UNITED STATES

NUCLEAR WASTE TECHNICAL REVIEW BOARD

WORKSHOP ON LOCALIZED CORROSION OF ALLOY 22 IN YUCCA MOUNTAIN ENVIRONMENTS

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Las Vegas Marriott Suites
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I N D E X

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(Continued)

P R O C E E D I N G S

8:00 a.m.

DUQUETTE: I'd like to welcome you all back this morning, and glad to see all of these smiling faces this early in the morning. On behalf of the Board, welcome to this morning's session on localized corrosion.

Yesterday, we had a lot of introductions, and there's one more I'd like to make, and that is one of my colleagues who's on the Board just arrived this morning, Dr. Andy Kadak, who is Professor of the Practice at MIT in the Nuclear Engineering Department, is here. Andy is over here.

So, without any further ado this morning, what I'd like to do is introduce the first speakers. There are a couple of changes to your program. One of them is at 8:55, Maury Morgenstein made his presentation yesterday, and Don Shettel is going to do it this morning, so there's been a flip of speakers for the State. And, at the end of this morning's session, we're going to be privileged to hear a very short presentation by Russ Jones on Sulfur Segregation to Surfaces and Alloy 22. And, so, that's going to be an addition to your program. It's going to be a very short presentation at the end of the morning.

Yesterday session was I thought very interesting. I think a couple of things that came out of it, and with lots of qualifiers, it may not be justified to FEP out at this point the possibility of having deliquescent salts, and it may not be possible to FEP out the possibility of those salts being persistent. And, I put big capital letters and quotation marks around the may at this point. But, I think that the session yesterday was very good.

I think it was interesting that one of the things that seems to be coming to some kind of congruence is the fact that there is at least some agreement on what the environments probably are going to be in the mountain. And, again, lots of qualifiers on that, although there was at least one presentation, as you know, that seemed to think that the salts that are being examined are not those that are going to be there. So, there's still some controversy on that issue. However, it's interesting to see that at least some of the parties are coming to convergence on the issue.

The first talk this morning is by Raul Rebak of Lawrence Livermore National Laboratory, who is working for the Project, and the title of his talk is New Alloy 22 Data and Their Relevance to High-Temperature Localized Corrosion.

So, Raul, without any further ado, if you'll take the podium?

REBAK: Thank you. The title was actually given by, I think, Carl Di Bella, so I just gave the same title, New Alloy 22 Data and Their Relevance to High-Temperature Localized Corrosion.

Next, please? So, these are the people that work at Livermore regarding the gathering of the data, Gregory Gdowski and Susan Carroll were managers at the time this data was gathered. Tiangan Lian, who is seated in the audience here today, was part of the electrochemical testing for high-temperature sodium and potassium based brines. Joel Hayes, Sarah Roberts, Kirk Staggs, Christine Orme work in the autoclave tests, and then Phil Hailey, Kirk Staggs also work with Tiangan Lian. And Dixit also of course works with the autoclave tests. And, Sean Felker was part of the high-temperature volume solutions of the brines.

Next, please. So, the outline of this talk today will be one slide of introduction, and then what is the possible environment, what is the physically possible environment based on sodium and potassium salts. Then, the results from the autoclave tests, the Dixit report, what is the general and crevice corrosion susceptibility of Alloy 22. And, then will be the anodic polarization at high temperature to prove that nitrate is an inhibitor at high temperatures. And, then, some conclusions.

Next, please. So, this is more introduction, one slide only. We know that Alloy 22 is susceptible to crevice corrosion and chloride-containing aqueous solutions. The susceptibility of these is strongly influenced by chloride concentration, temperature, electrochemical potential and nitrate concentration, and may be other inhibitors as well.

Nitrate inhibits crevice corrosion initiation and propagation. And, a minimum of this ratio may be needed for localized corrosion inhibition to occur. So, at temperatures below 120 degrees C, this ratio is between .5 to 1 or 2, depending on other variables.

Next, please. So, the first part will be the environments based on sodium and potassium salts, the Felker report. There is a UCRL-number there for this report. And, this is what will happen, this slide, is temperature as a function of the molality of nitrates, and what are represented here by these points are boiling points of different types of solutions. And, we have here the molality of nitrates, and here, the molality of chloride and their different symbols. zero molal chloride, which is pure nitrate, is the dark, the black diamond, and the highest molal of chloride, 9, is the circle, the black circle.

So, what we have in this slide is data gathered by half molal of potassium chloride and half of the total molal of chloride will be potassium and sodium, and the same for the nitrates. Here, we see that when the molality of nitrates is below 20, the solutions could be rich in nitrate--or rich in chloride, I'm sorry, poor of nitrate. So, nitrate over chloride is between .125 and 2, so you can have boiling points below 120 degrees C.

To have boiling points higher than 120 degrees C, and up to 160 degrees C, you need higher and higher amount of nitrates. You cannot form high chloride solutions in these areas. And, for example, for 160 degrees C area, what is the lightest point, you have a nitrate over chloride ratio of 100, more or less. And, you cannot have in nitrate, a chloride rich solution with this high boiling point, only in this area where there is the yellow circle.

Next slide, please. So, the notes from these environments for potassium and sodium brines is that using sodium and potassium salts, it is not possible to make chloride-rich brines that would have boiling temperatures higher than 120 degrees C. All sodium and potassium based brines with boiling points higher than 120 degrees C will have nitrate to chloride ratios higher than 5.

Crevice corrosion was not observed for Alloy 22 using short-term tests for any nitrate over chloride ratios higher than 2, even up to 150 degrees C. So, except for the closed autoclave tests, which were performed at chloride ratios lower than those in stable solutions, which we saw crevice corrosion, you will see in the next few slides.

So, this is the autoclave experiments, the Dixit report. Why were the autoclave experiments run? The very first autoclave experiment were actually done at instances of suggestions from the Board and Carl as well, and they were done by Chris Orme in 2002, 2003, and the latest autoclave experiments were designed as a follow-on of the previous tests to determine the general corrosion rate at temperatures higher than 50 degrees C. That was one of the points that the Board had previously.

So, at that time, in 2004, October 2004, or September, crevice specimens were also included in the autoclave to test the hypothesis that a nitrate over chloride ratio higher than .5 would not initiate crevice corrosion. The autoclave experiments were not designed to mimic the high nitrate brines described in the drift environments because the autoclave tests are not physically possible in the natural environment.

Next slide, please. So, the autoclave experiments, as Ron mentioned yesterday, are available in that report on the Livermore website. The only specimens in the autoclave were a non-welded polycrystalline materials. There were three types of specimens. Polished pucks, which are designed for use for non-creviced and were highly polished to be used to determine surface composition. And, then, we have two types of foils, non-creviced foil that were used for weight loss tests, and then the creviced foils were used were creviced with alumina washers, not teflon, and were used to determine crevice corrosion initiation.

Next, please. So, there were three autoclaves.

They are purged with nitrogen before the heaters were turned on. Autoclave 1 has about 18 molal of nitrate and 2.5 chloride at a ratio of 7.4, 160 degrees C. Autoclave 2, 220 degrees C, with exactly the same composition. Then, Autoclave 3 was a lower amount of nitrate and higher chloride, a ratio of .5, also 220 degrees C.

Based on our previously knowledge, we wouldn't expect crevice corrosion in Autoclave 1 and Autoclave 2, but we found. And, in Autoclave 3, we may have expected and also we found.

Next slide, please. This is again the same slide about experiments. This is the boundary of temperature for each molality of nitrate, and each value of chloride that can be expected in a natural environment. Autoclave 1, which is this little autoclave here, 160 degrees C, was done at the total amount of nitrate, about 18 molal, and then autoclave, you see it's very far removed from the physical environment, and then Autoclave 2 and 3 was done at 220 degrees C, which is outside of this chart, and were, one, the same amount of molality of nitrate, and another one is much lower, about 3 molal of nitrate. So, if you extrapolate these 220 you see, this is about 500, I guess, molal of nitrate.

Next slide, please. So, the autoclave experiments, the specimens were tested in the vapor and the liquid region in each autoclave. There were a total of 30 specimens per autoclave, and the total testing time was 267 days, or about nine months.

Next, please. So, there are three types of results from these autoclaves that was intended for. One is the crevice corrosion initiation susceptibility. Another one is about what is the composition of the surface. And, the third one is what is the corrosion rate by weight loss of the non-creviced specimens.

Next. So, crevice corrosion intiation results from the autoclave. The creviced specimens show deposits from the dissolved crevice formers all over the specimens, as you may know from the report. The specimens exposed to all the tested conditions had crevice corrosion, both in the vapor and the liquid phase in all three autoclaves.

Next slide, please. This is how the specimens for Autoclave 1 looked like. This is 7.4, 160 degrees C. You see the specimens, a little bit cramped because of the thin foils, about 2 mils or 50 micrometers thickness only, and then, the one in the liquid phase. And, you see the footprints of the crevice former in each one, and the crevice corrosion mostly happened in the inner part of this footprint, a very small amount, and it was a very shallow attack. But, there is no doubt of this type of localized corrosion.

And, here, is how one of those sites looked like, this is a very high magnification, 4000 magnification, you see this typical, maybe crystalline attack of crevice corrosion, surrounded by perfectly passive film around it.

Next, please. This is the data for Autoclave 2. You see the deposits all over the specimens, mostly coming from the crevice formers, and this is in the liquid, this is in the vapor phase. The same nitrate to chloride ratio, higher temperature.

And, then, the Autoclave 3, next slide, please, we see the similar things, deposits, a smaller amount of crevice corrosion attack, and always on the end of the footprints of the crevice former, and you see this is an SEM picture of one of those tooth, maybe not here, because this is a different specimen, and all these marks are all deposits coming from the crevice formers.

Next slide, please. So, these are the results from the surface composition. So, there was another specimen with strong signals, of course, of oxygen and carbon, which is always there, and then aluminum and silicon, which are the foreign elements that came from the crevice formers. All the metals from the solution were also found, sodium and potassium, of course, from both salts, and there were also some levels of calcium and magnesium.

The profiles show nothing unexpected, I will say, from what is known from the reaction of this alloy with the environment. For example, thinner surface oxides in the vapor as compared to the liquid. And, in the Autoclave 1, which has the lowest temperature, has the thinnest oxides. And, then, of course, nickel, chromium, iron and tungsten were also detected on the surface in the form of oxides and hydroxides.

Next, please. Regarding the corrosion rate, this has the weight-loss experiments for the thin foils without crevicing. All the weight-loss foils of the three autoclaves show mass gain, even after the 30 times acid washes of cleaning steps. And, these are very hard to remove, I think mostly because there are foreign elements deposited on the specimens.

The weight difference, the maximum was 70 micrograms, but always positive, so this is an equivalent of a negative corrosion rate maybe of 10 nanometers per year. So, we couldn't get actual corrosion rates from this test.

Little or no general corrosion by observation after nine months at these two temperatures, and that's easily seen, because when you have transpassivity, for example, you can see with the naked eye under the microscope, and we didn't see that. And, this implies that maybe the corrosion potential, we'd never measure it because it was a closed system without any electrochemical connection, but it was probably not in the transpassive region, since no transpassivity was observed.

Next slide, please. So, the notes from the autoclave tests that all the creviced specimens in the three autoclaves showed crevice corrosion initiation. The tests were conducted in environments that are physically impossible in the repository. It may be unanticipated results for Autoclave 1 and 2 where the ratio of nitrate to chloride was 7.4.

We know from short-term, fully immersed, cyclic potentiodynamic polarization that in that same ratio of nitrate over chloride, at 120 degrees C, that thing would not happen, crevice corrosion, because that's the maximum temperature you can reach with that solution.

So, to reach a stable solution at 160 degrees C in a repository-type environment, like in Autoclave 1, you would need nitrate over chloride ratios near 100, and that doesn't cause localized corrosion.

Next. So, why did crevice corrosion occur in the autoclave tests? We are not really sure why, but there are some explanations that are given also in the report. It could be a chemical modification of the electrolyte or the passive film due to the crevice former dissolution. We don't know that for sure, but it could be. And, the other one is that at the temperature the tests were performed, which is 160 and 220 degrees C, the absolute amount of nitrate that may be needed to provide inhibition could be higher, because the absolute amount of nitrate we had here is only about 18 molal. At those temperatures, you may need 100 molal, because a solution like this will not exist at this temperature.

Also, as Ron mentioned yesterday, the ratio to provide inhibition of nitrate over chloride may be temperature dependent. As the temperature increases, that ratio could not be .5 or 1, but may be, you know, 7 or 10.

There may still be a need to investigate in the physically attainable natural conditions, what is the effect of crevice corrosion initiation and propagation for these ratios of higher than 1 in the dust-like environments. To see, you know, do they initiate, yes. But, do they propagate, we don't know that.

Next, please. These are some electrochemical tests done in fully immersed specimens in sodium and potassium based brines. Short-term test result data was done by Lian and co-workers.

So, these are data done mostly in sodium chloride, potassium chloride, sodium nitrate, potassium nitrate brines. We did also some quaternary salt mixtures, including calcium chloride in some of them, because we couldn't reach certain compositions and temperatures based on any of those brines.

Temperature tests of 110 to 150 degrees C, with several types of solutions – more than 30 solutions - were tested, from pure chloride, 8 molal, to pure nitrate, 42 molal, to mixtures of chloride and nitrate from 0.005 to 100, and some pHs were even adjusted to 2 and 4, with HCL.

Next slide, please. These are some of the results of slides from Lian. We have potential here as a function of current density. This is the cyclic polarization curve. In the red curve, we have pure chloride solution. We have a corrosion potential, the passive region, the breakdown, and then the repassivation. For all of the slides, we use repassivation potential of ER1. In the reverse curve, which is 1 microamp per square centimeter.

You see that if you keep adding nitrate, .1, the breakdown potential increases. Maybe the hysteresis here doesn't change much, but in the blue curve, the hysteresis gets smaller, and when the ratio is .5, the black curve, the breakdown potential is high, and the curve returns without hysteresis. There is total inhibition to crevice corrosion.

Here, we have how the specimens look after the test. At pure chloride solution, the zero ratio, crevice corrosion in the crevice former, after you start increasing the amount of nitrate, this is all tested at 110 degrees C, the amount of crevice corrosion starts to decrease and then practically disappear for the ratio which is 1, even though these specimens were polarized to potentials to near 1 volt.

Next slide. Here, we have at 125 and 150 degrees C, cyclic polarization curves. The first one, we have 42 molal nitrate, 4 molal chloride, which is a ratio of 11, and you see a very clean curve, no hysteresis, very high polarization potential, no crevice corrosion. This is at 150 degrees C, at a ratio of 33, again, very clean curve, no hysteresis or crevice corrosion either.

At a ratio of 25, this you cannot see from here how much is the temperature, again, there is no localized corrosion and no hysteresis. And, this is the pure nitrate solution that somebody asked yesterday, again, without any chloride, we only see, you know, this transpassivity outside because of the high applied potentials, but there is no crevice corrosion of any sort, no localized corrosion outside the crevice formers either.

Next slide. As I said previously, from two slides ago, we are taking parameters from the cyclic polarization curve, which we call the repassivation potential, and we plot here as a nitrate over chloride ratio here. And, we see that with this nitrate over chloride ratio increases, the repassivation potential increases. And, in the green oval here, this is all brines at 110 degrees C, in the green oval, we see absolutely no crevice corrosion with a ratio of maybe 10 and higher.

And, then, in this other plot, we expanded this area to see the effect of nitrate over chloride from zero to 1, and we see that the repassivation potential is minus 200 millivolts for pure chloride solution, and increases rapidly, about 600 millivolts, only where the ratio is about .5. So, at .5, we see this inhibition, you can see this inhibition, because the repassivation potential is so high. And, so, this area, you have crevice corrosion. In this area, you may have or you may not, depending on who looks at this specimen. But, I will say when the repassivation potential is higher than 300 millivolts, you will call that no crevice corrosion.

Next slide, please. This is a similar representational figure, but at a higher temperature, 125 degrees C. We have a few calcium based brines here because you cannot prepare this solution less than 10 in nitrate over chloride at this temperature for use in only sodium and potassium. You have to use calcium. So, again, you see that you have localized corrosion here, in this case, pitting at the ratio of maybe, I forget how much it was, maybe .2. At a ratio of .5, you may have some small amount of crevice corrosion, but when the ratio is 1 and higher, all this pink area, or whatever the color is, there is absolutely no crevice corrosion.

Next slide, please. This is a similar representation of repassivation potential as a function of nitrate over chloride, 140, 150 degrees C. You have highly concentrated brines. We have two data, the green dots are 140, the red are 150 degrees C. All the repassivation potential at higher than 600 millivolts, this is incredibly high values. It's almost physically unattainable in nature. And, you see that none of them have crevice corrosion, absolutely none.

Next slide, please. So, the conclusion for localized corrosion tests in sodium and potassium brines. The repassivation potential results shown were determined for fully immersed specimens in bulk electrolyte. So, there's unlimited amount of solution reaching the specimen.

We used forced corrosion using a potentiostat source, unlimited amount of cathodic reaction to the specimen. At atmospheric pressure, crevice corrosion was not observed for any of the ratios higher than 1 in any of the tests shown here today. And, we see that the most detrimental range of temperature for Alloy 22 regarding localized corrosion would be below 120 degrees C, where these lower nitrate over chloride ratios could be naturally reached.

Next, please. So, the final remarks, we see that from these tests, the inhibiting effect of nitrates, active at high temperatures. So, it's not true that it stops acting. The results shown are for fully immersed specimens in the electrolyte, we have unlimited amount of solution to corrode. And, in the real repository, the amount of brine in the container would be small. We know that. That is what Charles talked about yesterday.

Crevice corrosion is inhibited for these nitrate over chloride ratios at these values, regardless of the temperature, we tested up to 150 degrees C.

Dust deliquescence brines also will be highly concentrated, so the activity of water in the brines will be very small in the dust. So, you can expect very small amounts of metal being dissolved into these brines because it will be so concentrated.

And, as a final remark, which is I think very important, current results continue to support the localized corrosion model for degradation of the waste package. We didn't see in any of these studies, anything that we could say is not true with the current model.

Thank you.

DUQUETTE: Thank you, Raul. Let me start with a couple of questions. One of those has to do with, perhaps my memory doesn't serve me as well at my age anymore, but I don't remember anyone reporting pitting before in these solutions. Is that a new observation?

REBAK: Say it again?

DUQUETTE: I don't remember anyone reporting pitting in these solutions. Is that a new observation?

REBAK: No, it's actually not very new. We've been saying for a while that about 120 degrees C, the localized corrosion mechanism may be changing from mostly crevice corrosion--these are forced experiments, so it's very hot experiment. When you do cyclic polarization, above 120 degrees C, you may start, the attack will happen outside the crevice former, under the crevice former. And, if you do another type of test, a more gentle like, a galvanostatic type of test, or the Tsujikawa method, you may shift that pitting corrosion into crevice corrosion. So, it depends on how the current is applied to the specimen.

DUQUETTE: Okay, thank you. The other comment I might make is your 1, 2, 3, the comment about dust deliquescence, the amount of metal, that brines can dissolve will be minimal.

REBAK: Yes.

DUQUETTE: But, if you do get dissolution of the metal because of the alloy components, I would expect that the crevice would turn very acid. Do you have any comments on that?

REBAK: Yes, but then you have the inhibition from the nitrate. Nitrate may, you know, may form nitric acid, which is good for C-22, actually, the corrosion rate of C-22 in nitric acid is about, I forget how much, but about 10^3 lower than the hydrochloric acid. Also, nitrate may reduce to nitrogen, or even ammonia, or something like that, and that consumes protons as well. So, it is not a big deal.

DUQUETTE: Thank you. One comment I'd like to make.

Yesterday, Ron asked for opinions, and there was some reluctance on the part of some folks to express some opinions because it might be tied to their organizations. This is an informal workshop, and I can promise you that at least the Board won't tie comments of the organizations. We're looking for, as you probably know, when the Board expresses opinions as individuals, those are exactly that. They're not Board positions. And, so, I'd like to have--I'd like to request, as much as possible, because it is a workshop, that people be as honest as they can, and we try not to tie that to organizations, but just to individual opinions.

Having said that, comments from the floor--from the table first?

AHN: Ahn, NRC. Do you have--what pressure do you have with salt solution, not water? That's the first question. The second one is: your test was done under deaerated conditions. Do we have any idea the oxygen pressure there?

REBAK: Actually, both of the questions, I actually don't know. In the report, if you read the report, I think they mention how much could be the pressure under those conditions. But, I think that we didn't take the values of the pressure when the tests were done.

Regarding deaeration, Joel Hayes did the test. He said that he purged the autoclaves before that, but we don't know to which level and what would be the oxygen concentration at the end. So, we don't know the content either.

AHN: Okay, thank you.

DUQUETTE: Bryan? Oh, sorry.

MON: My name is Kevin Mon with Areva NP.

I think the pressure was estimated in the report to be about 23 atmospheres at 220 degrees?

AHN: That's water, and with the salt water, do you think you have the same pressure?

BRYAN: This is Charles Bryan. I can respond to that.

I think it was 8 to 10 atmospheres. The calculated activity of water in the brine is about .4 to .44. At 1 atmospheric pressure, of course, at 220 degrees C, you'd only be able to obtain about 4 percent RH, would be 1 atmosphere of water vapor.

DUQUETTE: Thank you, Charles. Any other comments before we move on on the experimental--from the Project, before we--I think the next question was Ron's, and then--

LATANISION: If we could put up Figure 28? I'm interested in the same issue that Dave brought up, and that is observation of pitting. I understood your explanation, but I would like, in the spirit of a workshop, I would like to know, of the others in this room who have done research, testing on this material, has anyone else seen pitting? You have? In the absence of a crevice?

MORGENSTEIN: Oh, yes.

LATANISION: This, to me, is--at lower temperatures? Let's see, we have a couple hands in the back. David? Use the microphone. We're going to be really religious about that. You have to use the microphone so that we can identify you.

MCMILLAN: Glenn McMillan, University of Nevada, Reno.

We've conducted some experiments where we have heated a two inch diameter piece of Alloy 22, and placed simulated concentrated water, that is a J-13 well water, on top of the specimen, and heated it to dryness, and on that specimen, we do see pitting corrosion, and not at the edges where we had a crevice former.

DUQUETTE: Thank you. There's another comment over here, I think, someone else has seen pitting in the--same, okay, thank you.

REBAK: May I make a comment?

DUQUETTE: Yes, please.

REBAK: I'm not a convinced that in SCW, you will see pitting corrosion, but, you know, I cannot contest their results, but--a form of crevice corrosion under the crevice former, or something like that, yes.

LATANISION: No, I understand the crevice issue--

REBAK: Outside of the crevice former, we see this high temperature, 120 degrees, in this case, where it's low nitrate, you can see pitting corrosion.

LATANISION: To me, it really is a surprise. I mean, I have to admit, on the basis of all the testing I had seen to this point, my impression was that there was no evidence without a crevice--

REBAK: No, we've reported before. We have papers saying in 5 molar calcium chloride, even at 90 degrees C, using the cyclic potentiodynamic polarization, as I told Dave before, where you move the potential pretty fast, so you have to move a lot of current in a short time, you can see pitting corrosion. We used to call it like a massive attack, or something, it starts in the edges of the crevice former and propagates towards the outside rather than inside. But, if you're doing exactly the same solution, 90 degrees C, 5 molal calcium chloride, using a more gentle galvanostatic type of test, 2 microamps per square centimeter only for three hours, the attack tends to go under the crevice former rather than outside. So, it depends how you do your test.

DUQUETTE: Lietai?

YANG: Lietai Yang from the CNWRA.

For the electrochemical test, I'm really interested in learning what kind of reference electrode was used? Because the temperature, 150 degrees C, atmospheric pressure, so what was the reference electrode used?

REBAK: We used a saturated silver chloride electrode with some external electrode that was cooled with water, with a water jacket to keep maybe about 15 degrees C, and then had the bridge towards the solution.

YANG: This salt bridge is still chloride, is it? Is it chloride and it would be dried at 150 degrees C.

REBAK: No, the salt bridge is the same, I think the same solution--Lian, could you clarify that, please? Is it the same solution generally that we have in the--

LIAN: Tiangan Lian with the Lawrence Livermore Lab.

To answer the question, the salt bridge we used, replaced with a 5 molar calcium chloride at a higher temperature. Otherwise, like you said, bridge would be boiling.

YANG: Thank you. The other question. May I? Can we go to Page 12, please? So, here in this diagram, you indicated the solution used for the autoclave test--

REBAK: Yes.

YANG: It was impossible if you do not pressurize it?

REBAK: Yes. In the real world, it would not exist.

YANG: Yes. But, we have a report, the Dixit report, the report only recently came out. I took a look. It looks like the solution was made at the test temperature. It took solution test--that means it was open to air. It was not pressurized at that time. If that is the case, the solution, you have indicated, it was stable and fair condition.

REBAK: But, not at those temperatures. It was stable, you know, you can have a solution at ambient temperatures. I imagine you can dissolve that amount of salt, off the top of my head, at ambient temperatures, but then you have to raise those temperatures. So, those solutions where the test was done didn't exist at those temperatures.

YANG: The other thing, did you observe any crystallized or solid in the system? Because during the test, if you heated evaporate water, then the composition may change, and may be different than the testing reported.

REBAK: Yeah, that's true. We don't know exactly the environment inside the autoclave. Yeah.

YANG: Thank you.

DUQUETTE: Russ Jones, and then Maury, and then we'll--

JONES: Russ Jones with GT Engineering.

Raul, I know you have a protocol for surface preparation, but you don't say much. Could you just summarize a little bit how you prepared the surfaces? Because anything where you're looking at the kinetics or the rate at which initiation occurs is, I mean, really dependent, even if you allow lots of time, dependent on that surface.

So, if you could say a few things?

REBAK: Yes. Regarding the electrochemical tests that we did, it's always the same procedure. We grind the specimen with 600 paper, wait about one hour before running the test. So, it's always the same controlled surface finish. Regarding the autoclave test, I cannot know exactly for sure, but apparently, there was some touching of maybe 600 paper to remove some of the oxides, or something, but I'm not exactly sure.

DUQUETTE: Thank you. Maury, then all the way at the end, and then--oh, all right.

MON: This is Kevin Mon from Areva NP.

I mean, according to the report, the non-creviced foil specimens were, you know, in essence, reused and they were polished down to 3 micron paste, and the creviced foils were just as received.

DUQUETTE: The paste that you used was alumina or it was diamond?

REBAK: It was alumina.

DUQUETTE: Alumina? So, some of the aluminum that was detected could have been from a paste rather than from a crevice former?

REBAK: That's possible.

DUQUETTE: Okay, thank you. Maury?

MORGENSTEIN: Morgenstein, State.

Could you tell us something about the time of exposure under the autoclave test?

REBAK: Yes, I'd say the time, we have exactly the start date and shut-down date, and it's 267 days, nine months.

MORGENSTEIN: Have you varied that at all? In other words, run different tests at different points in time to see if time affected the nitrate to chloride ratio for initiation?

REBAK: You are saying start the autoclaves and take a sample, and things like that? No. No, the start time and end time, nothing was done to the autoclaves.

MORGENSTEIN: Thank you.

DUQUETTE: Fraser?

KING: Fraser King, Consultant to EPRI.

I have a question on Slide Number 27. So, on the left-hand side where you have that green area that says no crevice corrosion, I just want to clarify that's under potentiodynamic conditions where you’re driving this with a potentiostat?

REBAK: Yes.

KING: For a waste package not connected to a potentiostat, that way, you can't attain those sort of potentials. The critical nitrate to chloride concentration would be much lower?

REBAK: Yes. So, those potentials are incredibly high, you know, well in the transpassive region of potential. But, we reported those values, saying no crevice corrosion, but in most solutions, natural environments, you will never reach those potentials. I don't know, ozone, you will have some experience with that. I don't know if you always get that high potential.

KING: For the waste package, the potentials are going to be 200--

REBAK: Yes, that's about--I think we have SAW, some ppotentials after three years, and the maximum was about 380, or so.

KING: So, in those cases, the critical nitrate to chloride ratio would be much lower?

REBAK: Oh, yes.

PANG: Yi-Ming Pang, CNWRA.

I have a clarification regarding the surface analysis on Slide 19. You do show the much thinner oxide former in the vapor phase.

REBAK: Yes.

PANG: Much thicker in the liquid, also in the bullet, you mention you detected different types of oxides and hydroxides.

REBAK: Yes.

PANG: We do know the protection of the passive film is formed by the thin CR203.

REBAK: Yes.

PANG: Three parts.

REBAK: Yes, this is the whole oxide, everything that, you know, until you get oxygen, to about half of that curve, I think that is how Charles Evans estimated the thickness.

PANG: And, in terms of the oxide, you used CR3 or 6?

REBAK: No, I don't think we looked into that, or we saw anything of that. So, this is the whole corrosion product on the surface, up to until you reach metal, but many times, you know, you meet the thin chromium oxide in between.

PANG: So, you're not sure of whether this formation of CR203 is in the inner layer?

REBAK: No. I'm sure it's there, but we may not have seen it, the results.

PANG: Thank you.

XIHUA HE: This is Xihua He from CNWRA.

I have two questions on Slide 26. On Slide 26, outside the crevice region, there's some green to yellow film.

REBAK: Yes.

XIHUA HE: Formed on the surface. Would you please comment on this slide. Did the film--what caused the color change?

REBAK: We always see that whenever you go into transpassivity, and in this case, you know, high nitrate, you don't see much dissolution. We don't know exactly what those colors are, but you see all the bluish and the yellow a lot. The yellow, it could be a chromium oxide or maybe transpassive chromium, and the blue could be associated with molybdenum, but we actually don't know. We never look into those things in detail. They always form in high potential, all those colors.

XIHUA HE: So, if you comment that because of a transpassive dissolution, I have a follow-up question, is what are the transpassive dissolution or (unintelligible) repassivation potential you measured in your tests?

REBAK: No, in this case, we didn't do too much. Yeah, we did a few things, because, let's see what the slide will be, maybe next slide. Yeah, this slide. At the same time, we did some of the Tsujikawa-Hisamatsu method here, the CRP, the squares, which are not cyclic polarization. And, with those tests, what you do is you polarize only two potentials. You never reach into the transpassive region, or it's more gentle type of applying current. So, you don't force the specimen to very high potentials very fast. And, in that case, you see the repassivation potentials are similar to the cyclic polarization, in both cases, here in this area, and in this area.

And, from that, you can conclude that the transpassivity in the cyclic polarization curve doesn't affect the repassivation potential of the alloy in the environment. It's kind of a property of the alloy, but is not affected, it goes into transpassivity or not. We have the same conclusion for lower temperatures as well, sodium chloride and potassium nitrate brines, 100 degrees C, and below, we see the same thing. The Tsujikawa method gives exactly the same value as the CPP method. So, there is no different in the repassivation potential.

DUQUETTE: Ron?

LATANISION: I'd like to get something of an integration of all of what we've heard this morning. So, if we could turn to Slide 31? The very last bullet, "Current results continue to support the localized corrosion model for degradation of the waste package." As I understand what you presented, there has been observation of crevice corrosion in some circumstances where it was unexpected.

REBAK: Unanticipated, I used.

LATANISION: Sorry?

REBAK: Unanticipated.

LATANISION: Unanticipated. All right, the difference is subtle, but meaningful. And, the argument is that perhaps that might have been in environments that are unlikely to occur in a repository environment?

REBAK: Yes.

LATANISION: And, even if it did occur, you would argue that stifling would--well, you don't know, but perhaps stifling would inhibit the propagation of localized corrosion?

REBAK: Yes, the stifling and also the amount of brine that you may have, because it would be varied in the microliters that Charles presented yesterday would be very small amount, and those brines would be also a very low activity of water. They cannot dissolve much metal into them, and things like that. So, there are all these other arguments that even if you initiate, you cannot have enough dissolution to cause any damage to the containers.

LATANISION: Okay. So, that is what you mean by supporting the current corrosion--

REBAK: Yes.

LATANISION: Okay.

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

BRYAN: This is Charles Bryan.

DUQUETTE: Charles?

BRYAN: I'd like to make another observation about the autoclave experiments, especially with respect to the atmospheric corrosion, the corrosion in the vapor phase.

As I stated earlier, within the autoclave--the relative humidity was about 40 percent corresponding to a maximum pressure of about 8 to 10 atmospheres. At one atmosphere pressure, the maximum relative humidity is about 4.4 percent. It's not at all clear that--in order to get the corrosion in the vapor phase, you have to have capillary condensation within the crevice. It's not at all clear that capillary condensation would have occurred had the relative humidity been limited to 4 percent.

DUQUETTE: Thank you. Any other comments? Comments from the audience? Questions from the audience?

(No response.)

DUQUETTE: None. So--please.

AHN: Yes, regarding yesterday's discussion of the decision tree, I think that applies to the last bullet here, too. I would like to mention that the question, it should be very clear, at least to me, the deliquescent brine forms, it can be from several monolayers to all the way near the layer. It was very unclear to me how to answer to that question.

The second one is in NRC's 10 CFR 63, that is the rule for the safe disposal of the high-level waste at the potential Yucca Mountain Repository. You can have screening out in two different ways--actually, three different ways, but technically, two different ways. One is events, sequence, process, FEPs screening, either by, one event or a combination of any of these events. At low probability, you can screen out.

Also, there is another way you could screen out.

If those consequences are extremely slow--low, I mean, and also you can screen out. So, that goes to--

DUQUETTE: Thank you. Any other comments or questions?

(No response.)

Then we're just done a little bit early. Thank you, Raul.

The next presentation is by Don Shettel on the "Update of the State of Nevada Research on Corrosion of Alloy 22."

SHETTEL: Roger Staehle apologizes. He was supposed to give this talk. I'm a last-minute substitute. Roger is enjoying a conference in France at the moment. I think some of you probably know what that is, but I don't.

The next slide, please. Roger initially initiated and commissioned a study and supervised a study on the effects of concentrated hydrochloric and nitric acids and sodium fluoride on the corrosion of C-22 alloy at 25- and 90-degree C and developed the model for the rapid penetration of C-22. The purpose of this was to develop a basis for modeling the phenomenological results that we already obtained with the Catholic University--that'll be Pulvirenti and Barkatt--for the accelerated corrosion of C-22 under some fairly concentrated brine compositions from accumulations of corrosive solids, which resulted from the evaporation of unsaturated zone pore waters, presumably hitting heated surfaces as a hot metal, which we believe were applicable to the conditions at Yucca Mountain. And this work utilized the electrochemical methods, SEM, and electron dispersive spectroscopy.

Next slide, please. I'm going to get right to the conclusions of this study. A model, meaning the spherical perforation pitting, or SPP, was developed for explaining and quantifying the rapid perforation of C-22 in concentrated mixed acids. The model is based on the continued nucleation of spherical domains that move through C-22 without being stifled.

The SPP is consistent with all work that was performed at Catholic University.

Number 3, the SPP is capable of perforating C-22 in times as short as 10 years or less, assuming that the environment of concentrated mixed acids can be attained.

The SPP occurs over a broad range of compositions of the mixed acid, HCl and nitric, where these concentrations exceed several molar in concentration.

And, 5, the activation energy for the SPP process indicates that it can occur over a range of temperatures including room temperature.

And Number 6, attention, he felt, should also be given to the terrace-ledge-kink process that occurs in concentrated hydrochloric acid, and this process can produce high rates. The propagation of intergranular corrosion also occurs, but this process was not nearly as quantified as the SPP.

And Number 7 is a rather important one. They found that there was no evidence of nitrate inhibition or the anion is functioning as an inhibitor or mitigating the corrosion.

And we would like to do some additional experimental work he's recommending should be undertaken to establish the applicability of the SPP mechanism as well as the intergranular corrosion and possible the terrace-link-kink corrosion to C-22 containers. And he feels this data that he has developed here provides a credible foundation for early penetration of the C-22 container.

And just a few examples of some of the SEM pictures from this work. We have SPP, spherical propagating pits. This one indicates--and this is a cross-section--indicates how he's formed. You get initial spherical pit at the surface, and at some point you propagate another spherical pit, and this keeps on propagating like a worm hole through the metal. And these other ones are just surface representations of the same thing, different magnifications. This one is actually from the Catholic University work.

Next slide, please. This is an example of terrace-ledge-kink dissolution. I think Roger may have shown some of this before. Yeah, this slide he's shown before. This one results from the present work. This is very similar. I believe it's a higher magnification. This just shows the theoretical mechanism for this process.

Next slide, please. And some examples of intergranular corrosion. The right-hand slide is just a blowup of this area here. It shows corrosion at the grain boundaries.

Next slide, please. I thought I was going to be talking yesterday and more on environments, but I got switched around to today. I wanted to discuss a few features that may support the development of the corrosive, highly concentrated solids that--the work at Catholic University shown was very corrosive, and I think one of the first assumptions that we might question is that of the capillary barrier that's at the rock void interface.

It turns out we don't really have a rock void interface. What we have is wall rock contacting the ground support, which is the stainless steel sheet here. And DOE assumes that there's a good capillary barrier here but basically, I think, ignores the ground support in modeling. The ground support--you can see the rock bolts here--but the ground support is a stainless steel sheet 3 millimeters thick, and this is snugged up against the wall rock and, I believe, compromises the capillary barrier to some degree, depending on how good the contact is.

If there were no slot--you can barely see that this is slotted material here. If this weren't slotted, it might be a better liquid barrier, except it also has rock bolts going through it. And with the slots, we believe this might increase the dripping of water onto the EBS; and when a ground support fails, then a rock fall occurs. And, again, the rock fall affects the capillary barrier. And the conclusion from this might be that the wall rock capillary barrier is not a conservative assumption.

The next slide I'm going to--and some other, what I would consider, optimistic non-conservative assumptions DOE makes is that no water contacts the EBS above boiling. And I think prior or up to the peak of the thermal pulse, you get a lot of pore water that's essentially moved out of the matrix into the fractures over a fairly short period of time. It's conceivable that there could be fingering of this water into fractures and faults which reach the wall rock-ground support barrier, and therefore that may increase dripping.

We also assume no episodic flow below the PTn, but the Chlorine-36 is considered fast-path or, in other words, is an example that there is episodic flow occurring in Yucca Mountain.

I've already discussed Number 3.

A lot of discussion on dust deliquescence on the EBS assumes that none of the water in the system reaches the

EBS until long past the thermal peak; and I feel that based on some of these other assumptions the DOE makes, it is possible to get mixed salts that may be highly concentrated by hitting the hot metal surfaces prior or shortly after the thermal peak.

Oh, and another thing on Number 1 here, there's a large range in the temperatures of the wall rock and the canisters, depending on where the canister is located, whether it's at the edge of a panel or in the center of a panel. And I think a lot of the diagrams the DOE uses show the maximum temperatures that may be obtained and not the range of temperatures. As you get close to the edge of the repository, the system barely gets above boiling for a much shorter period of time.

And all these assumptions affect whether you can have pore water contacting the engineered barrier system.

Roger feels, at the bottom here, that the environmental conditions for C-22 corrosion have not been bounded by the DOE and that one should expect the worst conditions for corrosion and not the best, based on all his experience in the nuclear industry.

And that's all I have.

DUQUETTE: Thank you, Don. Let me go out on a limb for just a minute and say that of all the corrosion work that's been done in this area so far, I think the Catholic

University work is the one that has been labeled with the most skepticism at the present time as being an environment that's just not possible to ever occur in the vault.

I know you've made comments about that before. At our meeting in 2004, you tried to justify those environments, but there may be some new people in the audience. Would you tell us why you think that environment is a possibility?

SHETTEL: Well, I think that all of these comments I made on DOE's optimistic assumptions here explain in more depth than I think I went into before, although I haven't gone into much detail in these except for Number 3 here. I thought--again, I was speaking yesterday, and I didn't have as much time as I had today--but I think these assumptions provide a possible condition for more UZ pore water contact in the EBS than DOE has assumed or modeled.

DUQUETTE: Ron, you had a question or comment?

LATANISION: Don, I know in Roger's absence you're at a disadvantage in presenting this work, but I'm curious about, let's see, slide--well, the conclusion slide. It was the first one you showed, the second one maybe.

SHETTEL: Number 3.

LATANISION: Number 3, yeah. Item 7 is really a very important statement, and I'm wondering what--there is no evidence that nitrate is functioning as an inhibitor. What is the evidence to show that? I mean, is there something other than these micrographs that are shown on the next--let's go to the next slide. Is this the basis for that comment? Because we're looking at a nitrate chloride environment, we're seeing pitting?

SHETTEL: No, I haven't shown you the basis. I believe that the State is going to release this report to the Board under certain stipulations so that you will have a chance to look at the evidence for that.

LATANISION: Okay. This is a report we do not have at this point; is that right? This is when we should have it, right now.

SHETTEL: Does Susan have a comment?

LYNCH: Susan Lynch, State of Nevada.

We're in the process now of deciding if we're going to release the China work that we've done to the Board under the stipulation that it goes no further at this time. I have talked to Bill Barnard about that; my boss, Bob Loux, has talked to Bill about that; and he suggested we wait till after this meeting to do that, and that's what we have done.

DUQUETTE: Without wanting to prejudice what you'll present to the Board by making a comment, is there any particular reason, that you can share with us, as to why the data would be so secretive that it wouldn't be shared with other participants in this workshop?

LYNCH: You could ask DOE the same thing of why they don't give any of their data out until they deem that either--

LATANISION: I just have one other comment, and I'd like to address this not so much to Don as to the metallurgists in this room who may know more about the metallurgy and microstructure of C-22 than I do.

But as I look at that top right micrograph, and I see the very high twin density, this looks like a much lower stacking fault energy material than C-22. Am I off base or does someone have a comment?

SPEAKER: --

LATANISION: Yeah, these are annealing twins.

SPEAKER: Yeah, they're annealing twins.

SPEAKER: --

LATANISION: Say something into the microphone, Russ.

JONES: Russ Jones, GT Engineering.

Annealing twins aren't related to stacking fault energy.

LATANISION: We should talk. I think they are.

JONES: No. Copper is a good example.

DUQUETTE: Let me ask the question differently. Has anyone else who is working on C-22 that's been heavily annealed seen this particular microstructure?

Yes. So the answer is--

LATANISION: All right. That's an alternate--.

DUQUETTE: Okay. Other questions or comments, please?

PAN: Yi-Ming Pan, CNWRA.

I think in the--report, we also characterize the microstructure in Alloy-22. Without looking at pitting--the pits--I think the microstructure is very common--

LATANISION: That's why I asked a metallurgist.

MCMILLAN: Glenn McMillan, UNR.

I've seen this twinning structure in materials that I've annealed at 1200 degrees C; and, of course, the longer you anneal it, the larger the twins grow. The reason I began doing that is because mill annealed material that I had received from Haynes I found very often had grain boundary precipitates that would, in fact, increase the likelihood of localized corrosion; and so I began solution annealing all of my specimens before I used them.

And that's another remark that I wanted to clarify on what I said earlier about us having seen pitting corrosion--not crevice corrosion, but pitting corrosion--away from any crevice formers under heavy salt deposits. And it's very likely that that may be due to inadequate annealing of the as-received material that we got from Haynes.

And I also wanted to comment that in this test where we saw pitting corrosion that this was under a salt deposit that was perhaps 20 to 30 millimeters deep, and we had cycled it from wet-dry-wet-dry many times where we had a lot of solution available to dissolve the metal.

And I think that's a very important point that we need to make here is that my understanding of the work that has just been presented in front of us is that there was essentially an unlimited amount of liquid available to carry away dissolved metal. And I don't understand how that can apply to the service conditions that we expect to see in the repository.

BRYAN: Charles Bryan.

I would also like to make a comment about--

DUQUETTE: Charles, could you pull the microphone a little closer? I can't hear you well from up here.

BRYAN: This is Charles Bryan.

I'd like to make a comment about these conditions. Of course, these solutions would not be stable in an open environment for very long. The acid gas partial pressures are so high for these that they would evaporate within hours at most on a waste package surface.

DUQUETTE: Thank you.

PAN: Yi-Ming Pan, CNWRA.

I just want to provide an additional observation. According to our testing—I think DOE also did some testing--if you use a very aggressive test solution, for example ASTM G-28 with a boiling hydrogen chloride solution, you definitely will see the pitting corrosion on the test specimen, especially for the aging or weld sample. But of course, our testing—indicated another type of possible chemical composition we--would definitely not see this pitting corrosion occur on the specimen.

DUQUETTE: Russ?

JONES: Russ Jones, GT Engineering.

Question about the Roger--and I realize I'm not speaking to Roger Staehle here, and maybe this will get back to him and I can talk to him directly. But the question of the fast corrosion rate because you have a terrace-ledge-kink kind of model, in the absence of a passive film, it's my understanding--and I'm not a corrosion scientist per se, but I'm of the understanding that the activation energy for corrosion of a bare metal surface is relatively low, and it's all dominated by film formation. So to find another process by which active corrosion occurs in the absence of a film, it doesn't seem like it would affect the rates that much. That just surprised me that he'd put that in as a mechanism, that he needed some special mechanism to accelerate corrosion rates of bare metal surfaces.

Doesn't seem like that's a necessary step, but not talking to Roger, I'm sure he'd have some explanation.

DUQUETTE: Don, do you want to make a comment of any kind on that?

SHETTEL: Well, I believe Roger does have some rates in the report, and I think the same corrosion occurs at 25 degrees as at 95 degrees, so it doesn't seem to be much of a--

JONES: That's consistent with a low activation energy--.

SHETTEL: Yes.

DUQUETTE: I think Russ's comment really has to do with, your solutions don't allow a passive film to form, so you're going to have a different corrosion mechanism than one would have if one expected passive films that are broken down by localized corrosion. I think that the Department of Energy, in the very first slide that Raul showed, indicated that, yes, C-22 will crevice corrode in certain environments; and I think one of the purposes of this workshop is to say that in this environment it may not be probable. That's as gently as I can put that comment.

PAYER: Joe Payer, Case.

Taking a page from Maury yesterday, I guess I would totally agree with these results that are up on the board. I don't think that's at all debatable. If you put Alloy 22 in 3-molar hydrochloric acid and concentrated nitric acid at these temperatures and dip it in a teacup, this will occur. There will be no passive film, and it will corrode very rapidly.

I think the key is: How do you generate these environments in Yucca Mountain at any given time? And apparently the State has a rationale for that that will be shared, as Susan said, at the right time, and we'd look forward to that, to analyze that, and see what that means. In the absence of that, I'm not sure.

But one of the main focuses of this workshop is high temperature deliquescence. And with the thin layers of dust that are on the metal surfaces under those conditions and the open conditions in the drift, I don't see how one could ever sustain these environments for any appreciable time. They're just not stable, and you wouldn't have enough environment to do that.

SHETTEL: These environments are dependent on getting pore water to the surface of the hot metals.

PAYER: Well, then maybe that would be more relevant to seepage conditions, but it's not relevant to high temperature deliquescent conditions. And so, again, I think we just have to separate the two regimes and what possible mechanisms are there. And then, again, if we're talking with dripping and seepage conditions, then, again, I think we still have to talk about the stability of these environments, how are they maintained, why don't they acid vaporize and--.

SHETTEL: Well, I believe that some of these pore waters--if the pore water is going to reach the EBS, it's got to do that pretty much before the thermal peak, and that means it's going to be above boiling possibly.

PAYER: Well, that's fair, but--

SHETTEL: And there are mechanisms for that to finger through the boiling zone.

PAYER: Well, is it coming in as 16-molar nitric acid and 3-molar hydrochloric acid? Is the picture that the drop of water that comes in as that?

SHETTEL: No, no. If pore water can penetrate the fractures because there's an abundance of it above the boiling zone and kind of shoots through the fractures and drips on the hot metal, then that concentrated acid is developed on the hot surface, as the experiments at Catholic demonstrate.

PAYER: That's the part we don't see. I mean, one of things we have seen from the Catholic University was a Soxhlet experiment.

SHETTEL: No, that's not all they've done.

PAYER: On our--, you're not talking about that again, but that's the one we've seen. And, again, nobody disagrees that that's what would happen in that experiment if anybody else reproduced that experiment that way--.

SHETTEL: They have a lot of other experiments that aren't Soxhlet.

PAYER: I understand. That's the mystery right now.

DUQUETTE: Just a comment, Joe. While the thrust of the workshop is on deliquescence, the real thrust is the integrity of the container. If there is evidence that it will fail by some other mechanism and we can bring that out-- I understand it's not where we're going, but I think it's somewhat--.

PAYER: I don't disagree with that, and I'm not saying we're--, but it would be useful, I think, if we talk about, is high temperature deliquescence an issue, is seepage an issue, is there some other mechanism an issue, or else we start talking about processes that can't occur at the same time.

LATANISION: Dave, just to add a footnote. My point with this workshop is to determine whether we have a technical basis for screening out localized corrosion, and deliquescence is certainly a part of that equation. But any source of liquid or corrosive environment that may be realistic ought to be on the table.

DUQUETTE: That's what I thought I said.

DUQUETTE: Since Maury's name was used in vain a couple minutes ago, Maury, you had another comment to make?

MORGENSTEIN: It's totally correct to assume that an environment such as exhibited here with what we did at Catholic would be difficult to produce in a drip scenario or in a dust scenario by itself to the extent where it could sustain itself over long-term sufficient in one location to arrive at penetration. Actually, even if we move the high temperature regimes and go down to 96, the same comment could be made that I just made.

There are situations, however, where you pond sufficient amount of dust, and if you had, for example, a rock bolt sitting above you which gave you an automatic drip system, you could sustain long-term drip over the same location. In a condition where you have a heavy dust accumulation on the surface and a drip over that dust, you form microchemical phases in some of those unit cells of pore that can go to acid in a fairly consistent way. That, in itself, is probably the largest problem that would occur in a drip system, and it's self-mitigating in the sense that eventually you precipitate enough salt so that you remove the liquid from the surface of the metal, so it eventually stifles itself.

The time it takes to stifle depends on the chemistry of the water coming in and the temperature of the system. There are situations where you can penetrate without stifling. The amount of penetrations that could occur for the number of packages you need to penetrate is a totally different type of issue that we haven't gone into.

So this is a situation where we can be extremely realistic, and we can show where you could receive this kind of failure in a very common scenario that could occur. If we move from a drip system to a flowing system or a very fast drip system, then the problem of finding a scenario that will work simply with this acid system is alleviated.

DUQUETTE: Thank you, Maury.

Charles, I can see you're anxious.

BRYAN: I think I would argue with that point. In the open system it's very difficult to generate any kind of concentrated acids. The materials de-gas very rapidly, the fluids de-gas very rapidly. You can't maintain a concentrated acid in an open system. I don't think there's any way to obtain or to maintain these solutions in the drift.

DUQUETTE: Thank you. Maury?

MORGENSTEIN: What we're saying is it's not an open system if you're dealing with pore size. Capillarity is equally capable of holding an acid as it is a non-acid.

DUQUETTE: Charles, do you want to comment any further on that?

BRYAN: No.

DUQUETTE: No? Okay, thank you. Other questions or comments from the Panel? Yes?

BROWN: Neil Brown with BSC.

I've heard a couple comments that seem to suggest that we're screening out all localized corrosion, and I just want to make it clear that, as you'll see from my talk later today, BSC is only screening out localized corrosion due to dust deliquescence, that localized corrosion due to pore waters and seepage is accounted for and is modeled with consequences.

DUQUETTE: Thank you. That's a good comment, because it goes along with what Ron and I said earlier, that the integrity of the container and what that does is really the important aspect here and not whether it's one specific mechanism that we're addressing.

Any other comments from the audience? Panel?

Thank you very much, Don.

DUQUETTE: The next talk is on corrosion in salt environments at elevated temperatures from Lietai Yang from CNWRA and Southwest Research Institute.

YANG: Thank you. Good morning, Ladies and Gentlemen.

My talk this morning is corrosion of Alloy 22 in salt environments at elevated temperatures. Before I start, I would like to acknowledge the contributions from these people.

Next please. This is the key point of this presentation. First, I would like to share some experimental results obtained in sodium chloride, sodium nitrate, potassium nitrate system. Temperature range 150 degrees C to 180 degrees C. We conducted this experiment, under we think a representative condition, which is ambient pressure, no deaeration.

The main conclusion was general corrosion was found to be the major mode of attack for Alloy 22. The corrosion rate was from 1 to 10 microns per year. Of course, uncertainties exist in the susceptibility to localized corrosion for Alloy 22 in this environment.

Next, please. This is a background, as presented yesterday by Charles Bryan and Bobby Pabalan. Sodium chloride, sodium nitrate, potassium nitrate, they are present in atmospheric dusts. And, this salt system is highly deliquescent. Boiling point can go as high as 220, or even higher.

Based on the model for the waste package temperature, this is a maximum, therefore, deliquescence may take place during the thermal pulse, therefore, corrosion of Alloy 22 in the system may affect, if it's present, it may affect the performance of the waste package.

Next, please. This is the experimental setup for the test. This is sodium chloride, sodium nitrate, potassium nitrate, equimolar, we chose equimolar. We have about 1 kilogram of these salts, a lot of salts, placed in a glass vessel, and then we added some deionized water to form about half of the volume liquid, the other half of the volume solid. This system is not pressurized. It's open to the open air. Note no good filling here. Therefore, it contains some air.

From time to time, we added a little bit deionized water to maintain the half liquid, half solid because of this criteria. And, also, the vapor pressure here was maintained close to one atmosphere condition, therefore, the composition of this liquid is fixed. That's thermodynamics.

We took some samples at 150, and also 180 degrees C. We analyzed them. The ratio of nitrate to chloride was from 16 to 20, which is a lot lower than what Raul just presented this morning. So, that is 16 to 20 molal ratio. It was stable at 150 to 180. No pressurization.

We have specimens in the liquid, and specimens in the vapor phase. Some of them creviced. Some of them, some of them with no crevice, totally uncreviced.

Calomel electrode was used to measure the corrosion potential of Alloy 22, in the liquid phase, of course. And, also, we did some polarization tests.

Next slide, please. This is the corrosion potential measurement from the system of Alloy 22 specimens. We have uncreviced mill annealed specimens. We also have creviced, welded plus solution annealed, solution annealed, this one here. You are going to hear this from a colleague, Xihua He. She is going to present this in a moment. Solution annealed means that the specimen was heated to 1100 degrees C, then quenched in water.

Also, we presented here, we have the electrochemical potential measured on platinum electrode, platinum electrode in the system, to indicate how oxidizing the system is. You can see about 500 millivolts against the calomel. It's quite oxidizing. Also, the corrosion potential at this temperature is high, about 300 millivolts.

Next, please. This is a comparison of the corrosion potential measured in our test, no pressurization, no deaeration, compared with the corrosion potential presented last year, last November, at the Board meeting. You can see these results were obtained under deaerated conditions. There is a big difference. 600 millivolts difference.

The other thing I'd like to point out is we're in high concentrations of nitrate, no chloride. The potential is minus 400 millivolts. We have been thinking about nitrate is a very strong oxidant, but it does not appear to be oxidizing in this environment, minus 400 millivolts.

Next, please. Since the results I'm going to present are based on--the corrosion rate results are based on weight loss measurement, I'd like just to spend a minute on the cleaning procedure for the measurement. We cleaned the specimen with hydrochloric acid according to the suggested ASTM standard, and also we cleaned with this solution. We have base metal with unreacted or uncorroded metal in the same test. It does not show that this solution was causing weight loss for unreacted metal. So, from our cleaning procedure, after the--this is a one cycle cleaning, the second, third. After the third cleaning, we got level. Therefore, our weight loss measurement was taken after the third cycle of cleaning.

Next, please. This shows the corrosion rates. Corrosion rate in the liquid phase, and corrosion rate of the vapor phase. Temperatures were 180, 160, 150, and these are the given days. We have welded, because this was initially a scoping test, we put as many different kinds of specimens as possible. So, welded specimens, thermally aged specimens, thermally agedthen we heated the specimen to 870 degrees C for 30 minutes, then quenched. We have creviced specimens, we have uncreviced specimens. These are welded plus solution annealed that I mentioned previously.

The big difference is vapor phase corrosion. Notice it is lower. The liquid phase corrosion, it was higher, about ten times higher, and the corrosion rate was from about 1 micron to about 10 microns per year. This is a very high corrosion rate.

Next, please. This shows the corrosion of Alloy 22 specimens, thermally aged specimen. This is the line, vapor up there, the liquid down here. You see no corrosion. Here, we can magnify the section here, more corrosion in liquid phase, less corrosion in the vapor phase. And, also, in the vapor phase, you'll see twin boundary attack.

Next, please. This is the crevice specimen. We didn’t polarize them with immersion test at straight corrosion potential. Crevice former. You can see here the black area. They were underneath the crevice former directly. This white area, this was the exposed area. If you magnify this section here, you'll see underneath the crevice, you can see clearly machining marks However, outside of the creviced area, the exposed area, there was no machining mark at all.

Therefore, a lot of corrosion going on outside, very little inside. If we magnify the interface, we can see it. There's some dark spots in this area. However, when we do the depth measurement, we find that the depths in these areas, it was about the same as depths in the open area. Therefore, our conclusion was that general corrosion was the major mode of attack, not crevice corrosion, for this environment.

Next, please. This shows the corrosion of Alloy 22. This is a welded specimen, this part in the vapor phase, and this part in the liquid phase. You can clearly see the difference. This is welded area with base metal. And if we magnify the interface, we can see corrosion in the welded area. It's along the dendritic structure.

Next, please. Because we conducted the tests at different times, we thought we could get a trend. This is the plot of the corrosion rate at different temperatures as a function of time, because we didn't have enough data, it's hard to draw a conclusion from this test. We do have other tests going, and hopefully, we can get more results soon.

Next. This is the comparison of the corrosion rate with the--measured in the air condition, with the corrosion rate measured in the autoclave condition. For the liquid phase, and you can see the condition, 160 degrees C, autoclave, so there was a difference. The difference was about, if you measure the corrosion rate in the non-deaerated condition, the rate was about 10 to 50 times higher. Of course, we realized our test was conducted in a little shorter period. The DOE test was conducted at 120 days. Our maximum time, 80 days. And, also, there are some microstructure metallurgical treatment differences. But, at this time, we think it looks like the deaeration is an important factor.

Next, please. This is the summary. The experiments were conducted in sodium, potassium, chloride and nitrate systems under ambient pressure without deaeration. Corrosion potential under this condition was about 600 millivolts higher than under deaerated conditions.

General corrosion was found to be the major mode of attack, and the corrosion rate was about 10 to 50 times higher than if you do not deaerate the system. We have tests ongoing to characterize the evolution and the stability of the salt system under this condition. And, also, we have a relatively longer-term test ongoing to verify the high corrosion rate we have measured, and also to verify the susceptibility of Alloy 22 to localized corrosion under this environment.

Next, please. Acknowledgement. With that, I'd like to take questions. Thank you.

DUQUETTE: Thank you very much.

Could we go to Slide Number 8, please? You indicated that the--there's two things I'd like to comment on on this slide. Number one is that you indicated that general corrosion was more rapid than crevice corrosion. But, if we look at your highest corrosion rates, that would indicate that the crevice corrosion and the mill annealed test at 160 degrees celsius had a much higher corrosion rate than any of the ones that were just annealed.

How do you account for the fact that the crevice corrosion sample shows such a high corrosion rate, and yet you conclude that general corrosion is the problem?

YANG: Yes, that's a good question. I have shown that the specimen, the crevice specimen, the corrosion from the crevice specimen, it was not into the corrosion underneath the crevice. It was outside of the crevice area. For this sample, we measured the high corrosion rate, I believe the rate was scattering. We saw this within the scattering range, so we cannot--

DUQUETTE: So, you think this is a scatter problem rather than anything else?

YANG: Yes.

DUQUETTE: Okay. Go ahead.

LATANISION: Well, is the rate that you're measuring here a uniform corrosion rate on a creviced sample, or is it corrosion--it's not corrosion under the crevice; right?

YANG: This is weight loss--total area--

LATANISION: See, that's not a localized rate that's listed up there. It's a uniform rate.

DUQUETTE: I understand that. I understand it very well, since they're all just weight loss measurements.

YANG: The crevice area is a very small proportion, fraction, of the total surface area.

DUQUETTE: Right. And, so, if I take it out--this is a little bit higher, but he's comparing it to the first sample, which is just a sample without a crevice, apparently, 49 days at 160, and there's a factor of at least five difference, and you're saying maybe that's in a scatter.

YANG: Yes.

DUQUETTE: Do you have a mechanism for why your data at

160 is so bad, or I won't say bad, shows higher corrosion rates than at either 180 or 150?

YANG: For these facts I tried to correlate them, I was not successful. Cannot explain.

DUQUETTE: Okay, thank you.

LATANISION: May I ask some questions? This is Latanision, Board. If we go to Number 14, please?

As I understand your observations, your corrosion potential is 600 millivolts higher than those measured in the DOE experiments, and your observation is that that's because your system is aerated. Their system is effectively deaerated. Is that corrrect?

YANG: That is fact.

LATANISION: Okay. And, following that general corrosion is a major mode of attack, but what seems to me to be unclear here is that if the environment is more oxidizing in your experiments, it would seem to me the probability is that you would be above either the critical potential for crevice corrosion, or above the repassivation potential, in which case, I'm not sure why you're not seeing crevice corrosion. Am I missing something, or do you have a--

YANG: Because--do you want to--

DUQUETTE: No, let him respond first, then I'll come back to you.

YANG: Thank you. Because we think this environment is so corrosive, is corrosive, it destroys the passive--it's not truly passive anymore. So, it's corroding. The corrosion is going all over the place. You do not have a catalyst to support localized corrosion underneath the crevice. So, the other part is corroding. And, we do not--we don't polarize it. It's not connected to a potentialstat. It's like a free corrosion potential. So, you don't have catalyst.

LATANISION: No, I understand that. But, the free potential is above the repassivation potential, presumably, isn't it?

YANG: That is correct. And, the other thing is that the repassivation potential, if we compare the repassivation potential measured by the—presented last year during the Board meeting-- our potential was still low, lower than the repassivation potential. But, it's high, just looking at the slides that Raul presented this morning, he showed, if I'm not mistaken, he showed 400 millivolts of repassivation potential. That's slightly lower. Our potential is still slightly lower.

DUQUETTE: Let me take the Chairman's prerogative for just a minute, and only indicate that we had done some experiments on C-276, which is a slightly different alloy, using ozone as the oxidizer, and saw very similar results, that crevice corrosion could not be initiated. We got general corrosion outside the crevice, and total protection inside the crevice. If the oxidizing environment goes high enough, you're above the transpassive potential, and it corrodes uniformly and you don't set up a cell between the inside and outside.

But, Raul, now it's your turn.

REBAK: Raul Rebak, Livermore.

The reason, I think the main reason is because he says that in his solutions, he has 16 to 20 nitrate over chloride ratio, so that in his is no matter what potential you went on, we also have tests, like a constant potential, with a potentiostat, we have a passivation potential that would be 500 millivolts, and we run at 800 millivolts for one week, and we only can produce transpassive dissolution. You never nucleate localized corrosion on the crevice former, and the reason is because the solution is not for that. So, it's the property of the metal and the solution, no matter what potential you apply, if you have the conditions of the ratio, nitrate to chloride higher than a certain value, you will not have localized corrosion, no matter what you do.

DUQUETTE: Thank you. Russ, you had a question?

JONES: Russ Jones, GT Engineering.

Can you go back to Figure 9? You commented on this, but didn't explain why. What's the reaction occurring at the green boundaries in the vapor phase, do you know?

YANG: Because the vapor phase, the relative humidities were low, but you still have equilibrium of vapor and liquid, there is condensation on the metal. Make it very simple.

JONES: So, is this like the canary in the coal mine? I mean, is it something showing up that you would see eventually in a liquid environment?

YANG: There is a thin film on the surface.

WALTON: John Walton, Nye County.

My question, I'm just trying to understand, is that it would appear that you didn't get corrosion, general corrosion, as rapidly into the crevice system, and, so, a part of this area was creviced and it was protected from corrosion, so what would the general corrosion rate be if you normalized for the area that was protected underneath the crevice?

YANG: As shown in the diagram, the corrosion rate underneath the crevice, it was a lot lower than the corrosion outside of it.

WALTON: Right. But, if you got the measurements by weight loss, then presumably, the area outside and inside the crevice, you're giving an average for the rate for both of those areas.

YANG: Slide 10, you can see it here. This is the creviced area. You can still see the machine mark. However, outside of the exposed area, there's no machine marks. So, it was deeply corroded here. Not much corrosion here.

DUQUETTE: I think the question was did you take out, in your calculation, did you take out the part that was under the crevice as far as calculating your total corrosion rate. Did you normalize for just the exposed area rather than taking a regional size of the sample?

YANG: We take the whole area.

DUQUETTE: The whole area.

WALTON: So, the general corrosion rate would be higher than we see on 13?

YANG: The fraction of the crevice is a--the fraction is very low. The fraction of the dark area compared with the whole surface area is very small.

WALTON: Okay.

DUQUETTE: Raul?

REBAK: Raul Rebak, Livermore.

Yes, the same comment. If you calculate only for the area exposed, the covered area is such a small value, less than 5 percent, it will not change the general corrosion rate very much.

DUQUETTE: Questions or comments from the audience? From the Panel first, and then from the audience? Yes.

DI BELLA: I've got a number of questions about the apparatus--

DUQUETTE: Identify yourself, Carl.

DI BELLA: I'm Carl DiBella of the NWTRB staff. It's

Slide Number 4.

Okay, you said this is a glass vessel. Did you have one separate vessel for each temperature, is that how you did it, or did you run 150 in this vessel, and then come back and run 160, and come back and run 180?

YANG: We have four vessels altogether.

DI BELLA: Okay. And, did the vessels have agitators in them?

YANG: No.

DI BELLA: Did you ever take a sample of the liquid and analyze the liquid in the vessel, not the condenser, and determine what the compositions were?

YANG: Yes. For 150, we got a ratio of 16-something, I don't remember, 16 point something. And, then, for 180 degrees C, we got 19, the ratio was 19.

DI BELLA: Okay. And, did you take samples from a number of different points inside the liquid to determine that you had uniformity?

YANG: Very good question. In this experiment, I draaw here, you can see a definite separation of solid and liquid, actually solid is a--so we tried to get our liquid from the deepest spot we could find. So, we didn't try different areas. We think the composition of the liquid is, we think, the liquid is the same. If it's solid, it might be different, but the liquid, we think it's the same.

DI BELLA: It's a glass vessel, you could observe the liquid. Was it very viscous, or not very viscous?

YANG: We could clearly see the liquid. It flows very well. Yes.

DI BELLA: Okay, thank you.

DUQUETTE: One quick question. We mentioned the transpassive. I don't remember what the transpassive potential is for this alloy in this solution. Are you above the transpassive potential when you're getting this general dissolution?

YANG: Can I go to the backup slides, please? This is the corrosion potential, about 300 millivolts here. The transpassive--yeah, this is two specimens, one is a weld creviced specimen. The other one is uncreviced specimen, mill annealed. So, you can see it. This is below the transpassive region.

LATANISION: This is for the ternery salts you are looking at?

YANG: That is correct.

DUQUETTE: At that temperature.

YANG: 160 degrees C.

LATANISION: Latanision, Board.

Just to follow that, where do you think in your tests you are relative to this cyclic polarization diagram? What potential--what open circuit, what potential would you be operating at during your test?

YANG: About 300 millivolts, corrosion potential.

LATANISION: Okay, thank you.

DUQUETTE: Yes? A question from the audience?

APTED: Mick Apted with Monitor.

Slide 12. As sort of a consumer of this type of information on corrosion rates and propagating them into consequences, I think it's very encouraging to see. Trying to get some idea of time. Certainly, repository time scales are a bit longer than 80 days. The only data that I see that sort of we can look at a time change here is the 150 data here with the liquid uncreviced. And, it certainly seems like it's falling quite a bit over 80 days.

I don't know, how do you look, in terms of propagating this forward to repository time scales? What type of rate should we come away with in terms of trying to look at long term general corrosion based on, I realize limited data, but it seems to me that--is this a general phenomenon that these rates strongly decrease with time?

YANG: From what I have seen and what is presented by DOE, that was the case. For this one, I really do not have enough data. It's true low here, high here, but it's low here. I really do not have enough data, because this one was a scoping test, we put as many kinds of specimens to see if we may catch that here.

APTED: Sure. But, I see in your conclusions, you know, you're saying 10 to 50 times higher corrosion rate. You know, I don't know whether it's based on the early data, later data, and if we had data at two years, whether we could say--

YANG: Yes, the comparison with the data--the data we compared with was not that old,--it wasn't (unintelligible) the 120 days. So, not a lot longer than what we have.

DUQUETTE: Ron, you had another question?

LATANISION: Yes. If we could go back to 17? This is Latanision, Board. In the spirit of our workshop, this is really quite an important polarization diagram, and I'm just curious, do you have a nitrate to chloride ratio for this?

What would it be in this case?

YANG: I do not have it for this temperature. But, this is 160 degrees C. We have measured 150 degrees C. The ratio was 16, a little more than 16.

LATANISION: 16 to 1. Okay. But, you don't have it in this case. You just suspect it's similar?

YANG: It should be very similar, because, you know, the test, I must admit, our test to control within 10 degrees plus or minus, it's difficult, because we wanted to control the volume of water. If you add a little water, the temperature drops.

LATANISION: Yes. And, you're getting a corrosion potential that looks like 200 millivolts positive. Could we go back to Rebak's presentation, Slide 26? This is a workshop; right? We're trying to get through a workshop, workshop-spirit conversation here. Number 26.

Raul, I think you would agree with this; is that correct? If we look at Number 26, here on the bottom left, you've got, at 160 degrees, you've got a ratio of about 33, and you're showing negative hysteresis, which suggests you're not experiencing crevice corrosion; right?

REBAK: Yes.

LATANISION: So, it seems to me there's some common ground here.

REBAK: Yes. Again, yes, there's no contradiction between their results and our results.

LATANISION: Okay. So, the real question is what is the operational nitrate/chloride ratio that we're anticipating.

REBAK: Exactly.

LATANISION: Because it's very clear that in your cases, you do see crevice corrosion in some circumstances. Your solutions are presumably deaerated relative to his.

REBAK: Yes.

LATANISION: He's saying no evidence of crevice corrosion in these aerated solutions under circumstances where you, too, see no crevice corrosion.

REBAK: Yes.

YANG: There is another point here. That is in the results Raul presented, the autoclave test, the ratio was 7 and .5. In our case, our ratio was more than 16. This is other difference.

DUQUETTE: Right. But, I think Ron's point would be that this discoloration, and so on and so forth, in a short-term test could translate into the general corrosion that he reports after 80 days.

LATANISION: That's exactly right.

DUQUETTE: So, the data are consistent at least at this point. I think everyone agrees with that.

LATANISION: Thank you, Mr. Chairman. That's exactly my point. Thank you.

AHN: One more thing about the difference. Raul's case is pressurized.

DUQUETTE: Yes. Thank you. Fraser?

KING: Fraser King, consultant to EPRI. Can I go to Slide 4 on Lietai’s presentation? This is the one where you have the experimental setup. I think you were saying that you had an equal volume of solution to an equal volume of solids?

YANG: Tried to keep that way, yes.

KING: So, I think we're going to hear this, and we have heard that the amount of liquid in the deliquescent brine in the dust deposit will be very much smaller. Have you done any experiments with a smaller solution volume? And, if not, do you have any suggestions as to what might happen to the corrosion rate if you had much less liquid than you do in these tests?

YANG: This condition, because in the Yucca Mountain condition, you have a vapor, and that vapor you are going to evaporate, and there is a state you go, from diluted to concentrated. This is one of the states it has to go through. But, in our experiment we have to immerse the specimen in liquid so we have control, and then we want to compare the result with one another, so we chose to control a one to one ratio, volume ratio.

KING: Right. I understand that. I was thinking more of the dust deliquescence situation where you have very small volumes of liquid, which this would not represent. Do you have any--can you sort of speculate as to what might happen if you had much smaller volumes of liquid, as you would do in a dust deliquescent system.

YANG: The concentration, if we have a small volume of liquid, it might be more concentrated. However, because the eutonic point limitation, so the concentration, the composition, the dryest you can go, the most concentrated you can go, is that eutonic point. And, that eutonic point is the limit. Therefore, we don't see a lot of difference from this composition to that. There is difference. I don't have the diagram to show, but there is a limit.

KING: Yes, I wasn't thinking in terms of composition, but just the actual amount of available water.

YANG: The actual--it really depends on the amount of the salt, and then the thermodynamics.

DUQUETTE: Carl?

DI BELLA: Carl DiBella again, Board Staff.

As long as we've got this slide up, I have another question about the apparatus. The condenser, did you see any evidence of acid degassing by sampling the condenser water? And, if so, which was coming off faster, nitric acid or hydrochloric acid?

YANG: We analyzed the water here. So, we set out to capture all of the gasses coming out, not all, most of the gasses coming out here, because it's low temperature solubility. It far away from solubility. It's like a scrubber. For this test, we found the pH was low, about 2 to 5, and the ratio we found, the data was scattered. We found that nitric acid was higher. However, we repeated the test. We found the data was scattered, so we need to have more data to get a conclusive result.

DI BELLA: Thank you.

DUQUETTE: Rob Kelly?

KELLY: Kelly, Virginia.

Could you go to Slide 17 of this, your backup slide? Maybe Ron and Dave can correct me if my memory is wrong here. But, for most alloys, a microamp per square centimeter is about half a mill per year. And, from your dotted line where your corrosion potential is, that's hitting at about a microamp per square centimeter, which would be about half a mill, that's about 10 microns per year. So, it seems that you're not really undergoing transpassive dissolution, you're not high enough in potential, you don't have localized corrosion, as you showed, it's a passive dissolution phenomenon that you're seeing, but at rates that maybe we're not all that used to at low temperature.

YANG: If we take the polarization curve, it's like this, it goes there, it goes there. If you take this current, it's about 20 microns, we calculated it, it's about 20 to 50 microns per year. So, this current density is very close to the weight loss measurement. The other thing is that this is--it's below the transpassive region. We think that you can call it, it's a passive dissolution, or simple passive. The current is a simple passive dissolution.

DUQUETTE: So, it's possible, I've seen systems with two transpassive regions, depending on what dissolves. So, it's possible you're seeing that.

Any other questions or comments? Yes.

LIAN: Tiangan Lian from Lawrence Livermore Lab.

In your Slide Number 9, you show there is a specimen with both vapor phase and the liquid phase. I don't see that in your setup. Can you clarify that?

YANG: That's a good question. That setup is too simple. It was typical, the setup was for typical specimens.Some specimen was halfway.

LIAN: Okay. Now, my next question is not. In your setup, I assume you're going to see, I mean, you already said a lot of the solids on the bottom. So, I would assume you may see some slurry in the lower part of the setup. Did you see this kind of a heavy, I mean, the slurry solution, a co-mixture of that, kind of a floating, and it may have somewhat of an abrasive motion on the specimen?

YANG: Sorry, I didn't catch your--

LIAN: What I'm saying is that in your setup, you continued to have a mixture of a solid and liquid.

YANG: Yes, sir.

LIAN: So, are there solid particles kind of floating in the cells?

YANG: If we let it settle, then we can stir it. If we stir it up, we may see particles floating around. Most cases, the particles are settling down to the bottom, or to the edge, crystallized at the edge of the bottle.

LIAN: So, your solution temperature is just marginal, I mean, right on the edge of boiling. So, I assume the boiling motion may have a stirring mechanism.

YANG: Not much boiling. There was not much boiling.

LIAN: Thank you.

DUQUETTE: Any other questions or comments?

(No response.)

DUQUETTE: If not, let's take a break. Let's reconvene at 10:15.

(Whereupon, a brief recess was taken.)

DUQUETTE: Anyone who doesn't take their seat fairly quickly will have your data ignored. I notice that's the only thing that works with technologists.

Now that you're all refreshed and had your coffee and are back awake again, we'll continue with this morning's session. The next presentation is by Xihua He from CNWRA on crevice corrosion initiation and propagation tests. I hope I didn't do too badly with the pronunciation of your name.

XIHUA HE: Good morning, everyone. My name is Xihua He, and I work at the CNWRA.

Previously, just now, Lietai Yang gave a presentation from our center on his corrosion tests, were focusing in their temperature regime above 120 degrees C. For this presentation, many focus on corrosion tests conducted in the center in the temperature range from 25 to 110 degrees C.

Before I move onto the presentation, I would like to acknowledge the contributors for this presentation.

Next slide. This is the outline of my presentation. In the introduction, first, I will give you the key points of this presentation, and I will briefly introduce our model for Alloy 22 localized corrosion. And, then, I will introduce our test methods and the test results to look at the localized corrosion initiation and the propagation in the low temperature region. And, I will wrap up my presentation with the conclusions, and some uncertainties related to Alloy 22 localized corrosion.

Next slide, please. The key points for this presentation is, the first one is localized corrosion susceptibility of Alloy 22 was affected by several factors. These factors include temperature, pH, the ratio of chloride concentration to concentration of inhibitors, and here, in this presentation, inhibitors are referred to as the nitrate, sulfate, carbonate, and the bicarbonate. Another factor is the fabrication process.

In our tests, we observed a strong tendency toward stifling and repassivation of Alloy 22 localized corrosion in 5 molar sodium chloride solution at 95 degrees C, and we believe a 5 molar sodium chloride solution, is a very aggressive solution, which can be attained at room temperature for only chloride solution. And, at 95 degrees C, which is close to the boiling point for 5 molar sodium chloride solution at the atmospheric pressure, but uncertainties remain in elevated temperatures and more aggressive chemical conditions.

Next slide, please. This slide introduces our NRC/CNWRA model for Alloy 22 localized corrosion. In this presentation, I refer to crevice corrosion as one of the major attack modes as well as localized corrosion. For a typical crevice corrosion process, ther’re two steps, initiation and the repassivation. So, in our localized corrosion model, we also have two parts for this model, for the initiation, it is considered that localized corrosion initiates when a corrosion potential is greater than the crevice corrosion repassivation potential, and the E_{corr} is corrosion potential, which we measured in an aerated environment, and the E_{rcrev} is repassivation potential for crevice corrosion, and that is (unintelligible) over the critical potential to initiate crevice corrosion.

For the propagation part, typically in the literature, localized corrosion propagation conforms to an equation listed on the right-hand side. d is equal to K times the T^n. D is the penetration depth. T is the time. N is the time exponent, typically, it's between zero and 1. And, the K is the coefficient, which is typically temperature dependent.

For a diffusion controlled process, according to the literature results, mostly N is equal to .5.

Next, please. In our Total System Performance Assessment code, because in the literature no data for K and N available for Alloy 22, especially in the Yucca Mountain repository condition. So, we assume that in this equation, the N, the time exponent, is 1, and that the K is .25 millimeters per year. So, it suggests that if localized corrosion initiates, the localized corrosion will propagate with a constant rate at .25 millimeters per year, and we recognize that this is a conservative approach through our independent tests. We want to obtain the data for K and the N to improve our model realism.

Next slide, please. First, I want to introduce the data on how we look at the localized corrosion initiation. The figure shows in this slide part of the corrosion potential as a function of pH. In this figure, if we look at the pH dependence, it shows two distinctive regions. First, I would like to look in the acidic region. In the acidic region, the corrosion potentials decreased with increasing pH. But in the alkaline region, the corrosion potential appears to be a weak function of the pH. In the acidic region, the corrosion potential is significantly higher than what we measured in the alkaline region. The difference is about 300 millivolts.

And, for this test, we also looked at the dependence of surface condition and the chloride concentration. From this figure, the corrosion potential we conducted at this condition, 95 degrees C for mill annealed Alloy 22. It's weakly dependent on the surface condition of Alloy 22, and the chloride concentration.

Next slide, please. And, we also conducted some tests to look at how the corrosion potentials change with the temperature. The dependency is shown in this figure. All these tests were conducted in air saturated 4 molar sodium chloride solution using mill annealed Alloy 22. Mill annealed Alloy 22 is referred to as as-received material.

We conducted this test in temperature ranges between 25 to 95 degrees C. From here, what we show here is the corrosion potential decreased with the increase in temperature. And, the corrosion potential values at the 25 degrees C were approximately 150 to 200 millivolts greater than the values at 95 degrees C.

Next slide, please. We also measured the repassivation potential to find out the critical potential to initiate localized corrosion. The test method we used was adopted from ASTM G78. As I show, the crevice assembly on the left-hand side, the top is a crevice specimen, and this crevice specimen is sandwiched between two teflon crevice washers.

During our measurement, we used a combination of potentiodynamic polarization and the potentiostatic hold to measure the repassivation potential. As I show, two typical examples in the figure at the right-hand side, what typically we do is we scan the potential up to a value which is below the transpassive dissolution, and that then we hold the specimen, and it's at the potential for a period of time in the range of probably five to eight hours, and that then, after that holding period, we scanned the potential down to about negative 500 to negative 700 millivolts.

The red line shows one example we conducted using this method. We used the mill annealed Alloy 22 in 4 molar sodium chloride solution at a 95 degrees C. Using this method, we defined the repassivation potential as a potential when the current density reached a 2 microamps per centimeter squared. For this test, repassivation potential measured is negative 92 millivolts.

And, the second example I show is the blue line is in 4 molar sodium chloride solution, but with addition of .5 molar sodium nitrate. From the current density we recorded, it showed the current density is much smaller than what we obtained with chloride containing only solution. And, in this case, the current density was suppressed, and the opposite test, we didn't observe any localized corrosion from the nitrate containing solution, under this test condition.

Next slide, please. This shows the repassivation potential we measured from the tests--using the test methods

I described previously. And, we looked at how the chloride concentration and how the fabrication process affects the repassivation potential. If we just look at the chloride concentration--for this test, I need to mention that we conducted it at 95 degrees C, and in deaerated solution, and we used four types of metallurgical conditions. The four types of metallurgical conditions include mill annealed--as I mentioned, mill annealed basically is as-received Alloy 22 material, and as welded is basically what we did, is we just put two pieces of Alloy 22 plate and welded the material together, and we take the material from the welded region to do the test.

And, another metallurgic condition we studied a welded plus solution annealed, and that this is also one type of material, Lietai Yang also used it in his high temperature tests, and one, it's thermally aged, and thermally aged, we do have the two conditions. One is we thermally aged the material, we used the 870 degrees C, but the one we conducted for five minutes, and the other, we conducted thermal aging for four hours.

For all this data, at the different metallurgical conditions, we used linear regression to draw those lines over there, and basically, for those lines, you can see it started reaching into two areas. One is the susceptible region, which is at the right-hand side in the figure, and the other is reaching the immune region. For the top line, the top line corresponds to the mill annealed Alloy 22, which is at the higher chloride concentration region, and the lower line we show in this figure it's for the thermally aged material.

So, from this figure, what we have--the crevice corrosion susceptibility increases with the increasing chloride concentration, and it's a fabrication process, as we show here, such as the welding, post-weld heat treatment, and the thermal aging increases the crevice corrosion susceptibility.

Next slide, please. We also looked at how the nitrate to chloride concentration affects the repassivation potentials. For this test, we conducted it in 4 molar magnesium chloride solution at 80 degrees C, and 110 degrees C, and for the nitrate, we added magnesium nitrate, we added a different amount of magnesium nitrate to change the ratio of chloride to nitrate.

For this figure, it's a figure--on this slide, what I show, those open symbols represent after the electrochemical tests, we didn't observe crevice corrosion. And, for those closed symbols, we mean that after the potentiodynamic polarization, we observed crevice corrosion.

At 110 degrees C, what we observed is for the mill annealed material, when the nitrate concentration--when the ratio of nitrate concentration to chloride concentration is greater than .1, no localized corrosion was observed. But, for thermally aged material, when the ratio of nitrate concentration to chloride concentration is greater than .3, we didn't observe any localized corrosion.

But, at 80 degrees C, for both mill annealed and thermally aged material, at the ratio of .1, we didn't observe any crevice corrosion after the electrochemical tests.

Next slide, please. In the repository, according to the present designs of the waste package, the outer container will be in contact with a point made of Alloy 22, and the Alloy 22, the titanium drip shield will sit on a base made from Alloy 22. So, potentially, there's some similar and dissimilar metal crevices present in the repository. So, we also did some tests to look at how those metal to metal, and the dissimilar metal crevices, to effect that crevice corrosion resistance. This slide shows the hardware we used in the tests. And, for the crevice specimen, we sandwiched the crevice specimen between crevice washers, but those washers are made from either Alloy 22 or titanium Grade 7 to form similar or dissimilar metal crevices. And, we also machined some titanium Grade 7 washers with larger crevice area to simulate the Alloy 22 contact with the larger cathode in the potential repository.

Next slide, please. This slide shows the corrosion potentials and the repassivation potentials we measured using the metal to metal crevices. The corrosion potentials I show you in the figure. At the left-hand side, we measured this in 4 molar sodium chloride solution at 95 degrees C. We also measured the crevice corrosion--this is the corrosion potential for uncreviced titanium Grade 7 and the Alloy 22. Basically, we didn't see much difference between the creviced specimen and the non-creviced specimen.

So, we, from this test--next slide--we show that no effect of Alloy 22 to titanium Grade 7 crevice couple on the corrosion potential, and we also measured the repassivation potential using Alloy 22 to titanium Grade 7 crevices, and compared them with previously obtained data using a mill annealed Alloy 22 with teflon at the crevice.

After the electrochemical tests for the metal to metal crevices, we observed crevice corrosion only in one case, and for that case, when the crevice corrosion was observed, the repassivation potential is slightly above what we have observed previously using our test run as the crevice washers.

So, basically, from this test, we concluded that the Alloy 22 crevice corrosion resistance was not degraded by forming crevices with titanium Grade 7.

In addition to the localized corrosion initiation, we also conducted tests to look at the localized corrosion propagation behavior of Alloy 22. This shows the experimental setup we used in the test. We used two setups. The main concepts for this setup is we used teflon to form Alloy 22 to teflon crevice, and for this creviced specimen, we coupled it to a large Alloy 22 plate through a zero-resistance ammeter.

During the test, we monitored the corrosion potential and the current density to monitor the crevice corrosion processes. And the difference for these two setups, the one on the left-hand side, there's only one single crevice, and the one on the right-hand side has a 24 crevice sides. The solution, we used these 5 molar sodium chloride solution with a small amount of cupric chloride. The reason to add a cupric chloride is to raise the corrosion potential and to initiate the crevice corrosion so we can observe how this localized corrosion propagates. The temperature we used in this test was 95 degrees C.

Next slide, please. This shows one typical example we obtained using the single-crevice assembly. From what we show in the figure on the left-hand side is after the addition of cupric chloride, the current density increases to a peak value. After that, the current density decayed. Correspondingly, the corrosion potential also decreased.

And, when we look at how this current density decays in the time region starting from about a .5 day to nine days, the current decay behavior, as shown in the figure at the right-hand side, and we fit the current decay with the exponential equation, and for this exponential equation, the time exponent as determined from this test, it's negative .8. And a negative .8,I want to highlight one point is a negative .8 is smaller than negative .50, which is for a diffusion controlled process. So, this suggests that for this localized corrosion propagation process, it shows a strong stifling under this kind of a test condition.

And, for this test, I show on the left-hand side, at the time, about nine days, I wanted to point out the current density decreased. Correspondingly, the current potential increased to a value which is close to the previous value, and this simultaneous current density and the potential change indicates the repassivation for Alloy 22 localized corrosion.

So, from this test, we saw after adding the cupric, we initiated the crevice corrosion, but the crevice corrosion showed a strong stifling tendency, and we also observed crevice corrosion repassivation in this test.

Next slide, please. And, for this kind of a test, we conducted at specific time intervals. After the tests, we used our optical microscope to measure the maximum penetration depth. Part of the maximum penetration depth begins at the penetration time, as shown in the figure in this slide. The open symbols represent the experimental data. And, for this experimental data, fitted with exponential equation for fitting the equation, as shown on the right-hand side, the maximum penetration depth is equal to .0912 times $10^{0.233}$. T is the time in days.

And, I want to point out, one typical feature is the time exponent, .233, is less than .5 for diffusion control process. This also suggests that for Alloy 22 localized corrosion propagation under these conditions, it shows a strong stifling tendency.

Next slide, please. These are the conclusions, based on the experimental tests I showed in this presentation. Localized corrosion susceptibility of Alloy 22 was affected by several factors, including temperature, pH, the ratio of the chloride concentration to concentration of inhibitors, and the fabrication processes.

We observed a strong tendency toward stifling and repassivation for Alloy 22 localized corrosion in 5 molar sodium chloride solution at 95 degrees C. And, from our similar or dissimilar metal crevices tests, the localized corrosion resistance of Alloy 22 was not degraded by similar or dissimilar metal crevices.

Next slide. From our tests, we achieved some understanding of aeration to localized corrosion in the lower temperature region. But, uncertainties remain related to localized corrosion of Alloy 22. The first one is impact of dust deliquescence brines. This also was presented by Lietai Yang in the previous presentation.

The second uncertainty remains the tendency toward stifling and the repassivation at elevated temperatures and in more aggressive chemical conditions. And, for all the tests, they were obtained in fully immersed conditions, so the last uncertainty is the applicability of data obtained from experiments in fully immersed condition to water-film systems.

This is the acknowledgement and a disclaimer. That's my presentation. Thank you.

DUQUETTE: Thank you very much. In the spirit of this being a workshop, let me ask what I think is a probing question. Your colleague, your co-worker, just a few minutes ago presented a presentation that said crevice corrosion is not a problem, that uniform corrosion is a problem. You just made a presentation that analyzes crevice corrosion. Do the two of you want to come to some kind of conclusion as to whether either of your sets of work is relevant?

XIHUA HE: May I comment first? In Lietai Yang's presentation, first, he said what he observed is general corrosion is a major mode of attack in those tests. And, the uncertainties remain for localized corrosion, such as we're getting.

DUQUETTE: Okay, thank you.

PENSADO: This is Osvaldo Pensado from the Center. I want to make a comment about the distinction of the two regimes. On one hand, we have the elevated temperature regime that Lietai talked about. On the other hand, the environment Xihua addressed are more applicable to the scenario where we have seepage in contact with the waste package. So, those have two different scenarios. And, this one is important we're not ruling out the possibility of localized corrosion on the latter scenario where seepage could come into contact with the waste package, and I'll go into that in my presentation.

DUQUETTE: Okay. Ron?

LATANISION: Yes, if we could turn to--

DUQUETTE: It's Latanision, Board.

LATANISION: Yes, Latanision, Board; right. Sorry, I lost the slide. Oh, it's Number 13, please.

This refers to tests performed in 5 molar sodium chloride containing copper chloride; right?

XIHUA HE: Yes.

LATANISION: And, you added copper chloride for what purpose?

XIHUA HE: Okay, in 5 molar sodium chloride solution at

95 degrees C, without the addition of any oxidant, localized corrosion will not occur based on our experimental tests. So, usually you have to apply a potential to initiate crevice corrosion, or supply an oxidant to raise the corrosion potential. It bounds the critical potential to initiate the localized corrosion.

LATANISION: Okay. So, this was not an attempt to look at an environment that was representative of repository conditions. This was an experiment to look at the question of stifling?

XIHUA HE: How--cupric chloride will not be present in the repository conditions.

LATANISION: Right.

XIHUA HE: So, to view a little bit oxidant in raise up the corrosion potential, then we start at how the localized corrosion propagates.

LATANISION: Yes. Let me try to understand the potential. The bottom left curve, you show potential as a function of time.

XIHUA HE: Yes.

LATANISION: And, in the period where repassivation occurs, you show a very precipitous--well, a steep increase in potential.

XIHUA HE: Yes.

LATANISION: Do you understand--how do you interpret that?

XIHUA HE: In the beginning, or after the test?

LATANISION: No, the increased--I don't have a pointer, but where you show the potential increasing--right.

XIHUA HE: Yes.

LATANISION: How do you interpret that, given--okay, thank you. Ask and you shall receive; right? How do you interpret that?

XIHUA HE: My interpretation for the potential increasing, we still have cupric chloride in the solution, and after the crevice corrosion repassivates, the acidity in the crevice increases, so your corrosion potential increases.

DUQUETTE: Okay, thank you. Raul?

REBAK: Yes, Rebak, Livermore.

The reason that the corrosion potential increases is because the crevice corrosion dies. Whenever you have crevice corrosion, the system was to be in an active region. Whenever crevice corrosion dies, it goes back to the passive region where it was before crevice corrosion initiated. So, it moves to the original surface. It passivates inside the crevice. So, the film that you form inside the crevice is the same as the film outside.

LATANISION: Driving the potential in the oxidizing direction--

REBAK: Exactly. Yeah.

LATANISION: Why?

REBAK: Because it passivates. You start there in that value.

LATANISION: But, you want to be below the repassivation potential.

REBAK: Exactly. So, that cycle, if the condition endure, that cycle may be repeated. But, we don't know, if she didn't keep it long enough, it may be initiated again. But, the conditions are not exactly as they started. So, maybe it's dead for good, or maybe the conditions are there and they may start the time again to crevice corrosion. We have at Livermore for more than two years, the (unintelligible) and you see those cycles frequently, the passivation dies, repassivation.

LATANISION: So, in this context, what does stifling physically mean? I mean, this is not a relevant environment in a--

REBAK: No.

LATANISION: In your experiments--

REBAK: Stifling means that you slow down in certain ways. It could be different, a very different mechanism, the crevice corrosion, it doesn't propagate is because you eliminate a cathodic reaction, or because you eliminate--the crevice opens up, and then you cannot form a localized corrosion anymore there, because you cannot form the acidity to sustain it. There are different mechanisms by which it dies.

LATANISION: Okay. We're going to come back to stifling later on, so, I'll pass that. Thank you.

DUQUETTE: Fraser?

KING: Fraser King, Consultant to EPRI.

Sort of following up on that, now, I guess there's two possibilities in the way that crevice could be propagating. One is that you have one large crevice site, which is gradually slowing down with time, and then all of a sudden at nine days, you reach the very last vestige of propagation and it goes passive.

The other possibility is that you have a number of discrete sites within the crevice which are propagating, and sequentially, during the nine day period, one is stopping, and at nine days, it's the very last one that suddenly passivates, stifles or passivates, and that's what accounts for this rapid increase back to the passive potential.

And, I'm wondering, Xihua, if you have any evidence or whether you're having one large crevice propagating, or do you see individual sites within this crevice assembly when you disassemble it at the end?

XIHUA HE: After we disassembled the crevice assembly, most of what we saw is the crevice region was attacked, and the crevice corrosion is not uniformly distributed across the crevice region. And, in the crevice region, there's some deep sites, and there's some shallow sites. And, so, the deep sites appear like a--it appears like a pitting corrosion in the crevice region. So, it's not uniformly across the crevice. Even in the crevice region, some of the region is not attacked at the crevice corrosion.

KING: So, you're saying you have a number of individual sites, and that perhaps sequentially shutting down during the nine day period?

XIHUA HE: I think so.

DUQUETTE: Joe Payer?

PAYER: Joe Payer, Case.

To follow up on that, Fraser, we have done crevice corrosion tests, and with multiple crevice formers, and we have seen both the instances you have talked about. There's cases where certain contact areas activate and shut down, but there's also cases where only one contact area started, and even that showed areas of not the entire part of it. I think there's a time. One of the advantages of this is you don't have potentiostats on this, and that's why the center went to this copper chloride. When you do use a potentiostat, however, the additional information you get is the current versus time behavior to go along with the potential. So, it's not a good or bad. It's just a different way to run the test.

DUQUETTE: Rob Kelly?

KELLY: Kelly, Virginia.

Is this from the single crevice samples, or your multiple crevice samples?

XIHUA HE: This is from the single crevice assembly. We do have a report related to localized corrosion propagation behavior, and in that report, we presented some results using the multiple crevice assembly. The main difference between the single crevice assembly and the multiple crevice assembly is for the single crevice assembly, most people have observed this kind of propagation behavior once it repassivates no initiation after a long time. But, in the multiple crevice assembly, in some cases, once the localized corrosion repassivates sometimes we get re-initiation within the multiple crevice assembly.

DUQUETTE: Fraser?

KING: Fraser King. I have a question on Slide Number 9. Really a comment, it's the same comment that I made around these nitrate to chloride ratios that you were defining here are defined on the basis of potentiodynamic--potentially driven experiments with the potentiostat.

XIHUA HE: Yes.

KING: I think we just have to be a bit careful about putting up ratios for the waste package in the repository, which is not connected to a potentiostat. The potential that we're concerned about is the corrosion potential, and that will retain its natural value depending upon the environment. And, so, the nitrate to chloride ratio that would inhibit localized corrosion for a waste package in a container would be different from this, and it would be lower, perhaps substantially lower, because you can't drive the potential so positive. So, I think we just have to be a bit careful about putting up these ratios based on the observation from an experiment which is driven by a potentiostat, and comparing those with what will happen on a waste package under fully coating conditions.

XIHUA HE: Yes. For this test, basically, when we got the potential up to about 550 millivolts to try to drive the crevice corrosion process under postive conditions. The corrosion potential typically is much lower than 550 millivolts. This is driven by the potentiodynamic polarization.

DUQUETTE: Other questions or comments. Yes, sir. Please use the microphone.

GOPAL DE: This is Gopal De. I work for BSC.

Would you please go back to your potential process-time plot?

XIHUA HE: Next one. Is it this one?

GOPAL DE: Yes. Did you actually do any potential balance? As soon as you add cupric chloride in the system, the potential jumps. And, then, because of IR drop, and so forth, other solution effects--it goes down. And, then, you are saying that copper still stays in solution as cupric chloride; right?

XIHUA HE: Yes.

GOPAL DE: And, the potential goes up. Did you do any potential balance calculation? Before and after-- It has to be the same. Input has to be equal to output.

XIHUA HE: You mean, for the cupric chloride?

GOPAL DE: Yes.

XIHUA HE: For this test, we didn't do any potential calculation. But, we did conduct some trial tests to look at how the cupric chloride can be maintained in the system. So, we added the cupric, and after the initiation of crevice corrosion, the corrosion potential went up. That shows that the cupric chloride, which is still left in the solution, and for some tests, we left it for a long, long time to observe if the cupric chloride will be consumed in the test or not. But mostly what we observed is for this amount that I showed, it's about a 2 times 10 to the negative 4 molar cupric chloride, we can maintain the high corrosion potential in this test. And, I'm going to say, I wouldn't say it's absolutely not a concern. We can still maintain the high corrosion potential in this system.

GOPAL DE: Before you added this cupric chloride in the solution, the potential was around 400 millivolts; right?

XIHUA HE: The corrosion potential?

GOPAL DE: This test that you did is actually a galvanic cell.

XIHUA HE: A galvanic cell, yes.

GOPAL DE: So, the galvanic cells potential was where? Before the addition of cupric chloride--I see it's a little less than 400 millivolts; right?

XIHUA HE: After the test?

GOPAL DE: No, no, before.

XIHUA HE: Yes. I didn't really show the corrosion potential tested before we added the cupric chloride. It's about--it's about less than 200 millivolts, without the addition of cupric chloride in the 4 molar chloride solution. It's about a negative 200 millivolts to a negative 100 millivolts.

GOPAL DE: So, maybe 200 millivolt, and after additional cupric chloride it raised to--

XIHUA HE: To about a 400 millivolts.

GOPAL DE: Okay, then, as the corrosion process progresses, the potential goes down?

XIHUA HE: Goes down, yes.

GOPAL DE: And, then, it comes to--then it makes the balance of 630 millivolts; right?

XIHUA HE: Yes, a potential drop we observed from--650 millivolts--

GOPAL DE: And, now, the crevice corrosion has stifled, repassivation complex, okay? And, so, it is going up again?

XIHUA HE: Yes.

GOPAL DE: Now, did you make a calculation for initial true maximum for coming down, and then going up? Did you make a balance? That's what I mean by a potential balance calculation? Did you do that, or not?

XIHUA HE: I'm sorry, I didn't catch your last part.

GOPAL DE: Did you do any potential balance calculation on this? The cyclic process?

XIHUA HE: No, we didn't do a calculation.

GOPAL DE: That was my question.

DUQUETTE: Ron?

LATANISION: Yes, could we go back to Raul Rebak's presentation, Slide 25? Okay. Well, I'm trying to understand what we're talking about in terms of stifling. Let's just take this red cyclic polarization diagram as a case in point. This is the corrosion potential. We drive the potential in the oxidizing direction. This would be the critical potential, right, for crevice corrosion? There's a positive hysteresis. This is the repassivation potential. Okay?

REBAK: Yes.

LATANISION: If stifling occurs, I would take that to mean that somehow we've driven the potential below the repassivation potential in this range. What Xihua has just shown us is that the potential is increased, and that would be above the repassivation potential. What am I missing?

REBAK: No. What happens in this--this is cyclic polarization curve, driven by a potentiostat.

LATANISION: Yes.

REBAK: Actually, what you have in the real system with an open circuit system, what you have here, potential is driven maybe near the critical potential, as you said here, maybe around zero.

LATANISION: Use the pointer.

REBAK: Oh, okay.

LATANISION: This is a workshop.

REBAK: What you have in her system, in Xihua's system, where the corrosion potential increased to let's say around that value, and then you initiate crevice corrosion. At that moment, and only in a system that is open, which is not in this case, because it's controlled by the potential--

LATANISION: Yes.

REBAK: The corrosion potential drops here, is the active region. So, it corrodes in the active region, and then--

LATANISION: That's not active. That's passive.

REBAK: No, no, no. Here, you have this little bit where you have the active dissolution at the corrosion potential. So, her potential, from whatever you have, 400 millivolts, drops to this value, and this is the value where crevice corrosion occurs. When crevice corrosion dies, the potential goes back to this value where it was originally. That's what happens in an open system. So, this is just a cyclic plot controlled by a potentiostat, so you will not see the same thing that she sees there. What you see, again, is the potential is here. What she has goes back there, crevice corrosion initiates, so, the mixed potential goes back here in the active region, which is the corrosion potential. And, then, when the crevice corrosion is stifled, for whatever the mechanism, the potential goes there again.

LATANISION: You're saying that when localized corrosion initiates, it drives the potential into the active regime?

REBAK: Exactly, yeah. It's always like that. Because what the system sees is the acidic solution inside the crevice, which is hydrochloric acid, or whatever, and this is in the active region. Whenever the hydrochloric acid corrodes, the alloy goes away by whatever--

DUQUETTE: We have too many pointers. Let's ask someone without a pointer. Joe Payer? Give him a pointer while he's up there.

PAYER: We'll have to get color coded pointers.

I think, Ron, your point is important to get across here. And, the rationale for understanding and studying this localized corrosion is to use the cyclic polarization curves to identify the crevice corrosion potential, as you pointed out at the top, and the repassivation potential. And, then, in a well established mechanism, as you compare the corrosion potential of the sample to that repassivation potential, and if it's more negative, we don't get crevice corrosion.

LATANISION: Right.

PAYER: So, the other way we can examine that is to take these multi-crevice assemblies, or other crevice corrosion specimens, and hold them at constant potential now. And, when we do that, if we hold them in a constant potential below the repassivation potential, we don't see any crevice corrosion.

LATANISION: I'll buy that.

PAYER: You know, so it's consistent.

LATANISION: Yeah.

PAYER: If we expose a constant potential above the repassivation potential with a potentiostat, you see the passive current density, and then when the crevice initiates, you see a rise in current, and then it decays. And, it's that decay above the repassivation potential that we're calling stifling.

So, you're holding--you initiate the crevice corrosion, as we would expect it to, you get a rise in current density, but it doesn't stay there in all instances. In many instances, it decays with time, as Xihua's work showed, and Raul showed some of those, and we'll be showing some of those in our work. So, that's what we mean by stifling. The conditions are not maintained.

LATANISION: I'll buy that explanation. I have no problem with that. I'm just really struggling with the idea that the potential in the crevice has actually been driven down here--

PAYER: Well, what happens, another way to look at it, and, again, there's a slide either in Rob's part of this or mine next, but this is the polarization curve for the passive metal. But, you would have an active polarization curve for the metal in the crevice solution. And, that would be more like the corrosion potential in one normal hydrochloric acid.

LATANISION: Well, why don't we table this until your presentation.

DUQUETTE: I would just make one quick comment on it. This is a chemical potentiostat and that's what you expect would happen to the chemical potentiostat versus an electronic potentiostat, which fixes potential. Potentials are allowed to drift or whatever, it is allowed to drift--

REBAK: Yeah.

DUQUETTE: And, that's what you would expect for potential shift if the crevice weren't active. I don't have a problem with that.

REBAK: Yeah, the potentiostat that Xihua used is the old style potentiostat of 50 years ago, before the electronic potentiostats….

DUQUETTE: I guess I'm just showing my age.

LATANISION: Well said, David.

DUQUETTE: By the way, I want to make one comment in observing all of this, and stifling is going to be very important in the next talk as well, everyone should keep in mind that the crevice that one expects to see in the repository is not the same geometric crevice we're setting up here, which is a fixed crevice with a clamp on it that's going to be geometrically different from dust settling on a surface that can expand. Everyone should understand that, and in the context of any kind of modeling we do on stifling or anything else, if you have geometric effects that prevent diffusion down the crevice, it can be a different situation than if you have the possibility of diffusion basically almost from the top of the crevice with a sponge sitting on the surface. So, everyone should realize that in terms of these stifling experiments.

With that, do we have any other questions from the Panel or from the audience?

(No response.)

DUQUETTE: If not, let's get on to the next multimedia presentation by Payer and Kelly on "Localized Corrosion Data and Analyses from the Materials Performance Thrust of the OCRWM Science and Technology Program." Joe is going to start it off, and Rob is going to wrap it up and explain everything.

PAYER: Thank you, David.

Inviting two professors to make a presentation in 25 minutes is quite a stretch for the Board, but we'll do what we can do here to get you back on schedule.

That's the title. The next slide is a disclaimer recognizing that this work is funded by OCRWM Science Program and carried out under a cooperative agreement.

Next slide. This is the outline. We've heard enough about decision tree, so I'm going to go through that pretty quickly. I want to focus on what some of the requirements are for localized corrosion, and then we're going to talk about those properties and processes and particulate layer; and then we'll pass the gavel to Rob, and he'll talk about factors influencing cathodic, anodic, and coupled processes.

Next slide. And this is the beast we're talking about. This is a waste package surface in a cartoon, and onto that dust particulate deposits have occurred. We're representing insoluble species and soluble species. This is dry at this point. And in that deposited dust layer, we can have more dust deposit, or that's how it built up originally. Moisture can move in and out of this, oxygen can move through it, and what we're trying to understand and model and also develop experimental data to support is how will a corrosion cell--in this case just showing nickel--how will a corrosion cell operate under these conditions? So that's what this is about.

Next slide. There's two points there. The decision tree, we think, is very valuable to look at that; but there's a separate decision tree that you would use for deliquescence conditions.

Next slide, then, what you would use under seepage conditions. It's the same decision tree approach, but there's some different parameters on the electrolyte and such. And, again, we've been trying to keep the discussions focused on which of those conditions are we talking about.

Next slide. Just a couple slides here to show--this is a cartoon of a metal crevice. This is the creviced area, this would be open surface at higher magnification, and like any corrosion cell, there's four requirements. We need some area that becomes an anode. That's where the potential gets more negative, and when Xihua's surface initiated, this became more negative, dragged the potential of the couple down. You need an electronic path, an ionic path, and you need this external cathode.

In order to initiate crevice corrosion, you'd have to build up an aggressive environment in this crevice with time, you need a tight impermeable crevice, the corrosion potential has to be greater than the repassivation potential at the mouth of the crevice, you've got to separate the anode and the cathode and keep them separated, and then you have to develop that critical crevice chemistry to get things going.

In the propagation mode, you've got to maintain the critical crevice chemistry, you've got to maintain sufficient cathodic capacity out on the free surface to continue to drive that anodic dissolution, and you have to maintain the separation of the anode and cathode and this tight impermeable membrane. So that's our picture of both the initiation and propagation.

Next slide. This addresses what we were just talking about. Here's the cartoon of the crevice. This is the anode area, the area that's dissolving, and that has some localized corrosion current flowing out of the crevice, the anodic current. That has to be balanced by the cathodic current out here. The polarization behavior of this cathode is the polarization behavior of a passive metal with a cathodic curve. The polarization curve for what's happening in the crevice, once you've developed this critical crevice chemistry, is an active polarization curve. And so when the metal is all passive, as Xihua showed, you get a high passive current potential. When this kicks in and becomes active, you now have this, what you could look at as a galvanic couple between an active area and a cathodic area.

Next slide. One of the things that we'll focus on throughout this talk is, the demand of the anodic crevice has to be balanced by the capability of the cathode to provide that current, or you'll get into a situation where the cathode can limit how much of this dissolution will occur.

Next slide. And so we're going to focus in this talk on the post-initiation. We're going to conceptualize this and say, okay, we've started the crevice by however we've done that, we've got an active area that's got a current demand, we've got an external surface that's providing the cathodic behavior, and we're going to talk about what's going on in the electrolyte layer, what's happening at the cathode, what's happening at the anode, and then what happens when you couple those together. And one of the things we'll do throughout is demonstrate a number of processes that can affect that propagation and stifling an arrest.

Next slide. So I'm going to talk about some of the things going on in the particulate layer and then pass the gavel to Rob, and he's going to talk about the cathode and anode.

Next slide. This is a cartoon of some of the things we've been sort of waving our arms about and trying to talk about. This is our picture conceptualization of dust having settled on the waste package surface, and that dust is made up of inorganic particles, the dark brown ones in this slide, and soluble salts that, when water came in, could deliquesce or could form moisture. The particle sizes and shapes, how much of that is on the surface, what the temperature and the relative humidity is, the activity of water, what sort of solution properties are what are going to govern the corrosion behavior.

So this is the dry situation, and what we find is at the very earliest stages of deliquescence, you're going to have small droplets of moisture that form. A couple of those can be in contact with the metal surface, but many of those are going to be isolated in the particulate layer. This occurs at high temperatures. These solutions under these conditions are highly concentrated brine--50, 60, 80 molal--and there's limited contact with the metal surface. As you go to lower temperatures, these brines become less concentrated, the volume of brine increases, and you could get into a situation where you would have wetted particles. The blue is much thicker than it really would be, but we're trying to represent that you would have unsaturated particles, void spaces partially filled with brine, and perhaps some liquid surfaces. As you go to still lower temperatures, less concentrated brines, you could have this situation where you have a particulate layer that is completely flooded.

Next slide. This is just to show that there is a technical basis, and there is a rationale for understanding the high temperature behavior of solutions and temperatures. You've seen this plot before. This is the inaccessible relative humidity and temperatures in an atmospheric system; and depending upon the assemblage of ionic species, soluble species, you can have these very high temperature deliquescent salts at very low relative humidities. If you've got potassium nitrate, sodium chloride, you're limited to deliquescence in this area and so forth. And so there is a rationale for tracking and determining the solutions available.

Next slide. This comes out of the May 2004 Board meeting, and I think it's one of the more important concepts that were introduced there, because it links the history of the waste package, the temperature and relative humidity that the waste package is experiencing, and this is the temperature ramp, this is the relative humidity. This is a log scale, so we're going 100 years, 1,000 years, 10,000 years. That's fairly well established. And we can link that to the types of water chemistry data that we have, and we can follow trajectories from a very hot package, could start here, and its temperature/relative humidity follows this, we can map that onto the solution chemistry. So the temperature and relative humidity at any time determines the possible water conditions. We can follow that trajectory, and the solution composition can be related to the corrosivity, so we can link these together, and I think that's an important aspect.

Next slide. What we're going to do is say, okay, let's apply those conditions to the real condition of dust deliquescence, as described in the analytical report by DOE. And this is the description of that dust layer that's in the dust deliquescence particle. The density of the dust ranges here--these are all various properties--the porocity of the dust is 50 or 60 percent, it's not fully dense, the thickness of the dust layer can go from to 10 to 180 microns thick, and so forth. You can see these various properties of that.

And so what we're going to do is say, okay, what happens under this condition? What sort of moisture can we form? What sort of volume of moisture can we form? It's interesting--we've got to keep coming back to this. I can't demonstrate this, Ron could. But a hair is about 100 microns thick, so we're talking about dust layers--and Rob can't demonstrate this either--we're talking about dust layers that are one- or two-hair diameters thick. So we're not talking about a large volume of material.

And in the dust deliquescence mode, that's all the salts, that's all the material you've got. You can bring water to it, you can take water away from it, but you've got no other way to add more chemicals, more minerals to that. As soon as you get dripping and seepage onto the waste package, that changes. Very important distinction.

Next slide. There's a series of slides here just showing that we are continuing, we've done experiments, and we're looking at changes that can occur in thin layers of moisture. If we form an electrochemical cell--this is the cathode, this is a simulated anode--it just shows that the conditions out on that cathode change with time, and this is just a pH indicator showing that the cathode becomes more alkaline, the anode becomes more acidic. And we can follow that with time and model it and so forth.

Next slide. We've done some computational work determining the effect of particulate on the conductivity in that thin layer of deposit out on the surface. If the cathode has to supply current to the anode, the conductivity of the electrolyte layer is an important parameter; and the particulate in that layer makes it more difficult to pass current, is the bottom line on that. There's a lot more behind this.

Next slide just shows that that's been applied to multi-particulate layers, and this is with no correction.

This is the I-net, the amount of current that can be supplied as the function of how many particle layers we have. And without correction you can get higher I-nets; and with the correction for particulate, those can be reduced by a factor of 3 or so in this scenario.

Next slide. The important set of experiments we've done, not unlike what Xihua is looking at, is looking at the effect of the crevice former on the severity of crevice corrosion we see; and the most severe crevice corrosion experiments we can do are with ceramic crevice formers with a thin layer of teflon tape in between the ceramic so it's tightly squeezed. And that's the way Livermore has run the bulk of their tests. A less severe condition is taking a solid teflon and squeezing it against the surface, and that's how the Center has done a lot of their work and a lot of other people do. That's the more standard test.

One of the interesting things that comes out of this work is, when we just press a ceramic against that metal surface under the same conditions, we cannot initiate crevice corrosion. And so the ceramic crevice former is much less severe than the accelerated laboratory tests--. And there's going to be rocks at Yucca Mountain, not pieces of teflon in contact with the metal. So that's an important distinction.

Next slide. This shows the variation of solution volume, so we start with taking a salted deliquescence that they order here of around 30 percent relative humidity. You get the isolated droplets of water that are highly concentrated droplets of brine; and as the relative humidity increases, as more and more water equilibrates with that solution, the volume of solution increases. And so we can see a trajectory here, and this is normalizing that for what percentage of the void space would be filled with solution.

And so that early deliquescence, we get isolated droplets of water, very small volume, less than 10 percent of the void space is filled with moisture, and the molality of that solution is like 26.9, highly concentrated, very small. But when we get out to 60 percent relative humidity, we still have less than 20 percent of the void space filled, and we still have a concentrated solution.

Out here where it starts to go up and we would go over to this sort of scenario, where we've got now more continuous moisture layers, now we're up to, in this case, 95 percent; 60 percent of the volume is filled, and the molality comes down. The point is, you can't mix and match these. The chemistry drives this. The chemistry determines this.

Next slide. And so what we say--you've seen this plot before here--this is the temperature and concentration. If you have deliquescent salts, no matter what their composition--and it's demonstrated here for the ternary and quaternary salts--if you're in this solution, you have to have extremely high molal solutions. And so these dust particles that have gotten wet by deliquescence can only form very small isolated droplets. If you come down into this range, then you have to be dealing with much more dilute solutions, and much more of that space would be filled up. But, interestingly, this is where the well-established technical basis for will crevice corrosion occur or not, and this is where there's an extensive database. And so the system, by its very behavior, drives us back into the region where we have the best theory and the most extensive database.

This solution up in this region is going to be highly concentrated, nitrate rich, small fraction of porocity filled, limited contact with the metal surface, a highly permeable layer. Because the porocity is primarily filled, it's going to be a low conductivity from an electrical conductivity, so it's going to be a poor cathode, and it's going to have a large surface area for reaction. If there is any reaction between these concentrated salts and the minerals that are insoluble, it's favored by a very high surface area.

So next slide. And it just goes through the conditions--we've seen this before--can a particulate layer act as an effective electrolyte? It depends on the composition and the amount of the moisture, the conductivity, permeability of the layer, and the separation of the anode and cathode. It's not just the chemistry of that solution, it's the distribution of it and its ability to act as a crevice former and an ability to act as a separator of anodes and cathodes. And when I look through that--and, again, we'll speak in the workshop mode here--when I look through that, I say that for high temperature deliquescent salts and deposited dust layer, there is too little moisture, it's unlikely to fulfill the requirements for localized corrosion, the answer is no, to which every one of those questions that box--that fits into. And that really is my bottom line.

I'll pass the gavel on to Rob to talk more about the anode/cathode stuff.

KELLY: Thank you, Joe. Joe is taller than me, so--

Okay. Next slide, please. Joe has outlined some of the factors in the particulate layer that can affect localized corrosion. What I'd like to do is to talk about the characteristics of the anode and the characteristics of the cathode that can affect localized corrosion stability and then talk about a way to couple the two together to ensure for a stable localized corrosion site that you have a compatible cathode for your given anode, given your scenario.

So this cartoon you saw before--Joe showed it to you before--but I wanted to reemphasize this idea of looking at localized corrosion as a galvanic couple, that you have a anode in the occluded region, and that's coupled to an external cathode. In order for stability to be maintained, the cathode capacity has to meet the needs of the anode at least. So you have to have at least enough cathode current to meet this anode need; otherwise, that critical crevice solution that Joe mentioned cannot be maintained. That critical crevice solution's developed by this I-LC, the dissolution within the occluded region and the hydrolysis thereafter.

So what I'd like to do is to talk about--this schematic will be a foundation throughout the rest. This is a plot of the cathode current capacity, I-net, versus the anode current demand. So there are three regions. In this upper region we have enough cathode current that we're not limited by that. The cathode can easily meet any anode demand, and so localized corrosion is controlled by the anode, and we'll talk about that.

Right along this line, the cathode can just keep up with the anode demand and maintain stability. And then below this line in this region, the cathode cannot meet the anode demand so it's cathode controlled; and, in fact, that will lead to stifling.

Next slide, please. As I said, the basis for stability is the maintenance of this critical crevice solution. And this shows some of Joe's data--some of his students--these are current versus time plots for C-22 multiple crevice assemblies in 4-molar sodium chloride at 100 degrees C. And you can see after an incubation time, there is initiation and then there are several arrest events until eventually in both cases you get complete repassivation.

Now, these tests were conducted potentiostatically, so there is no cathode limitation here. We've had constant conditions; but similar to what Xihua showed, you get repassivation. This is not unique to Ohio. Just in C-22 Xihua has shown it, Raul has shown it, Darrel Dunn (phonetic) when he was at the Center showed it before. So even though, in the standard Fontana and Green description of crevice corrosion, this autocatalytic mechanism, you can get repassivation. So what we want to talk about is what are the factors that can control that under natural exposure.

Next slide, please. So first we'll talk about the cathode.

Next slide. One thing to keep in mind is that atmospheric exposure represents a whole different set of criteria for stability or for constraints on stability that you don't have in full immersion, and this picture of water droplets on a surface helps to illustrate that. The first is that because you have a thin electrolyte layer and you have finite conductivity, there will be only drop within that layer that takes some of the cathode area out of play; that is, it cannot participate in stabilizing the localized corrosion site, and we'll talk about that quite a bit.

Time constraints won't let me talk about this, the fact that when you have a limited cathode size, that will limit the minimum pH you can sustain inside a crevice. But if there is interest, we can talk about that in the question and answer period. So now I want to talk more about this, this limiting of the cathodic current, because of the ohmic drop.

Next slide, please. So if we look at that, what we can do here is computationally separate the cathode here on the left from the anode here on the right. And we can go about calculating this maximum total current that a thin electrolyte cathode can supply. And we'll do that based upon the characteristics of that layer; that is, the water layer thickness, the conductivity of whatever the solution is, and then the interfacial kinetics of the cathode. And that's shown by these little arrows that represent the current density as a function of position.

If you consider only ohmic drop and you consider that the mouth of the crevice is held at a constant potential, you can derive the fact that the maximum current that you can get from this wetted cathode is described by this expression; that is, if you've reduced the conductivity or you have a thinner water layer or if you have slower cathodic kinetics, all of these will tend to limit the maximum current that you can sustain. This is the maximum current independent of how large the cathode is, and the reason for that is, once you get an area of the cathode where you have enough potential drop where you reach E-corr, there can be no net current from this portion of the cathode to the crevice, because that's circumstantial. And it doesn't matter if that's a millimeter or 10,000 millimeters, it simply can't participate.

Now, as Joe mentioned quite a bit yesterday, we can relate the conductivity and the water layer thickness to temperature as well as the relative humidity and the deposition density, the amount of salt on the surface.

Next slide, please. So these next couple slides, I want to use that framework to do some what-if scenarios. So here's our cathode again, again computationally separated from the anode. We'll reunite them a little later. Here are some cathodic kinetics for 316 stainless steel in concentrated halyte solutions, and you can see as you increase the temperature, the activation control region shows faster kinetics, the repassivation potential is a little bit lower, and the conductivity is higher.

And if you put all those together into that expression that I showed, you get a plot shown here. This is, again, the maximum net curve from the cathode as a function of sodium chloride deposition density; and you can see, then, going from 25 C to 95 C if you were, say, at 3000 micrograms/cm_2 of salt, you get a factor of about a 5 increase in the cathodic current available. And this is all due to this increased conductivity, faster electrokinetics, and a little bit due to the low repassivation potential.

Next slide. Now, we can look at a constant temperature and see what are the effects of cathodic kinetics. So on the left here are some cathodic kinetics for C-22 again in concentrated halyte solutions. The faster kinetics up here are regenerated on a clean surface. The slower kinetics were generated on a surface that had first been polarized to zero volts for an hour in order to grow an oxide film, and so that slows down the cathodic kinetics.

When you do that, you get the results shown over here that now begin picking a mythical 3000 micrograms/cm_2. Going from the faster kinetics, you get a beta factor of 8 reduction in the total current that this cathode can supply simply because you've grown an oxide film.

The next slide, please. Now we've looked at the cathode, so now let's take a look at what processes inside the anode can control crevice curves and stability.

Next slide. And we have to admit that the vast majority of crevice corrosion work has been done looking at the anode. People over the years have done the work potentiostatically, so that takes the cathode out of play and focuses on the anode. And this is generally accepted belief that crevice corrosion, to be maintained, you have to maintain a certain critical chemistry within the crevice, within the occluded region, and often that's described as a combination of a critical pH, a low enough pH, and a high enough chloride concentration; that is, this critical crevice solution.

The way that concentrated solution is maintained is by the existence of a critical dissolution current density at a given depth into the crevice. So the combination of this I-LC and X is a localized corrosion stability product. The two of those multiplied together give you a criterion for localized corrosion stability. As you increase the corrosion resistance of an alloy by increasing its alloying content, for example, that leads to the requirement of solutions that are much more aggressive to prevent the formation of oxide inside the crevice. So it needs a lower pH or a higher chloride concentration or, for a given depth into the crevice, a higher dissolution current density.

So as you start to run into trouble in maintaining this critical chemistry, that's when stifling occurs. Why might that occur? Well, some examples are shown here. If the position of the crevice attack with time moves toward the mouth, the crevice essentially commits suicide and eventually reaches the mouth and the gap opens, and the diffusion then dilutes the critical chemistry. Or if within the crevice as dissolution occurs you form a protective precipitate, that will reduce the dissolution current density at that position, and that will tend to repassivate the crevice. Or if the potential at the mouth of the crevice falls, that can lead to slower dissolution rates inside the crevice and, again, repassivation.

So the key that holds all these together is, you get stifling or you get repassivation when the dissolution rate within the crevice combined with the hydrolysis thereafter is overwhelmed by diffusion outside the crevice. So this is kind of the criterion that you need to maintain.

Next slide, please. So as example of one of these processes, this is a modeling from Uzi Landau at Case. So the geometry here is an external cathode and an internal anode. In this case the cathode is considered to be able to supply as much current as the anode needs so we're not cathode limited. And then here is the way he starts. Here's the crevice, so you have a crevice precursor, an active site, at some position within the crevice. And then for the conditions used in this model--and I repeat, for the condition used in this model--the evolution of the geometry shown here, so here's the initial active site, and these lines show the evolution of the dissolution front. And so eventually the dissolution front comes outside the crevice former, so the gap becomes opened and this crevice repassivates.

Next slide, please. Here are some kinetics for nickel-chromium-moly alloys established in solutions of matter. You need to establish these kinetics in a critical crevice solution. So these are some data from John Scully. So we have polarization curves for nickel-chrom-moly or nickel-22 chrom-moly alloys with different amounts of moly. One can see that as you decrease the amount of moly--that is, you're moving from left to right in these curves--the dissolution rate in any given potential increases; that is, it's easier to maintain a critical solution inside the crevice as you decrease the moly content.

This table on the right illustrates the effect that as you increase the localized corrosion resistance of an alloy, the critical solution that you need becomes more challenging. So as you go from 304 to 316 to 625, the critical pH that must be maintained decreases, and the critical chloride concentration that you need inside the crevice increases.

Next slide, please. So now we've talked about the anodes and anode control, we've talked about the cathode, so now let's look at coupling these two together; that is, we're going to look along this line and find out how we can maintain compatible anodes and cathodes.

Next slide, please. So for crevice corrosion we need, under natural conditions, not having a potentiostat connected to anything--as Fraser has mentioned a number of times--we have to balance these two. And so one simple approach to that is to calculate this net current that you can get from a cathode and then compare that to the anode demand. And you get the anode demand by knowing this I times X, and this is a material property for a given alloy to given temperature.

And so we've done this calculation for 316L at room temperature, and here are the criteria over here. So this solid line with the little diamonds, that describes the maximum current capacity from the cathode that you can get as a function of the amount of sodium chloride deposit. These are like the curves I've shown you before.

The dotted horizontal lines represent the anode demand for a crevice site located at the position shown. So if your crevice attack is at half a millimeter in from the mouth, for these conditions you need to maintain a localized corrosion current of around 10 microamps. By putting these together, what this tells you is that in order to get crevice corrosion half a millimeter in from the mouth, you need to stay in this blue area; that is, if you fall below, say, 550 micrograms/cm_2 of salt, you can't maintain crevice corrosion at that site, because you simply do not have enough cathode capacity to do so.

If, however, instead of being at a half a millimeter your crevice corrosion were occurring at 5 millimeters in, now you can do that with a much less active cathode; that is, now all of this pink area and the blue area allows for stable crevice corrosion.

Next slide, please. Before I give this summary, I want to emphasize something that Joe said, is that all of the discussion that we've given today has been dealing with post initiation. One way to think about this is, we've taken kind of a damage tolerance approach to crevice corrosion, saying, "What are the conditions that will control stability once a crevice has been established?"

And so what we've tried to do is to talk about a number of processes in the particulate layer, some in the anode and some in the cathode, that affect crevice corrosion stability and particularly affect crevice corrosion stifling. And then we've presented a simple methodology to try to couple those two together to find when will you have a compatible cathode for a given anode in the same scenario.

Our work tries to address the question: If you have localized corrosion initiate, will it persist? That's really the technical basis and the decision tree that we're addressing. And we want to emphasize for the record that all these analyses are scenario-specific, very scenario-specific. So if one wants to relate conditions at Yucca Mountain, then you need to put--conditions that are relevant to Yucca Mountain, because otherwise you get a--to pick up on something Maury said--"garbage in, --out" kind of approach.

So, with that, I'll thank you for your attention, and we'll be happy to answer any questions. As Joe has said, he'll take all the hard ones.

DUQUETTE: Thank you. Before we proceed, just let me make a couple of very simple comments.

If we can go back to Slide Number 7 of this presentation, I just want to point out one thing, and that's something we do with our undergraduates in the corrosion world. One of the things that Joe mentioned, you need to maintain a tight impenetrable crevice. A standard experiment that we do is to simply take some sand and put it on a sample in a beaker with some water and show that you can get concentration effects just from some sand sitting on the surface, which is not a tight impenetrable crevice. If you do that with stainless steel in salt water, you end up with pitting underneath the individual sand particles; and so you don't need, necessarily, to maintain a tight crevice in a particular case.

PAYER: That's very metal and solution dependent. If you did that same experiment with Alloy 22, the sand would sit there and look at you forever and won't ever--.

DUQUETTE: It certainly--

PAYER: And what we're trying to do is build a technical rationale for why is that so you can make those. So, you're right, it's very dependent on the particular system.

DUQUETTE: I fully agree. The other slide I wanted to look at was Slide Number 20 just briefly, just because of my age and experience in this kind of thing. These relative humidity numbers, again, are site-specific, because there is really old data that shows that at about 60 percent relative humidity, dust is corrosive. Just conventional dust in rooms. That's very old data, and it's been around for a long time. And dust typically will become deliquescent--just room temperature dust will become deliquescent at about 60 percent relative humidity.

And so, again, I think the last bullet that Rob showed is the one that's really important for our discussion, and I agree with that, but I think one ought to be very careful about making generalities.

PAYER: Well, sure, you like Rob better.

DUQUETTE: Actually, he has the most--.

PAYER: I think, again, your point's well taken, but the 60 percent critical relative humidity goes back to the early--you know very well--the early 1900's, Evans' work, but that was iron in SO_2 industrial environments; and under those cases, if you get moisture, it'll corrode, but Alloy 22 would sit there and look at you forevermore, so it's very metal-specific.

DUQUETTE: No, I understand that.

LATANISION: Latanision, Board.

But just to add to that point, Joe, you certainly don't require puddles of water on the surface in order for atmospheric corrosion to occur. I'm wondering whether the--maybe I should address this to Rob--that illustration was meant to suggest deliquescent puddles representing deliquescent salts, or what was the point? Atmospheric corrosion occurs when you have monolayers of moisture.

PAYER: Certainly. Of active metals. We're talking about localized corrosion of a highly resistant chrom-moly alloy, and then can these conditions support crevice corrosion.

LATANISION: Yeah, I'll buy that.

PAYER: If they can't support crevice corrosion, then we have to analyze pitting corrosion, and that's another several hundred millivolts more positive and much more corrosive environment. That's what we're trying to--.

LATANISION: Okay. I just didn't want people to think that you needed puddles of water on the surface in order to get atmospheric corrosion in a general sense.

But let me return to Number 7. I'm not finished yet. Hold that. I've got a couple of questions, Mr. Chairman.

Stifling, as far as I'm aware, does not appear in any textbook at this stage in history. And so maybe we are writing a new chapter in terms of the control of localized corrosion phenomenology, and perhaps it's due. But I do want to make the observation that--and what we're seeing here is probably the traditional lore--oh, this is green, I didn't realize--okay. It's sort of green. Well, maybe it's running on a visible--.

The traditional philosophy or, maybe, point of view is that when localized corrosion begins to occur, as in this situation, the population of metal cations in this crevice geometry increases because, as everyone has correctly pointed out, this is the anode. That population of metal cations attracts anions from the bulk solution into this environment, and you can see the increased population of chloride, and so the net effect being that you have a change in the chemistry in this local geometry, which makes it unlike the chemistry in the bulk solution.

These metal cations can hydrolyze, and the contemporary philosophy is that that would increase the local acidity. And so you actually end up with a solution that may be more acid and more chloride-containing than the bulk solution, and this is experimentally verifiable. This has been done experimentally on cracks, on pits, on crevices. It's part of the tradition in corrosion engineering.

What that says is that this environment may become more aggressive with time; and, in fact, I think the general attitude is that localized corrosion is actually somewhat autocatalytic. In other words, once it begins because of the metalline hydrolysis and the need to balance cationic and anionic populations, you actually generate a more aggressive environment in local geometry as a crack or a crevice or a pit propagates.

And so I didn't hear anything in the discussion this morning that--well, two things--I didn't hear anything that was dated. It was relevant to a repository environment specifically. But I also did not hear anything in a generic sense about the question of the local chemistry change. And if we now go to Slide 32, I think that becomes important when you talk about this issue. More corrosion-resistant alloys require solutions that are more aggressive to avoid stifling, and I think all of those things can happen almost in a catalytic sense as a crevice propagates.

So how do we balance what is the more or less traditional view that localized corrosion has almost on a catalytic behavior to the concept of stifling? There seems to me to be, at least on a first order basis, a contradiction there. If you were to tell me that the crevice dries out and there's no electrolyte, then I can imagine stifling. But if there is still electrolyte present, then I'm not a hundred percent sure I understand this.

PAYER: Let me just take the first part of that and then pass it to Rob to explain why.

Empirically, experimentally, Xihua presented results, Raul Rebak has presented results with co-authors, and Xihua as well, and we've presented results where if you--

LATANISION: Xihua's data was on a copper chloride containing solution.

PAYER: We've done it in concentrated chloride solutions at high temperatures. And the reason we do that is we're driving it not to realistic repository environments, but environments that were in that range of--it's possible to get those environments under some conditions.

And so if you don't go to those environments, you get no stress corrosion cracking, students don't write papers, they don't get degrees--. One of the deals is, we've got to go in--you drive the system into a regime that's not so--I mean, it's an accelerated test, but it's how do these behave in halyte conditions.

But what I'm saying is, empirically we see and can demonstrate repeatedly that stifling does occur. There's an incubation time, the critical crevice chemistries build up, the crevice corrosion starts as measured by the increase in current, and it stops, it shuts down, and that specimen repassivates.

LATANISION; Where does the change in local chemistry enter into the picture?

PAYER: Rob.

KELLY: Let me do that. And, actually, Ron, I'm hurt that you don't know that in the technical that Scully and I wrote, we talk about stifling.

LATANISION: Oh, you do. Okay, I accept that. I think on that basis, I need an autographed copy by the authors. How's that?

KELLY: It's a 175 bucks a copy.

PAYER: 200 if it's autographed.

KELLY: But on Ebay you can get it much cheaper.

LATANISION: Oh, okay.

KELLY: The point is, the reason you can lose that chemistry, this autocatalytic mechanism of Fontana and Green assumes that you have a cathode that is willing to supply as much current as you want. Okay? And if you have a cathode that fails you--if you go back to Slide 7--if you have a cathode that fails you--because this is not the only place that chemistry change happens. One is producing hydroxyl out here, so the pH is rising. That inhibits cathodic current. That slows cathodic kinetics.

And so if you're not in the potentiostatic mode where you have some counter electrode over here that will just merely move to whatever potential you need, you will tend to slow down localized corrosion simply because slowing of the cathodic kinetics. And you can see that in stainless steels and in copper alloys that have been exposed for long periods of time in sea water, where the first year or so the pit growth rate--if you take the five largest pits or whatever parameter you want to use--the pit growth rate is very high. But then if you take exposures that are now not one year, but three years, five years, ten years, the biggest pits don't get much deeper; and the reason for that is this stifling phenomenon.

LATANISION: Rob, I'll buy that, but I still haven't heard any conversation about the chemistry in a propagating crevice, and I think there is good evidence that the chemistry can become far more aggressive than the bulk environment.

KELLY: Oh, absolutely. Absolutely.

LATANISION: Well, where does that enter into the whole conversation we had this morning about stifling?

KELLY: I guess it's back to 32. This is where it happens. You have this critical chemistry, it can be sufficiently aggressive, and you cannot have a protective oxide on the metal, and then one of these things can happen. An example, a protective precipitate can form that slows down the dissolution rate. If that slows down the local dissolution rate for the depth where the attack is occurring so that you get below this critical I-X, you're done, because now you can't maintain that critical concentration. That's what it's all about, stability in the crevice, all about maintaining that critical concentration.

LATANISION: It's not all about that. I mean, it also includes changes in pH and chloride and anion population in a--

KELLY: But that's all tied up in this. That's all tied up in this.

REBAK: May I make a comment?

DUQUETTE: Raul?

REBAK: Rebak, --.

Looking the very simple way, the only thing that causes crevice corrosion in Alloy 22 is hot hydrochloric acid. If you have cold hydrochloric acid, will not cause crevice corrosion or any way that you can eliminate if there is no hydrochloric acid from the crevice will stifle crevice corrosion. One of the things that Rob was just saying about this precipitation, you precipitate chromium and molybdenum oxides inside of the crevice, those are insoluble species in hydrochloric acid, so they stifle crevice corrosion.

Another way, when you have that anions that you said migrate inside of the crevice, you would have also nitrate or sulfate or carbonate. They also migrate because they neutralize the pH; or in the case of nitric acid, the nitrate can form nitric acid, which has very low corrosion in Alloy 22--.

So anything that will keep the chromium oxide film stable in the crevice, you will stifle crevice corrosion.

LATANISION: I will buy that, too. But there is a mechanism by which, I think, I would expect the local chemistry to change pretty dramatically, and it could easily become an acid chloride.

REBAK: And that's hydrochloric acid?

LATANISION: Right. And that's what you--

REBAK: And if you eliminate that, it will stop.

LATANISION: But I don't see that you've eliminated that. You're talking about a nitrate to chloride ratio. You've got a crevice, a localized geometry, you've got metal cations, they may hydrolyze, you've got chloride anions which presumably should be attracted to neutralize the charge imbalance. It seems to me you have all of the ingredients to actually give rise to an acid chloride environment in a propagating crevice. Have we ever looked at the crevice chemistry?

REBAK: No, actually, we never looked at that, but-- hydrochloric acid--. When you have nitrate there with hydrochloric acid, the nitrates are slightly weaker--nitric acid than hydrochloric, so it wins in the fight for protons. So then what you have is nitric acid--inside the crevice.

LATANISION: Let me just say. This may sound contentious, but this is a workshop, and the whole idea here is to learn something, so I don't think anyone ought to feel inhibited about asking questions.

Go ahead, Joe.

PAYER: Joe Payer, Case.

If we'd have brought the other guy from Virginia, Scully, the one that's taller and with hair, he is focusing--and other people in the co-op are focusing on that exact issue with the anode chemistry, the anode chemistry required as a function of alloy composition. So they've got a series of iron-chrom-molybdenum alloys that have been made, and Rob--where's the anodic polarization curves?

KELLY: The next slide.

PAYER: The next slide up there.

KELLY: 33.

PAYER: The next slide up there shows--the next one there.

Those anodic polarization curves on the left hand there show you that as the molybdenum increases, you get to a point where, in that particular solution--I can't read that far--the ph=0 HCl--that at a certain molybdenum concentration, that material is passive, so you would need a more aggressive acid condition for that particular metal. So it's a function of the metal.

And that is being studied; it is being looked at. But in order to maintain that critical chemistry, you need a certain amount of anodic current density that has to be balanced by the cathode, and it has to be balanced by the I-R drop down through the solution. And if you put all that together, you can reach conditions where it's unstable, and it will repassivate. When it repassivates, you no longer have that critical chemistry. You've moved away from it.

DUQUETTE: If you treat each dust particle as a separate crevice, some of your geometric effects are going to go away. I mean, if you make the crevice long enough, I fully agree with you. But I think you've got some local geometry situations that you're not duplicating in the laboratory. I think the laboratory tests do show some stifling, and I think it's a laboratory effect.

PAYER: Payer, Case.

So with Alloy 22 you will not initiate crevice corrosion under individual sand particles. You can't separate the anode and cathode. You won't do it. Unless you dip it into 6-molar nitric--I mean, Maury showed us what solutions you have to dip it into to initiate corrosion on that. You need these highly acidic environments, but now we're not talking about crevice corrosion. You're talking about a bulk environment.

DUQUETTE: Maury, a quick comment?

MORGENSTEIN: When you get into a crevice situation where you have developed a strong enough acid to eat the metal, what you're really looking at is what we showed you occurs in the Soxhlet. We already know what happens there. And aqua regia-- actually works very well, so it doesn't have to be a pure chloride acid in those conditions.

DUQUETTE: I'm going to allow two more questions. We're running out of time. We've got another short presentation.

WALTON: All right. Slide Number 28. It would look like your corrosion model and your cathodic current model and your pictures suggest that it's all one-dimensional cartesian that you're doing, and I'd suggest that most crevices at Yucca Mountain are more likely to have a cathodic area that's much more nearly radial and two-dimensioned. And if you put a radial solution in here, you get a lot more current coming in--you get a lot more current.

KELLY: Yeah, that's not different in concept, that's different in implementation. And that's why none of our--as I said before, it's scenario-specific, so I wouldn't do anything with the numbers that we've put up here, and you would need to model it in whatever the geometry that's relevant to your situation. Absolutely.

AHN: This is Tae Ahn. --for information. I've heard you modeling in the last Las Vegas meeting and here as well. Given the initiation site inside a crevice, do you have any information on distribution of current or potential chemistry inside crevice?

KELLY: We've done some calculations where we've either decided where the initiation point is and looked at current potential distributions as what Uzi is doing, or started with the critical crevice solution inside filling the crevice and then seeing what current potential distributions develop. So we've done some of that work. We haven't shown it, but we'll give presentations, I think, on both at the ECS meeting at the end of October in Cancun.

DUQUETTE: Maury, 30 seconds.

MORGENSTEIN: One might even take a look at the degradation of a rock bolt as--debris as opposed to just dust. Well, we can look at it as dust, because it may come down looking very much like that. And certainly that would have a different geometry situation than just sort of aerosol dust. The question is how much of that is going to be available and how does that enter into pictures that we're describing here.

DUQUETTE: And in the unique context of yesterday at the end-of-the-day discussion.

Before we put the last speaker on, because it's a little bit different from crevice corrosion initiation or propagation, how many people in the room think that in the repository environment crevice corrosion will probably initiate?

How many of you think it will not?

And how many of you don't know?

The last speaker this morning with a very short presentation is a guest of the Board, Mr. Russ Jones, and he's going to talk about some chemistry changes that can occur in the surfaces of nickel-based alloys.

JONES: Basically, the genesis of this work actually goes back to an earlier Waste Board workshop on long-term stability of passive films. We weren't at the workshop. My team, a group I worked with at Pacific Northwest National Lab at the time, we weren't at the workshop, but our answer to that was, yes, there is a concern with a phenomena that we had observed before we had studied, and the ones that worked with me were Don Baer, who is a surface chemist, Chuck Windisch is a physical chemist.

The work and the experimental work--very limited work--I've got limited results here--they are only from very limited experimental work that we did--was done at our Environmental Molecular Science Lab at Pacific Northwest National Lab, using some surface analysis equipment that we had developed over many years working with Don and other surface chemists. We developed the capability to do surface modification and transfer to a corrosion cell under controlled environments, so you could go back and forth, okay, and modify your surface and go into a corrosion cell and then go back and measure your surface chemistry. And it's been modified and upgraded in this repository facility, and they use it quite a bit.

So going on, we knew at that time that sulfur can be damaging to the stability of a passive film on nickel alloys. We knew in some circumstances that sulfur at the PPM level could enrich on a surface, because it's a very surface active element, under limited conditions, granted, okay, so the questions were: Will they occur in this alloy under these kinds of circumstances? We have a limited answer to that. I apologize, but that's all we've got.

Some Roger Staehle work, which he's published, which just shows part of the answer to that question about the role of sulfur on the stability of--film, and it depends very much on the valence of the sulfur. Okay? So it takes reduced forms--and these are two different pH's in an Alloy 600 solution of alloy. The sulfur must be in the reduced form, not in the oxidized form. So as you oxidize it, it becomes sulfates and so on, and they're less effective. Metallic sulfur, S-zero, is very effective adsorbed on the surface.

Next slide is some of our own work where we took--this is nickel with PPM levels of sulfur in it, and you run an active corrosion experiment, not a passive film, okay. In active conditions sulfur will continue, so this is really time building up and then sulfur enriching. It lists current, but actually there's a time element in here. And as the corrosion rate starts to go up with time, we would pull the sample in and out. This is this experimental capability we have to go in and out without exposing to the atmosphere, and you get a build-up, and then you reach a monolayer and it starts to saturate.

At this previous workshop you had Phillipe Marcus from France also made the same kinds of comments and observations. They are the other team in the world that have done the same kind of work that we had.

The next slide, though, was used to sugges--that, okay, this Alloy 22--this isn't going to be an issue, because there is evidence that molybdenum will form a complex with sulfur and will reduce the amount of sulfur in the surface. And that is shown by his results here that the coverage of sulfur as you go in is affected by the presence of the molybdenum.

Now, this isn't a binary alloy and a lot of conditions that aren't at all the same. It's not as complex as the Alloy 22. So that was the basis of the question: What would happen if you put sulfur, and you could look at this enrichment issue in the Alloy 22?

Going on to the next slide, mainly I want to show--this is the sputtered profile in an OJ experiment. We've sputtered a profile into the sample, and I really want to just look at that profile. The way we do this experiment is we take about a one-centimeter square of sample, and we polish it to a one-micron finish and then send it out for ion implantation with sulfur. That's how we perform this experiment; it's how we've done it for years.

What we're doing is trying to jump-start the process to get more sulfur than the 100 PPM or so that's in the alloy, which in Alloy 22 would take hundreds of years at the corrosion rates that you'd see in a passive current or condition to build up a monolayer on the surface. So what we do to jump-start it, we put some extra sulfur in there, and that's the profile, and we get to about two percent at the maximum.

The way we run the experiment is, we then take these samples, and we put them in the OJ instrument, and we sputter down to this depth. We then transfer under vacuum--we have a system that attaches to the OJ--then transfer the sample into it under the same ultra-high vacuum conditions, take it to a glove (phonetic) box, and then release the pressure back up to a cover gas, and then in the cover gas we run the corrosion experiment. So you do expose it to some oxygen. I mean, it's not totally pristine, but that's the way we run the experiment. So we've profiled down to where we get to the maximum sulfur concentration.

The next slide, then, shows some of our results. And we ran tests--and they're very limited--we ran tests in three pH's. For the sake of time, I'm only showing the most acidic. We saw no effect--again, no effect--at higher pH's of about 6 and 8, only at the lower pH. So that's what I'm showing, just a look at the worst case, if you will. And, really, the only real result we see in this condition is that there is a shift in the open circuit potential of about 50 millivolts.

We saw one perturbation, which I've never seen in the corrosion work that we've done, a perturbation like this in a polarization curve. We went and looked at the sample and looked for some evidence of pitting or some kind of event that went with this and found none. So at this point in time we assume that there's very little affect on the passive current density at this 2 percent level of sulfur. Two percent is only 1/50th of a monolayer, so you're at a fairly still dilute condition relative to a monolayer, but at least you're much more than the 100 PPM that's in the alloy that you would be able to study if you just took this material and cleaned it off, got the oxide off, got down to pristine metal, and ran this experiment.

The next slide just shows that the effect of implantation is a factor. You cause atomic displacements as you put the sulfur in. So we always run a standard or a calibration with argon or some inert gas in order to create the same amount of displacement damage. We have never, in all the experiments we've done, ever seen displacement damage cause a change in the corrosion performance, and that's what this illustrated.

The last slide, then we ran one experiment at the end of our effort; in fact, this was beyond the extent of funding that we had, and we just ran this. We took a sample--this was one that was not sputter profile; it had about 1 percent or so at the front surface, okay, the beginning of that sulfur profile. We just put it in there for about a month, then took it out and did OJ analysis. And what you see is, this would be the original control implant, and this is what we got after 29 days.

So the question then--it revealed that sulfur was enriching. We don't know much about it. It was a very simple analysis, so we've seen two effects. One, we see a small shift in the open circuit potential of 50 millivolts when we're at 2 percent sulfur; that's 1/50th of a monolayer. And we do see accumulation from 1 percent up to 5 percent over a long period of corrosion at the open circuit potential in our sodium chloride solutions at a pH of 3.6.

So is this like an iceberg that you've observed and there's a whole lot more below the surface--sorry for the pun--or is it like a little chunk of sea ice that's going by and you say, no, never mind, we don't need to worry about it? You can look at this as a good news result. We got to 5 percent on the surface and no breakdown in the film. Nothing deleterious happened to that sample. It didn't start corroding very rapidly.

You could look at it as more of a concern result, and that would be that, gee, it's collecting, and it will continue to collect perhaps over longer periods of time. We saw a 50 millivolt shift in the--circuit potential, so there's something happening, but we don't know much about it yet.

That's all I have.

DUQUETTE: Thank you, Russ.

Any comments? Yes?

AHN: In your polarization you indicate the current. It means current density?

JONES: Yeah or--

AHN: Its--?

JONES: Yeah.

AHN: Okay. Second question is: Five percent means coverage fraction is 5 percent?

JONES: If you've done OJ analysis, it's actually your peak heights, so it's the peak height of the sulfur peak relative to all of the other elements in the alloy.

AHN: Last one is: You show the moving this sulfur with moly. Could you tell me what time frame is there lost?

JONES: That's Phillipe Marcus's results. I could get you the reference for that--yeah, go back to the reference. I don't recall the time period.

He does his experiments a little differently, by the way. He starts with a surface where he's adsorbed at least a monolayer or more of sulfur. Sometimes he gets a sulfide by thermal reaction, by high temperature reaction with H2S. So his starting point's a little different than ours.

DUQUETTE: One more comment.

PAN: Yi-Ming Pan, Center. I am very interested to notice your XPS profile on Slide 5. It looks like the chromium seems to deplete near surface. Did you have an explanation for that?

JONES: It's typical of lots of surfaces that have been prepared by polishing and so on. You can get--you know, we've cleaned it down--you'd have to ask Don Baer in his analysis and how he got that.

PAN: Well, the reason I ask, you know, typically this sample should be exposed to oxygen. You would suspect you have oxide film from there.

JONES: This is after the oxide film's been removed.

PAN: Right.

JONES: Right. So once he gets to his metal surface. It has been annealed--they were thermally annealed and then polished. So that's the preparation for that baseline condition, and it's also been implanted, so you've had one more step in the process. We did not pursue that, and Don might have a better answer than I would.

PAN: My concern is whether you are damaging the passive film. That's the bottom line. I don't know.

JONES: That doesn't really matter to our--we go down to here when we start the experiment.

PAN: Right. But the concern is whether that change the passive film, and the protection is not there and whether that affect--changing the corrosion--.

JONES: This is a sample that's as implanted. We then put it into the Auger spectrometer and sputter profile down to here, so that's the level of chrome, so you get rid of all of that when you start your experiment, so that's gone.

PAN: But typically you would see the--if there is chromium oxide there, you would see the chromium-enriched inner layer maybe.

DUQUETTE: Perhaps the two of you can talk about this over lunch.

We're just about on time. I want to thank the speakers, except for the Case Virginia presentation, for staying on time. And I'd like to thank the discussions--very lively discussions. We obviously could have gone on for much more.

We're going to break for just about an hour. We're going to reconvene at 1:15.

(Whereupon, the lunch recess was taken.)

AFTERNOON SESSION

LATANISION: Let's get started.

All right, we're going to continue with our discussion of localized corrosion, and this afternoon, we'll hear some conversation regarding models. And, we'll begin with Osvaldo Pensado from CNWRA. He's going to talk about Corrosion Models to Support Total System Performance Assessments.

PENSADO: Thank you.

This is actually a corrosion model, only one, to support the Total System Performance Assessment, the one that is developed by the NRC.

I acknowledge my contributors. This talk is closely linked to the presentation by previous speakers from CNWRA, and is closely linked to the one by Bobby Pabalan.

Next slide. This presentation is focused on linking the dots from the previous speakers, and summarizing how the information that we got from those studies is used to support the Total System Performance.

Now, I'm going to try to go one step beyond and try to see if the--presenting what will be the probability, and what will be the possibility for the development of some brines that could support localized corrosion. So, I'll try to go one step, only one step, and the consequences, although

I'm not going to touch into releases or dose assessments.

Next slide. The key points of the presentation, there is agreement that localized corrosion should be considered in performance assessment, and that there is the probability of localized corrosion that's linked to the feasibility for water to come into contact with the waste package. And, we acknowledge that there are uncertainties, uncertainties in the persistence of localized corrosion, and namely issues related to stifling and repassivation, and there are questions related to the extent of the attack.

To describe the model, we have developed, or we have split the time period into a number of periods. First, we focus on--well, first, let me slow down. All these lines are not hard lines. You should consider these lines more as envelopes, as shadows. There is uncertainty. But, these lines are given to give you an idea of what is the time frame that we're talking about.

First, we have initially there are elevated temperatures and we have been focusing some attention on the elevated temperature period, where temperatures could be above 120, 130 degrees Centigrade, and relative humidity in the system will be enough to support the formation of deliquescence of salts present in dust, and support localized corrosion, or some general corrosion.

And, then, when the system temperature goes down, there is the probability, the possibility that seepage could come into contact with the waste package. We grant that there is the protection of the drip shield, and that is an item that has to be considered, has to be kept in mind that the drip shield is present. But, if for some reason, the drip shield was not present and water was going to come into contact with the waste package, then there is a second period where brines could develop.

There is a competition between an evaporation rate and a seepage rate, and when the brine period ends, it's uncertain. In the performance assessment, we just assume that this is long enough to cover the period for localized corrosion. The period for localized corrosion is shorter, because as the temperature goes down, the possibility of localized corrosion, the feasibility of localized corrosion is reduced.

So, there is a temperature, possibly 70, 80 degrees Centigrade, where localized corrosion, inducing localized corrosion is highly unlikely.

This transition time is a function of--we have questions on--or it depends on the solubility of the brines, and the salt components, and it also depends on uncertainty in corrosion potential and repassivation potential.

So, with respect to the model assumptions, how do we go about modeling localized corrosion performance assessment. This is the stage and this performance assessment is lagging behind with respect to information, but we acknowledge that there is uncertainty in the elevated temperature process. At this time, we regard elevated temperature corrosion in the performance assessment. We need to gather more information, and this workshop hopefully will give additional insights on what should be the appropriate approach to elevated temperature corrosion.

Now, when the system--the temperature is down and the probability of seepage coming into contact with the waste packages, is that we assume the formation of brines. Now, for the concentrations that we use, we selected those simulations that Bobby Pabalan discussed yesterday for the concentration of the different chemical components. In reality, in this case, as an example here I have chloride. In reality, as the relative humidity goes up, and as the temperature goes down, what is expected is that the concentration will go down with time.

As a first approximation, we assume a constant concentration in this localized corrosion period. An implicit assumption of this model is that deliquescence--does deliquescence corrosion, localized corrosion is disregarded? It means that if the drip shield is present and is protecting the waste package, then the performance assessment model assumes that localized corrosion is not initiated.

This plot, Xihua already presented. I'll just tell you how I see that this information was incorporated. We acknowledge the presence of two different material types in the system. We have the welded areas of the waste package and the mill annealed waste package. So, we use a repassivation potential expression for the mill annealed body, and an expression for the repassivation potential. We use the same equation for the two material types, we just select different parameters.

The welded material is, as you see in this, is scattered--the data are scattered. So, we use as a surrogate to represent the welded material, we use a low bound that is given by the thermally aged data. And, in the performance assessment, we don't use a single line. Instead, what we use is an envelope, it's a shadow to account for uncertainty.

Xihua also presented these data to account for the presence of the inhibitors in the system. The repassivation potential increases dramatically with the additions of inhibitors. The inhibitors that we consider are carbonate, carbonate/bicarbonate, nitrate, and sulfate. The sulfate concentration is never high enough and can be ignored in the description.

Increasing the repassivation potential, we compute the increase as a delta. It's added to the repassivation potential expression, presented in the previous slide. And, we assume partial independent contributions to the repassivation potential by the different ionic components, carbonate, sulfate, and nitrate.

Next slide. Similar also in consistency with the presentation by Xihua on the corrosion potential. We derived an expression for the corrosion potential based on a mechanistic argument, and we derived the parameters for the corrosion potential using data in the literature and also fitting some of the parameters to some of the kinetic constants, to get a fit that would be consistent with experimental data. What we have is that the corrosion potential is a decreasing function of the pH. It decreases with increasing values of the pH. The corrosion potential is a decreasing function of the temperature. As the temperature goes up, the corrosion potential goes down.

I just make the caveat again. This is for the lower temperature system. So, I'm not describing the system that is above 110 degrees Centigrade. I'm describing a system up to 110 degrees Centigrade. Beyond 110 degrees Centigrade, this equation is not necessarily accurate. It may not be possible to extrapolate this equation.

I just draw your attention to a couple of terms, that is, the anodic current density, the corrosion potential is an inverse function of the anodic current density, which means that you have a high anodic dissolution rate, a high current density, then the corrosion potential goes down, and that's consistent with experimental observation. There is direct dependence on the concentration of oxidants in the system. Again, at higher temperatures, there is going to be a competition of the solubility with the different ionic components, so probably salting out may reduce the concentration of the oxidants. And, that will have an impact on the corrosion potential. So, that's why this expression should be treated with caution and shouldn't be extrapolated to temperatures beyond the range of validity.

The uncertainty in the corrosion potential is assumed to be due exclusively to the anodic current density. This is an approximation, so we fixed all the parameters as constant with constant values, and the only one that we consider uncertain is the anodic current density, and that's what brings the uncertainty in this corrosion potential.

You see a discontinuity here in the acidic range, and the neutral-to-alkaline range. This was modeled by selecting a transition pH and selecting different values of the parameters for the acidic range and different parameters for the neutral-to-alkaline range.

Now, so, the model is for the initiation of localized corrosion, and you have all the chemical, you know the concentrations of your ionic species. You know the pH. You know the temperature. You can compute a corrosion potential. We define the corrosion potential as a function only of temperature and pH. We define the repassivation potential as a function of temperature, and as a function of the inhibitors and chloride concentration.

So, if you know the concentration, the definition of the environment, we compute a corrosion potential, and the corrosion potential exceeds the repassivation potential, we assume that localized corrosion is initiated.

So, to quantify probability for localized corrosion, it’s a function of two terms. On one hand is the probability that seepage may come into contact with the waste package during that potential localized corrosion period, and another term that is the probability that the brine develop that the corrosion potential may exceed the repassivation potential. Only this probability is quantified in this work. So, the idea was we were trying to answer a question is this probability significant, or could be used to support some thermodynamic argument. If this probability was small, then this would be sufficient to decide to screen out localized corrosion. And, what we found in the main point is that this probability was not necessarily negligible.

The total probability is not quantified in this work, and that requires the Total System Performance Assessment. It depends on drip shield failure. So, the probability of the drip shield failure needs to be quantified, or the presence of initial defects.

Now, this is the model for the environment, and is closely linked to the presentation given by Bobby Pabalan yesterday. He presented this information in the form of box and whisker plots for--I'll explain briefly. He described that the numerical simulations, what he did was consider a set of ambient pore waters, pore waters at 25 degrees Centigrade. And, those waters were evaporated, and were numerically reported to do numerical simulations. And, as a result of the simulations, there were three brine types that developed at 110 degrees Centigrade.

There was 8 percent of the pore waters resulted in calcium chloride brines, 24 percent in neutral brines, and 68 percent in alkaline brines. So, those numerical simulations, you can imagine, that those were put in a single bag and shook, and by interpolation, these numerical distribution functions were constructed.

This distribution function, you see that it has some coordinates here. The reason for these coordinates may become more apparent if you overlap these plots to the box and whisker plots that Bobby Pabalan presented yesterday. You will see where these coordinates are happening.

Also, the calcium chloride brines have a feature that are concentrated in chloride and seem to have a low pH. So, there is a correlation in the way that the concentrations are defined. There is a correlation between pH and the chloride concentration, and we computed, well, what would be the correlation coefficient. The correlation coefficient between the chloride and the pH, and there is also a physical correlation between the carbonate and the pH.

There is a negative correlation between the chloride, pH and, again, this is just to represent that the concentrated chloride is also associated with the low pH.

Now, Bobby Pabalan only considered 150-something pore water compositions. We wanted to explore, okay, what if you generate random compositions that are consistent with these experimental data that preserve a proportion of the 8 and 50 percent of the different brine types, preserving the proportion but interpolating to new and different concentrations that are feasible and may be consistent with experimental data. So, to account--to have some account of uncertainty.

The only feature that we requested was preserving these rank correlations, this negative .8 and this .9. So, in the numerical experiment, what we did was sampling 10,000 vectors--by vector, I mean a value of pH, chloride, nitrate, total carbonate, and sulfate--and, again, the reference temperature is 110 degrees Centigrade. So, we have all the information to compute the corrosion potential. We have all the information to compute the repassivation potential. And, then, we asked how many times from these 10,000 sampling vector, how many times the corrosion potential exceeded repassivation potential?

We accounted also for uncertainty in the anodic current density. As I said, that introduces uncertainty in the corrosion potential. And, also, uncertainty in the empirical parameters that define the repassivation potential.

So, I'll focus on this plot on the right. This is a complementary cumulative distribution function of this difference, the corrosion potential minus the repassivation potential. The point at which the cumulative distribution function intercepts the vertical axis is the number of times that our sample exceeded--the corrosion potential was greater than the repassivation potential, so we got 26 percent of the times that that happened for the thermally aged material. And, it happened in 3 percent of the times for the mill annealed material. So, this is the P, P_C, probability that I was talking about previously.

Now, the main point of these two probabilities is that just looking at the environmental conditions, it may not be possible to screen localized corrosion. And, the initiation of localized corrosion in that scenario where seepage could come into contact with the waste package at a high enough temperature, high enough, again, over 110 degrees

Centigrade, may give rise to conditions that could initially support localized corrosion.

Now, we have to acknowledge the uncertainties, and we have uncertainty of the initiation of localized corrosion, does not equate to propagation. We have questions on the stifling of repassivation. Also, this probability shouldn't be interpreted at all, like the waste package. How many waste packages are affected by localized corrosion?

There is a question of, okay, what's the other presentation of that uncertainty in my probability distribution functions for the chemistry, what does it represent. We have a seepage point on our waste package, and seepage points are independent, if they evaporate, do they give rise to different chemical conditions, or do we have a given area in the repository that may be affected by similar pore water compositions. We need to account for that interpretation in order to have an interpretation of what this represents with respect to initiation of localized corrosion in the waste package.

So, those uncertainties are acknowledged. The other uncertainty is the uncertainty in the distribution functions for the chemistry. Note that we used the ambient pore water compositions. We evaporated those, and it led to a distribution function for the components. This is different than the approach that DOE took. They allowed equilibration of ambient pore water with hot rock, and you've seen some reactive transport computations and complemented those with equilibrium computations from EQ3/6 simulation to simulate the formation of brines.

And, you compare that, for example, with--pull out the presentation yesterday by Charles Bryan--and you see that in time, there are some bins that develop, and the bins that correspond to the localized corrosion time are not so aggressive. So, there is another possible interpretation, and we're going to update the thermodynamic analysis to see if that could change the contributions here, or how would those probabilities be affected if we consider that possibility of the reaction of ambient pore water with hot rock.

So, in conclusion, I presented an approach to estimate the probability for the onset of localized corrosion. We accounted for feasible brine chemistries. And, here, the key word is feasible because I'm interpolating some distribution functions. We considered components that promote, chloride ion, or inhibit localized corrosion, nitrate, carbonate, and sulfate, and we considered also fabrication effects.

The conclusion is that localized corrosion should be considered in performance assessments if seepage water were going to contact the waste packages during the thermal pulse.

If the drip shield is robust enough to survive for a few thousand years, then the probability of localized corrosion, at least in this interpretation, for the lower temperature system is greatly diminished.

So, we acknowledge the uncertainties in performance assessment. We have the question of elevated temperature corrosion, and this question, we're going to take with us and we're going to continue analyzing what would be the effect on the performance assessment. We have-- certainly you want to do a full assessment, and you have to link to other parts of the system, and the drip shield lifetime is one question that will affect this link to localized corrosion.

We have uncertainty in the composition of solutions in contact with the waste packages. We already mentioned we're in the process of updating our analysis. The question of localized corrosion persistence, if you initiate localized corrosion, does it propogate. We have some evidence that the stifling and repassivation are possible processes. And, the question also what is the surface extent of the localized corrosion attack. We made some assumptions to incorporate into the performance assessment, but the uncertainty in this process should be recognized.

And, acknowledge this report of the NRC. This is an independent product of the CNWRA and does not necessarily reflect the view or the regulatory position of the NRC.

LATANISION: Thank you. Okay, any questions? Thure?

CERLING: Yes, on Slide 11, I was just wondering how you correlated the points. Did you take the original water compositions and then generate some compositions, and then evaporate them in the model? Or did you make a distribution after you--

PENSADO: Yeah, can we go one slide before? That one.

What we did was we took initially few pore water compositions, and you look in Bobby's presentation, he presented in the diagram, the triangle diagram, where is it that those initial pore water compositions fall. And, those pore water compositions at ambient temperatures, and those were evaporated to a reference temperature of 110 degrees Centigrade. So, the initial data set is only 156. And, then, we computed these three brine types, the calcium chloride, neutral and alkaline brines, of this 156 map into three, and this has ranges. So, I preserved the hot ranges, and, so, I preserved this percentage and then I put everything together and I looked at the total chloride concentration, and I looked at the percentile, how this chloride concentration appears, how often in those 156. But, this is the initial data set.

LATANISION: John?

GARRICK: Have you attempted to make a similar model for propagation?

PENSADO: Yeah, we have the--Xihua explained these. In the propagation model, what we have is we have a propagation rate that is consistent with stainless steels. So, once localized corrosion occurs, the propagation rate that we assign is so high that it just happens in two or three time steps. So, we assume a pretty high propagation rate. We are considering whether we should update with more realistic (unintelligible) measurement of the corrosion rate that considers the stifling and repassivation. In the propagation of corrosion rate, you have to touch on those questions, the stifling and repassivation.

GARRICK: Wouldn't you think that this approach, this general approach of trying to view with the question of the likelihood of localized corrosion would be a good way to handle it?

PENSADO: Oh, yeah, it's--

GARRICK: Rather than an arbitrary screening process?

PENSADO: Sure. I think that here, I put the probability part just to give an insight. What the performance assessment contains is a description of the processes that would trigger localized corrosion. Again, you gather the data from the performance assessment, and you count how many realizations localized corrosion will trigger, you will get something similar to what we have. And, I'm pretty sure that also in the DOE model, you look at the number of realizations that may trigger localized corrosion. And, you can also get the probability. So, you can fit it into an offline analysis to see independently whether a process is relevant or not. But, this is consistent with the performance assessments.

LATANISION: Maury, and then Russ.

MORGENSTEIN: Two questions. Why did you use 70 to 80 degrees for the break point in localized corrosion, and, two, when you broke down the waters to three types, with 8, 24 and 68 percent of probabilities, do those three types only represent vadose water that is likely to come in contact with the waste package, or is that general Yucca Mountain water?

PENSADO: The pore water composition is vadose. So, it's unsaturated zone pore water. So, it's not general pore water composition. There are other samples that are available that we have not considered in the analysis. So, you asked me for--the other question was on the 80 to 60 degrees. Again, that was only to give you an idea of where localized corrosion is a relevant process.

The performance assessment does not include a threshold temperature for the initiation of localized corrosion. The performance assessment is only based on the repassivation potential and corrosion potential. And, then, it's with those equations, you can compute at which temperature the corrosion potential is not likely to exceed the repassivation potential. So, there is no threshold temperature, and I just give you, by my experience is that where I see that these curves cross is below 70 degrees Centigrade, it's quite difficult to develop localized corrosion. And, this is consistent with experimental data.

LATANISION: Russ?

JONES: Russ Jones, GT Engineering.

Just a question of clarification. So, for any value of the E_{corr} greater than the reversible crevice potential, the probability is, one, that localized corrosion will occur? They're all equally probable once you exceed that value?

PENSADO: Is the initiation of localized corrosion, and, yes, we don't--probably you are getting into the difference, and more likely, it is. No, we don't need that.

LATANISION: Charles?

BRYAN: I would just like to comment to remind you that we did just review all of these waters over the summer, and that a great many of them were affected during storage by microbial activity. We had, from the unit of interest, the Topopah Spring, we had on the order of 120 waters, and only 34 of those we felt were minimally or unaffected by microbial activity. So, I suspect that as our results become available, these CDFs will change considerably.

CERLING: Can you share with us what sort of trends the microbial activity had out of the distribution that Roberto was showing?

BRYAN: Well, I mentioned this yesterday. The cores were stored. They were wrapped in plastic. They were placed in core tubes with packing to minimize the head space. They were wrapped in plastic. The conditions went anoxic in the tubes. The P_{C02}s went up to as high as 10 percent. Denitrification occurred. The nitrate concentrations went way down relative to the more recent samples, which were sampled, and analyzed much more rapidly and weren't stored the same way.

Calcium concentrations went way up. The trends that we tend to see is that the new waters--or the reduced sample, which we feel were minimally affected, have higher nitrate concentrations. Over half of them have nitrate to chloride ratios above .5. Calcium concentrations are generally lower. Sulfate concentrations are higher relative to the other samples. And, the pHs tend to be higher.

MORGENSTEIN: Just to follow up on that. Morgenstein, State.

How is this going to be handled in the QA?

BRYAN: In terms of? Well, we're screening those samples out. We're quite confident that the microbial activity occurred during storage. There's a lot of evidence for that now. We're not going to use those samples. We're going to look at the samples that weren't affected, or were minimally affected. We're using fairly conservative cut-offs for what we consider to be the effects of microbial activity.

MORGENSTEIN: To what degree of certainty do we have that maybe a naturally low nitrate water would be weeded out in this process?

BRYAN: Well, that's not one of the parameters we're using. It happened to be that that was the case. The parameters we're using had nothing to do with the nitrate to chloride ratio at all. We're looking at trace element concentrations, manganese and Strontium values, the measured pH, and the predicted P_{C02}s, which are extremely high. We have six years of CO_2 pressure data from the repository unit from one of the wells, and the concentrations are always on the order of 10^{-3}. They never go up to 10 percent, 10^{-1}, which is what we're seeing in some of these samples.

The conditions are clearly anoxic in some of the samples, because of the presence of the organic acids, which are not produced under oxidizing conditions. They form by fermentating processes, and, again, all of the gas sampling that's been done in the underground shows oxidizing conditions in the unsaturated zone. Basically atmospheric P_{02}s.

LATANISION: Yes?

MON: This is Kevin Mon.

Do you, like, compare E_{crip} to E_{corr} at every time step?

PENSADO: No. Well, yeah, the--

MON: In the TPA--

PENSADO: Yes. Yes. What you saw is that the approximation that we made in this--the composition is fixed with time. The only thing that is changing is the temperature. So, there is an update of the computation for the corrosion potential as a function of temperature that's changing with time. So, yes, it is computed for every time step, the corrosion potential.

MON: So, meaning if the criteria for localized corrosion is satisfied at early time, at some later time, you might--

PENSADO: Right. If the (unintelligible) at the earlier time. At the later time, we may not be satisfied.

MON: In which case, you could turn it off in the TPA code?

PENSADO: Right.

MON: Okay, thanks.

LATANISION: This model input--well, it explicitly excludes deliquescence during the rise transient in the thermal pulse. Is there an equivalent, at attempt to develop an equivalent model for that potential event?

PENSADO: No. The deliquescence analysis is based on the analysis that Bobby Pabalan and presented yesterday, that the lower temperatures evidence that the nitrate is sufficient to support inhibition of localized corrosion. That is, again, for the lower temperature. For the higher temperature system there are uncertainties that we’re trying to address.

LATANISION: You're going to address it?

PENSADO: Uh-huh.

LATANISION: Okay. And, finally, if we could turn to Slide 6? I'm intrigued by the effect of thermal treatment. In each case, it appears that thermal treatment, whether it's at five minutes at 870, or four hours at 870, the effect is to make the repassivation potential more reducing than the case of the mill annealed material. Do you have an understanding of what sort of metallurgy is--

PENSADO: Yes, it's not more reducing. It is thermally aged, so there is a possibility of some phase formation that may be rich in chromium. So, the neighborhood area close to the chromium rich phases are depleted in chromium. So, you have a region that is not as chromium rich, and is more susceptible to localized corrosion. And, the longer you expose the system, the longer you thermally age, then you have more nucleation sites. It just is closed. So, there may be some--you want an opinion--

LATANISION: Go ahead.

PAN: Yi-Ming Pan, Center.

I would just add additional what Osvaldo says here. We did transmission electromicroscopy analysis on the sample, for example, the thermal aging at 870 C for five minutes, and we do observe the formation of the thin film type of precipitate, very narrow along the grain boundary. And, of course, with time and increase, you will see the formation of bond type of precipitates along the grain boundaries. But, nevertheless, repassivation potential may indicate probably after just 30 minutes of thermal aging at 870 C, it seems you remain a constant E_{RP}, repassivation potential.

LATANISION: Russ, do you have anything to add to this, anything you have observed in a metallurgical sense?

JONES: Well, we also did some high resolution TEMs, and it can be very difficult to detect very narrow depletions in elements by high resolution, even one nanometer beam size instruments, just because of the spreading. So, yeah, you might have precipitates, but you might have some depletion of an element that you almost have to fracture them and do an Auger, and that's not easy to do with this alloy. So, it's a very difficult problem to analyze what's happening.

PAN: Yi-Ming Pan. Just to add, we also did high resolution beam analysis and we do see the very slight chromium depletion along the grain boundary. So, we do have copies of that in the paper.

LATANISION: Okay. Any other questions or comments? Yes.

SPEAKER: I have one comment. Why you did not included sulfate is strong oxidant agent. Are we missing something here? Because if you have chloride and nitrate from the Center, part of the information which I’ve seen is high level sulfate is something would be present in Yucca Mountain, what that effect would be. So please look into that much more. Thank you.

PENSADO: If we can go to the presentation by Bobby Pabalan where he computes also sulfate--is reported in that presentation. And, for the system of--evaporated system, the concentration of sulfate was not that significant.

LATANISION: Okay. All right, thank you very much. Let's move on. And, Fraser, you're up.

LATANISION: Okay. All right, thank you very much. Let's move on. And, Fraser, you're up.

KING: Okay, thanks. So, my talk this afternoon will be a follow-on from Randy's talk of yesterday. And, taking the multiple environments and looking at the last three boxes in that decision tree, concerning the corrosion aspects.

So, EPRI's approach is to, for those of you who aren't familiar with EPRI's role here, EPRI's approach is to take an independent analysis and base that analysis on data available from both the DOE, the Center, and any other available data. And, what we try to do is we try to come up with the best estimate, in this case, of the waste package behavior.

So, as I said, we have used the decision tree approach. We used that in the 2004 discussions, and we have extended that approach, which was for divalent cations in 2004, to the multi-salt systems of interest here today.

So, just to recap what Randy said yesterday about brine formation and persistence, and then go on to say a bit about the localized corrosion consequences. And, following that, revisit the decision tree, then go on to talk a bit about the expected evolution of the corrosion behavior in the repository. And because my brain doesn't operate too well in relative humidity temperature space, I'm going to convert those to temperature time composition space. That for the evolution of time--for these various postulated multi-salt systems, and also say a bit about degassing, the likelihood of degassing, the benefits of degassing.

So, here's the infamous decision tree. This is for the 2004 one for the divalent salts. But, we revisited this again, as I said, for the multi-salt systems. What this lays out, as you know is, we've heard multiple lines of argument, all of which must be answered yes for the consequences to be considered. And, the first couple pertain to the development and persistence of the environment, and then the last three or four are for the corrosion behaviors.

So, first we start with summarizing what Randy said yesterday. We also have used the EQ3/6 geochemical modelling to look at these three corrosive salts. They have identified these three possible salt assemblages, and the EPRI model concurs with these, under certain circumstances, but not in others. And, the discussion yesterday was about the role of degassing and the loss of HCl and nitric acid, and the consequence for whether these are appropriate assemblages to consider.

I shant go over that again, only to say, though, that in our EPRI II model, if you remember from Randy's talk yesterday, some of the alternative assemblages that we predicted are that deliquescence is at much lower temperatures, and, so, it takes us out of that high temperature range.

So, now, getting onto the issue of persistence, in that sort of second decision box there, and the issue of acid degassing. And, we heard several times and we've seen it in experiment evidence this morning from the Center, that acid degassing does occur under certain conditions, and these volatile species will be removed from the surface of the waste package in the drift by advection down the drift or diffusion away from the waste package surface. And, we believe they will be consumed by reaction with the overwhelming mass of minerals in the drift walls as they get lost in the drift walls, the sodium tuff.

Of course, acid degassing is favored by neutral to acidic pH because the partial pressure of the gas is much higher under those conditions. And, we believe there's reason to believe that calcite and other mineral phases buffer the pH, and that near-neutral pH would promote continued acid degassing. If that does occur, and of course there's obvious advantages from the corrosion point of view, in the sense that you lower the overall salinity of the brine, you may get preferential degassing of the HCl over nitric acid. We heard about that this morning. In which case, nitrate to chloride ratio is increased, and because you're losing these highly deliquescent salts with the salt version of these acids, your remaining constituents would deliquesce at a much lower temperature. So, there's a possibility of drying out.

So, that was a recap of the environment that Randy was making yesterday. Now, let's get on to the lower decision boxes, and firstly, the third one in the row is, are these supposed deliquescent brines corrosive? I'm making the assumption that these high nitrate rich, high temperature brines will be formed. But we would argue that nitrate has been shown to inhibit initiation of localized corrosion over a wide range of temperatures. And, this we'll explore here whether we can extend that range of temperatures to these higher temperatures of interest here.

So, here's a chart of the compilation of data, vis-a-vis crevice repassivation potentials as a function of temperature. The solid lines--the lines are model predictions fitted to the experimental data. The solid lines are from the DOE's model, the dashed lines are from the Center's model. And, the different colors here are for different nitrate to chloride ratios.

So, the first thing we see is, for the model anyway, quite good agreement between the two sets of models, showing some consistency. The individual points here are recent data from Lawrence Livermore, and these are, I think are calcium based brines. This is from this paper here, a recent publication that Raul was involved in. So, these are calcium-based nitrate rich brines, going to temperatures of 160, and the color coding again corresponds to these same nitrate to chloride ratios.

And, so, these pre-existing data, these previous data, which were fitted to--I'm sorry--the pre-existing data which were fitted to these model predictions, are quite consistent with these subsequent data, which has just been reported in these calcium nitrate brines.

KADAK: I'm sorry. Would you just explain why the green line is down the data--

KING: Because these points are not fitted to these lines. These fitted lines were from earlier data from which, in this case, the DOE came up with a model for the repassivation potential as a function of temperature. There was subsequent data, with individual data points, which I will show you here. So, these are individual data points and they're not used in that fitting.

KADAK: So, which do you believe?

KING: I not saying I believe in any--I'm just saying these are consistent with these previous set of data. If anything, the repassivation potential is sort of independent of temperature.

So, as we discussed this morning, for a waste package which is not connected to a potentiostat, the criteria for localized corrosion is whether the freely-corroding corrosion potential exceeds the repassivation potentials. So, this is some of the previous data. I have excluded the Center's crevice repassivation potential data, just for clarity. So, I've kept the DOE data. But, in addition, these three dashed lines now are the predicted corrosion potential, the temperature dependence for corrosion potential, based on the DOE model, up to the temperature of 120, which we used to fit those data.

And, so, the criterion for localized corrosion is, and, again, these colors each represent a particular nitrate to chloride ratio. And, so, for instance, where the green curve crosses--and that green curve you see, nitrate to chloride ratio of .05-- where the green dashed line crosses the green solid line is where the models were predicting to initiate localized corrosion. And, so, that defines, for that particular nitrate to chloride ratio, a critical temperature, if you like, of maybe 105 degrees, for the nitrate to chloride ratio of .05. And, so, we can use that critical temperature in the subsequent analyses to see if localized corrosion is going to be feasible in these systems.

So, what we see here is to what extent can we extend these data beyond the range for which they were measured. And, so, the green curve with a ratio of 0.05 is within the data-- is within the range of the measured data. In extreme cases we would extrapolate this by a few tens of degrees, we would predict for a nitrate to chloride ratio of .15, that this critical temperature was of the order of 150.

If we go to higher nitrate to chloride ratios, say .5--yes, of .5, here we'd have to make a longer extrapolation, and if you were to, just based on these models, we extrapolated the corrosion potential model, or the repassivation model, you would predict a critical temperature at, oh, 250 degrees, or whatever. All I'm suggesting is that based on these data, based on this extrapolation, this critical temperature where these lines would intersect is quite high, and I'm saying it's up here somewhere. And, for some reason, it's important that. Here's one measure, the one measure that I could find, of the corrosion potential in these nitrates rich brines at 160 degrees. And, as you can see it’s quite positive; it's 550 millivolts.

But, it's still below some of these repassivation potentials that are measured in the same series of experiments. And, so, there's reason to believe at this high nitrate to chloride ratio, that the critical temperature is in this region, and you can argue and debate how far up it is. So, really, what I'm trying to do here is extend the existing model to higher temperatures, and to claim that nitrate will continue to act as an inhibitor at these higher temperatures.

And, to support these data, on the next slide, some suggestions as to why nitrate might be doing that. So, the argument here is that nitrate would continue to be an effective localized corrosion inhibitor at elevated temperatures, partly because of the nitrate reduction within the crevice. And, so, we've heard a bit this morning about nitrate reduction, and if nitrate is reduced all the way to ammonia, an 8-electron reduction, it consumes vast amounts of protons, so it's catalyzed by acidic conditions, of course by a high temperature, as well, but it results in a large decrease in pH.

So, nitrate reduction on the external surfaces and outside the crevice will be slower than that inside the crevice. So, this is a mechanism because the lower the more acidic pH in the crevice, we would expect this reaction to proceed preferentially inside the crevice. But, in doing so, it consumes many of those protons, increasing the crevice pH. And, consequently, reducing the rate of anodic dissolution, which is what we were saying this morning, is another mechanism for losing this critical crevice chemistry we need to sustain in order to get continued crevice propagation.

Another argument here is that the nitrate concentration inside the crevice will be maintained because unlike oxygen to the classic differential aeration cell that leads to localized corrosion involving oxygen, the issue there is you can't get oxygen--there's no effective transport mechanism to get oxygen into the localized region, because it's an uncharged species. And, that's why you get chloride, for instance, building up in the crevice because that is brought in by that electromigration to do the charge balancing.

Here, we have a potential oxidant, nitrate, which is in fact charged. And, so, there is an effective transport mechanism to get that nitrate into the crevice, where we're suggesting that it will be reduced because of the low pH, but in doing so, it's going to drop that pH, and so, it won't--we won't run into a situation where we can't sustain the cathodic action inside this crevice. And, this is another potential mechanism for why nitrate acts as a localized corrosion inhibitor.

And, in fact, the rate at which anions are drawn into the crevice, are a function of the mobility of those ions. And, in fact, the mobility, or the transference number, of nitrate is higher than that of chloride. So, there's a possibility, a likelihood, that in fact nitrate will enrich in the crevice over chloride, because the transference number is higher.

And, as an aside, my Ph.D. thesis many years ago, was involved in the measurement of transference numbers in concentrated aqueous electrolyte solutions. And, this is the first time in 25 years that I've ever been able to use any of my Ph.D. work--. [Laughter.]

So, this is good supporting evidence for claiming that this inhibitive effect of nitrate should be effective at these higher temperatures. And, justification for extending the existing model to go up to 120, 140 degrees, up to higher temperatures.

And, so, a lot of the subsequent slides will be based on this, and so this is now taking these critical crevice temperatures, and this is the critical temperatures for localized corrosion, based on that intersection with the corrosion potential and the crevice repassivation potential as a function of nitrate to chloride concentration for nitrate free solution--I didn't show you those data. We have some data there on two slides ago to the .05, and there we saw the intersection occurred at about 100 degrees--the intersection for the .15 was about 150, and this is the .05 ratio, and those are the red lines where the intersection was somewhere on the right hand side, and I'm not suggesting that it's quite a high temperature. I'm not sold on that temperature, and you'll see in the subsequent analyses, it doesn't really matter if it's not quite that high.

But, what this line defines is a region of protection, and, so, if our deliquescent environments are below this line, we should not initiate localized corrosion. If we're above that line, then we could do it.

I just want to touch briefly on the recently published Lawrence Livermore data. These solutions they did these experiments that Raul talked about this morning. Here's an SEM that I stole out of that paper. My impression of this was I was overwhelmed to still see the polishing lines. I had to look for dissolution, and I can see the dissolution in parts--or evidence of dissolution--perhaps some dissolution here. But, compared to the (unintelligible), this is 1 to 2 microns. And, so there could be features here which are consistent with dissolution. But, overwhelmingly, you will still see the polishing lines, the original surface preparation.

Now, the authors themselves had some questions about the artifacts in the study, and I am not going to gainsay their opinion. All I would say, though, is that the evidence presented amounted to a few microns of attack at most. It's a closed system and we're concerned about this accumulation of acid gases as a consequence.

And, I did also note, these crevice samples were added to the solution a year after the experiment started. The experiment was started, I think, in fiscal year 2004 as a general corrosion study. And, as we said today, might get extensive dissolution, it's possible, I don't think that it's--it's possible that when the creviced samples were put into the solution a year later, that solution was now quite oxidizing because of the presence of dissolved chromium six, and that may have temporarily boosted the potential--artificially boosted the potential to give us this minor amount of initiation. But, otherwise, these tests were done up to 220, and I would say they are consistent, not inconsistent, about this inhibiting effect of nitrate at these high temperatures.

Okay, so let’s just revisit some of the arguments we made in 2004. And, this was one of the arguments we made for why these dust deposits weren’t effective crevice formers and couldn't initiate localized corrosion. And, some of you may remember this. This is a very simple model that we had, and the idea here was to try and determine whether you could form that differential aeration cell that you need to initiate localized corrosion.

And, our argument was that under this permeable dust deposit we might form a deliquescent solution, but that the rate of oxygen consumption due to passive corrosion prior to initiation on this Alloy 22 surface would be a lot slower than the rate of replenishment of oxygen by diffusion through this dust deposit and this thin deliquescent film.

So, we looked at this in the calcium chloride brines. We revisited it in these nitrate rich brines, and the two issues that that affects are: firstly, the solubility of oxygen/salting out effect is a bit greater because the concentrations are somewhat higher, and of course we have a higher temperature.

So, here’s the results of that update of the analysis. So, what we show you here is a function of temperature, and I’ve sort of extended the temperature range from the previous analysis up to 180 here. What this shows is the current density. Firstly, for the rate of consumption of oxygen due to passive corrosion, this is the line used in 2004. This is the rate from the Center. I took the corrosion rate that was in Raul’s recent paper, and these nitrate rich brines at 160 degrees, and that falls very nicely with same trends, and we think we have a good handle on the rate of oxygen consumption due to passive corrosion. And, these three red lines are for comparison are the rate of oxygen replenishment by diffusion through this dust deposit, but more importantly, the thin deliquescent solution, and there's some uncertainty in the thickness of that, or some variability perhaps in the thickness of that deliquescent solution. And, so, these are for three possible thicknesses. I think this is 1 micron, 10 microns, and 100 micron thick deliquescence solution. But the point here is the difference between rate of consumption and the rate of replenishment is several orders of magnitude, it's two to three orders of magnitude at least, suggesting that you can't consume the oxygen faster than it's replenished.

And, so, based on this conceptual model, you can't set up a differential aeration cell under dust deposits. A dust layer is not a good crevice former.

I'm touching on stifling, now. We had some discussion about that this morning. As you remember, stifling has long been the component of the EPRI model, and that was based by analogy to other materials. But in previous EPRI models we've had this stifling component for localized corrosion, and we have used values for the time exponent between .1 and .5. Again, by analogy with other alloy systems.

We're pleased to see that now we have some data on Alloy 22, and in systems with some relevance to Yucca Mountain. And, indeed, this dependence is being born out. Here's the DOE data which is, in FEP screening AMR. A range of time exponents here. I assume that the Center data, which Xihua talked about this morning, and that is an exponent of .23. So, there seems to be some consistency between the various sets of data, and the previous range, but--that EPRI has used. So, we believe the stifling is a real phenomenon in these systems.

Here, this is just bit more discussion on that, the Center paper from this Las Vegas meeting, and Xihua showed this data this morning. So, the mechanism of stifling is actually still unclear. Rob gave some discussion about that this morning. IR drop, mass-transport effects, loss of the critical crevice chemistry is the thing that Rob was focusing on, possibly by catalysis of hydrogen reduction. That's what happens in titanium alloys. That's a 7 degree (unintelligible) titanium alloys, especially with the palladium containing alloys, the palladium catalyzes the hydrogen reduction and it loses acidity, and that's why crevice corrosion of titanium stifles.

I suggested another reason a few slides ago that nitrate, the addition of nitrate within the crevice might have a similar effect by raising the crevice pH. And, someone suggested that that negative shift in corrosion potential when crevice corrosion initiates could be involved as well. That was suggested by the Center.

For the waste package, of course, there's additional stifling mechanisms. There's the time dependent evolution of the environment. So, the environment changes with time, although slowly, but it is changing, and perhaps pH buffering by minerals in the dust. The additional stifling mechanisms which aren't apparent in these experiments. But, regardless, we believe there's strong evidence to believe that stifling will limit the penetration of localized corrosion were it to initiate on the waste package.

This is now getting down to the prediction of performance. So, what was shown here is if localized corrosion does initiate and continues to propagate, what does stifling tell you about how much penetration we get. And, in blue here, the dashed line and the solid line, these are the range of values that EPRI is using in its performance assessment model for some time. And, this now is the Center's prediction, it falls nicely in between our range.

And, if localized corrosion continues for 2000 years, unabated, at a decreasing rate with time, you get a maximum in this case, of 5 millimeters penetration, compared to 20 millimeter wall thickness, so even if localized corrosion does initiate, stifling is affected, and even if it were to continue for a long period of time, it wouldn’t dramatically impact the life of the waste package.

Okay, so that's sort of a wrap-up of where we are in terms of updating our decision tree. Now, for the second half, we just want to take some of the salt assemblages that DOE has suggested could form, and see what the consequences might be for the corrosion behavior of the waste package. And, so, as I said, my simple left temporal brain doesn't operate very well in this space, temperature and relative humidity, so I'm going to transform those into temperature versus time and put, place, on these temperature profiles with points in space where we can form different environments, and see what the corrosion consequences will be.

For illustrative purposes, we assume that the DOE Assemblages A, B, and C can exist, and see what happens in those phases. But we could apply this to any salt assemblage, and (unintelligible).

So, here's salt Assemblage A, and just to remind people it's a 2-salt system, sodium chloride and potassium nitrate. Here in this complex temperature RH space for the hot waste package in red, and the average waste package, and the actual averages taken from the DOE temperature profiles on the previous slide. Here, the temperature RH trajectories for those two particular waste packages, the hottest one and the average one, and what we say for the 2-salt system is that deliquescence is first predicted to occur at temperatures of 113 and 118 for the hot and average waste packages. This is based on EQ3/6 calculations.

And, so, deliquescence first occurs at these points A, then if no degassing occurs, the surface of the waste package stays wet, but as the relative humidity rises, those solutions become more dilute. So, along this trajectory, and I'll convert this into time-space in the second, along this trajectory the surface is still wet without degassing, but the solution is becoming more dilute. Until you reach a point B, and then the EQ3/6 calculations tell you that some other salts, these chloride rich salts, potassium chloride, sodium chloride, will precipitate, and you get a different system, and the small table down here--I apologize for the small size--this table down here gives you the solution composition of the points A, B, and C for the average waste package, A prime, B prime, C prime, for the hot waste package.

So, at Point B, you have a system which has sodium chloride and potassium chloride salt deposits, with that composition of brine. And, again, as time goes on, the temperature decreases, but the RH increases, those brines, if they don't degas, will dilute until they get to Point C, at which point you will just have sodium chloride. The potassium chloride will have dissolved. So, with an evolution of time and the absence of degassing, a general dilution of these solutions on the waste package as time progresses.

So, the next slide, I've taken those points, A, B, and C, A prime, B prime, and C prime, and put them on this temperature/time profile. So, here is the hottest waste package, and this is the--this average waste package. Both points in that RH/temperature space put into time/ temperature space, this is just a relative humidity profile, so the dashed lines just complicate things. But, these are these three points in time represented by these solutions that were calculated into EQ3/6. And, what I've also done here is I've taken the nitrate, the temperature, the pH, the chloride concentration, and the nitrate/chloride ratio, calculated using the DOE corrosion potential model, what the corrosion potential would be for that case, and in this case using the DOE crevice repassivation model, calculated what a corresponding crevice repassivation potential would be.

And in all cases you can see the corrosion potential is many hundreds of millivolts lower than the predicted crevice repassivation potential. So, in Salt Assemblage A, what this is suggesting is that even though the surface of the canister would be wet at this point, you would not initiate localized corrosion.

Now, on the next slide I've taken those three sets of points, the A, B, and C for the hot and the average waste package, and tried to plot them on this previous slide that we showed, which is this critical temperature for localized corrosion to initiate, which is the nitrate to chloride ratio, and--perhaps we could just go back quickly. You will see here the nitrate to chloride ratio of these mixtures is very high. It's greater than 1, 1 or greater, which is off of my scale. So, these points here are over here somewhere, and that's even further. But, the point being they're well below this line where localized corrosion is initiated. So, our argument would be, because we're in this protection area, those salt assemblages at Points A, B, and C, and subsequently any diluted version of those would not be sufficient to initiate localized corrosion.

So, now, we move on to Assemblage B, and of course as we move from A to B to C, we move up higher in temperature because we have a higher amount of nitrate in the system. But, we can go to a similar argument, sort of our argument, and we get the first deliquescence here at temperatures now of 130 and 122 degrees at Points A and A prime, and as we go up in RH, those solutions are becoming more dilute, if there's no degassing. We get other species--species precipitating at Point B or Point C, and again, variational evolution of the brine chemistry given by the table at the bottom here.

So, again, we can transfer those, yes, next slide please, and calculate using those nitrate, the chloride, the pH, the temperature and the nitrate to chloride ratio, calculate the corrosion potential based on the DOE model, and the crevice repassivation potential, and again, these values are mainly in the very high nitrate to chloride ratio, show that again repassivation potential, the calculated repassivation potential is many hundred of millivolts more positive than the predicted corrosion potential. And, so, here on the temperature/time plot, A, B, and C for the average and hot waste package--under none of those conditions, although the waste package surface is wetted, do we believe, would we believe that localized corrosion would be initiated.

And, again, on the next slide, we are again attempting to plot those on this summary slide--but, again, because of the very high nitrate to chloride ratios, these corresponding temperatures, the points would be somewhere in the hallway, but, again, well below this line of this critical temperature for localized corrosion initiation as a function of nitrate to chloride ratio.

So, primarily here, we are protecting, because of this high nitrate concentration. Now, we're still within the temperature range here, and this is about 130, where we're only 10 degrees above the corrosion potential data. So, we're still within the range where we believe that the data were measured.

This, however, is without degassing, and we had some discussions about degassing, and some questions about the kinetics of degassing, and, so, we--conservatively simpler model to try and calculate how long might degassing take. So, this is a very simple model.

We have assumed that the gas phase, the HCl and the nitric acid gas above the deliquescence solution is in equilibrium with the dissolved species. That acid gas is removed from the surface by transport across a thin boundary layer adjacent to the waste package surface; a stagnant boundary layer. And, the rate of static diffusion across that boundary layer. whose thickness is a function of the rate of advective flow down the drift.

Now, qualitatively, low flow you get a thick boundary layer; for a high flow you get a thin boundary layer, and I don't have exact numbers for those, but I'm going to look into some sensitivity analyses.

Next slide. Now, just to see what effect that has, our assumption is that on the far side of that boundary layer, there's a mechanism for removing that acid gas, so, really, it's just a steady state diffusion profile across this hypothetical boundary layer.

Next slide, please. This just attempts to show in pictorial form, so you have brine solution here. We have sealing equilibrium and kinetics here, the brine--this layer here represents our stagnant layer. So, exsolution and dissolution kinetics. And you have a boundary layer here whose thickness is dependent upon the rate of flow down the drift.

Next slide. And, so, I mispoke, I won’t be presenting any sensitivity analyses, I’m presenting one particular calculation. What we're doing here is estimating the flux of acid gas out of that brine layer, and this gives you the flux of acid gas. Based on these assumptions, the partial pressure is of the order of 10^{-8} bar, and I'm not distinguishing between HCl and nitric acid--more of a magnitude calculation. And, that's taken from Lawrence Livermore. So, these are high temperature partial pressures, which are assumed to be constant, and .2 centimeters squared per second gas phase diffusion coefficients.

And, here, I'm assuming a fairly thin boundary layer thickness due to high mass transfer, advective flow down the drift. So, that's the flux. Now, how much acid--how much of these species do we have to exsolve, or what would be removed from this brine? And, for a 1 micron thick brine solution, a 10 milligram solution, it's still about 10^{-6} moles per square centimeter. And, so, dividing one by the other, we come up with complete degassing in about 24 days.

This is, under these assumptions, a relatively rapid process. So, the most important parameters here, in determining the time is the boundary layer thickness, which depends upon how much advection you may have down the drift. And, also the partial pressure of these acid gases. Now, this essentially assumes that we're maintaining near neutral pH conditions in order to maintain such high partial pressures.

Now, we would argue that precipitation very of various salts, buffered by mineral phases in the dust, could well maintain a near-neutral pH and sustain that high partial pressure. We can debate that point later on.

But, under these assumptions, based on this relatively simple model, a relatively fast process. And, so, if that occurs, what will happen to those mineral assemblages. And, this is Assemblage B. So, we start off deliquescing at the same point as we did previously at Point A to 130 degrees and 122 degrees, and now, though, what we are saying is instead of the surface staying wet as the RH goes up,we have an effective degassing mechanism. And, so, within perhaps a 24 day period, that solution would lose the nitric acid, the mineral assemblage changes, the solution composition changes, and, in fact, the surface will dry out.

So, now under this degassing assumption, between point A and the next Point X, the waste package surface will be dry. And, what Point X is is there is a point in temperature/RH space where you would next get deliquescence, and that's due to primarily carbonate rich system, it's mostly sodium carbonate, and no low-RH deliquescence, and a much higher RH, much lower temperature. And, so, now we can put these Points A and X onto the next one. So, again, the time and temperature profile. And, so, we first get deliquescence here, but under this degassing assumption, we would get a dryout because of the acid degassing, and that between Point A and Point X on each of these curves, the waste package surface will actually be dry, only to redeliquesce, if you like, at Point X, as sodium carbonate.

But, similarly, we can go through the same exercise and calculate what the corrosion potentials and crevice repassivation potentials will be under those circumstances, and those are shown in these two right hand columns in this table. And this time, I again used the DOE corrosion model to predict the corrosion potential, but for the case of the carbonate salt, I'm trying to take into account the inhibition provided by the presence of carbonate, and, so, I've used the Center's crevice repassivation model, which we saw in Osvaldo's presentation, does include carbonate species, and, so I’ve used their model to calculate these crevice repassivation potentials.

And, on the next slide, we see that again, in most cases, the nitrate to chloride ratio is so high that it's off the screen. This is for the hot waste package. This is particularly low nitrate to chloride ratio in that particular case for the temperature of the deliquescence of certain carbonate solutions quite low, it goes to 80 degrees, but again, it's well below that cutoff for protection from corrosion. So, with this acid degassing we don't believe Assemblage B would initiate localized corrosion.

So, the last assemblage, Assemblage C, gives us a bit of trouble because it deliquesces at temperatures above the valid range for the EQ3/6 calculations. And, we heard that yesterday. And, so, when we try to do that calculation, the code fails to converge. And I can't show you a similar analysis because the code fails.

But qualitatively, we would expect the initial brine, if such a complex assemblage was present, would--it would as a consequence of degassing--transform into a carbonate-rich system. And, by analogy, the previous analysis of Assemblage B, we would argue that calcium carbonate precipitation plus the other minerals would maintain a pH near neutral, and we'd expect the surface to dry out after that initial wetting, only to redeliquesce at a much lower temperature, higher RH, to be a carbonate system. But, again, we would argue that the high nitrate to chloride ratio is likely to inhibit localized corrosion. But, I can't show you specific data because the code--.

In the event that localized corrosion did initiate, we'll just revisit this table one more time. And our argument is still is in that last box on the decision tree, and we still have stifling that would limit the extent of propagation.

So, in summary, based on the EPRI decision tree, we don’t believe that the issue of high temperature deliquescent solutions and the consequent possibility of localized corrosion is an issue. We have some differences of opinion about whether these complex, especially these four-salt systems, will be present along the surface. If they are present, we don't believe that they will lead to initiation with or without degassing.

In the unlikely event that they did initiate, we see strong evidence for stifling from a number of independent sources. So, we believe there's multiple lines of evidence, and particularly the argument is robust because we're taking data from several different sources, mutually consistent, and we believe this a strong argument, and, again, we don't believe that localized corrosion will initiate or propagate.

The last slide is just the decision tree.

LATANISION: Okay, thanks. Okay, let's take some questions. Charles?

BRYAN: Charles Bryan, Sandia.

I just had a couple comments. First, I'd like to remind you and other people that we do have experimental data that shows that the Assemblage B brines do deliquesce at, you know, over 200 degrees Centigrade. They transition to aqueous--to hydrous melts at 220. So, the modelling doesn't do an adequate job. We know that. Our model can't adequately predict deliquescence of those salts. The same thing with Assemblage 3.

KING: I'll just comment on that. There's still plenty of room between points where brines would form and protection versus corrosion cutoff, so--

BRYAN: Also, with respect to how long the brines last, we did the calculation, too. I'm not--our results are different. We did not show that we would expect it to get dryout under the conditions in the repository. And, I'm not sure about your calculations, but I would like to point out that at 10^{-8} bars, p-acid gas, our calculation suggests that the maximum amount of salt on the waste package would be about 2.8 milligrams per centimeter squared. That's equivalent to about 10 grams of nitrate on the first waste package. And, at 10^{-8} bars, in the atmosphere, you will require a equilibration of about 4 million cubic meters of air to degas all of that.

The calculation that this--I realize that would be a steady state, a closed system, you have a diffusive system, but I think there may be some problems there with the calculation if you're having it degas within 24 days.

KING: With our calculation or with your calculation?

BRYAN: One or the other.

KING: This is really a conceptual model.

BRYAN: At 10^{-8} bars, 10 grams, that's 4 million cubic meters of air.

KING: Well, like I say, our QA procedure, and I’ve rechecked those calculations several times.

LATANISION: Dave?

DUQUETTE: Figure 7, please. I only want to point out that Payer presented this morning--indicates that when the atmosphere is oxidizing, that--Duquette, Board.

I only want to point out that this morning's data presented by the Center, that red and blue dashed line that you have that indicate the corrosion potentials, moves up at least 200 and probably as much as 300 millivolts, once you have an oxidizing atmosphere versus a reducing atmosphere, which is what that data was based on. So, I think it's the autoclave data for the ternary system, so it doesn't change your entire model, but it does indicate that if you're going to do those comparisons, your nitrate to chloride ratio has to go up.

KING: Yeah, correct me if I'm wrong, these are the DOE corrosion potential measurements--

DUQUETTE: Correct.

KING: Which were in aerated systems.

REBAK: No, deaerated. Long term or short term?

KING: These are long term.

REBAK: Long term they are all aerated.

KING: So, these are aerated systems.

DUQUETTE: But, then, they're quite different from what was presented this morning, because those are at least 300 millivolts more noble than those numbers.

KING: I can redo the calculations, with the Center's corrosion potential.

DUQUETTE: Yeah, it doesn't change your story very much. It just changes the nitrate to chloride ratio, somewhat lower to somewhat higher values.

KING: And, very shallow slopes at this point. I think these are aerated data. Raul?

REBAK: For the corrosion potential, yes.

DUQUETTE: Okay. The second thing I want to look at, and I keep seeing these crevice propagation rates, and I think it's on Slide Number 13. And, that has to do with the stifling effect. Keep in mind that when you do these calculations, you're talking about a crevice that's growing, if I can do a conceptual model, the way it's normally presented, it's a horizontal crevice that's growing in the horizontal manner. You then go ahead and take that data, which is growing horizontally, and you start to talk about penetration into the package, with the other curves that you've indicated where you show the penetration rate of the package.

If you treat that crevice in a slightly different mode, because our laboratory results do a fixed crevice type experiment, and if you can think of a piece of dust, and I know you don't think that dust makes a very good crevice, but for my discussion, let's assume that it does. You create corrosion under that piece of dust, and you eat away some metal, and the piece of dust settles down and forms a new crevice, and keeps moving into the metal.

It's not the same as the stifling types of experiments that are indicated here, where you're talking about a crevice growing basically linearly or in a planar manner along the surface. I think one has to be very careful about applying these equations.

KING: Okay. I believe, and again, the experimentalists will correct me if I'm wrong, that these penetration depths are into the metal.

DUQUETTE: Yes.

KING: Are into the metal. They're not naturally across the surface, and, so, the data that we're using here are penetrations into the crevice.

DUQUETTE: Yes, it's that lenticular shape that you get coming out of the metal.

KING: So, under certain circumstances, precipitation of the corrosion product is an effective crevice.

DUQUETTE: Correct.

KING: But, those would have been taken into account in these measurements, and, indeed, often times we do see the deepest penetration not underneath the original crevice former, but around the edges of it, because that's where that nice precipitate is formed, and formed by that tight of crevice.

DUQUETTE: That's right.

KING: Those effects would have been taken into account in these experimental measurements. There were, in the EPRI model, which is my analogy, but I think with the Center's data and the Project's data would have taken that into account. These are penetrations into the metal not along the surface.

LATANISION: Raul, did you have a comment to make? I think you were about to comment when we--

REBAK: No.

LATANISION: All right. Yes?

XIHUA HE: Would you please go to Slide 15--Xihua He from CNWRA. Would you please go to Slide 15? May I ask what is the temperature for you to do the extrapolation?

KING: What was the temperature?

XIHUA HE: Yes.

KING: There's no particular temperature involved here. This, for the EPRI model, again this is my analogy of behavior of the other materials, the greatest variability here is the value of the exponent. The K term, or the B term, as you tend to call it, was I think determined by analogy of the materials at about 100 degrees Centigrade. This red line, that is your data. So--

XIHUA HE: Yes, 95, yes.

KING: 95. With the cupric chloride.

XIHUA HE: So, based on your--I'm asking for your extrapolation. Do you think it can be applied to high temperature region, or not?

KING: So, I don't have data--if you go back to the previous one? These are only three sets of data that I have. I can extrapolate that to higher temperatures. What I would suggest, I would remind you, we have arguments that nitrate will continue to be a good corrosion inhibitor at higher temperatures. And, as the temperature goes up, and the rate of nitrate reduction in the crevice increases, we see no reason why this would suddenly start to get a more rapid propagation of localized corrosion. But, I don't have data to support that.

LATANISION: Let's see, John?

WALTON: Okay, John Walton, Nye County.

Could we have Slide 8? What I didn't follow here is you have one process, nitrate reduction--it means a loss of nitrate in the crevice, and then down below you have another process that the transference number is higher for nitrate, and would increase nitrate relative to chloride in the crevice. So, since you have one process that decreases the ratio, another one that increases the ratio, how can you conclude what will happen to the ratio? On the relative rates of those two processes?

KING: We haven't done coupled transport model. I think you did a model once of crevice corrosion containing that.

WALTON: Yes, I have.

KING: We have to do something like that to see if the nitrate rate of consumption inside the crevice, due to the cathodic reduction, is greater than the rate of nitrate-- the electro migration--I shouldn't be so adamant, but those are counter-posing processes, you’re right. But, I want to point out that this is not a critical oxygen differential aeration cell. We have an effective mechanism here to get cathodic oxidant into the crevice. And, we believe that will be--that's one of the reasons why nitrate is good inhibitor of localized corrosion.

LATANISION: You're just taking the position that that dust shown is totally transparent, oxygen transparent?

KING: That was the other argument. That, and producing the dust layer to act as an effective crevice former. And, when you compare the rate of oxygen consumption due to passive corrosion to the rate of replenishment through the dust layer, we see a two to three order of magnitude difference. And, so, our claim is that an oxygen differential concentration cell won't be established because of the dust.

LATANISION: Go to Number 11--I jumped in. I'll come back. I mean, the oxygen differential, if you're interested, the oxygen on the fault surface, and the oxygen in the electrolyte here; right?

KING: Right.

LATANISION: And, are you assuming that this is totally transparent? There's absolutely no barrier between the oxygen--

KING: Well, I guess what I'm suggesting is that if you take into account the fact that this is, to some degree, a mass transport barrier, the rate of oxygen consumption here was, let's say, in the middle of this crevice former. The rate of consumption of oxygen is very small in comparison to the rate of diffusion through this dust layer and through this film of deliquescent layer. And, so, the oxygen concentration here is 99.9 percent of what it is here on the outside of the crevice. And, so, this will not form a--an oxygen differential cell between that point and this point, which is--I mean, that causes --one of the requirements in classic--

LATANISION: I agree. But, it is saying it's a transparent barrier.

KING: Well, yes, and it's 99.9 percent transparent, three orders of magnitude.

LATANISION: Yes.

YANG: With regard to the formation of concentration cell, you mentioned your argument made by salting in effect. Is that salting in effect--

KING: Yes, salting out.

YANG: Yes, salting out effect. Is that salting out effect based on mass transport, or is it based on thermodynamic potential?

KING: The salting out effect here is simply to say--it would be inappropriate to say that the oxygen concentration in that deliquescent solution is the same as that in water, because you have such a high salt content, you get salting out and so the oxygen concentration, the saturated oxygen concentration in that brine, is somewhat lower than you have in water is the salting out. And, what I'm saying is I'm taking that into account, and it lowers the solubility by a factor of four, or something. So, the solubility of oxygen in 10 molal calcium nitrate is one-fourth of what it is in water.

YANG: But, the chemical potential will be the same, the same fugacity--

KING: Yes. So, I'm not doing a rigorous calculation here. I'm using concentrations, no activities or fugacities at all.

YANG: Yes.

KING: In the concentration phase.

YANG: For a mass transport.

LATANISION: Other questions? Yes?

PENSADO: On Slide 15, your comment on the validity of this setup relating the propagation rate of this empirical equation to thousands of years? I see the propagation, and we have some limited data, and that if it's propagated to thousands of years may not be the reasonable approach. I'm asking your opinion on this.

KING: We don't know from Xihua's data, the crevice started in nine days, and I'm not saying here that it will propagate for 2000 years. Quite the opposite. We don't believe that it will. But, what I'm suggesting here, even if it did, I have no other data to go on, other than the short-term data that you, yourselves, and the Project, and from the literature. Based on that analysis, if it would continue for 2000 years, which we don't believe it would do, it would still get limited amount of penetration.

PENSADO: But, the equation in time, you've got the form of the equation of t to the Nth, do you think that when time goes to infinity, that the corrosion rate is equal to zero?

KING: Yep.

PENSADO: So, my question is whether that is appropriate due to propagation, given that we know that the limit is zero?

KING: Well, Xihua's data--you reach that number nine days. At nine days it repassivated.

PENSADO: Nine days it forms that trend, but my question is whether that can be propagated to a longer term?

KING: I'm not saying that it's going to propagate in 2000 years, this is just a mathematical extrapolation. In my opinion, Xihua's data shows it passivated after nine days. That, I think, is a better representation of what will happen on a waste package than this arithmetic calculation.

LATANISION: Okay, I have one final question I hope will be quick. Could you put Number 5 up? The question of preferential degassing of HCl over HNO_3, I thought I heard yesterday just the reverse.

KING: Yes. In some DOE documents I see the partial pressure of HCl is higher than that of nitric acid. But, yesterday, I forget who it was, was it you Leitei, said that sometimes you have variability in the data.

LATANISION: Yes.

YANG: Yang from the Center.

We measured the acidity. Also, we measured chloride and the nitrate in the condenser. We used that one to determine the degassing. We do not have consistent data.

KING: Calculations from the Project suggests that the partial pressure of HCl is higher than that of nitric acid, and, so, if degassing did occur, it would tend to increase the nitrate to chloride ratio in the remaining brine. Isn't that correct?

BRYAN: That's correct. That's based upon our thermodynamic database. There have been recent studies that have showed that potentially, that's not correct, that potentially, the nitric acid degasses more readily.

LATANISION: There's a comment in the back.

PALMER: David Palmer from Oak Ridge National Lab.

We've made measurements for Joe Payer's group, and measurements of partitioning constants of hydrochloric, nitric and hydrochloric and sulfuric acid, and they show that at least up to the temperature range up to 200 degrees, nitric acid is three times more. The partitioning constant for nitric acid to the steam is three times that of HCl. Hydrochloric is two or three time higher than that again.

I'd just ask one question, this may be a trivial one, but we spent ten years working for EPRI back in the 1990's measuring partitioning constants of acids and bases and salts. This work was done mainly for wet steam pipes. But, sodium chloride has a finite partitioning constant, even to 200 degrees C. And, we had a closed system, but we could still measure sodium chloride in the steam. With your open system with a thin layer where you have a high surface area to volume ratio. I wonder if any of the models consider the leakage or the loss of potassium nitrate, sodium chloride from those liquid films into vapor.

KING: What we have now, as you can see, is a very primary, simplistic, conceptual model. You're right. I used to work on steam generator corrosion, and I that partitioning of a certain chloride into the steam phase, and I think the partition coefficient we used was 10^{-6}. So, it does occur, and we didn't take into account here. But, if anything that’s enough to lead to faster drying out. It depends on the rate of removal from the vapor down the drift.

LATANISION: Okay, let's take a ten minute break. Thank you.

(Whereupon a 10 minute recess was taken)

LATANISION: Let's continue. Neil Brown, you're up.

BROWN: The title of my presentation is, "Development and Implementation of the Localized Corrosion Model." I've tried to combine just the raw mechanics with some pictures and drafts to make this presentation a little more interesting, so please bear with me.

I'd like to thank Kevin Mon and Raul Rebak for helping put together the presentation.

For the outline we're going to talk a little bit about in-drift exposure conditions, recognizing this is a repeat from a lot you've already heard, talk about the localized corrosion model for seepage conditions, and then the localized corrosion model for dust deliquescent conditions. It's important to keep in mind that on the project we do differentiate between the two corrosion regimes and then finally reach some conclusions.

The in-drift exposure conditions, as we've talked about many times before, the waste package goes through an initial thermal pulse followed by cooling, and the temperature where we get drift seepage is around 105 degrees Celsius--waste package's temperature, which is occurring between 100 and 2,000 years in the future depending upon the temperature of that particular waste package. I have included some brine solutions just for edification purposes.

Next slide. One thing that we haven't talked about today is general corrosion. It's important to note that the general corrosion model is always left on. We initiate general corrosion at the time of closure, and I have provided here a curve showing the blue curve is the best fit of the 60- and 90-degree Celsius data, and then it's extrapolated as a function of temperature.

Next slide. Now, the localized corrosion model for seepage is similar to several you've heard already today. We compared the long-term corrosion potential with the crevice repassivation potential; and if one's greater than the other, then it will initiate localized corrosion. It's important to note that once we initiate localized corrosion in seepage conditions that we do not turn it off. We leave it on. We don't resample as a function of chemistry or temperature. And the model is applied to 105 Celsius, which is the maximum possible temperature of the waste package when seepage could occur.

Another nuance that's important to recognize, however, is that if seepage were to occur at a relatively low relative humidity of 77 percent, we're concerned about salt separation, as we've heard from several people today and yesterday. So if salt separation were to occur, we're no longer quite certain where the nitrate--where the chlorides are going; and to account for this uncertainty, if seepage were to occur onto a waste package at low RH, we will initiate localized corrosion regardless of chemistry to account for salt separation.

The entire waste package surface is assumed to be susceptible to crevice corrosion, and this is conservative because crevice corrosion thresholds are less than pitting thresholds.

And then, finally, the model is fit to experimental data and accounts for associated uncertainty. We're not trying to screen out localized corrosion for seepage conditions.

Next slide. We haven't really talked about it much, but the long-term corrosion potential testing, as Rollo (phonetic) indicated, these are aerated conditions; and you can see the E-corr tends to drift upwards with time. To account for this, for our E-corr model we only use corrosion potential for experiments run for at least 300 days, and you can see the C-corr for various solutions.

Next slide, please. So with that said, C-corr is determined by long-term tests of at least 300 days. Now, this might sound a little schizophrenic as I talk, and the reason I say that is, we're in the process of redeveloping the model. So what we have available for modeling for our revision is over 55 different test conditions, and you can see the range of conditions, temperature up to 155 C, a very wide range of pH, nitrate, chloride, nitrate to chloride ratio. And then, finally, down below our corrosion potential model. I've left off the coefficients, because they're going to be changing, but basically it's a function of temperature, pH, chloride concentration, and nitrate to chloride ratio.

Next slide, please. So the crevice repassivation model, these tests are obtained from cyclic polarization. We have over 90 test conditions available, once again a wide range of temperature, pH, nitrate/chloride ratios, and you see the repassivation model is based upon a base model plus the effect of nitrate, and the two equations are shown below. The important thing to note here, once again, is--of temperature, pH, chloride, nitrate, and nitrate/chloride ratio. We do not account for sulfate, primarily because we weren't certain at the time the model was being developed how much sulfate would be present, and we recognize it's conservative to ignore the sulfate contribution.

Next slide, please. So with that said, just to throw in a slide to show--and this was shown by Raul earlier yesterday--you see that as nitrate/chloride ratio increases--all these are at a 110 degrees Celsius--as your nitrate/chloride ratio increases, the quantity of localized corrosion is greatly reduced and stops.

Next slide. So taking all of the data, fitting curves to the data, we arrived at the following conditions. Upper left-hand corner, this slide view is a non-representative solution. As Charles mentioned yesterday, we expect to have a pH of around 4 to 10; but given some uncertainty, as he said, plus or minus 1 pH, then it is conceivable that we could sample this regime. So we have a fairly low nitrate/chloride ratio, and you can see the corrosion potential is above the repassivation potential for all temperatures. So if this condition were to occur, our model would initiate localized corrosion.

Going down to the lower left, we've kept the conditions the same. We're at a 0.5 nitrate/chloride ratio, we have a pH of 7 at this point, however, and you can see that the localized corrosion is going to be possibly occurring starting at 100 degrees--I'm sorry, starting at about 70 degrees on up.

And then going up over to the upper right where I've increased the amount of nitrate, kept the pH the same, we now see the E-rcrev is above E-corr for all temperatures, so the model would assume that no localized corrosion occurs for that particular conditions.

And then increasing both the nitrate ratio and lowering the pH to 3, you can see at this point that E-corr is above E-rcrev, depending upon where you are in probability space, so we would expect to see some localized corrosion somewhere around 100 degrees Celsius.

The important thing to note here is that we're sampling for uncertainty on the E-corr and E-rcrev separately, and we do use the covariance matrix, so we've accounted for all uncertainty.

Next slide, please. With that said, for seepage conditions, how are we treating propagation? And we're treating propagation very conservatively. Once localized corrosion initiates, we apply that corrosion rate until penetration occurs. In other words, we don't take credit for stifling, we don't resample to see if it should have turned off due to new temperature or new chemistry. The rates that we use are, as you can see, 12.7 to 1,270 microns per year. This is sampled log uniformly. Lacking project data, we went to handbook data and chose the following solutions to represent our penetration rates, and you can see the boiling hydrochloric acid or iron chloride solution. So we believe that these adequately represent extremely aggressive environments that you might find inside a crevice.

Next slide. Just bringing it back to what we've talked about before. The nitrate chloride ratio is required to go up as your solution temperature goes up; otherwise, you would have boiling. And so the region in the yellow is the region we're talking about for seepage conditions where we expect to have nitrate chloride ratios above .125. And then as we move into the dust deliquescence region, which is the rest of the talk, the nitrate chloride ratios by definition have to be significantly higher.

Next slide. For dust deliquescent conditions, as we said before, above 105 Celsius liquid can only exist as the result of salt deliquescence, and we screen this out on the basis of low consequence. I've really liked other people's, and I wish I had not thought of that myself--the fault tree--but bear with me. We've all seen the fault tree, so you can imagine it over here on the left-hand side. In order for localized corrosion due to dust deliquescence to occur, we must answer yes to all five questions.

We've talked about question number 1: Can multiple-salt deliquescent brines form at elevated temperature? The answer is "yes." I think a subset of that question would be: Can they exist for Yucca Mountain salts? That's not on the question list, but clearly for number 1 we have to answer "yes." I'm not certain it's the case for salts contained in Yucca Mountain dust.

However, question number 2: If they form at elevated temperature, will they persist? Our answer here is "sometimes." It depends upon the composition but "sometimes" isn't a fair answer, so I guess we'd have to say "yes," because we can't exclude the possibility of them persisting.

On question number 3: Will they be corrosive? The project's answer to this question is "no." As we have been talking about ad nauseam, your nitrate chloride ratio has to get significantly higher as you move up in temperature. And

I've put up here just to remember the autoclave test where we did see minor amounts of localized corrosion, and you can see those autoclave tests really have no bearing on physical reality, because, first of all, their molarity is too low, and their nitrate chloride ratio is too low. Those conditions just can't exist except in a pressurized system.

On some more relevant data, we've shown here at 125, 150-degree Celsius at various chloride ratios, you can see we don't see localized corrosion or historesis on the curves, showing the high nitrate brines inhibited localized corrosion even at high temperature.

And then question number 4: If they were potentially corrosive, will they initiate localized corrosion? Well, first of all, since the answer to number 3 is "no," we probably shouldn't even be answering this question; but if number 3 were "yes," what would this answer be? The answer would be, "no, not under relevant repository conditions." As we've talked about, there is a very limited volume of water, approximately 18 microns thick at the maximum volume, and much of the brine will be held up in the dust. And as we've heard at a much more scientific level than I've got time to go into today, the small-scale and rapid mass transport will hinder establishment of chemical gradients. We heard earlier today that several orders of magnitude on transportation rate on oxygen, so we would not expect there to be oxygen depletion, and so we would not see separation of the cathode and the anode.

And then once initiated, will localized corrosion penetrate the waste package outer barrier? Our answer to this question is, "no." As EPRI just presented, once you start to use a power law using experimental coefficients, the rates are greatly reduced as a function of time; and the limited experimental results indicate that the depth of attack may be limited. And, finally, limited brine volumes and sequestration in corrosion products, this limits the amount of chlorine available for reaction. And corrosion products can also limit the extent of the crevice corrosion.

And just to keep some other data, this is showing current as a function of time for several different conditions up to 155 degrees Celsius. And you can see with time that the current slows down, indicating that localized corrosion is stifling and we're approaching steady state.

So with that said, our dust deliquescence screening argument--and this is all documented in our report--we say that brines can exist, that they sometimes will persist, but they will not be corrosive under relevant environments, they won't initiate localized corrosion, and if they were to initiate, they would not penetrate the outer barrier. And, therefore, on this basis, we've screened out dust deliquescence.

Next side. So, finally, in conclusion, the department's localized corrosion model is based upon experimental data that's implemented for seepage conditions. It takes into account uncertainty in both the environment, which is accounted for through other models, as well as experimental uncertainty for corrosion; and it's unlikely to occur in nitrate containing neutral brines, as we saw. If the pH is dropped significantly, we might get some initiation, which is similar to the results shown the Center. And then we screen out localized corrosion due to dust deliquescence.

So with that, I'm open for questions.

LATANISION: Any questions? Yes, John.

WALTON: John Walton, Nye County.

So could you just briefly tell us, if you've screened it out from dust deliquescence but you have a localized corrosion model, I think very few people in here really understand what localized corrosion model you're actually going to include. Could you just briefly tell us what that is and how often it's likely to occur?

BROWN: I can describe the mechanisms but not the probabilities. The mechanisms are, if seepage water were to contact the waste package. So when seepage water returns to the drift, seepage occurs if it contacts the waste package, then we would initiate that localized corrosion model, compare crevice to E-rcrev, and see if localized corrosion initiates.

WALTON: So if somehow the drip shield failed or got crushed or something and seepage got through, then you'd have some localized corrosion; is that right?

BROWN: Yes.

LATANISION: Let me understand that. Are you talking about pitting corrosion, or are you talking about crevice corrosion in that situation?

BROWN: Crevice corrosion.

LATANISION: What creates the crevice?

BROWN: We model crevice corrosion even if a crevice is not present, because the likelihood of crevice corrosion is greater than pitting corrosion, so we model crevice corrosion even in the absence of a crevice.

LATANISION: So just to follow that, if there were, for example--I mean, this is a welded structure--so if there were, for example, a weld defect, that would constitute a crevice that could become activated.

BROWN: Yes.

LATANISION: But at this point you have no specific crevice geometry in your focus?

BROWN: That is correct. No specific crevice geometry.

LATANISION: And your penetration rate would be, then, what your table was or that exponentially declining rate?

BROWN: It would be what the table is. We do not exponentially decay the rate. We believe we could with further data, but do not have sufficient data to do so at this time.

MON: Kevin Mon.

Let me see, I guess the waste package pallet is a potential crevice, as are mineral deposits on the waste package, what have you?

LATANISION: Non-deliquescent mineral deposits.

MON: Yeah, right.

LATANISION: Okay. Dave.

DUQUETTE: Duquette, Board.

Let's go back to Slide Number 19, which, of course, is your decision tree. We heard some data this morning--and this may be changing my mind about some of the thoughts I've been having over this couple of days of corrosion work. We heard some comments this morning that you might get general corrosion rates as high as 10 microns per year, and we also saw from Raul's data that he's getting at least some discoloration in short-term tests even if he's not getting crevice corrosion.

I think, relative to localized corrosion, you may be able to deal with 3 from the deliquescence point of view; but you may not be able to from the general corrosion point of view. And if we go to--I think it's the next slide--maybe it's not, maybe it's the slide before that--yeah. And Joe Payer may want to address that. That's, of course, a logarithmic plot, and it's not really fair to put zero over there on the left. I think that's 5 times 10 of a minus 5; and I think if you were to take those currents and divide by the actual crevice areas that are present, you might come up with some pretty high corrosion rates if that really is 5 times 10 of a minus 5.

PAYER: I could comment on that. It's a little misleading in the way it's--

DUQUETTE: So what are those current densities--current densities, not currents--in that area?

Joe, do you want to--

PAYER: This is Raul's data, but in some of the other tests we showed--but my guess is it's a similar story. On some of the slides that we showed in the Payer-Kelly presentation--that showed with the multi-crevice former, there is an incubation time. Prior to the incubation time, the current to the sample to hold it at constant potential is the passive current on the order of 10 to minus 8 amps/cm_2 based on entire. That can go up to 5, 10, or more microamps during the active stage, and then it decays back on down to that passive corrosion rate, currents down on the order of 10 to minus 8, 10 to minus 9. And I believe Xihua's single crevice data also showed where she showed it started and then arrests. When it arrests, it arrests back down to the passive corrosion range.

BROWN: And with regards to the rest of your question, we are accounting for general corrosion. We do turn it on irrespective of seepage condition.

DUQUETTE: Well, this isn't in the deliquescent stage.

BROWN: We turn on general corrosion at time of closure regardless of condition.

LATANISION: Let me just follow up on Dave's comment. If you're getting 10 microns per year, that's a half a mill per year; right? Half a mill and you've got 2 centimeters of C-22, what's that, about 8/10 of an inch, 800 mills? In 1600 years you're gone. Is that correct?

AHN: 2000 years.

LATANISION: 2000 years. The C-22 disappears in--the C-22 is gone in 2000 years?

YANG: Lietai Yang from the Center.

If you talk about the general corrosion, we say it's general corrosion, but don't think as uniform corrosion. Always not uniform. You have valleys and you have peaks, but you need to characterize it as a general corrosion, but still it's not uniform. So if you calculate--2000 years, maybe you don't use the--you need to--

LATANISION: Maybe I'm missing just--and I didn't hear all that.

YANG: I just want to clarify. When we say general corrosion or localized corrosion, for general corrosion most people think it's a uniform corrosion. So my point is, even though it is characterized as general corrosion, still it's not a uniform corrosion.

LATANISION: Well, if it's any corrosion at a half mill per year, and it's penetrating in 2000 years, does that not represent a problem, or am I missing something? Go ahead.

AHN: Tae Ahn.

Also, we are talking here only corrosion penetration actual--there are other mechanisms which can lead to waste package failure. For instance, in this presentation--and I will reiterate that--if you think the waste package layer, rock--may cause a mechanical failure--so the corrosion here, just corrosion penetration.

LATANISION: I'm only concerned about this now, I think, because we really--the Board had a workshop before I joined the Board on long-term passivity, and I think that meeting concluded with an estimate that there would be a million years of uniform corrosion resistance. All of a sudden I'm hearing some sort of corrosion. Whether I'm missing it or not, I don't know, but some form of corrosion is going to compromise 2 centimeters of C-22 eventually in 2000 years. That's a big difference.

SANTOS: Al Santos, NRC.

Lietai's data is for 160 degrees C. So that's only for about a 30- to 50-year, maybe, window. So it's not 2000 years.

MON: This is Kevin Mon.

So let's suppose above 160 degrees, you get 10 microns per year, what do we have? 200 years?

SPEAKER: 2000.

MON: We have about 2000 years of--

SPEAKER: It's gone in 2000 years at that rate; right?

MON: Yeah, but we're not at 160 degrees for 2000 years. We're above 160 degrees for maybe 200 years--maybe--and you can see that for most of it, we don't even get to 160. So if only a small fraction of the water packages are going to see this high rate, if it is indeed 10 microns per year, it's only going to be--

LATANISION: Do we have a temperature dependence of the uniform corrosion rate?

MON: Okay, so this is what is currently implemented in TSPA. As Neil said, we are refitting the corrosion rates, and obviously we're going to evaluate the corrosion rates measured by the Center. But you can see the rule we get at 220 is more in the range of .1--well, in the median maybe .2, .25. So this is the lower bound and upper bound CDFs.

KADAK: What's the unit--

MON: Millimeters per year.

KADAK: So you're off by a factor of what?

MON: Well, if 10 is correct, it's off by about--a little less than that.

KADAK: Kadak, Board.

What troubled me about the earlier data that the Center put up was the trend, and I think you even raised the point. And that is, as a function of time, apparently the corrosion rate goes down, and we only ran it for--I forget the number of days it was. And I guess I don't understand the quality of the experiments to be able to have such performance upon which we may be basing an opinion about whether or not generalized corrosion is a problem even if there is elevated temperatures.

So could you just comment on the quality assurance of your testing program as well as the implication that the corrosion rate is not going to change with time--has changed with time?

YANG: Lietai Yang from the Center.

Our test were performed according to our quality assurance procedure, which was audited once a year. As a matter of fact, this report was audited just four months ago. The other thing I'd like to mention is, our test was done short-term. So if we talk about 2000 years or 1000 years, longer term test should be conducted, so the rate may be--

MON: I suppose I should clarify. Yes, the CNWRA comparison was with, I think, 49 to 60 days your tests were, and they compared it to our maybe 120-day tests. These data here are based on the five-year long-term corrosion test facility--and let me fit a CEF to it--and then using a number of polarization resistance tests, we managed to get a temperature dependence. So that's how we're getting, you know, extrapolating out to higher temperatures.

LATANISION: These are the autoclave tests?

MON: No. These were the long-term corrosion test facility five-year immersion data points here, and so those were at 60 and 90 degrees, and then we basically did a lot of temperature-dependent tests between, I guess, 25 to 160 or so and extrapolated a little bit if we were to go to this 220.

KADAK: So how do you explain the difference?

MON: Well, which difference in particular? First off, one reason the--rate might be lower is because of basing the five year, so longer time periods. So lower overall corrosion rates would be expected after five years of exposure versus 50 days.

Is that the answer to your question?

KADAK: You're talking about significant different areas of magnitude between corrosion rates. Now, is that just purely a function of time?

MON: Indeed, it can be

KADAK: Even with elevated temperatures? So what should the safety case be made on? Which is the corrosion rate? What is the corrosion rate? Are we looking at package in 2000 years that will be full of holes, or are we looking at a million-year package?

MON: Well, I don't think you're looking at a million-year package, but you're not looking at a 2000-year package.

KADAK: Help me in the middle.

BROWN: This is Neil Brown with BSC.

The project at this time stands behind our data. We just recently became aware of the Center data. We've got some concerns about the Center data. The trends don't seem to match between temperature and time. There is a large scatter in their data. We're going to be evaluating to understand their data, but at this time our model is going to remain with the long-term corrosion test facility data. But we will be considering that data.

MORGENSTEIN: Maury.

Based on your data, I presume then, in a conservative way, we would enter the NRC's potential blind period with about a 10 percent loss in C-22, just based on general corrosion. Is that correct or not?

BROWN: Can we put that up--the temperature transient showing the brine period? I think that came from--

MORGENSTEIN: So do we have a 10 percent loss at least or thereabouts due to general corrosion during that period?

BROWN: Not using the Project's data. If you were to use the Center's data, perhaps as much as 10 percent.

MORGENSTEIN: But what are we doing at--for 200 years?

BROWN: Our model currently uses the Project's data and applies it from time of closure onward using the general corrosion rates that we showed on Slide 4.

LATANISION: Okay, let's go on to Joe.

PAYER: Joe Payer, Case.

I'm not sure how it's handled in the model, but in the mountain there is no seepage that occurs during this time period. You can't have seepage at 160 degrees on the waste package, so we're talking about the time period of dust deliquescence, and you don't have the samples immersed in beakers and liters of solution. So it's just saying, okay, I can put a sample in a liter of solution in a teacup, and it corrodes at this very high rate. The reason it corrodes at so much higher a rate in this versus the data the Project's using is the environment. So his long-term test facilities weren't run in these nitrate chloride-type environments. They were done for environments that are more likely to occur during the seepage period.

So it's apples and oranges or chickens and oranges. You cannot have these conditions. You don't have that solution in contact with the waste packages during that time period. The amount of those solutions--again, we've gone through it on several occasions here--are microliter droplets distributed in aluminum silicate particles, and so it doesn't compute. You don't have that. So you're not going to have perforated waste packages due to this general corrosion.

Now, the Project appears to have an issue here of how they're going to treat general corrosion and rethink that based on some of this data, I would guess.

LATANISION: Yes, go ahead.

RUBENSTEIN: Jim Rubenstein, NRC.

I'm going to say things that are similar to what Joe said. The question is not the quality of the Center data, I don't believe. I think it's the purpose of the experiment. They measured general corrosion in an experimental design to look for localized corrosion under these conditions. And I think if your department is going to evaluate all the data that are out there and select what they consider a reasonable range, they can encompass the uncertainty and justify what data they use and what data they think is relevant.

So I'd just caution people not to focus on whatever number happens to turn up in the last hour and extrapolate that--.

LATANISION: I think you and Joe have both made a good point. On the other hand, it is a little unsettling that I don't think you expected to see localized corrosion--

corrosion in those crevice corrosion tests. The corrosion is outside the crevice. That wasn't on my mind when we organized this meeting as a potential issue. So I am a little surprised, but--go ahead.

WALTON: John Walton, Nye County.

Could you explain to me--when the Center brought out their data, they--into oxidizing conditions, so--under oxidizing conditions exposed to the atmosphere somehow or what?

BROWN: Yes. On Slide 4, this is based on long-term corrosion tests at 60- and 90-degree C five years aerating conditions. And these are aerated--part of the difference is they were running theirs at 160 Celsius. We do have long-term tests where we--corrosion potential. We'll go look at those to see if we can form conclusions from those and try to make sense of this.

KING: Fraser King, Consultant for EPRI.

Can you tell me what the activation energy is?

BROWN: Kevin can.

MON: This is Kevin Mon.

I believe this activation energy is about 26 kilojoules per mole.

KING: So is there a reasonably high temperature dependence, and so--will decrease with--decrease in temperature, so--10 microns per year for 2000 years--10 microns per year for a few years decrease--.

MON: Right.

KING: The second question, on Slide 7, the corrosion potential model, you said you were revisiting that, extending the range of conditions or temperature range or--

MON: Since the last time our report was published, we've gathered a lot more data, and we're looking at all the data. We haven't decided exactly what we're going to do. You asked to extend the range. We're not certain it makes sense to extend the model upward to, say, 150 Celsius, because those conditions can't exist with low nitrate chloride ratio. But we're going to be looking at all the data and determining what data to use for the model. We might not extend the model upwards in temperature.

AHN: I would like to mention that--to understand--deliquescent conditions. However--simulate--to use the conditions to--. I believe this is beyond the scope of this workshop. That should be covered in other places where there are simulation--.

YANG: Lietai Yang from the Center.

Regarding the passive--long-term test. The other one use the short-term electrochemical test--. Now the short-term electrochemical test showing the localized corrosion under deaerated condition. However, these long-term tests show the localized corrosion, the ratio of nitrate to chloride was 7.4. But it seems to me there is no--12--16. There is no such long-term test to--the conclusion that no localized corrosion will take place.

BROWN: Well, we do have the long-term E-corr tests that have been run at up to 155 degrees Celsius, but to go beyond that you're forced to use something currently like an autoclave. The Project is looking at some other experimental conditions, but we don't have those to present.

YANG: For these tests--corrosion, what's the boundary? Under deaerated condition--. For the deaerated condition, you--you have--E-corr--we dry the oxygen out, we dry the air out. In those location, you--location--reducing the environment--autoclave test--is simulating that environment.

BROWN: But you still would have to have a high nitrate chloride ratio in order for a brine to exist in those conditions, and the autoclave test is--atmosphere, so it's just not relevant.

YANG: But based on Questions Number 1 and 2, they are all here.

BROWN: And we'd agree. 1 and 2 are "yes."

YANG: Yes. So you have a salt.

BROWN: We agree there is a salt.

YANG: And the salt may be persistent.

BROWN: And the salt may be persistent. We agree.

LATANISION: I'm glad we have agreement. I think, unless there is another burning question, we should move on to the final paper in this afternoon. And it couldn't be better timed.

AHN: Tae Ahn. This talk is by myself and Yi-Ming Pan. I want to summarize what the Center and the NRC side presented. I'd like to give some examples of how we consider this (unintelligible) in relation to waste package corrosion. In addition to our four speakers on the NRC side, I would like to also acknowledge three more people in the end --Xihua He, H. Jung and Osvaldo Pensado.

Next slide, please. I mentioned to you initially we prepared our presentation focusing on the localized corrosion. However, as you heard from the first experimental data, at elevated temperature up to 180 degrees C by Lietai Yang, we recognized that general corrosion is a major attack mode under those deliquescence conditions.

On the other hand, also we recognize by Xihua He, near the boiling point localized corrosion was really stifled and repassivated and slowed down on the propagation. Therefore, I'd like to give a couple of examples of the risk insights in relation to the issue. One is in general corrosion. The other one is localized corrosion.

Those two cannot be separated because the breakdown of passive film leads, most likely to localized corrosion. However, in the NRC's current risk insight report, it is suggested that the general corrosion or uniform corrosion has a higher risk compared with localized corrosion. The reason is that it could often be a bigger area to release the radionuclide. For instance, if you lose the passivity under some conditions, for example, Russ Jones mentioned about--you could increase the area open in the waste package that leads to more radionuclide release.

On the other hand, localized corrosion is very significant in terms of propagation, and under many instances, it could be very restricted area, such as near boiling point, you could have a crevice under pallet or a rock contacting a weld area such as (unintelligible), and the open area could be restricted.

There are a number of factors involved in these assessments other than open area. In the open area what you have is water inflow rate will be very restricted into the waste form to mobilize the radionuclide. Once you mobilize the radionuclide, the radionuclide is released out, and will be also restricted. Therefore, I would like to give you a couple of examples related to general corrosion and the restricted opening of the waste package. The risk can be assessed in many different ways. Osvaldo Pensado showed about 8 to 26 percent of the waste package purely based on rescission conditions of localized corrosion.

The waste package failure rate is one example of this assessment. The other one is dose calculations through the holes we have--radionuclide release can be calculated in terms of dose, and see what kind of release it sees. So, I would like to show you two cases. Then, I will go over the NRC work, considering how we considered the risk insights in its work. Then I will try to come out with – as of today - what kind of risk insights we have in relation to waste package corrosion, and I will summarize the path forward.

Next slide, please. This is the first NRC risk insight report. The uncertainties in long-term persistence of passive film has a very high risk insight here, especially as Lietai showed at high temperatures, this is true. Actually, this uncertainty is prevailing from very low temperatures up to 180 degrees C so far we saw. And, given the TSPA--given the passive current density, there is assumptions that the persistence of passive film is a very long time. Assurance of extremely low general corrosion rates is to be considered.

We are studying that, I would like to highlight a couple of issues involved. It could be propagated at--especially at high temperatures where Lietai showed the uniform corrosion on deliquescent solution. One case is structural change, micro-structure from amorphous to crystalline. Various defects, including point defects, compact and porous, or a void formation at interface between passive film and metal that can lead to spallation under certain conditions.

And, change of chemical compositions in the long term period time is another issue. For instance, de-alloying or--passive film composition may change. Thickness changes with time, especially at high temperatures. The contacted layer thickness could be very thin. They could change the corrosion rate or perhaps the passivity itself.

Other examples include anodic sulfur segregation which Russ Jones today addressed about that. Development of porous structure. Mechanical spallation at the film interface. And, development of large cathodic surface area from the corrosion product accumulation. Anion selective sorption in the corrosion product. I don't want to go over all of them, but one important thing is, especially at high temperatures, the uncertainties were further considered here. And, I'll give you one example; take anodic sulfur segregation.

Next slide. Formation of a sulfur monolayer may increase the general corrosion rate. Actually, I based that on Jones' paper, a recent paper. He showed that he--actually moly-sulfur can be removed as sulfur is accumulated at the film and metal interface. At that point, also, he showed removal of moly-sulfur--during that removal period we cannot consider the passivity. Therefore, we conducted simple calculations, slow passive corrosion rate times the time period of slow corrosion, plus fast corrosion rate during the removal period. It's a more active corrosion or increase the passive corrosion rate here times the time periods of fast corrosion. These two terms will be cyclic. Therefore, you should sum them to assess the penetration depth, counting in the sulfur monolayer segregation.

The slow corrosion rate is from passive current density of Alloy 22, and that the time period is basically sulfur segregation time. Jones postulated one time 500 years. And, fast corrosion rate obtained that from potentiostatic current transient of Alloy 22. And, again, from that transient, the average time period of passive corrosion.

Under normal conditions for passive current density time period for slow corrosion here of 500, from the current transient, you don't decrease the penetration time. You could increase the fast corrosion time, as shown in a different case, or (unintelligible) and/or increase the surface induced passive corrosion rate, as well as the prolonged active corrosion time, such as when the sulfide will not be dissolved rapidly with moly, you could expect longer time of active corrosion rate. Then you could see some sensitivity of rates after the penetration time.

What I'm presenting is not for prediction. I'm giving you additional information, maybe leading to rule out the formation of a sulfur monolayer.

The next example is--our next slide, please? Restricted opening of the waste package surface. At higher temperatures, above 150 degrees C, under deliquescent conditions, we observed uniform corrosion is prominent corrosion mechanism. Around the boiling point, however, crevice corrosion initiates, but quickly stops except for a very limited number of pits. This is Xihua's paper, measured current density and potential, within a single crevice assembly for Alloy 22 specimen in 5 molar NaCl with an addition of copper chloride at 95 degrees C. Initially, the crevice corrosion was over a wide crevice area. However, as time goes on, the potential drops and current density decay away. And, in this particular test, only one single corroded site persisted and grew to a greater depth than the area.

Xihua's propagation rate decreases with time. Also, that was obtained at constant temperature, at least remember that the constant temperature also decreases as time goes on. As long as the propagation rate at 95 degrees C is slow, at some point as temperature drops the pit propagation may stop. Also, even if you continuously propagate, a very limited area will be opened. This could happen, and any situation--one possible reason there will be potential distribution inside a crevice if I ask where there might be potential distribution in the future.

And, there are other limitations, too. Many people talked about limited groundwater volumes, restricted crevice area. This is from seepage water, therefore, the crevice area is very restricted, only the welded area perhaps easily susceptible to crevice corrosion. Also, there's rock fall contacting the pillar, a very limited area. Therefore, overall, the opening area is very restricted. I assure you the opening area has in terms of radionuclides release. As I mentioned water intrusion will be very limited. Also, we believe the radionuclide will be very limited as well.

Next slide shows the sensitivity analyses of restricted opening of the waste package surface. This was conducted using NRC performance assessment code, TPA4. Sensitivity study of restricted opening shows a clear relationship to dose. And, analysis assumes a log-uniform distribution of crack opening, I mean perforation opening, to simulate the pinhole or hairline cracks. The sensitivity study simulates a range of pit sizes 10^{-4}, 10^{-1} centimeter, and density from 10^{-1} – hundred number per square centimeter from the literature data. That literature data was from pitting. It's stainless steel, if you're into pitting. Some of them are from NIST long-term underground corrosion test results. But there is no specific data for Alloy 22 except what Xihua is right now considering to measure some of the restricted area.

The next slide shows using the literature data, the upper curve is the--almost 87 percent of the waste package failure, or 100 percent opening of each waste package shows the salt about 3.5, 3.7 milligrams per year. However, you can see the crevice, very conservative type area because it was obtained from propagating pits for underground corrosion. You could have much lower dose, less than .5 milligrams in the time period of 10,000 years.

Dose, the opening area data are very conservative here. We conducted more numerically lowering the opening area fraction. One is the pore opening-- .1, 10^{-2} t. You can see the reduction of the dose in order of magnitude along with this shift in the opening area. It's up to 100,000 years. This indicates there is a good correlation of the dose versus the opening area. What I would like to mention here is we proceeded--two things. One is the persistence of a uniform passive layer is needed to be evaluated further. We have somebody that will need to be evaluated further. Also, if we consider the restricted area or stifling or repassivation of the localized corrosion, we couldn't see the higher risk in uniform corrosion.

The next slide shows--keep in mind passive current - persistence of passive film in (unintelligible) corrosion, in restricted area from localized corrosion. I'd like to go over (unintelligible).

Brines formed from salt mixtures at elevated temperatures are more likely to result in general corrosion than localized corrosion. And, the failures here are 1 micron, 10 micron have only very narrow window of high temperature. It doesn't persist, you know, a very long period of time because the rise in temperature will decrease gradually.

And, as I indicated, mechanical interaction as the waste package becomes thinner, we need to take into account in the total risk analyses. Longer-term tests are ongoing to evaluate uncertainties in general corrosion rates, and the localized corrosion susceptibility, especially at elevated temperatures.

The next slide shows brines that form by evaporation of the seepage water are most likely benign. This is presented by Bobby Pabalan. But, some compositions, this is near the boiling point, compositions could initiate localized corrosion of the waste package. However, the contact of seepage may be prevented by our drip shield, you know, for a long period of time. The localized corrosion, also, susceptibility decreases with decreasing temperature. However, there is a potential of drip shield failure in longer period of time. As Osvaldo mentioned, the seepage would contact the waste package at close to 100 degrees C, localized corrosion should be considered in performance assessments.

Next slide, this is Bobby Pabalan's. Discussions were made by other people, the importance of nitrate here. And, again, near the boiling point, we show strong tendency of the stifling and repassivation. However, at elevated temperature, uncertainty needs to be further evaluated.

Next slide shows as of today, general corrosion appears to be a more significant process than localized corrosion. Uncertain effects from long-term chemical or structural changes in passive film stability warrant additional consideration. Crevice corrosion showed a strong tendency of stifling and repassivation near boiling. Crevice corrosion of the waste package could be the result of a small opening area, which limits potential for the radionuclide release. However, once the brines contact the waste package, we need to consider localized corrosion in performance assessment.

Path forward. We understand and better constrain conditions and mechanisms of localized corrosion and general corrosion. To reduce data and model uncertainties, additional model support and data will be continued in many different areas. An example is effects of long-term chemical or structural changes in passive film stability, and elevated temperature effects on corrosion rate, especially monitor localized corrosion susceptibility on the deliquescent conditions.

And, the next slide. Chemistry of the water contacting engineered barrier, we may update thermodynamic analyses. We need to consider the effect of drift degradation, which we're not really discussing in this workshop. Further sampling and characterization of Yucca Mountain dust may be needed.

And, crevice corrosion initiation and propagation tests. Corrosion supported by dust deliquescent salts and thin film water, and tests to monitor further stifling and repassivation. Measurements of opening area from crevice corrosion.

Corrosion model to support independent total system performance assessments. Long-term stability of passive film as bases for our general corrosion rates, and stifling and repassivation, and extent of surface damage.

Finally, to conduct integrated confirmatory tests on corrosion and evolution of near-field chemistry will be presented in the near future.

Thank you.

LATANISION: Okay, let's take some questions. Charles, let me ask you what's your sense of review from corrosion, general corrosion issues?

BRYAN: Well, I'm the wrong person to ask about that.

I’m not a corrosion expert. Raul can answer.

REBAK: I thought this was a symposium or workshop on localized corrosion, not on general corrosion. But, yeah, people maintain, or the Board seemed to be surprised at these 10 micrometers per year. You know, from the industry point of view, that's nothing, of course. And, the point of view is they take the short-term, you know, it’s about 49 days, or something like that, and at 150 degrees C seems to be decreasing in time, and fully immersed specimen, so there's unlimited amount of brine there for a small specimen. And, the point is also regarding those conditions for 150 degrees C, and that nitrate over chloride concentrations, so that's not a long--so, the waste package is not going to be a long period of time that it will be in those conditions.

So, things are very preliminary right now and we may have to--our data that we use for the model is much longer term, five years, and now we are having ten years data. So, we are going to analyze those one and see how they fit together with this data.

BRYAN: I would add a comment with respect to generalized corrosion. At least with respect to the dust deliquescence, that there will be very, very small amounts of liquid, the generalized corrosion rates that we're using are based upon inundated conditions. In these very small amounts of liquid, there is no reservoir for dissolved oxides. You know, if generalized corrosion can be characterized--or the thickness of the oxide layer can be characterized as a function of dissolution of the oxide relative to oxidation of the metal underneath. In the case of dust deliquescence, there is no reservoir for the oxide to dissolve into. So, I don't know how relevant--the generalized corrosion rate measured in saturated inundated conditions are.

LATANISION: Yes?

YANG: Lietai Yang from the Center.

Regarding the reservoir, unless you have a mechanism to remove the salt, I don't understand how that reservoir works. If you have a corrosion product--if there is a mechanism to remove salt, then I agree with you. Otherwise, the salt in the (unintelligible), the salt is not participating in the reaction, it is not being consumed> If you form oxide, oxide just deposits. So, you still have salt. You have to have a mechanism to remove salt.

REBAK: Which salt are you talking about, the metal salt, or the solution salt from the environment?

YANG: I'm talking about the deliquescent salt.

REBAK: The deliquescent salt? That will not be there. That will be there, yes, but, you know, you have metals, and the metals react and they also form salts, and they have to go somewhere. If there is no reservoir for those salts to migrate, they will dissolve in the environment, there is no further corrosion. Because it will form, instead of having, you know, potassium chloride or sodium chloride, you will have like a chromium chloride, or nickel chloride, or something, and those salts have to go somewhere. So, in fully inundated condition, and even if reservoir where those things can move away, some more corrosion can happen. But, in dust deliquescent type of thing, they don't have anywhere to go, so they will stay there and they will be a barrier for further dissolution.

LATANISION: Are you arguing that those salts provide something of a stifling effect?

REBAK: Yes.

YANG: I'm interested in seeing some of the mechanisms by which you can remove the salt. Is the chromium salt oxide, hydroxide, chromium precipitated? Anyway, thank you.

BRYAN: With respect to sinks for the components of the brine, there are a few. Of course, acid degassing will remove some of the brine components. We're not sure how important that is. There's some variability on that. When localized corrosion occurs, conditions become very acidic within the crevice. It's not clear how much that could affect the rate of degassing outside of the crevice. Or if it could.

Also, some of the corrosion products that form may contain chloride. For instance, in some of our experiments, layered double hydroxides have been identified and layered double hydroxides are anion getters. They contain chloride, nitrate, carbonate, and other species. And, so, there are some sinks available for components in the brine, and we haven't evaluated and we're not sure how important those are at this point.

YANG: Thank you.

LATANISION: Questions? Rob, what do you think about uniform corrosion, what's your thought on what you heard today?

KELLY: Kelly, Virginia.

It seems to me there are a couple of points that are important. One is this volume question. In a chloride environment, you do incorporate anions in corrosion products. And, unless that's different at 140 C than at room temperature, those get incorporated.

I guess the other is what kind of potentials you'll be at in these environments, and how that potential – open circuit potential - changes with time. So, while the 10 microns per year seems to be kind of a scary rate, it's not at all clear to me what kind of a distribution is on that rate. Is that a 1 percent, a tenth of a percent or 50 percent?

LATANISION: Fraser? What are your thoughts?

KING: Fraser King, Consultant to EPRI.

I guess what I would like to see is some plot of time versus temperature, and then superimposed on that, the corrosion rate, and integrate that to see how much corrosion actually occurs. You know, there's a temperature dependence on 30 kilojoules per mole. There's not a huge temperature dependence, but there is some temperature dependence. But, it seems to me, Rob asked this question yesterday, it seems that the potentials in the passive range, so, it we’re not looking at transpassive dissolution here, this is just a higher rate, and this is still in the passive range, and we seem to just have a particularly high passive current density under these conditions--there's no long-term degradation of the passive film. And, as the temperature decreases, the passive corrosion rate will decrease. If you do that integration of time versus temperature versus corrosion rate, my assumption is that it's not only a 10 percent loss, I haven't done the calculation, but--you may have, I don't know what that number is, but I don't think it's a huge number, is it? That you'd lose in that fairly short transient during the thermal pulse.

LATANISION: Do you want to respond to that first? Go ahead.

MON: He's correct, I don't have the numbers at my fingertips. So we shouldn't respond.

CSONTOS: Al Csontos, NRC.

We should note one thing. In the DOE general corrosion AMR, there are three sets of data. One is the long-term corrosion test data, one is the medium-term test data, another one is a short-term electrochemical test data. The electrochemical short-term test data, I don't know how long that was, showed corrosion rates up to 1 micron per year. So, this isn't a big surprise. I mean, Lietai's work, 10 microns, was three tests. If you'd put up his slide again, you will see the vast majority of them are 2 or 3 microns.

Can you put up Lietai's Slide 8? There's two test data over 4 microns. All the rest of them are 4 or less. So, the upper range of DOE's short-term corrosion test data, which they did not use in their abstraction, or in their model, they use the long-term test data, and whoever else wants to discuss that, but I just want to bring that up here.

LATANISION: Okay, thank you. Dr. Payer?

PAYER: Joe Payer, Case.

I guess I'm confused, which is not unusual. But, the tests were done to examine high temperature dust deliquescent environments that can be formed at 150 C, 160 C, 180 C. These conditions can't form under seepage conditions, because you can't have seepage at 150, 160 centigrade. And, so, I think we're mixing, again, these very small volumes of solution that can form, and then taking that and saying somehow we're going to form a teacup of that and immerse the waste package. And, how can this happen?

LATANISION: Just to be clear on that, these samples are creviced samples. There is no dust involved in these particular--

PAYER: No, the environment formed, can only form from high temperature dust deliquescence. That's the only way you can get these environments. This can't be a seepage water because it can't be 150 Centigrade. And, so, the only way you can get these waters is starting with sodium chloride, sodium nitrate, potassium nitrate salts, as they do, and you mix those up and you put them in a beaker at 150 Centigrade, and you get these types of environments. But, the only way you can get those is by the high temperature deliquescence. And, in high temperature deliquescence, you're limited to that amount of water, and, so, you can't get it under seepage conditions.

LATANISION: Are you comfortable with that?

YANG: Yes. These tests were done in one kilogram of salt. That’s a worst-case scenario. It's a lot of salt.

AHN: I would like to add a couple of things what I learned from Lietai the last couple years. At low RH, these are kind of a combination of salts, which will deliquescence first. That's why he chose that. The comment is whether you have sufficient water vapor. I don't think that is the problem. This workshop was discussing other UZ flow areas related to that.

YANG: May I just add one point. These salts, although we measured a lot of salt, we added a lot of salt. But, if you have a layer of salt, you don't know if you have 1 kilogram, if you have a layer of salt, that thermodynamics law, you are going to form the solution – concentrated solution. So, there is the other argument that we see we have not answered yet whether or not that thin film salt will support continuous corrosion. We don't know. But if that argument--if that assumption is true, so this amount is not important, as long as you have a layer of these mixed salt mixture. You could have the liquid there.

BRYAN: If you have a kilogram or so of liquid, even if you have very minor complexations of some of these salts, these metals in solution, chloride complexes forming, you may have a significant amount of metal relative to the amount of corrosion that's occurring, actually dissolved in the solution. Have you measured the amount of metal that's present in the solution, and done a mass balance? And, then, seen whether it's possible that you're actually having a high corrosion rate because you're dissolving a lot of metal into the solution.

YANG: So, with this test, we didn't do the measurement, because we have so much liquid, a small amount of dissolution of metal may not have the effect you just mentioned, because the metal you've not--we don't have a lot of metal.

AHN: I'd like to add a couple of things. Also, Lietai measured the corrosion rate in vapor environments as well. Also, recently he added silicates to simulate a more realistic--

LATANISION: Go ahead.

MON: This is Kevin Mon of Areva NP.

Let me see... I think during your talk, you said that these were open to air, and yet I think you also said that the pH was in the range of 2 to 4, and that there was probably condensation of acid gases on top of the apparatus running down into the solution. Is that true?

YANG: That is correct.

MON: Okay. So, decreases in pH have a tendency to increase the corrosion potential and the corrosion rate. So, it's possible in the repository environment, where there’ll be a flowing air, those acid gases would be removed, the pH of the remaining solution, if it could exist, which it wouldn't because, you know, this is too high for seepage. So, do you have any comment on that possible mode of enhancement to the corrosion rate?

YANG: I'm not sure if I captured your question. The pH we measured from the condensate during the initial test, they were low. So that means degassing. However, we were not able--we didn't do enough testing, the data was not reproducible. Some of data shows that it was close to neutral. If that was the case, close to neutral means degassing is going to take a long time. We got mixed signals.

LATANISION: John Walton, yesterday, you talked about cyclic efflorescence and deliquescence. Has what you've heard today changed any of your thoughts on that?

WALTON: No, I mean what leads to the cyclical behavior has to do with vapor transport in and out of the rock, which is, you know, done by a different set of people than is around the table, for the most part. And, so, I don't see any reason to change that. I did talk to Bobby about it briefly, and what we talked about is perhaps having someone at the Center look and see if they can mimic what George Danko has done to try to stimulate the change in relative humidity.

AHN: Let me add that, as I mentioned to you, actually NRC side evaluated one of the two parts he studied, actually he presented only on the rock side, not presented on the waste package area. The waste package area we considered your work, however, as Bobby mentioned, we continue to improve the drift area as well.

WALTON: Which part of my work? Are you talking about the flow separation--

AHN: Yes, flow separation.

WALTON: Yeah. Well, I think we were talking about the cycles of relative humidity. That’s a different process. And, so, I think we'll have to wait and see if somebody else can reproduce George Danko's results, and confirm it or deny it.

APTED: Can we go to Tae Ahn's presentation, number 7? Again, on that decision tree, there's one question that's not on there that was on the bottom when we first put the decision tree forward to the TRB, and that was the question: does it make a difference - so what? And, I think Tae Ahn answered that question for us very nicely here. And, maybe we can all go home. Number 7, please.

If I remember correctly, the EPA standard is somewhere here, 50 millirems, and maybe larger after 10,000 years, even in this diagram we're somewhere up in that sort of space. And, these are really--the Center's assumptions are very conservative. This is sort of no credit, and so on. This is very similar to the plot that Tim McCartin has already shown the TRB a few times ago. What's the problem? I mean, it seems like we're straining very hard here for--you know, yes, there's some--it's nice to have this extra order of protection. I think, you know, a best-estimate case is very similar to EPRI analysis is down in this area as well when we factor in these same sort of processes. So, maybe we're worrying an awful lot about features and, here, this is very early time failure, and yet the peak doses are not really out of compliance with what we need to be. Just an observation.

AHN: The right one.

RUBENSTEIN: Jim Rubenstein, NRC.

Mick, I just want to remind everyone that this was a hypothetical dose calculation. The sole purpose of this was to compare the two different cases, and the absolute scale is not relevant. This is not to demonstrate compliance or non-compliance under any kind of conditions. This is to compare the effects of the different size openings in the package, and it's a relative comparison. So, don't interpret this in any sort of absolute sense. It's a relative compliance.

AHN: You see the correlation of those (unintelligible).

LATANISION: And, here, we're ready to declare a victory and walk away? That is the ultimate question, isn't it? I mean, what is the best statement we can make about a release, and I'm not sure we can do that at this point. But, that is ultimately the point.

Let's see, any other questions?

(No response.)

LATANISION: If not, then I think we'll turn next to the period in the program where we allow for public comment.

And, Judy Treichel, I think, is the only one listed on my agenda.

Just for reference, is there anyone else who would like to make a statement?

(No response.)

LATANISION: Okay. Judy, welcome.

Treichel: How many people are out there that can make it this far until public comment.

One of the things that I see that's very strange is you've got a table full of people, and you're trying to bring this down as tight as you can, and you're trying to eliminate something to be considered, and I don't think anything should be eliminated, obviously, but it becomes so specific, and you're looking through such a tiny microscope at this little bitty thing, and we do have to understand that while you look at the alloy 22, some of the speakers said you've also got to be considering the other things that are around. And, you can't count on the drip shield to be the answer for everything, and if you do, or if you're counting on the drip shield at all, all of the same tests, it seems to me, should be going on with the drift scale--the drip shield at the very same time.

And, that would include anything brought in by the rock bolts. And, if you look at any of the pictures, there's zillions of rock bolts throughout this thing, and those are different kinds of materials. And, you've got whatever lining is going to be in the tunnels, and if you come to bad rock while you're building this thing, you might also have steel sets going in. But, there's all sorts of things that could be introduced, whereas people just look at this graphic of the tunnel sitting there, and at the same time, you have to understand that this thing is going to be being built, being filled, and having waste in it all at the same time. All of these things are going on together.

So, as we saw in the drift scale tests when you went down there, there was a time when it started getting real wet in the place where people could go that was just outside where the heaters were, and it got to the point it was real, you know, there was drips, and so forth, and finally DOE put up a poster on the wall saying, "Why is it raining in here." And, I would think that you're going to have that situation. If you have a few tunnels that are built, and start putting waste in, and you start moving that water out, it's going to be at those next tunnels where you're putting more waste in. The water would be moving toward the new tunnels where the waste would be going in. So, the packages might get drips on them right off the bat.

And, there's all sorts of things that happen in conjunction with other things, that it doesn't seem like people are considering right now. And, I don't know if radiation plays any part in this thing over time, or if anything happens because of the high radiation fields that are in there. But, there's so many things that happen together that it seems like you make a mistake when you try and narrow everything down, and have specific specialists to look at a little snapshot of something, when so many things are going on that require other experts to be looking at them.

So, thank you.

LATANISION: Any other comments? In that case, this gives me an opportunity to wrap up, and--we have a lot of time. I can take quite a while here, can't I. I'll think about that.

I do want to provide some sort of commentary on what I've heard over the last day and a half. But, let me first thank all of the presenters I think the conversations here have been very candid, and that's something I appreciate. I want to thank you all, not only for being here, but for taking the spirit of this meeting into account in terms of your presentations.

Somebody asked me at one of the breaks whether we've made some progress in the last day and a half. Yes, I think we have. On the one hand, I think this has been by far the most comprehensive conversation we've had about localized corrosion; and, in fact, it evolved into conversation that included uniform corrosion, too. But it's certainly the most comprehensive conversation I've had since I've been a member of the Board on this issue.

So I think we have a lot of things on the table. They're not all a hundred percent clear to me. Maybe they are to others. And I want to talk about a couple of those.

But I want to preface what I am about to say by a personal observation. During this past weekend I spent most of the weekend with a group of people from the U.S. Army. The United States is signatory to a treaty that requires us to destroy our chemical munitions. There are a couple of ways of doing that. One is to incinerate them; the other is to consider alternative technologies, and one of those involves supercritical water. It's high temperature/high pressure water above the critical point, great solvent for organics, poor solvent for inorganics; so it's a very convenient separation medium, but very aggressive. When you put agents like VX and mustard into these systems, they're extremely corrosive. We're not talking about microns per year; we're talking about centimeters per year.

The difference, however, is these systems only have to last for a few years; and, in fact, the current attitude about how to deal with supercritical water oxidation of waste is to use a titanium lined Inconel 625 reactor and to replace the titanium liner from time to time. So a different situation we're dealing with here. We're talking about thousands of years of engineering life.

But the problems are similar in one very important respect. They're both at a stage where the issue is really the engineering design. It's not science, it's not doing more science studies. It's really solving the engineering problems. I think the Army is well on their way. At one point they were actually considering using platinum lined vessel reactors. They had an agreement with the Franklin Mint to borrow the platinum. I say "borrow," the attitude being that they would return it after five or six years. However, even platinum corrodes in these environments, they discovered to their surprise.

And so I just it very interesting how similar yet different these two projects are. We've got a tremendously different time horizon, a lot of the same problems, and most of the problems are really engineering problems.

Now, I've heard a couple of things along the lines of these engineering questions that I think do need to be considered a little further. John Walton mentioned one of them, the question of efflorescence and deliquescence on a cyclic basis. I don't know whether that's a real issue or not in terms of the lifetime of these systems, but I think it deserves some consideration, and I did ask John and Roberto to consider a little further. I hope you'll think more about that. I hope you'll look at the work that was done by--whose work was it? Danko's, right?

SPEAKER: Oh, George Danko.

LATANISION: Yeah. I hope you'll look into that and come to some deeper thought on that whole process.

We also heard from Randy Arthur--I guess Randy's not here at the moment--but we heard yesterday what appeared to be contrary information on the issue of the presence of nitrates. And so there seemed to be some disharmony in the sense between what EPRI's thoughts were and what the Project's thoughts were.

I had asked Randy and Charles to talk about that. Charles, did you guys have a chance to talk? What's the consensus at this point, to put you on the spot?

BRYAN: We talked about it. I think there were two points in the discussion. The first one was that we don't really know what the nitrate and chloride phases are that are present. We haven't analyzed them. All we have are the chemical analyses of --.

And the second point was that EPRI feels that degassing will occur much more rapidly than we do, and that's certainly something that we'll take another look at.

LATANISION: That's a pretty important point. One of the major arguments about control of localized corrosion is related to the nitrate to chloride ratio. And if there's disagreement on that point, I think it's a pretty important issue to resolve. So I just hope you and Randy or the Project folks and the EPRI folks will compare notes more fully on that.

I really did think when we began this conversation that we were talking largely about localized corrosion. We've heard a lot about uniform corrosion that puts a slightly different perspective on that topic. I think we're going to have to consider that somewhat further. The issue of stifling. Whether we talk about stifling in the context of localized corrosion as a consequence of deliquescence or localized corrosion as a consequence of seepage, the issue of stifling still remains an important concept.

I made the point this morning that I think, from the point of view of the history of localized corrosion, which is often treated as being not a catalytic process that accelerates in terms of rates with time, we're talking about something quite different here if we can demonstrate and argue the case that the propagation rates actually decrease with time. And, in fact, if stifling is a possibility and we can demonstrate that either because of repassivation or because of dryout or whatever the reason is, obviously it's a very important point.

But, personally, and I'm speaking only personally, not as the Board, but from my own perspective, I really think we need to look at the issue of environmental chemistry and propagating localized corrosion issues, whether it's crevice corrosion or pitting or whatever we consider it to be. And I don't consider that to be a finished issue. As far as I can tell, there is still work going on at Virginia--Joe, I think that's what you mentioned--and I'm going to wait to hear some more about that.

Both the NRC and DOE models have explicitly excluded deliquescence. That's what we heard this afternoon. At any rate, as far as I can tell, that's the case. That seems to be an important conclusion from the point of view of those two organizations. But localized corrosion remains in the performance assessment. I guess the question that that begs is: What is the origin of the crevice? If it's not deliquescent dust, is it weld defects? Is it some artifact of the fabrication of the package? What is it? This is an important issue. It comes back to Mick's point that does it really matter.

I think these were the kinds of questions that still require some answers, and it would not surprise me if in the licensing process they'll become important issues.

At any rate, those were the kinds of things that are on my mind. Someone else has asked me whether there will be a report issued by the Board on the conversations we've had over the last day and a half. I don't have an answer to you on that one. The Board will consider what we've heard and how we want to memorialize it, I suppose, or not over the next day, day and a half. So we'll have a little bit better sense of where we want to go with that when we have our own conversations.

I think, from my point of view, this has been a very useful day and a half. I do want to thank you for being here.

Dave, as co-chair, do you want to add some of your thoughts?

DUQUETTE: Duquette, Board.

I'll keep it very brief. I'm a little bit concerned in what I've heard and had been hearing for some time that there are groups that would like to make the problem go away entirely and other groups that would like to make it be a damning effect on the repository.

I have to say that of all the talks I heard here--and I've heard some of it before--but Osvaldo's talk on allowing a certain number of containers to fail and seeing what that does to the total dose, to me, is more important than whether it's going to happen--whether you can FEP it out or anything else. I personally think there is going to be some corrosion problems in the repository, whether they be local or general corrosion problems. I think a certain fraction of the containers will fail, and I think we're spinning an awful lot of wheels to try to show that it can't happen when most of us in the corrosion world have dealt with situations that weren't supposed to happen and did.

And so I was more comfortable with a probabilistic model that says, "I'm going to have some that fail. What does it do?" And I think I'll close my comments here.

LATANISION: Let me just ask: Any comments from the Project point of view? Charles or Ernie? Ernie's not here either, I guess, is he? Oh, are you? Ernie, you want to add any comments?

HARDIN: I would, thank you. Hardin, Sandia.

I've been really good today. I haven't stood up once to take the microphone, but I will say this, that what I've learned from this meeting was that, number one, everyone in this room does not have the same understanding of the environments. It's clear that we're talking about complex mechanisms. Thermodynamics comes into play, but we tend to fixate on thermodynamics without due attention to kinetics or mass transport. And the differences among the experiments that we talked about today must be due to kinetics.

So I think there's more experimental work to do, and it's gratifying to me that the protocol that Dr. Yang presented today can be repeated at 90 degrees for comparison to reams of project data. So I'm looking forward to that. Thank you.

LATANISION: Tae, from the point of view of your--

AHN: Actually, I don't have any comment. You captured most of them. We appreciate our participation here to present our understanding, also learning what other parties are presenting here, and we will consider the comments we received here in our future studies.

LATANISION: Thank you.

AHN: Thank you.

LATANISION: Yeah.

RUBENSTEIN: Jim Rubenstein.

And if I could just add to Tae's comment. We thank the Board for letting us come and present the work the Center's been doing. And I also wanted to point out that it's important to remember that the performance assessment codes that the NRC runs and the performance assessment codes that the Department runs serve two different purposes. Ours is to guide our understanding of the system and aid in our review. DOE's is to make their case under the regulation. So they're really two distinct purposes.

LATANISION: Thank you.

Maury, from the State's point of view, any parting comments?

MORGENSTEIN: We thank you for our participation, and we have no comments.

LATANISION: John, Nye County?

WALTON: Same thing. We appreciate being involved in the process. That's it.

LATANISION: Thank you.

Fraser, from EPRI's point of view? From your point of view on behalf of EPRI; how's that?

KING: I should defer to my senior colleague. We appreciate being involved, and we'd like to continue to be involved, both in the corrosion area and in other topic areas. Thank you.

LATANISION: John, as Chairman of the Board, are there any comments you'd like to make before we close?

GARRICK: Not many. I'm sorry I didn't get my answer to the question of what does it all mean in terms of overall performance, but I will keep working on that.

LATANISION: Thank you.

Yes, sir, go ahead.

KADAK: Kadak, Board.

I'm not a metallurgist or a corrosion expert, so I just sat in to understand better the debate. And I guess what I came away with was, everybody was doing their own experiments that they knew how to do, but little of it was relative to what the repository environment really is. So I would urge those of you who are working on future experiments to try to understand what the true water is, what the true deliquescent materials are, and what the Alloy 22 really is that we need to worry about relative to the performance of this waste package at appropriate temperatures. Everybody can kill a rat with poison. It's just how much poison do you want to give it before it dies?

So I think you need to focus in on what the real repository conditions are, do the appropriate tests at the appropriate temperatures, and then I think we can have a sensible conversation. And I would like to recommend to the various teams that are doing all these studies is, talk about these things after this meeting is over so the next meeting that we have, we can start from the same page if that's possible. Thank you.

LATANISION: Thank you.

All right. Let me call this meeting adjourned. Thank you all for being here.

(Whereupon, at 5:00 p.m. the meeting was adjourned.)