, durations, ratio of sample surface to leachant volume and leachant types, and this data, if you run it long enough, may form part of the larger body of data that are necessary in the logical approach to the long-term prediction of waste form behavior, which is another ASTM procedure that I'm going to talk about at the end of this presentation. And it was through PCT-B, actually, that the Stage III was actually first discovered. Whoops.

All right. So this is our process control system. You can take any frit, Waste 1 which comes from our salt waste processing facility, and our sludge, which comes from the tank farm, and we control, of course, the glass properties, the viscosity, and we don't want the glass to crystallize in the melter. But this is the durability model here, and this is the homogeneity model here. The important thing is that all of these are based on first principles. I'm not going through everything that’s on here.

Everything here is done by -- it's not empirical. It's done by what's known about glass crystallization and glass structure and glass polymerization; okay. And so if it were empirical you would have to run in the center of that quadrilateral, because we have very, very high confidence in these models, and I'll get to that in a minute. We can actually run right down there where you maximize how much waste you can put in it. So the statistical process control not only accounts for modeling error but analytic error, tank transfer error, and heels, and so that solid quadrilateral is 95% confident that you're going to make a good glass and an acceptable glass at the maximum waste loading.

So process control is used by the producers to demonstrate acceptable performance by what are called "linking relationships." Process control means composition control. Composition control, because you're in a narrow range of composition, gives you dissolution rate control, which gives you performance control, which will give you acceptable performance. So we use that model that I showed you on the previous slide. This one here is this model in two dimensions. This is the release of boron from a glass, from a multiple of glasses. I've taken all the points off of here so you could see it. We use the thermodynamic hydration energy reaction model, which is sensitive to glass composition. You basically write equations for the different components in the glass. I will also have a slide about that towards the end of the talk. And this is the model and these are the upper and lower confidence bands on the model.

The benchmark EA glass, which I'll talk about in the next slide, lies up here. You have to be 95% confident that you're below that, and then you have to take into account the upper 95% confidence level of your model. So you key off of that point there and come down here, and when you calculate your glass composition you always have to be to the right of that line. And, in essence, most of our glasses are way down in here. We're not anywhere close to this two sigma that's required in the labs. And, again, the repository modeling uses a variety of test methods, including PCT-A and B, but this model, which is the process model, only uses PCT-A.

So I want to talk a minute about this not simplified glass, called the "EA glass." We went for our environmental assessment and our environmental impact statement in July of 1982. I had just gotten to the site in April of 1982. This is Table 1 out of this document, and the fractional release rates that were given to the glass that was -- the glass composition that was in the same document said that it had a fractional release of 10 to the minus 5th to 10 to the minus

4th based on plutonium leaching, assuming that there were no solubility constraints on the plutonium.

And so this is the glass that corresponds to those properties that I showed you in the previous slide. It had had uranium in it to make this simpler, since I had to shift some of this around the DOE complex we eliminated the U-308 and normalized the composition. This glass had manganese and other transition metals in it. We run at the a reducing flowsheet so this glass has an iron(II) to total iron ratio of 0.18, so we asked Corning Glass Works to make us a glass of this composition at that REDOX without uranium in it. They made me a thousand pounds for usage throughout the DOE complex. I still have about 900 of them if anybody needs any of this; okay? And other standard glasses can also be used to ensure that your PCT-A or PCT-B tests are in control. These include the Approved Reference Material-1 and ARG-1. This one's nonradioactive. This one has uranium in it.

PCT-A and B have been compared to each other by various people. PCT-A has been related to long-term burial tests. PCT-B has been related to shorter-term higher-temperature vapor hydration tests. This is from John Bates at Argonne back in 1996. The EA glass reaches the same stage of durability within 56 days at very, very high surface area to volume, or 313 days at 2,000 -- not crushed quite so finely -- when tested by the PCT at 90, or within six days when tested by the VHT at 200. So this way you know that you are, indeed, getting the same mechanistic information out of these different tests.

And then the rate of short-term crushed glass testing PCT-A has been shown to be an upper bound for accelerated durability behavior, that resumption of dissolution or Stage III leaching behavior by Ebert. And Bill will be talking about this more this afternoon. But what's interesting is that this came along, this piece of information came along 13 years after the PCT was developed and eight years after the EA glass was developed. So it just turns out that the short-term PCT-A on the EA glass bounds the repository modeling.

You asked me to talk about databases. The only database that's out there is one that I started compiling back in

2003. I called it "The Accelerated Leach Testing of GLASS (ALTGLASS)." This is because it was composed of mainly short-term PCT-A and long-term PCT-B, some of them up to 20 years, that had been run at the Vitreous State Laboratory. Most of the data came from the literature. Some of the data came from the joint EM-NE-SC International Technical Evaluation of Alteration Mechanisms, which Joe Ryan will be talking about this afternoon.

Right now, the database for inversion three contains 490 glasses. I have a poster about it later this evening. 113 of those are high-level waste, and 377 of them are LAW waste, low activity waste. Some exhibits say it's Stage III and some do not. That database is being used to understand many aspects of the relationship between glass composition and leaching. That includes people are using their rate equations that they've developed and using this data in this database to see if those rate equations actually hold up; okay?

What I am using it for is to look at what the potential mechanisms are in Stage III, and what I found is that by the time Stage III you've got some kind of ion exchange and diffusion. In Stage I and II you've created some kind of hydrogel layer. This layer will ripen into clays, which don't seem to cause an acceleration of the long-term durability because there is very little interaction between that and the leachate species, because the leachate solution is buffered, and I'm going to show you that on the next slide.

The hydrogels do ripen or precipitate zeolites from strong interaction with the leachate, what I call "solution mediated," especially the excess OH that's in the leachate, if there is excess OH in the leachate, because that acts as the mineralizer. And that causes the acceleration of the long-term durability. And I have two very recent January 2017 papers on that out in the literature. The solution is basically not buffered. There's excess potassium, sodium, lithium, OH in the leachate. It interacts with that alumino-silicate gel and whatever aluminum is in solution. This mimics the industrial processing of zeolites from gel, and from sodium hydroxide.

There are also papers in the geologic literature where they have harvested some gels off of natural basalt, and they put them in a lower pH and a higher pH. And in the lower pH they create clays, and in the higher pH they create zeolites. So there are natural analogs out there that also do this.

So back in 1995, when I developed the THERMO model, I also developed the Strong Base-Weak Acid Model for PCT-A. And that's all the light gray points on here. And what I found was that all of the glasses that I tested in THERMO were buffered. This is strong base minus weak acid, and I defined strong base minus weak acid as the sodium, lithium, potassium and cesium in millimoles in the leachate, minus the boron and the silicon in the leachate. And so you see that these leachates are all buffered until you get up here to the EA glass, and they're not buffered because the EA glass is actually a very high sodium glass, and so it gives off a lot of excess base. And so you're up here.

When we then overlaid some of the PCT-B data -- and I've only shown two of them here -- this is the SON68 glass, where it went from seven days to 600 days in testing; all right? It continued to give out weak acids and continued to go in this direction, and so no zeolites form on the surface of this. This is something that you would only see clay-rich layers. With the AFCI glass, you've got from seven days to 450 days. You've got a tremendous amount of excess strong base, and so you see this huge rise in zeolite-rich phases on the surface. Now what's interesting is that the cutoff that I had set back in 1995 was right here at about 10.8 in terms of pH. The other interesting thing about this is, if you would measure the pH of all these tests, the pH isn't changing very much, but the OH is changing. And over here the pH is not changing very much, if you just come straight down here to about 11. But the OH is changing radically. Actually, this is a weak acid that's changing. That's the strong base that's changing.

So it appears that this zeolite-rich material, versus the clay-rich material agrees with the information in the geologic literature about harvesting gels and putting them in low pH and high pH. So the other thing that I did with the data in the database was say, okay, I've got a population of glasses, I've got a population of glasses that

I know which have strong bases, and which has weak acid; okay, and I did a step-wise regression. And I believe that these are the activated aluminum and silicon concentration. The step-wise regression gave me aluminum and silicon ratios that I've got plotted here; that when you are in this range you make these clays, and when you are over in this range you make these zeolites. And just to save some time, I'm not going to go through the reactions that I think are controlling that, but they're in the presentation.

So down to last two issues that I'm supposed to discuss, the influence of glass chemistry on crystallite precipitation and our approach to designing glasses, and then a last wrap up on the natural and archaeological glasses. If you have homogeneous glass you only have one vector from which boron or any radionuclide can come out; okay? If you have an amorphous phase separated glass you're going to have a second vector. And if you have crystallized glasses you might have radionuclides in that crystalline phase and you might have radionuclides in the glass around the grain boundary. So how do we control all that? Ideally it would be nice if we could just get rid of all of these. That's why I have the circle with the bar through them. Because if you have these, then it requires that you know the distribution of radionuclides among the phases, between the homogeneous and the inhomogeneous, or between the homogeneous and the crystals.

Crystallization of spinel turns out to be one of the exceptions. It has no impact on glass durability, and many, many laboratories have tested this. It does not deplete the surrounding glass, the glass-forming species that can degrade the durability. This is some work that I did. This is a spinel crystal with some acmites hanging off of it. We leached it. I pulled half of the leach layer off with Scotch tape and left half of it on, and what you see is the gel layer here has grown over all of those crystallites and sealed up all of these boundaries, the grain boundaries up underneath that particular crystal.

And we did some testing of high aluminum waste, composite waste, high iron waste, the effects of spinel. So if this is your quench glass you've got a response of one. Everything that's shaded is a response of two. And we're not seeing any response up here in the region of spinels. We are seeing very, very little of a response in the regime of spinels in acmite, because sometimes you get these acmite intergrowths around the spinels.

The one that you do have to be careful of is nepheline, sodium aluminosilicate. It is not isometric. It does impact glass durability, and it does surround the depleting glass of glass formers, so we use a nepheline discriminator as part of the process control to avoid high-level waste compositions that could precipitate nepheline.

And then the only thing I'm going to say about natural analogs is we use the ASTM C-1174 Roadmap to predicting long-term behavior. There is a block over in here for the use of natural analogs. Block one up here is problem definition that this blue block is testing. This is modeling. This is prediction, and this is model confirmation where you might use that model in an actual repository. And so the next slide is a blow up of that so that you can see that you have to identify your natural analogs and you have to examine your natural analogs and you've developed a model for your waste glasses, and the natural analog data is supposed to feed into that model.

At Savannah River, we have actually looked at natural analogs. This is a paper that goes back almost 35 years. I know Argonne has also looked at natural analogs. We've looked at natural analogs. You heard a lot about natural analogs in the previous talk, and you're going to hear more about natural analogs this afternoon. But basically, we looked at obsidian, basalts, tektites, ancient Libyan desert glass that we got from Vanderbilt University, and ancient and Medieval glasses that we got from Corning Glass Works, and, of course, other glasses like window glass, and Pyrex. And what basically you're looking at, you know, you can look at the leached layers. You can look at the hydration rinds on obsidians, on naturally-reacted glasses, so you take whatever test you're doing -- this is an MCC-1 -- subject your natural glass to that, subject your waste glass to that and see if you're getting the same kinds of reactions and the same kinds of phenomena, observing the same kind of phenomena.

So, going back to my thermo model, I've now flipped the axes on you. I apologize for that. These are more durable. These are less durable. What we did was we looked at the medieval window glasses. We know they've been around 10 to the 3 years or so. We know our waste glasses are in here, and we know that the natural basalts, obsidians, and tektites are down in here. Remember, this is a composition model and this is how you calculate the terms for the X axis. This is the boron released from whatever test you're doing; all right?

So we have basically a historical context. We use a natural analog as a historical context to say that our waste glasses are going to be durable to somewhere between 10 to the 3 and 10 to the 6 years. And I think the rest is just my responses to the Board's questions.

BAHR: Okay, thank you, Carol. So we have about ten minutes for questions. I think we went over in the talking time a little bit.

JANTZEN: Sorry.

BAHR: That's all right.

JANTZEN: It's a lot of ground to cover.

BAHR: Yes, indeed. I have a question on that last slide. You listed things in terms of boron release rates, but there is no boron in the window glass or the basaltic glass.

JANTZEN: Yeah, you're right. That should have been silicon. I apologize.

BAHR: Okay. Thank you. Okay. Questions from the Board? Sue.

BRANTLEY: Sue Brantley, Board. So you've given us a real nice overview of the last X years, 35-40 years.

JANTZEN: 35 at least.

BRANTLEY: What do you think we should be doing now?

JANTZEN: I think, having heard the talk before mine, I think perhaps one of the things we should be doing is compiling all of the data from all of the different laboratories that have done natural analog glasses. I mean, there seems to be a real interest after the first talk in the natural analog area. But, unfortunately, there's not a lot of funding out there for that.

BRANTLEY: So, you know, what kind of meta-analysis would you like to do if you were going to do that? I mean, you've collected a database and you've started looking at it. But what further meta-analysis -- what's the argument for more meta-analysis, like some of the work you've already done?

JANTZEN: Well, I think with the natural analogs it's different than it is with the ALTGLASS database. With the ALTGLASS database you can see, because it covers stages one, two, and three, that you can use it to test a model, test the 2003 model, test the GRAAL model, test, you know, various models against the data in that database, because it's not just my data. I mean, I pulled a lot of it out of the literature. I had to go mine the literature. And, unfortunately, I think any database that you construct you have to mine the data. You have to have somebody who is dedicated to mining the data, you know. And like I said, there is not such a database on the natural glasses.

BRANTLEY: And what experiments do you think still need to be done?

JANTZEN: I think there needs to be some refinement, I think, of what Stage III is all about. I think I've given, in the papers I just got published in January, there's been a lot of interest in them, and I think a lot of people are wanting to follow up on that. I know Bill Ebert will be talking a little bit about that this afternoon, and he and I have promised to work together on furthering that aspect of it, seeing if Stage III is really something that's going to happen in a repository environment. I think if your repository environment stays below, say, 10.8, those phenomena may not occur unless you've got a very, very high alkali glass that's giving off, because for every sodium in the glass you give off an OH into the solution. The only other way that you could get high OH in your repository environment would be if you have a lot of cement around, because you're going to get the calcium hydroxides out of there.

So, as I said, we have a lot of information in these different burial samples that I showed. A lot of that work was done, 25, 30 years ago. The samples are still at Savannah River. There are lots and lots of new analytic tools that could be used to look at those glasses. George Wicks has done these pineapple slices with glass and salt, and then something else and things, different combinations of things all in contact, and I have all of those in cabinets.

BRANTLEY: Thank you.

BAHR: Tissa, and then Paul.

ILLANGASEKARE: Thank you very much. I liked the chicken slides. So you're telling seems to be to use, like you said, use short-term tests to make long-term predictions, so that's what you're saying. So my question is that if you -- also I like the idea of that if you are working on first principles then it's easy to, on a theoretical model, to extrapolate long duration. My question is that if you have -- again, going to the repository scale, is it possible to have all three stages happening at different parts of your block?

JANTZEN: I think, remember, all of these tests are done on glass without the canister being there, so depending on how your canister corrodes, you know, I think your glass log inside is going to get exposed. Parts of it are going to exposed at different times, so, yeah, you could have definitely one and two happening together.

ILLANGASEKARE: So this means that the effective behavior, again, the large scales, depends on the heterogeneity created inside the block based on these processes happening at different locations.

JANTZEN: Yes. But don't forget, well, in this country at least, we are depending on the waste package that, by the time the canister corrodes, most of the radionuclides, not all, but most, will have decayed to some degree. So, you know, we do what I call worst-case modeling. You know, what are you going to do if the whole block is exposed to water at the same time? Obviously if different parts are exposed at different times, it's going to be a slower process.

BAHR: Paul.

TURINSKY: Paul Turinsky from the Board. My experience with standards are they do evolve with time, as we learn more and more; that if you're in a regulatory environment there's some resistance to changing standards because you've established some basis from the past test. Can you give me some feeling of how the standards have evolved in this area?

JANTZEN: Well, the environmental assessment glass standard, I think, has been out there the longest. Gary, are you here, Gary Smith?

SMITH: Yeah.

JANTZEN: How long have ARG-1 and ARM-1 have been around?

SMITH: Since the early '90s.

JANTZEN: Yeah.

TURINSKY: And there haven't been revisions to it?

JANTZEN: Well the ARG-1 and ARM-1 are used to prove that your test is in control, because we control chart the standard response to your durability test. That's what we use those for. We run the EA glass simultaneously with our unknown glasses so that we know where we are on that thermo plot that I showed you. And almost every lab in this country is using the EA glass. It's over in the UK. It's over in Korea. It's over in several countries. I get a lot of foreign requests for it, because it is really the only high-level waste glass standard that's out there.

TURINSKY: And do you think, given what we now know, that that still is an appropriate approach or --

JANTZEN: Well, I think it's a benchmark. I mean, you've got to have something to benchmark against, and if you keep changing your benchmark, then you really -- you know, it's like changing your goal post at the end of a race, you know. Somebody thinks they've got to run a mile race and you've moved it a half a mile and they've got to run a mile-and-a-half, you know, you can't keep moving your goal post, so we've kept that. And I think it's actually turned out to be a good standard, because even before we knew about Stage III, that glass went to Stage III. You know, so it's been a very important benchmark for the repository modeling and for incorporating that Stage III, you know. And I guess I want to say, 20/20 hindsight you never know. You know, I certainly didn't know 35 years ago that that glass was going to become the benchmark, and used around the world, as it is today.

BAHR: Other questions from the Board? From the staff? Roberto.

PABALAN: Pabalan, Board staff. Carol, you pointed out that the initial stage corrosion rates, the data available for that are higher than the limited data available for the Stage III rates. Two questions. Can you think of mechanisms or processes that could make the Stage III rates higher than the initial rate. And follow up to that is, if you continue to use initial Stage I rate as your basis for, say, the assessments and that's acceptable for regulators, so is there any need to do anymore studies on Stage III corrosion?

JANTZEN: I think I'm going to defer that to Bill Ebert in his talk in the afternoon, because he's got a plot of the Stage III rates compared to the Stage I rates from all of the data that's in the ALTGLASS database. It's bounding. I mean, that's all I can say, is it's bounding. And we have not found any glasses in that database that go beyond that.

PABALAN: Okay. Thank you.

BAHR: Jean Bahr from the Board. You do these tests on each pour at Savannah River; correct?

JANTZEN: We have what we call a "macro batch concept." So we have a large tank that is agitated and stirred, so we have a large homogeneous tank full of waste, and we take one from each macro batch when the composition changes.

BAHR: And what would happen if the glass failed your test? I assume it has not so far. But what's the strategy if it actually fails the test when you do that?

JANTZEN: The repositories will take a canister that fails; okay? It just has to be identified.

BAHR: So, have any of these failed, actually?

JANTZEN: No.

BAHR: No? Okay. Thank you. Any other questions?

JANTZEN: That was one of my back up slide that said how many canisters we've made. But it's way up there, a couple of thousand.

BAHR: Any other questions from the staff? Okay. I think we're just right on time, then, to go to our next speaker. Let's see. Or are we? No, actually we have -- we were -- yes. Okay. Our final speaker for this morning is Stéphane

Gin, who has a PhD from Poitiers Université in France. And since 1995, he has worked for the French Atomic Energy and Alternative Energies Commission in Marcoule, and has been the lead since 2001 on the project on long-term behavior of high-level waste glass group at that department.

GIN: Thank you for the organization committee to invite me. So the talk of today's focus on the glass solution, although I'm aware of that, and you are aware that there are other key issues regarding long-term behavior of glass, such as radiation effects or some near-field effects that I won’t discuss in details here. So the outline of my talk is the following:

I will take time to discuss some basic mechanisms of glass corrosion, especially how to relate basic mechanisms to kinetic regimes, and I will give a very brief overview of some environmental effects, but very, very brief, and I will take time to discuss what could be done in the near future to derive a new generation of kinetic models to be more predictive, in the sense that we want to calculate the rate, just given a glass composition and environmental boundary conditions, but an a priori calculation, but not the case for the moment.

Well, just very basic things to start with, why glass dissolves. Simply because there is a huge difference, a huge shift between the chemical potential of the solid and that of the solution. And we define the affinity, that has been discussed previously, as the difference, the shift between the equilibrium constant and the ionic activity products given by the amount or the activity of the different elements released by the glass into the solution. And that basic simple rate law can be derived from this shift between the solution composition and the equilibrium. That is never achieved, so the question can thermodynamic equilibrium between glass and glass surface, even hydrated glass surface and solution be achieved? And the answer is simply, no, because, first, due to disorder within glass, the equilibrium concentration is much greater than for an equivalent crystal due to the high entropy of configuration for a glass compared to a crystal. And the problem is that secondary phases with low solubility and fast precipitation kinetics, will control solution chemistry, so the equilibrium between glass and solution or hydrated glass and solution will never be achieved, because the solution chemistry will be controlled by secondary phases, amorphous or crystalline.

And another important thing is that glass would transform into stable compounds by different minima -- following different energetic minima, leading to more and more organized phases. So, it turns out that the glass first transforms into hydrated material and then into gels, and later into crystalline phases. It could take time. And the question is how long it takes?

And one of the problems is that many, many parameters are to be considered to answer this question of how long it takes to turn a glass into crystalline phases. We can distinguish intrinsic parameters and extrinsic parameters. Intrinsic parameters are known, glass composition, of course, because especially for nuclear glass we have to consider broad domain in which major oxides can vary in wide ranges, and we have to consider from 20 to 30 oxides.

The glass structure also is important, the cooling rate that changes the effect of temperature, the homogeneity, the reactive surface area, also the surface roughness and residual stress within the material. And I've put in the intrinsic parameters the effect of radiation that change the structure of the materials with time.

And within the extrinsic parameters we have temperature. As Bernd said before, the glass can first be altered in unsaturated conditions, so with water vapor, and then with liquid water from the pH, the water composition, that also could be affected by the surrounding solids, the near-field materials, the flow rate, and in second order, less order of priority, the pressure, Eh, and microbial activity, as previously quickly discussed.

Okay. So, to make things simple, we can just distinguish four mechanisms to play with and try to understand glass corrosion. So, first, or one of those mechanisms are hydration, so water diffusion within the solid glass through small holes present in the glass. But you will see that it's very -- would correspond to very small diffusion coefficients. Ionic exchange associated with water diffusion and water dissociation within a solid, it corresponds to exchange between a charge compensator, especially alkalis in the glass and hydronium ions. We have also hydrolysis of covalent bonds, like silicon-oxygen-silicon bonds or silicon-oxygen-boron bonds and so on, also hydrolysis of glass formers.

We have the backward reaction, especially for silica, where silicon-oxygen, or two silanol groups can condensate to form a siloxane bond, silicon-oxygen-silicon bond. So it leads to the formation of the gel layer of the glass surface. But some other -- depending on pH, some other elements can also condensate to participate to the formation of the gel layer. And we have also at equilibrium with the bulk solution, at thermodynamic equilibrium, we have also to consider precipitation of secondary phases. As said before, it could be clay minerals or zeolites, CSH and some other precipitates, and generally on the top the hydrated glass of gel layers. So we can play with that and try to understand how to correlate the dominant phenomena with the kinetic regime.

So I said before I will go very quickly, we distinguish mainly three kinetic regimes: the initial dissolution rate, the after transition rate regime corresponding to the rate drop, the so-called residual rate regime that corresponds to a steady state between the formation of a passivating layer and its disruption, its dissolution into more stable phases, but with no passivating properties, no transport limiting effect. And then in some cases, especially at high pH, we can have massive precipitation of silicate minerals, mainly zeolites, that can move or -- yeah, move the rate to -- a rate close to the initial dissolution rate, but always less than this initial dissolution rate, so it remains a maximum. Okay. And we have to understand, for a given glass composition under given conditions, why -- so when we return from this regime to the residual rate regime, and if there is a risk to switch to the Stage III regime.

So as said before, we can distinguish where we have the result by a deep observation or in-depth observation of the alteration layers. We have information about where the dominant mechanism or the rate controlling mechanism under a given condition. And, generally we, at high reaction progress, we see the hydrated glass more porous and more reorganized, porous, hydrated, an amorphous gel structure like this, and generally on the top of the gels we can have some crystalline phases.

And it's hard to understand or hard to get all the local information about the solution chemistry at the different interfaces and understand the role of the different materials on the global dissolution kinetics, simply because of the transformation, especially under residual rate conditions, the transformation of glass into alteration layers or alteration products is very, very slow. I give, here, some figures about the R-77-type glass or international simple glass at 90 degrees Celsius just to give orders of magnitude, where you can see that water diffusivity in the pristine glass is very, very slow, or around 10 minus 20 square meters per second. The maximum dissolution is a fraction of micrometer per day, and the residual rate conditions, it's about four hours of magnitude lower than this maximum dissolution rate, so you have to wait for years or decades to have the thickness sufficient to perform solid state analysis, so it's very difficult. Or you have to accelerate process. But if you accelerate process, are you representative of real conditions? I don't know. So, yeah, it's a tricky question.

Recently it was shown that when the passivating layer is formed the diffusivity of water is much lower than in the pristine glass in similar pH-temperature conditions. It's about two to three orders of magnitude below the diffusivity of water into the pristine glass, so raising the question of how surface layer passivates glass and why it's so low compared to a diffusion in a non-hydrated solid. And the time to form passivating layers strongly depends on the full parameters I have listed below, so intrinsic and extrinsic parameters. So it can take days, years, depending on conditions.

Okay, one interesting thing is that if we derive performance assessment or a calculation of glass lifetime based on the initial dissolution rate you end up with very short lifetime, typically hundreds to a few thousand years, so it's not so interesting because the glass matrix is not an important barrier for the performance assessment calculation, and the only way the glass is a strong barrier, very efficient barrier for the retention of radionuclides is if we are able to derive a rate based on the residual rate regime, so with the formation of this passivating layer. But for that you have to have very strong argument or very good understanding of the basic processes controlling this residual rate regime. And as said by Bernd before, it's under debate. We have not a full understanding and a very predictive model for calculating the rate. Okay. But we make progress.

And bad news is that there is absolutely no relationship, no link between the initial dissolution rate and the residual rate. I've plotted here as an example, but PNNL has some examples with U.S. glasses. The initial dissolution rate is not correlated with the residual rate, and the reason why is because the rate-limiting mechanisms are not the same, so there is no relation, because it's completely different. It's controlled by different mechanisms. So it would have been a good idea if the two were correlated, because you measure short-term rate and you understand something about long-term rate. But you can see here that you can't do that. It's not possible.

So if you established things, we've identified from the 30 years of research in this field about three main processes causing the rate drop. This is before the residual rate regime, so why the rate drops by three to five orders of magnitude. So one reason is affinity effect, as discussed by Bernd Grambow. You can see here, it's very simple comparison between two tests; one run in deionized water. The other run in similar conditions, but with a solution pre-saturated with silica. We have the equivalent thickness of boron, so boron release, and you can see that just after a couple of days, the rates, the slopes of the rates are exactly the same, and the amount here coming from the deionized water experiments, is just the amount of glass that needs to be dissolved to reach saturation, and after the processes are the same.

Okay. The second reason why the alteration rate drops by several orders of magnitude is because of a dense passivation layer, so transport-limiting layer forms at the glass surface. Also, somewhere in the alteration layer, and now it's better understood. It's the rate-limiting transport effect is located very near the pristine glass, and we'll try to explain why.

And the last potential explanation is that because for some glasses we can observe a clogging, a closure of porosity within the gel by those backward reaction of condensation. So, by hydrolysis condensation, by reorganization of the porosity within in the gel, we sometimes observe a closure of the porosity. That is one explanation for some glasses to account for the low diffusivity of mobile species through the corrosion layer, through the alteration layer, so it's established for now about ten years. So three causes for the rate drop. Okay.

Another important question is why alteration doesn't stop in Stage II, in the residual rate regime. So once the rate drops then you start the so-called residual rate regime corresponding to a steady state between the formation of the distal and the dissolution of the passivating layer. So the passivating layer is amorphous. It's not the most stable compound. It will transform into more organized matter but nonprotective. So you have a steady state during which dissolution and formation of this transport limiting layer are the same. And the question, why is that?

So one hypothesis is because precipitation of secondary phases consume elements from the passivating layer. That's what I just explained before, yes. But we have some cases where no crystalline phases precipitate, and so it's not a sufficient reason. It works for some cases but it's not a sufficient reason.

The second hypothesis proposed in the literature for a while now is because ion exchange continues beyond the saturation of the solution with respect to silicon polymorphs, like amorphous silica. So, it was proposed that because of the high disorder of glass, ion exchange, the water diffusion in the glass and ion exchange will continue, and that's the reason why the release of mobile species can continue beyond the saturation of the solution. And we have shown these last years that, no, it's not a question of ion exchange, because chemical profiles within the alteration layer doesn't fit a model based on ion exchange. I will give detail, if necessary.

And a third hypothesis proposed very recently is that water accessibility or water transport within the dense part of the height of the alteration layer, the passivating layer, is hampered by the very low porous gel formed by in-situ reorganization of the silicate network after the release of mobile species, so I will go back a bit after. So it's a hypothesis that is studied in the frame of the EFRC with WastePD project, and there is a poster on that, and perhaps we'll take time to discuss this point a little later.

A few words about Stage III. One important question we were trying to answer this last year is, okay, we've seen experimentally that beyond pH 10.5, 10.11, the zeolite precipitation can trigger a glass dissolution to Stage III, but the question is, because we observed before the reason for alteration a long or latency period that depends on pH, so the lower the pH the longer this latency period. The question was at realistic pH for the disposal, so typically from seven to nine, could we have at very long term, so not accessible to experimental -- to laboratory experiments, but could we have in the real world a triggering of Stage III due to this precipitation of zeolites that couldn't be seen due to this long latency period?

And to try to address this question, we ran a series of tests with these. The idea was to bypass the latency period corresponding to the nucleation of zeolites by seeding the experiment with germs of zeolites. And we did see that the effect of precipitation was important at high pH, so above this typical threshold of 10.8. But by diminishing the pH up to the realistic pH conditions, the effect of the zeolite growth was diminishing until there was no effect near neutral pH conditions. So it was an experimental way to try to address this question of this latency period before zeolite can grow and control the dissolution kinetics.

An important point is that the mechanism of formation of amorphous layers change with pH. And we have also seen that beyond pH 10, we do have to consider dissolution precipitation reaction to account for the formation of amorphous gel layers, whereas below pH 10 we have -- the gel formation is controlled by in situ reorganization of the silicate network. And it was part of a recent debate in the literature, where two models were opposed. One, to explain or account for the formation of passivating layers, so within the gels. One was based on the classical inter-diffusion theory. So the gel here is formed by ion exchange and in situ reorganization of the silicate network, and whereas another model proposed that there is a very thin film of water, interfacial water, in which all glass elements dissolve congruently, and the less soluble reprecipitate to form, first, the amorphous materials and then the crystalline phases. So in this case, this is the precipitate. In this case it is a relic structure of the glass after reorganization. But it's more a relic structure.

And by looking at the literature, we do find example in favor of the two models, and the critical parameter is pH, typically -- or combination of pH and temperature. Typically, at very low or very alkaline pH, we have evidence of dissolution precipitation processes, so the gel is formed by precipitation. It's an example at pH 11.5. It's an example at pH zero. And we have completely different story at near neutral pH conditions, where in situ reorganization after the release of the most mobile species -- sodium, calcium, boron -- explain or -- yeah, explain the formation of the passivating layer. Okay. So I don't go into details because I think I have no time for that, but if you need, I will.

The last interesting thing we have obtained recently, so we have formed the so-called passivating layer in near-neutral pH conditions to deeply investigate this material, and especially follow the mobility of water molecules in the microporous structure formed after the release of mobile species and the in situ reorganization of the silicate network.

So you probably know that in porous media if pores are big enough, and the big correspond to a few nanometers in diameter, the diffusivity is not so much affected compared to self-diffusivity of water, so it's basically 10 minus 9 square meters per second. So it could go to 10 minus 10, 10 minus 11, but not the 10 minus 20 to 10 minus 23 square meters per second we calculate from leaching experiments.

And we have seen that by using spiked water molecules, so tagged with oxygen 18, that it takes a very, very long time to equilibrate the water present in bulk solution with pore water. We expected times corresponding to seconds or less than seconds if it corresponded to a self-diffusion of water. And you can see that it takes hundreds of hours to stay near or to reach near equilibration with pore water. But even after 500 hours, we don’t achieve equilibrium. It means – and we are currently working in the frame of the EFRC project to explain that using MD simulations. And the first calculations performed by North Texas University, Jincheng Du at North Texas University, show that there are atomistic explanations to account for this very slow mobility of water molecule in the microporous gel layers. For those materials with pores less than one nanometer in diameter, so it’s very, very small.

Okay, so a brief summary before I move to the last part and discuss what we could do now. So the initial – the brief summary – of what I said before, the initial dissolution rate is controlled mainly by hydrolysis of the silicate network. It remains the fastest dissolution rate for a given glass under temperature and pH conditions – or for a given set of temperature and pH.

The rate drops because of two effects. An effect of affinity on the hydrolysis reaction or dissolution reaction of the silicate network and by the formation of the transport-limiting phase within the amorphous gel layer.

The mechanism by which passivation layer and non-passivation gels form are strongly dependent on the pH. And the origin of passivation needs to be better understood, and that’s a key point to derive a better or more predictive kinetic model.

And, of course, the precipitation of silicate phases, clay minerals, zeolites, or some other silicate phases, is very, very important for the two stages, residual rate and Stage III, resumption of alteration regime.

Very briefly a few examples of environmental effects. Perhaps Joe will talk about that this afternoon. It’s hard to generalize because water composition, the pH, temperature, can affect and move the system from one controlling mechanism to another. I give here a quick example of the effect of calcium, at high and low pHs, and high and low reaction progresses, where you can have opposite effects. So depending on the pH and reaction progress, calcium can have a positive or negative effect because it can condensate with silicon to form a denser gel layer, or it can activate, especially at low pH and low reaction progress, it can absorb on the silicon-oxygen-silicon bonds and change the rate of hydrolysis, so the initial dissolution rate, and that accelerates, contribute to accelerate, to increase the initial dissolution rate.

So we can have different effects, and it’s hard to be general. And it’s also a reason why it is hard to derive a very general rate law to account for those different effects because, yeah, it’s very complicated.

It’s known, but just a reminder that iron in the vicinity of glass, especially due to iron containers, play a major role, especially due to the formation of iron silicates that control the solution chemistry and act as a silica pump that change the composition, the porosity, and the diffusivity of amorphous layer that could form on the glass surface. So it’s another reactive transport problem that needs to be taken into account for the evaluation of the long-term behavior of glass.

The glass composition effects, you will probably see some other example today. Just by the dissolution rate as a function of time for different glass composition. And my point is just to say that glass composition effects are not linear. So it’s hard to predict because one element can play in a direction by it is influenced by the whole composition or by some other – three minutes? Okay – some other elements.

And, yeah, just to finish. So Bernd talked about different models, GEM2001 or GRAAL model. For the moment we can’t say that those models are predictive simply because they have parameters that need experiments to be populate like for the GRAAL model, this passivating layer that is described by thermodynamic properties and diffusivity properties. And the parameters need experiments to be parameterized. And there is no link between diffusivity and composition. So if you ask the question, okay, I have this glass that will be altered in those conditions, what is the rate using the model? We cannot answer. We need experiments to parameterize the model for the system, so it’s not very mechanistic. But it can be used to address some problems, and there are many, many papers with this model showing that it is good help to make progress, but it is not sufficient to say that is a mechanistic model. And it’s the same for the other model available in the literature or used these last years.

And to finish, I’ve thought about what could be done to improve things and be more mechanistic. So I’ve prepared a few slides for that. So I think we can follow this kind of roadmap by following different steps. One I think very important is to have a better understanding of the rate-limiting mechanism controlling the Stage II and transition toward Stage III. And with that we could derive some general equations. And there are two for that, I will just show very briefly.

And then we can better understand or study the effect of composition, the effect of irradiation effect, the effect of nearfield material because we will be very confident in this understanding and we can base our thinking from the equation that could be derived from that. So this step one is very, very important.

So the need can be – split into different things – we need to better understand the role and properties of gels with especially the important part that is the where the reactive – or transport of reactive species is limiting. Also the role of secondary phases. The role of solution chemistry everywhere, so the bulk solution chemistry is understood, but what happened in nanoporous, microporous system is much less understood. And there also a need to bridge the different scales from molecular approach to more macroscopic approach.

And of course we have to design for that. We have to design smart experiments. Not so easy to think about or have an hypothesis and design an experiment for testing an hypothesis. And we have a bunch of very good or very advanced analytical techniques. We can spike the glass with different isotopes and use isotope-sensitive techniques to do that. And we have many examples, especially with APT or some other very advanced analytical technique that very help to make progress in this field.

Okay, that’s my thought for this tab.

And then we can try to link the glass composition to the rate limiting mechanism understood at the first level. And of course at this first level, we have to work on simple system well and assume with a limited number of elements, with many groups working on the same material to make this real progress. And then it will be easier to link glass composition effect to the rate-limiting mechanisms. And we can explore for example the ISG domain with the MD simulation. Now we have the North Texas University have developed an initial [inaudible] working in a six-oxide domain, and it works pretty well when we compare the glass simulation and the experiments by NMR, for example. That means that we can now substitute some elements, or add some elements, some other elements, to this simulated glass, and understand how it changes the properties. And then we can work on the parameterization of the model. And we could see effect of irradiation, or could see effect of near-field materials or other disruption of the reference case we have worked on in the previous steps.

So I’ll stop there. I’m sorry if I was a bit long. And just acknowledge my collaborators, CEA, and some other groups with which we work.

Thank you for your attention.

BAHR: Thank you.

Jean Bahr from the Board. You mentioned briefly these irradiation effects. Could you say a little bit more about what those are and how significant you think they might be?

GIN: Yeah, okay. Well simply speaking we can distinguish different effects on the – it’s well known now that the most important effect are due to – recoil nuclear due to alpha radiation in glass that creates cascades in the materials. And also the effect of irradiation effect on the containment properties of the glass itself are well understood. The effect of self-irradiation under dissolution is less understood, especially to what extent irradiation damage could change the properties of surface layers, and especially the passivating layer, is not really understood. We have some examples of the negative effect of irradiation on glass dissolution especially under this residual rate regime, but we don’t understand what is beyond that. We measure an effect, but we don’t understand why we are seeing an increase of the residual rate. So we need to link the structural effect of irradiation on the residual rate regime, and it’s, okay, it’s under study, so presently we don’t understand. It’s not a huge effect, but it’s an effect. Whereas beta and gamma irradiation have no effect or very, very slight effect on the glass structure and no effect on glass dissolution.

BAHR: Okay, thank you. Lee Peddicord.

PEDDICORD: Lee Peddicord from the Board. Following up a bit on Dr. Bahr's question, not so much the irradiation but the radioactive decay is introducing new elements into the mixture, and particularly when you were talking about the precipitation of secondary phases, over periods of time, long periods of time, are these affected then by the fact that the composition is changing?

GIN: Yeah, okay. So it is easy to calculate how much the glass will change in composition at different times due to the radioactivity effect. And the conclusion is simple. There is no – it's a third order effect because the slight change in glass composition are very small compared to the broad range of composition we have to consider for glass formulation. Especially – it's the same in the U.S., it's the same everywhere. We don't produce given glass, but we produce – glasses within a domain, and the change in composition are huge compared to the change expected due to radioactivity. That's a very small expected effect, yeah. But calculated. We know that it is there. It's very small.

PEDDICORD: Thank you.

BAHR: Any other questions from the Board? Sue Brantley?

BRANTLEY: Sue Brantley, Board. Thank you for that. It was very interesting. So I keep coming back to what could make a glass dissolve faster in the field than it does in our laboratory experiments because that’s, you know, that’s just something you worry about. And you did talk about stage III, but I got a little lost from the point of view that you, you know, you started talking about seeding experiments and when or how long the latency period was before stage III would start. But then you jumped to this argument, which I think is interesting, between whether the gel is formed by dissolution precipitation or whether it’s formed by some kind of in-situ reorganization. But I didn’t understand why you went from stage III to that argument. Like what’s the connection between that in terms of precipitation of these secondary phases?

GIN: Okay. So Carol said by using thermodynamic arguments we can say this glass will form clay minerals, or this glass will form – or can form zeolites. That’s a way to say that this composition could be sensitive to zeolite precipitation or another glass is not. But the question we tried to address here was is it – so the fact that the glass can turn to stage III, is it only related to thermodynamics or also kinetics. Because experimentally it was seen that before the glass switched to stage III, there is this long latency period with a very slow dissolution rate, and potentially corresponding to the residual rate before it resumes. So before we thought that this latency period was due to the same mechanism as the one explained in our recent papers with this idea that the layer inherited from the glass and just reorganized and be passivating because water cannot rapidly move into the gel. But we also saw recently that the – at low pH, or near neutral pH, will form the gel by this in-situ organization whereas in conditions where stage III can occur, the gel is formed by dissolution precipitation. And we don’t understand how an amorphous precipitate can passivate the glass and explain this latency period before zeolites precipitate. So there is something not understood at the present time corresponding to what gel or what phase controls the latency period before it transforms, dissolves, and form zeolites.

BRANTLEY: So just as a point of clarification, I think at the top, with the reorganization, that was circum neutral pH, I think.

GIN: Yes. Yes.

SUSAN BRANTLEY: And then at the bottom, it’s either high or low pH.

GIN: So the very over-acidic and the very –

BRANTLEY: And don’t we see the stage III precipitants in the second?

GIN: Yes.

BRANTLEY: Okay, so that’s the essence of the issue is we need to understand that lower picture more because that’s when stage III happens?

GIN: Yes.

BRANTLEY: Okay.

GIN: And for the French case, I mean for the R7T7 glass where there is no evidence – sorry I try to get back to this stage III – yeah. For the R7T7 where we have this resumption of alteration. It’s only at high pH. And the high pH, all the gels are precipitates. They are not as [inaudible] neutral pH, I mean in situ reorganized. So, yeah, we have to better understand what are the phases that can precipitate at a given pH and which of them could be a transport-limiting. You can see here that zirconium that was expected to be very insoluble, very – yeah, very insoluble, if you leach the glass at pH above ten, zirconium is dispatched or is precipitating everywhere, zone without and zone very enriched and zone completely depleted and some other – and we don’t what is controlling the formation of those phases.

And potentially one of them can be transport limiting for a given period of time, and once you have sufficient germs of zeolite that can grow, then it dissolve this layer and the global dissolution rate of the glass is then controlled by the precipitation of zeolites. And it is not understood. We don’t know.

Okay, but now the clarification is that we have a model or an understanding for the mechanism responsible for the formation of this transport-limiting phase, at near-neutral pH conditions and at high or very extreme pHs, we don’t know. And especially in France we’re not very interested in those cases because the design is or would lead to near-neutral pH conditions, whereas it is more interesting, or more pregnant, for the Belgium case, or especially the very alkaline glasses. But for science it is important to know the domain in which we have a given model and a given set of equations we can rely on and derive PA. But, yeah, the recent findings were that we have to distinguish, even for a given glass, it’s behavior depending on pH.

SUSAN BRANTLEY: And whenever there is a crystallite that forms, does that cause them to stage III or do some crystallites form but not affect the residual rate of the glass?

GIN: It depends on if crystals are made of silica or not. So the silica is the most important factor in the system. I don’t say that the other elements are not important, but if silica is not involved in the phases, I don’t believe that the other elements can be dominant in the glass dissolution behavior. The first order is to really well understood the effect of silicon. And, of course, some other elements can play a role. Especially aluminum at high pH is known that it becomes very soluble. And the stoichiometry of silicon/aluminum in solution can be closer to that of zeolites and then change the saturation index of the solution. So, of course, silicon is not the only player, but it is the most important element in the system.

BRANTLEY: All right. Thank you.

GIN: Yeah, you’re welcome.

BAHR: Jean Bahr. Just another question on this figure. So the profiles that you are showing for boron, sodium, and calcium in the upper case, that looks like a diffusion profile.

GIN: Yeah. Um hmm.

BAHR: And in the lower case basically the concentrations go abruptly down to some low thing so that implies that there is no diffusion limitation through that precipitated layer, is that correct?

GIN: Yes and no. You made a good point because in fact in the recent papers we discussed the two models, and I was too quick here. But this is not a good model because even if we say that we have preferential release of boron, sodium, and calcium, so the most weakly-bonded to the silicate network elements, from the glass and the other elements stay in place, we do observe a very sharp interface that cannot be explained by ion exchange. It’s more a dissolution front of those mobile species, and that’s why we try to revise and change what we call interdiffusion by considering that there is one limiting step in the interdiffusion to account for this sharp interface. But what I said that probably the rate limiting step is the mobility of water molecule in the dense or in the passivating layer. So the idea behind that is that the flux of water molecules is rate limiting. It’s not sufficient to dissolve the glass or to dissolve the mobile species at a fast dissolution rate. Then once water molecules reach the interface, they dissolve those species and they are released – the transport of the mobile species within the gel layer is not limiting. So once they are dissolved, they are leached out very quickly. The rate-limiting step is how much water can reach the reactive front. And that’s a limiting step. Okay?

BAHR: Okay. (Inaudible.)
GIN: That tends to be proven by those tracing experiments with the – tagged to water molecules. And also supported by MD simulation. It’s not yet published, but it will come.

BAHR: Other questions from the Board? Any questions from Staff? Bobby?

Pabalan: Pabalan, Board Staff. In one of your slides, I think maybe 20 or 21 or something, you mentioned that you will look at the effect of glass composition.

STÉPHANE GIN: Yeah. Again?

Pabalan: Next – uh, yes. So using molecular simulations. Is this the approach that you guys are taking for the WastePD project?

STÉPHANE GIN: Yes.

Pabalan: Okay. And you –

GIN: So just to complete for the moment, the North Texas University from calculation of the pristine glass, ISG glass, so the whole description of the short range, medium range, and long range order for the ISG glass with parameters for the six oxide components. And they have explored or started exploring the gels – I mean gels – for this glass. And they are very confident that they can keep the same potential for the six oxide to explore the whole

ISG domain. So but it’s not done but it’s within the – it’s a goal of – one goal of the product yes.

Pabalan: So if one is interested in the effect of the presence of actinides, are potentials available to simulate those?

GIN: Well, it depends on what you want to see. So you can have potential just to describe the structure. But if you want to describe interaction with water, you have to make sure that the potential are good for that. So it depends on what level of refinement you use for MD simulation. There are so many different approaches. For example, now when we start looking at interaction of pore, surface and water molecules, and we have many potentials for that. We can just consider that water molecules are rigid, they cannot dissociate. But there are more advanced potentials able to dissociate water molecules and react with surface sites. So they are comparing the different potential. So I can’t answer regarding the effect of actinides, but it has to be discussed depending on what we want to model.

Pabalan: Are there – you mentioned experimental validations. I imagine you will be doing some experiments.

GIN: Yeah, sure.

Pabalan: Is there any other part of the WastePD project that will do more experiments to evaluate the effect of glass composition?

GIN: Yeah, at PNNL, so probably Joe will talk about that this afternoon. The answer is yes, of course.

Pabalan: Okay. Thank you.

BAHR: Any other questions from Staff?
Okay. So I think we are at time for public comments. I don’t know if we have any one that is signed up. No one has signed up. Is there anyone who would like to make a public comment even if you haven’t signed up?

Okay, seeing none, then we have a lunch break now until 12:45.

BAHR: Welcome back from lunch. It looks like we may be missing a couple of Board Members who are still at lunch; but we have a pretty full schedule this afternoon, including the Poster Session afterwards, so I'm going to get started.

Our first speaker this afternoon is Dr. Ian Pegg, who is Professor of Physics and Director of the Vitreous State Laboratory at Catholic University of America. A number of us from the Board had a chance to visit that facility a year or so ago; and it's certainly an impressive operation with a staff of over 110 scientists, engineers, and technicians working in a variety of basic and applied research and development areas. They've particularly been doing a lot of work on glass formulation and durability studies, and we're going to hear about that this afternoon.

PEGG: Thanks for the introduction and thanks for the invitation. To the Board Members that are new or weren't able to make the last trip, we're still there; so I encourage you to come out and see us.

I guess it falls to me to try and keep everyone awake after lunch, so we'll see how this goes.

I'm going to talk about some glass formulation and durability studies that we've done over the years. The first part will be very brief because it's a whole subject in itself, but I will at least use it to set the context for where some of these glasses that I'll talk about came from. The picture in the background there is the lab itself, so just for a little change of scenery there.

So a quick overview…I'll mention quickly some of the projects we've been involved in and where these glasses came from; the glass corrosion tests that we've been doing over the years; a little bit about the composition ranges involved; and then some of the…I really had to pick from a very large set of information here, so I picked a couple of subject areas. One is this issue of resumption, which I think is current and still important. I'm going to say a little bit about a pet interest of mine, which is the role of ion exchange…even in the long term believe it or not; and then some interesting aspects of this affinity term, which may or may not be a little more complicated than we think; and then I'll summarize.

In terms of background where these glasses came from…going back to the early '80s, we've been involved in glass formulation first and foremost for the West Valley Project, where we developed the formulation that was used there; later on in the '90s, the M-Area facility at the Savannah River; worked for Sellafield from the '90s to currently…a range of different wastes, but it was high-level and intermediate waste; worked for the DWPF and for Rokkasho in Japan; and the work for West Valley goes back to the 1980s, and then Hanford from 1996 to the present, Rokkasho from 2005 to the present, DWPF from 2009 to the present. So these are ongoing projects.

The baseline vitrification technology in the United States is something called Joule Heated Ceramic Melting technology as distinct from the hot wall and cold wall induction technologies used in France and the hot wall also in the United Kingdom. That baseline technology, believe it or not, at the Vitreous State Lab in the middle of Washington D.C.

we have the largest array of test platforms for that technology…five different platforms. We also have the single largest test platform in the United States; it's about half the size of DWPF. It's a one-third pilot scale system for the Hanford high-level melter systems.

What that means then is from the smallest to the largest scales -- we have three different scales -- that's a factor of 60 scale-up. So we can in the lab go from a factor of 60 scale-up, and then it's just a factor of 3 to full-scale HLW at Hanford.

One of the big breakthroughs in this technology area of the past few decades has been the ability to drastically increase throughput through these systems by the use of active mixing. This is what we call "bubbling" technology. Conventional melting technology – this is a finite element model here showing the molten glass and the cold cap area – relies on natural convection in a really quite viscous fluid, which is a slow process but it works. By driving this mixing process by injecting gas in an organized array, you can drastically improve heat and mass transfer or drastically increase the rates of reaction of this important glass cold cap interface here.

We've shown that we can get rate increases of about a factor of 5. So imagine the cost of space in a nuclear facility of the types we're talking about and being able to get five times the throughput through that same space. That's a big deal. That's largely why the Hanford Waste Treatment Plant melters are not even bigger than they otherwise would be. You may think that's a big facility; you take bubbles out and multiply it by maybe 4 or 5.

This was first used in the mid-90s at the M-Area facility, the first commercial implementation. The process was invented in the early '90s at the Vitreous State Lab, commercial developed, commercialized license to Atkins, and then sublicensed to both the Hanford site and the Savannah River site. It was incorporated into both the Hanford LAW and HLW melter designs. It was in 2010 that the Defense Waste Processing Facility, which started operations in 1996, in 2010 in a regular outage we retrofitted this technology into those melters and pretty much doubled the throughout overnight…so a really important technology.

I'll mention that in the following brief summary before I get on to glass corrosion. In the context, then, of where these glasses I'll talk about came from, from West Valley the glass formulation we developed for West Valley, about half a million kilograms of high-level waste glass was made at that facility. All the waste is now converted to glass. At M-Area, we developed all the formulations for that facility…about one million kilograms of glass. This was the first application of this bubbling technology and about a twofold increase in throughput because of that technology.

At DWPF, we did all the glass formulation qualification work for the last two Sludge Batches 8 and 9. The bubblers were introduced in 2010; and since that time, about 2.4 million kilograms of glass have been made in that way.

For the WTP, the Atkins LAW Pilot Melter, about 3.2 million kilograms of glass, all based on VSL formulations and about a fourfold rate increase demonstrated. At the WTP HLW

Melter, which is operated in the VSL, about 400,000 kilograms of glass all based on VSL formulations and up to 5 times rate increase. So this really is what gives us the basis for our expectations for the full-scale operations of the WTP.

In terms of the ongoing work for the WTP, there's a whole area of improvement of formulations to further increase throughput and, very importantly, to improve the loading of waste into the glass product, which is a huge impact on the economics of the process…whole story in itself, some very important work in that area but that will be for another day.

In terms of designing these formulations, we use a mixture of active and statistical design. These are some of the matrices shown up here…property composition models, component response properties, et cetera.

With that, so you know a little bit about where some of these glasses came from, what kind of corrosion tests are we doing on them?

The longest-running tests have been running for 36 years. They started in 1981; they're still ongoing. Many different tests…you've heard Carol talk about many of these earlier…in the case of PCT, we're talking about thousands of glasses; in VHT, hundreds; TCLP, about 1,000 – so large number of glasses.

Moving on then, I'll say a couple about two particular types of these tests. Most of what I'll say will relate to the PCT test. These pulse flow tests are some of the earliest and longest-running tests that we have. One type is a 25% replacement; so each time you sample the vessel, you remove 25% of the leachate and replace it with fresh water. You do that on different intervals. We have about 187 different samples; I say samples because there are glasses, there are rocks, there are obsidians, basalts, tektites…you name it.

There are 4 different temperatures; 13 S/V ratios, powders and monoliths; not only deionized water but ground waters, including EJ-13 well water from Yucca Mountain. The replacement intervals are 1, 3, and 12 months. We have both

Teflon and steel vessels; and, as I mentioned, it includes the natural analogs.

These plots at the bottom here are some data over 4,000 days on one of these types of tests…as you can see, pretty linear cumulative response for this replacement, more or less linear, two different surface-to-volume ratios. Interestingly, on a normalized basis, what comes out fastest? Not boron but sodium.

Another test, which is an IAEA test…it's similar but it's 100% replacement. These tests have also been running for about 36 years; 52 different samples; 5 different temperatures; 6 S/V ratios; and the rest of the story is rather similar…so a large set of data there.

Moving on then to PCT, which is the dataset I'll show you some of the data from, we have about over 2,300 glass compositions…all in triplicate. So this means about 7,000 individual tests; 4 different temperatures; many different S/V ratios, from about 20 to 40,000. The durations of these are up to 25 years; that's about the time of the existence of the PCT. It started as soon as it existed, and we've been running ever since.

What this means is about 17,000 records. Since Carol mentioned the ALTGLASS database this morning, there are about 2,000 records in that database; 75% of those records are ours. The data came from the VSL. And 100% of the records in that database for times beyond 600 days, 100% of that data came from the Vitreous State Lab…so just to set this in context.

In terms of composition coverage, this is a scatterplot matrix. If you haven't seen these before, it may be a little confusing. But it shows the major glass constituents plotted pair-wise. What this means is this plot here is boron against aluminum, and you see the coverage here. So boron goes from zero to about 20%, and aluminum goes from about zero to about 30%...so very wide coverage of many different constituents. And that's not all the constituents in this class; and that's on a weight percent basis, by the way.

Okay, so let's look at some data. I've got to pick out just a few phenomena that I think are interesting. So here are two glasses, which are replicates of each other. These are the same composition; we made them two different times, we leached them two different times in triplicate, and we ran the PCT for a long, long time. You see they track each other fairly nicely, and this is up to about 9,000 days. Pretty boring but that's good; boring is good for glass. What this axis here is, is the percent of altered glass, which is just an easy way to digest how much glass is reacted…so probably about 5% of the glass has reacted by about 9,000 days.

Okay, here are two more glasses, replicates of each other. This one rises to a little bit higher level here. Everything looks still fairly good until about 2,000 days, and then something very strange happens. It just decides I'm done being boring now; I want to be interesting…and leach very, very quickly. What's significant here…this is 100% alteration of the glass. So by this point here, essentially all of the glass has reacted. You went from almost nothing to all of it, just like that. It's like turning on a switch. It's a very, very striking phenomenon; and I must say a little bit disconcerting when you're thinking about performance in a repository.

So dispositioning this, understanding why it happens, when it happens, can it happen in an actual disposal scenario certainly is a very important question.

So stealing Stéphane's picture, which gets a lot of air time these days, what we're obviously talking about is this Stage III resumption region. A while ago, drawing on what Bernd had found in the late '80s, I believe, is the key to this is secondary phase formation and, in particular, zeolite formation. We did an analysis of about 98 different West Valley glasses…looked at the characteristics of when this happened, when this didn't. One thing we found was there was a key pH; at about 10.7 is where you start to see this phenomenon…below that you don't. And once you get above about a pH of leachate, pH of 11, pretty much all glasses will run away to this resumption stage.

In this stable region over here, what you tend to see is the glass is covered with these clay-like minerals, smectite phyllosilicates. Once you get into this regime here, you're seeing massive growth of zeolites of various kinds. Here are 12 different glasses, all of which have gone through this resumption stage; and it's pretty clear that there's a common feature here. They're all showing this massive growth of zeolites.

So let's go to a different glass. All of those were high-level waste West Valley-type glasses. This actually is a very different glass composition. This is a Hanford WTP LAW formulation, a high-sodium formulation. And as I'll show you in a minute, you see the same kind of thing; and the same site kind of phases…a little bit more prevalence of these things, these (inaudible) things…very characteristic of analcime, but otherwise a regular array of zeolites. This hexagonal platelet here is probably gmelinite which is a little bit like chabazite. Then underneath you're seeing residual clay-like phyllosilicates on the surface.

Basically, the suggestion here is that these clays that are forming in the long term, if the leachate pH gets high enough, you get hydrolytic attack and modification of the clays into these zeolites; and that apparently is a bad thing for continued reaction of the glass matrix.

We can sample and analyze these solids. You won't be able to see much of this from a distance; but suffice to say that compositional analysis the character is consistent with what I was just saying about the basically phyllosilicates versus the zeolites. One of the key differences is the silica to aluminum ratio. The zeolite phases tend to have a lower silicon to aluminum ratio than the phyllosilicates that you see.

This little plot here is an XRD pattern of these phyllosilicates, and the broad XRD peaks are pretty well explained by an array of really quite similar phyllosilicates from (inaudible), stevensite, nontronite, beidellite, et cetera. And you can see the spread of those lines here; they're all very similar type phases is what's giving rise to that broadening of those lines.

Okays, so this is a phenomenon; is it unique? Is it only those glasses?

Well, no, there are a couple more different West Valley glasses. There's one that behaves…or at least behaves for 9,000 days. Here's one that didn't. Here's a Hanford high-level waste glass…one that shows resumption, one that hasn’t yet; a Hanford LAW glass…one that does, one that doesn't; and DWPF…this is just an array of glass that does not show resumption, one that does. And then several glasses in between that differ by maybe a percent or so in composition, and you see the range of different resumption times you get as a consequence of this. So it's really very sensitive to composition…so a very complicated phenomenon that's going on here.

Okay, so what I'm going to try and address a little bit now is obviously in translating this observation to its potential relevance in the repository, you really need to understand what's causing it. What are the factors that affect this, and are those factors such that they might prevail in the repository environment or not? Maybe this is unique to these accelerated tests that we're running, and maybe it's just not possible in the repository. But to draw that conclusion, you really need to understand what factors are at play.

One of them certainly is glass composition. Here's a set of glasses where if I take this one, which shows resumption of about 1,500 days, if I add some boron to it…a few percent boron…I suppress the resumption. If I add some aluminum, I make it earlier and much sharper. If I add some calcium, I make it yet earlier…very sensitive to a few percent changes in composition.

Another series of glasses here where the base glass is this first blue line; now I add some boron…that delays it. Curiously, I add aluminum to this one; and it delayed, not accelerated, the resumption. So aluminum…it can do good or bad, depending on…so that's the challenge right there.

Zirconium is one of the things that's consistently – in everything we've seen, zirconium is one of the consistent beneficial actors that will delay resumption…I've not seen an exception to that yet.

Another thing to point out is this little plot here is the early portion of these data here, right? I'm just exploding this, and these first points here are the seven-day data. So one thing to bear in mind from this is if I take these seven-day data and say which is the good glass/which is the bad glass, well, clearly the blue one is less good than this one and this one and this one. So this is the ordering, right? Blue is the worst…unless you keep testing. If you keep testing, blue is…I'm sorry…did I get this backwards?

My point is the order changes here from what you see on seven days to the order of resumption…which kind of relates a little bit to the connection that Stéphane was making to the early rate versus the processes that you see later on.

Okay, another factor, certainly an accelerated test, is we run these tests typically at high temperature…a higher temperature than perhaps in the repository. What's the effect of temperature?

This is a little bit busy, but it's fairly easy to follow. This first set, there are six glasses on here. All the group of data points, the plots on the top, are at 90 degrees Centigrade; and you see different resumption times for each glass…so one that's early, later, later. All of these data here relate to the same glasses tested at 20 degrees. So it's purely six glasses tested at 90 degrees and 20 degrees.

The first thing you see is resumption at 90 degrees and so far, at least to 6,000 days, no resumption at 20 degrees. So maybe that's good news. Temperature slows things down…maybe not a surprise; but that certainly leaves the question, how long do you have to go before the resumption that you saw at 90 degrees occurs at 20 degrees…or does it ever occur?

Here's another set of data for temperature. This is actually EA glass, and EA glass pretty much runs away right from the beginning. You look at it in a log-log plot; there's actually a steady period before the resumption. Resumption is at about 50 or 60 days. If you run that at 20 degrees, this is what you see; so this is out to about 5,000 days; and it's really still quite stable. So temperature is a big factor here.

Another set of glasses…these are Hanford LAW glasses, where we see resumption at 90 degrees but not at 40 degrees. So again, all of the glasses that take off, the 90-degree data, this tight little set of data here are the same glasses at 20 degrees. So far, we have never seen resumption at 20 degrees…another five or six decades of funding might be necessary to address that problem. Talk to me later. We've never seen resumption at 40 degrees.

What if we push the whole story – what I'd like is resumption at two different temperatures for reasons I'll mention in a minute. So what if we push everything to higher temperature?

Okay, so these are tests where we ran glasses at 120^0 and at 90^0 …obviously sealed vessels under pressure at the 120^0. And lo and behold, we have several examples now where we have definite resumption at two different temperatures. So this is one glass right here where it takes off at about 25 days at 120^0C and it goes out to about 125 days at 90^0C…and likewise for this glass here. So you can see where I'm going with this. Once you see an effect, and it's the effect of temperature on that effect, you're wondering about, okay, well, can I use some activated process arguments?

So with a lot of caveats, we don't know what the elementary processes are. We don't know if this is an activated process. But let's assume it is and that there is some kind of aggregate effective activation energy. What would that look like?

We can do a number of things. We can certainly take these data, where I have two numerical data points and calculate an activation energy. I know the time it takes, so I have a rate; analyze that and get the activation energy. But even these other data, where I have a "yes" at one temperature and a "no" at another temperature, I can say at least this has not happened up to here. If it happened on the next day, what activation energy would that give me? That gives me a lower bound on the activation energy.

If I do that, these are the kind of numbers we get. The West Valley data, the bound is not very good; we're in the now 10 to 20 range. DWPF data, the bound is a little better, about

57. For the LAW glasses in the 11 to 40 range, and these glasses where we have two definite data points, it's about 60 kilojoules per mol.

What does that mean?

Well, that's a pretty typical activation energy for matrix dissolution. For these glasses that it happens, it's also pretty typical activation energy for ion exchange. The general thinking is the ion exchange activation energy is significantly lower. At least for these glasses, that's not what the measured data is saying; they're both about the same. So there's an interpretation aspect to this; but perhaps more importantly, there's a pragmatic aspect that if you do know the temperature dependence, now you can start to extrapolate to repository-relevant temperatures, albeit on limited datasets.

Another accelerating parameter is the effect of surface to volume ratio. Short story here as you change the surface to volume ratio, you can go from no resumption to resumption;

and the time of resumption depends on S/V…two different glasses, we have many examples of this.

Again, I'd like to take this parameter, which is very high in the laboratory and probably much lower in the repository and I correlate resumption time to S/V. With the data we have that I've just shown you, this is a log-log plot of S/V versus resumption time for two glasses; and for whatever reason, it follows a power law. For the two glasses, the power law exponent is really fairly similar. So one is very close to 1.0; the other is about 1.2. What you can now do then is say what does the repository scenario look like in terms of what S/V is likely to be?

To the extent it's down here, you can say, well, yes, I'm seeing resumption after about 5,000 days here; but in the repository, it's likely to be hopefully a million days or something. So this is starting to put the flesh on the bones of that skeleton. So if we can look at the temperature effect, the S/V effect, we can start to project into repository scenarios.

Another important factor…we mentioned the importance of pH. Well, what about buffering then?

Well, these are tests where we ran tests in steel and in Teflon. Teflon is permeable to CO2. It allows CO2 from the atmosphere to breathe in. What we see here then is in steels versus Teflon vessels, the buffering by CO2 delays the time of resumption; and the effect of that is shown here. These are not resumption plots but just show you the stark difference between with and without this effect. So this is a particular LAW glass showing in steel versus in Teflon. All of these are at 20 degrees Centigrade. This is the EA glass in steel versus Teflon. So this buffering effect can be very, very significant in terms of glass leaching.

Let's see, I have a couple more minutes; I'll try and squeeze in a few more points.

One of the striking effects we've seen with S/V is as the glass leaches, the pH rises and reaches a steady state; and that steady state pH depends systematically on the S/V. Strangely, it does so in a way which is not consistent with affinity effects alone. This is something we pointed out in 1994. We looked at six different glasses; and the supposition we came up with…I'll make this long story short…is that the other piece that's important is ion exchange. This is a very simple model, just keeping in the essential elements of the affinity term with a pH-dependent rate parameter and adding in a diffusive ion exchange term with, again, a pH-dependent rate parameter reflecting the fact that the higher pH lowers proton concentrations; so ion exchange rates should go down.

To make a long story short here, when you couple these together through the solution speciation and the moving boundary problems that are involved in the rapid ingressive diffusion profile of the slower matrix corrosion profile, that moving boundary problem ultimately comes to steady state with a fixed thickness separation between the boundaries. And then both boundaries move at the same rate. The key is what determines that rate then is this…not this. It's the ion exchange that determines that long-term behavior in this simple model.

Another important point is the steady state pH then you can show the limiting behavior of these equations. There's a power law in S/V, and that power is 1 over 1 plus alpha; it's not 1, which is what you get from affinity alone. It's 1 over 1 plus alpha, and this alpha is the power of this pH dependence here. What we see experimentally is that, yes, indeed, this is not 1; it's two-thirds. And that implies alpha is one-half, which is exactly what you'd expect on the basis of the Doremus interdiffusion model.

So the key here then is what goes on here?

Very quickly, this affinity equation very quickly comes to saturation, where the affinity essentially goes to zero. So this just sits there in the background not doing much. This thing is still diffusively releasing alkali. Every alkali that comes out, a proton goes in; and that means that another orthosilicic acid can dissociate. That's now under saturation by 1 molecule, so more glass dissolves. So the diffusive release of alkali is actually dissociating orthosilicic acid, which is driving the matrix dissolution reaction forward. So this is very, very suggestive of a long-term residual rate, which is nothing more than ion exchange.

Now, I know this is controversial; and people are saying ion exchange doesn't explain the diffusion profiles. I'm not convinced. I can't see how this cannot at least be a portion of the problem. Ion exchange doesn't stop.

Okay, so the long and the short of this then is that the long-term behavior is driven by ion exchange under this very simple model. The bottom line is then the way these equations scale, there's a simple KD times S/V scaling. Once you do that, there's a one parameter fit to the data for five different glasses that show this. And this slope here is not one based on affinity; it's actually two-thirds, which is what the ion exchange equation would tell you.

One last point…I'll mention this even though I'm out of time because I think it's an important point to leave you with. So the Hanford Low-Activity Waste Performance Assessment is based on this version of the prototypical rate law model, which includes a very simplistic implementation of ion exchange release. We, together with PNNL, are supporting the performance assessment for that facility; and to correct the parameters in this rate law, we use glass flow-through testing. A number of glasses have been tested this way. What I want to focus on here is an aspect of the affinity of term, which is a little bit troubling.

So here we're plotting the rate versus orthosilicic acid spiked into the influent solution. And what you'd expect, based on this equation, is that this would just decline linearly as you increase the orthosilicic acid. Well, we see for certain glasses, for many glasses it behaves nicely; what I'm showing you is the ones that don't. That's more interesting. This is sodium and boron. You see it actually rises, and now it starts to decline. Here's one where it declines and then rises. This is a rate that is rising with added orthosilicic acid concentration. How you can make that consistent with this is the least of questions.

These are data from PNNL. As you can see here, there's a decline. But this rate certainly is not zero. It's in fact probably 30% to 50% of the forward rate. So I don't have an answer to this, but I certainly have questions. There is a possibility some of these glasses that have been looked at may have nanophase separation; I'm not sure how this would explain this, but at least it's a question.

Okay, I need to stop. In summary here, I don't think there's anything on there that I haven't said, so let me take the last couple of seconds in acknowledging a few people. Quite a number of people helped me put this together: Isabelle Muller, Adonia Papathanassiu, Konstantin Gilbo, Miguel Penafiel. I should mention certainly these two people here, Xiangdong Feng and Shiben Xing; both got their Ph.D. with us many years ago, and they were responsible for setting up some of the earliest PCT tests which are still running…worked very hard on the database of these.

Then many other people and lastly, Ronnie Barkatt and Pete Macedo, who had the foresight to start some of these tests in 1978 and 1981 and to keep them going…particularly the natural analogs. I should mention Pete Macedo, who passed away a couple of years ago, would have been heartened to have heard all the talk of passivation layers; so thank you, Stéphane. This was something Pete believed deeply in the early '80s…that of course glasses react and form passivation layers; and he never really liked the whole affinity story.

I'd like to thank all the staff of the VSL. This is unusual to thank yourself for funding; but believe it or not, none of my proposals for our 36-year leach test ever got funded. So we fund all of these long-term data ourselves.

I'd also like to thank our DoE friends…EM, ORP… and then various projects…the supporters of the projects that I mentioned. I apologize for going over time. If there are any questions, if there's time I'm happy to take them.

Thank you.

BAHR: Okay, thank you.

[Applause]

BAHR: It looks like we've got about 15 minutes for questions, so we're in good shape. Any questions from the Board first? Mary Lou?

ZOBACK: This is just a point of clarification. Early on you said you didn't see resumption in the high-level waste glasses unless the pH was above 10.7. Then you went on to show how different parameters influence that. So all those tests you showed were above pH 10.7?

PEGG: Just to clarify, what I'm meaning here is the pH I'm talking about is the natural pH the glass comes to; it's not a control parameter. So what we found was that if we took glasses and just let them leach and just look at that leachate pH, if the leachate pH stayed below 10.7 we did not see resumption. In all the cases where we did see resumption, the pH had gone above 10.7; and if it was above 11, we always saw resumption.

ZOBACK: I see, thank you.

PEGG: That's a little confusing perhaps the way I—

ZOBACK: Yeah, you were going kind of fast too.

PEGG: Yeah, sorry about that.

ZOBACK: I admire how many words you got into that time period.

I have another question too, another clarification. When we were talking about the ALTGLASS database, I thought you said you had 17,000 points; and then you said the database had 600 points or something. So are all your data in that database?

PEGG: Oh, absolutely not…no, no, no. That database has about 2,000-some records.

ZOBACK: And you have 17,000?

PEGG: 17,000…that's just PCT…that doesn't count all the other tests.

ZOBACK: Okay, how come…and this isn't assigning blame or anything, I'm just curious. If a database exists, then are all the researchers working on glass contributing to it; or do you need funding to get the rest of the data in?

PEGG: As I said, these data that we've collected have been internally funded. As we get to aspects of a particular story, we will publish it. We have no support to – we have periodic support. So probably two-thirds of the ALTGLASS database comes from one of our reports from 2011, which was funded specifically by the Hanford Low-Activity Waste Glass Performance Assessment Project. So we were expressly funded to go back into our database and select data that may be important for that PA, which included leach data and secondary-phase data.

So there are 253 glasses running out to probably 4,000 days in that 2011 database…that report. And that constitutes two-thirds of the ALTGLASS dataset.

ZOBACK: Then if I understand you correctly, of your 17,000 or whatever data, the ones that would be important to be in that database could be in there; but it would require funding to have someone go through and…?

PEGG: As you can imagine, these are long, long…sometimes to even figure out – it's an exercise in itself to go back and mine just for this kind of presentations=.

ZOBACK: But there aren't any priority issues…it's just an issue of getting funding to—

PEGG: Essentially, yes…I mean, we're engaged in other projects; and each one of these studies we do in this area there's kind of a side project that's usually not funded.

ZOBACK: Okay, thank you, that's helpful.

BAHR: Paul?

TURINSKY: Paul Turinsky of the Board. I'm wondering what other sort of experiments do you do, other than these -- I'll call them dissolution experiments -- to get a more fundamental understanding of the mechanisms that are going on here?

PEGG: I think that's an area where great progress has been made over recent years, with the greater focus on the solid phase. So the old story of glass leaching was exactly that…leach in glass and measure what's in the solution. A certain amount of secondary phase analysis – scanning electron microscopy, x-ray diffraction – see what phases are forming.

But more and more we're seeing, as Stéphane showed, some of these advanced techniques with atom probe tomography, advanced SIMS techniques, to look at the residual glass, the alteration layers, the structure of those layers, and making that correlation between one you see in solution and how the glass itself has altered, not just in terms of the crystalline phases but all the hydration zone. And as you saw from this morning, it's actually very complicated; there's an awful lot going on.

So the material that is leaching, the simplistic idea is it's glass and it's dissolving. Well, no, it's glass that's changing into something else over time, as well as it's dissolving; the surface layer is changing, may become passivating. When you look at anything involving a diffusion profile, you're now talking about diffusion in a compositionally and morphologically stratified medium with diffusion coefficients which are probably spatially and temporally variant. So it becomes a very, very challenging problem; but the techniques are becoming more and more available to make those kinds of measurements and make those correlations.

TURINSKY: And do you have collaborations with other institutions were you take some of your glasses that have been leached and send them out for analysis where they have instruments that Catholic University does not have?

PEGG: We have over time. In fact just a few weeks ago we were talking about with colleagues at PNNL of looking at some atom probe tomography on some of these. Again for the LAW glasses where a lot of this information is really key to the performance assessment, the on-site shallow land disposal facility. There's probably greater initiative than need in that area, so that's one of the areas of focus that we're looking at, yes.

BAHR: Other questions from the Board? Sue.

BRANTLEY: Sue Brantley, Board. So this is following what Mary Lou was asking. I'm still confused. You had like 17,000 dissolution experiments, but mostly they were not supported by DOE, is that what you're saying?

PEGG: Yeah, so how did we get started in this? This is a little bit of a labor of love. You start a leach test – so designing glass compositions, as Carol mentioned this morning, usually you're designing a glass that goes to the melter, has the right viscosity, conductivity, it's got the waste loading you like, all those (inaudible) parameters. And then there is a product consistency type test, which is the seven-day PCT test, for example. Now at that point, if you like the contractual requirements of the facility, that's a compliant glass. And so what we were faced with

early on was rather than go through all this pain to set up a test, you run it for seven days and then pour it down the drain. Usually not literally, but something like that.
So we elected to, once we’d set up those tests, keep them going for longer. Now the project, it’s just the way it worked, the project wouldn’t support that because it’s not adding value to the compliance short-term requirements. So we simply kept many of those tests going. That’s, in a way, how this happened. And in the early days there were a whole bunch of tests that were set up because of our support to the Yucca Mountain Repository Program -- that kind of ebbed and flowed, but largely speaking what’s happened is the tests we’ve set up we’ve elected to keep them going on our own nickel. For 36 years. Yes.

BRANTLEY: So what do you think causes stage III? What are the causes?

PEGG: What do I think –

BRANTLEY: With all of the experiments –

PEGG: Aren’t I out of time?

BRANTLEY: We’re talking about it a very essential scientific level. Is it – I mean, what is it that causes stage III? Or make it more specific, you showed I think the rate of one glass increasing as you added silica in the solution. What caused that?

PEGG: Yeah. So now I have this Hobson’s choice, right? You’ve asked me two terrible questions, which one to choose. I will take the question one, please. Can I call a friend? What causes stage III? I think this idea of getting into a phase field and solution or in the reaction zone where the solution enters stability with respect to a new phase, that phase – the growth of that phase, may or may not be depleting constituents from this passivation layer, which then, you know, becomes a vicious cycle of this new phase, grows, starts destroying the passivation layer and the reaction picks up again. I think that’s a very plausible argument to me.

One of the things that would mean, though, is that inherently in that process there are nucleation and growth phenomena of these complicated phases which, you know what, you think then of predicting that, you know, the time to the critical nucleation growth of a phase, that starts to get very challenging. But I think in terms of what causes it, that, to me, seems very plausible.

Now there were old ideas in terms of a very strongly-protective passivation layer, which, as it grew thicker and thicker, actually cracked. Just became just a mechanical problem when the phase cracked, and you got new contact of the leachate with the glass was an old idea.
I think the phase precipitation is a more plausible.

BRANTLEY: In the experiment where you added silica and then the dissolution rate increased?

PEGG: That really is perplexing. And, you know, there's a multitude of sins thrown into this Q term. So in this affinity equation, it's one over Q, one minus Q over K, and you know everybody says transition state theory, blah, blah,

blah, and Q, and then we’ll take Q as the ion activity product and we’ll just replace it with the orthosilicic acid and forget about everything else. Um, well maybe we shouldn’t be forgetting about everything else. Maybe it truly is an ion activity product that includes not just silica but other species. We may be in a region where silica by itself is not the sole controlling constituent. But, again, that is a very troubling observation because it’s just in stark contrast with that affinity term.

So, yeah, I would agree with earlier comments that early stages, by and large, are in comparison very well understood, but at least not in this respect.

TURINSKY: I’ll take a second shot. Have you looked at the impact of glass making, in other words, the same compositions but different procedures for making that glass? The cooking times and pouring rates, and that sort of stuff?
PEGG: That’s a good question, yeah. So we have, I didn’t show any of the data, but we have tests on glasses that were made in a crucible, platinum crucible, melted for two hours, continuous stirring. And glasses of the same composition

that were made on melters of four different scales. So tens of kilograms, hundreds of kilograms, thousands of kilograms a day. We have parallel tests on those glasses. And by and large they track really quite well. I must say I have not gone to pains to look at the very, very long-term data for that comparison. And certainly the melter data won’t extend to the very long periods that I’ve been talking about. But as far as I recall, there are no big differences.

Now one of the differences that you could see, however, is it’s certainly known that you can get somehow water into glasses, believe it or not. So you can get a few tenths of a percent into glasses. And one of the differences with a crucible melt is generally it’s from dry chemicals, and in the slurry-fed melters, you’re feeding the waste and glass formers in a suspension in water, so you have a high partial pressure of water in the overbearing atmosphere of the molten glass. So you are actually tending to put more water in the melter-produced than the crucible-produced glasses. And that’s something we have also looked at.

BAHR: Jean Bahr from the Board. First question that I have, and this may just be an artifact of the size of the experiments that you were doing, in some cases your stage III then seemed to level out.

PEGG: Um hmm.

BAHR: And I can see it leveling out at a hundred percent, but it basically reacted everything. But in some cases it seemed to plateau at 70 or 80%. What’s going on there?

PEGG: Again, not absolutely sure, but I mean the guess would be that we’ve reached a situation where we’ve run out of some limiting constituent in the glass to continue to form the mineral that’s being formed. So we may have produced a depletion zone that just maybe there’s not – there’s no longer enough aluminum there to continue to continue to make those zeolites would be my guess.

BAHR: And then my second question is if you were able to put all of your 17,000 experiments into the ALTGLASS database, what do you think the value of that would be? Would that –

PEGG: The value?

BAHR: Or what could they do with that database with all of the data that – or, you know, is there a question of whether the data that are in there are representative or not? Would they be more representative for analyses that one might want to do with that database if you had the whole universe of data that have been collected?

PEGG: Well, obviously more data is better. There’s nothing wrong with the data that’s in there. At least I can only speak for our data. It was all collected under very high-quality assurance controls.

BAHR: But are there holes in composition space –

PEGG: Oh, very, very, very likely, yes. Yes. I mean a lot of the data that’s from us that’s in that database are LAW glasses, so they tend to be the high-sodium glasses. There are a number of West Valley glasses that are HLW glasses. But, yeah, these glasses are 20, 30, 40 component systems, so the more data you have, the better hope there is of understanding these composition effects.

BAHR: Okay. So then if one wanted to get all of your data into that database, what kind of a person-year effort would that require? To mine the data to get it into that database.

PEGG: I'd rather not speak off hand. It's a fairly substantial – of course it could be done But it's a substantial undertaking.

BAHR: Okay. Mary Lou?

ZOBACK: Mary Lou Zoback, Board. Just to follow up on that, and I'm asking you, maybe the question should be to Carol, but so you have a lot of data. I guess what has impressed me is that you've had it run for so long, so I would say you have some unique data, at least from what I've seen yesterday and today so far. What about the international data? To your knowledge is that in the database as well?

PEGG: There are data from the UK. There is NNL. Plus Sellafield glass data. I don’t recall there being other international glass data.

ZOBACK: French data?

JANTZEN: No. I can only take what’s available in the open literature. National Nuclear Laboratory gave me their datasheets.

Bahr: Can we – maybe we can get Carol to repeat that answer into the microphone.

JANTZEN: That one or that one?

UNIDENTIFIED SPEAKER: That one. That one will be fine.

JANTZEN: I can only reproduce or put into the database what’s actually out in the open literature. And National Nuclear Laboratory was kind enough to send me their Excel datasheets with their raw data before it has been published.

So that is the only international data that we have right now.

BAHR: Other questions from the Board? From the staff?

Pabalan: Pabalan Board staff. Ian, you mentioned earlier that the initiation of stage III likely involves the nucleation and growth of a more stable phase. And it would be useful to understand much better what these phases are. I’m guessing this kind of study or process would be experimentally or analytically inaccessible just because it may be a short term or maybe a very small amount of phases being produced. My question is are there other techniques like molecular simulations that would make these kinds of studies more accessible. And maybe I don’t know if you know the answer. Maybe Joe can answer that later. So are molecular simulations able to maybe provide information that we need for this nucleation and growth?

PEGG: Certainly there’s great strides that have been made in those kind of calculations with improved potentials and density functional theoretical methods. I think the complexity of these problems we are talking about, just the unit cells for some of these things can be very, very big. Lots of substitutions, solid solutions. It’s a challenging problem. In principle, probably yes. In practice I think, we’re still probably years away from making that tractable would be my guess.

Experimentally, and you can see the challenge here, is that, you know, if you are looking at these resumption problems, first of all you need to take a glass, figure out when the resumption occurs. And then you’ve got to do it again so you can sample it before and afterwards. So at least having a library of these glasses, this is when the resumption occurs. If anybody wants to repeat that. I mean, the kind of things you’d like to see is well, what do things look like right before resumption, and then what happened right after. Maybe even during the resumption process.

So now if it’s something that you have to wait for 2,000 days for it to initiate, that’s a problem.
So there’s been some nice experiments in France where they were looking at taking glasses and seeding them with zeolite

seeds to try and trigger this process earlier. So there are some deployment techniques that may help shed more light on this.

Pabalan: Okay.

BAHR: Okay, I see that we’re over time, so thank you Ian.

PEGG: You’re welcome. Thank you.

BAHR: So our next speaker is Dr. Joe Ryan from Pacific Northwest National Lab. And we had a chance to visit some of his laboratory facilities yesterday. And he has been working on a whole variety of surface-related techniques looking at properties of glasses and ceramic materials. And with lots of exciting instrumentation. Joe is an active member of the American Ceramic Society, and he is a graduate of the Penn State University.

RYAN: Okay. So thank you very much for giving me the opportunity to speak today. I’m going to be giving a kind of a summary on some of the work that has been done throughout the DOE complex on improving the understanding of rate-limiting mechanisms throughout this whole process. So it will build on a lot of the talks that you’ve seen earlier, and that will really help us kind of be able to bear down on some of the areas that we’re looking at.

So the background of the team that has been kind of put together, the most recent team, is that it was put together in about 2010, but this is only the most recent incarnation of this work. As you heard from Bernd and Carol, this work has been going on for a long time, and occasionally we come together in groups like the GLAMOR Study, or the JSS Study before that, to investigate problems in long-term glass corrosion in a collaborative manner.

But this group that we put together, and here’s a couple of summary papers, the report and two more recent summary papers. What we’re trying to do is identify the mechanisms that control glass dissolution over many different conditions and in many different times. And then perform the fundamental research and apply that to modern materials, modern choices of glasses, and use the modern materials science techniques that are being developed to understand the mechanisms in question using targeted experimental things. And then critically evaluate the test methods, the data, the interpretation, and the models as a group so we can come together and develop more of a consensus on what the critical problems are, how to solve them, and what the mechanism – how to interrogate various mechanisms in glass corrosion.

So the critical question that we’ve all been asking today basically is what’s the rate-limiting mechanism for radionuclide release from the waste form and how should models represent that rate-limiting mechanism in various time periods?

The corrosion behavior of glass results from a combination of processes, as we’ve seen throughout the day here.
And more remains to be known about which processes dominate under which conditions. And which ones do the models have to take care of, and how.

And so we’ve developed this coordinated approach that leverages particular national and international expertise along with particular national and international needs. So each group might have a different need for which conditions they would be looking at and which mechanisms would be most appropriate to study.

So this is the diagram you’ve all been seeing, but in this case I’ve kind of lit up which mechanisms are kind of operating at which conditions. And you can see that over the lifetime of a glass corrosion experiment in a static solution, this is static solutions right here, that all of these mechanisms operate but some of them operate more than others at certain time periods and in certain areas of behavior.

And so the idea here is the behavior of glass when you take it from a holistic standpoint at all times, it’s believed to be a result of a combination of several processes at work at any given time. And all of these, if you take it in a holistic fashion over the entire lifetime of the material.

So the different processes dominate in different conditions. And the key thing here is we want to account for that in model development. So you want to take a look at which processes will be operating in each condition.

So we’re trying to use a mechanistic approach and mechanistic experiments to get at this question.
As Carol mentioned, the activities are planned based on the overall strategy in the ASTM C1174 document that tells how waste forms should be evaluated for performance and how to basically do that activity. And the goal here is to provide a mechanistic foundation for our models. Determine which mechanisms control glass degradation rate, and provide a technical basis for each model that we are putting together.

And to insert flexibility, the research really hasn’t focused on an individual set of environmental variables. In fact, it’s gone the other direction to take a look at the environmental variables that are most appropriate for the teams working on each individual glass area.
So the experiments are necessarily – they were designed to include those that are targeted to explore individual

mechanisms and more general examination of behaviors similar to what Ian was mentioning where you really need to know what happens over a long period of time, that experiment might not be targeted towards an individual mechanism, but it helps to understand what the long-term behavior is for as long as we can actually do the study. Which when you figure out the lifetime, it’s not that long, but when you try and do these accelerations, you can get a good idea of what the behavior is in general.

So I’m going to go through – I’ll go back a couple – and say I have this list of mechanisms here. And I’m going to go through the areas, each area, and talk about the work that has been done in each area of these mechanisms. And in each case I’ll try and give one or two examples of a targeted approach taking a look at that mechanism, and then a more general overview of the work that has been done.
So a targeted approach for the dissolution of the network, a good example of that is a report by Peter Zapol from Argonne National Laboratory where he was trying to use a first principles approach using density functional theory to examine the glass-water interactions at a bond-per-bond

standpoint. So basically he developed a set of energy barriers for modeling glass dissolution, which, for example if you had a silicon atom that’s completely connected to the glass network except for one bond that’s exposed to water, what’s the difference in energetics between that one and one that only has one remaining bond left to the glass network? And so he developed an entire series of simulations using quantum mechanical calculations to take a look at the energetics for each of those bond states. So basically you have this transition state that takes you from the solid state into a broken-bond state, and he examined what the size of that energy barrier is to move from one state to another.

Interestingly he also took a look at the probability of moving backwards. Because we do see condensation events happening to form that gel material on the surface of the corroded glass.

So that’s a way to use one of these more targeted experiments. You can’t get simulations to examine a 30-component glass, but what you can do is take a look at each

individual bond and get predictions of probabilities and see how that will affect the dissolution as a whole.
So other recent findings. Those of you who are familiar with geology, and I know that there is a number of you, will not be surprised that we are taking a look to see if there is more of a pH dependence than was currently incorporated into our models. It’s not a surprise that water, hydroxide, and hydronium all play a role in the rate model from some of these more recent findings.

We’re also – a really nice new paper from Stéphane that examines the roughness at the buried interface between the gel and the unreacted glass using a multitude of techniques. Also looking at the impact of composition on both of these. And then Stéphane mentioned several times that we are working with Jincheng Du at the University of North Texas who is an expert in molecular dynamics simulation. And just to put together this MD model of the international simple glass is really quite a feat that required a lot of work. But he hasn’t stopped there. He’s actually using those models to populate some Monte Carlo work that Sebastian Kerisit here at PNNL is doing to examine how water then interacts, again using kind of these kind of probabilities to inform how the Monte Carlo will work to generate porous gel structures.

So the theory of a passivating layer, that’s another aspect. So here’s some experiments that were targeted to explore that phenomenon. It’s a difficult thing to explore because if you are looking at transport between them, the idea is, how do you tell the difference between the ions that were in solution and the ions that were from the glass or the gel to start with. And what has been done over the last probably ten years, and a little bit more, is the increasing use of isotope tagging experiments and isotopic enrichment to examine that study. I’ll give an example here of one piece of experiment. This was a nifty test where we took two different glasses that had the same chemical composition but differing isotopic ratios. We made glasses, coupons and powders from each glass, put them into a vessel with kind of controlled conditions, and allowed them to corrode for a little while.

These are the various isotopes we substituted in the glass, so you can see that we tracked seven different types of ions. That includes formers like silicon that are part of the network, the mobile former of boron that is more mobile than silicon in terms of solution. We have an alkali, an alkaline earth, and then several transition metals.

And what we did was we allowed those to corrode over time, and we do a characterization of the experiment. But the key thing was when they corroded for quite a long time, around 200 days, we decided okay, they have an alteration layer, now let’s start our tracing experiment. So what we did was we took the solution from each one, just switched the pipettes, and put the solution back in. So now you have a – the isotopics of your solution are different from your isotopics of your solid. So then you can monitor the progress of your experiment over time, and monitor the isotopic migration into and out of the solid phase, the concentrations in solution, and continue that experiment. These actually are ongoing for three years now after that swap.

So right off the bat one of the things we noticed was the silicon isotopic ratios, pre-swap it was kind of consistent through the alteration layers of the glass, but after the swap, even one day, it started to penetrate right to the corroding glass interface, and then didn’t change very much, except for getting deeper, as the experiment proceeded over time. So it seemed to be that the silicon went close to the glass reacting surface.

Another thing we noticed was the isotopic evolution of lithium. That was a little bit different. Within one day you can see this – I made this dash line the same place as it is on the silicon plot – but you can see within one day it actually penetrated well beyond that dash line from the previous plot. Seven days it was in even further, and as we got over to about a half a year it was more than half of a micrometer into the sample with that isotopic change of silicon. Obviously different ions behave very, very differently in their transport through the gel and into the solid state glass material.

So these experiments conclusively showed that the gel wasn’t a transport barrier to these particular ions. And it showed that the tracer ions behaved quite differently. I didn’t show most of them. The ones I didn’t show were kind of boring. They behaved how we expected them to. Boron was the least at the gel-glass interface, and transition metals just kind of stuck where they were from the glass. They didn’t really go into the solution. And they didn’t come from solution into the gel or the glass.

But what we realized is we didn’t have the resolution to answer many of the questions we had. How is this proceeding? So we wanted to develop a new characterization technique. So the one we did was Atom-probe Tomography, which you’ve heard a couple times just mentioned. The idea here is that you have a technique based on field ion microscopy, which was the predecessor, oddly enough, to scanning electron microscopy, they decided electron microscopy was a better way to go. But what you do is you create a small tip. And when I saw small, it’s on the order of 20 to 100 nanometers across and about 400 nanometers in length. You make this tip. You put a large field on it. You tickle it with a laser, and that sets off the ions which are accelerated through a local electrode and detected on a detector in the back here. And the idea here is what you get is a three dimensional elemental map with single atom sensitivity and sub-nanometer position accuracy. And the effort that we did produced the first atom probe results for multi-component amorphous oxides. It had never been done for multi-component glasses before. And so we really developed this technique, and now it’s being done fairly routinely in France and at PNNL to give us this information with really, really high spatial resolution.

And what did we get from that? Well this is that same sample. This is at – I think this is the two-week post-swap sample. Again you can see that lithium penetrating into the glass material. One of the key results was this blue line, and that is boron. One of the neat things is taking a look at the X axis here, it’s extremely small, very, very small, resolution. So you can see that these are single-digit nanometer fronts here.

So we saw that the boron was not really a diffusion front. It’s a very, very sharp reaction front. It is offset from where the silicon starts to equilibrate with solution. The silicon goes beyond that front as the full glass component and then starts to equilibrate with solution. This was a much more complicated interface than we had been giving it credit for. There’s a lot of mechanisms that are ongoing, and this is still an area of research.

One of the key things here is ion exchange. We talked about. You can see atom probe can take a look at hydrogen profiles. And this is a test. Same glass, similar conditions, temperature and everything. There’s the hydrogen profile at one year inside the reaction front. There’s one at two years. It’s about the same distance. There’s one at 26 years from the experiment done at CEA. Again, very similar profiles from one to two to 26 years. It doesn’t appear that ion exchange is penetrating any deeper into the material with time. For these experiments anyway.

From that, now we wanted to know more about the gel and the impact of an interfacial layer. So Stéphane came to work at

PNNL for a while. He came up with the idea to create the gels and then perturb the system, basically to poke it. Monitor various ion molecular transport through them using dye tracking, isotopic tracking. And start out with conditions where you take a glass and put it in saturated solutions and create the gel from the get-go.

And one of the neat things that was seen here was that there was very little silicon isotope equilibrium throughout the system. That’s this line here. Except at the very, very surface, and there’s not even much at that, the solution didn’t talk to or incorporate itself in – the silicon in solution did not incorporate itself into the growing gel material.

So a very interesting result showing that the gel formation was not possibly how we had thought before. It’s not a precipitation event when you do the test in this manner. Again, as Stéphane mentioned, as you go to really higher pHs, that changes, but in these conditions it showed us that the gel is a restructured version of the glass. And this just shows that in more resolution and a picture of that layer as it is forming.

The gel structure, also we found that it is notably different from the glass. This is just a Raman spectra and the big takeaway here is that this black line is very different from those colored lines, and that's the pristine glass versus the structure of the gel. So you can see that the silicate structure is very, very different in that gel area. It's a highly porous material with specific surface areas ranging from 11 to 800 square meters per gram. Because of that different structure we know it's not a relic of the glass structure. You don't just simply leach things out and this is what remains. It's actually reformed material.

And then we found that the structure formation depends strongly on composition and the pH that it's going on.
So there's a lot to see, and as Stéphane mentioned, this is an area of active research to see how does that gel form and how does it impact the glass corrosion from that point.
So elemental profiles. We're getting really good with our characterization is the key here. We've shown that the boron profile is very, very sharp. It's most likely a reaction front. And then alkali ions behave differently from each

other. And so this is a decent summary. And then again I’ll plug the recent paper by Stéphane where he used multiple characterization techniques to illuminate the fact that there might be an intrinsic surface roughness that forms at the interface below the gel.

So it means that the breakdown of the glass waste form occurs via dissolution. But don’t think that it takes transport properties out of the equation because if transport is impactful, it probably impacts via dissolution. So you have nanoporous materials. You have very different chemistry in those nanoporous materials than you do in the bulk. So if you have a transport impact, it’s probably because of that, that you have different chemistry in those nanoporous regions rather than just simply a limitation of transport in that area.

So this is just a summary of those findings on the alteration layers. I think it’s one of the major findings that we’ve had in the last five or ten years or so.

Also there’s been some targeted work on ion exchange. It’s a demonstrated phenomenon, and pretty much everyone agrees that the mechanism plays a role, the question was how much, and how do we model it.

So that previous experiment showed lithium quickly diffusing into the glass in a similar, if faster, method to hydrogen, so Jim Neeway and Stéphane and I actually came up with an idea to say well maybe you can take a look at that and knock out the impact of corrosion and examine only the diffusion of lithium into the material.

So we decided to do a non-aqueous method. Again this is very targeted towards one particular mechanism. It doesn’t have anything to do with corrosion from a water standpoint because there is no water in this experiment. We knocked it out of the equation, right? So we wanted to look at only one mechanism. And we designed this test to put glasses in this non-aqueous solvent that is spiked with an isotopic version of lithium.

And so we got the results. We had different durations in the solution, and different temperatures. And you can see that we have some neat profiles that grow with time.

And so we tried to fit it to Fick’s second law, just isolated diffusion experiment. And you can see it kind of fits, but it didn’t fit all that great. Until we started using an interdiffusion type model. And that says that the ions coming in are different from the ions going out. And when we started doing that, these models tend to fit a lot better, and we got good diffusion coefficients for the various mechanisms that were going on.

And one interesting thing here, these are two different – this is – these particular ones were ions going into the glass. We also modeled, of course, the ions going out of the glass, and these are the profiles the other direction. One interesting thing that we modeled, when we did the experiment we thought these little humps at the top here were experimental artifacts. But when we used the interdiffusion model we actually found out that that was predicted by our model. It shows that there is a little pileup that occurs in interior of the sample just as a result of those differing diffusion coefficients of the different ions.

And then it fit also the sodium. One interesting thing of the sodium, there was an exchangeable sodium content. Only a small amount of the sodium was available for ion exchange. It was about 20% of the sodium that was in the glass was available for ion exchange. The rest of it didn’t appear to behave with that at all.

I mentioned we did this at different temperatures. So we got an interdiffusion activation energy. These activation energies are very high compared to glass dissolution. But what we found is they are almost exactly the same as molten salt ion exchange for making your gorilla glass for your iPhone, how commercial entities do to chemically strengthen glass. So it seems to be a very similar process of ion interdiffusion in the material.

So these are the general findings for this, as I mentioned. The nice thing about it is the findings led to a model for solid state alkali interdiffusion and it is published. The downside to it is it is with lithium. We tried to do it with hydrogen. Failed in multiple spectacular ways. Basically it’s difficult to get hydrogen in a non-aqueous solvent that acts the same way as you might expect for an alkali material. And so the applicability of the model for hydrogen is part of ongoing work. And work remains to examine the reaction that introduces hydrogenated species into the solid glass. How does that first exchange at the surface proceed? So other recent findings in this area. Ion exchange mechanisms, the entire process takes two steps. One of them is at the surface and then the other one is diffusion in the glass. And that various alkali behave differently.

I also want to bring up medium-range order. There is a paper Carol wrote kind of in the – when was the year? 2010. And it has this figure in it. That’s where I got this from, actually. And the idea is that there are certain compositions that might produce channeling and/or percolatable kind of order within the sample, and that’s an idea – this isn’t phase separation, this is actually the structure of the glass itself just sort of having preferential order at a medium-range scale that might impact the glass.

Some models in simple systems predict this type of behavior. And some solution data, actually it’s the solution data is similar to the stuff Ian presented, suggested this might happen. But only minor and tangential evidence has been observed in waste glass material. We don’t really have any major evidence for this yet.

So when you are talking about crystalline alteration phases, here is a targeted approach towards stage III. You guys have all seen the behavior kind of diagram that we’ve all seen as we go through. It’s really nice to get an actual set of data points that shows that that is the case that’s going on. You just have the full set of data points when we examine our system using Raman spectroscopy. One interesting thing, you know, phase I is kind of below concentration limits of the technique, but we show how quick it is to get to a certain level of concentration. And then at some point with this glass, this is a terrible glass by the way, which is why we chose it. The glass takes off and accelerates due to the precipitation of zeolites. And these little gaps in the spectra here are actually indicative -- we know it’s a precipitation of zeolites because they coated the window of our probe and knocked out our signal. So we can evaluate in-situ, mentioning just having the ability to sample before, after, and during the initiation of stage III, now we have a technique that can actually show it as it occurs. So this is

fairly brand new. We have a paper that is in draft – it should go out next week actually. But just to give you an idea of how we’re trying to develop new techniques to examine these problems one mechanism at a time.
People have also mentioned there are seeding experiments. Maxine Fournier was a great grad student and is now a great staff member at the CEA. He’s got some really nifty ideas on how to study the impact of crystalline alteration phases and model those. And then of course we’ve all been talking about an informatics-based approach using large amounts of historical data to examine trends in this – trends in when stage III starts, trends in its rates, trends in its extent, and trends in the local conditions that cause it. And then in-situ examination, having an approach that is coupled with the kinetics of phase precipitation. And then the idea is to do this all on an open basis so that when we’re done we have large-scale international agreement that what we’ve done is good, that it represents the mechanisms that are operating, and we have a good model.

So I’d just like to point out, I’m sure it’s been said, that whether or not stage III behavior occurs contributes to the highest uncertainty to calculated rate. If it doesn’t occur, glasses are good in almost any repository condition we can think of. If it does occur, it’s less certain and it depends on the repository that you are considering.

To that end, I’d like to talk about a targeted approach. This is actually from our friends in Belgium on the super container concept that Bernd talked about in the first talk where they basically created a series of cement rings with steel containers, and then the glass in the middle of that setup, counting on the cement to modify the corrosion of the steel itself and leaving the glass kind of at the end of all of that creation. But they wanted to take a look at what happens when – if the glass were to contact these ground waters as a function of time. And so they took a look at several pHs which account for what the pH of the solution would be at several different time periods in these cement conditions. And what they found was the glass didn’t dissolve as – it wasn’t as terrible as we thought it was going to be is the end result here. We found out that there actually still is kind of a stage II that is reached even though your pH is 13.4 to 13.6 throughout the entire test.

That was a very interesting result. We do find even where, you know, the SON68 here didn’t appear to be accelerating yet, this aluminum decrease suggests that it might start to fairly soon. But these experiments are very helpful because they are kind of relevant to waste form options of disposal where cement materials might be nearby to the waste form if we want to have some calculations of mechanisms in the U.S. standpoint where you have cement lurking around glass waste forms. We can use these studies from our friends for whom it is more important to educate ourselves on what the options are there.

As Stéphane mentioned and I think Aurélie is going to talk about, the impact of iron corrosion products is a major area of research in several different countries. So there’s the ancient study of a smelter, which I think is going to be coming up, and then our Japanese colleagues took a look at the corrosion of a buried sword to examine the various alteration products that the glass might come in contact with given a particular kind of steel. And basically relate it to the impact of canister corrosion on glass.

People are also looking at the presence of magnesium and how that impacts glass dissolution. Our Japanese colleagues are interested in that mainly due to the fact that there is a lot of magnesium in their groundwater due to the fact they are so close to the sea. In the UK, they are also interested because they have, of course, magnesium in their waste glass. And so people have different interests and they examine different aspects.

One of the questions was on the Board taking a look was how to impact glass – how you take analog systems and apply that to our corrosion understanding. So this is one study, it was in Applied Geochemistry in 2013. Dennis Strachan and a couple others took a look at glass from a shipwreck called the Iulia Felix off the Italian coast. And what we found, you can see this is a piece of glass, and it’s got this lump of sediment that’s around it. And the reason all of this stayed together and it doesn’t look like sand was because it was cemented together. And it was only cemented together kind of nearby the glass. So we did a study to see why that might be, and we found that the silica that was coming out of the glass material, you could take the rate at which it was coming out and then use geochemical modeling with the composition of the seawater and the composition of the sand that was around there, and find that it dissolved certain parts of the sand and then reprecipitated with those components that came from the sand to form an interstitial kind of solid phase that was composed of the silica from the glass and other elements from the sand material that was around it, and it cemented all of the sand in a near field around the glass.

This is a – it’s nice confirmation of how our models worked. That was really good. And it also kind of shows how you can change your percolation of water through the near field. In some cases you might actually have a benefit from the glass that is actually decreasing your percolation of fluid through your near field materials. But all of that can be modeled with our more advanced geochemical modeling that we are doing lately.

When it comes to modeling and rate model parameterization, this is just an example of a targeted approach that we’ve been doing. This one is just submitted that took a look at the rate model parameters from the transition-state-theory kind of based rate model that we have.

We took a look at three different glass materials and examined how far away from the parameters that we have regressed from the data that we got using flow-through data, could we be before that experiment didn’t work anymore and the data didn’t fit. Or the model didn’t fit the data. And what we found was that the parameters, as I think it was Bernd who mentioned earliest, that parameters are highly correlated. You always have to worry about, if you are doing especially empirical parameters, are those parameters that you have developed for your equation independent? And in this case, they are not independent, but the set of them actually reproduces the data quite well. And the idea here is you have a flat ellipse, and anywhere in that ellipse you fit the data pretty well. If you go off that ellipse in kind of a Z direction, if you can follow my meaning, if you go just a little bit above the set of parameters that fit your data, then you’ll be wrong and you won’t fit the data anymore. On the other hand, you can a pretty far distance as long as you stay in that plane and still have a reasonable fit to your data.

So the nice thing about that is that all of the three glasses that we studied were on the same plane. And we have ongoing research to examine other glass compositions, again needing more data and having more data really helps with this effort. We might be able to find that you can get a general set of composition space that parameterizes most borosilicate glasses – or boroaluminosilicate glasses – and be able to basically nail down that portion of the rate model for most glasses that we work on.

We’re also doing model development validation in other ways. You’ve heard a lot about several models in here. The models basically have different approaches to how glass dissolves, and in doing so they use different equations to account for that. And what we wanted to do is develop a program where you could evaluate these models, head to head, same datasets, same way of dealing with the data, same way of dealing with the models. So we came up with a system where we can insert the models into a particular computer program, use a database of long-term experiments, the bigger the database, the better, so that we can examine how these models behave, which conditions they excel at, which conditions they fail at. And a lot of that can really inform where our next targeted experiment needs to go. So once we find out that, oh, we have an experiment here and it starts to fall off the actual data at this point, or in these conditions it doesn't really work well, or at high pH it doesn't work as well as at lower pH, we can start to examine why, and how to change our function of our equation so that our equations and our models work over the entirety of composition space and the entirety of predicted environmental conditions that might occur. It's all about getting these models to be more universal and more technically based in each time step and in each repository condition.

So a key question remains, how do we do all those mechanistic models and incorporate them into all of these, but at least we have the framework to be able to study that. So that's all I have. I'm sorry it was so quick, but the idea here is we're still looking for the information on what rate-limiting mechanisms occur in each condition. It’s a complicated problem. I think that’s what all of these talks put together come out with is that it’s a complicated problem. But it’s really moving along, I believe, because of the coordinated approach between a really good group of scientists that leverages particular national and international expertise and priorities. And it’s really nice to have a group where we can talk and limit the duplication of our efforts. We trust each other to do the experiments right, but then examine them to make sure that that happens. We maintain confidence in our abilities and our data. And knock our heads together at least once a year to come up with new ideas for how to attack certain mechanistic issues that are part of the – that are still remaining questions. So thank you very much.

BAHR: Questions from the Board? Mary Lou.

ZOBACK: Thanks. My question is about this collaboration, and it seems like the benchmarking of the different models and assuring there is adequate data to do that is really important and that’s where you really draw on the expertise of everyone in the group. So is there dedicated funding to run those models, either from the DOE side or the international side, or is everybody kind of, you know, bootlegging this on top of another project?

RYAN: Well, the nice thing is our sponsors from – at least our sponsor from Nuclear Energy, this whole international – and Environmental Management, I would say – this whole international approach and the collaboration is very important to them. And so they don’t see it as bootstrapping to their funding. They see it as yeah, we’re funding you to be a part of this and to make sure that this goes well and that it works. Yes there’s dedicated funding to model the data. Of course you always say, well, it’s not enough to do that modeling because then you’re like, well, I also want to do this experiment and this person wants to do that experiment. So there’s always a balance to how much funding each individual part gets. But there is dedicated funding to do that model evaluation.

Now getting the data from a different country or from a different institution, they have to have funding as well.

And so, you know, there’s points at which funding drops off for certain organizations, and then they can’t do as much work for a while, and we don’t end up getting some of that data incorporated.

So it’s really – it’s very much helpful when all of the organizations are well funded. It makes the whole thing work better. But we understand that that’s a limitation that we all have to live with and we try and live with it.

ZOBACK: But it seems that by benchmarking – you know, running these different models and benchmarking them against common datasets may help direct the research as well when you really see the gaps in the rate-limiting processes.
The other question I have is with regard to the natural and analog – the natural glasses and man-made glasses – oh, I forgot to say Mary Lou Zoback, Board, excuse me – you know, everybody talks about it but we kind of saw the process you would do in Carol’s talk, and you did mention the natural and analog glasses, but I’m an earth scientist so it seems to me – I love all these experiments, but I also trust the earth.

RYAN: Yeah.

ZOBACK: And I guess I’m not getting the sense that that data is really being utilized. It’s kind of thrown up as yeah, we’re looking at this, too, but – so it’s – is anybody – I mean we don’t have a talk here about results, you know, or analysis of natural and analog glass.

BAHR: Yes, we do.

RYAN: Yeah we do. It’s the last talk.

BAHR: It’s our final talk.

ZOBACK: Oh, thank heaven! Okay, thank you.

RYAN: Yeah, so Aurélie will give you a great – they probably have the best study that’s ever been done that really takes a natural analog system and uses our glass corrosion models to validate what was seen from that natural analog system.

We’re always looking for good analogs. One thing I would like to put a plug in for people who know geology better than us material scientists is if you can think of analog systems that would tell us more information – I mean the key with an analog system is you have to know the history, right? You have to know what conditions it’s exposed to over all times. We’re always worried about boron. Boron is a different one and it’s not – doesn’t occur in the natural glasses to a great extent. I’ve heard tale of some materials from the Smithsonian, they found some tektites somewhere that did have a little bit of boron in it, maybe a meteorite hit a boron-rich area. I don’t know how it got in there. But I haven’t been able to get a good portion of that sample that I knew the history of, of how it reacted. It tends to come from word of mouth almost when you get these samples, and when, you know, and who has the ability to jump and say, oh yeah, I would love to work with, you know, someone in Turkey, I would love to work with someone in Sweden. You’ll see a poster out there about a national analog from Sweden that Albert Kruger is funding. It kind of is when the opportunity comes along with a good natural analog we jump on it. But usually it’s not in the funding cycle to say, oh yeah, we’re going to plan two years down the road to have this perfect sample that we can then study. It’s hard to do that. It has been done, and that’s where some of our best results are, but you’ll hear a lot from that from Aurélie.

BAHR: Lee?

PEDDICORD: Lee Peddicord from the Board. Following up on the international collaboration group you showed us, are you all coming together on a more or less ad hoc basis or are you under the auspices of something like the OECD, Nuclear Energy Agency? How do you keep this all glued together and functioning?

RYAN: It’s kind of in between. So what we do is we have – it’s been most often in correlation with probably the largest glass science conference in the world. It’s called the Glass and Optical Materials Division Meeting of the American Ceramic Society. It’s got a big name.

But every year we get together with that meeting and tack on two days of workshop, either on the front or more preferably the back end so that we can listen to everyone’s talks and then they come into the workshop and they say, oh, yeah, we also had this data and I had no idea what it meant. And we talk about how the experiment can then proceed. You know, they gave their talk during the conference, but then afterwards they say, well here’s what I thought for the next step. And then all of us, oh, wouldn’t it be cool if – and we talk about the data in a very frank manner, really go over the interpretation.

So we do it at least once a year. We’ve had more meetings when – usually when we find that several of us are going to get together at some spot, then we have a scale meeting. But we definitely get the group together once a year.

BAHR: So we have time for about one more question before the break. Is there a burning question? Tissa.

ILLANGASEKARE: Tissa Illangasekare, Board. So it is more for clarification for me. You had a slide with text (inaudible) in forms of dissolution and diffusion. So I’m trying to understand – I thought diffusion is part of dissolution.

RYAN: It is. And getting the reactants and the products to and from the area where the dissolution occurs. And having the concentrations of those ions be what they are at that interface rather than what they might be out in the bulk. It’s a very important part of the process. As opposed to, for example, diffusion through a solid state. And that’s a different beast where you just have atoms hopping from one site to another doesn’t have as much to do with a dissolution process when that’s the thing that is going on. But if you are talking about diffusion through pores to get the chemistry what it needs to be at an interface, you’re right, they are definitely coupled and related.

ILLANGASEKARE: Thank you.

BAHR: Okay, so we’re scheduled for a break for about 15 minutes. We’ll reassemble at 2:45.

BAHR: Okay. Welcome back. And get people into the room.
So now we’re going to hear about how these various rate laws and rate-limiting steps actually get incorporated into performance assessment models. And to tell us about that we

have Bill Ebert from Argonne National Lab. Bill has over 30 years of experience in Applied Research. He has developed test methods and degradation models for glass, glass ceramics, metallics, and cement waste forms. And that includes the model used to calculate radionuclide source terms for high-level waste glass and does calculations for the DOE license for the Yucca Mountain repository.

EBERT: Thank you. I’m going to focus primarily on stage III, which you may have heard about, and how the recent improvements of the DOE models, I’m going to focus on how we are now addressing the triggering and stage III rate in performance assessments.

So I have a long list of questions, so that’s going to form the outline of my presentation, but I’m not going to take these in order. I’m going to start off with introducing what the improvements to the DOE models for glass corrosion are. Again that’s mainly for stage III. And how we’re looking at the corrosion mechanisms that are responsible for that behavior.

So I’m going to start at the beginning, which was about 1985, the seminal work of Dr. Grambow on applying well-developed, well-established, mechanistically-based corrosion mechanisms for minerals applying that insight to borosilicate waste glasses. So what we did thereafter was mainly run experiments to measure the dependence of the kinetic terms in that rate expression on glass composition, the pH that was generated in the solution, the temperature. And we used short-term tests to measure those model rate parameters. And we used long-term tests to evaluate the thermodynamic terms in that rate expression. But at that time we had limited mechanistic understanding of what was going on with stage III. We knew it occurred. We knew it occurred for a lot of glasses. We weren’t sure why or how to model it mechanistically.

So the model that’s in existence right now, we use the probabilistic approach to represent the dependence of the solution composition on the glass dissolution rate primarily, including the uncertainty in whether the stage III behavior would occur or would not occur under particular corrosion conditions.

So what I’m going to focus on this afternoon is the new developments in the model where we can identify the mechanistic origin and basis of stage III behavior, its effect on the corrosion rate during stage III behavior, and model that deterministically.

So whereas the – in the same way that the original glass model is based on mineral dissolution understanding, the new aspects of the model are also based on the mineral transformation theory that we’re applying to glass behavior. So I’ll also touch a little bit on how we are starting to improve – to interface the improvements in the model with the generic disposal system analysis model that is being developed by DOE for performance assessments.

So, this is the mathematical expression of the basic dissolution model that we’ve used for many years. It includes a series of kinetic terms. It includes the dependence on the composition of the glass, the pH of the solution that is contacting the glass, temperature of the system, and then there is this thermodynamic reaction

affinity term. So the Grambow approach to the model is to identify the hydrolysis of the terminal silica bond. The hydrolysis of that reaction is the rate determining step for glass corrosion. So the reaction affinity is populated by the solution concentration of orthosilicic acid as the Q term. And then the solubility stability constant for this reaction is used as the K term in the affinity term.
As Stéphane described, the glass cannot come to thermodynamic equilibrium with the solution because it is thermodynamically unstable. So we add this k-long residual rate term to prevent the calculated dissolution of the glass from becoming zero when this reaction affinity term becomes zero.

So I’m sure you are tired of seeing this reaction progress slide. But I used this about 30 years ago to understand how the model rate expression related to the results of experiments that we were running for a long time to show how we came to this stage III behavior. So I’m just going to quickly step through how this was generated to relate this equation to the experimental results.

So stage I refers to conditions that are far from equilibrium where the value of the reaction affinity term one minus Q over K is essentially one. So the glass dissolves at its kinetic rate, which only depends on the glass composition, the pH of the solution, and the reaction temperature. So that is essentially a constant rate if you keep maintaining constant pH and temperature so you get stage I is that constant initial rate.

So stage II refers to the buildup of glass dissolution products in solution which drive the value of the affinity term towards zero. So as the value of this overall term becomes smaller and smaller, we see the rollover in the test results until we reach this limiting value of the residual rate, k long, and it stops here.

So in this representation, the zero part is the initial system where you just have glass in water. And then the far right is when the glass has completely been converted to stable secondary phases in contact with the solution. So this transformation progress I intend is kind of a thermodynamic progress from the initial state to the final state. So any kinetics, mass transport effects, etc., are just affecting how quickly the system is moving up that curve.

So when you get to the point where the reaction affinity – the solution is very near saturation, the value of the reaction affinity term is very near zero. The rate is determined by this ad hoc term. And it can continue dissolving at that very low rate for a very long time.
So the fun begins when we precipitate particular secondary phases that somehow affect the dissolution rate of the glass, and we see this sudden increase in the dissolution rate that we call stage III.

So from the experimental results, we know that the value of this reaction affinity term is no longer near zero, but it is some constant value that is greater than zero, and that this combined rate is now significantly higher than the residual rate. And we see it from experiments, so Ian showed several and I’m going to show more data that show that the dissolution rate in stage III remains essentially constant. So that tells us that this value is essentially constant. So as long as the pH and temperature don’t change, you are going to maintain dissolution at that now constant stage III rate.

So somehow the form of this reaction affinity has changed in stage III. So we’re left with, now, we explain the origin of this progress plot and the uncertainty of whether a glass is going to continue forever at the low residual rate, or if critical secondary phases are going to form and the glass dissolution rate is going to increase at stage III. So we’ve seen stage III behavior in many glasses, but there are a large number of glasses where we did not observe stage III behavior during the tests and that low residual rate persisted for very long terms. So the objective of the work is to identify what are the conditions during the corrosion of the glass that trigger stage III behavior and how can we quantify the form of this affinity term for Stage III. So this now is how we're parameterizing and identifying the model values based on experimental data, how we're using the short-terms values to do that, in order to look at the long-term performance of glass for modeling in a repository.

Carol alluded to a large number of targeted test methods that are used to target the behavior in particular reaction conditions that we can identify different tests that are appropriate for looking at the corrosion behavior under the conditions where you see Stage I dissolution, the approach to saturation, and then when Stage III occurs. So we have different test methods, and mainly they generate fluids having different concentrations that put you in those different regimes for the reaction affinity terms.

So we run tests with different glass surface area-to-volume ratios by using monolithic samples or crushed glass samples to provide high-specific surface area. So we can maintain conditions far from saturation, we use monolithic samples with small surface areas to look at Stage I behavior, where we can go to very high surface area-to-volume ratios to look at the approach of the system towards saturation and then beyond into Stage III behavior. We use methods with static, semi-static, or dynamic solution conditions, where they flow through. We use those to control the evolution of the solution composition during the tests…differences in the behavior in static and dynamic and semi-dynamic test methods.

We can evaluate the relative contribution, the mass transport, and surface dissolution to the corrosion behavior, et cetera. We use various imposed leachant compositions. We can impose high or low pH concentrations. We can introduce spiked amounts of silica or aluminum into the solution. We can use leachants with different isotopic ratios to understand the aspects of the corrosion mechanism. We use elevated temperatures to accelerate the individual processes that contribute to corrosion behavior, and different processes will be accelerated to different amounts or different degrees. We can use that to accelerate the progress of the reaction during the test period and talk a little bit about excellent work done in France, with the seeding the tests with the minerals to look at the impacts of secondary phase nucleation on the test results. We've run tests with steel and steel components. We've corroded steel in the same tests that we've dissolved glass.

So there are a fairly good number of different test methods and test conditions that we use specifically to understand and parameterize the corrosion behavior of glass under different conditions of affinity control to look at the specific behavior in these different regions within laboratory accessible time periods. Joe went through some results where we maintained far from equilibrium conditions to measure dependencies of the kinetic rate on various terms and populate the parameters for the kinetic term.

So part of that was the effect of the glass composition on the kinetic term in the rate expression. I'm going to go now to how we're looking at the impact of glass composition on Stage III behavior.

This is a cartoon for the Vitreous State Laboratory modifications, the product consistency tests that Ian was talking about earlier. So it's basically crushed glass immersed in a volume of solution, and occasionally a small amount of that solution is withdrawn for analysis and replaced with demineralized water. Here is an SEM micrograph of crushed glass used in these tests. So it's crushed to the consistency of fine sand, and then it's meticulously washed to remove fines generated during the crushing so that we have clean surfaces here and estimate the surface area.

The purpose of these tests is going to be look at the impact of the affinity term and k-long residual rate for modeling this behavior. So here I've plotted normalized concentration…in this case of boron…where it's the concentration of boron measured in the test solution divided by the mass fraction of boron in the particular glass. So we're looking at the mass of glass that's dissolved per liter so we can directly compare the results from tests with different glass compositions. So I show here groups of high-level glass, and then I divided the results for low-activity waste glasses into three plots so you can see the data a little better. These aren't all the data but it's most.

So the maximum y values are the same in all tests. The tests with the high-level glasses plotted out to 20 years, the low-activity waste glasses out to 10. The dark filled symbols clearly identify the glasses that did go to Stage III during the test. The open blue symbols are results for glasses that did not go to Stage III during the test. I drew these lines so that the blue lines all have the same slope; and they're intended to show that the release rates of boron, the dissolution rate of the glass, is essentially the same for all glasses in tests that do not trigger the Stage III.

The red lines here are all drawn with the same slope, and they indicate that the Stage III rates for all these glasses are essentially the same and can be well-represented using the same slope. So here the Stage III rate was about 26 grams per liter per year, whereas the Stage II residual rate was about 0.37; so that's a difference of about a factor of 66 higher in the Stage III rate than you get in the Stage II rate. Again, these data are representing essentially that portion that we had in progress plot.

Let me go to the next one.

So I did analyze the tests with individual glasses specifically in order to extract the actual Stage II residual rates and the Stage III rates that were measured in the tests. So the solid symbols are the data that I used to fit these blue and red lines. You can see here with the open circles for boron, the initial increase and rollover occurs very quickly in these tests at the very high surface-to-volume ratio.

Let's see…the other thing here is in most tests, you see the release of boron is the highest; sometimes sodium is higher, but you always see sodium/boron increase in Stage III. The silica concentration also increases when Stage III is triggered. Aluminum is different. It's hard to see on the scale; I'll show a little more detail in an upcoming slide. But there's a small increase in the boron concentration, but then it starts decreasing before Stage III is triggered; and then after Stage III, the aluminum concentration remains fairly low.

The other thing to show on this plot, for the data…the samplings that I used to regress the Stage II and Stage III rates, I also looked at the pHs that were attained in the tests; so these are the pH values that were measured at room temperature. I used the highest pH that was measured in the group of tests to represent the pH for Stage III, and this used to represent the pH in Stage II…oops, too far.

So these are plots of the fractional boron release rates measured in Stage II and measured in Stage III, plotted against that pH value that was measured to represent those. Each one of these squares represents the rate for a particular glass composition. So plotting against the pH that was attained in the tests spreads them out. Each of these glasses had a different composition. There's no discernable correlation between either the Stage II or Stage III rates and the pH that are attained; likewise, there's no correlation between the Stage II and Stage III rates and the compositions of the glass, nor is there a correlation between the rates and the total concentrations of dissolved silica, aluminum, or sodium in the tests.

Analysis of the ALTGLASS database shows that a very wide range of glass compositions that reacted under the same modified PCT condition gave very similar Stage II residual rates; and they gave similar Stage III rates, but there was no correlation. So the major effect of the different glass compositions is if and when Stage III was triggered in the test. We didn't see any correlation between the time required for Stage III to be triggered and the glass composition or the solution that was attained in the tests.

So big question…what is triggering Stage III to occur in these tests?

We didn't see any correlation with the glass composition or the solution composition. I asked Jim Jerden to use Geochemist's Workbench and calculate the speciation of the major components from the measured test solutions, and I think this shows the smoking gun. We look at the aluminum hydroxide concentration solution, which is the only significant aluminum species. Plot here the concentrations of aluminum hydroxide that were attained at each of the measured solutions, but the reaction time was normalized to when Stage III was triggered. So on all of these blue curves, when it gets over to 1.0, that's the time where Stage III was triggered. So Stage III dissolution continued to the right, and aluminum kept decreasing in solution; but I excluded that from the plot.

This shows that all the tests that Stage III triggered attained a fairly high aluminum concentration in solution; but then for some reason, the aluminum concentration decreased. So the aluminum is falling out of the solution.

In contrast, the glasses that did not show Stage III behavior maintained essentially constant aluminum concentrations throughout the tests. There are two flies in the ointment here. There are green lines that get up here into the region and show this behavior. I'm very certain that these are tests where if they'd have been run for another year probably would have triggered to Stage III. So some of those tests weren't conducted long enough for this to happen, but that remains to be verified. We are running series of tests to look at the impacts of the pH, aluminum, and silica concentrations in solution as glasses dissolve to see if we can identify threshold concentrations that trigger Stage III behavior. The results so far are very promising; we consistently see this hump in the aluminum concentration that occurs before Stage III is triggered in the tests. So I think we've figured it out.

Here are some cartoons in what I think we figured out. This just shows the initial behavior as glass dissolution proceeds from Stage I for the clean glass and then into Stage II where you form your gel and eventually clays, and you reach saturation, and you get this residual rate. So everything is fine up to this point using the original model.

Here's the first step required to trigger Stage III. We see that the pH and aluminum concentrations get high enough somehow that the aluminum then is driven out of solution and modifies…you get an aluminum-rich surface layer. As Carol indicated, this aluminum oxide is the origin of the zeolite framework charge; and the hydroxide is a catalyzer/mineralizer for the formation of zeolites.

So that's the first step.

The second step, this aluminum rich layer continues to interact with the solution…probably mainly with the silica in solution, and there are probably some interactions with the gel as well. So you're changing the composition of the surface layer and the structure of that surface layer. Again, Carol pointed out the importance of silica as a building unit to form the zeolite framework; so all of this is lining up with Carol's analysis of the ALTGLASS database from the perspective of the evolution of the gel surface composition.

So the model is that this somehow matures until it reaches a Point P. When the Point P hits, that's when you start nucleating either the zeolites or a precursor phase that quickly evolve to the zeolites. We know from the ALTGLASS database and all the VSL results, when this happens that you start dissolving glass because it's boron that's being poured into solution in Stage III. This gel and clay layer, Stéphane and Joe showed, contain very little boron; so the boron that's going into solution is this. So looking at other samples that get into Stage III, we do see significant increase in the thickness of the clay layers that are formed at the same time that these zeolites are being generated.

When that happens, we get a coupling between the precipitation and growth of these zeolite phases, dissolution of the glass that's mediated by the solution composition. So we're putting enough fresh aluminum in the solution as the glass dissolves, but it's immediately consumed to grow zeolite. There's more sodium and silica in the glass than is going into the zeolites, so we're increasing the solution concentrations of sodium and silicon along with boron; but we're not increasing the solution concentration of aluminum. So aluminum is the key species that's being transferred from the glass through the solution to the zeolite that's limiting the Stage III corrosion rate.

Going back to the geological literature, there was some work done in the early '90s by Lasaga's group, looking at the coupling of the dissolution and precipitation of, in this case, kaolinite. They proposed a rate equation for the coupled dissolution precipitation reaction in this form. So I've adapted it in terms of the rate for Stage III. So the kinetic term now is a coupling between the forward dissolution rate for glass…so that was the kinetic term in the original Grambow equation that could be a function of the glass composition, pH, and temperature…and then an equivalent term for the precipitation rate of whatever phase is precipitating. We don't know what that phase is, but it's probably some function of pH and temperature for that precipitation rate and probably the concentrations of key nutrients, such as aluminum.

So we have this coupled term; and for the affinity term, the affinities for both glass dissolution and for precipitation formation are both included here. So this is the same equation, and it's instructive to apply limiting conditions to this equation. So first I looked at the conditions where the secondary phases precipitated instantaneously and remained in equilibrium with the solution, so this is the Helgeson partial equilibrium model from 1968. What happens there is the kinetic term then simplifies; it's dominated by the dissolution of the glass, and you only have the free-energy term for the glass dissolution. So this collapsed to the same equation that's been in the Grambow model.

The Zhu model looked at conditions where the secondary phases precipitated much more slowly than the glass dissolved. This term for the precipitation was much smaller than the dissolution of the glass, and this coupled term reduced was dominated by the forward rate for mineral dissolution; but you maintained both affinity term for glass dissolution and for mineral precipitation.

This is the important part, I think, of the Zhu model. Having these free energy terms coupled…he calls it "arrests," the reaction affinity term for the system and maintains a constant -- this should be value. So the value of the sum remains constant as glass is transformed into alteration phases because any increase in the value of free energy for dissolution is balanced by a decrease in the free energy for the mineral precipitation and vice versa. So you can increase and decrease one or the other, but the sum remains constant. That's exactly what we see experimentally for the Stage III rate and for the residual rate…that those are remaining constant cases of Stage III rate until the glass is completely dissolved in those experiments.

This may be the last time you have to look at this plot. I've repopulated the rate equations controlling behavior in

Stage I, Stage II, the residual rate, and Stage III, in terms of those models. So we now have rate equations for the coupled dissolution reaction in Stage III. I also propose that there's a coupled dissolution precipitation rate for clays and phyllosilicates that tend to arrest the system at the low residual rate.

So now the problem is how do we parameterize those rate equations, and this would be impossible to identify the precipitation kinetics of these phases. We don't know what those phases are; we don't know what the relative surface areas are, et cetera. But fortunately, the results of the tests in the ALTGLASS database indicate that this Stage III rate that we measure in those tests is constant. The Zhu model indicates that this affinity term should remain arrested and be constant. That means that the net value of this kinetic term must also be constant.

We can simplify this for Stage III as constant and constant, and then just look at the functional dependence of those constants on the pH and temperature of the solution and maybe the composition of the solution…and likewise for the residual rate. But if we look back at the other tests for the kinetic terms, we know that the impact of the glass composition is small. We saw from that wide range of glass in the ALTGLASS database that there wasn't a very strong compositional effect on the Stage III rate. In the pH values for those tests, we didn't see any correlation; but I'm sure there's some dependence of the rate on the pH. And then temperature is probably the most important variable controlling the Stage III rate and the residual rate.

The tests that we're running now try to see if we can use these simplified rate expressions to represent the experimental results that we're running in tests at different fixed pHs and different temperatures. In this case, we're using glasses that we know will trigger at a Stage III rate to see if we can validate these simplified rate expressions for use in long-term performance models. That's where I'm going to go now…how are the process models of glass corrosion integrated in the processes' assessment, how are these improvements helpful to the geologic disposal program, how are environmental conditions being investigated and incorporated into the performance models?

Here's a simple representation of the disposal system, where you had your waste form within the engineered barrier system in the near field environment of bentonite backfill, cement barriers, whatever; and then the far field environment, whether it's in clay argillite or a granite host system. So you're looking at the transport of radionuclides of interest that are released as a waste form, degrades, and then gets transported through these different barriers to the boundary of the repository where the regulations are applied.

So that transport is modeled here. I just wrote this in one dimension, where the concentration of your contaminant, your radionuclide of interest, would be affected by dispersion advection forces and then a series of source and sink terms. So the dissolution of the glass, the corrosion of the glass, is a primary source term for all of the radionuclides. So the model is providing this source term for the aqueous degradation of glass, a biodegradation which would be mentioned would be a separate source term. There would be other source terms. Radioactive decay could be a source term or a sink term, depending on which radionuclides you're looking at. Sorption is a very important sink; I've even shown that as a separate term for sorption onto different materials in the EBS or in the minerals in the near-field environment, et cetera.

Precipitation is important. This is where the solubility limits of different radionuclides are taken into account. Bernd mentioned earlier that we did not include solubility limits in looking at the glass dissolution rate. Those solubility limits were applied after the element had been released to freeze it. Things like plutonium would stay stuck on the glass surface, et cetera.

Radiocolloids could form where the plutonium could become attached to a colloid; so that would be a source term so there'd be more plutonium to be transportable, things like that. Size exclusion through the different porosities of the different barriers would be included. The bottom line is the glass degradation model that we're working on is going to provide the mass of each radionuclide as a source term in this transport equation.

This is a conceptual diagram – well, one of the questions is the benefit of the waste form model to the disposal model. But in this case, the system model is benefiting the glass dissolution model because it's being developed as a modular model, where the glass degradation model is in a separate module that interfaces with the system model. Then there are other modular models that interface, but this gives us the opportunity to track the chemistry of the solution that's contacting the waste form.

So for the first time, we'll be able to track the evolution of the pH, the silica concentration, whatever, in the solution so we can apply chemistry or utilize chemistry within the model. This gives us a method to use the evolution of the solution contacting the waste form to identify a solution composition that would trigger the formation of secondary phases that would impact the glass dissolution rate. So if we can identify what those triggering compositions are, treat that like an effective solubility limit, as part of the glass model simulation, we can identify specifically when the conditions are appropriate or the required conditions to form this rate affecting secondary phases are present, so we can change to Stage III rate.

More important than that, if we can identify what those conditions are, we can verify that condition is never attained during the simulation in the disposal system. So we can have technical confidence that Stage III would never occur, and then we have confidence in using the low residual rate throughout the simulation.

I don't know how clear that was; but again, the approach that's being used in the system model gives us a lot of liberty to include chemistry in the glass dissolution model. And we think we know how to make use of that chemistry in triggering Stage III and calculating what that Stage III rate is and have confidence that if those conditions are never attained that we don't have to include the Stage III rate in the glass dissolution simulation.

The other nice thing about that is that we can now include the contributions of outside elements to the in-package chemistry to include the chemistry of different disposal environments within the solution that's interacting with the glass. So we can…I lost my point here…oh, so we can include the impacts of other EBS materials in different near-field environments in different disposal sites deterministically to account for those effects on the glass dissolution rate.

This is then just a summary of responses to the various questions that were provided for this…and that's about it. Thank you.

[Applause]

BAHR: Do we have some questions from the Board…Sue?

BRANTLEY: That's the second time I've heard your talk, and I got it this time…that's great!

EBERT: That's pretty good…it took me more than that.

BRANTLEY: All right, so I think this is interesting. Let me just see if I really, truly have it. So here's what I'm hearing. Stage I…you're modeling it as the glass dissolves far from equilibrium at its intrinsic rate, and that's the fast rate that's been measured in your seven-day experiment.

EBERT: Well, no, that would be measured in single-pass flow-through or C-1220, where we're maintaining highly dilute conditions.

BRANTLEY: Okay, so intrinsic rate, okay.

EBERT: Okay.

BRANTLEY: And then at Stage II, there's a back reaction you think; and it's then you incorporate the affinity term because the silica is back reacting onto the surface. And then at Stage III, the part that's different is that then you're starting to form another phase that's pulling aluminum out of solution.

EBERT: Aluminum and silicon.

BRANTLEY: Aluminum and silicon…and so because the zeolite is acting almost like a "getter" for aluminum, that means that your silicon release rate can increase in that Stage III?

EBERT: I think, in essence, yes.

BAHR: You're releasing both aluminum and silicon; but you're precipitating more aluminum than silicon, right?

EBERT: Right, you have an excess in silica in the glass relative to the composition of the suite of secondary phases that you're forming. That's why we see the continued increase of silicon and sodium in solution, along with the increase in boron. But aluminum is limiting the transformation of glass to that suite of alteration phases, so that is limiting that transformation.

BRANTLEY : So, I guess, several pieces of it…you show clay in the gel layer. Do we know there's clay there?

EBERT: Oh, definitely, yeah.

BRANTLEY Okay, so there is definitely clay there.

EBERT: Yeah, a gel forms very quickly; but then there is some in situ transformation of that gel to smectite clays, depending on the composition of the glass, you see nontronite or whatever.

BRANTLEY: Okay, and is the zeolite precipitation only occurring on the surface of the glass or the gel or whatever?

EBERT: No.

BRANTLEY : Because I thought it also precipitated around the…

EBERT: No, once it gets going, it precipitates everywhere. Joe showed where it's precipitating on his probe.

BRANTLEY: So why do you emphasize the precipitation at the gel layer? What is that so important?

EBERT: Well, that's let me tie it to the work that Carol is doing…the effects of chemistry and her strong-base weak-acid model to what happening on the gel surface. So from the ALTGLASS database, we can estimate what the surface composition is based on what we measure in solution and the difference between what would have released to solution if the glass dissolves stoichiometrically. So that gives us our relative concentrations of silica, aluminum, et cetera, in the gel layer. So that gives her something to assess the evolution of those hydrogel compositions to result in hydrogel compositions that interact with solutions that support the formation of zeolites or those that don't.

BRANTLEY: But simplistically, it doesn't matter where the zeolite precipitates, right?

EBERT: Right.

BRADLEY: If it's acting as an aluminum getter and it's changing the affinity and causing network dissolution to accelerate, it doesn't really matter where it happens.

EBERT: Yes.

BRANTLEY: Except for maybe you have other experiments that show that…Carol's experiments that you were just talking about.

EBERT: Well, for years we knew that they didn't form only on the glass surface; but that makes a nicer slide.

BRANTLEY: And then the last thing that I want to ask, which is not really related…what about the worry that we've brought up before about biotic reactions? You know, I asked this morning Bernd; and he said that they probably wouldn't survive. What do we know about that?

EBERT: There was a lot of work – well, not a lot of work – work done previous, prior to the Yucca Mountain, that was considered in pretty good detail. And I think it was this tertiary effect is right, but it's very minor.

BRANTLEY : Biological growth is minor?

EBERT: In the deep disposal system with radioactive materials it was, I think, not considered to be a significant source.

BRANTLEY: So there hasn't been much thinking about that since?

EBERT: Not that I'm aware of.

BRANTLEY : Not that you're aware of, hm.

EBERT: But it was considered, and then the decision was made that it wasn't worth – it was a minor contribution.

BRANTLEY : So just going back to what I'm worried about as a citizen…not that I'm, like, losing sleep…but we've got a dissolution rate model for glass; and what I'm interested in is what could possibly make it happen faster in the repository than what we're thinking about today. So one thing could be this Stage III, and I see that there's been a lot of work and some thinking about that so that you can start to incorporate that.

Another thing could be if the glass starts fracturing or something in the repository…so the surface area goes up, something like that. Another thing could be biota. I just think the things that could make it go faster in the field than we're seeing in the lab are things we should think about.

EBERT: Well, I think that gets back to…it's in here somewhere…to this cartoon. A lot of the lab tests that are done and flow-through tests are measuring essentially Stage I rates of mineral dissolution, et cetera. Then in the field, your conditions are maybe out in here. We had about two orders of magnitude difference in the rate. So, yes, I did look at that very closely to try and understand why the field rates were so different than the laboratory rates. I think that was one of the main reasons…in most tests is you're just looking under different lampposts.

That seemed to be the orders of magnitude difference, so that seemed consistent to me that you'd see the same sort of behavior for minerals. For a mineral, you don't have Stage

III; but you still have this far from saturation and near saturation differences.

BRANTLEY: I think I agree. I feel good about the talks that we're hearing and the level of understanding.

EBERT: Thank you.

BRANTLEY: I guess the only thing I'm wondering about is what could make it go faster in the field? I think it's unlikely it goes faster in the field, but we always have to think about what could make it go faster.

EBERT: Yeah, that was another thing that I wanted to mention. Let's see, where should I do that? I guess when we're focusing on the affinity term for Stage III, it's very possible that when we get to Stage III conditions that the pH of the solution is much higher than in whatever test that you would measure the initial kinetic rate. So you could get a couple factor…10 or 20…increase if you have 3 or 4 pH units higher in Stage III. So you need to take that into account in your comparison. And I think that happens a lot because glass dissolution is going to drive the pH very high, as Ian has shown, and in the ALTGLASS data that I showed. And that's typical that you're going to get that order of pH unit rise increase or more during a product consistency test.

BRANTLEY: So you're saying that the intrinsic rate that you measure is measured at a more close to neutral pH?

EBERT: Oh, we measure that as a function of pH. So we have it measured over a range of pHs. So when the performance assessment tells us that we have a pore water at this pH with this silica concentration, we can plug the values of the pH and silica into this equation and say, well, you've got this rate.

But you're right, it's important that – and what Joe was saying, these sets of parameters are coupled as well. So your temperature, pH, and whatever you're using for your glass composition are a set of values to be consistent with the tests that they were derived from.

BRANTLEY: Thank you.

BAHR: Paul?

TURINSKY: Mine is more a question of clarity. Sue may get it, but I haven't gotten it. What determines the time for the onset of Stage III, and what all in the model – those parameters that determine that – where do you get those from?

It seems like it may be very (inaudible).

EBERT: Exactly, so we're not there yet. But…where did I…?

That is why I babbled on about the value of being able to track that solution composition. So the idea is we should be able to identify sets of aluminum/silica concentrations and pH that we can use as an effective solubility product.

TURINSKY: Isn't that tough to get in that cracked glass?

EBERT: No, we're talking about bulk. Yeah, we couldn't measure it in the solution within a crack.

TURINSKY: Okay, but isn't that the case…I mean, in a repository? Your surfaces are basically cracked glass surfaces.

(Multiple voices)

Modeling that transport seems really tough.

EBERT: It's going to have to be simplified; you're exactly right.

TURINSKY: And what is the actual time then for the onsets for the sort of glasses we're looking at and for some – I guess it varies by repository, where we're putting this stuff. But what are we talking about?

EBERT: I don't know; that's going to depend on temperature very strongly.

TURINSKY: But we have these integrated models. Have you looked at clay, granite – what sort of time scales?

EBERT: Well, it's going to depend on the evolution of those solutions; so that's going to depend on the relative volume of ground water that's contacting a surface area…how quickly that solution is going to – composition is going to evolve to get to whatever level is sufficient to trigger the formation of those phases. But right now, we're just trying to identify what those conditions are. Then once those are identified, we should be able to, for a particular system…where we can define the volumes and surface areas and temperature, et cetera…determine how long it's going to take to do that, to get to that point.

TURINSKY: Okay, so we haven't really taken these models and put them in a performance assessment model for a specific geological formation to figure out what those time scales are?

EBERT: We have not…so this is a very infancy of that.

TURINSKY: Okay.

EBERT: What I'm saying now is that we have the tools to be able to do that and I think we have a mechanistic model to pursue, to identify some of these triggering conditions. But that remains to be done.

BAHR: Okay, I think we have to move on to the last speaker. Thanks Bill.

So our final talk for today is Aurélie Verney-Carron who is an assistant professor at the LISA -- Laboratoire Interuniversitaire des Systèmes Atmosphériques which is a mixed research laboratory between Paris-Est and Paris Diderot University and also the French National Center for Scientific Research and she's going to tell us about archeological classes and natural analogs, which I know Mary Lou has been waiting all day for.

VERNEY-CARRON: So thank you Jean and thank you for the invitation to talk about studies on natural and archeological glasses and what can we learn about the long term nuclear glass corrosion. So, as you can see with this non exhaustive review there are many references dealing with the studies of ancient glasses, natural and archeological considered as analogs of the nuclear glass as they have been altered for a long time in real conditions and Ewing was the first to propose to use the basaltic glass as an analog of the nuclear glass. So I only mentioned the studies that really discuss the similarities between ancient glass and nuclear glass and not those even more numerous that mention the glass alteration of nuclear glass as a main issue of the general understanding of glass alteration.

So for ancient glass we can study the short term alteration by performing experiments in a laboratory and the long term alteration after a given time. But on the contrary for nuclear glass even if experiments were performed for two decades we cannot know the long term alteration. So to counterbalance this lack, reasoning by analogy, as stated by Aristotle, can be helpful and if the short term alteration of ancient glass is similar to the short term alteration of nuclear glass and that the ancient glass has some interesting features that could be favorable to the storage and that could help to assess the source terms of radionuclides and guarantee the safety of the storage, therefore probably the long term alteration of nuclear glass will also have these features. So first we will examine these interesting properties such as the long term durability of nuclear glass, the retention of elements possibly, the radioactivity in the alteration products and the contribution of internal surface developed by cracks due to the elaboration of conditions.

Then we will discuss the similarities between the different kinds of glasses and last, the link between short term and long term alteration can be made using a modeling approach and for nuclear glass these models are necessarily based on the experimental determination of mechanisms and the kinetic experimental data, implementing the geochemical models such as GRAAL for example, but we cannot verify the long term simulation by comparing them to ancient samples. On the contrary, this step can be made for the ancient glass and if long term simulation and ancient glass characterization match, this will demonstrate, validate the predictive capacity of the model and improve the confidence that we can give to the nuclear glass models.

The first property that is interesting for the storage is the long term durability of natural glasses and many natural glasses exist on Earth such as basaltic, more alkaline magma or more acidic such as rhyolitic glass or obsidian, as well as glasses created by the impact of meteorites and these find the tectonic that will inexorably lead to the recycling of the oceanic crust to the basaltic crust in less than 200 million year. We can find all samples on the continents and here's an example of a rock from Figeac which is presented here, of a glass dating from 289 million years.

Then here is a graph with the alteration layer thickness as a function of the alteration duration for the basaltic glass and I have to say that the same results were highlighted for minerals by Susan Brantley and at right for other minerals as a feldspar of biotite if I remember and hornblende and we see that the apparent alteration rate of whole samples is lower than the rate measured in the laboratory at the same temperature. So these can be explained by the measurement here of initial dissolution rate and here the control medium will favor a residual rate that can be extrapolated from a measurement in the laboratory and can be explained by the precipitation of secondary phases that sustains slow hydrolysis.

Then, even if the glass is altered, we can expect that some elements will be retained in the alteration layer and not dispersed in the medium. So for that, stained glass windows were studied, they were buried close to churches and here is an example of a French stained glass window dating from the 12th century and here this is elemental profile and this reveals the partition of some elements, especially transition elements and heavy metals.

So here you have the lead and the zinc and we see that they are retained in the alteration layer and the same results are obtained for iron and titanium for stained glass windows and basaltic glass. And then in the storage we were seeing that the glass package can interact with other materials such as iron and actually experiments performed on nuclear glass have shown detrimental effect of these elements, here is an experiment at 50 degrees in a synthetic clay-based ground water with glass alone, glass with magnetite, glass with twice the quantity of magnetite and we see the increase of the alteration rate and this was explained by the precipitation of iron silicates that will consume the silicon and prevent passivating layer to be formed and this is confirmed by the model using GRAAL. And here this experiment with glass, iron, argillite and water and kept at 90 degrees for 18 months.

We also observed the formation of iron silicates and the alteration thickness corresponding to the initial rate divided by two and not expecting the residual rates. So in order to assess if the detrimental effect of iron is transitory or a long term effect these visual slides were studied, they were produced in the blast furnace, working during the sixteenth century at the ironworks site of Glinet in Normandy, and altered since that time in a soil saturated with anoxic water. You see here the glass in contact with the metallic fragment and corrosion products as well as the presence of cracks. So it's a small analog of the storage with the glass package and the corroded stainless steel container.

So the results of these vitreous slides show that the same morphology observed in the nuclear glass experiment with the prisms of the gel of iron silicates and siderite. Concerning the alteration rate, the alteration thickness is 20 micron in the external cracks, which is a high alteration thickness, which confirms the detrimental effect of iron. But, this thickness is thinner in the internal cracks, so iron silicates precipitation is a long-term mechanism, but there is a drop in the alteration cracks in a confined medium.

So, then, in order to infer these properties to the nuclear glass, it is important to discuss the similarities between the different kinds of glasses. First we have to give up the analogy of composition, as nuclear glass is made of boron, but it's important to discuss this analogy in terms of phenomenology mechanisms and in a lesser extent kinetics. So, for nuclear glass here and for basaltic glass, we have a similar alteration surface with a rough interface between the pristine glass and the hydrated glass. The presence of gel called palagonite and here a well-known gel layer and the presence of crystallized secondary phases and especially smectites.

The same, we've already talked about it but, the same methodology based on use of 29-silicon was applied for nuclear glass, SON68, and ice tea glass, for the stained glass and after for basaltic glass. And the solution is enriched in 29-silicon and the glass is composed mainly of 28-silicon and so the analysis of the 29- over 28-silicon ratio in the alteration layer allows the different sources of silicon to be traced.

So here is a secondary ion mass spectrometry profiles of the silicon isotopic ratio as a function of depth. For nuclear glass and for stained glass, we see the same result. The silicon isotopic ratio is lower than the range of variation in solution. So this suggest that this gel layer is formed by inter diffusion and local hydrolysis and condensation reaction and is not in thermodynamic equilibrium with the solution and so formed by dissolution and precipitation process.

I have to mention that these experiments are performed in solution that are not initially saturated with respect to amorphous silica. And when these experiments are performed in saturated solution, here for the nuclear glass, we see that even if the solution is saturated, the glass still corrodes with hydration here, and the release of sodium, boron, and calcium. But the 29-silicon weakly interacts with the gel layer, except in the external zone that corresponds to secondary phases, and with thickness that is less than 200 nanometers.

For the basaltic glass, we have also here the silicon isotopic ratio. Here you have the secondary phases and there is an equilibrium between this signature with the solutions, so they are formed by dissolution and precipitation process. But, in the internal zone, corresponding to a mixture between secondary phases and altered glass, there is an enrichment here, in 29-silicon.

So the alteration mechanisms look like somewhat different for the basaltic glass, the alteration proceeds by internal diffusion and hydrolysis followed by the precipitation of clays and amorphous silica and then the remaining silicate network dissolves and amorphous silica precipitates, and then the layers of secondary phases grows up sustaining the glass dissolution. And the isotopes could not observe the formation of the passivated layer or gel, so the mechanism controlling, limiting the alteration rates is different for the nuclear glass. This is the diffusion of water in the nanoporous layer, and for basaltic glass, this is the precipitation of secondary phases, not a sustained dehydrolysis.

So, however, concerning the kinetics, we see here that the measured initial or forward dissolution rate is very similar for basaltic glass and for nuclear glass, you have the data, as well as the activation energy of the dissolution process. For the residual rate, both were measured in the laboratory and they differ by one order of magnitude.

To summarize this examination of similarities, I think that the virtue of studying other kinds of glasses is mainly to go to a unified understanding of glass alteration. However, the alteration process are very similar. Some differences exist for the degree of structural reorganization of the gel, but similar secondary phases. It's alteration products are formed by similar mechanisms, and the relative contribution can vary as a function of glass composition and environmental conditions, but we have seen that this can be translated in terms of kinetics that have to be measured for each glass, and this kinetics depends on the glass composition and glass structure.

The last objective of the analogy is to improve the confidence that we can give to a nuclear glass model. Two of views can be structured first to give a simple geochemical model that can account for the glass alteration of analogs and to apply the nuclear glass model to other kinds of glasses to extend its range of application. So, I will focus on the first case as the second is in progress. For example, for the application of the GRAAL model to basaltic glass, in the PhD work of [inaudible] this year. During my PhD, we used Roman glass blocks. You see here a picture of these blocks of a few kilograms each, and they were collected in a shipwreck in the Mediterranean Sea close to the Embiez Island at a depth of 56 meters. They have been archeologically dated from the second century [inaudible], and so they have been for 1,800 years in a known and stable environment that is sea water at 15 degrees. Interestingly, they present morphological analogy with the nuclear glass package as they are fractured due to the fast cooling after they were melted. What is the state of alteration of these Roman glass rocks after 1,800 years? In other words, what do we have to model?

The steady block here displays three zones -- a non-fractured and non-altered core, an internal zone and a border zone. The border zone is mainly composed of large, altered cracks with an average thickness of 400 microns. They are mainly composed of smectites and the total altered –the percentage of alteration of the whole block is 12%. But these large cracks contribute to 84% of this alteration. In the border zone, the cracks are thinner between 5 and 20 microns. They are composed of hydrated glass here and smectites in the center. Even if this zone is 6 times more [inaudible] fractured than the border zone, they only contribute to 16% of alteration.

There is -- Sorry. There is a low contribution of internal cracks to the global alteration and this alteration is not proportional to the reactive surface area and further more they are filled with alteration product that has been shown to decrease the permeability and probably the diffusion coefficient in these cracks by one of two orders of magnitude.

In order to give [inaudible] the geochemical model we have performed experiments to determine the mechanisms and the kinetic parameters in a newly elaborated Roman glass. The model was developed using the HYTEC software. Here is a general principle of the model. The Roman glass turns into a leached glass following an experimentally determined diffusion law for the release of alkalis that depends on pH and temperature. Then the hydrated glass will dissolve following this rate law based on a classical first order law with an initial rate that depends on pH and temperature and an infinity term based on the equilibrium between aqueous silica and a silica phase of cristobalite-beta.

The released elements can react alone or with also elements from the environment to form secondary phases and in the experiments we have characterized magnesium smectites and calcium carbonates in agreement with what is observed on the ocean samples.

First we use the new set of experiments to validate the model under short term and in summary, the release of alkalis and pH were well simulated and pH is a very strong parameter -- the coupling between the glass alteration, the chemistry, and the transport in solution especially in the cracks. We have here an example of an experiment performed in sea water at 15 degrees -- in red is the simulated pH and in blue the experimental data.

For calcium, in some conditions, especially low pH, it was shown to be underestimated because it can be released by inter diffusion and the model only considered dissolution. However, it's not dramatic. Has calcium is highly concentrated in sea water so it's not a limiting element to form secondary phases. For silicon, it was over estimated at high pH due to interaction with calcium that can decrease the solubility and in sea water due to a difference between the stoichiometry of the thermodynamic database and the observation, but this can be corrected in the database. Know that chemical model can be coupled with transport and tested on the long term.

Here are the results of the long term simulation. We simulated two cracks representative of both population of cracks in the border zone and in the internal zone. Here with different initial aperture and distance from the external surface. Here it's a large cracks with initial aperture was 100 microns and located at one centimeter from the surface. Here were thin cracks with an initial aperture of two microns and located in the center of the block at 5.6 centimeter.

Here are the results for the pH, for the large cracks, the pH of sea water is maintained, and for the thin cracks, this pH rises until 9.4. The diffusion, the renewal of the solution by diffusion, is too low to counterbalance the increase of pH caused by inter-diffusion. This has an effect on the total altered thickness. For the large cracks the thickness after 1,800 years is 450 microns and for the thin cracks it is only 30 microns. This result is in very good agreement with the observation. Here a large crack in the border zone. This external cracks are in contact with a diluted medium. The blocks lay on the sea floor and so they are altered at a 4:1 rate and in the external zone there is a strong coupling between the chemistry and the transport with an increase of pH and a decrease of the alteration thickness.

There is a good agreement between the simulation and the observation. This validates the predictive capacity of this geochemical model for this glass in its environment.

If we use these results and consider the reactive surface of each zone of the block, we can simulate the evolution of these blocks over 100,000 years. Here is the contribution of external cracks controlled by the diffusion in the crack. Here the contribution in red of the external surface and external cracks and in black the sum of both contributions. In [inaudible], corresponds to our whole sum [inaudible] of 1,800 years and for the blocks that are still in seawater, we can predict or hope to predict the evolution and we see that if only the internal surface here in blue were leached, more than 650,000 years would be necessary for complete alteration of the block. External surface alteration would limit this lifetime about 20,000 years.

If we transpose this simple transposition of these results to nuclear glass alteration shows that here if the glass would be altered at an initial rate regime, the expected lifetime would be 7000 years but fortunately in the geological disposal this will favor a residual rate and we can expect 30% of alteration after 100,000 years. If like the Roman glass, the internal surface is controlled by the diffusion, only 5% of alteration, after 100,000 years.

So, to conclude, it's important to study other kinds of glasses in order to achieve a general understanding of glass alteration and maybe even minerals. And if the similarities reinforce the analogy between the different kinds of glasses, the differences raise interesting question on the impact of the glass composition and environmental condition on the glass alteration.

So it's also important to continue the modeling work, and for me the objective is not to find the closest glass in the closest in composition in the closest environment, and it's interesting to model, for example, a stained glass in atmosphere or basaltic glass in hydrothermal event to demonstrate the feasibility of the modeling and to validate the predictive capacity, and especially to extend the range of application of glass alteration, long-term modeling. And just to finish, yesterday we visited a theater with Stéphane, and we saw these skylights here and we find that it could be a good analog to study the interaction between glass and the cement and the glass and the iron. So, thank you for your attentions.

BAHR: Thank you. You mentioned glass and iron and you showed some intriguing results early in your talk that suggests that the presence of iron can accelerate the glass corrosion rate -- Nuclear glass is mostly being poured into steel canisters and I don't think that the iron is being accounted for in any of the models of nuclear glass as far as I know. Is that correct?

VERNEY-CARRON: No. These experiments were modeled using a grand model so this shows that this model is able to account for this iron effects. So I don't know exactly the progress of the model, but this effect will be considered in the running. Yeah.

BAHR: Yeah, and it's not a criticism of you. It's more that I don't know if the U.S. program has accounted for that in their models. So it's good to know about that.

Questions from Board members? Questions from staff? You convinced us all.

VERNEY-CARRON: I was afraid of the questions.

BAHR: Do you want a question?

VERNEY-CARRON: Yeah.

BRANTLEY: So, this is a general question. What do you think the most important goal of these kinds of studies should be in terms of nuclear glass? You know what I mean? Like, we're not going to -- It's not exactly the same kind of glass, but what should we be doing with these kinds of experiments? Should we just be testing our models? Or --

VERNEY-CARRON: For me, there is two major points. Testing a model -- If we can model the alteration of Roman glass but also basaltic glass in seawater and in contact with meteoric water -- I don't know, it was difficult for the pro slides because the glass was complex and very different. But if we can do this for a large number of glass, I think that it will improve the confidence. If we know modeling for different kinds of glass, probably we can do it for the nuclear glass, and in a sense it's the only way to improve the confidence of the long-term simulations, so I think it's important to study a large number of analogs and to succeed in the modeling the alteration in various compositions and various environments.

And the second point is I think after this day of talks is to understand the long-term mechanisms that will control the residual rate, and I don't speak too much of these results here, but in the PhD of [inaudible] he measured residual rate in the laboratory, and he extrapolated the result using a linear rate, square root of time rate, and we cannot determine the mechanisms using a mathematical fit, but this indicates that it's probably more hydrolysis that control the residual rate than the portion of interdiffusion under long time.

BRANTLEY: So the hydrolysis was more important than the interdiffusion.

VERNEY-CARRON: Yeah. Because the evolution is linear. And in the future, I think it would be important to complete this figure to have more maybe younger basaltic glass samples, and to see the effect of the zeolitized samples or calcified if it plays protective role of stage three or -- I don't know.

BRANTLEY: So, you think that it clarified in your mind which of the different steps really is important, namely hydrolysis, you think, based on this. And it clarified what element in the environment might be precipitating or somehow poisoning the surface that might warrant more experiments. Was there a parameter that you had to get of thin air to put in your model to make it fit? Is there a parameter that you really didn't understand?

VERNEY-CARRON: Sorry?

BRANTLEY: Was there something that you needed for your model that you didn't know how to estimate and that you had to just estimate out of thin air, almost?

VERNEY-CARRON: I think that no -- Before modeling, we have to understand the mechanisms before to apply this model --

BRANTLEY: What about surface area? Didn't you have trouble estimating the surface area to put into your model?

VERNEY-CARRON: No.

UNIDENTIFIED FEMALE: How did you estimate surface area?

VERNEY-CARRON: I can't say too much about this, but in the work of [inaudible] there is some tests with modeling using different flow rates or S over V ratio, and to see which one is close to what can be in the field.

BRANTLEY: So you varied the S over V ratio until it fit?

VERNEY-CARRON: Yeah.

BRANTLEY: That's typically what you need to do. That surface area. To fully find the ratio, we just don't know --

VERNEY-CARRON: It's difficult to know in the field. I agree.

BRANTLEY: Thank you.

BAHR: Any more questions? Oh, Tissa?

ILLANGASEKARE: Yeah, Tissa Illangasekare from the Board. So in your alteration phenomenological model, so you have three zones: the border zone, internal zone, and fracture zone. So if you look at the observation glass, so if you look at glass I assume that these three zones are dynamic, they change with time. So what other timeframes involved in those changes, how long -- They keep changing all the time, is that correct?

VERNEY-CARRON: Sorry --

ILLANGASEKARE: So there are three zones. So these zones will change.

VERNEY-CARRON: Yes -- No. We choose a block that will representative of the other blocks and the -- Actually, the question was -- Are these cracks seen now because they are formed after, during the alteration, or are they here from the beginning, and they are seen now because of the coupling between chemistry and transport? And so the modeling is important to demonstrate the feasibility but also sometimes to understand the observation, and with the model we were able to simulate, to explain this in alteration thickness, after 1800 years. So we can answer that these cracks using also mechanical arguments, and for example constraints and stresses but we can observe that they are formed from the beginning and they are seen because of the alteration.

BAHR: Thank you very much.

VERNEY-CARRON: Thank you.

BAHR: We're now going to do our quick look at the posters, and probably the easiest thing would be if the poster presenters will kind of line up here, and I will call you in order and you'll have two minutes along with a slide to give us a little pitch for your poster and tell us why we should come talk with you.

First up on my list is Carolyn Pierce. And then the next person in line will be John McCloy, and then Margit Fabian, and then Claire Corkhill, and then Clare Thorpe, and then Matthew Asmussen, and then Sarah Saslow, and then Joe Ryan, and then James Neeway, and then Nikolla Qafoku, and then

Jonathan Eisenhower, and then Cory Trivelpiece, and finally Jerry Frankel.

So, Carolyn. You're up.

PIERCE: [inaudible]

BAHR: You don't have these -- There's a PDF file? Bobby?

Male Speaker: [inaudible] Posters, PDF file. [crosstalk]

BAHR: We won't take it out of your two minutes.

PIERCE: I'll be quick.

Yes, that's great. Thank you. So, yes please, I'd like you all to come visit this poster to find out about an EM International project that we have through Albert Kruger at ORP to look at these pre-Viking hillfort glasses as analogs for nuclear waste glass. The site is in Sweden, it's called Broborg, and there's some representations of the site as you can see here. It's from 1500 years ago, and so it's a hillfort of the local granitic gneiss geology, piled up, and then some amphibolite rocks placed in between and set on fire to melt that assemblage and basically strengthen the walls of the fort. And the fort still stands today. You can see a picture of it today. I was there a couple of weeks ago. And the glass is helping to hold those rocks together.

We're very interested in these glass samples because of their age, and also because of their compositions. There are multiple different compositions present here. There's a silica-rich glass that is representative of the low activity waste glass that’s proposed for the IDF here at Hanford. There's also a dark glass that's rich in iron and calcium that's more similar to high level waste glass. We can look at how these two glasses have corroded over very long periods of time under the same environmental conditions.

This project has two goals because it's an international project. The first one is to look at the long term durability of these glasses so that we can use that information to support putting low activity waste glass into the IDF. We also have partners in Sweden who are interested in the anthropological and archeological interpretation of the site. That helps us as well because we need to know the entire history of the site to be able to interpret how these glasses have changed and also how the glasses have formed. You will hear more about that from John who will follow me next [inaudible].

These glasses are considered as historical artifacts because they tell us about our ancestors and have been around for a very long time. We have to be very careful when we analyze them and we developed a series of protocols so that we would not alter the glass in any way that we didn't want to. We'd also preserve as much of the artifact as possible. We employed a dry-cutting technique to not change any of the alteration layers and we downsized to the point where we have a fib thin section and we can actually look at those alteration layers.

Here you can see representatives of both the clear glass and the dark glass. We do micro-XRD to verify that there are amorphous regions. Then we analyze the samples for the alteration layers and we see very different results depending on what's on the surface. This doesn't come out very well but hopefully you see it better in the poster. This here is basically microbial colonization of the surface of the glass. There are fungal hyphae, there are microbes, there are amoeba and it's a whole community existing on the glass surface. That interacts with the glass itself to generate these alteration layers. Please come and stop by and I can tell you more about this exciting project.

BAHR: Okay. Thank you. John McCloy and Debra has the end sign.

MCCOY: Thank you. I'm John McCloy from Washington State University and I'm going to talk a little bit more about this Hillfort Project. My role at the university is really the second goal that Carolyn described and that is to really look at the cultural technology of this wall building. As she mentioned, the understanding that we have is that there was a metamorphic rock called an amphibolite that was melted to fuse these rocks together. There's a number of hillforts around the world that are vitrified in this way. There's different ideas about how this was done and if it was done on purpose. They have different geologies.

This one happens to be metamorphic igneous rocks. There's others that are melted, basalts, and there's others that are melted metamorphic sedimentary rocks. What we did at WSU, you can see clearly in this X-Ray, computer tomography image that was done at PNNL, you can see the rocks that were glued together and then this what we believed to be melted amphibolite which outgases and glues these together.

We also took some of these samples and did thin sections on them and looked at the mineralogy that comes out and we have high under cooling here. These assemblages are similar to contact metamorphism. We also looked at another sample that looks very different and there's just beautiful microstructures here. Pyroxenes that come out as well as spinels. If you could go to the next slide please.

What we did as well was we had some amphibolites that were collected from the site and we measured their phase composition and they vary quite substantially. Not all of these amphibolites would've worked. Some of them have too high a quartz content for instance. The other part of what we did is we took the measured microprobe compositions of some of these glasses and then we tried to melt them from oxides in the lab and found that the temperatures that these melt are much higher than what would've been achievable in ancient times. There's something else going on here that we haven't captured whether it's an effect of iron redox or it's some volatiles. For instance, water that's lowering the viscosity. Those are some of the future experiments that we're going to do as well as we have some collaborators at the Institute for Rock Magnetism in Minnesota who are helping us to measure the paleo magnetic dating of the spinels that crystallize out so we can get a very good dating on the site within plus or minus 50 years. So that will be very important for the later modeling of this. Please come and talk to us about this.

BAHR: Thank you. Next up is Margit Fabian.

FABIAN: Thanks. I'm Margit Fabian from the Center for Energy Research from Hungary. We have also a national program for nuclear waste management which is coordinated by a public limited company for the radioactive waste management. We are the center for energy research and together we are involved to a huge project.

First is macro and microscopic investigation of very stable clay site which could be our geological repository site and another is conditioning of high level radioactive waste dedicated [inaudible] with the vitrification process.

Here I would like to show some results and to invite to see my poster. We tried to find a simple composition for this process. Step by step we only got to prepare this type of composition called matrix system. We've different kind of methods like neutron, x-ray diffraction, NMR spectroscopy, reverse Monte Carlo simulation, we are able to define our basic network structure of our glassy samples which is built up by 3- and 4-coordinated boron and 4-coordinated silicon sites. Here you can see a very random network but also we have this very nice units.

We are very happy with these results and we try to add actinides. First of all uranium oxide because we have uranium oxide. Step by step we add 10, 20, 30, 40 weight% uranium oxide to these core matrix system. We apply sort of methods to see how it's changed our basic network. Beside the first distribution correlation function and coordination numbers, we find very characteristic secondary distances between uranium and network formula atom sites silicon and boron atoms. This showed that uranium can take back on our basic structure. Also we try to do leaching test for 20 and 40 weight% uranium oxide samples for the back and the [inaudible] samples with different time and temperature conditions and also I would like to present these samples.

Second, it's not allowed to use real actinides, therefore we use chemical models. We had cerium and neodymium oxides up to 30 weight % and we also get nice results. We can see that these cerium and neodymium ions can accommodate in both silicon and boron sites our structure. Thanks.

BAHR: Thank you. Next up we have Claire Corkhill.

CORKHILL: Thank you. I'm Claire Corkhill. I'll be Claire Thorpe for the next poster. I’m from the University of Sheffield in the UK so this is another international perspective. My poster is going to give some insights from our UK nuclear research program which is funded by EPSRC Diamond and Distinctive program which I'm really happy to say that Ian Pegg and John Vienna who are here in this room are advisors on our UK program on durability and nuclear waste disposal and decommissioning. This is what our geological disposal facility will look like when eventually we do have one. It's a co-located repository where you have intermediate level waste and high level waste together. The intermediate level waste portion has very very high contents of calcium and of cement, and calcium in high pH ground waters. As Bernd mentioned this morning, we're very interested in the coupled processes that occur when you dissolve glass in these very high pH cementitious environments. That's one of the main purposes of my poster is to talk about the mechanisms and kinetics of glass dissolution in these high cement environments. I also have a part of my poster, which will talk about the dissolution kinetics of multi-phase waste forms, these are glass ceramic materials, or if you have multi-phase glasses in your material, how can you work out what the dissolution of those different phases is. We've been using some imaging techniques to try and understand dissolution kinetics in those environments.

Finally, one section of my poster talks about some work that we've been doing at Sheffield on the vitrification of unconditioned plutonium-bearing wastes. This is really interesting because we have a very nice natural analog study for some of the very high metal content waste that we're generating, not that have plutonium in, and non-plutonium containing. We're doing some work to try and understand the long term performance of these new materials by looking at 200-year-old archeological samples. If you're interested in hearing about that, please come and see my poster.

If you go to the next slide. This is the second poster that I'll be presenting on behalf of my post-doc Clare Thorpe. I can be two Claire's at once. This is research, again, that we're performing at the University of Sheffield in collaboration with Pacific Northwest National Lab and

Vanderbilt, funded by the US Department of Energy. This is related to the integrated disposal facility at the Hanford site, and the immobilization of LAW in glasses.

At present, one of the pass-fail criteria for these glasses, in terms of their performance, will be measured using a vapor hydration test, which is one of the ASTM standards that Carol talked about earlier today. It is stated by this statement here. Unfortunately, this test really is inconsistent with assessment of glass durability under the disposal conditions of the IDF facility at Hanford, so mainly the temperature is very different, 200 degrees versus 15. There also can be very high variability between laboratories and even between operators within the same lab. It's not very reproducible. This means we'd get large uncertainties in, I should say, prediction of glass durability from using this test.

The purpose of the research that we've been doing at Sheffield is to try and evaluate an EPA method that could be used instead of this test. What my poster will present is a critical analysis of this test and whether it's feasible to use this as a pass-fail criteria for LAW glasses.

BAHR: Thank you, Claire. Next up, if I am in the right place here, I have Matthew Asmussen. Okay.

OSMUNDSON: Hey, I'm Matthew Asmussen from PNNL. What my poster's going to go over is looking at what we do to treat waste streams that are produced at the back end of glass vitrification processes. What this is, this is a program that is sponsored by Washington River Protection Solutions that a collaboration between us at PNNL and Savannah River National Lab do in looking at developing and testing cementitious waste forms for treating secondary wastes, which are produced as a result of vitrification.

What my poster's going to go over is how we go through development of formulations for a specific waste streams, down selecting proper formulations that are candidates for eventual testing, how we test these waste forms for their physical properties and their radionuclide retention capabilities, how this data feeds into performance assessment models of the integrated disposal facility at the Hanford site, and how us at PNNL go about incorporating some of our advanced scientific techniques towards furthering our technical understanding of cementitious waste forms. How they age with time, how these changes release behavior. If you stop by my poster I'll be happy to walk you through the history of this program, where we are currently, and where we see ourselves going in the next couple of years. Please stop by.

BAHR: Okay. You're not Sarah Saslow.

SMITH: Hi, I'm not Sarah Saslow, but she couldn't make the meeting. I'm Gary Smith. The poster that you're going to see out there that Sarah pulled together is a collaboration funded by, Matt went over the background pretty well. We're doing a lot of cementitious waste form work for Washington River Protection Solutions, the Chief Technology Office, and we're doing it in collaboration with Savannah River National Laboratory. Specifically what we're looking at is disposal of effluent management facility, evaporator concentrates, if you go to the next slide.

Right now, to get direct feed low activity waste vitrification facility up and running, they're building an effluent management facility. The off-gas stream that comes from the submerged bed scrubber and the wet electrostatic precipitator is going to be high in chlorides, fluorides, sulfates, technetium. That's going to be cycled back in front of the LAW vitrification facility. It'll give fluctuations to that facility. It'll also increase the halides, et cetera, which will decrease the waste loading. This work is looking at breaking that recycle stream and sending that to a grout formulation, making cementitious waste forms and then disposal at the Hanford site and the near surface integrated disposal facility.

The driver behind it, the modeling shows that you would increase the direct feed low activity throughput by up to 22%, and you would not be sending approximately 3.2 million gallons back to the tank farms. Big advantage in this in time and cost, if successful, and our preliminary work does show that it looks pretty successful.

BAHR: Next up we have Joe Ryan.

RYAN: All right, I'm back up here again. I will have a poster out in the room about some work I am also doing with Washington River Protection Solutions. The impetus behind the work you'll see out there is basically the instructions given in the 2001 performance assessment where they say that the performance assessment activities will continue to collect additional data on long term performance. They basically will take data and knowledge that was present in other avenues of research, for example all the other stuff you heard today, and produce better estimates for the low activity waste performance assessment that is being done.

If you go to the next slide, we basically came up with three different areas for reducing uncertainties in that performance assessment. The first is composition impacts for the wide range of compositions that will be done at the low activity waste melters. For example, determining how these four different parameters you see here will change with composition of the glass and how much that impacts the performance assessment. Basically, how much if you change glass composition you get more waste in, how will that effect the performance assessment.

The second one is ion exchange impact. You heard a lot about that today. The idea here is that there's a term in the performance assessment they use today that says that there's constant sodium released due to ion exchange. In reality, we know perfectly well that it's a diffusive mechanism and might be better incorporated into the model through a diffusive term.

Then the third one is secondary phase impacts. You saw this plot in Bill's talk earlier, and it basically says that there's a significant number of glasses when tested in accelerated conditions, it's always accelerated conditions, always high temperatures, but in those conditions they do go and show that latent acceleration. That's called stage three dissolution. We want to know is that going to happen at the 15 degrees that's present in the integrated disposal facility where the low activity wastes will be disposed of.

If you want to talk to me about these three effects and the strategy behind the updates in the performance assessment, please stop by. Thank you.

BAHR: Next up is James Neeway.

NEEWAY: Hello, I'm Jim Neeway from Pacific Northwest National Laboratory. My poster pretty much goes with what Carol was talking about this morning, of these standardized tests and how these standardized tests are actually used to support the performance assessment that's being conducted at the Hanford site IDF.

This work is a multi-laboratory effort between PNNL, Catholic University, Atkins, and us, supported by the WRPS Chief Technology Office. Simply put, you've seen this equation a couple times today in various forms. Basically our efforts are to give these parameters for different glass compositions, and we do that by performing flow-through tests, the single-pass flow-through test. And also, within this model, though not explicitly given here, there is the effective secondary phases that form in the system that may then alter for instance the pH or the activity of orthosilicic acid. And so I'll just talk through how the product consistency test is used and a couple unsaturated tests, because many of the tests we've been discussing are in saturated conditions. There are a few options to study glass alteration in unsaturated conditions. So, if you stop by, I can discuss those.

BAHR: Thank you. Nikolla Qafoku?

QAFOKU: Thank you. Sure. Thank you. My name is Nik Qafoku, I am from PNNL. I will present a poster today about some field scale lysimeter studies that we will be starting pretty soon, hopefully next year, to test glass and cementitious waste form performance. There is a facility at the Hanford site, a lysimeter facility, and we intend to use that facility to conduct a study to look at the glass corrosion and cementitious waste forms put separately in different lysimeter units, or put them together in the same lysimeter unit.

This is a brand new study. We are just in the very initial phases of putting together the test plant and other supporting documents. The study will be conducted in collaboration with the Washington River Protection Solutions, and Dave Swanberg and the others are here in the room.

Can we go on the other slide? The idea here is to use the Hanford site field lysimeter test facility to try to replicate field conditions of IDF at Hanford, and then we will use simulated different types of glass and cementitious waste forms. If you are interested in discussing what type of glasses are we thinking of using, and what kind of cementitious waste forms, please stop by my poster. And there are other -- I mean, there's a set of other questions that we are trying to address right now, so I would be more than happy to engage in conversation with you. The lysimeter unit will be irrigated so again we will have an accelerated corrosion conditions supplied, in the lysimeter, and then we will follow the changes in the chemistry, and the changes in the transport parameters as a function of time in those lysimeter units.

Please stop by. There is a lot of items to discuss. I'll be more than happy to go over them with you.

BAHR: Thank you. And we have Jonathan Eisenhower?

EISENHOWER: All right. Okay. I'm Jonathan Eisenhower. I'm from Sandia National Laboratory, the Carlsbad branch, down in Southeastern New Mexico. Actually in close proximity to the Waste Isolation Pilot Plant, or WIPP, and it is a working nuclear waste repository in rock salt.

So, for that reason, we're interested in all things having to do with sodium and chloride, and -- next one please. And just to be really brief here, the objectives of the study was to look at the dissolution rate of borosilicate glass as a function of sodium chloride and magnesium chloride in flow-through reactors, and we wanted to see if sodium chloride will enhance the dissolution rate as it does for the silica polymorphs. And just to kind of give you an idea of what I'll be discussing on the poster is that sodium chloride and magnesium chloride turn out to be very important in terms of being able to either enhance or suppress the rate, and the effects of one of those dominates over the other, and if you're curious as to what does which, please come by my poster and I'll discuss it with you. Find out.

BAHR: Perfect example of a teaser. Perfect teaser there. Cory Trivelpiece? No? Carol Jantzen?

JANTZEN: Well, even if you didn't know who I was already, Cory's about a foot taller than me and he shaves his head. Okay. So I'm not going to go there. I'm going to be talking about the database that you've heard about most of today, the ALTGLASS database, and what we have done in terms of using it as an informatics tool.

Now for people who don't know what informatics is, it's been long used in the biological community for looking at huge populations of data, looking for trends as to why people might get cancer, or why people might get a particular type of disease. And so it's now being picked up, the informatics approach, by the material science community. And so I put together the first three versions of this ALTGLASS database. I have now turned it over to Cory, which is why he was supposed to be here giving this poster, but he couldn't make it.

And so, if I could have the next slide? Again, what he was trying to indicate here was that we're using this informatics approach, combining it with geochemical modeling, and with prediction, and using the ALTGLASS database as the source of the information. As I said earlier today, I started to develop it in 2013. I did versions 1, 2, and 2.1. He did version 3, which is the newest release, which has the international research data in it. It has about 490 different glass compositions in it, and then Cory is actually my co-author on these two papers that I spoke about this morning. I have one more slide.

Some of this is what I showed you in my talk this morning. By digging into the database and saying, "Okay. If I've got a population of glasses that do go to stage three resumption, and a population of glasses that don't go to stage three resumption, and then I do some statistical analysis on them with a stepwise regression, what is that telling me about the aluminum/silicon ratios in those gels?" And what it does tell you is that the ones that form the clays are in this regime with aluminum to silicon less than one, and that the ones that go to zeolitization over in here have aluminum to silicon greater than one, and that this is mostly related to the leachate strong base, weak acid. So the weak acids are down here, the strong bases are up here, and it's a more sensitive parameter than the pH, which is what I said this morning. [inaudible] pH, which is what I said this morning.

So if you want to hear some more about it, and exactly what I think is going on, and exactly where we're going with this, which is to try and relate this all back to glass composition, stop by.

BAHR: Okay. Thank you, Carol.

And last but not least, it looks like we have John Vienna.

VIENNA: Thank you very much.

Hi. Our poster is to present the early results from a new center that just started this fiscal year. It's the Center for Performance and Design of Nuclear Waste Forms and Containers. This is one of the Office of Science funded Energy Frontiers Research Center.

And the objectives of this is to develop a more fundamental understanding of the mechanisms of waste form performance, and then develop tools that can be used to design better waste forms, or other materials in general where performance is important. And this center was started by Gerry Frankel, who's here in the room, and he brought together experts in metals corrosion, and in ceramics corrosion, and in glass corrosion with the vision that we would work together collaboratively to help use the best science in all of those fields to better understand the corrosion mechanisms in general. And we're starting by focusing on those things that are common. Were there commonalities in the mechanisms of corrosion of the three material classes?

And so, although we're a relatively new center, we have already made fairly significant progress in the glass corrosion, as part of a collaborative effort. And you've heard a few of these today already. And so the poster will talk, generally, about the center and its objectives and who's on the team and several in here: Joe Ryan, Stéphane Gin, Jerry Frankel, and myself. And several others: Penn State University, University of North Texas, University of Virginia, there's many. So you can talk to us at the poster, and some of our early progress already is, we've studied the properties of this passivating layer on glasses.

We've used multiple techniques to look at the effect of different ions in solution and how they affect the residual rate of glass corrosion. And these are solutions that have, sort of, fixed pH, fixed silica concentration, and we see a vast difference in corrosion rates with, for example, lithium, or potassium, or cesium ions in there. And we've done analyses and modeling of that alteration layer and the analyses have shown dramatically different optical spectroscopy of those layers. The models show different structures, so we're just -- we're not finished with that, but we've started, and it's fairly interesting.

Stéphane mentioned, already, the water mobility within passivating layers that he studied using tagged oxygen 18 water. And the preliminary results on that, which are shown on the poster suggest that during this residual rate regime that the transport of water through the layer to the glass surface is probably limiting.

So we've also done molecular dynamic simulations of the glass, the reacting glass surface for the international standards glass. And also, we're in the process of developing a sexy new technique where we can flash-freeze a corroding glass with the water on it, and make amorphous water. And it has all of the ions and all of the layers in this sample, and then without letting the sample warm up, we take it and we go into an atomic probe-tomography, and we can analyze atom by atoms sort of the structure and composition of that reacting interface at really high spatial resolutions.

So if you're interested in any of those things, come see us by our poster.

BAHR: Okay, thanks to all the poster presenters. The last thing on the agenda is an opportunity for public comment. I don't know if we have anyone who has signed up for public comment. Is there anyone who would like to make a public comment who is not signed up? --

State your name.

VIENNA: Thank you, Jean. This is John Vienna. You asked this question earlier, and I had to hold my breath -- You had asked about looking at iron impacts on glass corrosion in the U.S., and we have done that. So it was done back in the time of the Yucca Mountain studies, and very recently Joe showed just a real slight flash of it on his slide summarizing very recent work. But I just wanted to point out that that has been done, and is being done. I won't say that we answered all the questions, but we have incorporated them.

BAHR: Thanks for that clarification. Are there any burning questions for any of the speakers that we didn't have time to get to? Bobby.

Pabalan: Pabalan, Board staff. I have a question for Bill Ebert. Is he still here? Bill, can stage three corrosion rate be higher than stage one?

EBERT: Well, yeah, it can if the pH is higher in stage three than what you measured in stage one. The range of the affinity value is still between zero and one, so I think that is an upper limit constraint.

Pabalan: So, okay so --

EBERT: At the same pH, no.

Pabalan: Okay, that's, yes. So really if you still stick with the initial or forward rate in your safety assessment or performance assessment, it bounds-

HUBERT: That would be a highly conservative upper bound, yes.

Pabalan: Okay, thank you.

BAHR: I think we have another comment on that question.

GRAMBOW: Just [inaudible] my comment is also on the stage three question, and from my point of view, one should also look how to avoid it by technical constraints. That means either for example, having glass composition, which for the sodium to boron ratio it allows by its composition to have more buffer effect built into the glass. Someone from my point of view the strengths of the French glass, which has a large boron and much less sodium in the glass. It will not drive the pH to very high levels, which is a question of essentially the sodium content in the glass. It's one point, from technical point. But even if you have a glass with a high sodium content, maybe you can have buffer medium around, which limits the pH to go to such high values. So maybe by technical constraint one could [inaudible] fluxes.

BAHR: Thank you. Anything else? Okay, then we will adjourn -- Oh, sorry.

KRUGER: Albert Kruger with the Department of Energy. I just wanted to state that in terms of the sodium to boron ratio, our program, which will take over during the operational phase of the treatment plant, as opposed to the initial commissioning, does have very high boron alkalis. And so we should be able to avoid any detrimental effects, plus accelerate the mission.

BAHR: Thank you. Anyone else? Okay. That being the last call, the public meeting is adjourned, but I invite everyone to head over to the poster session, which is just in the lobby out here. Okay, thank you all.