UNITED STATES
NUCLEAR WASTE TECHNICAL REVIEW BOARD

INTERNATIONAL WORKSHOP ON LONG-TERM EXTRAPOLATION OF PASSIVE BEHAVIOR

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Hilton Arlington & Towers
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Arlington, Virginia 22203

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Question 1: On the effects of long-term passive dissolution.

-Since commercial allows are being used to manufacture the waste packages and due to "atmospheric" corrosion conditions in the repository, it has to be assumed that most of the effects described in the speculative scenarios (defect sweeping, vacancy build up, debris accumulation, potential ennoblement) do not necessarily occur uniformly over the whole passive surface of a WP (Waste Package). Therefore, if these effects are really occurring during the long-term exposure, and if these are also effective to promote passive metal dissolution, they will lead to some degree of inhomogeneous metal loss. In case of oxide spalling, it is assumed that repassivation occurs fast enough and no localized corrosion takes place.

-According to our experience from exposure tests in long-range alpine road tunnels in Switzerland and in France up to 25 years, we never observed this scenario on passive metal surfaces. Instead, external debris accumulation from environmental influences occurs much faster and may lead in case of hindered repassivation to enhanced localized corrosion processes. These debris accumulations are not necessarily connected to the passive state of the materials, but are rather caused by the environment in the repository.

-Our results from the field tests in the Mont-Blanc Tunnel lasting for approximately 8 years show that the nickel-base alloys (Inconel 2.4856, Hastelloy C4 2.4610) do not corrode at all in this heavily contaminated atmosphere of long-range alpine road tunnels, contrary to 304 and 316 SS which show severe corrosion already after one year. (Pollution: Chlorides, sulphates, sulfides, nitrates, RL plus or minus 78 percent, T plus or minus 35 degrees C.)

Question 2: On the long-term preservation of conditions preventing localized corrosion.

a)

-Critical pitting potentials quoted in the literature are usually threshold potentials at or above which stable pit growth occurs. Pit initiation processes followed by metastable pitting may already occur at much lower potentials. This leads to the concept of "metastable pitting". Therefore, Question 2 should be rewritten more precisely: What is the lowest potential where metastable pits can be transformed into stable pits under certain given environmental conditions. (In case of Ni in highly conc. $NiCl_2$ - solutions this potential is approx. -50 - -100 mV sce at RT)

-If the transformation from metastable to stable pitting is mainly controlled by the chemical composition of the pit or crevice electrolyte, the pit or crevice geometry of the initial pits and crevices, together with the mass transport in the bulk electrolyte are of decisive importance. High Cl concentrations (saturation) in the water films strongly promote this transition and decrease the corresponding critical pitting potential. Therefore, the expected environmental conditions in the repository, including temperature, play a key role with respect to the critical pit growth potential. It is important to consider these surface conditions as function of time. Our experience in long-range road tunnel investigations indicate that we get a gradual increase in concentration over the years.

-The open circuit potential is mainly influenced by the oxidizing conditions in the repository, in the present case probably air or eventually products from radiation.

b)

-Transition from metastable to stable pit growth depends on many parameters, such as potential, pH temperature crevice or pit geometry, etc. Some of them may not be directly related to Ecrit. Therefore, the necessary conditions for stable pitting always result from the behavior of the whole system. It also has to be looked at from a stochastic point of view.

c)

-Corrosion tests and surface analytical investigation of worst case repository conditions.

PROCEEDINGS

(8:30 a.m.)

BULLEN: Good morning and welcome back to the continuation of the International Workshop on Long-Term Extrapolation of Passive Behavior. I would ask that anyone who wants to continue their conversations can take them out in the hallway. I'll ask my Board members and Panel members to have a seat.

My name is Dan Bullen. I'm a member of the Nuclear Waste Technical Review Board and the Chairman of the Repository Panel of the NWTRB which is the sponsor for this workshop. I want to welcome you back and I just have a couple of housekeeping announcements to begin with.

There will be a public comment period at the conclusion of this morning's session. The session ends today at noon. The public comment period is scheduled for 11:30.

If you would like to comment, please, sign up at the public comment registry which is at the table outside of this room. Ask one of the Lindas out there to provide you with help and she'll get you signed up.

I wanted to welcome you back. Again, this is a workshop on the long-term extrapolation of passive behavior and this morning's agenda calls for us to actually take a look at Question #2 which is listed on the back of the agenda for those of you that want to follow along. This is actually the question on the long-term preservation of conditions preventing localized corrosion. I'm going to summarize the three points of the questions before we begin and I've actually had one of our esteemed Panel members volunteer to be first. So, I'll call upon him in just a moment.

The questions say, Part (a), "Can you propose any plausible mechanisms relevant to the waste package that would cause over long periods of time shifts in the open circuit and/or the critical potential such that stable localized corrosion could develop?"

Part (b) of that question is, "In addition or as an alternative to (a), can you propose a localized corrosion process that could develop over long times such that the initiation and propagation are not amenable to description in terms of a critical potential?"

And then, (c), "What experiments and/or theoretical treatment would you propose to investigate the issues identified under (a) or (b) for Alloy-22 under the proposed repository conditions?"

Now, we did hear yesterday in a number of presentations about the localized corrosion. And, in fact, I'm going to maybe give a little fair warning to the members of the Panel that we'll probably go around the table and ask for your professional opinion on the answers to the questions. So, we'll get a little bit more straight forward answer today.

But, with that, I'd like to turn the podium over to Dr. MacDougall who has volunteered to be first with respect to these issues. And, Barry, it's all yours?

MACDOUGALL: Good morning. The reason that I wanted to go first is to perhaps say one or two things initially with regard to some of the comments, finishing off of yesterday. I don't think we can separate passivity from breakdown and that sort of thing.

We talked quite a bit yesterday about the so-called passive current, whatever that might in point of fact be. But, I'm showing you here to remind people, I guess, because it's--I'm sure most are quite aware, in fact, that if you do a potentiostatic experiment, constant potential on a metal or alloy that passivates and the potential is in the passive region, and you monitor the current as a function of time, you're going to get a series of curves depending upon the electrolyte condition, the temperature, the potential that you're at, the pretreatment of which metal or alloy you have.

This is the case of nickel, in fact, and it's a sulfate solution. It's a pH 2.8 sodium sulfate. This is in a buffered pH 7.4 solution. You can certainly see in this case here, I mean, the current is falling (coughing) as a function of time. It follows a log I/log T relationship. So, I don't know where the passive current is. Is it there, is it there, is it there, there? I mean, supposedly, if you waited long enough, this thing is beginning to bend over here and the reason for that is, I think, because we're reaching some kind of a constant state of condition of the film, not necessarily in terms of thickness, but in terms of defect character.

I think many of these things have implications for alloys like C-22, in point of fact. This one here, the pH is higher and the thing is bending over earlier. If you had the right conditions, this thing could go on for long periods of time. This experiment was only done for one week. So, it's done for, I guess, a short period of time in comparison to 10,000 years. But, the interesting thing here is that during this particular profile, this log I/log T that many of you have observed and talked about, a lot of people in the audience here have looked at things. I think what's going on is you have a change, in fact, in the so-called defect density of the film as a function of time. The stability of the film is increasing because the defects, their number are decreasing according to, I guess, a logarithmic function, the N-1 reciprocal of number of defects being the stability of the film and the current falling according to this. And, what ties the log I/log T together is the stability of the film which is like a thickness, but it's not thickness, in point of fact, because during this particular period of time here, the majority of the charge that we see flowing isn't actually associated with nickel dissolution even during this log I/log T period. So, we aren't thickening the film. 90 or more percent of the charge is going towards a change in the perfection of the film.

Now, we talked yesterday about strain in these films. I think that if you have a very thin film, like this case here, it's a 10 angstrom NiO film, and you have that film on a metal, nickel oxide on nickel, the difference in the lattice parameter between the two is 18 percent. Now, there has to be some strain there. I mean, you can't fit something on something else with an 18 percent difference and not get a certain amount of strain. And, the way people look at this, the way, in fact, I have and others, I guess, over the years, is to look at something called the lattice parameter of the oxide. What I've seen, in fact, in terms of the lattice parameter of the nickel oxide in the very early stages, in fact, what you have is an expanded lattice, 2.53 percent expanded. It gradually gets better and better, in fact, in terms of approaching the lattice parameter for NiO.

Along these points here--that's where I showed those defect charts of yesterday. So, if you were here, you had lots and lots of defects, you had fewer and you had fewer down here, in point of fact. So, I mean, why do you have this 2.5 percent going to 1.5 percent going to 1 percent expansion of the lattice going to 0.5 and then it's difficult to measure much beyond what 0.2 percent expanded going towards NiO, the lattice parameter of NiO. We measure that by reflection, high energy electron defraction.

It's because in that oxide, what you have when you're forming it initially are vacancies. It's a p-type semiconductor, as I understand it. People have talked about semi-conductive properties. When you have cation vacancies, you have to have Ni3+. You have to have charge balance in the film. So, you've got Ni3+ long before you would think in terms of the battery application. So, you have this higher oxidation state there. Now, these nickels, because you have the cation vacancies, there are repulsive interactions between the oxygens in that film and it expands the lattice; the fewer the vacancies you have, the more the lattice approaches that of NiO. But, the important thing is that we have Ni3+.

Now, I don't know about chromium; I know iron. I've looked at iron; I don't know chrome. I don't know if--I forget if chrome is a p-type or an n-type semiconductor, but --it's n-type, is it? It's n-type. So, it may be different in point of fact. The question again as to whether you can have chromium in a higher oxidation state in the early stages. 6+, I don't know. But, some of these minute little defect sites, in point of fact, might you have something? I don't know.

I want to say about strain and films, you have to be careful. It's again something--maybe it's a detail. I don't really think it is. You could have a measurement of an average strain in a film of zero percent and it still has strain because it has what's called inhomogeneous strain. It means that there's +2 percent here at this interface. The older interface, there's -2 percent. The average strain is zero. There's still inhomogeneous strain in the film. You can measure that. People can measure that. They know how to measure that from defraction patterns and that sort of thing there. But, I think there is strain. I think we,ve relieved the strain. What happens later on, I certainly don't know.

I think these things can be important and I think one has to keep in mind that in this particular system here we're probably dealing with defects, in fact. We have things which maybe we don't understand. It looks to me as though one has a very good alloy material. An air formed film that's extremely stable, and I would imagine that perhaps the only way to get that film off is by some kind of a mechanical failure, abrasion. And, from what I understand is that, in fact, when these things are lined up or something of this nature for 10,000 years, there is the possibility of rocks falling, them falling over and things of this nature. So, that very protective air formed film can--with time, it would seem to be, be disrupted, fail after conditions, or perhaps ripe for something which is not so nice. It has to reform. That's why I presume repassivation experiments have been done and perhaps they should be done in point of fact on this particular material in environments that relate to what we have to see if the pits actually develop in that particular case there. I think usually it's in this early stage that things are pretty susceptible to, in fact, the localized corrosion. So, if you have this mechanical failure going on, you would have to check under those conditions there.

The other thing, just to remind you, in point of fact, that's what pitting is all about. Most of you are aware of that, in fact, that there are defects, that things happen, and what's going on to actually trigger that event. The other thing which most of you know and certainly I'm as fond of cyclic voltametry as anybody else, but I think you've got to be careful with it. It's a very fast scanning method and this is a curve which shows pitting in nickel and sulfate solutions. In fact, the pit initiation, as Susan calls it in her book, the ENP begins here, the nucleation potential. The repassivation potential is way down here, in fact. Once you begin to get nucleation, you're in a bit of trouble in this particular thing because there's a tremendous hysteresis because of the conditions that you develop within those particular pits.

I think the species that I would be nervous about also in this particular environment in terms of the long term, in terms of driving the reaction, we talked yesterday about peroxide, H_2O_2, certainly a possible species, but this is also an environment, I guess, where one can have radical species. They can be short-lived, but I mean HO radical--which I work with a lot now in terms of destroying phenolic compounds, organics, and they can destroy almost anything--

this particular thing has a potential of 2.4 volts. It's very, very high. Other species HOO star, these things are possible radical species which can be involved in the reactions there. And, I think if they can drive the potential high enough, there could be problems. There may not be, but I think these radicals, very short-lived, but they are tremendously potent species. And, under the right set of conditions, I would think they could--as I say, I was amazed when I found that the hydroxide radical had a potential driving force of 2.4 volts above zero for hydrogen. This is a tremendous driving force, in fact.

And, I will now sit down after taking this off.

BULLEN: Thank you, Dr. MacDougall. I appreciate that. We can actually ask a few questions around here.

This morning's session, I would like to run like yesterday afternoon. So, if you have some presentation material and I know Gustavo has already elbowed me here to be next. But, Dr. Newman, did you want to make a comment or two?

NEWMAN: It's perhaps slightly off the point, but may I just write a little equation on the board?

BULLEN: We would never stop you from writing an equation. Go right ahead?

NEWMAN: Actually, this is slightly off the point, but since everyone else has been grandstanding here, I should, as well (laughter). I just wanted to write a little equation which is, we call it in my university, the corrosion equation because it's often the only equation in a thesis when a student graduates. This equation just says the maximum depth of corrosion. I mean, there's more subtlety in this than actually meets the eye because, of course, this results from an extreme value type statistical study, in fact. But, it says the maximum depth of corrosion is proportional to time to the M where M is equal to 0.3 to 0.5. There's a question mark as to whether for atmospheric pitting, which may be what we're dealing with here, maybe it can be as high as .7.

And, on the back of my envelope, it just says that if we have a corrosion allowance--this is what corrosion engineers call this is a corrosion allowance--of, say, 20 millimeters--that's the thickness of your thing--and we're allowed 10,000 years to consume that corrosion allowance, and you ask yourself, well, how long will it take--how deep should the corrosion be--I mean, after how long should the corrosion be 1 millimeter deep? All right? Well, for M equals .5--I wish I'd used 10 millimeters instead of 20, but I can't do the calculation now. But, I believe if the average is .5, your answer is 25 years. And, if M is equal to .33, the answer I believe is 5.4 years. Somebody will have to check my arithmetic there. So, as far as I'm concerned, what that says is that if you're worried about failure by pitting corrosion, you only have to do an experiment for up to 25 years and you know right away how much is going to happen up to 10,000 years.

Thank you.

BULLEN: Thank you. You've got to be close to the microphone.

Jerry, you had a comment?

KRUGER: Roger, that equation deals with uniform corrosion really, the corrosion allowance, and--

NEWMAN: It refers to pitting.

KRUGER: You said it's a corrosion allowance. For pitting only?

NEWMAN: Well, I'm referring to pitting corrosion, but maybe the same thing applies to uniform corrosion.

KRUGER: You see, all of that corrosion could occur in a very small area of the pit or a few pits.

NEWMAN: No, no. No.

KRUGER: And, that 1 centimeter would be much, much larger.

NEWMAN: Well, it wouldn't be because the--well, it's hard to--that equation is--

KRUGER: It has to be the amount of corrosion per unit area.

NEWMAN: That equation is an empirical rate loss of pitting corrosion. That's all it is. And, I've just inserted 20 millimeters as the--

KRUGER: Oh, it's for pitting corrosion--okay, fine.

NEWMAN: Yeah, the depth of the pit after 10,000 years. It's probably a very facile argument, but I'm just pointing out that you might only need to do experiments for a few years to be able to say that you're not going to have any 20 millimeter pit after 10,000 years.

KRUGER: You didn't say it was for pitting.

NEWMAN: Sorry.

CRAGNOLINO: Let me clarify the point even further. I'm Gustavo Cragnolino. This equation that Roger put there really was used by Marsh in England within the high-level waste program to calculate the penetration by pitting corrosion of carbon steel. And, he used experiment that lasted for three years to use the approach, that is the Campbell approach and Dr. Shibata know very well this, in terms of extreme value statistics, he derived equation, he has a way to correlate the result because this is implicit in the treatment of Campbell, it's more applicable -- to a large surface and work very fine, and you can correlate with experiment in the same way that Roger was mentioning.

BULLEN: This is Bullen. Gustavo, just before you get started, Alberto had a comment or a question.

SAGÜÉS: Actually, it was before Gustavo's. So--

MR. BULLEN: The chairman is at fault, as always.

Alberto, go ahead?

SAGÜÉS: No, I just wanted to mention before this gets going farther. I wanted to keep the members of the Panel aware of the following question. Have you ever seen any pit in something other than carbon steel that went through 20 millimeters of anything? I'm talking here about like stainless steels or alloys, like that.

NEWMAN: Usually, we can't talk about it if we've seen something like that. We're not allowed to.

SAGÜÉS: Okay. Well, maybe, have you seen any that you can talk about, I guess? That would be the next best thing. But, I really would like for that to keep in mind because I would like to avoid today--I mean, if we're getting into this very seriously, it would be very interesting to learn whether it's something fictional or something that has actually been seen to happen in actual practice.

The other item, and Gustavo brought this up, is I would like also for you to keep in mind the extremely large surface area we're dealing with which was, what, a couple hundred thousand square meters or so. It can vary. Also, to have an idea of not just the time element, but of the surface element, which may concern some of the--what Roger Newman just mentioned, maybe doing some experiments in that equation is fine, maximum depth corrosion, but that is, of course, for certain assumed--of overall size populations.

BULLEN: Bullen Board. Since I'm not going a good job as chairman this morning, I'll try to get better at it. I want to remind the speakers to go about five minutes, maybe 10 minutes, so that everybody has a chance to talk and we can stay on task.

Gustavo, it's all yours. You have your whole seven minutes left.

CRAGNOLINO: The answer the question that was posed by Alberto, I think that in one of the last TRB meetings Sridhar precisely showed the case of the beautiful pit in a stainless steel pipe that was a quarter of an inch in thickness that went through very fine. I will not--quarter of an inch, 6.35 millimeters.

SAGÜÉS: Right, right. We're talking about basically an inch.

CRAGNOLINO: Well, we are not far from the 20, but you know, it's something to consider.

I wanted to come back to my slide yesterday, I made some corrections last night--I don't know after the wine or this morning--and I want to emphasize a point here. I want to emphasize two points. That, I think, that this is a powerful approach to make sure that you are not going to confront the risk of localized corrosion that could lead to failure in very short time. And, I calculated clear correction here for this type of material that we're dealing with. It is not pitting, but crevice corrosion, the main form of attack that we have to be concerned with. Therefore, I made a correction here in order to clarify the meaning and I used the term repassivation potential for crevice corrosion in the same way that Dr. Shibata expressed it yesterday and with the same approach to make sure of this value because this is a powerful bounding parameter. This parameter depends--and we have demonstrated this for a limited range of conditions of temperature and concentration of the aggressive species chloride--will depend obviously on the presence of inhibitors like nitrate and of metallurgical factors.

And, the other parameter I would have to consider is the corrosion potential. I'm not going to go into detail, we can discuss this later in more detail. But, you know, I indicated here that while the repassivation potential is practically not dependent upon pH, this is an important conclusion. The corrosion potential is strongly dependant upon pH. It's dependent upon the concentration of the reducible species of the oxidant that is prevailing air in our system because we have air circulated condition. And after you have the radiolysis problem sorted out, this is what is going to control the potential. It says the presence of oxygen at atmospheric pressure. Obviously, the chain current density for the oxidation-reduction and the water reaction, too, these are subject to further analyses and all the kinetic variable that should be included here--I'm not going to deal in the detail--is very important. The surface state--obviously the metallurgical factor. And this is the way to depict an evolution. I'm going to go into more detail into this.

And, what I'm trying to emphasize is this that I put with some sort of concern, semi-empirical model of localized corrosion. I believe I have a solid mechanistic basis. Probably, we have more knowledge at the present time about the mechanism controlling localized corrosion. Therefore, we can make prediction about repassivation potential that passivity of long-term passive corrosion rate or other phenomena that is not the subject of this meeting--that is the stress corrosion cracking in which there is no clear agreement with respect to theories and models. For localized corrosion process crevice pitting, there is a basic agreement in terms of mechanism and for that reason we are, I believe, on much more safe ground.

I emphasize repassivation because in the approach of the DOE, there is use of the word critical. And, critical has many meanings. If critical is initiation, it's the wrong concept to decide the process of localized corrosion because it's a matter of the past pacing (phonetic) of the investigator to measure the critical potential, in this case the pitting initiation potential, depending upon scan rate, depending upon the conditions of the surface, many factors, but is not the case of the repassivation potential with the approach suggested by Dr. Shibata yesterday or some variation of that approach. This should be clear.

Here, I listed factors that I included yesterday. You can go into more detail. I'm not going to spend more time because Dan is going to get impatient with me. I only add fluoride in the list. It deserves some consideration after what Dr. Strehblow said yesterday, and we have to consider the possible synergistic action in between the chloride and fluoride and other eventual inhibitors. By the way, carbonate is a very weak inhibitor. I put this for completion, but it is very weak inhibitor. If there is an important inhibitor in our wet system, the system under consideration it's really nitrate. But, you have to consider activators and I put here thiosulfate salt symbolizing all the type of sulfur species that are detrimental. I don't mean necessarily that should be thiosulfate. It could be form of absorbed sulfur. That may be or not, may be or not, I'm not sure related in the long term with sulfur reducing bacteria, but it is only a caution here.

This is the important thing. The redox potential of the environment that will affect the corrosion potential will be essentially controlled after the initial period by what you have as the concentration of oxygen from air. Radiolytic species will decay and will be not important, even though initially you have an effect increasing, as I mentioned. Here, they're all factors that I've related to materials--and I think that we have to pay enough consideration--and this factor that was added yesterday following the discussion and I think I can anticipate with direction the current for all the corrosion potential, but it's pretty sure that we may, in fact, this repassivation potential will have some effect-- especially when you accumulate some sort of detrimental species from the environment.

These were not yesterday in my figure, but are now and this is an issue. This is a very important issue. You have this repassivation potential for the received material and there is something done wrong with the thermal treatment of the welds. A few minutes at eight hundred seventy during its long cooling, maybe, has a significant decrease in the repassivation potential. Practically everything changes in the few initial moments. These are not really all the five minutes at this temperature really. Here, the heating of the specimen in the previous state was part of this time.

At well, it's not that important, but this is the message. The result of the message is this. Inside the crevice area even at very low chloride concentrations where you have this significant development of intergranular-- attack. In three of the 24 crevice sites, there is a collection of pictures that show also some attack at grain boundaries. It's usually such a grave concentration doesn't happen, but, it's something that has to be paid good, good attention and--

BULLEN: Bullen, Board. Before you take that one off, Gustavo, I have a question. Did you do an analysis to determine if there was change in the microstructure at the boundaries there after the heat treatment was--

CRAGNOLINO: Right. These are the--

BULLEN: Is there some kind of segregation effect that's going on?

CRAGNOLINO: Right. These are what we are going to explore afterwards.

BULLEN: Okay.

CRAGNOLINO: Obviously, in this alloy it's very well-characterized the fact that there is a precipitation in the grain boundaries of intermetallic phases, probably combined with some carbide precipitation, too, and we have to explore this in more detail. But, the physical metallurgy of this alloy is not completely well understood, but we have enough basis and this is work that has been done at Lawrence Livermore to understand many features associated with this process.

The other process before was in the more low temperature regime to try to predict what happens in the long term. There is a concern, too, but I think that is partially dissipated. Now, concerning what happen when you are processing the alloy plus welding is you got a grander risk by trying to improve things making them worse. This is what I wanted to emphasize.

For that reason, to conclude, I strongly believe, we strongly believe in our group work and I think that this is something that has been put very well together by Professor Tsujikawa in Japan with his group, that this passivation potential is a very strong concept.

SHIBATA: -- measure the ER crevice on how --.

CRAGNOLINO: Well, you have a good point. I think I've taken enough of time. This is done potentiostatically and the repassivation potential are not so high as presumed before, but are not so low to have proration (phonetic) in the open circuit condition in the presence of this.

SHIBATA: Very close to the--

CRAGNOLINO: It's getting close.

SHIBATA: I see.

CRAGNOLINO: It's getting close, but I think that this is the last part of my message. It's getting close, but it's not there. We have to watch these because we don't know exactly how is going to be this evolution with the aging of the film. And there are two factors. Here, I indicated very briefly pit growth or crevice corrosion growth is affected by dissolution kinetics and mass transport process without the crevice growing and we can model this. We are in the condition of modeling this. But, it's also, as Digby will insist all the time, has to be balanced by the balance of charge. That means that there is a cathodic reaction that fit this process and the kinetic of the cathodic reaction is very important and the cathodic area available and the conductivity in between these. I mean that this is the second part of the thing that we'll have to keep in mind. But, this is, more or less, it's an emphasis in the approach and it's a response to the question. The only thing that I can anticipate that could lead to a phenomena and I cannot be certain with this localized corrosion, that I cannot be certain with this repassivation potential concept, is what Phillipe indicated yesterday about the potential segregation of the impurities that lead to localized corrosion in the form of intergranular penetration, that maybe there is no such a threshold potential, or something like this.

BULLEN: Gustavo, thank you.

Dr. Strehblow, did you want to--do you have a quick comment, go right ahead?

STREHBLOW: No, it's a little presentation.

MR. BULLEN: No, that's quite all right. You're next.

Alberto, did you want to make a comment before?

SAGÜÉS: I've got a question for Gustavo. While Gustavo is still up there, I wanted to ask Gustavo a question. This has to do with the open circuit potential. Did I understand that when you have your little transparency there, you refer to the oxygen as being the main species responsible for--the main species providing a cathodic reaction or some kind of a couple up there that would determine the open circuit potential above and beyond the metallurgical factors?

CRAGNOLINO: Uh-huh. (Barely audible response away from microphone.)

SAGÜÉS: How about anything else happening over there?

For example, in the old repository concept when there was a carbon steel shell proposed, several people expressed concerns about, oh, maybe having, who knows, ferric/ferrous couples and so on that would drive potentials very high because there was--I understand that now the Yucca Mountain Project is beginning to obtain some measurements on open circuit potential on specimens exposed to a long term time, something like--that stuff was so preliminary, but I understand that one of the concerns may be that other things in the juice maybe surrounding the waste packages may elevate potentials. How about all those ions that come out of the Alloy-22 itself? Could that be creating over the long term, some kind of a system that would have a very high redox potential?

CRAGNOLINO: Well, to tell you the truth, I didn't give it thought in that direction as a product of the dissolution. The concern with ferric ions is legitimate depending upon the acidity of the media to have enough concentration available of iron three plus, otherwise they tend to precipitate in the form of complex salts or mineral rocks, oxyhydroxides, but it is something that has to be looked at, no doubt. To dissipate concern, nitrate has a very low kinetic for reduction. I don't anticipate, for instance, the nitrate having influence in the cathodic kinetic reaction that control the corrosion potential. But, if this is like ferric three plus, we can think about something else. I don't know. It has to be looked at carefully.

NEWMAN: This is Newman. May I make a small comment on that? I think the first one is that I think Fe3+ can be solubilized a little bit by fluoride in the environment. So, you can have a buildup of Fe3+. But, the other comment relating to fluoride is that it wouldn't surprise me if fluoride were to be an inhibitor of localized corrosion of this material, not an activator. Do you have any direct evidence one way or the other on that?

CRAGNOLINO: No. Let me answer to him first. No, we don't have any evidence. It's important for titanium drip shield. That is not the subject of this discussion. But, let me tell you that is extremely important for titanium drip shield and there is no inhibitor there to control the site. You control nitrate, you control sulfate, you control everything but fluoride affecting this because it's a different type of process altogether, you see? Generally, solution in phase like fluoride is complex titanium in the form of hexaphase -- fluoride titanate. But, I don't know. It would be interesting study to do it.

BULLEN: Dr. Strehblow?

STREHBLOW: Just a short comment to the fluoride story.

If you have iron 3 in the--well, if you like to solubilize iron 3, then it's forming a very strong complex and then this is no longer a strong oxidant because it's a strong complex and doesn't react. And, on the other hand, I have to say that the fluoride is really a very dangerous species. It's attacking the surfaces generally by dissolution. Dissolving the passive film and by thinning the passive film and increasing the passive current density, that's one thing. And, the other thing, it can result in a complete removal of the passive film. This could lead to general dissolution of the metal surface in the case of iron and nickels like that. Or if the pH is a little bit high, you have localized corrosion and we have published this 20 years ago or something like that.

NEWMAN: That was on nickel, I thought.

STREHBLOW: That was on nickel and iron. But, you mentioned also the iron dissolution possibility and then you have a complex, a strong complex which would not really react.

CRAGNOLINO: I try to avoid generalizations. You know, I understand very well the chemistry of iron chloride complex. It have a beautiful reddish color since we are talking about color. But ferrous cyanide is a very stable complex. Nevertheless, you can have a very well-defined kinetic reaction of ferrous cyanide, far greater than ferric anion. I mean that dissolution you have to look because always in this type of system--and even if you have a species that the conditions aren't right for the transformation will carry the equilibrium down. And, this is the thing. I think that we have to stop this comment here.

BULLEN: I was going to refocus the discussion, but I see my colleague, Alberto, has one comment. So, I will let him sneak one in.

SAGÜÉS: And, this is a comment again I want to say to the other speakers. Yesterday, we saw some very good reasons why Alloy-22 would become better and better as time progresses and the nice passive layer forms. If that is indeed the case, the material is just great and it keeps on passivating and becomes more and more like a nice, noble material. Of course, what is going to happen then is that we're not going to have a baseline anodic reaction to keep that potential down and then the potential will creep up to whatever is--to something that will approach the equilibrium of the couples that maybe exist in the system. I would appreciate it if the Panel members would keep that particular sub-question in mind. What if the passivity gets so good that now we are at critical potential on that account.

BULLEN: Okay. Thank you, Alberto.

Dr. Strehblow, do you have a less than 10 minute presentation, I hope?

STREHBLOW: Oh, not that long, a very short one.

I had yesterday a little discussion with Jerry Frankel and he dug out one of my old results about 30 years ago when I was studying pitting on nickel and iron. Nickel is related to the Alloy-22 so I'm mentioning this one.

We have two kinds of critical potentials which I would like drawing attention to. This is the pitting potential of the lower limit. We have to exceed the lower limit to get pitting which is well-known. But then, if we have inhibitors in there like the nitrate. We have an upper limit which we call in these days inhibition potential. So, if you get too positive, then the pits will repassivate. These results, we have found, were received by potentiostatic measurements, by potentiostatic pitting, and repassivation by changing the potential with potentiostatic measurements.

So, with the nickel, we have a certain range between these two lines which is acceptable to pitting. If we exceed this range and we get out of this red region, then we have passivity. If we are below that, we have passivity again. This is the story with nickel. We have done this also with iron, with chloride, bromide, iodide, and as inhibiting anions nitrate and percolate. Both are effective in this sense.

Now, if we look for a brief moment to stainless steel, that's what has been taken from a file of Jerry Frankel. It was checked in SSW, and I'm sorry, I forgot to ask what SSW is, but you might know that.

BULLEN: Bullen, Board. Simulated Saturated Water. So, it's saturated J-13, as I understand. Did I get that close, Dr. Gdowski?

STREHBLOW: Saturated in what?

BULLEN: Simulated saturated--in all the salts that are in there, right? No?

GDOWSKI: Chloride and nitrate.

BULLEN: Saturated in chloride and nitrate.

STREHBLOW: Uh-huh, okay. So, now in this case, you also see pitting, a pitting potential. Then, you have a region that pitting occurs, and if you exceed this critical potential, the inhibition potential, then you have a passive range and then you have transpassivity. So, you have a large range where you don't have any pitting.

Now, if we go to Alloy-22, we don't see that in the SAW, whatever this is, and you might know it.

BULLEN: Bullen, Board. That one is acidified. It's a Simulated Acidified Water. So, I'm guessing the pH is less than 3 or that sort of ball park.

STREHBLOW: Very good. So, in this case, you just have passivity and then you have transpassivity. Now, the idea is if we are looking to Alloy-C22, we have a lot of chromium in there. So, it's not nickel; it's nickel chromium. Perhaps, we have a shift of this V type structure to the right where the concentration ratio of aggressive to inhibiting anions should be much larger in order to get pitting. So, if we check that, the Alloy-22 with a high chloride concentration and small nitrate, we might end up with a situation where we could get pitting if we are getting to the right range of this curve.

And, that's what I wanted to say that we should pay attention to the lower critical potential and the upper critical potential which we called inhibition potential in these old days and we should perhaps check whether the stability of nickel chromium alloys and especially Alloy-22 is just course, because we need a higher chloride content to get pitting. And, we should perhaps study some dependence like that, what I have shown here. That's all I wanted to say.

BULLEN: Thank you. Comments from the Panel? Questions? Dr. MacDonald has requested a little time; less than 50 minutes, I hope.

MACDONALD: Okay.

BULLEN: How about less than 10? Thank you, Digby.

MACDONALD: After I presented the material yesterday, a number of people expressed surprise that I was able to get--well, not me, actually, people at SRI were able to get C-22 to pit. Okay? So, I wanted to show another example--in fact, two other examples of C-22 pitting. One will be stable pitting and the other is metastable pitting. Actually, the metastable pitting work was done in Moscow. Also, I'd like to comment on the various factors that are important.

This is an additional example of C-22 pitting. This is at 80 degrees Centigrade, pH 3, saturated sodium chloride solution and again at .9 of a volt on the SCE scale. This appears to be associated with some sort of an inclusion. We haven't identified what that inclusion is, as yet.

The work that Alexy Davidoff is doing at the Frunken Institute (phonetic) involves--part of it, at least, involves metastable pitting. If we take C-22 and saturated sodium chloride solution at 30 degrees Centigrade, you don't see any metastable pitting. It's just a simple passivation phenomena. And, these measurements are done at .3 of a volt on the silver/silver Chloride saturated KCl scale. However, if you go to 95 degrees Centigrade, that's what you find. So, metastable pitting clearly occurs at 95 degrees

Centigrade.

The reason why we're doing these experiments is to get the survival probability and these experiments will be carried on. By the way, this is just simply the time scale repeated on the bottom here. Eventually, of course, we hope to find a pit nucleate, in which case we will count all these metastable events and determine the survival probability. That's due to a process that, at least we refer to, as prompt repassivation. Prompt repassivation is the situation where the embryo or the nucleus fails to achieve critical conditions necessary for conversion to a stable pit.

I did point out yesterday that there is a different or a separate repassivation phenomena that has great implications for the production of pitting damage and I'll just review that very quickly again. That's this value gamma. And we refer to that repassivation phenomenon as delayed repassivation. Okay? In this particular case, we assume that it's a first order process. In other words, minus dn/dt is equal to k n or gamma n. So, this is where no delayed repassivation occurs. Prompt repassivation, by the way, is responsible for populating these initial bars here. If you have very strong, prompt repassivation, then very few of the breakdown sites convert into stable pits. So, this bar becomes smaller.

But, gamma, this delayed repassivation constant is responsible for how many of these pits will populate the larger dimensions, the greater depths and, hence, will determine when failure occurs. So, that's the case where gamma equals zero. And, this is a case where gamma equals 10^{-3} years to the minus 1. In case anyone missed what this calculation is, this is thousands of years, here's the thickness of the container canister wall, and these are increments in depth. So, in this particular case, there's still some living pits up here and they've got to 1.5 centimeters.

Now, the real question comes and this is something we're just starting on now is what's responsible for delayed repassivation? There's at least three processes that I can think of and I'll just use the board over here to illustrate them.

The first one is death by old age and I'll use the analogy with people because it's quite apt. When a pit grows, it ejects positive current from the cavity and this positive current has to be consumed by some reduction reaction. And, it's possible to solve the equations which we have done to describe the potential and current distribution in this system. But, what happens is that you define a hemisphere of influence for each pit. As the pit ages, this current increases and the hemisphere of influence expands. It's like a nation-state. Okay? It expands and it consumes the resources on the external surface. It needs to consume those resources to keep itself viable.

However, as this current increases, a greater IR drop occurs within the pit and in the external surface. So, less of the potential available occurs as a potential drop across the interface and, hence, facilitates that reaction. So, as the hemisphere of influence keeps expanding and the pit is demanding more and more resources on the external surface, it becomes increasingly difficult for the external surfaces to supply those resources. Eventually, when it can no longer supply the resources, then there isn't the separation between the anode and the cathode necessary to maintain the pit viable and the pit dies of old age. Okay? So, that's the first one.

The second process that occurs is what I call death by misadventure and that's essentially an unpredictable phenomenon. For example, say, if the surface dried off, then the pit will die. Okay? So, in a sense, that's a trivial one, but in fact, it may have important implications for prediction of pitting damage over a very long period of time.

BULLEN: Bullen, Board. A quick question then, if you have the pit that died by drying, when it rewets, does it initiate at the same potential and the same rates or--

MACDONALD: Don't know.

BULLEN: Thank you.

MACDONALD: Okay. The third one is death by competition. This is a very interesting phenomenon. Let's say, I have two pits next to one another. Then, as those pits age, their hemispheres expand, and ultimately these two pits compete for the same resources. Okay? And, survival becomes survival of the fittest. It's Darwinian in nature. So, there is ultimately a limitation to the number of pits that can exist on a surface.

And then, just as a final statement, I'll point out that we've looked at a lot of these pits. You can actually see these hemispheres of influence in quiescent systems by getting the lighting right under a microscope and you can actually watch these hemispheres expand because of difference in refractive index. Okay? Nickel, for example, this is a solution of nickel 2 plus.

Now, one of the interesting things that you find is that the pit protects its surrounding surface so that you never find pits nucleating underneath the hemisphere of influence. Never nucleate under the hemisphere of influence. We're just in the process now of trying to model this theoretically. These are very, very difficult problems to model, theoretically.

So, with that, I'll end. Except I do want to make a comment to all of the community involved in this business concerning experiments versus theory. Okay? I think that we should do our utmost to insure that there's a confluence between experiment and theory. Let me explain what I mean by that.

In all theories, certain assumptions are made usually so that you can solve the mathematics and so forth. Okay? I guess the plea that I'm making is that people who are doing their experiments be aware of what those assumptions are so that the experimental data that are produced can be used to test the theories. Because, ultimately, this question will be decided on the basis of models being used to extrapolate corrosion damage over a long period of time. Likewise, those who are developing theories, you know, must bear in mind what's possible to be measured and not produce theories that are impossible to test because, ultimately, these models and theories need to be tested in order to extrapolate.

The final thing I would make a plea for is that we are now carrying out experiments at temperatures significantly above ambient; in fact, significantly above 100 degrees Centigrade. The reference electrode, the choice of reference electrode, and how the reference electrode is connected to the cell becomes critically important because we can negate all of the work if we don't understand how to convert a potential measured, say, at 140 degrees Centigrade to 25 degrees Centigrade. There's various combinations. Some people have the reference of electrode actually stuck into the system so it's at the same temperature as the system itself. Other people use a salt bridge so that you have a non-equilibrium salt bridge. You've got a serray effect, thermal diffusion effect along the salt bridge, and that can contribute a potential to the measured potential that can be quite large depending upon the nature of the salt bridge.

So, I think, first of all, you have to state very, very clearly the potential scale upon which the measurements are made. By the way, these ones are made with the reference electrode at the same temperature. I think we, as a community, should decide upon some sort of a standard for reference electrodes so that we all are measuring the same thing.

BULLEN: Digby, before you leave, Dr. Strehblow had a question, then Alberto, and then Jerry Kruger.

STREHBLOW: Some remark to your question, your personal question, on drying the electrode and whether it will continue to grow when it is wetted again, the pit will continue to grow. We did some time ago some measurements where we pulled out the electrodes and apparently in this case, the high chloride concentration within the pit was the reason for its stability. And then, when we reintroduced the electrode, it immediately continued to grow to the same current density. Once the surface has a chance to reform a passive film, for instance, by rinsing with water and to get the high chloride concentration out, then it has to start again. This is a question to that what you answered.

The second thing is if there's a pit and if there's a second pit in the vicinity, then they compete for the resources. That might be true. But, it could be also the opposite. If you have a pit which is growing with a high intensity--which accumulates chloride because it ejects cations into the solution so it has to attract anions and it could be the chloride, for instance--then, in the vicinity of one pit, you have a high chloride concentration and this could create new pits. So, in their potentiostatic condition, it could be just the reverse that you have an awful lot of new pits around one pit due to the accumulation of that aggressive anion.

MACDONALD: Well, we've looked at nickel extensively and we've never seen that scenario that you described. I'm not saying it doesn't occur. Okay? It may very well occur.

But, what we see of the two pits that are close together, one of them eventually dies and no new pits nucleate underneath this hemisphere of influence.

STREHBLOW: But, we have seen many of these cases that the accumulation in the vicinity of a pit was increased when we have high chloride content due to the growth of this central first pit.

SMIALOWSKA: We have seen the same situation.

BULLEN: Susan, just right up to the microphone, please?

SMIALOWSKA: Okay. We have seen the same situation as he described. So, it is not unusual that you have around one pit several pits around this big one.

MACDONALD: Well, as I said, I'm not saying it doesn't occur.

SMIALOWSKA: But, I would like to ask you if in your experiments did you have the open pits or the covered by some residual of passive film?

MACDONALD: Well, you know, this was a non-electrochemical experiment. Just open circuit--

SMIALOWSKA: No, open circuit, but what kind of pits you have, open? It means not covered by passive film?

MACDONALD: Let's see, what kind of pits did I have? I think most of them were open here.

SMIALOWSKA: Yes, because when you have--

MACDONALD: Well, I said most of them.

SMIALOWSKA: Most. But, because if you have such a situation like on stainless steel--on different material with very resistant passive film, usually you have film which are covered by passive film, and in this situation what you have, you have one pit which is going left to the material and then the pits are going below the passive film and started--

MACDONALD: Sure.

SMIALOWSKA: --so they are quite close to each other. So, it's not--

MACDONALD: Yeah, but that's a different scenario than what I was describing. I was describing nucleation on the outside surface.

SMIALOWSKA: This is also on the outside surface. So, it means that--

MACDONALD: You're talking about--

SMIALOWSKA: --it is only this very special case which you described, not usual case.

MACDONALD: Well, I mean, we haven't looked at all that many cases. So, I don't know whether it's special or not.

BULLEN: Alberto and then Jerry and then Ugo and then Gustavo. Alberto, please?

SAGÜÉS: A question of numbers. When you show your distributions by assuming certain gamma parameters, I looked at the numbers and it looks like you're looking at the tails of distributions, when they hit or they not hit except at threshold --

MACDONALD: This one?

SAGÜÉS: Right, right. And, those numbers are pits per cm/square. Now, you have ten thousand centimeters square and one meter square, you have about 10^5 meters square. So, we seem to be having like a 10^9 multiplier.

MACDONALD: Oh, yeah, yeah. Don't worry too much about this because this will be subject to change depending upon what we determine for the survival probability.

SAGÜÉS: But, of course, you know, it isn't that you don't get anything. I mean, those tails keep going, right? Is that right?

MACDONALD: No, eventually, you've got to have--you know, pits come as integers. Okay? So, if the probability or the number predicted is less than 1, we put it equal to zero. You can't have half a pit. Okay? So, pits always come as integers. This may look to be continuous, but in fact, it's a digital.

BULLEN: Jerry Kruger, did you have a comment?

KRUGER: Yes. Yesterday, I proposed that metastable pitting is a possibility where you could get pit growth at potentials below the repassivation potential. In light of what you've said, is that still viable or reasonable?

MACDONALD: Yeah. I personally don't use the repassivation potential; I use the pitting potential. And, let me just point out that the extensive work done by Professor Shibata here and others, Hoisler and other people, demonstrates that the pitting potential is a distributed quantity. Okay? And, you know, its distribution is over .1 of a volt or .2 of a volt depending upon what the system is. So, there is no such thing as the pitting potential. If I were to carry out 100 experiments sort of similar to the way Professor Shibata has carried them out and I plot the data on probability paper, I end up with a near normal distribution in the pitting potential. It's near normal, not normal.

KRUGER: But, for example, the potential that Gustavo was talking about, say, at a potential much lower than that where you do get metastable pitting, could you get pit--

MACDONALD: I would expect so, yeah. I would expect so.

KRUGER: Because until your talk just a moment ago, it's been ignored completely, and even though I personally like the repassivation potential, from what you show--

MACDONALD: The distribution and the pitting potential is incorporated into these calculations.

KRUGER: Uh-huh. No, I think greater attention should be paid experimentally certainly under the repository conditions.

MACDONALD: Absolutely. And, you know, it's not even certain that--well, in fact, it's uncertain that if you carry out, say, one experiment that you actually sample the mean in the distribution, it's not necessary. You may sample one of the two sidearms in the distribution. I think that unfortunately leads to a lot of error or scatter in data that is probably there for a very good physical reason where people don't appreciate it nor can they define it because they don't repeat their experiments enough.

NEWMAN: I'll just directly address that question. Roger Newman. I think more than one of us yesterday or perhaps Gustavo and myself, certainly, I think were implicitly making the assumption. When we talked about, for example, surface deposits influencing pitting, the way they influence pitting is by stabilizing the metastable pit. So, in other words, in the limit what happens is that's exactly what a crevice or deposit does is it makes the stable corrosion occur at the potential where you first see the metastable corrosion on the nice, clean, shiny surface. When you have a dirty surface, you find that you get the stable pitting corrosion at the same potential where you would have gotten the metastable.

KRUGER: Boehni has found, for example, in crevices that metastable events also are important.

NEWMAN: Yeah, but I think there's a lot more people that have factored that into their thinking than perhaps you were--

MACDONALD: What happens, these numbers would change. Okay? These numbers would go up. Okay? But, it doesn't affect the shape. The shape of these curves is affected by this value of gamma which is the delayed repassivation. And, you know, it's conceivable, in fact probable, that gamma is also affected by having deposits on the surface.

NEWMAN: Well, I can certainly say I've seen one practical case. It was in rather a sensitive installation--I can't say exactly what it is--where the very reason why the pitting was so stable is that it managed to find a way of growing where the current didn't increase with time. So, the potential didn't keep dropping as you pointed out in your--was it the death by old age? I think it was the death by old age. And, pits are very clever, as you pointed out, as this competition and natural selection element. And, there's also this other element that I don't think it's possible to be sure that over a long period of time a pit will grow in such a geometry that the current--that it needs an increase in current. What you find is that pits always grow on the edge. They grow exactly in the shape that exactly consumes the available current. If the available current decreases, what you find is that part of the pit repassivates and it makes a little tunnel and you get these very ramified shapes that don't look like pits, at all. They look like kind of trees. And so, I think there's an interesting issue there as to--I don't think one should assume that the gamma parameter which probably applies to hemispherical type cavities applies to these real pits. They're a lot cleverer than that.

BULLEN: Dr. Bertocci and then Gustavo?

BERTOCCI: I think that I have seen cases where it looks like competition in the position of pit. But, one of the questions is that in this case you presumed that there is an equal probability everywhere for pitting and in a number of cases--

MACDONALD: I'm sorry, equal probability--use the other microphone.

BERTOCCI: An equal probability for initiating a pit at any point if you--

MACDONALD: No, no, no.

BERTOCCI: Well, if you can have this kind of competition, it means that you don't have points which are privileged or have reasons for any shape--

MACDONALD: No, no. They can be separated initially at a sufficiently large distance that the hemispheres don't overlap. So, you might have to start with one pit, the hemisphere of influence grows, then another pit nucleates. There's no overlap. There's no competition. Then, as they both age together, then they start--

BERTOCCI: I understand that, but any point on the surface has essentially the same probability of pitting. So, inclusions, things like this, are not considered in this case.

MACDONALD: No, because they're never the same. If the pitting potential is distributed, the potential at which you -- passivity breakdown, if that's distributed and you have a fixed corrosion potential because the rate of nucleation depends upon that potential difference, then there's not equal probability.

BERTOCCI: And then, I wanted to make a comment about the other -- you showed this pre-pitting in the case. I notice that they start rapidly and decay, more or less, exponentially. There are a number of cases where people have presented exactly the opposite. Williams, for instance, in which you have the current increasing and then decreasing very rapidly.

MACDONALD: Well, yeah. What he's talking about is the current during the actual birth and death, prompt repassivation.

BERTOCCI: I have seen the same thing in my experiments, but there has been always controversy about which way they go.

MACDONALD: And, in fact, you can see both types of behavior. I mean, these, too, can be at one of these little transients.

BERTOCCI: Yeah. I tend to consider this as the real passivation cases for a metastable pit rather than the other ones.

BULLEN: Gustavo?

CRAGNOLINO: Yes. I offer a comment to try to reconcile this point of view difference in terms of the proximity of another pit and I think that you are talking about two different things. One thing is pitting grows under potentiostatic condition in which you can have the situation that Professor Strehblow has just mentioned where you have pits accumulated one to the other. The other situation is clearly what Digby has in mind and the growth of pit under open circuit condition in which you have this type of situation that created the protection around. And, this was demonstrated in a very elegant work many, many years ago by Gross and Philandanigo (phonetic) and came this idea that the pit protects the areas around it. That is only on the open circuit potential--

MACDONALD: That's right and--

CRAGNOLINO: When you have a potentiostat, which is the common way, any imperfection will be a site of nucleation, nobody care--

MACDONALD: That is predicted theoretically when you breakout the (inaudible) environment--

BULLEN: Don't walk away from the microphone.

MACDONALD: When you solve all the equations for the current and potential distribution, you predict theoretically that the potential surrounding the pit mouth will be shifted in the negative direction. And, that greatly decreases the nucleation rate for new pits.

BULLEN: Thank you. I did not want to imply that everybody has to get up and give a presentation. If you want to make a few comments from your seat, that's fine. I actually have been ignoring the other side of the table and I had comments from both Drs. Kruger and Davenport early-on. So, since Dr. Kruger didn't want to be first and he didn't want to be last, I thought I'd put him in the middle and ask him if he had comments that he's like to make on Question 2 right now or do you want to defer 'til later?

KRUGER: I'll defer 'til later.

BULLEN: Okay. Dr. Davenport, would you like to make comments or do you want to--

DAVENPORT: Sure.

BULLEN: Okay. Go right ahead?

DAVENPORT: Yeah, I just want to make a couple of comments from here rather than a presentation. I was very encouraged to see Digby show a picture of a pit initiating at a metallurgical imperfection because I'm firmly convinced that that's something that's extremely important here. I was again very much impressed by Gustavo's images of intergranular corrosion. I think we really shouldn't undermine these factors, at all. I think the idea of Phillipe's concern about sulfur, and, I think, both at the surface and at grain boundaries are very important. That's something, I think, is going to affect both passivity and also localized corrosion here.

Thinking about Digby's comments about the growth of pits and pits consuming larger and larger amount of current, I mean, there's evidence in other alloy systems that as pits develop, the shape of the pits does follow the microstructure. So, you have the possibility of pits going down, preferentially down, grain boundaries which may or may not have species segregated to them. That could be a circumstance where pitting could persist and you don't get the same. It's just like very thin people being able to live longer. I mean, if you were going to use the human analog there.

BULLEN: She wasn't commenting about your longevity, Digby.

MACDONALD: No, I couldn't agree with you more. What we really need is somebody who can comment on the metallurgical state of C-22 and the aging effects that are likely to occur in the 10,000 years, if any.

BULLEN: Do you want to hear comments from DOE? I mean, Tammy Summers is sitting in the back. She's our resident expert. Did you want to stand up and tell us how wonderful the intermetallics won't be or do you want to just let it pass? Dr. Summers, it's up--do you want to shoot from the hip and give us a little bit of information on what you think is going to happen over the course of fabrication and emplacement? Nothing like putting you on the spot, right?

SUMMERS: Summers, Lawrence Livermore. As Gustavo mentioned earlier, we've looked at the aging in C-22 in order to predict what would happen under repository conditions. This alloy has a number of phases that form what you've been calling intermetallics are the TCP phases. They tend to be rich in chrome and moly. There are several that form, mostly, mu phase and P-phase. There's very little carbide formation because of the low carbon. At very high temperatures, you get sigma phase. And, at low temperatures you get ordering.

If you evaluate the kinetics, the formation these days is at higher temperatures. You have to do that because they don't form in very short times at the lower temperatures. The data does not indicate that these phases will form under repository conditions. That's the same for the ordering.

BULLEN: Bullen, Board. Actually, so what you're saying is if we make it through fabrication and you've done all the post-weld heat treats and you've survived the anneal process, although I'm interested in Gustavo's results at 870 because that means that near the heat-effected zone of that induction anneal at the end, you might end up with a problem? I guess that's the question I'd like to, at least, have you address.

SUMMERS: At higher temperatures, the phases form faster and we do have to look and are looking at formation of phases during the induction anneal. I think during the solution anneal because you have a cooling, phases form more slowly when the temperature is changing during cooling. So, I don't think that will be a problem, but we are looking at induction annealing. Keep in mind that the phase that forms at these higher temperatures is different. It's not the stable phase at the lower temperatures. So, even if it does form, the question is, you know, how quickly it may dissolve or transform to the other phases. But, we are looking at that.

BULLEN: Bullen, Board. One of my colleagues just whispered in my ear and had me ask you about inclusions or other phases that might occur metallurgically, these other imperfections that Dr. Davenport has alluded to.

SUMMERS: As far as the inclusions, I've looked at a lot of commercial Alloy-22 and I don't see a lot of inclusions. Sometimes, you'll see them at the center of the plate because you get less mixing during rolling in the center of the plate, but very few at the surface of the plate. We do have in our plan to characterize inclusions because we recognize that pitting at inclusions is important.

BULLEN: Dr. Davenport, did you have any other questions? Go right ahead and then we're going to go to Alberto.

DAVENPORT: Right. It wasn't so much additional questions. It was just a followup comment. That is something I think I mentioned to you last night and that is the question of how many canisters are allowed to fail? Is it a disaster if one or two fail?

Let me give the reasons for asking that question first because if one canister failing is a disaster, then we have to consider all kinds of extreme problems. We have to consider what one possible large metallurgical imperfection or one serious weld problem might occur in thousands of canisters. So, we have to consider very extreme conditions.

Going back to some of the discussions yesterday about fluctuations in the environment, is there one point in the repository where there's a particularly nasty lump of rock that's going to drip really nasty things onto one canister? If we're concerned about one canister failing, then we have to consider very wild, extreme possibilities. Whereas if one or two failing is not completely catastrophic, then we have pushed much more in the direction of things that are likely to affect most of the canisters and that very much narrows the range of possibilities that we have to consider in terms of where corrosion is going to take place--fact most of the canisters and that very much narrows the range of possibilities that we have to consider in terms of where corrosion is going to take place.

BULLEN: This is Bullen, Board. And, I will take off my repository chair hat and put on my performance assessment chair hat and speak to you as I understand the performance of the system.

We actually focused your question very narrowly and we made this group look at waste package passive film behavior and extrapolation thereof. In reality, the repository is required by law to meet EPA standard and the soon to be changed NRC standard for dose rate to the public at the accessible environment for a 10,000 year period. So, we look at the total system performance and we look at both the engineered and the natural system performance. And, as I understand results from the current models from performance assessment, one or two or three or a handful of waste package failures do not compromise the system and exceed the dose.

Now, Rob Howard may be sitting in the audience and can tell me the exact number of 97.365 containers can fail before we do it and less after that. But, in my estimate, we can withstand a few failures before the regulatory limit and still not exceed the dose limit. So, it's the distribution of the tails that you're actually asking about is how far in --do we have to go 6 sigma out to make sure that we have absolutely no failures or can we go a sigma or two on the standard deviation and determine that.

Rob, could you maybe address that?

HOWARD: Yeah, and I'm not going to give you an exact--

BULLEN: Five significant digits. I want five significant digits, Rob.

HOWARD: Okay. Five significant--we have about 10,000 waste packages in this system that's being envisioned at the moment. Whether at a high temperature or at a lower temperature, you could design a system for about 10,000 or

12,000 waste packages. To meet the regulatory standard for 10,000 years, it's certainly possible to fail on the order of 30 to 40 percent of those waste packages and still meet the standard. Now, it also depends on the nature of the failure. If you're talking about having a couple pits in each package, you still have to figure out a way to transport the radionuclides out of it either by advection or diffusion. Those processes can be very slow in a pitted material.

BULLEN: Bullen, Board. I actually have to apologize to Rob also because it also depends on the distribution of failures. I mean, if you failed 50 percent of the packages on Day 1, it would be a lot different than if you distributed it over the 10,000 years and failed all of them on Day 9,999 plus 364. So, I realize there's a distribution.

But in answer to your question, no, we don't have to worry about the extreme tails of the distribution. If there's one or two packages that are sitting under a big lump of lead dripping on the top of the stainless steel or the stainless material, the repository itself would survive those types of failures. Did that answer your question, Dr. Davenport?

DAVENPORT: Yes. I think that's really very reassuring in terms of what kinds of extremes of conditions we have to work with here. Going back to some of the metallurgical issues, I mean, it's quite clear that quality control on the welds and post-weld heat treatment is going to be something that's extremely important here. But, if that can be maintained to a pretty high level such that again there's only a low fraction of them where there are flaws that are likely to cause serious metallurgical and then potentially corrosion problems, again if that quality control can be maintained, then I think that helps us mitigate worries about these kinds of metallurgical effects here.

BULLEN: Bullen, Board. I think the quality control issues dealt with your quality assurance plan, NQA-1. There are going to be nuclear grade quality control for all of the fabrication processes. So, there are criteria that are set up and inspection and the like. So, I think that those kinds of issues have been addressed.

HOWARD: Yeah, we are looking at--in fact, our most recent analyses are early waste package failures come from an improper heat treatment of that welded area and that's a Poisson distribution failure rate. It's on the order of 2 to 5.

BULLEN: Okay. Thank you.

I notice we're approaching the break and so I want to give one more opportunity for--you do not have to stand up and make a presentation. Would someone like to make--oh, Alberto, I'm sorry. Alberto was after Dr. Davenport. Alberto, would you like to close us out before 10:00?

SAGÜÉS: Yeah. Since Tammy is here, I want to show a picture. And, this has to do with a question of phase stability and so on. I want to show to the Panel the kind of arguments that are being made concerning--not being concerned--about metallurgical evolution in the package over a long term. I would like to see what the Panel feels about this.

And, this is just an example of several things done in this model. Tammy could answer questions, I'm sure, on this. This is for just one particular kind of metallurgical evolution, and namely, what happens with welded areas and whether a given type of transformation may happen over a certain amount of time. These are the kind of data that we have, of course.

We have information here between one year and about, in this case, 4,000 hours--this is about like half a year or so in this particular case--at different temperatures. And, in this case, we have this indication in here. This is the ground truth information and this is the kind of extrapolation regimes that are being made to see whether or not at the temperatures of interest we may be having a certain amount of precipitation. Now, these are the kind of empirical information that we have. I'm sure that we have a body of knowledge in physical metallurgy of phase transformation that goes together with this. Of course, what is not in here is whether there would be some metastable phenomena or whatever that may happen at Time X that we just cannot observe with our present knowledge of phase transformations and metallurgical evolution of the systems.

The question is, of course, and Tammy, I'll ask you very quickly if you could answer this. How do we know that we are not going to encounter some metallurgical break in here that is going to do this kind of a job or this significant type of phenomenon? These kinds of uncertainties, we have to deal with in our thinking as to whether we're going to have Phenomenon X happening in the not so remote future. Can you comment on this, Tammy?

SUMMERS: I can tell you about what evidence I do have and that is a natural analogue that's been formed about 150 million years ago. It's a two phase structure and it has its high temperature structure. It hasn't changed since it formed at temperatures between 350 and 400 degrees C. This is a nickel/iron system. The phases are actually fairly similar. They're solid solution FCC just like the nickel in C-22. There's also an ordered phase which is very similar to the ordered phase that forms in Alloy-22 and that has seen--

it formed during igneous activity--it's seen a temperature profile similar to that seen in the repository but extended over much longer time periods and much higher temperatures. So, the fact that that structure hasn't changed in 150 million years provides evidence to us that there's no unknown mechanisms, no very rapid unknown mechanisms.

SAGÜÉS: In that particular system in a nickel/iron alloy, about 60 percent nickel and about 40 percent iron?

SUMMERS: Right.

SAGÜÉS: Now, of course, we have to find a C-22 analogue that will be--we have had this kind of argument before. I'm saying this for the benefit of the Panel. Yes, that's a good example of what is happening. I'm sure that when people were building, say, tin organ tubes in the 16th century, they were not aware there was a--you know, they discovered later by bad luck that there was a transformation of 10 degrees Centigrade where there were two different phases of tin that would cause that to crumble and so on and so on. I'm just saying there are examples of corrosion in the history of science and engineering which an unknown transformation took place and they didn't have an analogue for that to deal with presumably, for example.

So, anyway, indeed, your argument is a good one. And, that is that there is one system in which things behave as expected.

BULLEN: Tammy, did you want to make one more comment?

SUMMERS: I was going to say, you know, this extrapolation looks rather severe and I'm probably the first one to say that extrapolating four points out of three decades in time is a bit tenuous, but we do have theoretical modeling that backs this experimental work up. It's a much firmer extrapolation. It, of course, is based on our understanding of the mechanisms that occur. We cannot model a mechanism we don't know.

BULLEN: Dr. Newman?

NEWMAN: Newman. I have a question for you about this type of phenomenon. Is the thinking that this is a potential embrittlement phenomenon or a potential corrosion phenomenon since we're talking about corrosion here?

SUMMERS: Well, actually, we're worried about both. The TCP phases form on the grain boundaries first and this has an impact on the toughness of the material. And, also, because it's chrome and molybdenum rich, tends to deplete the matrix of those elements and impacts the corrosion. But, again, we don't see any indication that this would form under repository conditions.

NEWMAN: Because we've done a little work on sigma phase and so forth, chi phase, and so forth in duplex stainless steels. It's awfully difficult to get people's attention to talk about corrosion of these materials because what they're worried about is huge manifolds under the seat breaking in half and so forth. So, it's a different--corrosion can seem like a very small concern compared to that, I guess.

BULLEN: Thank you. Now, as chairman's prerogative, I'm going to ask that we take a break now. I'm going to ask you to come back at 10:15 knowing full well that it will be 10:20, but please try to get back in the room by 10:15.

Thank you.

(Whereupon, a brief recess was taken.)

BULLEN: I'm changing hats now. I've taken off my hat as a Nuclear Waste Technical Review Board member and I've put on my Professor's hat.

And so, I want to ask everybody that's a Panel member, 14 of you, to take one of those pieces of paper that says Nuclear Waste Technical Review Board on it. Everybody gets one of those pieces of paper, a blank one. Okay? Now, this is a pop quiz. I don't want your name on this quiz, but I want you to basically consider the following.

This is the temperature distribution that we were shown by Carl Di Bella yesterday and what I would like you to do on your piece of paper is to make a column that looks like this that says Waste Package Survival. And, this is a

Chance, all right? So, being the true Las Vegas meeting person, the chance is from 0 to 10, okay? Then, I want to know what your plus or minus some percentage which we'll call your uncertainty. Okay? So, I want the chance of it surviving 100 years, 1,000 years--I apologize for the comma; to the Europeans, it doesn't go there in your country, I know--10,000 years, and 100,000 years and I'd like you to write it down. So, if you think--

SPEAKER: What does chance--

BULLEN: If you think it's going to survive, very high probability of survival, for 100 years, you put a 10 here or a 9 or an 8 or whatever. If you think it's going to have a very--my plus or minus zero there, tells me that I know it's going to be exactly 10. Okay?

NEWMAN: And, survival is having no penetration?

BULLEN: Survival is having--is the waste package itself. It's not worried about whether or not I have tails of the distribution and I would actually probably look at this as saying--I'm going to ask Alberto about this. The average waste package surviving, can we look at that? I mean, I know it's going to be a distribution around some statistical mean. So, I don't want you to argue about what the tails look like or anything. Will the average waste package survive 100 years, yes or no, or 0 to 10? Will the average waste package survive 1,000 years, 0 to 10? Will it survive 10,000 years, 0 to 10? And, what you think.

This is our way of forcing you to extrapolate. We asked you to comment on extrapolation and I didn't see as many people answer the question yesterday as I would like. So, after you've done this--and you don't have to put your name on it--I'd like to actually collect them and then I'd like to discuss it as part of the continuation of the meeting.

So, I always give my class, at least, three minutes to take a quiz. So, you guys can take the next three minutes. You can kibitz among yourselves if you want or you can just do it as a straight "this is my answer". But, I'd like you to fill out numbers here.

SAGÜÉS: If we catch you watching the person next to you, you're going to get an F.

BULLEN: That's right. We will immediately throw you out of the class.

SAGÜÉS: That's right.

BULLEN: Oh, I'm sorry, I meant to tell you what--there should be two numbers. I messed up. This is a hot number and a cold number. See, I messed you--this professor is terrible. I'd like to see two numbers here. You know, there's another number that says plus or minus zero, this one is a 1, plus or minus, you know, 5. I've got a big distribution and I don't think it's going to be right. So, I want a hot and a cold column, too. That's why I made it that wide. And, green is cold and red is hot. Okay?

So, actually, we could look at this and say, okay, up to 100 years following this line, what's the probability of survival? Following the red line up to 100 years, what's the probability? Then, go to 1,000, then to 10,000. You can imagine that 100,000, these kind of keep going, and they go back to ambient which is, I don't know, 35 or 40 degrees in the mountain. What's the ambient in the mountain, Rob?

HOWARD: 30, plus or minus 10.

BULLEN: Thank you. That's a big range.

(Pause.)

BULLEN: This is Bullen, Board. We had a comment. Did anybody in the audience want to take the quiz, too? We've got extra paper up here or you can use your own if anybody is interested. This would be a nice survey. You're relatively intelligent technical people. We will segregate the results, though. We don't want to intersperse with our Panel. But, if you'd like to, we'd appreciate it.

(Pause.)

BULLEN: I'm collecting the quiz now.

(Pause.)

BULLEN: This was not to develop a consensus. This was to see what the range of opinions of the scientific community were. So, we're not going to basically say everybody has to agree that, you know, Dan Bullen says it's a 10, so darn it, it ought to be a 10. I mean, if you think it's a 2, tell me it's a 2. And, actually, I don't think it's a 10, but I didn't say that. So, we want a range of opinions and that's the whole reason that we're doing this.

Let me see a show of hands? I see Professor Rapp is still--the last one? Anybody else still have the quiz over there? Oh, excuse me, Dr. Shibata, are you all done? Keep thinking, that's fine. I don't want to rush you.

CRAGNOLINO: I have a comment. I think that this has not been done under the proper QA (laughter).

BULLEN: Bullen, Board. That's the beauty of being a TRB member. We can put together a meeting like this and ask any questions we want without worrying about that QA, right?

SAGÜÉS: While we are getting finished with this, I would like to again ask the members of the Panel to keep in mind the scope of Question #2 which has two parts. The first one is whether you can think of any mechanism whereby the potential could creep up--either the open-circuit potential creep up or whatever is the critical potential come down during that very long period of time. We're trying to get answers to that. We have seen some wonderful descriptions of potential pitting mechanisms and the like, but I really would like, if at all possible, to try to go to that further step of trying to anticipate whether such a thing may be happening. And, of course, what kind of experiments or what kind of analysis could be conducted to elucidate the validity of those possible mechanisms. So, please, keep that in mind because that's the kind of thing that may eventually be part of driving our collective societal search for an answer to this.

And, the other one I would like to hear again, if you can think of anything that would not be amenable to that kind of a mechanism and I think that Professor Marcus mentioned something and some of you have mentioned something else, but again the technical community has been very much focused on some kind of a threshold of critical mentality. And, if that is the best thing that the community can come up with, that's great, but if there is something else, this is a very good time to bring it up and at least plant the seed of that alternative way of thinking about it.

BULLEN: Bullen, Board. I just missed what my colleague said. So, I'm going to actually ask that if there's anyone else in the Panel who would like to address either the issue that he raised or anything else that they'd like to say, we do have--let me tell you one housekeeping issue. We're tabulating and taking averages. That's what you do with data like this. So, I handed it off to the staff and we'll come up with a number that gives you, you know, numbers, plus or minus percentages, by the end of the day.

Professor Rapp, did you have a comment or question you'd like to make?

RAPP: Yes. Last night when Alberto and I were enjoying the wine, he told me something that I would not have imagined that--and I don't know whether I believe. But, it's important to this issue of what is the potential in the film. He said that when this hole in the ground gets closed up or sealed that there will essentially be no air in there. I would like to hear about that. And so, only humidity so that the principal oxidant is any condensation of water. I just cannot imagine that air can be excluded. Maybe, a clarification?

SAGÜÉS: No, let me clarify. Many of the projections assume that the system, the drifts, are going to be sparged by steam. Whether there is going to be or not air in there is another question and there is all kinds of evidence. But, at least, many of the projections assumed over a certain amount of time, the air is going to be sparged out by water vapor. At what moment the air comes back and how much oxygen comes in is another issue. But, effectively, a predominance of water vapor is--as far as I know, it's still pretty significant in the TSPA projections.

BULLEN: I'm going to ask the PA people. Rob, does relative humidity go to 100 percent and air partial pressure go to zero at any time?

HOWARD: Partial pressure of air never goes to zero.

BULLEN: You always end up with 20 percent oxygen, 80 percent nitrogen, and a bunch of water?

HOWARD: I mean, the relative humidity goes up to--

BULLEN: Basically, the mountain breathes, right?

HOWARD: Yeah, yeah. It's an open system.

SAGÜÉS: How much does the relative humidity go up at, say, the Year 100 in the hot concept?

HOWARD: Relative humidities for either system, whether it's warm or less warm, go up to around 99 percent on the order of 200 to 500 years dependent on where you are in the repository. I mean, it is variable over time. But, relative humidities go up on these time scales, I would say, rather rapidly.

SAGÜÉS: But, doesn't the TSPA--doesn't the near-field environment calculation assume that by that time around Year 100 or so you have mostly water vapor and most of the air has been spurged out?

HOWARD: No.

SAGÜÉS: No?

HOWARD: No.

GDOWSKI: The limit on the water vapor pressure is atmosphere pressure. You can never go above that. So, once you're above 100 degrees C, the relative humidity is always decreasing. But, there's always a small fraction of air in there. It never goes to complete water vapor. There's always some air in there.

SAGÜÉS: And, how much?

GDOWSKI: Oh, that's a good question. I would think it's anywhere--I don't think it gets less than 10 percent of atmosphere as air.

SAGÜÉS: I seem to recall earlier in the TSPA-VA, at least, didn't they have like 100 percent water vapor--

GDOWSKI: I think they have modified their models now and so there was always some air there.

BULLEN: Bullen, Board. I kept asking that question with respect to the drift scale heater tests because the projection was that there would be 100 percent water vapor in the tunnel. And, what they find is that the mountain is very fractured. There's a lot of flow. They couldn't seal off the bulkhead. All those kinds of things happened. So, in reality, you always have oxidants that are air, if it's not--

I mean, it's never 100 percent just steam. It is steam or it is relative humidity--high relative humidity air at higher temperatures.

RAPP: Since water condensates gives you the expected corrosion, why don't they blow it out with nitrogen instead, dry nitrogen?

BULLEN: Well, the problem is that the mountain itself is a natural system that fractures and so you can't keep it--

RAPP: Fine. So, you won't be able to do that anyway, but I don't understand putting steam into a system where corrosion seems to pose such a problem.

BULLEN: The steam occurs naturally because the water comes in contact with the hot rock and the hot--it's the groundwater percolation in there that vaporizes water.

RAPP: Fine.

SPEAKER: Oh, you're not adding steam?

BULLEN: No, no, no, nothing is added. This is just the natural system.

RAPP: That's what I just heard.

SAGÜÉS: But again, TSPA people, please. Are we saying that supposedly in the hot curve over there around the Year 100, don't the present projections say that maybe--of the molecules of gas in the tunnel in the present projections, which percentage of those are water molecules like, at least, 50 percent?

HOWARD: Can you ask the question a different way? I don't understand it.

SAGÜÉS: Well, you have a one meter cubed of air in the drift, you're at Year 100, of that one meter cubed of air, which fraction of the molecules are water molecules, and I would say it's a significant fraction, a very large fraction, isn't it, in the present TSPA projections?

GDOWSKI: No, it's probably--it varies across the repository. I mean, every waste package is different. But, if you look at the range, it's probably about 75 percent relative humidity at 100 degrees C. So, assuming that at 100 degrees C, you have one atmosphere of water, you have about 25 percent air in there.

SAGÜÉS: Okay. So then, about 75 percent of the molecules are water molecules, roughly, right?

GDOWSKI: That's a range. I mean, that's the nominal value--

SAGÜÉS: Yeah, something of that order, about three-quarters, you know.

RAPP: You didn't say that right. What's the temperature of the gas that you're talking about? Relative humidity 75 percent does not mean you have 75 percent water.

GDOWSKI: I said 100 degrees C.

RAPP: Oh, you said--

GDOWSKI: Yes, I did.

RAPP: The gas in the tunnel is 100 degrees C. So then, you've got 75 percent water vapor, you're guessing?

GDOWSKI: Right. That was just a convenient number for me. I mean, I don't have the calculations with me.

SAGÜÉS: Adding the earlier projections in the early models, the models indicated 100 percent, right? -- also spurging out, but that has changed.

BULLEN: Basically, it changed because of the results of the drift scale heater test, as I understand it. Is that a misconception?

(No audible response.)

BULLEN: Dr. Newman?

NEWMAN: Newman. Since we're dealing here with what seems to be essentially atmospheric corrosion, although we've not used that word, I'm not--probably because of my ignorance of thermodynamics, I don't quite follow, as yet, what relative humidities--well, the relationship between the relative humidity and the tunnel thing, the relative humidity that's appropriate to the surface temperature of the canister, which will be a different one, presumably, and the choice of the proposed concentrated environment for carrying out corrosion testing. Obviously, there must be some sort of mental process linking those three things. Is it possible to explain in a few words what that is?

GDOWSKI: I think the calculations that Rob gave to Professor Rapp show the actual relative humidity on the waste packages.

NEWMAN: On the waste packages?

GDOWSKI: On the waste packages.

NEWMAN: All right.

GDOWSKI: The waste packages are always hotter. So, the relative humidity is always lower on the waste package because we're assuming constant water vapor pressure inside the drifts. So, there are projections on what the relative humidity would be on the waste package.

NEWMAN: Right. So, your magnesium chloride solution, for example, would--what Henning calls his Q brine which is all concentrated magnesium chloride would form at some particular humidity and then your other brine would possibly form at some other humidity and so forth. Is that correct?

GDOWSKI: That's right. And, as you go up in relative humidity, the brines become more and more dilute because of the--

NEWMAN: So, there is a period there where you can get something approximating to this Q brine type of environment?

GDOWSKI: That's right, and it's transitory. I mean, as you go to lower and lower temperatures, the relative humidity for all the projections go up. So, the brines become more dilute.

BULLEN: Bullen, Board. I have a question. Can you get that same relative humidity in concentration if you don't go up in high temperature, if you hit the green curve instead of the red curve up there, Dr. Gdowski?

GDOWSKI: I'm sorry?

BULLEN: You have two questions. If I don't boil the water, can I hit the brine concentrations in the same manner?

GDOWSKI: It's a function of relative humidity. It's not temperature.

BULLEN: Not temperature.

GDOWSKI: It's relative humidity and that controls the brine concentration.

BULLEN: By the way, could we all get a copy of that handout that was given to Professor Rapp?

NEWMAN: I think that's an extremely important handout.

RAPP: Let me ask one more time to be sure.

BULLEN: Go right ahead?

RAPP: Is this tunnel going to be purged with steam or with something more reasonable like dry nitrogen or--

GDOWSKI: No, it's not purged. The rock itself contains between 10 and 20 percent water by volume and, as you heat the rock, you're vaporizing that water and that's what's causing the water vapor pressure to rise.

RAPP: All right. I understand that, but just before the tunnel is sealed up, is anything done?

GDOWSKI: There is a ventilation system that's purging with outside air, the desert air.

RAPP: Okay. So, air is always there.

BULLEN: Yes, that's correct. Air is always there.

RAPP: Yeah, okay.

BULLEN: Any other questions about this--Gustavo, did you want to make a comment?

CRAGNOLINO: No.

BULLEN: Okay. I want to thank the project for illuminating that way.

Other questions or comments with respect to Question 2 or the issues raised by Alberto? Some other people that wanted to make comments that haven't yet or do I have to twist--okay, Professor Marcus.

MARCUS: Well, actually, I have a few points which are more related to what has been discussed earlier than to just the last point.

I would like to return to the question of aging, not aging of the material, but aging of the passive film. It has been pointed out here aging of the film is beneficial, but this--I think it's been proved only for very short time periods. This beneficial effect is due--for chromium containing alloys or stainless alloys including probably C-22--is due to increased chromium three plus contained in the film. This has been known for some time. But, also, increased crystallinity. However, I would like to point out that again this has been proved only for short time periods. I'm asking whether these improvements would, say, continue for longer time periods is completely known. And, of course, this is very important in terms of breakdown of the film because the improvements can be seen in terms of, for example, the pitting potential increases with aging, but again over short time periods.

Another point is that this has been proved to my knowledge only on alloys containing chromium and perhaps molybdenum like the 316, but not for alloys containing both molybdenum and tungsten. So, I would suggest that more work be done to, even for short time periods, look at the aging of the film on such an alloy, and see if tungsten has a beneficial or non-beneficial effect on aging. I think this is unknown.

The second point is again the sulfur species which have been mentioned, that I mentioned yesterday, and Gustavo emphasized that. And, I would like to re-emphasize that if sulfur species are present, pitting can definitely occur at potentials which are much lower than the pitting potential measured with chloride solutions. It is known, for example, for iron/chromium alloys that if you have both thiosulfates and chloride in the solution, then there will be stable pitting at potentials where, in the absence of thiosulfates, you will have only metastable pitting. So, at the causlos of the stabilization of the pits is the thiosulfates. So, even at potential where you will observe only metastable pitting, you would get stable pitting in the presence of thio-sulfates or other sulfur species.

BULLEN: Pardon me a second. Bullen, Board. You mentioned thio-sulfates. Are they microbiologically influenced or are they just--

MARCUS: That was the next point is that I think this issue has not been raised and I don't know if it's an important issue or not is whether microbial induced corrosion must be taken into account. This point has not been raised, so far. But, of course, if we are talking about sulfur species in the environment, we cannot disregard the possibility that micro organisms could produce such species.

The last comment I wanted to do was on again the wet and dry cycles and how they may modify the composition of the oxide layer and the resistance to breakdown. I think that if we go up to temperatures about--I could not get a clear idea of what the maximum temperature on the waste package surface would be, but I understand it could be up to 200 or 220 degrees C. Perhaps, slightly thicker oxides could be formed. I mean, thicker than the passive film formed in the aqueous solution. At this temperature, of course, it would be probably a dry oxide. I mean, the outer hydroxide layer which is normally present on the passive film will probably disappear at this temperature. And, one concern could be what would happen with this oxide layer, thicker, anhydrous layer, would be exposed again to the aqueous environment containing all the salts we've been talking about and I don't know if such a film could perhaps be much less resistant to initiation of pitting than what the normal passive film would be.

So, these were the comments I wanted to make.

BULLEN: Bullen, Board. Thank you, Professor Marcus.

Jerry, did you have a comment?

KRUGER: Yeah, I would like to get back to the issue of metastable pitting. I think it should either be more emphasized or laid to rest. And, I hope laid to rest because I have always felt that the critical potential or the repassivation potential is really the key element. You have lots of repassivation incidentally with metastable pitting.

And, I think, for example, Roger mentions that it's involved in the beginning of the process, but once you have deposits, the pit stabilizes. But, that's a serious thing, too, because once you have a stable pit, I presume you mean a growing pit, and some metastable pitting is involved in creating a growing pit. But, all these issues have to really pay attention to things like, just as Phillipe Marcus mentioned, the role of impurities like sulfer, which is a terrible impurity, does that enhance or stop metastable pitting? It probably enhances it. And, the metallurgy that's been talked about, the welds and etcetera, inclusions, and so forth, what role do they play? And, of course, the repository conditions, what roles do they play? And, wet and dry, for example.

So, I think this is an issue that is important because if we can minimize the effects of metastable pitting, then the ideas that Gustavo Cragnolino and Professor Shibata has mentioned with regard to repassivation becomes the all important thing that one has to measure and lay to rest the phenomenon that would rule out depending strictly on the repassivation potential. So, we need a lot more information on whether this is really something to worry about.

BULLEN: Dr. Shibata, did you want to make a comment or two? Please, use the microphone.

SHIBATA: I think that passivity people like to expect good quality of passive film, but if you note lifetime here, this is the potential, and we can suppose such kind of figure for expecting the crevice corrosion and the pitting corrosion here. Here is the crevice area and the no crevice. Pitting is expected around here and this is lifetime. And, I would expect the incubation time for pitting initiation here that--we don't know how long this time, but some time will tend to the crevice. But, if you can expect the worst case of crevice formation after long time, the crevice is created around here. So, I ask Gustavo what corrosion potential or open circuit potential is what position? He said around here or here, I'm not sure. So, if the ER crevice exists around here, if we can include this kind of ER crevice by our technology, this material can survive for long time after 10,000 years. But, if the ER crevice is much higher, we can easily expect crevice corrosion. So, we cannot expect it for a long time. So, I think we need much more data on ER crevice for this material.

Of course, good passivity, can expect for a long time of incubation time. But, we can now predict the incubation time for the pit initiation or pit formation. So, I think that we have to accumulate much more data on this crevice potential. Again, I have emphasized the importance of ER crevice data.

Thank you.

BULLEN: Questions for Professor Shibata? Susan, do you want to make a question or comment? Very close to your microphone, please.

SMIALOWSKA: It is rather a comment. I am very much confident that repassivation potential, it is very important thing to find if the crevice corrosion will occur or will not occur. However, crevice corrosion, crevice pitting, critical crevice corrosion will depend on many different factors like metallurgical factors, surface effect, like environment conditions.

SHIBATA: Yes, yes.

SMIALOWSKA: And so, we will have different repassivation potential depending upon these factors. What we can do, I think that we can very much probably improve the materials and it will be very easy to find if materials is good without inclusions, without the second phase precipitation, and so on. So, this would be the easiest way to control. The control of surface roughness, it will be also easy. But, environment effect is not very easy to control.

SHIBATA: Yes.

SMIALOWSKA: And, therefore, I think that we have to do the experiments in extreme conditions. So, the extreme conditions, it is the dry and these very wet conditions and different combination of this. I know the effect which is very, very important, what I mentioned several times, it is aging. However, again, how to model aging time? It is very difficult, but not impossible. And, I think that in this venue people who are working in passivity and electrochemistry can do this.

So, I would like to once more emphasize that I believe strongly that the critical potential for crevice will give you the right conditions when pitting will occur and will not occur. However, pitting potential, just pitting nucleation potential, even if you are doing statistical way, like you said, it is not good for predictions. This is my--

SHIBATA: That's right. Yes, I agree that the pitting potential is just located around here. So we can, of course, improve our techniques, alloy addition, something like that, and of course, depending on the environment. So, we need much more data for the crevice. Of course, this is a function of the metallurgy and environment, but Gustavo said that not so much depends on the pH, but of course, it will depend on the chloride or some other species and the metallurgical conditions, I think.

SMIALOWSKA: Maybe one more.

BULLEN: Go right ahead?

SMIALOWSKA: Once again, I would like to emphasize that this critical crevice potential is depending mostly about the composition of the film because what kind of aggressive solution you can produce in the localized corrosion? But, you must remember that also passive film is important because you have to have such a passive film which will keep this aggressive solution in the localized--

SHIBATA: Yes, I understand. But, I think there are two approaches. One is expecting the good passivity, this is one scenario. Another scenario is expecting the worst case. That means that after pitting initiation or after crevice initiation, even then, we can expect it for a longer time. So, the two scenarios; one is, of course--this is very important techniques; two, inhibits pitting initiation in improving the environment and also improving the alloy, the --

BULLEN: Digby and then Jerry?

MACDONALD: Yeah, let me state my objection against repassivation potential. You have to ask the question what is the initial state in that measurement? And the initial state is an existing pit.

SHIBATA: No, in this case, the crevice formed already, so that the stopping potential here--the worst case.

MACDONALD: Okay. Okay. But, we talk about repassivation potential for a pit. Okay? Then, the initial state is an existing pit. Okay? It's not a passive surface. So, the parameter is not measuring passivity breakdown.

SMIALOWSKA: No.

BULLEN: Susan, go ahead?

SMIALOWSKA: No, it is a completely different story and there are different models which assume which way the breakdown of the film occurs. But, breakdown might occur without chloride anions and without aggressive solution. And, in your point defect model, you assume also that breakdown of the passive film without any aggressive solution.

MACDONALD: I assume what?

SMIALOWSKA: You assume that breakdown of the passive film occurs without chloride solution. You only say that when you have chloride anions, then this agglomeration of the vacancy at the metal and oxide interface is going much more faster. This is what you said in your model.

MACDONALD: I didn't catch the middle.

SMIALOWSKA: I said that you said in your model that the passive film can be this--breakdown of the passive film occurs without any aggressive solutions or any chloride. And, chloride, what are doing, it has increased the--

MACDONALD: Although, Susan, there's a number of processes that can give rise to the generation of vacancies. There's a number of processes. If you have oxidated ejection of a cation from the barrier layer into the solution, okay, that generates vacancies.

SMIALOWSKA: But, you generate the vacancy without any aggressive solution.

MACDONALD: You can generate vacancies without chloride ion.

SMIALOWSKA: Yeah. As you said, that this is the breakdown of the passive film.

MACDONALD: But, chloride ion greatly accelerates the generation of vacancies.

SMIALOWSKA: Yes, yes. Accelerate only.

MACDONALD: Yeah.

SMIALOWSKA: Accelerate only. Okay.

MACDONALD: Yeah. Let me come back to this question of repassivation potential because in a sense it violates the principle of causality. Okay? Because what causality says is that the system should have no response before time equals zero. The transition from a passive surface to a pitted surface has occurred before time equals zero. Time equals zero, being your reverse (coughing) potential. And so, it violates causality. The repassivation potential is not measuring passivity breakdown.

SMIALOWSKA: Passivity breakdown, no, we agree on this. But, when you have metastable pits, what was done by several people that metastable pits in the crevice are formed when you have no crevice corrosion, but metastable pits grow there and you have then--the metastable pits they join themselves producing crevice. This is on everything time dependent. So, if you will wait many, many days and years, then you will have pitting in the region between the repassivation potential and this nucleation potential which is quite--

MACDONALD: It's because the pitting potential is a distributed quantity.

BULLEN: Bullen, Board. I love the give and take, but we actually have a little bit of time limit. I want to go to Jerry--and then I have to ask do any of the Panel members have to catch an early flight? I know that Professor Pickering does and so I'm going to go to him next. Anyone else have a time constraint that we need to make sure?

SPEAKER: Susan and I.

BULLEN: Okay. So, I will make sure that everybody gets a comment. Jerry, do you want to make your comment and then we'll go to Professor Pickering?

KRUGER: Yeah, a very fast comment. First of all, with regard to repassivation potential and the role of the initiated pit in the first place, there are ways in which you can determine the repassivation without that happening. For example, you can do it mechanically or you can do it electrochemically by going to a very high potential and then looking at the transient as it goes down as a function of the open circuit potential.

Secondly, Toshio Shibata said that there's no role of pH in repassivation. That's not necessarily true in a crevice, for example, where you have occluded cells which build up very, very low pHs. So, pH does indeed play a role there in terms of repassivation.

BULLEN: Professor Shibata, do you want to comment?

SHIBATA: I have no data on the crevice corrosion potential. So, I'm not sure I can say.

KRUGER: Well, if you talk about the bulk solution, yes, the pH does not have any role. But, if you talk about inside the crevice, you have very, very low pHs developing. So, that would play a role in the crevice. That's basically all I--

SHIBATA: Because the outside pH, it does not affect so much on the inside.

KRUGER: I agree with that.

SHIBATA: So that the apparancy (phonetic) does not change.

KRUGER: I agree with that.

BULLEN: Professor Pickering, do you want to make a little presentation? Please, use the microphone.

PICKERING: On this last point, it's not the reason I'm up here, but I would say that what Jerry says fits right at what I want to talk about and that is understanding better what's going on in the crevice when you measure your repassivation potential. Does it suddenly passivate when the pH goes down to 3 or gets up to 7 or what? Or the chloride or whatever it is that's in there.

So, I'll go on now to the few data I have here. I just wanted to share with you some data that I gave you yesterday actually, but I didn't talk about. I'll start with the slide you saw yesterday and the point just deals with the composition like Phillipe and others yesterday and myself were saying about the possibility of the composition of the electrolyte changing on the wall. And, we're bothered here by the fact that we don't really know what's going on in the crevice. This is a crevice now. That causes this passive film to increase with time during the induction period. So, we like to know that.

Now, you know, we couldn't make the measurements 10 years ago when we did these measurements of the chloride concentration in the pH. We can now, but that's too late.

But, we did do something else about a year ago and what we did was we artificially changed the chloride concentration in the system that's very dependent on the chloride concentration for the breakdown or the onset of the crevice corrosion process and that's what I'm going to just show you now.

We kind of spike this solution and I'll first tell you about the system. If I had thought about this problem a year ago, I'd have picked nickel because we could have just as easily done it from nickel. This is iron pH 5 solution. I just show you here the polarization curves when you increase the chloride. You see the current density changes quite drastically with increase in chloride concentration. So, you go from, say, the starting blank solution here in the 10^{-5} range, amps per square centimeter, and I'm going to show you what 22 millimolar--that's close to 20 millimolar here. With 20 millimolar, you see what happens; you're way up here somewhere. And, the experiment I'm going to use, we're going to apply the potential at the outer surface. It would be right here at .8 on the calomel scale and hold it and see what happens then inside the crevice when you spike this system with 22 millimolar chloride.

Obviously, crevice corrosion starts and I wouldn't be showing you this otherwise. What we have here now is the

800 millivolts applied at the outer surface. So, we're along this boundary here and potential. This is time here, but just focus on this region right here to start with. We won't say how we got there, but we have a passive wall, a totally passive wall. You can see that. First of all, this is potential at the bottom of the crevice, 1cm deep crevice. The potential is very close to the outer surface potential. There's only 25 or, roughly, a 25 millivolt IR drop. And, that corresponds to a passive current. You can see that the current is coming out of the crevice. It's down here at 10^{-5} amps per square centimeter, the passive condition on that crevice wall. So, it's a totally passivated system. At this point in time, we added a drop of the blank solution which now is spiked with 22 millimolar sodium chloride. That caused the current to go way up because, as you saw in the polarization curve, something you'd expected, the current goes way up and you see what's happened to drive that. The reason is the potential at the bottom of the crevice has dropped precipitously down here at 1.4 volts roughly to -600, well-below the active-passive transition for this particular iron system in this pH 5 solution.

So, this is the sort of thing that I can visualize happening inside the crevice with Alloy-22 or nickel. As I say, if I do this with nickel, I don't have any doubts we won't get the same thing if we have the right ion. If it's the chloride that Phillipe mentioned--or not the chloride, the thiosulfate or whatever it was and the sulfur species, and that changes the polarization curve like I showed you, then I can expect that we'd have something like this one.

BULLEN: Thank you. Questions for Dr. Pickering? Roger?

NEWMAN: Well, it wasn't really a question for Howard, a comment. If someone else has a question, that's fine. I wanted to get back really to this issue of the repassivation potential and crevice corrosion. And, just sort of in the spirit of Devil's Advocate, I'll ask the question.

To what extent is the project relying on the inhibiting effect of nitrate to get the optimistic results that they're getting? Because I have some doubts about the longevity of that. Or, longevity is probably the wrong word. But, some doubts about the ability of nitrate to exert that inhibiting effect in extremely occluded geometries, such as you might get underneath a deposit or a layer that develops on the surface.

The reason I say that again relates to a practical instance that I came across where nitrate was added to a water system in order to arrest very large growing pits and these were pits that you could put your finger into. Well, you couldn't really. But, these were large pits and I don't know what was done in the actual plant, but some laboratory investigations were carried out and it was found that nitrate was remarkably poor at inhibiting the growth of pre-existing very large pits. So, I just wonder--I know Digby is going to say I'm violating causality even more by assuming a huge initial pit. But, if you get the surface deposit buildup, you might get what amounts to a sort of super crevice situation. I just have some doubts as to whether nitrate would really work.

So, I just wanted to know, suppose there was no nitrate in the water, how differently would we be thinking?

BULLEN: Gustavo would probably defer to the project. Does anybody from the project want to talk about the absence of nitrate and its potential for pitting? I see Dr. Gdowski took a big deep breath; that must mean no.

GDOWSKI: Yeah.

BULLEN: Okay. Jerry Gordon?

GORDON: We have done almost all our testing in what we think are relevant environments which in all cases have nitrate. Gustavo and the Center have done a lot of work in relatively pure sodium chloride solutions. There is less margin between the breakdown potentials and the corrosion potentials without the nitrate, but there's still margin.

NEWMAN: Okay. Thank you.

BULLEN: Professor Sato asked to make a few comments.

SATO: Just a short comment. Considering the discussions we've had, so far, I think one of the most probable type of corrosion will be crevice corrosion because the clean surface of the canister doesn't last for so many years. So that finally we've got dust and deposits and precipitates on the metal surface so that we have certainly a number of crevice on the metal surfaces. As Professor Shibata and other panelists have mentioned, I think your potential for prediction of crevice corrosion will be very important in this case so that controlling the open circuit potential is one of the most important issues to control the long term corrosion of the waste package. And, I would like to point out at this point this is really the same things that I had mentioned yesterday.

You see, in the corrosion system, the open circuit potential which we've called the corrosion potential is determined by the anodic reaction and cathodic reaction. And, that's the corrosion potential, the anodic reaction, and cathodic reaction current is balanced each other. This situation is established when we have no radiation, no radiation at all. But, when you have the radiation which excite the corrosion system, if this corrosion system container that I mentioned yesterday, the oxide, solid state oxide on the metal surface, the open circuit potential is forced to change toward the point which is very close to the flat band potential of the oxide. This is caused by what is called photo (phonetic) potential. Then, no matter what corrosion reaction is taking place, the open circuit potential under irradiation is forced to be very close to the open circuit potential--excuse me, flat band potential. This flat band potential depends upon the type of semiconducting properties. So, finally, as I mentioned yesterday, the open circuit potential is not only the function of the aqueous solution, but also depending on the oxide present on the surface of the canister metals.

Thank you.

BULLEN: Questions for Professor Sato? Go ahead, Alberto?

SAGÜÉS: Yeah, I have a question here. I think that, if I understand correctly then, you are proposing a potential mechanism to develop open circuit potentials that could conceivably be higher, and therefore, that that would, of course, be an important possibility. And, do I understand then, that you're basing this on a possible interaction between some of the radiation that is emerging from the repository and the passive layer itself?

SATO: Not passive layer. We are talking about only the deposits. Passive layer is very thin so that there's probably no effect, at all.

SAGÜÉS: So, this will be on the deposits that will be on top of the passive layer and so on?

SATO: Yes, that's right. That's right.

SAGÜÉS: Okay. Now, someone brought up the issue of cross-sections and radiative interactions. Things like gamma radiation, would be just way too high energy to interact with something. And, now, could it be that you have gamma that interacts with something else, and as a result of that interaction, you get photons of lower energy? Is that--

SATO: Yes. You see, radiation comes from the nuclear waste. It is a very high energy, 1,000,000 electron volt. This high energy radiation has nothing to do with the corrosion reaction itself because of so large energy. But, usually, around this line, we have secondary formed low energy radiation which excite the electron holes within the oxide. Oxide is usually a semiconductor and has a bond gap. The size of bond gap is usually several electron volt. So, it is, you see, very close to the chemical reaction. Okay?

BULLEN: Thank you. Other questions for Dr. Sato?

(No audible response.)

BULLEN: Thank you. Are there other Panel members who would like to make a comment? We are fast approaching 11:30 which is our public comment period and I know that some people have to leave. Anyone else want to make another comment? Dr. Kruger, you said you were going to defer, but you kept jumping in. So, do you have anything else you'd like to say?

KRUGER: No, no, nothing.

BULLEN: Okay. Does anyone else have a comment? Oh, Gustavo? Gustavo has one and then I'd like to actually ask Carl Di Bella to tell us how poorly I wrote the quiz because I know there's some problems here. Gustavo?

CRAGNOLINO: My colleagues at the Center prohibit me to show these because they claim it's been shown so many times that I'm boring with this figure. I will make an effort.

The only difference is that we are increasing the time now. You can see here that we are at the 10^8 seconds--

BULLEN: Use the laser.

CRAGNOLINO: We are at the 10^8 seconds now.

SPEAKER: Potential of scale.

CRAGNOLINO: Sorry. Potential. And, here, you have a bunch of data point that are data from repassivation potential type of experiment. The potential of the sample are held to a high value, you initiate, and then move down, and in very short time, of the order of a few seconds, 100 at the most, you repassivate. But, above certain potential, you can't repassivate and this is what this point is indicated here is a long time for repassivation. Here is for a small size, here is for larger size.

We can put more data points, but there is an uncertainty this repassivation potential measured at such and this is indicated here. This, as Susan clearly indicated, is environment dependent. It was done in 1,000 ppm chloride, 95 degree for Alloy-25 that was the initial alloy. But, this try to demonstrate the concept. These are, by the way, potentiostatic experiments. You see here it took more than 100 days to initiate under crevice corrosion condition, and for pitting, at this potential, we have not yet initiated. But, you have data for pit initiation here and we've have gathered more initiation points. This is under crevice corrosion conditions.

This is potentiostatic, but we complete these for some selected data point using open circuit potential measurement in which we've got, in addition, an oxidant in the system to raise the potential to this regime. This is a demonstration that this has to be done systematically over a variety of possible environment, but indicate that this is a powerful approach to demonstrate condition which after, in this case, was a very short period of time, only 1000 days.

You don't get the localized corrosion even though you have all the conditions in terms of crevice and so on that we would require. I think that this illustrates an approach that we considered that could be valuable to this type of assessment.

BULLEN: A question for Gustavo real quick? Go ahead?

SAGÜÉS: Gustavo, I notice in this meeting no one has uttered the expression critical crevice temperature. Do you have any comment about that?

CRAGNOLINO: Well, the critical crevice temperature is a constant that comes through this type of approach. You can define as a much more simplistic way, but critical pitting temperature at a given potential has been standardized by ASTM, for instance, using a solution that contained chloride ions and an oxidant to keep the potential at a certain value, it's ferric chloride. Roger knows very well this because he has been working around this concept on this idea. But, you can do a critical crevice temperature by holding the potential potentiostatically. But, it's containing the same concept. The fact that this repassivation potential is a function of temperature, chloride concentration, inhibiting action, and the point that you raised before, about the concern of one pit that's been, or one crevice that's been, initiated that an inhibiting species could be important or not, is something that deserves further attention, I believe.

SAGÜÉS: I mention the question because for a while, I think, that the critical crevice temperature had begun to adopt maybe a much more important role than perhaps it should have.

CRAGNOLINO: Well, it can be used, for instance, in some total system performance evaluation in a very simplistic way to abstract the model for corrosion and come out with some result, but not necessarily has more significance than the parameter --.

BULLEN: Thank you. Before we get to the public comment period, I would ask Carl Di Bella to come up to the front, and before he flips that chart around, I'd like him to flip the page down and show the one that I wrote because there was a flaw in the quiz that the professor wrote here.

You'll notice that as I wrote the description, and you can tell this after you grade. Actually, the answer plus or minus a percentage, right? But then, when I wrote the example, I gave you an answer plus or minus a number and I didn't put a percent on it. So, some people used percentages and some people used numbers. So, we have a range of data.

And, with that, I'll turn it over to Carl. He's going to explain the range of data that it looks like we have.

DI BELLA: Thank you. It is a little tricky when people put like 2 plus or minus 10. What that meant, it could be 10 percent or it could be 2 plus or minus 10. So, I interpreted it as being percentages and equivalent to 2 plus or minus 1. With that in mind, this is a tabulation of the upper and lower ranges and I didn't trust myself, frankly, in the period of the time that we have to try to get any sort of mean to this, but I eyeballed the mean.

Let me explain the ranges. I think they're pretty clear. I picked out the highest, 10 in this particular case, and the lowest, 7 plus or minus 2. I took that as being lower than, say, if somebody put a 6 because 7 minus 2 could be 5. Now, with that interpretation of the tabulator, these are the range of values that the 14 panelists expressed. As far as the major overall question for the conference, I think you can definitely see a trend here in either column, whether you're a hot or a cold bug. You can see a trend of decreasing confidence with time or increasing risk, however you want to express it.

Then, if you want to look across this way to compare hot and cold, you can see the differences in the ranges there, too. I did eyeball the means, and in all cases, I have to say these are evenly distributed.

SAGÜÉS: Carl, I don't understand.

DI BELLA: Okay, sorry.

SAGÜÉS: What is the 10 plus 4? What does 10 plus 4 mean?

DI BELLA: 10 plus or minus 4?

SAGÜÉS: Yeah, that means that someone wrote a 14?

DI BELLA: I'm writing it the way that the vote was expressed. I assume it means 10 plus 0 minus 4, but the electors were rushed.

BULLEN: And, the professor wrote a poor quiz. So, we had all of the issues associated with bad pedagogy in the development of the testing program here.

SAGÜÉS: We are not going to get accredited this way--

BULLEN: I know. ABED (phonetic) will never review this appropriately.

CRAGNOLINO: I have a comment. I told him that it was not proper QA.

DI BELLA: I'm just trying to show you the tabulation and you can interpret it any way you want. If you want to interpret that as 14, that's okay. I did eyeball the means and most of these were evenly distributed. There was a skew to the right for the 100,000 year. So, there are the results.

BULLEN: Some pessimists and some optimists. We have a range in the hot from 10 to 0, right?

DI BELLA: On the hot versus cold issue, I do want to say of the 14 votes, 3 had identical hot and cold columns, no difference, no difference.

MACDONALD: Did you find any hanging chads?

DI BELLA: No, but there is one voter from Florida who didn't even bother voting.

BULLEN: Alberto would like that. Thank you, Carl.

We are approaching 11:30 and I would actually like to take this time to turn the meeting over to Dr. Paul Craig to run the public comment period. We had a little discussion about that. We had one signup, but it may not be a member of the public. So, we'll see how he handles it. Paul?

CRAIG: All right. Are there members of the public who have not signed up who would like to speak?

(No audible response.)

CRAIG: Apparently not. Going once, going twice--in that case, Dan, I turn the matters back to you for Joe Payer.

BULLEN: We decided the one member who did sign up was not rally a member of the public. So, Joe Payer, are you in the audience somewhere? Joe, we'll actually let you come up and stand in front of the group or take that--whichever location you'd like. Do you want the podium, you want--

PAYER: That's fine.

BULLEN: Okay. Joe Payer would like to make a few comments and you can keep it to less than 50 minutes so we can get out of here, Professor Payer?

PAYER: I can do that, sir. Thanks for recognizing me. If I'm not a member of the public, I'm not sure what that means, but maybe I'm an alien. I think what that means is that my role as chairman of the waste package performance panel which is a DOE commission performance panel, not unlike your workshop participants here, makes me not a pure publican, I guess, or whatever.

A couple comments. With hoping not to offend our host here right at the start, other than this vote thing, I think this was an outstanding session. And, the vote thing--and I'm serious about that. I mean, you talk about garbage-in and garbage-out, I don't understand how you could do that or, you know, get anything from that vote. But, if it means something to somebody, that's kind of cool for you.

I'd like to, first of all, acknowledge the workshop panel and the organizer. This has been a stimulating day and a half. It's been delightful for me. The interaction has been very positive. A lot of the issues have come up. Just as a point of reference for knowledge, I'm the chairman of a peer panel on waste package performance that's commissioned by the Department of Energy. We are an independent peer panel from the standpoint that we're asked to look at and to evaluate the technical bases for waste package performance. Our scope is somewhat broader than the scope to this group. You were asked to focus on passivity, long term passive behavior, and understandably you wandered off into some other areas, but that was the intent of that focus. In our panel's efforts, we're to look at not only long term corrosion processes, but also other failure degradation modes. And so, one of the things that came out here that we are taking a look at is the long term metallurgical stability of the alloy, the effect of aging--and, Roger, your points were well-taken--both the mechanical effects and the corrosion effects are going to be looked at and what's the technical basis for doing that?

I might just make a couple of comments. It was pointed out and certainly clear that this application, this potential repository at Yucca Mountain has some unique features. Some of those were pointed out and I'd like to point out perhaps another. Certainly, the long time frame, well-beyond what we deal with in a typical engineering fashion, is the unique feature of this. Trying to project performance out into 10,000 years and then even beyond that gives, I think, all engineers and scientists some cause and you can see that. As you go out to longer times, the uncertainty increases.

The other unique feature is the importance of doing this right. It's crucial that this material be handled and dealt with in a safe manner. The analogy I use back in the classroom is if, you know, my barbecue grill fails in the backyard on a Saturday afternoon, that might ruin a day, but it's not like a bridge collapsing or something. The crucial issue of doing this right and having the degree of certainty as great as we can is important.

From an engineering aspect, there's a uniqueness in this particular service. These waste packages are fabricated, filled, sealed, and emplaced in the tunnels, and then we go away. They're closed and they are exposed then to a relatively slow heat-up process and a very slow long cool-down process. It's a one cycle type of a deal. To quote Peter Andrasian (phonetic), it's the closest he knows to the ultimate static device. There's no moving parts, they sit in a tunnel, and go through this process.

For the water chemistry, which was pointed out was really a critical issue here, in my mind there's two scenarios that need to be dealt with. The first scenario is if the waste packages and the system perform as designed. And, that is the drip shield performs its stated function and it prevents drops of water from hitting the waste package surface. If that's the case, then the situation that pertains is during the emplacement period any ventilation that's done during the dry period, dust and debris accumulate, can accumulate, particulates on the surface. As soon as its closed, that should stop because there's no more dust being generated after closure. Then, the system cools down. As the temperature gets to a point where we can start forming aqueous phases, that's when the corrosion process can occur. Under those conditions, there's a finite amount of material on that surface. Whatever that dust and particulate brought to bear, you're adding pure water to it, condensing water vapor. And, you will get whatever chemical and interactions occur during that time period. That environment will be modified by any electrochemical reactions or chemical reactions on the surface and you will cool down.

The second scenario is if the waste package is exposed to droplets of water, the amount of the water, the episodic events of flow are highly uncertain. There's some understanding of how much and where, but it's a very stochastic event, but now you've got droplets of water on the surface to interact with that particulate and dust and you also have the incoming mineral and ionic species that are in that water. So, you've got a supply that can continue. Then, you will form scales and deposits and those effects.

Those are the two issues, I think, that really have to be addressed. They're significantly different, I think. The first one is clearly an indoor atmospheric corrosion problem and there has been a lot of work done on that, not particularly with nickel alloys, but there is some knowledge in that.

The design objective, it seems to me, is to determine the bounding environments and then control the damage modes; evaluate and control the damage modes within those bounding environments. That's the design goal.

You heard here in the last day and a half that there's different camps on that. One camp is that the environments are totally unboundable. They're just indeterminable and the conclusion from that is that there ain't no materials that are going to do this job. If you're allowed to go to any location on the potential pH diagram with mixed ionic species and so forth, then we've got no material to do that. You heard other folks express the situation that they believe that, in fact, the environments are boundable and that some limits can be put onto it. That's going to be a major point of debate, I think, technical debate in this issue.

This activity and the activity that I'm involved with with the waste package panel, I think has significantly engaged the corrosion science and engineering community.

There's a much greater awareness represented by our peers around this table and so forth. I think the Board is to be commended for that; the organization of this session and you folks that have taken your time and effort to come in here. I think the challenge to the corrosion community is to wrestle with these issues and then articulate the findings in an understandable manner to the rest of the community, to the rest of the technical community, and also to the public. I think the challenge to DOE and the other participants in this is to provide the resources to finish this job, to carry it to the point. There's efforts that are underway, there's plans on the table, and I think that certainly ought to be followed through to some reasonable point of completion.

I heard some very relevant and significant, I think, knowledge base for evaluating expected behavior of this repository in the last day and a half. And, let me just give you some examples. You could probably go through your notes and come up with a similar list.

The major concern stated and I certainly support it based on my evaluation of this is the understanding of the future conditions on the waste package. Digby stated that is the path that the package will take. Jerry mentioned the concern of the long term changes in the conditions that might overturn findings of low corrosion rates. But the ambient waters out at Yucca Mountain are fairly innocuous. The question is how are those going to be modified or modulated and how is the package going to then perform to that? Again, there's the two cases. Roger Staehle was a proponent that the environment is unboundable. We heard from Gustavo and Greg Gdowski that they feel the environment is bounded. Well, let's line up the technical information and let's see where that goes. It's not a personality contest; it's is it boundable or isn't it?

A major issue that came out is the effect of dust and accumulation on the surface because that's where the water is going to be added to it. The whole issue of electrochemistry, you know, we all know around this table and most of us in the room that corrosion is an electrochemical process, it can be understood in terms of electrochemical processes. The emphasis and importance of the cathodic processes, the cathodic reactions that can occur and the cathodic areas that are available, I think, is something that came out throughout the impression. It's the anodic reactions that cause the damage. But, as in most applications, many applications, it's the cathodic processes that really carry the day.

There's been some outstanding listing of the factors that affect the evolution of the corrosion and repassivation potentials. As far as quantifying localized corrosion which in many of our opinion is the greatest realistic threat to the packages, crevice and pitting corrosion, several people have said that that's something we do have a pretty good fundamental basis for understanding and controlling and determining. As pointed out, it's an initiation growth and repassivation process. The pit depth term is the term that Digby uses, other people talk about pit stifling or crevice corrosion stifling. The fact that once the process is started, it can shut off has a significant impact on the damage functions that we see. Professor Shibata pointed out that the potentiostatic step down method is a more conservative method than perhaps some of the methods that are being used for actually determining where crevice corrosion will shut down.

Passive film growth and behavior was another topic that was heavily covered here today. Allison pointed out that it's driven by the potential field across the--that pertains--the film dissolution in many cases is what will really dominate that behavior. There were several lists of processes given throughout the workshop that could lead to increased dissolution and then one can go down those lists and say how do those pertain to Yucca Mountain and so forth.

I think Bob Rapp made what I consider a significant comment that ought to really be looked at in more detail and that is one of the most realistic, I think, passive film or film breakdown processes that I had in mind was the issue of vacancy accumulation and the spalling of the film. I think, if I heard Bob correctly, he's saying that based on high temperature scales, that's probably not a very likely mode. Well, I think that ought to be looked at more seriously. Is it or isn't it? The selective dissolution and selective enrichment processes that are going on are very important. Professor Shibata pointed out the importance of semi-conducting oxides or other deposits on top of the passive film as they might pertain. And, the list goes on.

As far as the gaseous dry oxidation processes occurring, I think it's pretty well-accepted that the gaseous oxidation itself is not going to cause significant damage to the waste packages. It was pointed out that even carbon steel in the dry environment just with the relative humidity and dry air would survive these time periods. But, what became very clear is the likely major effect of that is that will be the film that eventually gets wet and that precursor state, the initial state of that film, when it gets wet could have significant effects on performance. And so, I think that has to be looked at.

So, anyway, all I did was try to go down through some of the notes that I made here. I think there's some very significant output, some very significant findings, and directions that you folks have provided. I commend you for that. It's been an outstanding workshop.

BULLEN: Thank you, Professor Payer, for your comments.

Any questions or comments from the panel about what we heard? He did a great job of summarizing everything that we seem to have discussed over the past day and a half. And, I think since it got read into the record, we really appreciate that service.

Any other questions or comments from the audience?

(No audible response.)

BULLEN: If not, I would like to actually thank the staff and particularly the executive director who is just walking in for agreeing to sponsor and pay for this get-together because this has been a very worthwhile effort for the four Board members who are here and will be very helpful for us in our deliberations with respect to decisions that will be made later this year. Again, I would like to thank all the panel members.

Do you have a comment, Professor Rapp? Go right ahead?

RAPP: One of Joe's comments, I know that there are aging studies going on with this alloy now at relatively low temperatures even--I think 400C or something like this--and you have coupons with scales on them, dry scales formed in dry oxidation. Because, as Joe pointed out, that's going to be the initial state, a dry formed scale for any aqueous corrosion, you guys ought to examine what you've got there from whatever samples you've been aging for a long time.

GDOWSKI: Those are actually planned experiments.

RAPP: Okay.

BULLEN: Thank you, Dr. Rapp.

Any other comments from the panel?

(No audible response.)

BULLEN: Again, let me express my sincere appreciation for the opportunity to meet all you and to interact in this last day and a half. With that, I would like to say that this session is closed and remind you that our next Technical Review Board meeting is September 9th and 10th in Las Vegas.

Thank you very much. This session is closed.

(Whereupon, at 11:45 a.m., the session was adjourned.)