UNITED STATES
NUCLEAR WASTE TECHNICAL REVIEW BOARD

INTERNATIONAL WORKSHOP ON LONG-TERM EXTRAPOLATION OF PASSIVE BEHAVIOR

Thursday
July 19, 2001

Hilton Arlington & Towers
950 North Stafford Street
Arlington, Virginia 22203

NWTRB BOARD MEMBERS PRESENT

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Dr. Alberto A. Sagüés
Dr. Priscilla P. Nelson

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Digby D. Macdonald,
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Barry R. MacDougall,
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I N D E X

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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. Thank you for your indulgence while we took care of some technical difficulties up here.

My name is Daniel Bullen. I'm a member of the U.S. Nuclear Waste Technical Review Board, and I'd like to welcome you to this International Workshop on Long-Term Extrapolation of Passive Behavior. This workshop is being conducted under the auspices of the Board's Panel on the Repository, which I chair. I will be serving as the moderator and facilitator for most of the workshop. It's my please to welcome you to a workshop which is a little bit of a departure from the normal meeting format for the Nuclear Waste Technical Review Board.

First, I'd like to say a few words about who the Board is and what the Board does. As you may know, Congress enacted the Nuclear Waste Policy Act in 1982. The Act made official the policy that the Federal Government is responsible for permanently disposing of spent nuclear fuel and high level radioactive waste, and that the owners and generators of the waste should pay for that disposal.

Among other things, the Act created the office of Civilian Radioactive Waste Management, or OCRWM, within the U.S. Department of Energy, and charged it with developing repositories for the disposal of the nation's spent nuclear fuel and high-level wastes for reprocessing. Five years later, in 1987, Congress amended that law to focus OCRWM's activities on the characterization of a single site for a permanent repository, Yucca Mountain, on the western edge of the Nevada Test Site, about 100 miles northwest of Las Vegas, in the State of Nevada.

In those 1987 amendments, Congress created the Nuclear Waste Technical Review Board as an independent Federal agency to review the technical and scientific validity of OCRWM's activities. The Board is required to furnish its findings, conclusions, and recommendations to the U.S. Congress and to the Secretary of the Department of Energy at least twice a year. We do this in Congressional testimony and through our written reports. We issued our latest report, a summary of last year's activities, about three months ago.

As specified by the 1987 Act, the President appoints our Board members from a list of nominees submitted by the National Academy of Sciences. The Act requires the Board to be a multi-disciplinary group representing a broad range of scientific and engineering disciplines related to nuclear waste management. A full-strength Board, which we now have, consists of eleven members. We meet as a full Board three or four times a year, usually in the State of Nevada.

I would like to introduce a few Board members and a few of the Board's staff at this time. As I mentioned, my name is Dan Bullen. I'm a Board member and a nuclear engineer in the Mechanical Engineering Department at Iowa State University. My areas of interest include nuclear waste management, risk modeling, and materials science.

Paul Craig--Paul, would you raise your hand please--is professor emeritus at the University of California at Davis. He is a physicist by training and has special expertise in energy policy issues related to global environmental change.

Alberto Sagüés--Alberto, would you raise your hand, please? Alberto is Distinguished University Professor in the Department of Civil and Environmental Engineering at the University of South Florida in Tampa. He's an expert in materials engineering and corrosion, with particular emphasis on the behavior of steel in concrete and in infrastructure durability.

We have one more Board member here. This is Priscilla Nelson. Priscilla, would you raise your hand? Priscilla is Director--or actually, yeah, Director in the Directorate of Engineering at the National Science Foundation, and a civil engineer by training. I want to say geotechnical engineer by training. Is that not correct? I don't have it written here, Priscilla, so I'm in trouble. I have to do this from memory. Priscilla is a Board member and previously served as Chair of the Repository Panel.

I also have a couple of staff members that I'd like to acknowledge. First, I'd like to introduce Bill Barnard. Bill, will you raise your hand? He serves as our executive director for the Board. Next to Bill is Carl Di Bella. Carl, would you raise your hand? He is the staff member who spent many hours on the phone and on e-mail organizing the many technical aspects of this workshop and communicating with our experts internationally.

I'd also like to introduce Linda Hiatt and Linda Coultry. Linda Coultry is right there. Is Linda Hiatt outside? The Lindas have been responsible for many of the logistical aspects of travel arrangements, getting everybody here, organizing the room, and I'd like to express our appreciation for that. Unlike Board members who are part-time, these staff members serve on a full-time basis.

I'd like to talk a little bit about the agenda for today and tomorrow. In a few minutes, I'm going to turn the meeting over to Alberto Sagüés, who will introduce our distinguished panelists and explain why the Board is sponsoring this workshop. Carl Di Bella will then summarize to the panel the current repository and waste package design and the environment that the waste package will experience in a repository. Alberto will provide an overview of research on Alloy 22 related to nuclear waste disposal, and he will repeat the two questions about long-term corrosion that were furnished to the panelists about a month ago.

Each panelist will then give a very brief five to ten minute presentation on his or her initial response to those questions. Following the completion of the panelists' presentation, which should be around lunchtime, the entire remainder of the workshop, with the exception of the public comment periods, which I'll talk about later, the entire remainder of the workshop will be devoted to a roundtable discussion of the question among panelists. So this is going to be like a brainstorming session. And a little bit of apology to the general public, because it might get very technical, but that's the purpose of this meeting, for us to understand the technical opinions of the international community.

As I said before, this is not a typical Board meeting. In a typical meeting, presentations are made, often by the DOE or its contractors, and the Board engages in a dialogue with each of the presenters, with the meeting Chair often leading that dialogue, or at least participating heavily in it. Here, my role as Chair will be somewhat different. I'll be more of a moderator, facilitator, timekeeper, and maybe even a referee, should we have some heated exchanged. Rather than ask many questions of my own during the roundtable discussion, I'll be more concerned about the questions asked of the panelists and questions by the Board members, Paul Craig and Alberto Sagüés, or the other panelists themselves.

I need to offer our usual disclaimer that everybody is clear on as we conduct this workshop. What you are hearing, and its significance, and the reaction by Board members are spontaneous by design. Those of you who have attended our meetings before, and I know many of you have, know that the members of the Board do not hesitate to speak their minds. I'm sure that goes for the panelists today, too. But let me emphasize that Board members and panelists are speaking their minds. They do not speak on behalf of the Board. They're speaking on behalf of themselves. From the Board's perspective, the purpose of this workshop is information gathering. Any Board position that may develop would be taken only after the full Board has had a chance to process this information.

Now, let me say a few things about the opportunities we've provided for public comment and interaction during the workshop. This is something that is extremely important to the Board. By "public" I mean those who are not Board or staff members, or members of the panel. We try to give the public as many opportunities as possible to comment during our meetings. Today's public comment period will take place at the end of the roundtable discussion of Question 1, and tomorrow, at the end of the roundtable discussion of Question 2.

Board Member Paul Craig will chair the public comment session. Those wishing to comment should sign the Public Comment Register at the check-in table where Linda Hiatt and Linda Coultry were sitting on the way in. So, if you're interested in making public comment, please sign up and we'll hear your comments either today or tomorrow. Both of the Lindas will be glad to help you sign up and be prepared for the public comment period.

Now, let me point out, and I'll remind you again later, that depending on the number of people who sign up, Professor Craig may have to set a time limit on the comments that are made.

An additional opportunity for questions or comments, and continuing something that we've tried pretty successfully before, is you can submit questions or comments or concerns in writing to either Linda Hiatt or Linda Coultry during the workshop. If there's time and the question or comment is relevant to the discussion at hand, then I will read that question to the panel members during the course of the workshop. If I can't get the question or comment worked in during the workshop, I will hand that question to Paul, who will reserve the right to read that question, the same question, during the public comment period.

In addition, we always welcome written comments for the workshop transcript, and this workshop is being transcribed. Those who prefer not to make oral comments or ask questions during the workshop may choose this route at any time. We especially encourage written comments when your comments are more extensive than our workshop time allows. Please submit these written comments also to either Linda Coultry or Linda Hiatt, and they'll be happy to help you.

Are there any questions from the panel about how we're going to operate the workshop?

(No response.)

BULLEN: Excellent. Seeing none, I will turn it over to my esteemed colleague, Dr. Alberto Sagüés to introduce the panelists and begin the process.

Alberto?

SAGÜÉS: Thank you, Dan.

Good morning. My name is Alberto Sagüés, and as Dan has explained, I'm also a member of the Board. I would like to welcome you, the panel, officially to the workshop, and tell you how absolutely elated I am that all of you could make it. We have truly work-class panel.

One of the things that pleases me the most is that so many people were able to accept our invitation to participate, despite the fact that there was two months or less notice. And several of you have long distances to travel. I think this testifies to the importance of the issue we are addressing, as well as its intellectual challenge.

Stating the overall issue is simple. In the United States Repository Program, and this may be true in some other countries as well, the waste package, that is the container the waste will in when its placed in the repository, has come to have a very important long-term role.

The proposed outer layer of the waste package is a two centimeter thick shell of Alloy 22. Alloy 22 is a very corrosion resistant material that depends on a nanometer thick passive layer for its corrosion resistance.

Now, mankind's experience with Alloy 22 is only a few decades, and mankind's experience with alloys like Alloy 22 spans only a few more decades. And mankind's experience with any metal or alloy that owes its corrosion resistance to a passive layer is at best not much more than a century.

By the way, I fully expect to be challenged on this particular issue during the workshop by members of the panel, and you're welcome to do so.

So if our experience is limited to a century or so, what are the theories and the assumptions that form the basis for extrapolating for thousands and thousands of years? In other words, what is the basis for extrapolating? That's what I'm trying to get at here. Do we really have one? Why or why not? And in a nutshell, that's what the workshop is all about.

I think everyone on the panel knows each other. But both for the record and to refresh our memories, I would like to introduce each panelist briefly, and I would ask you to please raise your hand when I call your name.

We'll start with Dr. Ugo Bertocci. He holds a doctorate in chemistry from the University of Milan. He worked for the National Institute of Standards and Technology, NIST, for more than 20 years, and retired about nine years ago. Now, NIST, of course, used to be the Bureau of Standards.

More recently, Dr. Bertocci has done research at the Federal Highway Administration, again at NIST, and he has collaborated extensively with the French CNRS. His research interests have always been in the field of electrochemistry.

Dr. Gustavo Cragnolino is a staff scientist in the Center for Nuclear Waste Regulatory Analyses at Southwest Research Institute in San Antonio, Texas, where he has been conducting experimental research and modelling of corrosion and thermal stability of metallic container materials for high-level radioactive waste disposal since 1990. He holds a Licenciado and doctorate degrees in chemical sciences from the University of Buenos Aires in Argentina, and has worked before in the Argentina Atomic Energy Commission, the Fontana Corrosion Center at Ohio State, and Brookhaven National Laboratory.

Dr. Alison Davenport is a lecturer at the University of Birmingham in the School of Metallurgy and Materials. Now, that's Birmingham in the UK and not in Alabama. She has a doctorate in Materials Science and

Metallurgy from the University of Cambridge. Her research interests include the structure, chemistry and stability of passive oxide films, and the effect of microstructure and alloying additions on corrosion and surface treatment of metals. She's also a Brookhaven alumna, spending eight years there as a scientist in the late Eighties and early Nineties.

Professor Jerome Kruger, Jerry Kruger, received a Ph.D. in physical chemistry from the University of Virginia, and joined the Naval Research Laboratory. Three years later, he went to the National Bureau of Standards, and eventually became Chief of the Corrosion Section. In 1984, he joined the faculty of John Hopkins University in the Materials Science and Engineering Department, becoming Emeritus in 1999. He's a fellow of NACE, National Association of Corrosion Engineers, the Electrochemical Society and the Institute of Corrosion in the UK.

Professor Digby Macdonald is a professor of Materials Science and Engineering, and director of the Center for Electrochemical Science and Technology at Penn State. He has a Ph.D. in chemistry from the University of Calgary and BS and MS degrees in Chemistry from the University of Auckland. His research interests include passivity, nuclear reactor technology, and high temperature aqueous electrochemistry. And, of course, he's the developer over the past two decades of the Point Defect Model for the growth and breakdown of passive films. Dr. Macdonald is a fellow of NACE and the Electrochemical Society.

Dr. Barry MacDougall leads the Electrochemical Technology Group at the National Research Council of Canada. He received his doctorate in electrochemistry from the University of Ottawa. His research interests include the formation and breakdown of passive oxide films on metals and alloys, with emphasis on the mechanism of film breakdown leading to localized pit initiation. His interests also include improving understanding of fundamentals of corrosion processes of metals and alloys through the use of surface electron spectroscopies to study the composition and structure of surface layers. Dr. MacDougall is a fellow of NACE and the Chemical Institute of Canada.

Professor Philippe Marcus directs the laboratory of physical chemistry of surfaces, part of the National Center for Scientific Research at the University of Pierre et Marie Curie in Paris, France. He received his doctorate in chemistry from the University of Pierre et Marie Curie. His research interests include the effect of atomic layers of absorbed sulfur on dissolution and passivation of metallic surfaces, the study of passivity of metals and alloys, the use of photoelectron spectroscopy toward the standard relationships between the chemical nature of passive films and their corrosion resistance, as well. He co-chairs the Corrosion Electrodeposition and Surface Treatments Division of the International Society of Electrochemistry, and also chairs the Corrosion Working Party on Surface Science at the European Federation.

Professor Roger Newman is professor of Corrosion and Protection at UMIST, which is the University of Manchester Institute of Science and Technology in the UK. He has a doctorate in metallurgy and materials science from the University of Cambridge. He's been at UMIST for 17 years, but is another of the folks spending time at Brookhaven, in his case, four years, as a researcher in the early Eighties. He's a fellow of the UK Institute of Materials and of NACE and holds a doctorate degree from the University of Manchester. His research specialties are passivity, localized corrosion, and stress corrosion cracking, especially the formation of oxide films on alloys, mechanisms of growth of pits and cracks, and prediction of pitting or cracking thresholds.

Professor Howard Pickering is distinguished professor of Materials Science and Engineering at Penn State University. He has a Ph.D. from Ohio State University. His research interests include selective element dissolution from alloys, localized electrochemical degradation processes, such as crevice, pitting and grain boundary corrosion, hydrogen evolution and its absorption and diffusion into metals, and surface reconstruction in metal electrodissolution and electrodeposition in aqueous solutions using the scanning tunneling microscopy and atomic force microscopy.

Professor Robert Rapp is distinguished university profession emeritus in the Department of Materials Science and Engineering at the Ohio State University. He has a doctorate in metallurgical engineering from the Carnegie Institute of Technology in Pittsburgh, a predecessor to Carnegie-Mellon University. By the way, our Board Chairman, Dr. Jared Cohon, is the president of Carnegie-Mellon these days. Dr. Rapp is well known in the areas of corrosion mechanisms, coating and protection, extractive metallurgy, and high temperature materials. He's a member of the National Academy for Engineering, and a fellow of four U.S. Societies, ASM, TMS, Electrochemical Society, and NACE, as well as two foreign societies.

Professor Norio Sato is emeritus professor at Hokkaido University. He received a doctorate in engineering from Hokkaido University in electrochemistry. He's an electrochemical scientist, specializing in corrosion and fundamental understanding of metallic passivity and its breakdown. Professor Sato is a fellow of NACE, the Japan Society of Corrosion Engineering, the Institute of Corrosion in the UK, and the Electrochemical Society in the US.

Also from Japan we have Dr. Toshio Shibata, who is professor emeritus as of March of this year in the Department of Materials Science and Processing of Osaka University. His doctorate is from Hokkaido University. He has been concerned with the passivity of stainless steel and its breakdown, including pitting, and stress corrosion cracking.

Professor Susan Smialowska is professor emeritus at Ohio State University, and also the director emeritus of the Fontana Corrosion Center there. She earned her doctoral degree in chemical engineering at the Silesian Technical Institute and University in Poland. Dr. Smialowska's principal research interests have been investigation of the kinetics of the mechanism of electro processes, pitting corrosion, stress corrosion cracking, corrosion inhibitors, hydrogen embrittlement, different types of aqueous corrosion at high temperatures and, of course, passivity.

Professor Hans-Henning Strehblow is professor of physical chemistry at the Institute for Physikalische Chemie and Elektrochemie at Heinrich-Heine University in Duesseldorf. He has a doctorate in physical chemistry from the Free University of Berlin. His research interests include electrochemistry, corrosion, surface analyses, and the physical chemistry of surfaces.

Now, we have one other distinguished panel member who unfortunately will not be able to be with us today. That was Professor Hans Bohni of the Swiss Federal Institute of Technology in Zurich, who was to have been a panelist, and he e-mailed us Monday afternoon that he has come down with an infectious disease with a fever and, therefore, would not be able to participate. However, he had gotten started on preparing some notes for the meeting, and he was kind enough to forward them to us. You should find them, it is one sheet of paper printed on both sides, in the package of handouts that Linda Coultry and Linda Hiatt set out for you this morning.

I have a couple more introductions to make for the benefit of the panel. And before I make those introductions, I first want to apologize to any of the other distinguished visitors and friends that may be present in the audience that I more than likely will be overlooking, but I wanted to highlight some of our participants that are involved in the project in one manner or the other.

First of all, Dr. Gerry Gordon, formerly of General Electric, he's the lead materials scientist for the Department of Energy. And he and the group that he's with have kindly volunteered to answer any questions about the materials DOE program, should they arise during the course of the workshop. Indeed, the work of that group is going to be discussed in some detail during this meeting.

We also have Professor Joe Payer. He's professor of Materials Science and Engineering at Case Western Reserve University in Cleveland, and he directs the Yaeger Center of Electrochemical Sciences at Case Western Reserve. He's chairing a ten month peer review of the DOE Materials Program, and we have some of the peer review panel members here as well. The peer review just got started a month ago, and some of you members of the panel may be serving as subject matter experts for the peer review as well.

I want to assure you that this workshop and the peer review are independent efforts. The workshop has a very narrow focus, and is a one shot affair. The peer review is much, much broader and extends for nearly a year. Even though the two efforts are independent, they do overlap, and we hope what comes out of the workshop will be helpful to the peer review, as well as the Board.

I think that we have Professor Gerry Frankel in the audience as well. Jerry? He's in the Materials Science and Engineering Department of Ohio State, and is the current director of the Fontana Corrosion Center. He's a member of

Dr. Payer's panel.

Do we have Professor Kelly as well in the audience today? Maybe later.

Dr. David Shoesmith is in the audience? David Shoesmith originally from England, he spends most of his time in London, but that is London, Ontario, where he's a professor of chemistry at the University of Western Ontario. And I know Professor Shoesmith because of his extensive participation in the DOE effort and as a contributor to a number of previous discussions concerning materials in the repository.

Let's see, we have also Dr. Roger Staehle in the audience. Roger? He's formerly an Ohio State professor, University of Minnesota dean, and he is also involved in Rickover's nuclear navy, and now he's associated with Roger Staehle Consulting, and he's also in the audience and he has been involved also for a long time in these areas.

We have, again, many other friends and distinguished people. Dr. Scully maybe is in the audience? Well, anyway, and I apologize for those whose names I may have failed to notice at this moment.

Okay, a couple of housekeeping issues. You might notice that the meeting is being transcribed, and this is standard practice for all Board public meetings. The transcript will be kept in our permanent archives and will be posted on our website.

Scott Ford, who is recording the meeting and his staff back in Denver have provided transcribing services to the Board for quite a while, and they're good and they're familiar with many of our technical terms, but there is something you can do to help them. Whenever you speak, members of the panel, please identify yourself, unless someone has just introduced you, just saying your last name is enough, but that will help keep the record straight as to who is saying what.

Now, just a couple of very brief comments introducing the next presentation and the overall orientation of the workshop. Now, the basis for extrapolating corrosion resistance thousands of years into the future has been a concern of our Nuclear Waste Technical Review Board for at least four years. And this is a concern that the Board has mentioned frequently in its writings.

We have encouraged the Department of Energy to begin some basic research on the issue, and the DOE has responded by beginning some basic research, but much of it only recently. You will need to consider that in detail, and we're going to be addressing some of that in some of our next presentations.

Why are we having the workshop and why are we having it now? Dan Bullen mentioned the Nuclear Waste Policy Act of 1982. This Act, and its subsequent amendments, set in place, among other things, a careful and detailed process involving the Secretary of Energy, the President of the US, the State of Nevada, the Congress, and other parties, for making the social decision on whether to proceed with Yucca Mountain.

The Department of Energy plans that the first step of the process, a decision by the Secretary of Energy whether to recommend the site to the US President, shall take place late this year. Clearly, the decision will have a technical component. The Board's views will be important for the decision, and we want to have as complete a basis for our views as possible.

Hence, this workshop. We are seeking a broad range of diverse opinions on the matter of extrapolating corrosion resistance far into the future. We are not seeking consensus, and we are not seeking agreement. We are seeking opinions.

What transpires during the workshop will form an important part of the basis for the Board's view on the extrapolation issue. And since we have to express that view before the Secretary's decision, you can understand the timing of the workshop.

Now, finally, the subject of this workshop is the long-term extrapolation of passive behavior. I know there are many tempting side topics that this group is eminently qualified to explore, for example, stress corrosion cracking, or the design of the waste package itself. But if we get off onto those topics, we risk not fully addressing the reason we're gathering here in the first place. Long-term extrapolation is our focused interest. Also, we didn't furnish you with the background information to address those other issues.

So, if we travel down the side road, I'm sure Dr. Bullen will feel obliged to pull us back before we go too far.

Thank you. And now I would like to turn the floor over to Dr. Carl Di Bella, who will describe briefly the waste package designs and the range of chemical, physical and thermal environments that the waste packages may experience in the repository. Then I will return to summarize Alloy 22 corrosion research, and repeat the questions for the workshop.

Before I turn the meeting over to Dr. Di Bella, do we have any specific questions on the part of the panel?

(No response.)

SAGÜÉS: If we don't, then Dr. Di Bella, please.

DI BELLA: Thank you very much.

Well, Mr. Referee, we're running just a bit behind, but I'm going to help.

BULLEN: I am keeping score.

DI BELLA: I sent to each of you about a month ago some information about the waste package design and about the environment that a waste package at Yucca Mountain would experience. I'm going to repeat that very briefly, more for the purpose of you asking questions, if you want to.

I don't have copies of my handouts because I've already sent them to you, and because I got them from the DOE website anyway.

So, first, let me remind you, particularly for visitors from overseas, where Yucca Mountain is. All right, Yucca Mountain is located in the State of Nevada about 150 kilometers northwest of Las Vegas. It's at the very western edge of the Nevada Test Site, which is blown up here--blow up I guess is a good word for it. Here is the footprint of the repository located just west of the Test Site on Bureau of Land Management Land, on Nellis Air Force Range land. That's where it's located.

This is a semi-arid location. There are about 17 centimeters of precipitation a year. Most of that evaporates off or runs off, but some does filter into the mountain and eventually reaches the water table, which is about 600 meters below the surface.

The repository would be located above the water table about 300 meters. So it's in the unsaturated zone, the vadose zone, as it's known. And the pressure at that level is essentially the pressure of outside air, or the atmosphere, and the elevation of the repository is about 1000 meters. So at that elevation, pure water boils at 96 degrees rather than 100 degrees.

The repository would look like this. This is an isometric view of the repository. I'll give you a little closer view in just a moment. The emplacement drifts are the drifts going east/west where waste packages would be placed.

This is another view that emphasizes the ventilation aspects of the repository. I'm doing that to show you that the repository would not be closed immediately after waste packages are emplaced, but that some period of ventilation would take place, and this period of ventilation could be as short as 25 years, could be as long as 300, or perhaps even longer.

The waste packages look like this. There's a person there shown for scale. They do vary somewhat in diameter and length, but they're roughly between one and a half meters to two meters maximum in diameter, and they're up to on the order of five meters long, about the size of a Lincoln limousine, if you happened to see them when you came into the airport waiting outside for VIPs.

The outer surface of the waste package is C-22, a two centimeter layer of Alloy 22. The inner layer of the waste package is 316-N stainless steel, five centimeters thick, and it gives the structural strength, or a large portion of the structural strength, to the waste package. Then there is a basket to hold the assemblies. And the entire waste package, with the exception of the lid, is annealed before waste is put into it. Then waste would be put into it, and the lids welded on, and then the lids would be individually treated to put into a compressive state. There's a double lid. One lid gets laser peened in the current concept, and the other lid weld gets induction annealed, locally induction annealed to protect the waste.

That's the design of the waste package. Let me show you one conceptual diagram of how the waste would be put into the repository. The diameter of the emplacement drifts is roughly five and a half meters. The diameter of waste packages remember is on the order of two meters. Selection of waste packages are shown here in an emplacement drift, and you might notice towards the back of the drift, this device, which is called a drip shield, which would be made out of titanium, and the idea is to place the drip shield after the ventilation period, just before closure of the repository. And it would be a continuous drip shield of segments that are hooked together, overlapped like shingles, so that they would prevent water from going onto the waste package. That's the concept anyway.

You might think, of course, that besides C-22 outer layer of the waste package depending on passivity, so does titanium drip shields, so does the stainless steel inner layer, so does, hence, and we don't have a picture of an assembly here, but so does the zircaloy tubing that consists the assembly rods. However, we're going to talk about Alloy 22, of course, for this workshop. What comes out with regard to that may well have application to passivity for these other materials, too.

There is water in Yucca Mountain. Even though it's above the water table, water percolates down through Yucca Mountain and there is water in the pores of the rock at Yucca Mountain. And I have here a very complicated table, a very data-laden table that has the compositions of two of the native waters in the Yucca Mountain area.

This column here is the water from the water table, actually several kilometers away from Yucca Mountain, but it's close. This water here is water that has been squeezed, or centrifuged I think, out of rock pores at the repository level. They're really quite different, and you can see the difference in when you evaporate the respective waters. This is an evaporation of this water. This column is an evaporation of this water right here.

You will notice in evaporating the water below the water table, that you basically get rid of all of the calcium and the magnesium. What happens is that they combine with the carbonate, and that it precipitates them out.

However, in the case of water at the rock level, in the pores, there's much higher concentrations of calcium and magnesium, and when you evaporate this, you basically get rid of all of your carbonate, but you still have calcium and magnesium left.

What's the significance of that? The significance is that the calcium and the magnesium, together with the chlorine anion, have very high boiling points as saturated solutions, or near saturated solutions in water. Whereas, the salt here that has a combination of cation and anion that would have the highest boiling point of the saturated mixture here, is sodium nitrate.

In this case, the boiling point approaches 150 to 160 degrees. In this point, the boiling point approaches 120 degrees.

Now, why am I bringing that up and what does it have to do with corrosion? Well, the salts that are deposited on the waste package, whether they are from ventilation air that comes in, whether they are from rock dust that comes onto the waste package over this 25, 50, 100 year period, may have some of these salts here in them, some calcium, magnesium chloride salts in them, or some sodium nitrate salts in them, which would determine the highest temperature at which is going to be aqueous condition on the waste package.

If this is typical of the kind of salts that are on the waste package, then pretty much 120 degrees you can safely say is the highest temperature that there's going to be liquid water on the waste package. If this does, then maybe 160 degrees is the highest temperature, and that has something to say about the corrosion.

For the purposes of the workshop, I think we're going to have to play it safe and say it's possible that maybe there will be liquid water on some of the waste packages, or some part of some of the waste packages as high as 160 degrees.

Now, there are many other trace components. These are just what I call a major species in the water, and they can be important, particularly if they find a way to concentrate, and that's simply out of the scope of the workshop, but it's an important issue.

Temperatures can be generated at Yucca Mountain. There are basically two schools of thought for a repository at Yucca Mountain. One is called hot and one is called cold. And I've tried to represent them both here with a plot of waste package surface temperature versus time for the hot case, which is red, for the cold case, which is green. And there are many, many of these different kinds of cases. This is just meant to be a representative or a sample case. The actual temperature of a waste package is going to depend on where it's located in the repository, and what's inside that particular waste package.

But let's take this. And so in the hot case, ventilation goes on for 50 years. Then the repository is closed. Ventilation is turned off. The decay heat from the package boosts the temperature up to 160, and there's a slow decay as the heat dissipates from then on.

In the cold case, ventilation is not turned off. The repository is not closed at 50 years, but instead, natural ventilation is allowed to occur, and this removes a portion of the heat from the repository, keeping the temperature below 80 degrees.

Again, this red case here is the DOE base case right now, although they have studied both cases right here. But I think for the purposes of the workshop, that it would be wise to consider the DOE base case as being the base case for the workshop, that is, one where the temperature will stay above 95, 96 degrees for maybe on the order of 1000 years. It's going to be 500 to 2000, depending on the individual waste package.

Now, I think that's really all I wanted to say. Really, I put this up more to give you an opportunity to ask questions, if you want, about the environment that the waste package is going to experience. Are there any?

NEWMAN: I just have a question, which shows my total ignorance of radiation. Does the stainless steel stop all that?

DI BELLA: Yes. Does the stainless steel?

NEWMAN: Does the stainless steel stop all the radiation?

DI BELLA: No, there is a fairly significant radiation field outside of the C-22, at least from a personal point of view. From a radiation damage point of view, I think the consensus is pretty strongly that radiation damage from the waste, either of the stainless steel or of the C-22, is not a significant issue.

However, radiolysis, which is ionizing of chemicals in either the water on the waste package or in the humid air, and then some sort of concentration of, say, the nitric acid or hydrogen peroxide that you get, that's a potential issue if you can think of a concentration mechanism.

Dr. Kruger?

KRUGER: Are there any scenarios where the waste package sees only hot air and steam, and no aqueous environment?

DI BELLA: The proponents of the hot repository hope, of course, in this period of time that all of the water is driven away, that it will condense someplace far away from the waste package, and drain in between the tunnels, and so that it's not an issue.

KRUGER; The issue is that the environment at 160 at least, hot metal, in gaseous environment, which I think is an issue as well.

DI BELLA: There has been a fair amount of study of that. And, indeed, dry oxidation, or dry air oxidation is what term is used inside the project, does occur, but the rate is infinitesimal, I am told, so dwarfed by any aqueous corrosion rate.

KRUGER: Okay.

DI BELLA: Dr. Davenport?

DAVENPORT: I just wondered how much variability there is in the solution compositions that you quote? Is there a sense that in different parts of the tunnels, there might be some areas with particular constituents that go significantly above the amounts that you've indicated?

DI BELLA: In my mind, just speaking for myself, neither the variability issue nor the uncertainty issue have been sufficiently addressed yet.

Looking at it from an overall point of view, the mountain is a relatively homogeneous kind of rock called tuff. But looking at it from an individual waste package point of view, and there's going to be more than 10,000 waste packages, each waste package is going to see different characteristics of the water around it. And what that spread is, I don't think there's enough data yet, particularly of water at the repository level, to answer the question.

Dr. Strehblow?

STREHBLOW: I wonder why you stopped your concentration of the brine action? I would guess it's some 10 to the minus 2 molar solution. You're talking also about dry situations, and it could be that the electrolyte is really concentrated, more concentrated, like a Q brine, or something like that, which is extremely high in concentration. It might be more corrosive. Is that a realistic situation? We can talk about that later. But you might give it some thought.

DI BELLA: I think it's an absolutely realistic situation. I only put that chart up because I had something to cite behind it.

And now may I give the floor back to Dr. Sagüés?

SAGÜÉS: Great. Well, we're getting closer now to the substance of the workshop, and what Dr. Di Bella showed you is another introduction of our mental parameters. By the way, we do have here in the audience Yucca Mountain Project scientists who might be able to clarify some of these issues. So I would invite the panel participants that if they have any additional questions on this, feel free to indeed ask if we can have some additional clarification. And that applies also to what I'm going to mention right now. I'm just going to highlight a couple of issues, and I don't pretend by any means to make this into an exhaustive presentation.

And what I wanted to do is to quickly address the question of what kind of corrosion performance is needed if a repository of this type would be somewhat successful in doing what it's supposed to do. And the first thing I want to mention is that the performance of the repository has become increasingly dependent on the integrity of the waste package.

Maybe a decade ago when the initial concepts of the repository were considered, at that time, the mountain was an extremely, and still is an extremely important part of the overall equation that would determine separation between the waste and the public, but the mountain, during the last decade or so, more evidence began to appear that the mountain had a lot more water than was initially anticipated. The flow of water, the flux of water was found to be quite significant. There was uncertainty as to how slowed down that water motion would be, and so on.

So, as a result, the present performance projections for the repository are relying strongly on that package being there and staying in very good shape for a very long time.

Indeed, at this moment, to have a very credible, a very robust repository concept, really, there shouldn't be any widespread penetration of the Alloy 22 shell during the first 10,000 years of operation of the repository. And we cannot give any specific time period, and the like, but indeed, a very robust package, a package that will stay for a very long time is indeed needed.

Now, things like localized corrosion would be very detrimental to the anticipated performance of the repository. If there were strong evidence that localized corrosion, big pits would develop in the system, if those penetration phenomena are really very fast, to get something that would be a workable repository concept, so, really, localized corrosion is something that the concept cannot afford very much.

Now, that leaves, of course, uniform corrosion. Now, uniform corrosion rate would have to be quite small. To be quite sure that there's no widespread penetration, well, we have to have corrosion rates that have to be much, much smaller than two micrometers per year. Two micrometers per year is, of course, the nominal kind of corrosion rate that would give you two centimeters penetration in 10,000 years.

So, you realize that we are asking here for the kind of performance that in many industrial operations may be something you could live with, but in this case, you couldn't.

Now, the challenge that we have here is an extrapolation challenge, because the package corrosion performance relies on passivity. And I'm going to show a graph in a second here to dramatize this. The empirical evidence that we have on the performance of passive materials is very, very low. We haven't used a trick for engineering, as far as I can think, and as far as from conversations with a number of individuals who should know, we don't have much more than about 100 years, maybe 150 years perhaps, the first applications of some aluminum alloys, and one could say that, well, yes, maybe steel and concrete, there have been nails or some small components of steel embedded in mortars and concrete for a long period of time, and that would be passive. But, again, we are talking about a fairly short time.

So I put together this graph some time ago, and this graph is simply an indication of the following. Here, we have, say, assumed uniform penetration rates in micrometers per year. Here would be the millimeters per year; here would be the micrometers per year. And here would be the nanometers per year kind of thing. To penetrate through 20 millimeters, well, you have this amount of time. So if you have 10 micrometers per year, then you are talking about a couple thousand years, and so on, and so on.

Well, the kind of desired performance is something that begins to get better and better the farther away we are from 10,000 years. So this is sort of like a desired kind of regime, that cloud of behavior over there. But the problem is that the actual empirical evidence that we have on passive materials doing their job is about 100 years.

So, we have here an extrapolation gap, and we have here a heck of an extrapolation gap. We are talking about one, two, maybe three orders of magnitude extrapolation gap. And, clearly, we cannot just rely on maybe ten years test and saying this worked for ten years. We have to have something to support that, and that something has to come from some fundamental understanding of the processes that are responsible for this behavior. And, of course, that's why you're here.

Let's talk a little bit about what is the available evidence on uniform corrosion. I'm just going to highlight some of the results that the Project has produced, and some of the -- . And, again, as I said before, feel free to ask some of the Project scientists in the audience, if you would like, some very specific detail.

The evidence that is available on Alloy 22 comes, quite a bit of the most detailed evidence comes from gravimetric corrosion tests, coupon tests, in a fairly large facility that is located at Lawrence Livermore National Laboratory. Over there, Alloy 22, among other alloys, has been tested, and in simulated repository environments, the corrosion rates that are obtained by gravimetric tests are distinctly below the tenth of a micrometer per year. And I'm going to show that much of them maybe show a hundredth of a micrometer per year.

There's also electrochemical evidence that provides similar evidence, and then there is a little bit of evidence on temperature dependence. So let me show you some of that evidence so you get a flavor of what is involved.

First of all, about gravimetric corrosion rates, those of you who have been involved in coupon testing know that when we are talking about those very low rates, we must be talking about very, very small mass differentials in coupons that can be quite heavy. And sure enough, when you have data from the first maybe couple years, or one year, you may get indications like this.

And, here, we have the evaluated penetration rate for a whole bunch of coupons, in this case, of Alloy 22 in a number of simulated environments, and this is the cumulative percentage of it. And, of course, what you see is that a number of your coupons are going to show a negative mass loss. They have gained weight during the test, even if you clean them up, and so on.

So, you realize that right there, you are in a situation in which you have to start making some assumptions. Maybe we have silica deposition on the surface of the specimens. Maybe we have to have some controls, and so on, and so on.

Now, this gets a little bit better when you go over maybe two or three years, and that is indeed what is happening here, are similar cumulative distribution curves, in this case, going up to two years, and now a number of things showing negative rates are becoming a little bit less.

Up here you have your corrosion rates. You have some kind of a median that is less than a tenth of a micrometer per year, but you have some of -- here and there.

And, indeed, this kind of information is being used now for a number of ways of assessing what may be happening over long periods of time. Indeed, also what you see is that as the time of exposure increases, the mean rate of corrosion of these coupons by gravimetric observation is, indeed, coming down. And, here, we are hitting more like maybe the hundredth of a micrometer per year. But, of course, you have this uncertainty that comes from this test, and of course means you're going to have also a spread of values.

So, so much for the kind of gravimetric information that is coming up for these periods. There aren't too many other studies of extremely low corrosion rates by gravimetric purposes of passive alloys in general. You do have electrochemical evidence.

For example, in Gustavo's group at the Center for Nuclear Waste Regulatory Analyses, they have produced information like this. I'm going now to the Yucca Mountain Project which provides information of this type. You go ahead and you potentiostat an Alloy 22 specimen, and then of course you look at the kind of current decay that you get, and in this particular case, we have, in this example, we have a couple of weeks worth of testing, and you see that the corrosion rate reaches some kind of apparent stabilization at the value that is maybe about a tenth of a micrometer per year kind of information.

Now, as many of you know this, you can get this, you plot a log of current density as a function of log of time, and in that case, well, maybe it still has a way to go on this. It may go to much, much lower value if you extrapolate in that fashion. And I'm sure that many of you have other opinions and may have conflicting opinions after having interpreted this kind of evidence. But this is the kind of evidence, direct immediate evidence that we have right now, sort of like empirical observations, that have to be meshed with some basic understanding to be able to go ahead and extrapolate this orders of magnitude into specific behavior.

And then, yes, you do have electrochemical, in this case polarization resistance to the impedance as well, and you see also corrosion rates approaching a hundred, maybe a tenth and a hundredth of a micrometer per year, and this is linear polarization. In this case, we're talking about a half a year kind of period of time. And this also indicates something which seems to be distinctly below the tenth of a micrometer per year.

So much for rates. This is the kind of information, the immediate information that is available. A little bit on temperature dependence of this kind of uniform corrosion.

The first indications of temperature dependence came from gravimetric tests, and those indications were really not very informative. These are rates, in this case in nanometers per year, from coupon tests that were conducted at a couple of temperatures, 90 degrees and 60 degrees centigrade, and this is the spread of the information. There's no really good indication about what might be the temperature dependence. Of course, this is a very crude method of trying to obtain that.

But on the other hand, we're talking about data that spreads over a couple of years of time. So you have something in one direction, and you have some in the other. But this was quite inconclusive. And in the initial performance assessment exercises that the project carried, it was assumed that temperature dependence of the uniform corrosion rate of Alloy 22 in these kinds of environments was not very great.

Now, yes, you can do short-term experiments, and this is an example of results from short-term experiments that were made at the University of Virginia by John Scully and his collaborators. And here, you have some potential scan tests performed in a relatively short time scale. We're talking here in the hours or maybe a day at the most kind of time frame. And, yes, in this case, you can get some indications of apparent corrosion rates. This is a natural log, by the way, so it's a little bit--it's not immediately easy to look at.

But nevertheless, yes, there seems to be an indication of an increase. You can go ahead and do what we'll do, just put a range of dependence, and you end up with about 30 kilojoules per mole kind of activation energy. It doesn't sound too outrageous, but what I want to indicate, this is very preliminary information. This is just quick kind of testing. We have some idea of what is happening, as one can speculate, but that's about the kind of bit of information that is available for this particular issue at this moment. More is coming, but we are not quite there to the point where we have very nice data after several years of exposure with different temperatures and very low margins, and so on.

So, I'm showing this primarily to give you a flavor of the kind of information that exists. And, again, I apologize to the Project if I am short-changing some of the information that is available. I'm sure they'll be glad to supplement some of it.

Now, I'm just going to say a couple of words about localized corrosion, and the kind of information that is available at this time. And I should say that at this moment, the Project approach to performance analysis, which is sort of like an extremely sophisticated overall durability projection type of model, and that approach uses a critical potential criterion. And that is, of course, to measure ranges of open circuit potentials, to measure ranges of repassivation potentials. If your open circuit potential is below the repassivation potential, well, you should be fine. If it is above, you're in trouble.

A lot of this information comes from cyclic polarization tests, and some additional information is now emerging, but again, we have to deal with what is available at this time. And the overall conclusion of what has been observed is that crevice corrosion will not sustain the temperatures on the order of 100 degrees centigrade, and at the kind of expected open circuit potentials, if you are balancing the chloride ion content of the solutions with a comparable concentration of beneficial ion, such as nitrate, for example, things of that order, if you put just sodium chloride at those temperatures, and it's highly concentrated sodium chloride, several molars, and so on, yes, you may develop localized corrosion even in Alloy 22.

But when you have the kind of balances that Dr. Di Bella showed earlier, then the localized corrosion doesn't seem to develop, at least within the time frame and within the limits of the information available to date.

There is concern, and Dr. Staehle has pointed out this, that there may be other substances, say, trace elements of lead in the rock, and the like, that may lead to surprises in not only the localized corrosion, but also perhaps uniform corrosion of these materials.

But what I want to do is I want to close this review of the highlights of what is know about corrosion of these materials by emphasizing something in here. A, we have a very long time frame. We mentioned this. 10,000 years, we want to get farther ahead than that. The other thing is something that I'm sure Dr. Shibata has sensitized many of us of that, and that is that each one of these packages, oh, has about some 20 to 40 square meters of surface, say 30 square meters of surface. There's about 10,000 packages, or so, depending on what kind of a concept we have. So, you can have 30 times 10,000, have 300,000 square meters of passive alloy here to deal with. And there's a little bit of an extrapolation from tests that you perform with 10 square meter specimens when you're going to 300,000 square meters of surface.

The other thing is welding. These things have welds that have been annealed, and then there's finally a closure weld at the end of the package. Well, each one of these packages will have at least some 6 meters, or so, of closure weld at one end. So you have 6 meters times 10,000 packages, minimal, so you're talking about some 60,000--about some 60 kilometers of weld to consider in here. We are talking a long time, and we're talking about a lot of material to consider. All of it has to stay--you want for it to be passive, and you certainly don't want widespread failures of that material.

So, having said all that, we went ahead and we submitted to this distinguished panel a couple of questions. And you have the text of the questions. I'm just going to show this to remind everyone of what is the general flavor of the questions. And the first question was can you propose a mechanism or mechanisms that would after a long service time substantially increase the passive corrosion rate of all the presently expected values.

You saw that if we go to -- in the micrometer per year, we are likely to have some kind of a very important question as to whether these packages will do the job that the repository would need to have done.

And the idea was, of course, that maybe we do have these very low corrosion rates, maybe a tenth or a hundredth of a micrometer per year. This is happening for a while. But then maybe there is some kind of an aging process that we don't know about. And, again, we're bringing you here to speculate as to what processes might occur, and -- may kick in after 100 years or 1000 years or 5000 years. And if at that moment we get something that starts boiling quickly through the container, we want to have an idea, we collectively, not just the Board, but the community, we would like to have some idea as to whether that might or might not be happening. And the best thing that we thought of was to bring you all here and ask you directly that question.

And then, of course, the other is let's suppose that we lay uniform corrosion to rest, well, could something be happening at the localized corrosion end? Is this open circuit potential, critical potential criterion, that works so well when you're designing a refinery for a chemical processing plant, will that work also for something that has such a huge time designed service life, if you want to put it in those terms, and also such a large opportunity for damage to develop from a surface area standpoint.

And, of course, if you come up with ideas of things that could happen, you thought about this or this, how could this be tested in a reasonable time frame? As you heard today, our society is getting very close to making some kind of a decision. Our representatives will make that decision. We're not going to make that decision. But they are going to have to be informed as to what may be happening, what may not be happening, what may go wrong, and also, of course, what can go right with the present concept.

I would like to finish this by pointing out a couple of questions which are a little bit broader, but have to do with this as well, and they have been posed by Dr. Paul Craig. And I'm just going to flash them here. We may put them back later. And I guess that someone decided to call these philosophical questions. That was not my choice, but we'll leave it with that name, and I think philosophical is a good idea.

And I think that the number one, this is addressed to the members of the panel, and this is more of a general flavor kind of idea, and that is what is, you know, when I think about this, what is the most significant unexpected result or surprise that you have experienced personally in the physical, chemical, materials science area. And then given this experience, why do you or don't you believe that unexpected results or surprises concerning Alloy 22 corrosion behavior will or will not occur over very long periods of time. I think that that's a very good point that Dr. Craig has made, because this is going to be a humbling experience of going through observations in this area.

And, now, number two, which is again a little bit more general, is what is your level of confidence in this kind of extrapolation that one would be doing. And then how far out in time would you feel confident extrapolating the corrosion behavior of Alloy 22. And, again, how far in time are the operational works in here? Because that is what makes this problem quite unique.

And I think those two particular issues are of quite significant importance, and we're going to have to be looking at them. And there may be one or two other questions that will be brought out that we can discuss later.

So, this is really the overall kind of introduction that I wanted to give you. And before we go into the individual presentations, do we have any questions or comments that you would like to bring up based on what I have shown up to now?

(No response.)

SAGÜÉS: Well, I think that you will have plenty to say on your own presentations, so I'm going to now pass the meeting to Dr. Bullen.

BULLEN: Thank you, Professor Sagüés. I appreciate you getting us right back on schedule. We are at 9:55, and that's the beginning of the individual responses.

Fortunately, I had a volunteer approach and volunteer before the meeting started to be the first participant, and that is Dr. Gustavo Cragnolino from the Center for Nuclear Waste Regulatory Analyses. And so I'd like to ask Gustavo to give us a five to ten minute overview presentation of the response to the two questions.

So, Gustavo, would you please kick us off?

CRAGNOLINO: I want to start raising the same slide that you have seen that Alberto placed here, and these are the results of our work, only to emphasize that in this type of extrapolation that was done on the basis of electrochemical measurements of passive current density over the period in which steady state conditions are very well attained, we are using Faraday's laws to extrapolate time of this nature.

However, these are the main issues that we have to confront, that we don't have any way to estimate defect generation or accumulation of metastable events that may lead to higher corrosion rates at longer times.

And at some point that he touched on at the very end on how this could be impacted by the effect of fabrication processes that we need to consider.

These concerns about the validity of these long-term extrapolations, either from the experiments that I mentioned as electrochemical or gravimetric - we believe they need a critical assessment of mechanistic models that could provide us a framework to try to understand new methods or approaches that can be used for the purpose of experimental verification.

And we have used this modified point defect model as a starting point, but we have to keep in mind consideration of other type of passivity models that should be placed in the perspective of providing us a way to find an experiment that can in some way test, within the limitation of time, the results.

And I will talk on one issue that we have to deal with very clearly is there is validity for high temperature experiments as accelerated tests for extrapolations to the low temperature regime. This is a question that has been posed for many systems. It's possible that we are confronting here times that are much longer than the time of the engineering experience. And there is another factor that can be used to accelerate this.

I'm not going to go into details because I can cover this later on, but to give you an idea, we started working with the idea of the modified point defect model to try to develop a concept about the stability of the passive film, and we came to the conclusion that by using this model, the only thing that can explain seeing that would lead to eventual failure of the passive film is the process of film spalling at irregular locations. And we propose an heuristic model to account for this process.

But the final conclusion by analyzing the process through this type of model is that the steady state passive dissolution of this film is stoichiometric in nature, even though initially, it would be a preferential dissolution of the most easy to dissolve species like the nickel in this particular case of the nickel chromium based alloy.

The important thing is that as we mentioned here, in this family of the Hastalloy alloy that may contribute to passivity of the chromium rich oxide type of film in which we can have a double layer in the interface with the aqueous solution that is essentially more of a hydroxide type of effect.

We went through this type of exercise using this theoristic model to consider the process of film spalling and the alloy at different thickness, and we can work with this, in which situation with particularly this type of thickness of this flat, thin material in the calculation, and the lifetime of the container will be a function of the critical vacancy concentration fraction. This fraction is the concentration of vacancy over the concentration of the other species present in the interface. And film spalling is assumed to have occurred under this condition.

We can come out with prediction in life that lead us to very long times, except for critical vacancy concentrations that are relatively long. This puts in question obviously to our thinking, that for one side, this is valued as a concept, or there are some essential flaws that we have to find out.

Our approach by using this model, and for that reason I emphasize the model as a good way to design the experiment, but as critical responses. If the model will not agree with the response that we are expecting, we have to change the model. But this is the only way that we can come out with an approach to predict this type of long, long time decay.

And we are doing an experiment in which we measure solution composition, you've seen capillary electrophoresis, to really evaluate if this concept of stoichiometry in the long term is maintained, or we have preferential dissolution of the alloying elements, and this is the type of cell that were used for electrochemical purposes. I'm not going to go into details. We can discuss it later.

We need to grow to have very high resolution of the passive corrosion density measurement over an extended period of time, because in my first failure, you see that even though the current density is steady there is a lot of fluctuation, indication that they are processes of film breakdown and repair, and in order to evaluate the possibility of metal vacancy accumulation, we consider the use of resistivity measurements in thin foils.

To complete my point, we have to consider any other possible processes leading to small increases of passive current density. That could be a superposition of cumulative metastable passive film breakdown and other repassivation effects. And another approach is consider other types of models. I mentioned initially if the modification of the outer deposit layer is able to create a local, more aggressive environment with time, that will promote this type of very localized fluctuation in the concentration of the variables that influence the breakdown and repair of the films.

Obviously, the possible methodology that we have in mind is this. Enhanced resolution of long-term either potentiostatic or zero resistance ammeter measurements. But we have to keep in mind that when we are using an electrochemical approach, this is a very important consideration.

The basis of the consideration that was mentioned by Alberto regarding the probability of events that we cannot capture using the smallest specimen - tied to this, we have to consider the important role of the cathodic area when we are talking about a very extended cathodic area, compared to the situation when we are doing this under potentiostatic control, in which we have a driving force for the process.

I'm going to go very, very briefly, and think that is a matter of further discussion, about certain semi-empirical approach that we have been using for localized corrosion. And I think that we have to distinguish very well in this type of approach. Here, we are representing this dry period that was mentioned before in the discussion, the situation of the formation of the liquid film that was the condensed layer, that is many times promoted by the deliquescent point of salts that have high hydrotropic properties, and the possible evolution of the corrosion potential or the repassivation potential.

But this critical potential is not the potential that you have for the initiation of pitting corrosion in the short-term experiment, but it's a potential that you define as the minimum potential at which a surface can remain active after having grown. And, here, there are some factors I've included in this, and what we have to consider is the stability of this type of parameters in the long-term, because, as I mentioned here, these parameters are environmentally dependent and the environment's change with time.

And to emphasize the point, here are probably the main factors that have an involvement in the definition of this corrosion potential and repassivation potential. The temperature of the repository will decrease with time. The corrosion potential will increase, but at the same time, will increase the critical potential, decreasing the possibility of localized corrosion.

But you have other types of events that could have an effect, like the well-known effect of chloride, or the effect of the aging of the passive film that will lead to an increase in the corrosion potential and promote conditions for the initiation of corrosion.

And, finally, two aspects that cannot be neglected, and depending a lot about the fabrication processes, and in particular, the post-welding type of treatment either in the stage of fabrication or as was mentioned by Alberto, in the closure welds, and this has a detrimental effect in particular on the critical potential. For that reason, I don't have a clear answer to the question in the way that it was formulated, but I think that I tried to provide the idea that we have to confront this issue by looking not only in terms of the projection in time and in the space, but the projection in space has to take into consideration the important variability in the condition of the material, as they seem to consider in the long-term.

Finally, I want to acknowledge the people that have helped me in this endeavor.

BULLEN: Thank you, Gustavo. I appreciate your brevity, and you were done in twelve minutes. That's great. I'll try to keep everybody to at least ten.

Now, at the risk of asking a professor who's usually programmed for 50 minutes to talk, because I notice most of you are faculty members, do I have a volunteer?

Digby Macdonald, I saw him rustling his view graphs there. So, Digby, if you could do it in ten minutes, that would be great, or less.

MACDONALD: Okay, I want to address this question in a somewhat philosophical manner by pointing out that repositories are unique. In fact, we haven't actually built one yet. And being unique systems, we have great difficulty in developing empirical models that are based on a statistically significant database. It doesn't exist.

Furthermore, the horizon is far too distant, 10,000 years, compared with our experience in any given system where we have a well established database, far too distant for any effective extrapolation. Accordingly, empirical models are highly unlikely to succeed in this business. And what we have got to do is to appeal to determinism as a prediction philosophy.

And what is determinism? Determinism in this context simply says that the future may be predicted from the past, provided that, and this is the caveat, the caveats in this business are very, very important, the phenomena are described in terms of viable physical mechanisms and models; that the solutions to the constitutive equations, those are the equations in a model that tell you how the model works, are constrained by natural laws that are invariant in space and time; and finally, that the path to the future state is continuous and can be specified. And that is part of the-- one of the major problems in this whole business. Can we accurate predict the path over which one of these canisters is going to travel for the next 10,000 years.

I'm going to show you a couple of models just very briefly that meet these criteria, and the first one is some work that I've been doing for Gerry Gordon and his colleagues on general corrosion, and it's just essentially a mixed potential model. What it proposes is that any corrosion process can be broken down, fundamentally down into anodic and cathodic processes, or oxidation and reduction processes, if you like, and that the constraining condition is that charge must be conserved at the surface.

So, the sum of all the partial anodic current densities must be equal to the sum of all the cathodic current densities. And that condition defines a very important parameter called the corrosion potential that Gustavo just talked about.

Without going through all the mathematics, and there are a lot of mathematics, I'll just point out that the model is based upon point defect model, which I and my colleagues have developed over a couple of decades, and I should point out that one important reaction, and this should actually be over here, is the dissolution of the barrier layer, in this case, chromic oxide, and that establishes a lower limit for the corrosion rate. The rate of dissolution of the barrier layer represents a lower limit, not a higher limit and not necessarily the corrosion rate, because there are parallel reactions that can occur, the transmission of cations by cation vacancies and the transmission of cation interstitials through the barrier layer.

Nevertheless, if one goes through the mathematics and carries out the prediction, you can predict the corrosion potential, which I should add is in reasonable accord with the experiment, and you get this classical "S" shaped, sigmoid shaped variation with log of the partial pressure of oxygen. And this is on a standard hydrogen scale, which is not a scale that is commonly used, but open atmospheric conditions puts the potential around here.

Now, why is the potential so important? Well, the potential is important because it determines the likelihood of localized corrosion occurring. I think as Gustavo has shown, and Alberto showed as well, there's a good argument that can be made that general corrosion probably will not represent the major threat, unless there's some process that is currently unknown in corrosion science that causes a massive increase in the corrosion rate.

But that's not true with regards to localized corrosion. The problem with localized corrosion is that we have very, very long periods of time available for the nucleation of localized corrosion events on the surface, and yet our experience of course is very, very short.

Just to show you some predicted corrosion current density plots, up to 120 degrees, you'll see that the corrosion current density is not a strong function of the corrosion potential.

But let me move on to localized corrosion damage. Now, the objective in localized corrosion damage is to calculate the so-called damage function as a function of time. The damage function represents a histogram of the number of pits that exist on a surface per unit area as plotted against the pit depth. The pits that cause the greatest damage and could ultimately cause failure are, of course, at this upper extreme of that distribution. The total damage on the surface is the integral of the distribution.

Now, the reason why the damage function is important is that you can see--and these are just schematic ones, but I'll show you actual calculated ones shortly, and by the way, this work was funded by--this type of work was funded by the Department of Energy's Nuclear Energy Research Initiative. The reason why this is important is it leads to a natural definition of failure. If you have a critical dimension, in this case 2 centimeters of C-22, then what you seek to calculate is the time at which the upper extreme of this distribution extends past that critical dimension, and that gives you the time of failure. And what we want to assure is that the time of failure is greater than 10,000 years.

Now, does C-22 pit? Yes, you can make C-22 pit. Here's a pit. C-22, this happens to in saturated sodium chloride solution at 80 degrees Centigrade and a pH of 3, and

I should point out a very high potential, about 900 millivolts on the saturated cal/mol electrode scale.

Here's another one. This one shows the remnants of the barrier layer on the surface, and you might also notice here that there's some very small pits associated with crystallographic features on the surface. We can actually measure the property. For example, we can measure the apparent breakdown potential as a function of voltage sweep rate, and the theory predicts that this should be a linear relationship, which it is. And from this, we can extrapolate to obtain a fairly accurate value for the breakdown voltage. And that's required in order to actually do the modelling work.

Now, the model assumes that passivity breakdown occurs via the accumulation of vacancies at the metal film interface, followed by just dissolution of the film. And I'll show you now a series of calculated damage functions. And I'll draw your attention to this parameter gamma. Gamma is the delayed repassivation rate constant.

What happens, you see, is that pits are like people. They're born, they live, and they die. And this parameter gamma actually describes how these pits will die after they're formed. So if gamma is high, the population dies very rapidly. If gamma is low, the population doesn't die very rapidly. Gamma being zero, this calculation says none of the pits die. They live forever.

The reason why you get a distribution is that pits are nucleating at different times on the surface. Now, if I increase gamma, and I'll do that drastically, let me go to this plot here, we now take gamma as being equal to ten to the minus 3, year to the minus 1. It's the first order rate constant. You can see that it has a very remarkable effect upon the shape of the damage function. But most importantly, it has a tremendous effect upon the population of pits at the upper extreme.

In this case, the pits do not extend to the critical dimension of 2 centimeters. And most of the pits in this distribution are dead. They're ones that have already died. And it's only pits here at the top of the distribution that are still living.

Now, I bring up this whole issue of gamma because it provides an avenue, I believe, for being able to control the rate at which localized corrosion accumulates on the surface. If you can devise a means of controlling the value of gamma, you hold within your grasp a tool for determining the ultimate amount of damage that will accumulate on the surface.

With that, I'll finish.

BULLEN: Thank you, Digby. Again, twelve minutes. You did a great job. I'll try and be more strict with the rest of you, I guess, otherwise we'll be here all day.

Let me also comment that if you have extra viewgraphs and you want to talk about them during the discussion period, feel free to bring those up. We'd like you to keep your comments to five to ten minutes right now, and I'm looking for my next volunteer. Any hands that are going to shoot up before we have--we'll do one more presentation. Professor Strehblow? And we will take a break after Professor Strehblow's presentation.

STREHBLOW: Everybody has to come up with ideas, and so I thought I'd come earlier so I can relax and listen to the remarks of others.

We have heard about the composition of these films, and I think the major point is that these films are highly chromium containing, and it depends on the pH whether there's any nickel in there or not. It's a bi-layer film. The nickel is outside the chromium, the oxide is inside. But in acidic electrolytes, when nickel has a chance to dissolve, we have a lot of chromium inside. So this is a good idea for the choice of the material, because chromium and its oxides are very resistant to any aggressive anions, so it does not dissolve. It does not pit. It has a slow dissolution rate.

And the deeper reason is that the complexing or the fierce coordination of such an ion is relatively stable, and it needs a high activation energy to make any changes, let's say, to chromium ion, to transfer the chromium ion from the oxide phase to the electrolyte phase. So this is a very simple model of a passivated metal to metal, oxide to the electrolyte.

We discussed about the corrosion rate in the passive state, and this is the transfer of metal ions from the oxide to the electrolyte.

The potential at that interface is also determining the transfer rate, because this transfer reaction sees the potential drop at the oxide/electrolyte interface, which is in the stationary situation, determined by disequilibrium of O2 minus formation.

And there is a very important point that we can expect that some aggressive or complexing ions will help the cation to be transferred into the electrolytes. So this is the case with the nickel. This is the case with iron, which is not a point of discussion for this material. But for nickel, it is, and that is the deeper reason that we accumulate automatically the corrosion resistant chromium oxide which is sitting at the surface, and once it has a chance to form a continuous film, it will stop corrosion.

But there is perhaps some other point which we have to mention, and that is the difficulties which may arise. One thing is the complexing ions that I said when there's a chromium oxide, we have a good situation. Mostly it's anorganic. As we know, the composition of the water in this repository are -- and I have seen fluoride and chloride, which is very important.

Another problem could be the temperature, and the accumulation of impurities which could also lead to a low local deficiency of chromium. Once we have not enough chromium, then at some part of the surface, we might not be able to reform this chromium oxide film once it has been destroyed by some event, it could be also mechanically, and in this case, we have perhaps a difficulty to reform this protecting chromium oxide film. And as Alberto Sagüés has mentioned, we have large surfaces, and these large surfaces could have also defects in manufacturing, in welding and preparing the metal, and so forth.

Another point which I would like to mention, which is very important in the test of corrosion rate, and could be important in the dissolution in the passive state, could be radiation damage. This has been mentioned earlier, and I'm just wondering whether this is a major issue or not. We have perhaps a difficulty to get alpha radiation through the thick shell, and we might have difficulty even with the beta radiation, but we will not have difficulties with the gamma radiation. And this could also perhaps cause voids and defects. Implantations would be with heavy metals, but this would be at the opposite side of our material.

And then last but not least, there is radiolysis, which is causing oxidizing species like the hydrogen peroxide, which could raise the potential if this is a major problem. But that depends on what is in the containers and what the situation is there.

We have heard about the composition of the water in the water table -- and the brines which could be formed. Then there was a relatively modest concentration of these special aggressive anions, like a 10 to the minus 2 molar for chloride, or four times 10 to the minus 2 for the fluoride, which I estimated from the amount which is there. And these concentrations might not be critical for our Alloy 22, or similar alloys, but we have also the situation, as Carl Di Bella said, there could be an environment where the concentration could be higher. If we, for instance, have a higher temperature and we concentrate more and more of these species, then the concentration could be higher and we could end up with a Q-brine, which is more or less a concentrated chloride solution. And that's also something that Cragnolino mentioned perhaps. But I'm sure that Digby has mentioned that, and he did pitting experiments with a high concentration of chloride.

And then we end up with a very critical situation. The fluoride is also very aggressive. We should call that in mind. It's very aggressive for the nickel, but not for the chromium.

Now, just to mention some few experiments which are in this sense and which could be important, is passivation transients with material which is relatively similar to the Alloy 22, this is Hastelloy C-4. It has 5 percent less chromium, but it is close to the Alloy 22, and it has a high chromium content. If we have a 25 centigrade electrolyte, and if we have this highly concentrated electrolyte, high in chloride, the Q-brine, then we don't see any pitting in these transients. The potential is just positive enough to have a transpassive situation.

Now, if we raise the temperature, then we end up with pitting experiments. This is the logarithmic growth of the current density as a function of the time, and with the preservation change, you should have a slope of minus 1, which is the case. But then if you have a slope of plus 2, then you have the typical pitting situation, and then you have a pit growing, and if this is the case, you can look to the surface and the pit is growing. So the potential is not very high. This is against a standard --. And then you end up here with a potential where nothing is occurring in this short time scale at 200 milliwatts, but this is 60 degrees. And I have another one which shows the situation for 90 Centigrade, and this is even more dramatic. Then you have already a beginning of localized corrosion at 200 milliwatts, which is about the open circuit potential for these conditions, as has been studied.

I also would like to mention that we have breakdown and repair events. And if we increase the temperature from 50 degrees to 80 degrees, and we make a temperature transient, then you see a strong increase in these oscillations, which is breakdown and repair, then breakdown and repair. And I just estimated if we take this amount of charge and extrapolate that, we are ending up also with something like a little bit more than a micrometer. It could be two or three micrometers if these oscillations remain as large as they are. But they might die out and get smaller, so I made a factor of .1 in there, but I'm still ending with 3.5 micrometers per year as a material loss.

And if there's a pit and we have a pit within the pit, it will deepen the defect. And then, finally, we may end up at up to 10,000 years with a breakdown.

Well, just to illustrate a little bit radiation damage, I brought along one viewgraph which is showing in principle the possibilities which may occur. This is the alpha radiation, which is not a big deal, because our radiation is coming from inside. This is the situation when the solution is contacting the corroding surface, and there is the oxide film, and there we have defects which will be formed. And this is something that goes in the direction of Digby's defect model.

You have also the formation of dopings, and then you have--I think that is the thing which we should discuss a little bit, whether this is realistic or not. We might have the formation of very oxidizing species due to radiolysis. If the gamma radiation is, for instance, getting through this material, and it will, then there might be a chance that we have oxidizing species which are increasing the potential, and then it could get above the pitting potential if the concentration and addition of the aggressive anion is very high.

Well, I think this should be enough for the viewgraphs, because we would like to have some little break, and then the others might add something else.

I just wanted to mention here at the end that the penetration depth for alpha is definitely too small to get to the other side of the container. The beta might be good enough if the energy of the radiation is high enough. The gamma definitely will get through.

Thank you.

BULLEN: Thank you very much, Professor Strehblow.

I'm going to keep us to a strict time table, so we'll take a 15 minute break, and reconvene at 10:45.

Oh, by the way, could I make the comment to all the presenters if you have additional transparencies or viewgraphs that we haven't made copies of, would you please make sure the staff gets them so we can get copies to everybody?

Thank you.

(Whereupon, a brief recess was taken.)

BULLEN: The second part of the presentations by the panel. Our next presenter will actually be Roger Newman, to be followed shortly by Alison Davenport. So, Roger, if you're ready, we'll get you miked up and ready to go.

NEWMAN: This is the second one of these events that I've been to, and I was very disappointed that the professor of philosophy wasn't here this time. That was really enjoyable having her here pointing out when we were talking bunk, which was most of the time. But, anyway, now the scientists are using the word philosophy.

I'd like to just say a few very brief words really about, rather conventional words about this topic. And to some extent, I think I've addressed the questions, although I must admit to some extent, I've made up my own questions.

The first question is what is this passive film that we're all talking about? And my view, which I think has been acted by one or two of the other panelists, is that this is essentially chromium III oxide. You can find a lot of other things in it if you look hard enough, but to this day, I don't think we have any understanding of whether these other things have any causal role in the passivation process. We have quite a lot of evidence that the chromium oxide is the thing that actually causes the passivity.

The second point, and I certainly would expect a certain amount of discussion with some of my colleagues on this point, is whether the molybdenum is good for the passive film. My view, and I think I'm not entirely out on a limb here, is no. This molybdenum that we put in this alloy prompts its resistance to localized corrosion. But I would certainly argue that that effect takes place when you already have a small dissolving cavity, in other words, a kind of protopit. It has absolutely nothing to do with the passive film. And, in fact, quite often, molybdenum just comes after the passive film. So it's really this chromium oxide film.

The third question, which I think we're coming to the actual questions gradually here, is that how thick does this passive film grow? Well, we often find this sort of 1/t, in other words, the growth rate of the film is proportional to time. And if you extrapolate some data that exists, you find this thing doesn't really grow at all. It will never get further than about six or seven nanometers.

On the other hand, the assumption in this 1/t extrapolation of the corrosion rate is that the passive film is not dissolving. Well, that's clearly a poor assumption. And I just point it out here. Suppose even though the film development is limited by some film dissolution process, and even if this dissolution, the equilibrium solubility, if you like, is only on the order of 10 to the minus 14 molar, this would still pin the corrosion rate up at one nanometer per year. And if all this stuff is re-precipitated, you could build up a layer on top of the film.

Now, so what, you might say. It wouldn't be shiny any more, but it would still be protecting the contents. And, indeed, my general view is probably the so what is probably right response to that, because I think this C-22 is pretty good stuff. And most of these discussions on localized corrosion probably are going to lead to the conclusion that it will last pretty well, for at least hundreds to thousands of years.

So, how could this mechanism of film growth change with time? Well, one aspect that's already been mentioned is that you have a steady outward drift in this thing called the corrosion potential. That's the steady state electro potential to metal. And not only do you have oxygen driving that up, you also have peroxide created by radiolysis on the surface of the container. And, in fact, this reaches the borderline of what I've chosen to call transpassivity, especially if the pH is a bit high. In fact, this transpassive dissolution is worse at high pH values than it is at neutral pH values.

And in the pulp and paper print industry, for example, when some people carelessly use peroxide as a bleach without thinking about their materials, they discover that these nickel based alloys would corrode at several millimeters a year. That was a lot more peroxide than you have in this system, obviously.

What is this transpassivity? Well, normally it's considered to be this chromium to chromium VI, and that might be possible, but the main thing that's going to happen is the molybdenum is going to dissolve out. So, to some extent, you're losing the beneficial effects of the molybdenum in the near surface layer as a result of this dissolution reaction.

So, in other words, the corrosion rate might level out instead of paring off and falling to 1/t.

Another thing that might do that is fluoride. Henning said that fluoride doesn't complex with chromium. But it certainly is an aggressive anion and might make the film continue to dissolve.

There are other things. Peroxide itself is a complexant of titanium. The same people that had the problem with the nickel based alloys in the pulp and paper industry, some of them replaced the nickel alloys with titanium, and promptly found that the titanium corroded away at several millimeters a year as well. And that's because the peroxial anion is actually a complexant of titanium. So there could be other things floating around in this water that you just have to think about, even organic materials, which are possible complexants that could make this corrosion rate level out instead of continuing to fall.

Having said that, I don't think that's going to make these things fall apart or leak all over Nevada, or anything like that.

But, can a thicker film be bad? A thicker film seems like it's good. It's a protective. Well, this is where we come to the issue of localized corrosion. And there is a strong possibility, and Professor Sato was the originator of this kind of idea, is that if you have this thick sort of nanoporous type corrosion product film that results from this long-term passive dissolution, it can act like a membrane. Well, in fact, specifically can act like an anion selective membrane, such that you will stabilize the pitting process.

So, if we say that pitting is stable at 90 degrees in normal conditions, over long periods of time, you might find that pitting is just as stable as crevice corrosion in these containers, because this layer, this membrane of corrosion product will enable the pitting to survive under conditions where normally you'd only get crevice corrosion, essentially because the chloride ions can get in through the layer, but the metal ions can't get out. You build up the aggressive metal chloride environment underneath the film.

On the other hand, if by that time the temperatures fall to 60 degrees, I wouldn't anticipate that these containers are going to suffer any dramatic corrosion. And, in fact, all this discussion neglects the actual cathodic reaction, in other words, the reduction of oxygen or peroxide, whatever is the oxidant in the environment. I consider it perfectly possible that when you build up these thick layers, that in fact that might shut off the oxygen reduction reaction and make it very difficult for the process to continue.

However, we should always remember this water is full of nitrate. Nitrate is also an oxidant. You can say, well, it's not very kinetically oxidizing, but it is there.

With regard to measuring these corrosion rates with electrochemistry, this water has enough redox activity in it that I would rather doubt the ability of electrochemistry to measure long-term corrosion rates when you've got nitrates and other things in the water.

And, finally, just a comment on metallurgy, is that we do have welds in these things. They have spatial variations in chromium and molybdenum are less corrosion resistant. I still don't understand why Henning's C-4 alloy pitted as easily as it did. It shouldn't pit like that at 60 degrees anyway. These large areas of metal will have large inclusions, fabrication defects, and so forth, in them.

And I'll just mention phase transformations because at one time, people were talking about higher temperatures for these containers. Maybe that was a long time ago. But I would think that the temperatures that are being discussed now maybe these transformations are not important.

So, just reverting then to the two main points, I don't think these things are going to fail by passive corrosion, but you will develop probably thick layers, microns thick layers, and these thick films will probably adversely affect the localized corrosion resistance, in other words, pitting resistance, they'll act like membranes, and you will, to some extent, have local, the possibility of local perforation of the material if it's exposed to the appropriate bulk environment. But, you know, I'd have one of these in my back yard, and if anybody wants to pay me to put it there, I'd be happy to discuss it with them later.

Thank you very much.

BULLEN: Thank you very much, Dr. Newman. We appreciate it.

Next up is Dr. Davenport.

DAVENPORT: Well, I think the issues that I've been considering are in many cases quite similar to a number of the ones that previous panel members have come up with. So I'll try and keep things fairly brief, so that it doesn't get too repetitive.

I'd like to start off by thinking about, very briefly, about how passive films actually form, and in aqueous environments, because obviously that's going to be the conditions where we're going to get the most severe attack, compared with dry conditions.

First of all, we're relying on a passive oxide film. The passive oxide film that does the job, that actually drops the current density down to a low level so the corrosion resistance is very low is very thin. It's on the order of nanometers. The driving force has to do with the overall potential drop across the metal environment interface. And we form the passive film by a solid state process here, and it's driven by the electric field, and then we are going to have dissolution of the film at the surface. And chances are, over long periods of time, we're going to get to the point where we'll get to a limiting thickness of this film, where when we get to the dissolution, we're going to get a bit more film growth to replace the material that's lost.

So, chances are, in terms of the average passive current density, the average penetration rate of a passive system, is going to be affected by the solubility of these metal ions into the adjacent environment. Very much as Roger said before, these dissolved species are going to probably precipitate with things from the environment, ions from the environment, and also get involved with dust and scale and any other debris from the environment, to perform a much thicker external layer.

So, thinking about the factors that could actually make corrosion take place at a faster rate than we expect, I think the thing that we need to think about is what the materials are that we're dealing with.

Now, the group of people here, I don't need to have to say this to, but to those of you who don't study passive films, it's very difficult to study passive films, and one of the first things that we do when we study passive films is try and work on a very, very well defined surface. So, a lot of us here spend a lot of time preparing single crystal surfaces or spotted thin films that are beautifully homogeneous, so we can test fundamental models.

And so I think there's a risk that we might possibly forget that we're dealing with real alloys, and we have to remind ourselves sometimes that the problem in these systems is going to happen at heterogeneities in the surface. These alloys have intermetallic particles. They have grain boundaries and dislocations which are high energy sites, where impurities can segregate.

When we're dealing with very large amounts of alloys, we're going to have big defects introduced from the processing of these alloys, and then when we have segregation and precipitation processes, we're going to get regions that are depleted in beneficial areas.

So, I think we have to remember that whatever theories that we're using to test these ideas, to test passivation processes, we have to remember what metallurgical heterogeneity will do to this.

So, being a little bit more specific, what are the factors that could increase dissolution of passive films? We've got the possibility of impurities in the alloy, and over long periods of time, perhaps with elevated temperature, perhaps with the effect of vacancies introduced by radiation, is there a possibility that elements that we know are damaging to passive film stability, for example, sulfur and phosphorous, these will increase the dissolution of the passive film, is it possible that these, over long periods of time, can segregate to high energy sites such as grain boundaries or dislocations, so that we get a local enhancement in the rate of passivation?

Similarly, as I mentioned before, could we have the formation of intermetallic phases or solute-depleted regions? Again, could these happen over the very long periods of time that we're concerned about here?

To reiterate what Roger said further, other issues we have to consider are the possibility of transpassive dissolution. And this, for transpassive dissolution to take place in the system, we have to have a somewhat elevated potential compared with the open circuit potentials that people expect for this material in the environments that we're considering.

So, I think we have to think about what sort of factors might increase the open circuit potential, and those are going to be things that affect the cathodic reaction. And in worrying about anodic dissolution, I think it's very important that we don't forget the importance of the cathodic reaction.

Again, people have already talked about radiolysis. Are there some sites on the surface which could end up being catalytic for oxygen reduction, for whatever reason? Is there a possibility of microbial effects that could do that?

And then, finally, my comment earlier, what is the variation in the water chemistry across the repository? Is it a possibility that there are some regions in the repository where we might have particularly elevated concentrations of some adverse species? For example, sulfur oxyanions are known to be very detrimental in affecting the reaction of nickel based alloys.

The factors that affect localized corrosion are in some ways going to be quite similar to the factors that affect passivation. Again, we're concerned about the open circuit potential, so we're concerned about the cathodic reaction driving up the potential. Segregation of impurities or loss of beneficial elements is also going to affect localized corrosion, as well as passivation processes.

And, again, we have to think about the effects of these thick scale-like deposits. Roger has already mentioned these two factors, the idea that could we get crevice-like behavior underneath these deposits, and some issues such as ion-selective action of the deposits.

So I think the two main areas that I'd like to highlight are the metallurgy of the alloy and how the heterogeneities in the alloy that could lead to sites that actually behave worse than the bulk matrix of the alloy and, secondly, to think a lot more carefully about the cathodic reaction and things that could influence the cathodic reaction, and take the open circuit potential rather higher than we would perhaps normally expect.

BULLEN: Thank you very much. I appreciate your succinctness. That's great. It keeps us on schedule.

Our next presenter who had volunteered is Jerry Kruger. Dr. Kruger?

KRUGER: I'm going to restate the issue as I see it, and that is that even though the test facility results are a rather narrow range of conditions, show--and I'm quoting from it--no discernable effects of solution composition, vapor space, or direct emersion of placement, or temperature, the main issue, as I see it, is can long-term changes in these conditions completely overturn this result.

And, being an old time government worker, I'm going to follow very precisely the kind of instructions that we were given.

BULLEN: Thank you.

KRUGER: Including using the plausible mechanisms that were suggested. And it was said that we could use the ones, and I'll one of my own. First of all, is the defect sweeping, and that's described in the attachment, and I won't describe it. But, anyway, what happens is that the passive film becomes a film with high vacant densities and leads to enhanced ionic transport.

And then we were asked is this plausible? And I say, well, possibly plausible when conditions change over time.

The second one is vacancy build-up. And what we have is different rates of dissolution alloy components, and that, as has been pointed out by the last two or three speakers, is certainly a possibility when the potential brings you into the transpassive region. So, these different rates of dissolution yield to vacancies at alloy passive film interface, causing film disruption, the kind of point defect model that Digby Macdonald, for example, has worked on. And this is more likely to occur at discrete sites because of the metallurgy and impurities and various variations. And so this would lead to localized corrosion.

So, in terms of uniform corrosion, perhaps not. But in terms of localized corrosion, certainly. It would lead to uniform corrosion if the disruption or the spalling of the film, which was mentioned, would remove large parts of the film, which I think is quite unlikely.

The third one of these speculative mechanisms is debris accumulation. And, here, the passive film is transformed into a film composed of corrosion products of hydrated metal ions. Henning Strehblow mentioned these. And the film is probably, again, the result of chrome depletion.

And as the work of, for example, Norio Sato showed, such films may be anion selective, thereby again promoting localized attack. So this is plausible for failure by localized attack. Again, the question number two. I looks like localized attack, is going to be a much bigger problem, of course. And as Roger Newman pointed out, the passive film is pretty darned good.

Incipient transpassive behavior. And this I think is maybe the biggest problem, because thermodynamics would predict that if the potentials become transpassive, you would get dissolution of molybdenum and chromium. They oxidize to soluble species, and this leads to an unprotective film, and the process is promoted at high pH, as Roger Newman mentioned.

So, this is plausible if conditions change that lead to transpassive potentials, and we don't really know. We really need more research to determine whether this indeed could happen.

And, finally, one of my own additions on mechanism, and one that has generally been ignored, and that is gaseous oxidation. And, here, we form thicker layers by oxidation mechanisms that would occur when the system is dry and contains steam and/or air. Now, these layers, it's found in the research that has been going on that Dr. Sagüés mentioned, that this is a minor effect.

Sure, I agree, but over 1000 years, it may not be, and the films would grow very, very slowly, but they would grow, and they may not be as protective as the original passive film. So you could result, once the environment becomes wet again, and that could go between dry and wet a number of times, you have aqueous solutions with chloride ions, and these films may lead to localized corrosion.

So, this is plausible when conditions change from gaseous to aqueous solution environments.

Now, the next thing we were asked to do was experiments and/or theory to assess the validity of mechanisms, and I would suggest the follow two. One, experiments and theories on the effects of environmental changes on the increase of potentials to transpassive values, leading again to the dissolution of the alloy components in the passive layer.

And, finally, the gaseous oxidation that I mentioned earlier in steam and/or air at temperatures, and we go to high temperatures just to speed things up a bit, 100 to 250 degrees C. to determine the nature of the film produced over long times, and whether these films can resist localized attack in aqueous solutions containing aggressive anions, as the solution goes from dry to wet.

Now we get to question number two. We had a choice of 2A or 2B, or both, and I chose 2B, because 2A is more difficult. And this question 2B is localized corrosion mechanism for the initiation and propagation not dependent on the critical potential. And it has been suggested that if you are below the critical potential, you get metastable pitting, and many, many experiments have shown that this is so, and this is considered by many workers, for example, Tim Burstein from Cambridge, to be the kinetic precursor to stable pit growth.

And it especially can happen, I think, for long times. So one of a number of proposed ways in which these events of metastable pitting leading to stable pit growth can be described is as follows.

One, the anion, probably chloride anion, moves through the passive film at local sites under the influence of an electric field, as Alison mentioned just a few moments ago.

We have the formation then of metal chlorides at discrete sites at the passive film-alloy interface. And the with the point vacancy model for pitting that Digby Macdonald has mentioned, we have initiation upon rupture of the film at the metal-chloride sites.

Then you get pit growth at the exposed sites sustained when chloride ions under diffusion control can prevent repassivation. And this would occur for the very large areas and below Ecrit. And our absent panel member, Hans Bohni, has also shown that crevice corrosion is considered by some to also be dependent on metastable initiation r-passivation events to sustain growth.

Now, finally, question 2C, experiments and theories to investigate the issues of 2B. And first of all, we need more experimental studies of metastable pitting by, for example, using things like Dr. Bertocci has done, electrochemical noise at environmental extremes that may develop in the repository.

We need theoretical treatment of the effects of environment on the chloride ion transport through the passive layer under an electric field to examine the build-up of metal chloride at sites of local film distribution.

And, finally, we need theoretical treatment of such events as those in air and steam for long periods of time.

BULLEN: Thank you, Dr. Kruger. I appreciate your brevity. Dr. Rapp--oh, I have one more, and then I'll go to you.

Dr. Marcus has volunteered to go next, and then, Dr. Rapp, if you're interested? Okay, we'll go around the table. That would be great. Thank you.

MARCUS: Okay, we've been asked to answer some precise questions in a very concise manner, and although I don't work for the U.S. Government, I also tried to do it in a concise manner. So I have written down a number of phenomena which I believe could be important in terms of mechanisms that may cause the long-term corrosion rate to increase. So that was question number one.

And the proposed mechanisms I have indicated here four possibilities, which I think should be taken into account. I think we have to consider the increase or at least the change in the surface and interface roughness during dissolution in the passive states. Usually when a smooth surface is passivated, there is an increase of the roughness, and I'm talking about roughness on the thermic scale, and this increase of the roughness is caused by competition between the dissolution of the metal and the formation of the oxide. So, there is a marked initial increase of the roughness.

Whether this roughness will continue to increase on the very long-term experiments, that is not known. Usually the roughness increases very much at the beginning, and then it does not increase very significantly over a time period of hours or tenths of hours, but over 10,000 years, I think we don't know.

And I think that this is an important issue, because there is no such thing as uniform dissolution in the passive states. In fact, dissolution of the passivated metal or alloys takes place at preferential sites, even without localized corrosion, on the atomic level, and any increase of the surface roughness will correspond to an increase of the number of defects. And, obviously, the dissolution current is proportional to the number of defects, and that could increase the dissolution in the passive states.

Now, similar reasoning leads to the consideration also of the roughness at the interface between the metal and the oxides, because that may be more important even for localized corrosion, because the dissolution of the cations from the interface through the film to the electrolyte takes place essentially at defects located under the passive layer. So that's important both for general corrosion in the passive states, and also for the possible initiation of localized corrosion.

Another point which has already been mentioned previously is the accumulation of vacancies below the passive film, which may result from the injection of vacancies during dissolution of the oxides, at the surface of the oxide, as Digby proposed. But that would also be due just to the fact that in the passive state, dissolution involves the transport of metals from the interface to the surface of the oxide, and of course that leaves the vacancy behind, and if the vacancy cannot be annealated, then there might be correlations, and that can lead to the formation of cavities on long-term time periods.

Another aspect is, in my view, the segregation of impurities. Any alloy contains impurities, and these impurities can segregate at the interface and weaken the chemical balance between the substrate and the oxides. And there are two mechanisms of segregation of impurities in aqueous corrosion. One is the anodic process by which an impurity, this is illustrated here, an impurity even with a very, very small concentration, which is in the material can accumulate at the surface, or at the interface with the oxide film while the metal is being dissolved.

So, even impurity levels of the order of the ppm, parts per million, can result over a long time period in the formation of very significant amounts of these impurities at the surface, or at the interface. This was found many years ago and called anodic segregation. This was found for sulfur on nickel and nickel based alloys. But this can also exist for other impurities, not only for sulfur.

Now, another, say, more classical process for surface segregation is, of course, the thermal segregation by diffusion, and perhaps we cannot exclude that if the temperature goes up to, say, 160 degrees, and that is an average temperature, I don't know what is the variability, and maybe in some local area that could even be higher. So if we reach temperatures of the order of 200 degrees Celcius, I don't think that we can exclude the possibility also to have segregation, interfacial segregation, under the effects of temperature, just by, in that case, with diffusion.

In the first case, there is no transport through the solid state which can take place at room temperature. Of course, in the second case, it would take place only in the case where the temperature becomes higher.

And the fourth mechanism which I think should be taken into account is that the composition of the alloy near the interface can change. It's known that just under passive layers, alloys have a different composition than the nominal composition. Usually, the area of the thickness in which this composition is modified is very small. It's on the order of a few atomic planes. But, again, that's for experiments that last just some hours or tenths of hours. And over 10,000 years, I think we have to worry about the composition of the alloy under the oxides.

I have indicated here just the chromium depletion, but other elements, they can also become enriched or depleted in the zone which is under the oxide surface.

So, here, the emphasis that you see is maybe more on the interface between the oxide and the substrate than just on the surface, but I think issue is on the interface, the oxide alloy interface, can be important.

We were also asked to suggest some experiments of theoretical treatments to assess the validity of these proposed mechanisms. So this is only some general ideas. I think that there is correspondence between the colors in these dots. I think surface roughness which definitely needs at least some short-term measurements. We don't know at this stage, at least I don't know whether the roughness will increase or not, and that can be important. And then, of course, we need to use simulation.

But I think that I don't necessarily agree with what Digby said earlier, that for any simulation or modelling, we need really to know the mechanisms. It has to be based on deterministic or mechanistic approach. So I think it's necessary to know the evolution of the surface and interface roughness, and then use the data in simulation.

The same would apply to the investigation of vacancies. We have been talking already a lot about vacancies under the film, but there are very few, and I think there is a real lack of data. There are now techniques capable of detecting vacancies under thin oxide layers, and I think experiments should be conducted, and then again the data should be used for simulation on long-term evolution.

Regarding the segregation of impurities, one way could be to produce alloy with increasing amounts of impurities, including sulfur, and then look at the behavior of some sort of accelerated tests on the effect of impurities. And I think we also need data on changes of composition for this particular alloy, changes of composition under the oxide layer, and again, data which could be used if they are based on a mechanism which could be used in simulation.

Now, about question number two, in fact, there are many similarities between phenomena that can increase the corrosion in the passive state and those that can lead to localized corrosion. It's not two separate worlds. And I have mentioned here the passive film breakdown which can be caused also by segregation of impurities at the interface. So this is very similar to the mechanism I have shown before for anodic segregation on surfaces. But this time, we have the passive film, and this interface, and this is mentioned in one of the scenarios, the interface here is just sweeping the alloy with time because of the dissolution, and then we can have the accumulation of any impurity that cannot diffuse through the oxide layer.

And, for example, it's the case of sulfur, which does not diffuse even under the electric field through the oxide layers, and will accumulate here. But in that case, we usually have fluctuations of the concentration, with higher concentrations at the defects, so the vacancies are also important for this mechanism. And that can lead to localized breakdown of the film, and that breakdown is not really well described by just using the concept of critical potential, critical pitting potential.

Another aspect is the local depassivation by aggressive ions other than the chloride ions. This has been mentioned already I think by Henning Strehblow earlier. I think we have to maybe worry about other anions than chloride, which can complex the surface. So, fluoride usually is not a complexing agent for chromium oxide, at least if we look at the general surface, but the question remains on whether maybe fluoride could have some effects on localized area over a very long time period.

So I don't want to say that it's only fluoride that should be considered, but say a number of anions present in the environment.

And now for the suggested experiments. I think that I have here brief suggestions. The answer is the same as for question number one. I think that for the localized breakdown of the film caused by progressive accumulation of impurity at the interface between the oxide and the metal where we could do some measurements with increasing amounts of impurities that could be considered as potentially detrimental, like sulfur, and that we'd also need some maybe more work on the mechanism of local depassivation by anions other than chloride ions which have already been studied a lot. Probably we need even more work on that, but we definitely need more information on the effects of anions other than chlorides in the perspective of long-term extrapolation of passive behavior.

Thank you.

BULLEN: Thank you, Dr. Marcus. Dr. Rapp?

RAPP: The panel members are well aware that I'm not an expert in aqueous corrosion, but I have studied for a while scaling and high temperature dry oxidation. And about four years ago, with Sylvain Larose, we prepared a review of low temperature oxidation of carbon steels, and low alloy steels for high level radioactive waste packages.

At one time, as I understand it, a thick steel, cheap steel container was considered, and they wanted to know what would be the corrosion prediction for 1000 years. And so I will make some comments concerning the growth of dry scales on steels, but you can generalize the comments to other alloys, for example, C-22, eventually. At least for these steels below 550 C., you only make magnetite and hematite, and the proportion of the two scales is something like three to one. Cations are the migrating species in each scale layer, and by vacancy migration in hematite, but both interstitials and vacancy diffusion in magnetite.

Well, the oxidation of pure iron had been studied very nicely by Caplan and Cohon, who's a world-class outfit for such studies, and they showed--this is a parabolic rates constant, Kp, this is the--the equation is the weight change squared is equal to Kpt. So the Kp is shown to be dependent upon the initial surface preparation, which has not been mentioned once here today, I don't think, and they found that here for temperatures down even 400 C., that there's about an order of magnitude faster oxidation when a metal is electropolished, pure iron is electropolished--excuse me--lower when it's electropolished, and reasonably defect free, compared to a surface which has been cold worked and deformed.

So, I think in these canisters that will eventually be made, if they are, we should certainly have some specific initial surface treatment, and I would recommend electropolishing if that's possible.

Now, these are the results of a study, a very nice study by Runk and Kim on the oxidation of iron chromium alloys. They used mechanically polished surface, which would not be the best. They had three kinds of high purity alloys, .2, .4, .8 carbon. In other words, these were not commercial alloys. They had three kinds of microstructures, fine pearlite, coarse pearlite, sparidized structure, and at low temperature, at really low temperatures, 200 C., they did get logarithmic kinetics, but only for a matter of hours, or a day or so.

After that, everything became parabolic. And so this is what I would call low temperatures of interest to this canister, and these are our extrapolations of the parabolic rate constants for a steel with .8 percent carbon to 1000 years.

Now, I'll tell you, by the way, if you look at this kinetic curve, this is the weight gain squared per unit area versus time, and this is the classic way that everybody gets a parabolic rate constant. They say when that becomes linear, that is an incorrect calculation, and we have corrected all of these.

You see, it is not parabolic unless this curve goes through zero. Then it is parabolic. Here, you see there's some initial rapid weight gain in both of these, and when you take the total weight gain squared, you have some initial, plus the time dependent W and you square it, there's always a middle term of 2W initial times W, which never is terribly small.

So, if you instead analyze the weight change in such an experiment as the linear weight change versus the square root of time, you will get a true parabolic rate constant, and you will find out when it is established. So, we have done that, and these are corrected weight constants.

And the important point is after 1000 years, for .8 carbon steel, these are all negligible. This is the weight gain, this is the thickness of the scale, and this is the recession of the alloy. These are all negligible, in my opinion, for 1000 years. And because it's a parabolic, if you want 10,000 years, just take a ratio of times, square root of a ratio of times, and it will still be negligible. So, even carbon steel looks perfectly all right in a dry environment for the protection at these temperatures.

We also examined the oxidation of a two and a quarter Chrome-1 moly steel. And these, again, were abraded surfaces. The only studies available were hot temperatures, 550 to 700, but it allowed us to get a corrected parabolic rate constant again, and look at its temperature dependence. And so we have extrapolated these high temperature data to low temperatures, and this is sort of a nice plot. It has three ordinate scales. One ordinate is the gravimetric parabolic rate constant. This is the recession parabolic rate constant. And this is the scale thickness parabolic rate constant. So, all of the data are on one plot.

But if you use that extrapolation, this is for a two and a quarter Chrome-1 moly steel, temperatures from 100 to 100 C., once more, 1000 years of oxidation. These are all about a half as much as plain carbon steels, and they're all negligible. And if you take a parabolic ratio, a square ratio of the times, they're still negligible after 10,000 years.

Now, there's been a lot of talk today about vacancy and diffusion and annihilate at the metal scale interface and accumulation, and I just want to point out for high temperature scales where you have a crystalline scale and a crystalline metal, the metal scale interface is a site where you have epitaxial relationship obeyed. And if you look at a really simple one, for example, for nickel/nickel oxide where you have a parallel arrangement, the FCC planes of the metal are carried into the FCC cation planes of the oxide, which is the dominant parallel relationship, you have what are called misfit dislocations, a grid of misfit dislocations.

The difference in lattice parameter between, for example Ni and NiO, is about 14 percent, or so. Therefore, you have one of these misfit dislocations which amounts to an edged dislocation in the metal reaching the interface, about every seven or eight lattice spacings. They are all over the place.

On the other hand, any place where a slip plane intersects the metal scale interface, there, dislocations of the opposite verterspecter can become part of the interface, and those are called misorientation dislocations, and they are equivalent to a minor tilt away from this ideal epitaxial relation. You could look at these misorientation dislocations as little steps, if you like, or otherwise just squeeze it down and then you've got a dislocation in the interface. And, in fact, these steps are also created whenever a, for example, a screw dislocation in the metal goes right through the epitaxial relation, into the oxide, and it sets up a spiral staircase of these monatomic steps.

In any case, the way in high temperature oxidation, and I'm sure it also happens in aqueous solutions if you have a scale that is at all crystalline and epitaxial, the way vacancies are annihilated is that vacancies arriving through the corrosion product climbs these dislocations. The misorientation dislocations climb in the plane of the interface. The misfit dislocations would have to climb, leave the interface and climb into the metal. But these dislocations are all over the place, and when I hear about vacancy injection into the metal as the way of getting rid of vacancies, I don't believe it and I don't--I just don't believe it.

So, now, what good can we make out of this--two more minutes, good. In high temperature scaling reactions, we have something called a reactive element effect. The reactive element effect says the following. For certain very large, highly charged cations, we observe a drastic drop in parabolic rate constant, very much better adherence, and the mechanism changes from cation diffusion out to anion diffusion in a fantastic triple positive effect, and this is the mechanism by which this works.

You see, if the scale can only grow by vacancy diffusion and annihilation here, it can't grow if you pin the dislocations so they won't climb. And this is what cerium and yttrium do in an alloy chromium interface, for example. These wrong sized cations, like yttrium and cerium, which are 45 percent too big, simply pin these dislocations.

If cation vacancies cannot be annihilated, then the scale grows by anion diffusion, which is the only alternative. Anion diffusion is very much slower. It makes a very nice adherent scale, and it's an excellent idea.

Here's an example for nickel oxide growing on nickel at a hot temperature. If you put 250 angstroms of calcium on the surface, just I mean spray it on the surface externally, the scaling kinetics go from this one to this one, and if you plot the weight gain versus the square root of time, you see you have reduced the scaling rate by a factor, parabolic rate constant, by a factor of 20. And this is extremely adherent.

And the same kinetics more relevant to the alloy 22, here is an alloy, iron 25 chromium, which grows a chromium layer. If you add only 40 angstroms of ceria to the surface by sputtering, you can reduce the scaling kinetics from this one to this one, and the adherence is great.

Another example, this is for a nickel 30 chromium alloy, getting pretty close to C-22. These are the ordinary scaling kinetics at a hot temperature, agreed, but if you will ion implant 10 to the 16th cerium ions into the metal, you will drop the oxidation kinetics like that.

And, finally, this is a cobalt chromium alloy. So I just want to show you the generality of this mechanism. Unimplanted oxidation to form chromium oxide follows these kinetics. If you will ion implant yttrium into the metal, you can drop the scaling rate by several orders of magnitude, and the scale adherence is excellent. I think that this sort of a doping mechanism should be considered in aqueous solution.

BULLEN: Thank you, Dr. Rapp. I appreciate--well, actually, Dr. Smialowska is next, and then Dr. Bertocci.

SMIALOWSKA: What I would like to do is to say a few words concerning the property of the passive film which are of interest and importance for my further discussion.

So, what we know is that during the film growth, you have logarithmic growth of passive film. In fact, logarithmic growth of the thin films are always logarithmic. And initially, what you have is you have quite high current, and during these currents, you produce, you grow fast the film, and at the same time, you dissolve metal or alloys. So this is a non-stationary state when you have selective dissolution of alloy, and at the same time, passive film growth.

We know later on in stationary conditions, that the whole current in the passive range is going for dissolution of film, not film, but passive dissolution.

So, the passive film is, as everybody knows, not--the bi-layer films. There are two layers, an inner layer, which is oxide film, and an outer layer, which is hydroxide film. And, for me, the most important is the hydroxide, because hydroxide films stabilize the passive film.

Another very important phenomena is the aging effect. During the aging, you have improved the property, corrosion property of the film, and decreased the number of defects. I am not talking about this phenomena when we have increase of the corrosion potential and we reach the localized corrosion. I am talking about the general corrosion.

So, now what we have in the corrosion in the repository, so the people did a lot of measurements trying to find the corrosion rate, and these experiments were done usually by immersing the specimens into the bulk of the solution. There are some data also in vapor phase, but mostly there are these experiments by immersion in the solution.

In fact, in repository conditions, we do not have this kind of corrosion. We have the corrosion in very thin layers on the metal surface. And this surface, liquid layer, has no constant composition. The thickness also is not the same, because of different phenomena which can occur in the repository, like changing of humidity, changing of flow of air, changing of temperature, salt precipitation, and so on.

So, therefore, the corrosion in bulk solution do not necessarily represent the corrosion rate on the waste package. And we can differentiate two extreme cases. One, we have on this layer of fluid on the metal surface, we have solution, dilute solution, and we have precipitated salt film, which would be soluble in water, or insoluble in water. And, in fact, we're not--this would be dry corrosion. It means the water will be absent.

So, now, one, if you will do the experiments, the experiments in some kind of periodic way, one to have wet conditions and another time you have the dry conditions, then we will be much more closer to a real situation.

But what will happen during this time when we have dry conditions on the metal surface? We will have for sure some interaction between salt and oxide film, and between salt and this outer layer of the film when we have hydroxides. So we will have the degradation of oxide film, and we will produce in fact oxide film. And it is also quite known from the experiments that oxide film is much more susceptible to corrosion without this hydroxide film.

So, in fact, we will have destabilization of the passive film. And when we have this situation, we will change the -- wet corrosion, when we have electrochemical corrosion, to these dry conditions, then we destabilize this film very much, and we will have, in fact, a result of this procedure will be that the corrosion rate will be probably much higher.

So, I think that it would be very useful to do these kind of experiments, it's much more real in thin film of solution, and taking into consideration that we can have this situation when we will not have on the metal surface water.

Now, I have some kind of remarks concerning the increase of corrosion after long time by vacancy and defect accumulations. So, there are two propositions that we can have vacancy accumulation, either in the metal phase, either on the interface on the metal, either in the passive layer. So everything would be fine, even if I will accept another model. It seems to me that these models do not apply to the situation when we are doing the experiments for this very long time of exposure, because during the aging, what we know from the short time, we have improvement of corrosion resistance, and not increasing of the corrosion resistance.

So it is difficult to accept that during the long time of aging, there is different mechanism than in the short time of aging. If it would be like this, we should have some kind of changing of mechanism that is going on in short term, and long term. You can, of course, find some mechanism which would be okay, or relevant or not relevant to what we have. For example, we can assume that after this short aging time, the film is much more perfect.

But at the same time, you will produce in the passive film, some stresses, stresses and cracks which destabilize the film, and you will return to this condition which you have during the short time of aging.

So there is also a proposition that you can have during the longer period, longer time, you can have selective dissolution of the alloys. Again, if we will assume that the same mechanism is varied for short times and long times, you should not have, of course, selective dissolution, because selective dissolution occurs only in initial times of passive film formation.

These are my remarks concerning the general corrosion during the longer period of times. And now I would like to say only a few words about localized corrosion, which I think that the repassivation potential for crevice and repassivation potential criterion for pitting are valid to determine whether localized corrosion will or will not occur. But, again, only when you have defined conditions. But when the conditions are changing, that you have destabilization of the oxide film, then of course you will not be able to use this kind of criteria.

So, that is all.

BULLEN: Thank you very much, Dr. Smialowska.

Our next presentation is Dr. Bertocci.

BERTOCCI: All the previous panelists have already presented, I think, all the possible mechanisms, and so forth. So I hope to do it in much less than the five minutes that I have.

The short answer for the first question, if I look at that report, which is the one that Professor Sagüés showed at the beginning, the short answer is no, I don't really see how it could corrode. One could even say that maybe the thickness will increase, since there is certain probability that the weight increases according to the data.

But I would like to stress a certain point. Maybe I'm flogging a dead horse. And it's radiation damage. This thing is sitting in a gamma field for a long time, and there is also a neutron field that comes about, and I'm not an expert, but I would wonder whether this will affect the behavior of the material. After all, it's a metastable alloy on the things, and who knows what happens. Maybe there is -- inhibition of corrosion, as somebody has found, in certain cases, but who knows.

This vapor is not important in any way, but it's the case where the nickel passivity, here we deal actually more with the chromium layer, but it's reduced by foreign element. Do the neutrons create enough impurities in a certain time to cause problems? This is what I would like to hear.

The second, also the short answer is no. But, again, one is worried about the radiolysis field. We have a gamma field for years and years, which would create hydrogen peroxide and nitrous oxide, and apparently there will be ventilation for a long time, so part of these products might be carried away, but where? They might end up in the rocks and come back 5000 years later as nitric acid, or something like that.

Probably this is a crazy idea, but I'd like to mention it. And I think the main point, in conclusion, is that I would like to see models describing the behavior of the passive film, rather than counting on some parts which have been kept in solution for years. And in a certain sense, Gustavo in the beginning, and of course Digby have addressed this point, so there is no point in continuing talking about that.

But from the reports that you find on Yucca Mountain, you don't find any other information, except weight losses and maybe a little bit of elementary electrochemistry. I mention some of the things that could be desirable. Impedance measurements, and Gustavo is doing that. Noise, just to make a little bit of noise. The kinetics of the redox reactions on the passive layer, transports, and so forth. And we have now specimens which have been sitting there for a year. Do they behave differently if you take them and you do the electrochemistry on them?

I mention here an example of Schultze's laboratory, in which they look at the gamma radiation on titanium, which is probably not relevant here, but it would be nice to see their work done on these materials.

Thank you.

BULLEN: Thank you very much, Dr. Bertocci.

Our next presenter is Dr. MacDougall.

MACDOUGALL: It's certainly difficult to be as brief as Ugo. I will try to be a little bit brief, if possible.

This alloy, Alloy 22, is one I haven't worked on at all. But I have worked on other systems that I think have relevance in fact. I think everybody here today has talked about the fact that it has a thin oxide film, which confers passivity, and you have to maintain that thin oxide film on the surface.

I have a little bit of a cartoon at the bottom there showing, in fact, a metal or alloy with a very thin oxide film and defects associated with that particular oxide film, breakdown of the oxide occurring at the defects, most probably some chemical dissolution, or something like that, and some repair mechanism, and the current efficiency for that depends on how much of this parallel metal or alloy dissolution reaction there is, in fact, going to be.

I've done a lot of work with nickel and iron over the years, and I want to say one of the things that probably troubles me about this particular system, although I certainly hear that Alloy 22 is an outstanding candidate, and one of the things that I think has to be looked at a bit for that, and this, again, just simply shows rather the cartoon of a very thin passive oxide film on some metal or alloy, a breakdown, and then chloride migration interfering with the repair, an attack and the pits developing on that particular surface. And most of us are, I think, aware of that sort of thing.

In the case of nickel and iron, I did a lot of work years ago with my own hands looking at chloride induced pitting of nickel after I pre-passivated the sample, added the chloride at a certain period of time, and found there was a certain induction time for pitting. And this is in chloride.

In fluoride solutions, different, I pre-passivated in a non-fluoride containing solution, and then I added fluoride at time zero, and the current behavior is absolutely different in fluoride containing solutions. The pH, the composition, I won't get into at the moment, but there is a slow gradual increase of a current. This is a depassivation which is occurring, and the chloride and fluoride were quite different in terms of their breakdown modes, depassivation modes, in fact, this thing leading to one or two pits on the surface, this thing leading to massive depassivation and a very, very rough surface.

What I found was, in fact, that the worst combination that you could have for the nickel and the iron--I investigated this in iron, too--was a combination of fluoride and chloride in solution. There seemed to be some sort of synergism between the two of them where the total was more than the sum of both parts.

I'm showing here again chloride. What I'm doing here is in the case of nickel, stepping the potential from some oxide free region into the passive region, and monitoring the response of the current with time. This is in a sulfate solution, a background solution.

Chloride, you have an increase in the charge because the chloride competitively absorbs, interferes with passivation in the short term. Bromide is here also. Fluoride doesn't give that much of an interference initially in terms of the charge. But what fluoride is able to do is it interferes longer term. The current will not fall by this time, in point of fact, the seconds here, I guess, or whatever it is. The current, in the case of chloride and bromide, would have been down here if pitting had not in fact occurred.

So, the fluoride incorporation into the passive oxide film, I measured the amounts of fluoride I was getting in my NiO films. They could be as much as 15 and 20 percent in those films. Chloride, I never got those amounts. I got 2 to 3 percent.

Reasons for that complexation, but also the F-minus anion, in fact, has a radius which is comparable to that, an ionic radius of 02 minus at 1.3 angstroms. Chloride is, Cl minus is 1.8 angstroms. So you could get that. So what you have is in a case of a system where you have both fluoride and chloride simultaneously in the solution, you have the worst of all worlds. You have the short-term interference and long-term. If you could possibly do things in the short-term, the fluoride was still there to cause, in fact, the interference, and held that thing up so the chloride had a lot longer to work its nasty business.

And when we used to have people visiting from time to time, we would have senior officials come by, and if I wanted to pit a sample in a swiss cheese mode, it would be nickel and iron, not Alloy 22, obviously, but it would be in that particular concoction, that particular solution, a combined solution of chloride and fluoride.

So, I think it's very important for the people who are doing these experiments with the Alloy 22, which may indeed be resistant to many of these things, to work in solutions which contain simultaneously the fluoride and the chloride.

The question, and I'm not going to go into all the parts of this question number two, which I tried to address, in fact, but I would just concentrate on this part here, which is one of the complexation, the ability, and I'm using cyanide--thank God there's no cyanide in this particular system--but this is a very, very famous cathodic reaction, and I think that most of us know it, in fact. We may have forgotten it. And it's the stability complexes of the ferree (sic) versus the ferro cyanide.

And you can see by complexing with cyanide, you move the potential something like 400 millivolts, in fact, in the wrong direction in this particular system. You made iron dissolution that much easier, so you don't have to change the open circuit potential. In fact, in a case like that, the driving force has gone up for that particular reaction, the anodic iron dissolution reaction, by an amount of 400 millivolts. And, in fact, we have lots of complexing ions in this particular system, so that's something that should be taken into consideration.

And I would finish off by saying just there was a question asked about was there a result that you ever obtained which was a bit shocking, unexpected, or something like that. And I guess the biggest one that I had was quite a few years ago when I did work with nickel, and I was looking at pitting of nickel in chloride containing solutions, no fluoride, here just chloride. And I was measuring the induction times, and I pre-passivated a sample and then I looked at different potentials, and really what one has is a critical pitting potential range, I suppose, with sort of an exponential increase of the induction time. Obviously, as you go to more anodic potentials, the pitting is going to occur more and more rapidly.

This was the one done in a standard mode, pre-passivating in a non-chloride containing solution. This was the one where I pre-passivated in a chloride containing solution. I notice chloride in the film. It didn't pit, but I got chloride in the passive oxide film. And the trouble was this particular curve should have been down here, obviously, if all of the theories were correct, because chloride is a precursor to pit initiation. And because I obtained this result, I had to do literally hundreds and hundreds and hundreds of experiments, because people in the lab did not believe it, and it kept on coming up this way.

I think I have the explanation for it. I think I have one. I know others have others. But that result is true. So we have shifted the pitting potential range to more anoded values, making it more difficult for the nickel to pit, by incorporating chloride into that passive film before we did the pitting experiment. It was done in a sequence or series of steps there. And, as I say, if this result had been down here, it would have been a nice easy simple sort of experiment.

So, there can be times when you predict something and you're certain that chloride is a precursor, and maybe in some state it is a precursor to pit initiation. In this case here, the chloride in the film made the nickel metal more resistant to pit initiation.

I'd just like to emphasize again that I think it's extremely important, in fact, that one do these experiments in combined solutions, so the amounts of fluoride you have in those solutions is not small, the amounts of chloride is not small in those dried, evaporated modes. And in the case of nickel, I could get pitting with 100 or 1000 times less chloride/fluoride than what we have here. Of course, Alloy 22 is going to be a lot more resistant, but then one has an awful lot more time to do these things.

BULLEN: Thank you, Dr. MacDougall. Do you have a question, Gustavo?

CRAGNOLINO: Yes. The purpose of clarification of that plot, when you pre-passivate in a chloride containment solution, this will then have a potential obviously lower than 50 millivolts.

MACDOUGALL: Yes.

CRAGNOLINO: I mean, as you age the film, even in the presence of chlorides, but in a regime in which pitting cannot be induced.

MACDOUGALL: Cannot be induced. That's right. That's right. If there was any pitting, it would simply be null and void, and the result wouldn't be worth commenting on.

BULLEN: Next is Professor Shibata.

SHIBATA: When I received this agenda, I'm finding the premise that fundamental knowledge suggests that the passive layer on such material is thermodynamically stable. So, I think that this system is thermodynamically not stable. So, I think increasing the long term passive dissolution of alloy seems not to be expected, but still no definite evidence exists because this system is thermodynamically a very open system and there is a free exchange of matter and energy. Then, the system is not at equilibrium.

There are many explanations already presented. So, I'd just like to point out one factor. The alloy and the environment system is a very complicated, large component system which is difficult to reach a simple equilibrium state. An important point is the selective dissolution or selective enrichment of a specific element. And, Roger Newman said that the main point of this passive term is chromium oxide is a main player. So, I'd like to know about this process. Selective enrichment of chromium is very important, I think.

Unfortunately, we know the very short time enrichment process and we know the exact analysis over such kind of enrichment process, but know it's a long time or a long time exposure and its (inaudible) density is known. So, the compositional change will continue for a long time. So, we like to get definite evidence for this change.

Unfortunately, you know, the natural analog studies are done on the carbon steel and copper alloys, but still do not exist for the stainless steel. So, I hope the long term selective enrichment evidence will be accumulated.

So, I'd like to focus on the localized corrosion. In the document, I stated this condition is deciding the localized corrosion occurrence. So, it is well-accepted that the possibility of the initiation and development of a local corrosion could be judged by just comparing the open circuit potential with the critical potential here. But, of course, the open circuit potential is quite easy to measure. But, standardized method has have been known for measuring critical potential of pitting. But, still many discussions on the definition of the initiation and repassivation of crevice are discussed in the Report. In Japan, the same situation existed through 1980 to '90. But, this year, a method proposed by Professor Tsujikawa is standardized in Japanese Industry Standard.

This method for measuring the critical potential for repassivation of crevice is standardized in Japanese Industry Standard. The basic concept of this method is specimen with crevice former is used and preliminary existence of the crevice produced by the constant anodic current is necessary to measure or define the crevice repassivation potential.

The critical potential for stopping the growth of a crevice, we call this one $E_{R,CRV}$ and it was decided by the potentiostatically step down method. The anodic current decreases at the constant potential after step down and again increases if the potential is over $E_{R,CRV}$. When the potential is equal to $E_{R,CRV}$, the anodic current stops to increase. So, we can easily define $E_{R,CRV}$.

Here is a specimen with crevice former. We have some crevice here. The main point is that initially we increase the potential by potentiodynamic method, and if the current leads to the 200 microamperes, we kept it constant at the galvanic constant techniques. So, this corresponding to the potential decrease back here. After enough crevice is formed, the potentiostatically step down here just 10mV. So, if you measure the anodic current, anodic current decreases fast and again increases because this crevice is active. So, the anodic current increases. At this point, we again step down potentiostatically so the anodic current decreases, again increasing if this crevice is active. This process is repeated. Several step changes, the current decreases, and no increase is observed here. So, we can decide the $E_{R,CRV}$

potential here. This procedure precisely decided the crevice repassivation potential for the crevice. And, also, the method that is required to confirm the existence of 40 micrometer depth crevice after the measurement.

When we use this kind of method, we can decide the $E_{R,CRV}$. This is the dependent of the other function of chloride concentration. If you use the potentiodynamic method, you can decide such kind of crevice potential. But, this kind of crevice potential is much lower here. But, if you use the potentiostatic step down method or long time step down method, we can decide, like this one. But, if you use the higher speed of potential, a much lower value is obtained.

So, the criterion use that--if the natural corrosion open such potential here, then lower concentration can be a load for this kind of initiation or stopping the growth here. But, if the natural corrosion potential around here are much higher chloride concentration is allowed. So, this is a very good criterion.

But, why such method is not the standardized in our business--? Because industry people they just use such kind of idea because this barrier is so much severe, so ordinary stainless steels--like 304, 316 cannot be used if this kind of criterion used in the ordinary environment. But, a designer or a user still can safely use this kind of material, even if the $E_{R,CRV}$ is much lower, because the designer avoid to make a crevice condition and a user, of course, usually cleaning and avoids a crevice formation. So, in that case, we can use even with such kind of conditions.

So, I think that this $E_{R,CRV}$ measurement value is very suitable for the long time protection of the crevice formation for this kind of material. I don't know that Alloy-22 can be measured by this kind of method. But, this is a very-- a reproducible result can be obtained. And, also, this procedure can be the program by using the computer. So, this is a very good method to decide the $E_{R,CRV}$.

I'd like to add some comment to the distribution of natural corrosion potential or on the also critical potential. Of course, the natural corrosion potential, also distribution like this one, and the $E_{critical}$ is also distribution. This area can be pitting or crevice possible here. So, this is very important to decide what kind of distribution function can be observed for this alloy in the environment of a combination.

And, the probability density function of pitting potential, the experimental data on this pdf, many data is accumulated. And, normal distribution is observed for pitting potential. A general trend is observed at the higher pitting potential and seems to show a wider scattering, but, of course, some exception exists. Of course, just depending on the material, environment, or combination. But, the general trend, the higher pitting potential seems to show wider scattering. So, this material, Alloy-22, is a very high (inaudible) material. So, I think such kind of behavior will be expected.

And then, how the $E_{R,CRV}$--the probability density function, not so many data is accumulated of this $E_{R,CRV}$. But, normal distribution can be fitted for also. A more narrow distribution is observed for $E_{R,CRV}$ than pitting potential. This is possibly caused by the measuring method itself because a slower stepping method is used.

So, now I conclude that increasing the long term passive dissolution of alloy seems not to be certain, but still no definite thinking has existed. Changing the composition of the passive film including the subsurface due to selective enrichment should be clarified.

And, criterion of this condition can be used for assessment of possibility of localized corrosion. More discussion is required to deciding the critical potential for crevice corrosion.

We propose that the method which was proposed by Tsujikawa will provide a reliable and a confidential critical potential, $E_{R,CRV}$, for the repassivation of the crevice which was produced before the measurement. So, information about probability density function of $E_{R,CRV}$ should be accumulated.

Thank you.

BULLEN: Thank you, Dr. Shibata.

Could we move on to Dr. Sato now? I'm going to take some chair's prerogative and we're going to go through all the presentations before lunch. So, we hope to finish and we will give you an hour and 15 minutes for lunch. It just might be in about 20 minutes from now.

SATO: Thank you. Well, because of the short time, I would like to focus our attention on the open circuit potential, particularly. During long-term storage, it may happen for some reason that semiconducting oxides are formed and brought into contact with the alloy surfaces. The open circuit potential of the alloy depends not only on the aqueous environment, but also the semiconducting oxide present on the alloy surface. Here, two pieces of solid electrode. One is a metal and the other is the oxide. An isolated metal electrode sets its electrode potential at the so-called corrosion potential while the oxide electrode stands at its-- flat band potential. If you get in contact these two electrodes, then the mixed electrode potential come to somewhere between the corrosion potential and the flat band potential. And, when the oxide is excited by radiation or photo illumination, so that you have quite a concentration of excited holes and electrons, then the mixed electrode potential usually come to very close to the flat band potential.

Under illumination, as you see here, semiconducting oxide in contact with metal surface affects the open circuit potential of the metal. The oxide potential comes across to the flat band potential reaching usually more positive in the case of p-type oxide or n-type oxide. In the case of n-type oxide, the flat band potential is more negative than the potential of the passive metals. The oxide metal mixed electrode potential thereby shifts the potential in the positive direction. In the case of p-type oxide, while n-type oxide shifts the open circuit potential in the negative direction.

Here is the electronic level diagram for metal and p-type oxides. When being excited by radiation, in particular, p-type oxides may elevate the electrode potential. It opens up the potential (open circuit potential of the passive metals). And it may happen the electrode potential gets up to the point more than the passivity breakdown potential. We have two kinds of critical passivity breakdown potential. One is for pitting initiation potential and the other is the crevice corrosion. Usually, the pitting initiation potential is more anodic, more positive, than the crevice prediction potential. So that crevice corrosion really is more likely to occur when the electrode potential is going up.

Here is the schematic representation. When you have no oxide on the passive metal surface, your electrode potential is rather narrative. But, if you have p-type oxide on the metal surface, the electrode potential is going up then. If the electrode potential becomes beyond the certain critical potential, you have passivity breakdown. And, here, the localized type of corrosion occurs.

In addition, under the illumination, the excited electrons in the conduction bundle of the oxide are now incapable of reducing water molecule to produce hydrogen on the oxide surfaces. So that you have hydrogen evolution, cathodic hydrogen evolution, taking place on the metal electrodes which can be coupled with the anodic metal dissolution at the passivity breakdown sites. Therefore, you have a local corrosion cell, anodic metal dissolution, coupled with the cathodic hydrogen evolution on the oxide surface. So, it means this type of local corrosion is taking place even in the absence of oxygen. Of course, in the presence of oxygen, the local dissolution current is very much faster.

In the case of n-type oxide, you have the situation exactly the reverse to the case of p-type oxides. The n-type oxides shifts the open circuit potential in the cathodic direction. If your electrode potential gets down below the hydrogen electrode potential, then you have a higher evolution on the metal side, on the metal surfaces.

In addition, on the n-type oxides, excited holes in the valence band of the oxide are now capable of oxidizing the water molecule to produce oxygen gas on the n-type oxide surfaces. So, this oxygen evolution may be coupled with the hydrogen evolution on the metal side. So, you have oxygen, hydrogen, local cell, oxygen evolution on the oxide surface and the hydrogen evolution on the metal side. This type of local cell gives us a possibility of hydrogen damage in the metal electrodes.

This gives us the conclusion, p-type oxide may cause the passivity breakdown leading to a localized mode of corrosion. N-type oxide inhibits the passivity breakdown though increasing the probability of hydrogen damage. In order to prevent the p-type oxide induced passivity breakdown, the coating of n-type oxide layers on the metal surface will be effective.

Now, the suggestion I have made in this

presentation is based only on the thermodynamic estimation at the present time, but any direct experimental evidence except that n-type titanium oxide was found to inhibit the metallic corrosion in a number of cases.

Thank you.

BULLEN: Thank you very much, Dr. Sato.

I have a little apology to the audience, but we're going to finish with Dr. Pickering's presentation. His transparencies are being duplicated as we speak, but he does have a duplicate of his conclusion slide. So, he has agreed to go ahead and speak before lunch and we'll give him the option of first refusal after lunch if he wants to follow up on his presentation.

Dr. Pickering?

PICKERING: Well, I have this duplicate of kind of a summary outline, so to speak. And, what I will focus on is the crevice corrosion, #2, here; crevice corrosion rather than passive film breakdown and pitting which you've heard a good bit about already. I'll look at two things that I think are questions I would want to know about Alloy-22. And, mind you, these are now questions that pertain to the conditions inside the crevice, not the conditions outside the crevice that we've been talking about. I'd like to know, too, what the repassivation potential is, but I'm with the understanding of what the repassivation potential is, but right now, I'm going to talk about the conditions that we've measured and so forth inside the crevice and how they lead to criterions to susceptibility of a particular crevice in a particular metal electrode system.

And, there are two things that I want to say then about that, as far as characterizations, that I would want to know about. The potential distribution on the crevice wall, that is the electropotential, how it varies and how big the variation is as you go into the crevice? That's this on the left here. The potential is here at the outer surface. It could be applied potential or the actual corrosion potential. Then, as you go into the crevice in this direction, you find that the potential goes negative. And, the question is how much of the polarization curve do you have on the crevice wall? That depends on how big the IR drop is that is generated by the current from the inside of the crevice flowing through the electrolyte to the outside cathodic site or to a counter electrode if you're using a polarization technique. So, that's one question. How big is this potential drop under passive conditions on Alloy-22 in a given size crevice?

Okay. And, the other question is that alone will not produce crevice corrosion, but if you add the second condition, does the possibility exist that the passive condition shown here at times zero, just a straight passive, whatever it is for Alloy-22--10 to minus 8 amps per square centimeter, I've been told and we heard about that this morning, too--does the possibility exist as stagnation occurs in the crevice for an active peak to form at the lower potential region? And, if it does, then we know from those studies now--I don't have these documentations with me, but maybe this afternoon, I'll have them--that that peak can grow in some other systems like nickel and stainless steel, that peak can grow with time if the right buildup of concentration in the crevice occurs. And, when it reaches this criteria here where the IR drop is greater than this defined quantity right here of the voltage drop between the applied potential or the corrosion potential at the outer surface and the passivation--what I call the passivation potential, reactive passive potential of the system, that's when then crevice corrosion would start and that would be at the end of the induction period. That is a little bit beyond what we've done experimentally, this last statement about, but we have seen passive films grow in crevices, get larger, and kick off the crevice corrosion process.

So, as a result of criteria that evolves out of that--and this is essentially the criteria--the IR drop generated in the crevice, be it due to a passive condition or an active peak already in the system, we've studied mostly the active passive alloy electrolyte systems and we are starting now to study these (inaudible) passive systems, as well, like Alloy-22 is. But, that's for later.

Now, the next point to comment on is how big can this IR be in, say, Alloy-22? There are two factors I want to point out as I see are important. There are several factors that go into how big this IR drop is. I won't mention them all, but the one I want to comment on here is what's the size of the opening? And, we know we have to have a tight crevice to get crevice corrosion in all these corrosion-resistant alloys. So, that size opening, the generality is that the tighter it is, the bigger the IR drop will be. And so, how big can it be?

Well, these are two factors here that I would bring up. You certainly have the situation where one surface might be very smooth, but the other surface forming the crevice is rough. And so, the roughness determines the average opening of that crevice. The other case--and a big question for Alloy-22--is does hydrogen evolution occur inside the crevice because, if it does, then you form hydrogen bubbles. And, a bubble has the unique property, of course, of filling the space. So, now, we ask, well, what's the space between the bubble and the wall? Of course, you might say is it molecular dimensions? So, you what you can have actually when you have crevice--and we've seen this and I'll you some later this afternoon maybe. When we have relatively large openings, we still end up with a gap opening between the bubble and the wall which is very small and we can't measure conditions in there. But, we see crevice corrosion occurring in the center of the bubble on that passive wall.

So, that's where I'll stop and, as I say, we can kind of show you examples of all three of these things; of potential drop here; of the buildup with time as the acidification occurs or whatever; and, also, a lot of gas bubbles forming in, say, stainless less, not so many in nickel. That's interesting, isn't it, from a point of view of Alloy-22.

BULLEN: Thank you, Dr. Pickering. I guess we did find out how to limit the speakers to five minutes. We just take away their slides and it will get done.

Right now, I would like to recess the meeting for an hour and 15 minutes. We will reconvene at 2:00 o'clock and Dr. Pickering has first right of refusal.

Thank you very much.

(Whereupon, a luncheon recess was taken.)

AFTERNOON SESSION

BULLEN: We are going to digress a little bit from the written agenda. We have had one of our distinguished materials scientists who is interested was interested in making a comment, but cannot stay until the 5 o'clock hour. And, as such, we're going to allow him the microphone.

So Roger Staehle, who is working his way to the front of the room, would like to make a few comments for the benefit of the workshop panel. And, with that, I give you Roger. Keep it to less than three hours. Is that okay, Roger? How about ten minutes, just like everybody else?

Thank you, Roger.

STAEHLE: That's pretty restrictive. This will just take about five minutes.

I first discussed this meeting with Alberto maybe a month or two ago when he had suggested the idea of bringing a group together to look very carefully and thoughtfully at what innovative ideas there might be in developing loss of passive films. And my concern then is more now that one of the things we know about passivity is that it's very environmentally dependent, and so what the passivity is in a lead solution isn't the same as passivity in a sulfur solution, is not the same passivity, and so on and so on.

And zirconium, which is very good in some environments, when you add fluorine to it, it's not. And so the first point I want to make is that the passivity, the protective quality of the film is very environmentally dependent, which is something most of you know certainly.

But the second point I want to make is that the chemical situation on the metal surface is an absolutely unbounded chemical situation. And what you have to realize here is that the unboundability is related to the fact that you have a super-heated surface. And in nuclear steam generators, the super-heat, even in a very controlled bulk environment, produces environments locally which are virtually unboundable. And that's for a very controlled external environment.

Now, in this situation where the external environment is not controlled, but we don't know what's going to drip out of the mountain, except some part of the periodic table, and where we don't know what the composition of the deposits is on the fractures, which is quite different from the average composition, that means that the chemical composition on the surface will be an absolutely unbounded condition. And, so to make a prediction based on an unbounded environment is an impossible problem.

Now, the third point I want to make is that virtually all the work that has been done so far has been done in the general range less than 100 degrees Centigrade, like 95 Centigrade, or thereabouts. I think it was mentioned this morning possibly looking at 160 centigrade on the surface.

But let me back off a little bit and say that a lot of the low temperatures that people are thinking about today is based on the assumption that ventilation will be used. In fact, I think the assumption that ventilation is going to be used may be a very bad assumption, because the idea of ventilation means that if there's a leak, it will spread whatever the leak is around the countryside, and the chance of anybody putting up with spreading the results of a leak around the countryside I think is zero.

And so I think the possibility of using ventilation for a variety of reasons, not the least of which is lowering the temperature and lowering the humidity, is a very strained assumption. Therefore, the surface temperature will be at least 160 centigrade, and more, and that means the super-heat in the concentration process, and the environments that are there will be soupy saturated--this is soupy, not super--soupy saturated environments of undefined compositions. And, therefore, to conduct experiments in that kind of environment, or in something like that, seems to me a very difficult challenge.

And then on top of that, in this 160 centigrade plus range, the concept of modes of corrosion changes. Up to this point, as Gustavo mentioned this morning, and others have, that they're primarily thinking about pitting. In fact, in this range, I don't think pitting is an issue. I think we're looking at either major generalized corrosion, or extensive stress corrosion cracking. And I think the stresses will come from a lot of places. I think the idea that they can be eliminated or lowered is just a fantasy.

So, those are my concerns about making predictions, and sort of from the perspective of thinking about passivity, it seems to me the central question in making predictions is not to detail passivity, but rather how do we come to grips with an unboundable environment.

BULLEN: Thank you, Dr. Staehle.

Actually, before you leave, I have a question for you. One of the issues that the Board has raised is that cooler and drier and simpler might be better. Not regarding ventilation as the mechanism that you get cooler, would you agree that a cooler repository would be better or maybe easier to bound or to calculate?

STAEHLE: Well, I'd have to separate this question, because cooler and drier is better. But the question is whether cooler and drier is achievable.

BULLEN: Okay. Well, actually, let's start with the first part. If it is achievable, is it better?

STAEHLE: Well, any time you can lower the temperature, and the corrosion process in general, that's a good thing. So that's a good step. And if you can make it very dry and cool, that's a good thing.

BULLEN: But the concern is not to be able--if it gets cool, it may not be dry, is the comment you're going to follow up with?

STAEHLE: Well, you know, I have a hard time understanding how a person could achieve coolness in a situation where you have a super-heated possibility, because what's going to happen is you will very quickly start putting dust on the surface, and that dust will create an insulating layer, which will immediately lead you to a super-heated condition. And I was in that tunnel a couple months ago, and just my note pad ended up with a bunch of dust on the top of it, a couple microns of dust probably. So I think that the conceptual framework which is interesting has to be very carefully thought out in terms of whether it's achievable.

BULLEN: Thank you, Roger.

As Chairman's prerogative, I'm going to give, maybe with a little trepidation, Professor Pickering the opportunity to do an encore presentation, which he tells me is not 50 minutes. So we will let him have his viewgraphs and present--how about ten, is that okay? Ten minutes?

PICKERING: I could easily do it in ten. Okay, so I'll build on this dust, and consider those dust particles the start of a crevice, because I don't think there will be crevices deliberately built into the system.

So, if we have crevices, then just to illustrate quickly three things that I mentioned earlier, the distribution of the electropotential along the wall of the crevice, and if it falls--this is for the bigger peak I showed you here. If it's a smaller peak that you're dealing with, then this would be much more gradual, and it won't fall below the passivation potential and, ergo, you don't get crevice corrosion until that peak gets bigger to this point.

So, this line here is for the--by the way, the viewgraphs are a little bit--or your hard copy is a little bit mixed up. But the top viewgraph goes at the bottom. I'll get to that last, and they're mostly in order after that.

Okay, then I'll show you this process taking place, and I'll show you the effects of this gas, and then I'll make a calculation to see how big the IR drop is.

Here you have the results, and this is typical now. These are stainless steel actually in an acid chloride solution, which is a spontaneously active system, meaning it has an active and a passive region. And you can see at the beginning here, in both cases at the time, this is different times here, the profile of the potential distribution going into the crevice here is steeper as time goes on, because the current, you measure the current increasing. So the crevicing current is going up, so the IR drop per unit is going up. So at the end of the experiment here, the red curve, you can see the position.

Now, here's the active/passive transition measured on the crevice wall, the potential, and that means that the position of the passive region is going to be closer to the opening than that, and the position of the active region on that crevice wall is to your right of that, and the biggest penetration, corrosion penetration, is going to be where the peak currents are, which would be right to the right of this 3 millimeters.

We obtain these data by simply putting a microprobe into a relatively open crevice of .1 or .2 millimeters, which you can do for this duplex stainless. Here's just an example then of afterwards, a cross-section, and you can see that 3 millimeters down is where you get the attack. Okay? Just as you would expect, and as are indicated from the potential measurements.

Well, if we didn't have a lot of chloride in there, we'd have an all passive condition, like we do in Alloy 22. This is just sulfuric acid of two concentrations, A and B, and you can see there's no active peak whatsoever. It's a spontaneously passive system. If you add the chloride to the system, then you get the buildup of the passive peak, and the A curve is the lowest chloride concentration, the next highest, and finally the one that we used there to get the data I just showed you.

Now, when you use this active/passive situation with this chloride concentration, you get instantaneous crevice corrosion as soon as you polarize into the passive region for the conditions we used there, because that IR drop was larger right from time zero than the delta phi star value I showed you earlier is a criterion.

So that's the sort of thing with the buildup then. After you have the potential drop, you need to get the active peak to form. And you need to now also know how to measure the chloride concentration in the cavity. I'll just show you these data. These are the only data, and I'm just pointing out the blue curve here, because the red curve is actually the potential distribution as measured for now. This is iron in a pH 5 solution. It's an active/passive system. But the blue curve is--and these are the only data of the blue curve that are not--they're our new data and I didn't even want to present them on hard copy because I don't know if they're right. You know, they've haven't been reproduced.

But it looks like they're going to have a peak chloride concentration an order of magnitude higher--these numbers have to be reproduced also--an order of magnitude higher than the region where the metal dissolution rate is the highest. That's where the X pass position is, and the active peak is right here. And so you're seeing that the measured, using again a microprobe now for chloride going into the crevice, it's maximized there and it falls off to some value that's just a little bit higher than the bulk solution of 2 millimolar concentration.

Now, here is some data--all the rest of this data, this appeared ten years ago on the Electrochemistry Society, and it just shows now a passive situation where it has a small active peak in this system. It's iron in the pH 10 solution. A small active peak, but the IR drop wasn't big enough to push the electropotential down into the peak. So you didn't see anything but a passive current at time equals zero, and it's about 10 to the minus 6 amps per square centimeter here read on this axis here. We have it in milliamps here, so it's 10 to the minus 3 on milliamps. But 10 to the minus 6, and for this relatively open crevice, the IR drop is pretty small. Like I said before, you have to have a tight--or if you tighten the crevice up, the IR gets much bigger for the given current that's flowing.

And so the applied potential was this dash line, 200 millivolts on this scale, and the measured potential halfway into the crevice now, that's what we're measuring on this axis, is only 25 millivolts below the outer surface potential. But notice what happens with time. Up to 14 hours, the passive current is gradually increasing, and of course then the IR drop is increasing, and you'll see the measured current halfway in coming down.

At about 14 hours, suddenly, the current increases quite steeply, and we're getting up into the milliamp current range now, or the actual crevice corrosion. The potential drops way low. I didn't show you where the passive age potential is. It's right in here somewhere. It drops way below into the--below that boundary into the active peak region. And, of course, you have stable crevice corrosion indicated by the potential, and indicated by these high currents. So, there it took 14 hours to do that, and the reason for that we don't know, because we didn't have the chloride and pH that we do now, so we don't know what was causing the passive current here to increase with time. It might had been a pH decrease, or something of that sort.

And then the gas bubbles is the third item I told you I'd show you about. Here's a gas bubble, hydrogen gas bubble, formed in an iron crevice wall. By the way, we're looking through transparent plexiglass. And while we're doing these in situ probe measurements, we also monitor the appearance of the crevice surface with some necrolenses and a camera, and so forth. And then in this case, the wall was all passive in this region, but there was a hydrogen gas bubble that had formed there and lodged in place.

And knowledge you have after some time is very strong crevice corrosion at the middle part of the bubble. What you see here is grain boundary effect, which we also saw on the polarization curve when we did experiments at different potentials, getting close to the active peak. And here you see it blown up. You can see as you go in, you get slight intergranular effect. As the potential drops closer to the active peak, you get heavier intergranular effect, and then you have a boundary here where now you're in the active peak and you get an attrition.

So, that's the importance of the bubble, and that's why, you know, we would like to know whether hydrogen gas bubbles can form. Dynamically, they can form of course in any base metal, so also in C-22. We don't know, though, whether they form in there.

And the final question was how big of an IR might you get if you had really a low passive current, like C-22 has, and so I just made--I tried to make a calculation here using numbers we knew about. This is for one of our nickel systems. We had a pH 2 solution which was saturated with nickel sulfate in the crevice. And that has a measured resistivity of 23 ohms per centimeter, which is not a real high resistivity. You can get much higher resistivities in solutions that are more dilute, and so forth.

And we then had the relationship, a simple relationship where the IR drop, or the delta phi here to the bottom of the crevice, going from here to the bottom, is going to be just the average current flowing out of the crevice--I assume the average current. I assume the current was linear going, with increasing depth in, just to make a calculation, we're seeing results of the average value, and multiply that by the resistivity, times the depth, L, which we assume to be just 1 centimeter, and the cross-sectional area here of the opening, and that's A times W, divided by A times W, and you see that here.

So, that's just IR, of course, where R is L over AW. And so now we assume that 10 to the minus 8 amps per square centimeter of passive current on that wall, and there we chose not molecular dimensions. If we had gas in there, I don't know how big the crevice would be, but it wouldn't be very big. We took an order of magnitude higher than that, 10 to the minus 6 centimeters, and we end up calculating, if you plug the numbers in then into this equation right here, you end up calculating 230 millivolts, so a sizeable potential drop. You can't really rule it out just because you have 10 to the minus 8 amps per square centimeter.

So, I'll stop there.

BULLEN: Thank you, Dr. Pickering.

PICKERING: You're welcome.

BULLEN: Actually, I'm going to ask Professor Sagüés if he's going to help me out.

In your presentation this morning, you had a viewgraph of the first question. Could you dig that out?

SAGÜÉS: I don't have it. I have a summary of the question.

BULLEN: The summary is fine. I just wanted a talking point to put up there. And then as we dictate the procedure for the roundtable discussion that's going to occur this afternoon, I thought maybe we could start off by just asking each individual as we go around the table to make a few comments about what they've heard, what they haven't heard, but specific to question one. And I was trying to decide which side of the table to start with, and Dr. Davenport on the way in said she'd solved all the problems over lunch. So, obviously, we have to start over there, but I can't start with her, because she's not in the first position.

So, Dr. Kruger, because Dr. Davenport has already solved these problems, gets to actually take the first shot at question number one, which essentially deals with mechanisms--well, let me read the question specifically from the handout.

Question one basically states that can you propose any plausible mechanisms that would cause a long-term corrosion rate to increase once penetration under passive conditions reaches significant values, so that sustained corrosion rates may be no longer uniform, extend sort of greater than a micrometer per year?

And so specifically to that, we'd like to ask you to just say a few sentences, maybe a few words about what you learned this morning, if you think there are mechanisms that exist, if so, what? If you don't think they exist, that's fine, too.

So, we'll start with Dr. Kruger and just work our way around the table. That's a good way to start.

KRUGER: Well, since Alison has already solved all these problems--

BULLEN: That never seemed to stop you before, though.

KRUGER: Right, and it won't this time. But I was tempted.

Well, I think the thing that I heard, not this morning, but this afternoon, the things that Roger Staehle said is to me the most significant thing that you can say about question one. And that is that under the conditions that exist, you would really expect an increase in the passive current. Plus the fact that, and a number of people mentioned this, if the potential goes to the transpassive region, you dissolve a lot of the constituents of the passive film creating an unstable condition, and a large increase in the passive current density.

So, I'm not as sanguine as I was when I first came here that at least from a uniform corrosion standpoint, we really wouldn't expect any problems. I think we could expect some serious problems.

BULLEN: Bullen, Board. Actually, I'll follow up with the same kind of question that I asked Roger with respect to temperature dependencies of what you see, if you stayed away from the 160 degrees C. temperature regime, for example, would you find more confidence or less confidence in your expected performance for the long-term stability of the passive film?

KRUGER: You mean you were able to keep the temperature below 160?

BULLEN: Yes. Well, we saw two curves this morning that one was like kind of 80 degrees, 90 degrees C. maximum temperature. Do you have a little more confidence in that?

KRUGER: Yes, you would. But even under those circumstances, with the environment changing in very many possible ways, even at the lower temperatures, you could expect especially localized corrosion problems to exist even at those lower temperatures, which we have little experience with as well.

BULLEN: Thank you. Any other comments you'd like to make, or do you want to pass the baton to Alison next to you? You yield your three minutes?

KRUGER: Yes, I yield my three minutes to the lady from Birmingham.

BULLEN: Dr. Davenport?

DAVENPORT: I had a very interesting conversation with Gustavo Cragnolino over lunch, and this very much reinforced my view of the importance of metallurgical features, and in particular, what can happen along weld lines with thousands of meters of weld. It's not inconceivable that some of it may not be done perhaps as well as it could be, things may go wrong with the heat treatment somewhere, and I'm very much convinced that that is the most likely source of problems in terms of both local increase in passive behavior, and also in the risk of localized corrosion. But I think Gustavo can probably give more details about what the particular problems might be around welds. But I'm very firmly convinced that that's quite important.

Another couple of things following up on that that come to mind, and that is when people are doing measurements on pitting corrosion, any kind of measurements, and you have a hundred results and you look at the range, the spread, including some negative corrosion rates, or whatever that appears to be on that, I think the interesting ones are the outlyers where there are particularly high corrosion rates. And this again follows up with my interest in metallurgical features. When there are outlyers, is it worth taking a much more careful forensic look at the ones that seem to have corroded particularly strongly? Are there some features in the alloy, common or less common faults or defects or impurities in the alloy that can give sites where there's localized attack?

Again, we come to a size issue, and is a corrosion coupon of very limited size a very good analog for the canister itself? Metallurgically, they receive very different treatments. And also you're sampling a much larger area, and so rare defects can then come on and become a problem. So those are the features that I think have struck me going through today's proceedings, including lunch.

BULLEN: Bullen, Board. I actually had a couple of follow on questions that I had written down during the course of your presentation.

You mentioned that, you know, as a metallurgist and as a corrosion scientist, you try to prepare those perfect surfaces of single crystals, and then understand the fundamental mechanisms. How difficult do you perceive the ability to model the heterogeneities, to model the real world, to model the defects that you'd expect to see? And is it a realistic assertion that that can be done? Or is it an intractable type problem?

DAVENPORT: I'm not quite sure what you mean by model. I mean, I would say that the first thing to do is to actually have a look at the failures and see if we can identify particular problems. I mean, we're all very well familiar with the fact that pits in stainless steel initiate in manganese sulfide inclusions, but we don't have the same sort of common knowledge that, oh, failures always initiate at whatever kind of a particular in this particular case. So, I think a bit of forensics is needed first if we can go on to model anything.

I must say the other thing that very much struck me was actually in Bob Rapp's presentation when he talked about the importance of surface finish. And, again, the idea of electropolishing all these canisters is quite an interesting but probably rather impractical one. But there's an enormous effect of surface finish on corrosion behavior, because if you have a very rough machined surface, you've got deformed layers and bits where the metal is folded over on itself, and you've got automatic little crevices on the surface, not just with dust as well, so I think that's a very important feature, too.

BULLEN: Thank you. Actually, my emphasis in modelling stems from the fact that I'm a performance assessment modeler, so I was thinking extrapolation beyond 10,000 years and how well you do it, not the lab scale models, although those are the fundamental mechanistic models that we'd like to understand.

Anyway, thank you very much. You had a good intro for Dr. Rapp. Dr. Rapp, would you like to say a few words? Or do you just want to say ditto?

RAPP: It's a lot more complicated than that. This matter of surface finish I do think is important, and I don't know why these canisters can't be polished up before they are loaded up, you know. They don't--loading them up shouldn't make that much difference to the surface finish. So I think it could be done. I don't know why not.

KRUGER: They don't have to be electropolished. There's chemical polish.

RAPP: Chemical polish. And, in fact, I think you could dope up the surface with some cerium while you're at it. An anodic oxide on the surface with a little cerium doped in would be a nice idea.

Other than that, it seems to me like the most dangerous part of this service is the deposition and drying, and deposition--wetting and drying, and wetting a drying, which concentrates the salts. That's the critical thing. And if you do permit ventilation on occasion, you might use it as an engineering variable. You might let the stuff get hot, as long as it's not going to have any deposition to keep the water away from it until, by some monitoring system, you see that that period is over with. Then you might cool it down and let the water deposit on it, but not cycle evaporation deposition. Just either have it hot or else have it cooler, and you could use your ventilation system as the engineering variable to do that. I'm just dreaming here, of course.

But the other thing is, as was mentioned, no matter how this would be started out, it would be growing a little minor air formed product scale in dry oxidation at the very start, and I think that should be taken seriously, and experiments should use something like that, or simulated scale, as the initial condition for electrochemical aqueous experimentation.

And as Susan said, and I thought about anyway from my own experience, there's a big difference between atmospheric corrosion in an aerated film and deep solution in a vat of aqueous solution. And as I have heard, experiments are not being done in the atmospheric mode today, but they certainly should be.

BULLEN: Thank you. Professor Craig, did you want to make a comment, or do you want to just listen for a while and go around the table? Okay. Dr. Newman?

NEWMAN: Well, I don't have any particular qualms about the 90 degrees, or whatever it was, the lower of the two temperatures that we discussed. I don't think this stuff is suddenly going to start corroding generally, although I definitely hear what Roger Staehle says about the deposition and the evaporation issue. And I think 160 is kind of the minimum temperature where I would really start to be concerned about that.

So if somebody says, well, these things are not going to be ventilated and the temperature is going to go up to 220, I'm still a little bit puzzled as to what Roger thinks is the uniform corrosion mechanism that can operate there. But definitely in terms of promoting various kinds of localized corrosion, that then becomes a rather different kettle of fish then.

You know, quite clearly, if you have some conditions that persistently generate a highly alkaline environment full of peroxide from radiolysis, then you're going to corrode stuff at a significant rate. You know, whether it's a micron a year or ten microns a year, I don't know. But I think those mechanisms, I would say 150 or 160 is the threshold for what I would call a steam generator heat transfer mechanisms to really start switching on.

And you do see all kinds of stuff. I mean, just the other day, I was at a lab where they were using a new surface analytical tool to look at some alloys that have been exposed to these kinds of environments, and they were finding all kinds of stuff in the grain boundaries down to quite large depths, 100 microns, or so, lead, that kind of thing. And those mechanisms seem to be specific to these concentrated, I would going to say alkaline environments, maybe Roger can correct me here, but probably alkaline environments at temperatures in the 200 range and above. You can certainly get a lot of things happening to these nickel alloys that I wouldn't particularly want to be--I wouldn't particularly want to be associated with predicting that they were going to last for 10,000 years under those conditions.

BULLEN: Bullen, Board. Actually, you led into something that I was going to ask a little later. But Alberto mentioned this morning that the minor constituents in the groundwater, such as lead, or maybe mercury, or arsenic, or some of the other bad actors, could play a role in the passive film stability. And so I guess what I'd be interested in is maybe your interpretation of the importance of that role, and whether or not you would see it as more significant in a hot 160 to 200 degrees--

NEWMAN: Well, definitely the lead.

BULLEN: --versus the 60 to 80? Yeah, could you comment a little bit on that?

NEWMAN: The lead phenomenon, I mean it can be demonstrated at temperatures like 100 if you use the right kind of hydrochloric acid, and so forth. But as something that destroys materials, I'm not aware of any reports at temperatures, you know, in the 100's. But then on the other hand, the time factor always has to be taken into consideration.

STAEHLE: There's a lot of work on lead, as you probably know, up to about 300 centigrade.

NEWMAN: Yeah.

STAEHLE: Killian's work and Wong's work, it's pretty extensive. And the one thing that's of interest in the lead in a way is, you know, lead forms a lot of insoluble compounds. These compounds turn out to be very temperature dependent in terms of their solubility. And so you could have a compound which is quite stable at 100 centigrade, and at 200 centigrade, it's totally soluble. And so there's that kind of thing going on, without belaboring it.

NEWMAN: My concern would be intergranular corrosion. I guess if I have to summarize, if the conditions are what Roger says they're going to be, and they're going to close it up and forget about it, the temperature is going to go up to 200 and something degrees, I think one could have localized corrosion of the pitting type, but I think what Roger calls general corrosion, I think it would be more likely what you would get is this intergranular attack, or intergranular corrosion, and I would be concerned about that at a high temperature.

STAEHLE: Well, just to continue a point, we all work on different kinds of consulting problems here and there, and I'm working on a problem at the moment, a thing in Venezuela where the temperature is around 250 centigrade in a potassium carbonate heat transfer crevice. So, potassium carbonate is filling up in the crevice. It's corroding generally like made in this heat transfer crevice.

NEWMAN: The material being?

STAEHLE: Stainless.

NEWMAN: Stainless steel.

STAEHLE: So, you know, I'm not so sure the detail of the mechanism, but there's no question about what's happening.

NEWMAN: Well, you can get high corrosion rates in carbonate for well-known reasons, I think. I mean, it's a complexant, so, I mean, you don't need the very high or very low pH. But, yeah, I agree that that's the sort of thing that could happen. Carbonate is something that I think is not so aggressive to nickel, so that's not something to be so bothered about. I mean, you say 200 degrees. I'll jump to the other side of the fence.

BULLEN: Okay, thank you. Actually, Rob, before you sit down, I have a request for you. We had some questions about the testing program and the experiments that were being done, and Professor Rapp basically asked about the high temperature oxidation. Could you address maybe just a little bit of some of the experimental program that's on. Is that a fair question to ask you, or do you want to defer to somebody else?

HOWARD: Rob Howard, Integration Manager for Bechtel SAIC. I would like Greg Gdowski, who is one of the PIs involved in our experimental program, to just clarify a few things about what the testing program involves. And we do do testing in humid air environments. It's not just vat solution.

BULLEN: Okay, thanks, Rob. Dr. Gdowski?

GDOWSKI: Greg Gdowski, Livermore.

A few things about the environment that are probably not apparent initially is that we are bounded by atmospheric pressure. So you're not going to get superheated steam there. You're not going to raise the environment about one atmospheric pressure.

The reason you can go to high temperatures with the aqueous solution is because of the forming of the saturated aqueous solutions with mag chloride.

NEWMAN: The temperature of water is higher?

GDOWSKI: Yes. I'm not denying that. Other concerns that we are testing atmospherically, we do have a series of tests to address atmospheric corrosion. We are doing periodic wet and dry type experiments under high relative humidity conditions, where we're dripping saturated aqueous solution salts on the specimens, letting them evaporate, trying to characterize those environments.

We've also done a series of evaporative concentration experiments where we evolve these brines to very high concentrations. We're not, as Carl put it, they were at much higher concentration aqueous brine solutions. We're not at the .05 molar solutions. We're in the molar solution range on these salts.

I guess that's about it, unless you have some other questions.

RAPP: With what observations then? What are your results?

BULLEN: Identify yourself, Professor Rapp, and ask.

RAPP: Rapp is asking what results have you observed then under these test conditions?

GDOWSKI: Which tests?

RAPP: Well, any of them. Choose one.

GDOWSKI: Choose one. I could talk mostly about the evaporative concentration experiments. What we have seen under the wet and dry dripping is primarily the formation of the scale on the surface, with very little oxidation of the underlying metal. We've done these tests at around 90 and 100 degrees C. at this point.

Under the carbonate base waters, high silica, high carbonate, you form a very tenacious scale on these materials.

RAPP: As a deposit; right?

GDOWSKI: Yes, that's right, with very little indication of any corrosion underneath these deposits at this point.

NEWMAN: May I ask a question. This is Roger Newman.

Can somebody tell me what, given the constituents of the water, what is the highest temperature that you can conceive of maintaining a liquid environment on the surface?

GDOWSKI: It would have to be the magnesium chloride or the calcium chloride type brines. Calcium chloride boils at about 164 degrees C.

NEWMAN: Okay. Zinc chloride boils at a higher temperature than that. You don't have any zinc chloride.

GDOWSKI: Well, I mean, from the constituents at Yucca Mountain, from the groundwater constituents.

NEWMAN: Right.

STAEHLE: This bounding condition that Greg mentions of atmospheric pressure is certainly an important one. The question I was just asking him was whether or not in thinking about maximum temperature, you've got to think about some kind of a deposit build-up on the surface that has some dimensional substance to it, and maybe some capillary structure to it. And that may not change the temperature a lot, but it probably would be somewhat higher than 160.

GDOWSKI: Agreed. Agreed. It will raise it, but you have to, at these elevated temperatures, the size of the pores that you have to bring about a very large elevation in temperature are very, very small. You're talking sub-micron levels at these temperatures.

BULLEN: Thanks to both of you. I guess this maybe is a very good lead-in to the brine question that--oh, Alberto, do you want to say something?

SAGÜÉS: I have a couple of questions for Roger.

BULLEN: Go right ahead.

SAGÜÉS: Now, depending on what we get into, we may go into this later with some of the other participants.

BULLEN: Okay, feel free.

SAGÜÉS: You made a very quick estimate, Roger, in assuming a certain chromium solubility, and from there, you went ahead to try to obtain a guesstimate of the corrosion rate. Now, I assume that in doing that, you must have assumed that you were at some kind of a pH in the system, and you looked at how much the chromium oxide line interfaced in the--shift in the equilibrium, something like that?

NEWMAN: It's something like that, yes. In fact, I was just pointing out that you could have very low equilibrium solubility of the stuff, and yet over a period of hundreds to thousands of years, build up a layer of porous oxide, which a lot of people would probably agree might have some effect on the stability of corrosion. I wasn't really picking a particular point, but I mean, if you want to equate that to a particular pH, it would probably be anywhere near neutral, you could probably have 10 to the minus 14 molar solubility of something like chrome.

SAGÜÉS: And, from there, how did you work it out into a rate of dissolution?

NEWMAN: Just Pick's law, yes, Pick's first law. I mean, it's just a factor of the envelope diffusion.

SAGÜÉS: So, do I understand then that what you are suggesting with that kind of thinking, without making a very precise statement, of course, would be that that would be one way of having a non-conservative passive layer dissolution process at the passive layer solution interface.

NEWMAN: No, I don't associate that with some kind of accelerated general corrosion at all. I associate that membrane like layer with an increased probability of localized corrosion.

SAGÜÉS: Localized corrosion?

NEWMAN: So, over a long period of time, it seems reasonable to suggest that you would build up a thick, as to say microns thick, oxidized layer on the surface, which would be mainly a product of a re-precipitation process, simply arising from the passive current. And that that layer could promote a localized corrosion process.

SAGÜÉS: Okay, yeah, that I have followed. I guess another question, and this applies to you and then maybe as other members of the panel get through it, I think that one of the questions would be what is the thickest, maybe not the barrier layer, but the thickest passive debris layer that anyone may have seen anywhere that one can ascribe to a process like the processes we're talking about in here? Is there such a thing, or are we talking--what I'm trying to establish is are we talking about something that is totally, absolutely fictional, or are there any examples--

NEWMAN: Science fiction.

SAGÜÉS: --that we can look at?

NEWMAN: Well, I think the problem was that most of the practical cases where those happen at ambient temperatures have been where you are on the borderline of the transpassive dissolution. I once had to deal with a problem where industrial dishwashers were going blue. They actually looked much nicer when they were blue than they did before. This turned out to be due to peroxide in the detergent materials causing a kind of transpassive dissolution on the material. All the material was dissolved and then redeposited and it gave this blue film.

I don't know of any example, if you like, in the middle of the passive region where anyone has seen a similar thing. The best chance to get something like that would probably be at high temperature where the process is faster, the passive dissolution process. But, I do know that in acid environments, of course, you can see something like that. If you were at pH 1 and you passivate stainless steel, then the passive current is higher so it doesn't take so long to build up such a layer, and you could perhaps learn something by artificially growing such layers at low pH or something like that.

In fact, you know, you can actually make stainless steel go blue by cycling the potential. There's lots of ways to make stainless steel go blue and you cycle between active and passive. So, you're producing this sort of very finely divided re-precipitated type of material. That certainly makes pitting much easier. I've seen in lab tests that when you have that deposit, that blue material on the surface, it always pits prematurely at very low potential.

SAGÜÉS: I would like to ask the remaining members of the panel when it is their turn, if they know of any blue stainless experience or sighting, and I would like to hear that and it certainly would be very instructive to have some blue C-22.

NEWMAN: Well, I can supply it in different colors.

BULLEN: Then, we don't have to polish the containers. We could just have different color containers.

Go ahead, Professor Bertocci?

BERTOCCI: Is it then interference color?

NEWMAN: Yes, but it's always blue. So, it's something more than just--you know, you'd expect to get rainbow colors if it was--but it's definitely an interference effect, but sometimes you do see the rainbow colors. But, when you don't see the colors, it's always blue.

BULLEN: Gustavo, go ahead? Do you have a question?

CRAGNOLINO: Well, talking about colors, you produced this precisely for Alloy-22 when you go to the transpassive regime?

NEWMAN: It goes blue, yeah.

CRAGNOLINO: Goes to yellowish-blue type of color and this is associated with the transformation of the film under certain conditions, but we are talking a very high potential. So, I don't see that that's attainable by any means. You can obtain this potential in reprocessing units, but not in the condition of the repository.

NEWMAN: Well, I think, Alberto was just asking is it possible to speed it up so that you can do some experiments--was that the--

SMIALOWSKA: (Inaudible).

BULLEN: Please use your microphone, Susan.

STREHBLOW: Could I give a comment on that?

BULLEN: Oh, Dr. Strehblow, go right ahead?

STREHBLOW: Okay, sorry. If you have these interference colors, is it that you just dissolve the iron and you have the iron 2, and if you're back in the passive range, then you oxidize it to iron 3 oxide? I think that is the reaction which is occurring. So, if you by intention would like to have this layer, you also could add iron 2 salts to the solution, just oxidize it up and then at moderate pH it could be, let's say, 6 or 7, so that the iron 2 is still soluble. Then, you get this nice film and then you can study it in detail what it is doing to localized corrosion.

NEWMAN: Well, if there's any iron in the water in this mountain, it will certainly oxidize onto the surface of the alloy and produce a layer like that anyway, as indeed could one or two other elements. Any corrosion process that you propose here is going to be occurring under a membrane-like layer of something. And, you know, I think these, in general, would be just as aggressive as physical crevices for the corrosion, but not necessarily very aggressive. It depends on the temperature and so on and so on. Anyway, I took too much time there.

BULLEN: Thank you. Bullen, Board. Professor Strehblow, did you want to make any comments about Question 1 as we go around since we're returning to that?

STREHBLOW: Yeah, I just wanted to repeat also that--and support what the previous speakers have said--the higher concentration of the electrolyte is a very big danger and these wetting and drying periods which might concentrate the electrolyte. And this, in combination with a depletion of the chromium and the material by some wrong treatment, welding and whatever, you might also remember that you have chromium depletion at the grain boundaries for stainless steel by chromium carbide precipitation. And, things of that kind which might happen and which could lead to a local depletion of chromium is a source of danger because then the passivation mechanism by chromium oxide formation could be hindered because there is not enough locally, not enough chromium oxide. As Carl De Bella said, we have huge surfaces which have to be treated. There could be a weak point where this might occur. This is the first remark I would like to make.

The second, we heard something by Bob Rapp about high temperature corrosion and I would like to add some little remark which I didn't include in my short presentation because I didn't want to overload it. But, there is existing the possibility that also chlorides and high temperature corrosion could give a big danger of film breakdown and corrosion if the temperature is sufficiently high. When you have, for instance, HCl oxygen mixtures at 700 Centigrade, then you easily will corrode the metals and also the nickel-based alloys. We did a couple of these studies in the past. This will break down the material with a high velocity. Now, we have lower temperatures. So, it might on the long-term, there might be some mechanism of this kind. You might not have the HCl, but you might have the chloride sitting on the surface as a little crystal and then something of a similar kind may start and, as you have a long time, this may also cause some corrosion phenomenon in the dry at high temperature. This was the second remark.

And, the third remark was about radiolysis which somebody in the audience asked me or gave a remark at the end of the session and he told me that especially in the first time you have a danger of formation of high oxidants and electrolyte because then you have the high radiation. But, when it slows down, then this danger will be over. So, one has to discuss this in detail and there has been some work on it, as he said. I don't remember the name of the person.

BULLEN: Bullen, Board. Actually, with respect to the radiation field, and we started talking about point defect production, I wanted to sort of follow up on that. I know that a scientist named Rich Von Konynenburg at Lawrence Livermore National Laboratory had done in the late '80s an analysis of alpha, beta, gamma neutron damage, and, basically, same conclusions that were reached this morning. Alpha is not a problem because it's inside the waste package. The betas may or may not be a problem, but usually aren't significant. The gammas can cause some local ionization, but usually don't cause displacement damage. The only displacement damage you'd get would be from the neutrons. But, the conclusion from the Von Konynenburg paper is that the neutron flux is so low compared to the similar flux that you have in a nuclear reactor that in the 10,000 year kind of time frame, you may end up with sort of the equivalent of one or two reactor days of equivalent operation or radiation damage. And so, the kinds of point defect production rates would be, you know, maybe 8 or 10 orders of magnitude less than what you'd see in a reactor.

So, you'd ask yourself, you know, even though I have a factor of 5 increase in time, I'm still a factor of 10^8--or excuse me, a factor of 10^5 increase in time, I have an effect of 10^8 decrease in rates. And so, is that going to be significant? I guess, I don't know the ins and outs of point defect production and its impact--maybe Digby could comment on this--its impact on the stability of the oxide films. But, I would venture to guess that the neutron damage would not be a real big precursor to those kinds of issues. And, maybe, I should defer to Digby about that.

MACDONALD: No, you're right. Neutron damage isn't significant. About the only way that you could have a deleterious effect is if something like hydrogen peroxide kept building up, but, of course, the hydrogen peroxide decomposition is catalyzed by transition metals. Okay? So, it's a little far-fetched to see a massive buildup in hydrogen peroxide.

Just to put this radiation situation in perspective, a number of years ago, we did some modeling work on copper canisters and, of course, the wall thickness of copper canisters, much, much greater than the wall thickness of the C-22. The conclusion then was that there might be a very small shift, positive shift, in the ECP corrosion potential due to radiolysis. Now, of course, with the thinner C-22 wall, I believe that the dose rate of the surface is now about 2400 rad per hour, okay, compared within a nuclear reactor of maybe 1000 times that. But, nevertheless, it may be significant and that issue possibly should be looked at again.

BULLEN: Professor Strehblow, did that answer your question with respect to radiation?

STREHBLOW: Yes.

BULLEN: Dr. Rapp?

RAPP: May I comment on one of your comments, please? Relative to something like chloride cracking an oxide at a hot temperature, there were very nice experiments by Peter Hancock a long time ago where he took a metal wire and vibrated it to its resonant frequency and then put a drop of sodium chloride on it and it immediately cracked, but this was at a very high temperature, maybe 800 Celsius. But, the experiments are so easy to do that. I mean, if you want to try this at 300C, I think it only takes 10 minutes to find out whether sodium chloride will crack a film. So, that sort of experiment would certainly be reasonable, I think.

STREHBLOW: But, I think it is also very important in the context of the stability of a passive film because you are reaching perhaps 160 Centigrade or somebody told something about 220. So, we are approaching some temperature where this could be a danger.

BULLEN: Thank you. Dr. MacDougall, would you like to make a few comments about Question 1? You can show whatever you like because now we don't have a time limit. Well, maybe as a professor, you have a 50 minute time limit, but that's it.

MACDOUGALL: I'm not a professor.

BULLEN: Oh, well, we could promote you. Could you put the microphone on, please? Right there. It's right next to you.

MACDOUGALL: Well, it's about the passive current, in fact, and the nature of the question. I'm not again talking about Alloy C-22; I'm talking about nickel. I spent a good part of my life years ago decorating defects on passive films that were formed on nickel in sulfate solutions over various pHs and breaking those films down and open circuit. This is the nickel single crystal work that we talked about and it's a one-one-one. You have little arrowheads, and in point of fact, you can see them here. They're beautiful crystallographic etch pits which are developed, I believe, and I'm absolutely convinced, in defects within the passive film that are frozen in once you open the circuit you take the driving force away. There's a large number of them there. That was formed on a film that wasn't formed very long or it has low potential or something like that. You had fewer of them when the conditions of formation of the film, passivation conditions, were, in fact, longer or at higher potential. In this case, I believe it's longer. Then, when you went to very long periods of time, you had fewer defects still. You only had a few on the surface. In fact, it was 70 hours at 0.0 volts. You only had a couple.

Now, the passive current is obviously going to be lower here than it is for that, than it is for that one, but I don't necessarily agree that we're better off with this than we are with those ones because it's something that Susan alluded to this morning. In fact, I've had the feeling and qualitatively I believe that I've pretty much proven it qualitatively is a different story. This was done some years ago, many years ago now.

But, I think what happens is that the number of defects going from 100 to 10 to 1, the current doesn't go for

100i to 10i to 1i; it goes from, exaggerate, perhaps 100i to 30 or 40i to 10 or something of this nature. What I'm saying is that each of the defects here has to handle more--not more strain, but has to handle more activity because the strain of the film is not going down accordingly. So, the passive current that you see is going down. You'd say that's very good in point of fact. But, the activity associated with that defect, which was caused because of breakdown and repair, these defects are not static, they're mobile over the entire surface. They will eventually, when you have the potential applied, encompass the entire surface. The oxygen 16, 18 SIMS work proved that, in fact.

But, what I'm saying is that you would say, look, if a very low passive current here, but that doesn't necessarily mean, in fact, that you have a better scenario for localized corrosion which depends upon the current efficiency for the repair of any of those breakdown events. When you're on open circuit, it could be even worse because you have a larger cathodic area, in fact, involved in this particular case here.

So, I think just to say what of the passive current, the implication of the question is that it goes down, you're better off. That's not necessarily true. If it was up, you may be better off in some cases. I'm not sure.

I think with this alloy, C-22, it may have such a frightfully resistant passive film--and I don't know firsthand--but you may have to mechanically disrupt it or remove it in some sort of way like that which is perhaps not out of the realm of possibility. But, this is 70 hours and, as I say, the film, in point of fact, the defects in the film, I think, are getting, if anything, more prone to supporting some kind of a localized attack in that particular system that I was investigating. So, I think one has to be terribly careful of just looking to the passive current. It's an overall thing, I realize, but it has other things encompassed in it, in terms of the current efficiency for the repair of those events.

BULLEN: Bullen, Board. Just a follow up question. Because one of the things you look at is the drift in that current, do you think that it's the increase in the population of those types of sites in C-22 that makes that happen?

MACDOUGALL: This was nickel here in point of fact.

BULLEN: Right.

MACDOUGALL: It was decreased and the density was decreased in point of fact. But, certainly, yeah. Yeah. There are fewer defects in that, and I counted them up, you could count them. I'm sure today, if people were doing it today, they could do it much better. The ultimate would be, I guess, if one had, I suppose, only one defect. It may be so active that it would drill a hole in something in no time flat. So, maybe there's an optimum number of them or something of this nature in a system like this.

C-22, I certainly don't know, but I've used the analogy and again I have to be cautious because I don't know if this is applicable to this particular system here, but I think that one should, at least, consider it, the analogy with people. Some people have heard me say this before. Human beings, in point of fact, are those human beings who have lots of small defects, well, it's okay, I think they can get by in life and not do themselves or society any great injury. But, if a person has--perhaps, he's perfect, but he has one defect, it would be one deuce of a defect.

So, you perhaps, have to be careful that you reduce things--something to almost nothing. It's the strain in the film and, again, I mean, there were people at the University of Virginia years ago that looked at this Gwalfney and his group and people. It's a very difficult problem to look at, but just how is the strain decreasing within these films as time, in fact, goes on and the propensity towards this sort of localized corrosion.

And, I would agree that, in point of fact, if you have some kind of a porous deposit on a surface that Roger is talking about and others, then you could be in a bit of trouble, in fact. I mean, that's pretty nasty thing because the stews, the environments, the crevice situation, all of these places where you can have these occluded cells, that's something that could make things certainly much worse if they were to happen.

BULLEN: Thank you, Dr. MacDougall. It makes me happy for my small defects and hopefully not one big one that I seem to have. We're not all as well-engendered as you are, Dr. Kruger. So, we all have a few of these.

Dr. Smialowska, would you? Please, right to the microphone.

SMIALOWSKA: I would like to emphasize again the differences that can occur during these short time aging and long time aging because, in fact, we don't know nothing about what happens during the longer period of time. If you would take into consideration the mechanism of aging in this short period of time, you know that the corrosion properties are better which means resistance to corrosion increases. At the same time, there are a lot of mechanisms which showed that during the longer period of time, you should have rather higher corrosion than lower. According to what we know from short time of aging, it should be very small corrosion. But, we cannot say that after a certain period of time you have some changing in the mechanism of corrosion because some other phenomena appears.

This phenomena which I think could be, it is that after some time, we have this very small defect in passive film. Passive film is much more resistant, much more stiff, much more rigid, and what we will have then, we will have mechanical breakdown of the film which will be--first of all, we will have stresses in the passive film and later on cracks. And then, you will have destabilization of the film and it might be you start again to have high corrosion and then going up to the lower corrosion again.

So, I think that it is, of course, very difficult to model the aging after longer period of time, but it can be done some experiments which can show you that after special treatment, you have decrease of this defect, and later on, you might probably see this mechanical breakdown. I think that I know these kind of experiments.

Concerning other things, the surface preparation, of course, surface preparation is very important, but again this is very important in initial period of time. Initial period of time, I am saying about this 100 years or something like this. Later on when the corrosion starts, then the preparation of specimens will not play very much role, very big role. But, what I think it would be important, it is agglomeration of corrosion products of salt, salts films different which were these salts especially which are not dissolved in water and you have this calcium salt, and magnesium, also, not dissolved, and then you will have some specimen which is not uniformly covered by this debris and by this corrosion. Then, you will have non-uniform general corrosion which is some kind of localized corrosion.

So, it seems to me that quite a lot should be done to be able to model what is going on after longer periods of time. We don't know. For example, we don't know if the composition of film is changing and how much it's changing. Composition like you have at the beginning, everybody knows that it's agglomeration of chromium oxide on the film, but if it change during aging or not, we don't know nothing about this. We don't know also nothing about the physical property of the film.

SAGÜÉS: I would like to make a comment on a question. The first comment is that, indeed, the kind of things that you mentioned that we don't know about, the makeup of the film after long periods of time. It is part of the reason why we are here talking about this. One thing that you didn't mention and interestingly I haven't heard anyone mention, so far. It's sort of like the sore subject, sometimes, is whether the film starts as a crystalline and then goes into amorphous or it's amorphous and then goes into crystalline or where is it in this area? And, I wanted to ask what you may have to say about that particular aspect? Then, I have something else I wanted to ask you.

SMIALOWSKA: If I would know, it would be nice. Concerning the amorphous film and crystalline films, then when I know, it is all old work of Jurry who showed that when you have higher concentration of chromium in the film, you have much more--the film is much more amorphous. Is that right?

SPEAKER: That's controversial, but that's right, yes.

SMIALOWSKA: Yes. And so, however, after some time, maybe the crystallization can occur, but I don't know. It might be. It might be yes, it might be not. But, it would be some kind of the cyclic changes of property, I believe, in this. That it is not constant.

SAGÜÉS: Thanks for your answer. Before I ask you the other question, Dr. Strehblow had a comment, I guess.

STREHBLOW: To your aging aspects, I don't have experience with the Alloy-22, but with many other binary alloys. The chemical composition of these films is changing from--in many cases, we followed that from milliseconds to a week about. Even in the long-term, you may accumulate those species which are not dissolving. So, even after a week, we have still an increase, for instance, in chromium and iron chromium alloys. This is the chemical aspect. The other aspect is the question crystalline or amorphous and I think Phillipe can add many further arguments to that. We've studied together the situation on copper and you have a certain sequence. In a very short period of time, you see amorphous films forming at the very beginning, and then later on, at least in the case of copper where we have experience, it turns to a crystalline form when you see the crystalline structure with STM. There are changes and you can follow them with these methods you have today and this is giving us the idea that in many cases the crystalline film is not a bad film; it's a very good film and protective film.

SMIALOWSKA: Okay. I am glad that I was thinking in the right direction.

KRUGER: Copper is quite different from chromium, though.

SPEAKER: Of course, of course.

BULLEN: Okay. Dr. MacDougall?

MACDOUGALL: May I add just one caveat here in terms of the crystal nature of these films? The one on nickel, I certainly know rather well. On the Nickel 1-1-1 crystal, one has a film. The passive film is a particle size approaching, I think its about 10 angstroms, which is a pretty small particle size, in fact. But, it's perfectly epitaxed. If you look at the diffraction patterns, it's 1-1-1 on 1-1-1, the directions in the two major directions. What you have are very small angle boundaries. It's a mosaic. The boundaries between these particles are certainly less than a degree, much less. So, we're into a bit of a gray area what these things mean in terms of dislocations and that sort of thing. Are they sweeping the surface? And, we have very small particle sizes which indicate a lot of disorder. But, diffraction patterns indicate (coughing) tremendous order. So, you have to interpret these things in a special way, especially when you're dealing with films that are 10 or 12 angstroms thick. I mean, they aren't like bulk phases or anything like that.

BULLEN: Dr. Smialowska, did you have another comment?

SMIALOWSKA: No, I have--no, but I wanted to say something about the passive film.

BULLEN: Oh, please do?

SMIALOWSKA: Concerning the effect of potential on the passive film, in fact, you grow the passive film with potential, but this growth is not very substantial. It means you will have at the most 14 angstroms thick film and less. And, I think that if you will do some kind of experiments to keep the passive matter at potential which will be below the transpassive potential--so you have to be sure that you are indeed below this transpassive potential and keep it for long period of time--you might be able to see this mechanical breakdown. And, if it would be like this, it means that during the long period of time, you will have the same situation in your case.

BULLEN: Thank you. That's a very good suggestion.

I'm going to take some chairman's prerogative. I would like to ask Dr. Sato to make a few comments and then we're going to take the break that was scheduled for 15 or 20 minutes ago and I'll do that in just a second.

So, Dr. Sato, would you, please, make your comments on Question 1, please?

SATO: And, for uniform passive film dissolution is concerned, the accepted knowledge indicated that the passive film dissolution was controlled by the interfacial potential difference between the film and dissolution. So that anything that changed the interfacial potential will change the dissolution rate. For instance, aqueous environment, a different kind of composition, and also the absorption of hydrated anions. But, I don't think such a arrangement, the absorption gives us a dangerous increase of the dissolution current. I don't think so. So that I cannot see any specific mechanism that causes a great deal of increase of dissolution current.

Well, in addition, I think that the most important thing is that we have to keep the open circuit potential in the certain limit range where the passivity is maintained. If your open circuit potential goes outside the safety regime, you will get into trouble. For instance, going up, potential going up so you have transpassive dissolution region which you have a great deal of dissolution rate compared with the passive state. And, also, if you go down the potential, you will probably get into the active state. I'm not quite sure, your Alloy-22, how the active dissolution regime is-- .

BULLEN: That's a little difficult.

SATO: Except for hydrogen.

Well, I would like to add one more thing. That is the radiation effect. So far, we have been thinking only the electrolysis, radiolysis, which produced, for instance, oxidizing substances, such as hydrogen peroxide, which is one of the candidates which increases the electrode potential so that you get into trouble.

But, besides this electrolysis, we have to pay attention. The low energy radiation produces excited electrons and holes, as I told you in the morning. This excitation in the solid state--for instance, the electron and hole has an energy of the same order of magnitude, same order of the electron volt, similar electron volt, with the action of corrosion. So, it means this is direct effect to the corrosion process itself. But, we have quite a different kind of solid, you see, mostly probably the salt or oxide which are probably semiconducting oxide materials. So, it has, you see, band gaps so that the low energy radiation excites these solids. You have excited electrons and holes which have relatively high reducing and oxidizing capacity which affects the growth process itself.

BULLEN: Bullen, Board. I actually had a follow up question on the presentation you made this morning with regard to the radiation and radiolysis effects. This may be an inverse argument for temperature because do you expect the stability of the electron/hole pairs produced by radiation or radiolysis to be greater at lower temperature--and I'm showing you my ignorance of solid state physics now by asking this question--versus higher temperature?

SATO: I am not quite sure, but you see the high energy radiation with the energy median electron volt at the--not directly affected the corrosion process, itself.

BULLEN: Right.

SATO: Of course, you have radiation damage producing lattice defects or something like that. But, these point defect affects indirectly to the corrosion processes, but not directly.

BULLEN: Okay.

SATO: But, in the case of excited electrons in the hole, because the energy lengths, you see, similar electron volts so this is able, you see, to change the corrosion process itself.

BULLEN: Okay.

MACDONALD: Can I just make a comment on this?

BULLEN: Yeah, go ahead, Digby?

MACDONALD: You know, it has been found that irradiation of passive stainless steel surfaces inhibits pitting corrosion, inhibits the nucleation of the pits. Now, we've done that work, Professor Shibata has done that work. It does that by producing electron/hole pairs--at least, this is my interpretation--producing electron/hole pairs which essentially quench the electric field within the passive film, the barrier layer and, hence, reduces the driving force for the movement of vacancies across the layer. So, you have go to a higher potential on the metal in order to compensate for that effect. Okay? So, what would be interesting to do would be to find out whether that same phenomenon occurs in C-22, firstly. Secondly, if it can be induced with gamma radiation--I don't see any reason why it couldn't be induced with gamma radiation--and whether the shift in the breakdown voltage is comparable to the shift in the corrosion potential produced by radiolysis of water. I think if you were able to do those three things, you might be able to sort out that issue quite nicely.

BULLEN: Thank you. Actually, we are a little more than halfway through the panel roundtable type discussion of Question 1, but I want to introduce a break. I would like to take 10 minutes which means I know you'll be back in 15, but 10 minute break so everybody is back here at 3:35.

Before you leave, I'd like a couple people from Livermore or the project who have access to C-22 results to come talk to me, please? I think that may be Jerry Gordon or maybe Greg Gdowski or maybe even David Shoesmith who looks like he's a culpable individual there. So, I'd like to talk to them during break, please. 10 minutes.

(Whereupon, a brief recess was taken.)

BULLEN: We had a request from a panel member for some additional information. And so being as responsive as possible, the Department of Energy has identified Gerry Gordon as the opportune one who gets to come up here and give us a brief description of some of the results of the C-22 work that has been done to date. And, so I'm going to give Gerry the onerous task of going six to ten minutes max, and giving a quick overview of some of the general, or maybe even localized corrosion issues associated with C-22. And then I'll ask a couple of the questions of some other members of the audience. But, Gerry, you've got about five to ten minutes, please.

SAGÜÉS: Dan, excuse me.

BULLEN: Oh, Alberto, go ahead.

SAGÜÉS: Gerry, would you mind telling the panel members what is your exact capacity within the Yucca Mountain Program, and what are your technical responsibilities? Because I think that that may--

GORDON: Yeah.

SAGÜÉS: Thank you.

GORDON: I am the materials team lead in Las Vegas on the Yucca Mountain Project, with Bechtel SAIC BSC Company. That's primarily what I am.

This is just some of the environments that we are doing tests in. They represent concentrated salt solutions. This is the so-called J-13 groundwater at the site, concentrated to 10X, 1000X. This is similar, but with the pH adjusted to 2.8. This is about 50,000X concentration of the groundwater. It's fairly high in chloride. And this is a non-carbonate nitrate, sodium potassium nitrate chloride. This is wrong. It can't be more than a million parts per million, but it's very high in nitrate.

I think a key observation is that the molar ratio of chloride to some of the buffer or more beneficial ions is listed down below. It's on the order of one. If you go to pure sodium chloride, the environment becomes significantly more aggressive.

You saw a version of this earlier. These are the data based on descaled weight loss from the long-term corrosion test facility, and they covered the first three environments on the left that I showed on the previous slide over a limited range of temperature from 60 to 90 centigrade. And what's on here is the uncertainty band due to the very low corrosion rates. At two years, a mean rate is 100 angstroms per year. And so when you're doing descaled weight loss, the total weight loss is very low, and the air and the microbalance that does the measurement, and the dimensions of the sample, the descaling process, and so on, leads to this type of uncertainty, which with time is decreasing because of the total metal loss is increasing.

You saw some of these earlier, but they do represent independent confirmation of the magnitude of the general corrosion rate, the mean rate being on the order of

.01 microns per year, and being relatively insensitive to temperature. I think that shows up on a later slide. And these are some potentiostatic tests and unbuffered, so it should be .028, I think, molar-sodium chloride that show a similar kind of fairly low rate.

This is the surface from a specimen in atomic force microscopy after one year's exposure at 90 centigrade in simulated concentrated water. In this case, it was exposed in the vapor phase. There are also samples at the water line, and submerged. And this one had relatively little surface deposit. In many cases, you see silicate and some sodium chloride sometimes deposits when you examine the surface. This is a control sample, and this is a sample after one year's exposure. And you can see very little rounding of the sharp edges. These are 600 grid, I think, polished initially, and you can still see the polishing marks. And it's obvious the corrosion rate is very low.

Initially, the waste package will be exposed to dry air at maybe 160 centigrade. It depends on the final temperature mode that is selected. So, we've started to study the growth kinetics using the tunneling atomic force microscope. these are some results at Lawrence Livermore.

This is a surface. In this case, it's an atomic force microscope in which you're applying a bias potential and you're measuring the current that results, and it's a function of the oxide thickness. There are some calibration constants that need to get established for a given alloy system and oxide. This is conventional atomic force microscope. This is the electron current density map, if you will. It shows scratches, polishing scratches on the surface. This is after 45 days at 200 centigrade.

On the left here is the current versus the bias potential that's applied. These are calculated lines at one, two, three and four nanometers. The points are experimental data. The passive film, the air form film at the start was about 2 microns. After 28 days, it went up to something like 2.8--I'm sorry--nanometers. After 45 days, about 3.2 nanometers. And recently, they're 210 day data, and it's up to about 3.3. It's essentially leveled off to a constant thickness.

These are some data from the University of Western Ontario using time of flight secondary ion mass spectrometry. And, again, we're looking at--these are sputtered off and analyzed in a mass spectrometer, and you can see that for Alloy C-22 in the air grown films, it's rich in chromium oxide and molybdenum. At 200 millivolts, I think this was about 12 hours at 200 millivolts, and 1 molar pH 1 sodium chloride at 85 centigrade, similar to the air form film.

In contrast to Alloy C-4, which contains something like 15 or 16 percent chromium instead of 23, and somewhat higher molybdenum, you see the film is rich in molybdenum, and because of the lower chromium content, a lot lower chromium. But in Alloy 22, chromium, and in this case, molybdenum are present in the film.

At 500 millivolts, you're starting to get transpassive dissolution, and the chromium is dropping out. It's dissolving. The chrome 3, which is insoluble, is going to soluble chrome 6. So the ratio of chrome to molybdenum is decreasing.

In terms of localized corrosion, there have been a lot of tests and they're described in a lot of documentation, primarily done with cyclic polarization in a range of environments with and without these nitrate, sulfate, silicate, carbonate type buffer ions that are always present at least in all the waters that have been examined at the site. The groundwaters, the percolating waters, the pore waters all have roughly that one-to-one ratio of chloride to nitrate. You can get localized corrosion in Alloy 22 in pure sodium chloride at high enough potentials, especially if you crevice it.

This is an example of probably, along with magnesium chloride, the most aggressive postulated environment, and this shows the cyclic polarization curve with and without nitrate present. And it has a very marked effect. In this case, this is at 120 C., with near saturated calcium chloride and calcium nitrate. There are a lot of other data that show similar effects, that ratio of chloride to nitrate, plus sulfate, as it approaches one. There have been data done at 10 to 1, 100 to 1, and 1 to 1, and there's a very marked benefit of all of these oxyanions that are present in the water. So that needs to be considered.

These are some data generated again at the University of Western Ontario very recently, where these are potentiostatically polarized samples, and the current density after I believe it was 12 hours exposure over a range of temperatures from room temperature to, I think, 85 centigrade, and it's a comparison of a range of nickel based alloys. And at 200 millivolts, the corrosion potential is approximately that, so a little above the corrosion potential. There's very little temperature dependency over this range. There's some, but it's very small.

At 500 millivolts, it's somewhat higher. These vertical lines on some of these alloys, these were samples mounted in a plastic mount, and there was a crevice at the edge of the sample. In some of these samples, you could see crevice corrosion occurring. Alloy 22, at least under these conditions up to this 85 centigrade, didn't suffer crevice corrosion. Again, this is in one molar sodium chloride, pH 1.

BULLEN: Thank you, Gerry. I appreciate that.

Were there any specific questions on these types of results, or other questions from the workshop panel members?

Roger, go right ahead.

NEWMAN: I guess in terms of transpassivity, that's much less likely in acid than in alkali, I think. Is that you're experience?

GORDON: Because of chromium solubility; that's right.

NEWMAN: Yes. So I just wonder if the use of the pH 1 solution there might be deemphasizing the transpassive phenomenon quite a bit.

GORDON: Well, if you look at that very first table on the range of environments that have been tested, we've tested up to pH 13, and a very, very concentrated J-13. Can you go back to that table a second?

NEWMAN: Okay. You don't claim any credit for the OH minus ions there in that solution, that pH 12. You say that the inhibition is due to the nitrates and the sulfate. But I guess if you're at pH 12-point-something, are you also getting some inhibition of localized corrosion from the hydroxide ions?

GORDON: You likely are. You can postulate neutral or closer to acid environments that could exist. But the nitrates are always present, at least in all the waters that have been identified.

BULLEN: Bullen, Board. Any other questions from the panel?

MACDOUGALL: Could you leave on the conclusions for a moment?

GORDON: Okay. I didn't go through all the charts that led to them. But I certainly can.

I also didn't go into the path forward, the test program that's underway. There's a lot more experimental effort, modeling effort underway now.

BULLEN: Professor Davenport?

DAVENPORT: Just a quick question. In the absence of Professor Bohni, I guess somebody should ask is there much work being done on metastable activity in this system?

GORDON: Metastable pitting?

DAVENPORT: Yes.

GORDON: At the University of Virginia, Dr. Scully, under project funding, has done a fairly extensive study of metastable pitting over a range of these oxyanion to chloride ratios. And under potentiostatic, long-term potentiostatic tests, you do see a small amount of what could be metastable pitting that dies off with time and potential. It's pretty resistant to it.

KRUGER: Even at elevated temperatures?

GORDON: These were up to 100 centigrade.

BULLEN: Any other questions? Roger, I'm going to defer--I think I'm going to try and get around the table before we finish up.

So, thank you, Gerry. In fact, I'll apologize to David Shoesmith right now. He may want to make a comment in the public comment period, but I would like to get the rest of the way around the table on question one, and we still have six panel members left. So, if we could move to Dr. Bertocci? Please identify yourself.

BERTOCCI: The question is whether we can imagine mechanisms whereby the corrosion rate is higher than the expected one. And I think all day long, we have heard of possible mechanisms. I think that most of us would agree that if the conditions used for the test can be maintained for the whole time, probably the corrosion rate would be what the data said. But I think that we question, or a lot of people here have questioned the possibility of keeping these conditions, instead of having small samples which have been cleaned and so forth, we have these huge things which have been transported inside the tunnels, presumably not in a condition like the electronic industry, so we have dust depositing, we have the formation of films and scales, and what not.

And so the real point is how can--most of us I think are very doubtful that the conditions which have been used to do the measurements will be maintained in time and space.

BULLEN: Alberto, did you have any specific questions you wanted to ask? Or do you want to finish the rest of the way around the table?

SAGÜÉS: I would like to say something that pertains to what Dr. Bertocci was saying that may be for the other participants to keep in mind, and that is that maybe since we're going to be getting to the end of the day pretty soon, I really would like to hear an answer to the question that Dr. Craig formulated. And that is can we extrapolate over 10,000 years? And more importantly, say why we can extrapolate over 10,000 years. As a technical community or as a scientific group, and the like, do we feel that there is enough here to make a reasonable extrapolation? Or perhaps maybe the other way to say it would be how uncertain or how certain you will be that this extrapolation is in order? And, again, we're looking here for opinions, and maybe to frame your answer, so your comments perhaps around that kind of a question.

BULLEN: Do you want Dr. Bertocci to answer, or do you want to go on to Dr. Pickering? Dr. Bertocci?

BERTOCCI: I think that we have, a number of us have proposed quite a number of possible mechanisms which would be active if the conditions are not the ones that have been used. So, I suppose all of us would propose tests in conditions which were outside the range which has been used so far in order to have a better idea of what would happen if the conditions are not maintained.

A question I would like to ask also is what do we expect? That all the canisters will resist 10,000 years, or would be satisfied to have a few failures? I think that this would become an important point to decide whether or not the conditions and the materials in so far are sufficient or not.

BULLEN: Bullen, Board.

I'd actually like to address that one, because we really have a very focused nature for this workshop, which is how well do the waste packages work, and what mechanisms are going to operate over the 10,000 year time frame. But in the grand scheme of things, the project and the decision-makers who have to decide whether or not the site is suitable have to look at the legal criteria which are the EPA standard for performance, which is a dose based standard, or a risk based standard, for a population of people living down gradient from the mountain 10,000 years from now.

And, so to be perfectly honest, and this is a terrible way to put it, the solution to pollution is dilution, and so you would want to fail one can every ten years or so, and have a very slow release, and that would be the best. But that's obviously not a very licensable approach.

And, so in answer to your question, you know, we want to do the best we can in understanding the performance of the repository. But the actual performance itself isn't the waste package only; it's the waste package in conjunction with the natural system. And so we're asking you to focus very, very narrowly here, and we kind of apologize for that, but in a certain sense, no, because we want to get your expert opinion.

But, in answer to your question, sure, it doesn't have to last for 10,000 years. I mean, if one can fails, does the entire repository fail? No, that depends on how it fails and what time it fails and the release rates and the mechanisms, and all that. So, that's kind of beyond the scope of this. And I hope I didn't confuse the issue too much, but we are very focused here on passive layer stability, and long-term extrapolation. And, so that's kind of the focus here, and I hope I answered your question.

Did I raise any more that the rest of the panel have? Digby, go right ahead.

MACDONALD: If you ask the question can we predict, it begs the following question. To what accuracy? Now, there's another aspect of accuracy, and that is that if you were to build the canister with too thin a wall, of course, you couldn't ensure reliability. If you say, well, I'll go the opposite direction and build with a very thick wall, you may not be able to afford it. So what we haven't discussed here and defined is the accuracy with which we need to make these predictions. Is it a factor of ten? A factor of 100? It makes a big difference. Roger is going to say something.

BULLEN: Bullen, Board.

Actually, you get beyond the realm of science, into policy issues, with respect to certainty of performance and those types of issues.

MACDONALD: Right. But it's absolutely vital that somebody give us guidance as to what accuracy these predictions need to be made to.

BULLEN: I'm looking at Alberto now.

SAGÜÉS: Well, what I'm saying is the following. Suppose that you have this same group, and you say we're going to build this--or, rather, the Yucca Mountain Project is proposing to build a canister out of 1 millimeter thick 1020 carbon steel, and nothing else in between that and the waste, I have the feeling that we would be hearing some opinions saying this can never make it, impossible. It makes no sense to even think about it, et cetera, et cetera. That would be one extreme attitude.

The other would be to say we're going to build this out of a very thick and internally strengthened precious metal alloy, and I have a feeling that we may be hearing most people on this panel saying that, well, that is pretty much guaranteed as far as we know with all of our knowledge to last for a period of time that would be extremely long, and I would say exceeding, with a good degree of certainty, 10,000 years, if not maybe a much greater amount of time. And you get now into having analogs and all that that can show that. Evidently, we have something in between.

And what I would like to see, to hear a little bit more when you have an idea of the kind of evidence that exist, the direct evidence, empirical evidence, and so on, and of course this group has an extremely good idea of what is the present status of fundamental knowledge in the area of passivity. And what I would like to hear is maybe not a yes or no, and indeed we don't want to do that with this kind of a group, and maybe we'd like to hear a little bit more of how your answers are colored by this overall question. Are we having a reasonable chance of predicting durability over 10,000 years using our present empirical knowledge, and the knowledge that the scientific community has on the phenomenon of passivity and its stability?

BULLEN: Can I hand that one right to Professor Pickering as he sits here? You're on the spot. Dr. Pickering?

PICKERING: Well, I think I came in here with the feeling that we couldn't trust the passive current density to remain at the low level for many reasons, and we've heard many mechanisms. Certainly the one that seems to come out, at least to my ears, from many members of the panel is this deposition of debris, or reaction products, other things that might form this film.

Immediately, then I, you know, you see the possibility of composition of the electrolyte changing at the base of that film. And, you know, whether it's sulfur species or chloride or whatever that might accumulate, it's going to raise, you can visualize it raising the passive current density. And if you need 10 to the minus 8 amps per square centimeter to last ten years, then if you raise it only to 10 to the minus 7 amps per square centimeter, you're only going to last a thousand years, if my simple minded calculation is right.

So, yeah, I think it would be hard for me to say that we can extrapolate comfortably from what we know at this time.

That's all.

BULLEN: Okay. Dr. Cragnolino?

CRAGNOLINO: Yes, I have a comment, and I would try to concentrate essentially on question number one. I'll leave some of the issues related to number two in some way connected with what Alison mentioned before for tomorrow.

In some ways, even though I respect the opinion of Roger, I have to disagree in the sense that I believe that the environments are much more bounded than we tried to demonstrate. I learned not a long time ago that as a chemist, you do something called chemical divide, and allow then to discriminate what is the tendency of the environment and the condition of evaporation. What salt could precipitate and what you can expect as evolution, and we have two possibilities that were mentioned by Carl this morning in some way, but was not paid enough attention. One, is an evolution towards--an environment that is more acidic, or you could say it's slightly neutral, in which is magnesium chloride or calcium chloride, no zinc--chloride because it's not there, could predominate. And the temperatures--in this case, assuming that we have contact with air, because this mountain breathes, is going to be about 160 degrees C.

On the other side, we have the possibility of much more alkaline type environment, and this is a situation--in which we move--. Now, if we use short-term measurements of passive corrosion rate that are not in a steady state condition, we can demonstrate that this rate measured by electrochemical methods are almost independent upon the concentration of the chloride, and upon the pH, from a wide range of pH. And this is because chromium dominate the composition of the passive film under steady state conditions.

Now, this is telling us what happens under what we can consider a steady state condition that for nickel chromium alloys, contrary to iron--chromium alloys, you can get a steady condition in a couple of days at most. For nickel based alloys of this type, you need much more time.

However, you establish this condition, and you get films, as was mentioned some time, of the order of two nanometers, 3 nanometers, something like this, that I believe that is the real barrier film controlling rate of dissolution.

Now, we have these two problems. One, this possibility that was mentioned recently by Howard Pickering, and is connected with the idea of Professor Sato, of a membraine mentioned by Roger Newman, the possibility of having a membrane formed by corrosion deposition of products of the dissolution. And this is an issue that we have to deal with. But the main implication that I see is in relation to localized corrosion.

NEWMAN: May I just butt in there one second? I think when Susan before, or somebody referred to localized general corrosion, I think it could also be that.

CRAGNOLINO: Oh, okay.

NEWMAN: But it's a chemistry change type of corrosion. It's the type of corrosion where the anodic side becomes acid.

CRAGNOLINO: Exactly. I agree and I think that's an important consideration.

KRUGER: What about the potential going into the transpassive region?

CRAGNOLINO: I will touch up on that point later.

I'm going to bring up another point that Phillipe called to my attention, and was the point that was raised by Phillipe Marcus before, regarding impurities in the metal. And I think that this is important. This material has a specification has a sulfur content of .02 percent. But a good manufacturer of Alloy 22 will try to decrease significantly the number. It's one order of magnitude lower. It's 20 ppm. This is my question. Assuming this process that you mentioned of anodic accumulation of impurities due to the process of dissolution, do we have a risk that the stability of the passive film cannot be maintained. Not over a distributed interface, but at grain boundaries at a specific location. And this could lead to a form of attack that we didn't mention, for instance, localized corrosion in the form of intergranular corrosion that will lead to other processes that is not the issue here, but would be stress corrosion cracking, and so on. These are my concerns.

Coming to the corrosion potential, we have done experiment, obviously short-term experiment. We have done long-term experiment for Alloy 825. We have experiment for five year in Alloy 825, and the corrosion potential doesn't evolve beyond the 200 millivolts, in the calomel scale, that is in the passive regime of Alloy 22.

The addition of hydrogen peroxide can produce an increase, but is not substantial. And we are in that situation. A transpassive dissolution over a wide range of pH, and I forget the value but we can look later in my hotel room--, for Alloy 22 takes place at about 400 millivolts calomel scale, unless, unless, and here there are problems with the fabrication process, and the alloy has precipitation, modification in the microstructure, that would be possible, and will lead to problems.

That means that in dealing with the issue of passivity, I think that this is one thing that we have to consider as a possibility, and this is the process of accumulation of more information regarding factors, as was mentioned by Professor Sato, that could alter the corrosion potential for reasons that we cannot anticipate very well.

Now, responding to the philosophical question, I have one experience. The experience is an unanticipated process of irradiation growth of zircaloy. It's an alloy that is used in fuel elements as a cladding, but is not used very common as a structural material in the core of nuclear reactors. Well, nobody anticipated there was going to be a break-out rate in the kinetics of irradiation growth, and in the country I was working at that time, Argentina, a nuclear power plant was out of operation for six months because fuel channel broke down due to this that nobody was able to anticipate. This is regarding things that show that to have limit in our knowledge as you confront issues that could be catastrophic.

BULLEN: Thank you, Gustavo. Any comments from the panel on what Gustavo just said?

Seeing none, I will move on to Dr. Marcus.

MARCUS: As most or all of the panelists, I have proposed this morning a number of mechanisms that would or that could--I should say that may after long service times modify the passive currents, I think I proposed four mechanisms, and one of them was reemphasized by Gustavo, which is the segregation of impurities, including sulfur, at the surface or at the interface between the passive film and the metal. So I'm not going to repeat that.

Instead, I may make one or two comments. There was a comment this morning, I think it was Ugo Bertocci who said that, and I'll read my notes, that only weight loss and elementary--electrochemistry are available. Okay, we've heard a little more later this afternoon on the thickness and composition, but my concern is that we know really very little on the specific passive film which is formed on this specific alloy. We, around this table and the audience, know a lot about passive films on many metals and alloys, but not specifically on this alloy.

So I think it's quite hard to predict the behavior of something that you don't really know the nature of. We know very little on the thickness. We've had just a few data this afternoon. We don't really know the composition. Of course, everybody agrees that it's going to be largely enriched with chromium oxide because this is a general finding on chromium containing alloys in potential and pH conditions where chromium oxide is stable. But how much nickel do we have in the passive film? I think what we saw this afternoon with the SEM--data, in fact I was a little surprised. I saw that there seems to be a lot of nickel oxides in these. So it's far from being really a chromium oxide passive layer. I saw a huge signal which was assigned to nickel oxide, and I doubt that nickel oxide would behave very well under the expected environments.

Another point which has been raised I think by Alberto Sagüés earlier is the structure. We know absolutely nothing on the structure of these films. And to answer this question, I think this is something we must know, because the current in the passive state is largely determined by the defects, the structural defects which are present on the surface of the oxide film. In fact, most of the oxide films dissolved at specific sites, where the cations have low coordination, and that's of course directly related to the structure.

What we know from other metals and alloys in terms of structure is that for short-term passivation, as was shown a long time ago by Jerry Kruger, these films are amorphous. But what we have learned more recently is that aging of these films in the electrolytes will lead to partial or complete crystallization--, giving some long-range periodicity--with the structural defects, as was stated with these structures. And I think we definitely need to know the structure to really--predict the integrity of the passive films.

So, I think it's hard to conclude on that result, I mean, predicting the behavior of something that you don't really know the exact nature of.

Now, maybe a more general issue is to predict, what we have to do is to extrapolate on the long-term. But what do we have really to extrapolate? We have to extrapolate in time and space. So, what I have learned at school is that to extrapolate something, I need to have a plot of something as a function of time. And then if I know the mathematical law, I can extrapolate. And I have to do the same in space. But I have seen very little data of that type that would give some important parameters for the integrity of the passive films that would vary with time and that would vary with space derived from experimental data.

So, I'm not sure what exactly we can extrapolate. Okay, if we extrapolate the weight loss measurements, it seems to be that we can be rather confident that the passive dissolution would be low enough. But to my knowledge, I think it's the only curve where we have something as a function of time on which we can really apply mathematical extrapolation.

So, now, maybe another comment is that there seems to be a consensus around this table, and I would like to also share this consensus, that there's a risk related to the concentration of salts in the electrolyte. I think that seems to be an important issue.

And, also I would like to reemphasize the effects or the possible effects of wet to dry, and to wet transitions, in particular on the composition and structure of the film. It may well be that the film will have a different composition, under dry as compared to wet conditions, and that even the structure may be different. And when we will have this transition, I think it will be important to know what changes we can expect during these transitions.

That's all I wanted to say.

BULLEN: Thank you.

SHIBATA: I'll just make comment on the effect of temperature on the kinetics of the passive film growth. I have done it using the electroscanning electrode and I follow the kinetics of the film growth from room temperature to 250. Of course, I used the oldgrave (phonetic) system--and I found--and then, there are the materials, iron, iron nickel and iron chromium, binary alloy, and a series of materials are used. And, I found the logarithmic or inverse logarithmic type of film growth is observed from room temperature to the 150. Above the 150, the kinetics change to the usual--type parabolic law is observed. So, this is quite similar to the dry oxidation type. But, below 150, the inverse logarithmic type prevails. This is typically observed for iron system. Of course, iron chromium and iron-nickel is also the similar behavior. So, I think that in dry case also, the iron shows inverse logarithmic type near room temperature. If you increase the temperature, of course, these kinetics change to parabolic. I don't know exactly what temperature is changing the kinetics.

But, in the aqueous systems, I think that 150 is some critical temperature because the stress corrosion cracking or corrosion fatigues also very, very susceptible at 150. So, I think that this is connected to the nature of the passive film formed on the surface. So, recovery of the repassivation is some effect of such kinds of cracking behavior. So, I believe that below 150, the extension of the room temperature behavior might be expected, but I'm not sure in the instance of Alloy-22. This is my comment on the effect of the temperature on the kinetics.

BULLEN: Thank you. Bullen, Board. Go right ahead?

STREHBLOW: I wanted to say some remark to the outlines of Phillipe Marcus.

BULLEN: Oh, go right ahead, Professor Strehblow.

STREHBLOW: Is that too late or--

BULLEN: No, no. This is a roundtable discussion and we can all speak at any time. So, go right ahead?

STREHBLOW: Okay. I agree that we don't know anything about the structure because it has not been studied; for instance, with STM or AFM or whatever it is. But, the chemical composition of the films on, let's say, nickel at--20 chromium and nickel 34 chromium has been studied very intensively as a function of the potential, pH and time and these data are known from surface analysis, XPS studies. I didn't go into these data because that it is a whole story and I'm not prepared. But, roughly speaking, what you said, there is nickel in the film or not and how much and what is the film composition? Of course, it depends on the pH. If you are in a strongly acidic electrolyte, then the nickel is almost not there at the lower potentials and it enters at the higher potentials to some extent because then you have also the dissolution of chromium and you can play these games and you can follow that from a millisecond--we did studies from a milliseconds up to an hour passivation time. And, we know also the changes in that time range, not about years or something like that. But, in that time range and pH and potential, we know what the film is and its structure of the hydroxide composition and the oxide underneath.

MARCUS: Yeah, Marcus. That's right, but in this alloy, in addition, we have molybdenum and tungsten. So, we would like to know how much. As we saw earlier this afternoon that according to the SSIMS data that there is molybdenum in the film, but these are not quantitative data. We don't know really the composition of the film. We know what is in and what is not in. But, I don't remember if there was some tungsten in it or not.

STREHBLOW: There is molybdenum in the film. That's what I have seen. But, these are data of Schultzigan (phonetic) -- on hastaelloy C-4, but it's also not exactly the same alloy. If you are talking about Alloy-22 and nothing else, then you are right. But, if we are talking about nickel 20 chromium which is very close to that composition, then we know what the film is.

BULLEN: Alberto?

SAGÜÉS: Yes, a comment on Dr. Strehblow. I have no doubt that there are investigations that have looked at this in some detail, but I think that I'm correct in assuming that those are investigations that looked at relatively young films, maybe things that have been exposed to the environments for intervals of hours to days maybe. But, I would be surprised if this knowledge extends to mature films that have been in situations resembling service for many years or is there some--

STREHBLOW: These are basic studies, of course, and these are specially prepared alloys which have been subjected to special conditions and not to service or to field-like conditions.

SAGÜÉS: One of the things that the project, the Yucca Mountain Project, is generating is now relatively well-characterized, specimens have been exposed for periods of years to relatively well-characterized environments. Of course, they have a different kind of finish and they're not single crystals. But, there may be an opportunity there to learn things that couldn't be found otherwise.

BULLEN: Bullen, Board. I had a follow up to Professor Shibata's comments and maybe they tie in again to what Susan Smialowska had said about the structure and the kinetics of the film and its mechanical properties. You mentioned that you saw sort of different kinetics that occurred below 150 degrees C and you were concerned specifically about mechanical properties associated with the film as it grows. Would you have more confidence in a lower temperature if you never went above 80 degrees C during the operating phase of this? Would you expect to see perhaps better performance or perhaps better understanding or more confidence in the understanding that you'd see, as opposed to going to 160 to 220 degrees C? I'll ask Professor Shibata first, and then, Susan, if you could follow up, that would be great.

SHIBATA: This kind of technique, it just took a very, very short time and you cannot extend over this kind of behavior to the long-terms because of the very, very short time. But, even that kind of conditions, the kinetics changes at the critical temperature, so that I just confidence that the film growth kinetics is almost controlled by the passivity-like behavior below 150. And, of course, this is very much related to the mechanical behavior suggested by Ms. Smialowska. So, I think that the understandings of the amorphous nature or crystal nature of the structure of passive film as it depends on temperature is very important, I think.

BULLEN: Okay. Bullen, Board. Just to follow up on that. So, I guess the kinetics issue with respect to temperature is important, but if you had a longer period of time, would you expect to see similar types of changes in the mechanisms at lower temperature or you think it's actual fundamental mechanistic change? Susan, do you want to try that one?

SMIALOWSKA: Can you tell me what kind of material did you study because it's, I guess--because it is very--this 150 threshold, it is the change of the iron oxide from magnetite to hematite. So, of course, this might be because this, you have--

SHIBATA: Yes, I think that it's mainly the ion system. Yes.

SMIALOWSKA: Mainly this is because you change from one oxide film to another. So, it is nothing--

BULLEN: Not a good comparison?

SMIALOWSKA: Yeah.

BULLEN: Okay, thank you. But, with respect to your mechanical changes in the film, would you expect to see differences at different temperatures?

SMIALOWSKA: Let me think. Yes, I will. But, this is not how you can prove that you have mechanical changes. You can prove only when you keep the condition constant. It means rather high potential because, another way, you will not see nothing.

BULLEN: You won't see anything.

SMIALOWSKA: But, below this transpassive potential--so you have to do the experiments this way, that you have to be sure that you do experiments also to find what elements you have in the solution. Okay? To be sure that you have no transpassive dissolution. And, if you will take this kind of potential, then, of course, the time of aging should be much more shorter. And, if you will keep this for a long time, I expect that you will see some differences in the property of the passive film. Maybe, I am wrong, but I think you will.

BULLEN: Okay. Thanks. Dr. Kruger?

KRUGER: I have a question about these mechanical effects and I don't know the answer, but in these very thin films, you know, we're talking about 10 to, say, 20, 30 nanometers. I've always thought that developing stresses in such thin films is a very difficult thing to do. That you really can't talk about mechanical effects in such thin films. I may be wrong, but certainly with thicker films--

SHIBATA: I think that such thin films, of course, some stresses are generated and, of course, if you increase the temperatures, there is more thick film, thicker films--

KRUGER: Thick films, yes, absolutely. But, thin films, I don't know. Maybe you can, but it seems to me that it's very difficult to develop stresses in such thin films.

SMIALOWSKA: It will be difficult, but not impossible. Let's put it this way. The film which is flexible and not very--which will not go to very easy mechanical breakdown, there will be film which is hydrated. If you have this other, this hydrite layer on the oxide film--it would be double layer--then it will be much more difficult. But, when you are doing the experiments at a higher potential, the hydration is much less--and you will have just oxide only. And, in oxide, this mechanical breakdown could go much easier. So, if you will prepare, for example, oxide film using just high temperature oxidation. Yes? And then, put to the solution, then you have breakdown of the film, at once. Very easy.

KRUGER: Well, easy to get stresses and--

SMIALOWSKA: Yes. But, it is not necessary to have very --thick oxide film.

KRUGER: But, oxide films formed in aqueous solutions by electrochemical means are different than--

SMIALOWSKA: Yeah, it's completely different. I think it is possible to check this, you know. It might be just that nothing would happen, but this a rather easy experiment and so why not check?

KRUGER: Some experiments have been done, incidentally, many, many years ago by Vermillier, but looking at rather thicker film.

SMIALOWSKA: I don't remember Vermillier, but he did experiments--

KRUGER: And, Leach also did some.

SMIALOWSKA: Yeah, but he make experiments on the passive film, anodic films.

KRUGER: Thick films, yes, yes, anodic films on aluminum, titanium, things like that.

BULLEN: Okay. Dr. Strehblow?

STREHBLOW: It seems to me that this discussion is also showing the two opinions of a more simpler homogeneous film concept which has been used up to, let's say, five years ago and the further information about atomic resolution methods which show the details of such a film. Very often, you have stresses, let's say, between crystalline film and its substrate because the fit is not, at all, good and then the system reacts by faceting. We have studied this with Phillipe Marcus on the oxide film on copper, but he has also studied this with other systems. The situation was such that, let's say, in the case of the copper oxide, the epitaxial relationship between the copper 1 oxide and the copper metal substrate on a 1-1-1 orientation of a single crystal was not, at all, perfect. And then, the system reacts by a very interesting and nice-looking efaceting and so it overcomes this stress. If you have a stress, then perhaps you have faceting or slipping steps and so forth. And, if you study these systems and if this has been perhaps done with these methods for all these various systems which are of interest to this audience, then you might get an answer and further insight.

SMIALOWSKA: But, you know, I do not think that it is such a big difference between these different points of view how to study because, of course, when you are studying something in atomistic scale, then it's fine. You'll know what is going on exactly. Then, when you are doing these in microscopic scale, then you have many of these events on the forces and you measure some kind of film. Okay?

STREHBLOW: I didn't want to say that you should do one thing and not do the other. You should both and both concepts are not wrong, they are constructive to each other. That's what I wanted to say.

SMIALOWSKA: That's okay.

BULLEN: Thank you. Gustavo, did you have a comment?

CRAGNOLINO: It was only a clarification to the comment of Jerry Kruger. The experiment that he was referring to was Bupar (phonetic) and Vermillier was experiments done with films of the order of few nanometers in aluminum and other metals and tantalum--to try to discover what of the film were brittle or ductile, but subject to microscopic deformations. I mean, I think that the regime that we have to discuss here, in some way, is a different type of regime, a much more lower stress level and other --.

KRUGER: That's my point actually. I wasn't saying there were not stresses. I was just posing the question.

NEWMAN: May I just say something?

BULLEN: Roger, go right ahead?

NEWMAN: Roger Newman. Also in that Bupar and Vermillier (phonetic) paper, they found that when you anodize tantalum and you pull it, the film changes color (laughter) and it goes thinner. Remember that? That's one of the observations that have never been explained by anybody.

BULLEN: Bullen, Board. Does it turn blue?

NEWMAN: It depends.

BULLEN: Oh, okay. Thank you.

We still have one member of the panel to hear from and that's Digby MacDonald. He sat at the wrong end of the table after lunch. So, he gets the final say of the go-around. You can take out your viewgraphs now. So, Digby, can you give us your summary?

MACDONALD: I want to address the first question because I knew it was an important question. I actually did some calculations on it.

I showed you this morning by using a point defect model and a mixed potential model, you can predict the corrosion potential. So, the question is then what can I do to the oxygen reduction reaction in order to get the corrosion potential to exceed the potential for transpassive dissolution? Is there anything I can do?

Well, I can change the partial pressure of oxygen that will change the concentration of oxygen. And, by the way, this model assumes a very thin electrolyte film of saturated sodium chloride on the surface and it takes into account salting in and salting out and all those nice effects.

Well, the model also predicts the transpassive dissolution behavior. Let me just show you this one which I calculated current voltage curves as a function of pH. This branch up here is hydrogen evolution. This branch down here is oxygen reduction. Here is the passive current, here. Then, the model predicts that there's a sudden jump at this potential here which corresponds to the potential at which the oxidation state of chromium changes from 3 to 6, corresponding to dissolution as the chromate species. So, the question then is what can I do to the oxygen reduction reaction that will displace the potential of the -- ?

And, the origin of that effect also comes out of the point defect model. What happens when you change the oxidation state from 3 to 6, the model literally predicts the film disappears or becomes very thin. Okay? There's a sudden decrease in the thickness of the film. So, now, the potential just below that which is distributed across the film now becomes distributed across the interface where it affects a dissolution reaction. That's why there's a sudden increase in the rate of the dissolution reaction.

Well, it turns out that in order to displace the potential above the transition to the transpassive state, you need a partial pressure of oxygen somewhere between 100 and 1,000 atmospheres. That's the prediction. Okay? And, obviously, you're not going to have that. Okay? So, that doesn't seem to be likely.

There is, however, another possible way of doing this and that is what if you introduce something to the exchange current density? Is it possible to do that? And, unfortunately, I didn't bring those calculations with me. But, the answer to that question is no. There's nothing that I can conceive of doing to the exchange current density that would raise the exchange current density by the many orders of magnitude necessary in order to displace the potential above that transpassive potential. You have to go up 6, 7, 8 orders of magnitude. And so, I did those calculations for the specific reason that there are small concentrations of lead and mercury, but in particular lead, in this water. And, it's well-known in electro catalysis, that small crystallites of lead oxide on a surface is a quite good electro catalyst for the oxygen reduction reaction. But, even recognizing that, you'd have to move the exchange current density for oxygen reduction too much in order to get the potential above.

So, my personal opinion is that transition to the transpassive state is probably highly unlikely.

BULLEN: Allison?

DAVENPORT: Davenport. Digby, did you consider the transpassive dissolution of molybdenum?

MACDONALD: No. No, this is just purely chromium.

DAVENPORT: How much lower might that be? Do you have any feel for that?

MACDONALD: That's a good question and, in fact, I could put that in. In calculating the potential at which the transpassive dissolution process starts, I assume that chromate is in equilibrium with chromic oxide. Because you need a chromate activity in the thin oxide--in the thin liquid film in order to calculate the equilibrium potential. So, I assumed that there is equilibrium between chromate species and chromic oxide and oxygen in the air. From that, I can calculate the equilibrium potential and then applying the second law of thermodynamics, of course, potential has to be above that equilibrium potential in order to get dissolution.

And, one last thing, if I can, Allison, before I-- this plot here, we have good reason to believe that the calculated thickness of the barrier layer should extrapolate back to the equilibrium potential; in this case the chromium/chromic oxide equilibrium potential for the prevailing conditions. We found that that holds true for zinc and it appears to hold true for iron. In other words, for iron, if you measure the thickness of the passive film, it seems to extrapolate back to something that's close to the equilibrium potential for iron magnetite. And, certainly, zinc, that works very well. It extrapolates back to zinc, zinc oxide. Oh, and also for tungsten.

KRUGER: Looking at the Pourbaix diagram for chromium and molybdenum, you find that the potential where molybdenum becomes soluble is much, much lower.

MACDONALD: Is much lower, right. Right.

DAVENPORT: And, the other comment following up on that is you can also get transpassive dissolution of chromium when you've just got a little bit of band bending at the surface to produce just a little bit of chrome 6 actually at the surface layer.

MACDONALD: Yeah. Yeah, you know, this is sort of a semi-equilibrium argument. And, you could also argue that because you've got an inhomogeneous surface, there might be parts of the surface that have a different equilibrium potential for the chromic-oxide-chromate reaction than other parts of the surface. So, you know, this is a first order approach to that.

BULLEN: Roger and then Susan, please?

NEWMAN: Roger Newman. I guess, you weren't considering peroxide, right, because that would completely change the picture?

MACDONALD: Well, you could put peroxide--in fact, this model, its genesis goes all the way back to the model developed for calculating corrosion potentials in nuclear reactors, where, in fact, you do have hydrogen peroxide and the whole slew of radiolysis products. And, yeah, you know, the hydrogen peroxide question is a very interesting one, although I haven't done the calculation. Hydrogen peroxide being a much stronger oxidizing agent than oxygen, having a much more positive standard potential. It conceivably could shift the potential up. The only problem I have with it is that the decomposition of hydrogen peroxide is catalyzed by transition metal ions and it's catalyized very strongly. So, you know, whether you could get a significant concentration of hydrogen peroxide in that thin liquid film is problematic

--

NEWMAN: Some of the transition metal ions, because they would be complexed by fluoride in this environment, I think would be inactive for--I think fluoride is a stabilizer of peroxide.

MACDONALD: It could very well be. I think you'd need to get the concentration of--I'm just guessing at this point because I haven't done the calculation--but, I think you'd need to get the concentration of hydrogen peroxide up to well-above one molar.

NEWMAN: Well, I can tell you that at pH 11 and with 200 parts per million peroxide, stainless steel goes blue (laughter).

MACDONALD: Okay.

BULLEN: Susan, do you have a comment?

SMIALOWSKA: I wanted to ask you did you measure the exchange current density for all your experiments?

MACDONALD: No, we've taken values that we had measured previously on stainless steels. However, I do have in that pile of slides--and I'm sure you don't want to see it--data from Moscow. Part of the program--this is the NERI program, the Nuclear Energy Research Initiative program which is the other half of what I did. This model here was developed for Jerry Gordon and his folks. But, the NERI program is a joint effort between SRI International, me, and George Engelhard who is now at OLI Systems and also the Frumkin Institute of the Russian Academy of Sciences. A lot of experimental data are being measured in Moscow on C-22 and we actually have now quite a body of data on the kinetics of oxygen reduction, hydrogen evolution, and--

SMIALOWSKA: They measured the exchange current density for all these temperatures and--at partial pressure of oxygen?

MACDONALD: Right. And, hopefully, by the end of that program, you know, we'll have a significant database for that.

BULLEN: Gustavo?

CRAGNOLINO: Could you put back the plot that you have the thickness of the barrier layer?

MACDONALD: Thickness of the barrier layer?

CRAGNOLINO: Yes. I was surprised about the number, but I don't see well from here.

MACDONALD: Okay. This is 20 angstroms here.

SMIALOWSKA: 20 to 50.

BULLEN: Digby, before you leave, I actually have to call upon someone in the audience. Somebody from the University of Western Ontario, please, stand up back there, David Shoesmith, and maybe address a couple of issues. First, maybe the hydrogen peroxide issue, and secondly, maybe you could resolve some of the issues with respect to the ions that were identified in the Simms work? I mean, that was one of the questions that was raised.

SHOESMITH: Okay, yeah, sure.

BULLEN: Go ahead and address both, please. Identify yourself, too.

SHOESMITH: Yeah, I'm Dave Shoesmith from the University of Western Ontario, but I should confess also that I'm a consultant to the Yucca Mountain program so that you know where I'm coming from.

I just wanted to address the issue that's come up over radiolysis or radiation effects. We have reviewed that. It's been studied well on many materials in many different countries; Germany, Canada, Switzerland, Sweden, and the United States. It's not proven to be a particularly large effect. The dose rate level at which it was found to be effective on a reactive material like carbon steel was about 300 rad an hour and that was George Marsh in England. The present expected dose rate on the waste container for Yucca Mountain is about 1400 rad an hour at which level you should see no effect on passive materials based on the evidence from stainless steel, titanium, and some nickel alloys. The approximate half life is roughly about 50 to 75 years which means it should go down by a factor of 2 in less than 100 years. So, over a few hundred years, this should decay to effectively an insignificant level.

To put that into context with hydrogen peroxide, a dose rate of 10^4 rad an hour, which is approximately what you expect on this container, the models would predict about 10^{-5} or less moles per liter of hydrogen peroxide. So, it should go down from that level even if you wet the waste container in the beginning. Now, people have tried to simulate the radiation effect by adding hydrogen peroxide to experiments with passive materials and the only time they could find a shift in the corrosion potential to a more positive value is if they went to 10^{-1} moles per liter which is somewhere between 10^6 and 10^7 rad per hour equivalent dose rate. So, I don't think that there is a reason to believe that there will be significant hydrogen peroxide concentrations from radiation dose fields.

MACDONALD: If for some reason you had a G value, radiolytic yield value, that could give you a high concentration, I think the decomposition reaction would--

SHOESMITH: That's a good point. We studied in real detail on fuel because when you get inside the waste container, the radiation effect becomes more important. Where we're having a real problem is the models predict if you take a G value of 1, which is what the model would give you, all our experiments will tell us that all we can measure is something which is 2 orders of magnitude less than that.

We attribute most of that to a decomposition process which may be catalyzed by all the impurities which exist in your solution by glass surfaces, by all the properties of the surface itself. So, I'm having a real problem finding that the radiation dose rate effect is significant even at the model prediction level. It appears to be well-below that.

BULLEN: Roger Newman, go ahead?

NEWMAN: I'm sure your numbers were correct there, but I can certainly assert, if that's the right word, that one part per million hydrogen peroxide will significantly ennoble the open circuit potential of stainless steel in a whole variety of oxygenated solutions. So, I'm not sure where that 10^{-1} moles per liter comes from. That doesn't sound right to me.

SHOESMITH: Well, this comes from work by George Marsh and Bob Glass, both on stainless steel, who saw no effect on the corrosion potential at those high concentrations.

NEWMAN: Well, I mean, it's well-known in a variety of industrial contexts that once the hydrogen peroxide concentration gets to a few parts per million that it will dominate oxygen as the main thing determining the corrosion potential. Now, whether it goes transpassive, I--

SHOESMITH: Well, I have to argue with you, Roger, because we see exactly the opposite effect on uranium dioxide where the decomposition of the hydrogen peroxide leads to oxygen being the oxidant, not hydrogen peroxide. The oxidant dominates in that particular case. Now, that is a catalytic surface for decomposition of peroxide.

I just wanted to also address the point about the blue film. You can see that on titanium in hydrogen peroxide roughly around the 200ppm that you mentioned and there is an enhancement of corrosion rate which is roughly a factor of 2 to 3 in that particular case over the short term. In the long term, they tended to accumulate salts in the porous deposits which tended to block the corrosion of the titanium.

NEWMAN: Well, the reason is completely different in that case. In the case of titanium, the peroxile, if that's the right word, the hydrogen peroxide anion, HO_2 minus, is complexant. It forms a stable, soluble complex with titanium. So, that's a different effect from something which is due to the peroxide acting as an oxidant on the corrosion process. But, I guess I'll just have to agree to disagree with you and suggest that we go and do the experiment because I think my colleagues in a certain large British-Dutch company that makes soap powder would strongly disagree with any assertion that low levels of peroxide don't affect the corrosion potential.

SHOESMITH: Is the difference between us the pH? Are you talking extremely alkaline solution?

NEWMAN: This is mainly in the high pH environments, yeah.

SHOESMITH: Okay.

NEWMAN: And the blue stainless steel is--that only happens in high pH environment.

SHOESMITH: Yeah. Most of these observations are from pH 10 down that I'm talking about.

NEWMAN: Well, yeah, it could be quite critical as to what the pH is, but I think a little competitive experiment would be in order there (laughter).

SHOESMITH: I just wanted to address also the issue of the deposition of radiation energy directly in the oxide film. There is a difference between light and gamma radiation. It's about three orders of magnitude difference in energy. So that the efficiency you get for depositing the energy from light to form hole-electron pairs is quite efficient. For gamma radiation, it's orders of magnitude less efficient because the energy is too high to deposit as it goes through the thin film. We think we see this on uranium dioxide. We can't be certain. Which means that you need a much higher gamma dose rate to see the production of hole-electron pairs than you do a light intensity.

BULLEN: Thank you, David. Gustavo had a question or a comment. Go ahead?

CRAGNOLINO: I have a comment on the dilution data that is reported by precisely the DOE regarding this issue of the additional hydrogen peroxide. In what is called in the table that Jerry Gordon presented before, the saturated, no, the simulated concentrated water at 25 degree, the corrosion potential increased from -230 to -40 millivolt in the silver silver chloride scale is -275 to -85 in calomel with the addition of 72 part per million of hydrogen peroxide.

SHOESMITH: I was unaware of that result.

CRAGNOLINO: And, in the acidified condition, that is because there was this question of low pH, they increased from -80 to 150. In the silver silver chloride-- means -125 to 105 in the calomel that we are more familiar with. 345 millivolt difference in between the two scales with the same addition of 72ppm. We have measured these using precisely long ago the effect on Alloy-825 by using 5ppm. That was the number that came from the Glass and Konynenbeurg calculation, and we got increase of about 200 millivolt, roughly, of these.

SHOESMITH: That's really at odds with other published numbers.

CRAGNOLINO: Yeah. This is what--to put in context this, the problem is that is it going to be a stable hydrogen peroxide peroxide system or, as Digby suggests, is it going to decompose? And I think that this is what we never able to sustain this value for a long period of time.

NEWMAN: --oxide by decomposition. I remember there was something about one of those studies. I don't remember whether it was the Marsh one or the Glass one, which was a little fishy, and I would have to look that up. Am I allowed to use the word "fishy" in this?

SHOESMITH: Ariani's data showed that the effect of 10 to the 6th rad an hour improved the passivity on titanium.

BULLEN: Thank you, Dr. Shoesmith.

Alberto, did you have a few questions?

SAGÜÉS: I have a question, two questions for Digby. The second one applies to just about everyone. The first one is specific to the point defect model projections, which by the way, some of us are very glad to see that the project indeed is making attempts to obtain quantitative treatment, although we all know like in any other model, there are items open to discussion and interpretation. But, Digby, in the most recent calculations that you showed, what kind of steady state passive current densities is the model predicting? Like in this one, they were using it to look at the transition.

MACDONALD: Well, I actually fit the current density to experimental values--

SAGÜÉS: I guess they cannot hear you.

MACDONALD: I actually fit the model to the current density. So, you know, it's not fair to use the model to predict the current density.

SAGÜÉS: Okay. So then you're taking experimentally--

MACDONALD: Even I'm not that blatant.

SAGÜÉS: So you're assuming then current densities. Of which order are those?

MACDONALD: 10 to the minus 8 amps per centimeter squared at room temperature.

SAGÜÉS: Okay.

MACDONALD: About 5 times 10 to the minus 8 at 120 C.

SAGÜÉS: So those are fairly high passive current densities compared to the ones that may an order of magnitude greater.

MACDONALD: Well, this is pH 3. But pH doesn't seem to make a heck of lot of difference.

SAGÜÉS: pH doesn't seem to make too much of a difference. What I'm saying is that that may pull down your open circuit potential, and I'm wondering if that would affect the point at which your transpassivity would kick in. Because if you have a much leaner passive current, that would work together with the oxygen couple and send the potential higher up; right?

MACDONALD: If it's much lower, it will cause a small, relatively small shift in the corrosion potential in the positive direction.

SAGÜÉS: Okay. The second question is something that you and I have discussed on a one on one basis like a couple of years ago. But I think that it is very important to the overall question of long-term extrapolation. And I don't know, my personal impression is that if someone would tell me, would show me a piece of naturally existing material from a meteorite or maybe an artifact where someone, say, 5000 years ago by mistake cast a chromium iron alloy and it would show us this shiny piece of material that happened to have been exposed to a moist environment, not in an Egyptian tomb where everything is nice and dry, and say, hey, this thing is passive, look, we're looking at it and, darn it, here is a 5000 year old or a 50,000 year old or a 5 million year old passive layer, and this is what has been, you know, on top of it we have some blue stuff, and so on and so on. Well, I think that that would change, at least for some of us, that would change dramatically the nature of the question of using a passive material for very long-term engineering applications.

And the question that I'm asking you is can you think of anything that has been passive for a very long period of time, beyond the 100 years or so time frame that we could use? And I think that a couple of years ago, you mentioned something that many people wouldn't think that was perhaps passive material. We're talking about, for example, iron corroding in a regular moist environment.

MACDONALD: Well, I mean, there's that famous needle structure in India; right? What's that called? That has an exceptionally low corrosion rate. I would say that's--and that's been around for a few hundred years.

SAGÜÉS: Although one could argue that that's actually very slow active corrosion in the active regime, and not necessarily passive.

MACDONALD: One could maybe debate that point. You know, unfortunately, we don't have native chromium around. Chromium is too active. I'm not even sure where there's any native nickel. Is there native nickel around?

SAGÜÉS: There are iron/nickel alloys naturally occurring. It's called Josephinite. And that material is available as the native alloy. Whether that is present in the natural environment in a passive state, or it has been in a state of very low active dissolution, is another question. And that's something that is being investigated by a number of -- or by a few people right now.

But what I wanted to ask you specifically, and also

I would like to ask if there is any member of the panel here who may have an inkling of something that may have remained passive for extremely long periods of time.

MACDONALD: Okay, let me see if I can answer that as follows. In many situations, the passive film on a metal is in a metastable state. And you can see that from the Pourbaix diagram. In fact, it's in your explanation of Faraday's famous experiment. In about 1830, or sometime, Faraday carried out his famous experiment of placing a piece of iron in nitric acid and finding that it didn't dissolve, and then--in concentrated nitric acid--, repeated the experiment, and I actually looked it up in an encyclopedia, by the way, and he put the same piece of iron in dilute nitric acid, and it dissolved.

And, of course, the concept of acids had only recently have been developed, and he didn't have a pH meter or didn't have a reference electrode or anything like that, so he made a guess that the surface had been oxidized. Okay? But what he didn't know, and of course this had to wait until Marcelle Pourbaix created his potential pH diagrams, and I'll draw it for iron, we commonly label this as the stability region of iron, and this as the stability region of magnetite, Fe_2O_3, and even now you'll see people saying, aha, this is the potential, this is the pH. Aha, we've got a point here, it's active dissolution. Well, that, of course, is not true, because Faraday was actually up here somewhere in the concentrated nitric acid, and it didn't dissolve.

And the reason for that is that if you extrapolate this line here, that extrapolation of the iron/magnetite line into this stability region gives you the condition for the formation of magnetite as a metastable phase on the surface. Provided you're at a potential above this dotted line, magnetite can form as a metastable phase. Okay? Whether it does form or not depends upon the kinetics; the rate of formation versus the rate of dissolution. And that's where a lot of our passive materials operate. They operate with metastable passive film.

So, you know, passivity is a somewhat tenuous phenomenon, looked at that way, but nevertheless, it appears to be quite effective for many systems.

NEWMAN: You're sure it's not the second line?

MACDONALD: I'm sorry?

STREHBLOW: Shouldn't it be the stability between the formation of iron 3 oxide gamma Fe2O3 from magnetite, which is then causing the metastable situation?

MACDONALD: Yeah, if I extrapolate this line here--

STREHBLOW: I think the Pourbaix diagrams in this regard are even misleading, because, Digby, because it is a question of kinetic stability, and not of thermodynamic stability.

MACDONALD: Oh, no, it's metastability.

STREHBLOW: You call it metastable. I would call it kinetic stability because of dissolution rate or transfer rate of cations into the electrolyte is so extremely slow.

MACDONALD: The correct term is metastability. It's a metastable film. Okay? And if the rate of dissolution is high enough the phase disappears, passivity disappears.

STREHBLOW: Magnetite will dissolve immediately, and I think this goes back way in the Fifties, that Fetta (phonetic) tried to find even the magnetite formation by transient measurements, and he was not successful because FE304 is dissolving immediately.

MACDONALD: The rate of dissolution of magnetite has been measured under these circumstances, and it's on the order of about .01 angstroms per hour. And at the same time, of course, you're forming magnetite at the metal/film interface. And so the magnetite layer moves into the metal.

STREHBLOW: It is there, and then FE304, you have to--you need it, otherwise you would dissolve the whole thing, and then you have active dissolution.

MACDONALD: No, it's a metastable film.

BULLEN: Bullen, Board. We could actually--Susan, do you want to comment?

SMIALOWSKA: I would like to say that if you would like to have the metal with good oxide film take tantalum. You will not have dissolution in acid, not dissolution in neutral, not dissolution in alkaline.

BULLEN: Okay.

MACDONALD: But the point I want to make is that, you know, this is the region where the film is thermodynamically stable. It doesn't necessarily mean it will produce a passive surface, because passivity is a kinetic term. Okay? It describes a kinetic situation. It doesn't describe a thermodynamic situation.

And, of course, you are able to use iron based alloys, chromium based alloys under conditions where the oxide is not thermodynamically stable, because it forms as a metastable phase. And that led to my remark that passivity is a somewhat tenuous phenomenon, but it seems to be very effective. After all, we have a metals based civilization.

SAGÜÉS: Yes. Well, the society is going to have to make the decision as to how tenuous this type of phenomenon is, because it's a tremendously important decision that would affect our energy future. And one of the reasons we're having this meeting is partly to establish how tenuous and how useful, even if it is tenuous, it may be. I appreciate your comments.

BULLEN: Dr. Davenport had one small one she said, small.

DAVENPORT: I just don't think we should get too carried away with Pourbaix diagrams and thermodynamics here, because if we look at the passive film on iron, the stuff that we've done show that it isn't, you know, hematite or magnetite, as you've shown there, it's a different phase. So I think we should take all of this with a bit of a pinch of salt, and I think we should--

MACDONALD: But the principle is correct.

DAVENPORT: Yeah. But I think that what's going to really affect things is the dissolution of the films. We do have to look very carefully at the kinetics there.

MACDONALD: Yeah, but the principle is correct. Passivity is not a thermodynamic term. It's a kinetic term. It can occur because of a thermodynamically stable film, or a metastable film.

BULLEN: Alberto, did you have a brief comment?

SAGÜÉS: No.

BULLEN: Okay. Well, we may want to continue this over some fermented beverages a little later on this evening.

But I would like to turn the microphone over to Professor Craig. And even though we have no one signed up for public comment, we still have to ask on the record if we have public comment. And you can do it from your seat, or you can go to the podium, whichever you'd like. Paul?

CRAIG: There's something else I can do, however, prior to doing that.

BULLEN: Oh, go right ahead. I gave the meeting to you, Paul.

CRAIG: Since my hand was up, albeit not very far, a moment ago. By the way, do we have people who want to speak? Let's do that. Are there members of the public here who wish to speak?

(No response.)

CRAIG: All right. The formal part of the public is now completed. There are none. This means we have another 15 minutes, so I'll make my--so we have 15 minutes to talk before we break.

BULLEN: You get ten.

CRAIG: And I want two of them.

I've been listening to this discussion all day, and I'm absolutely fascinated, and I perhaps understood 10 percent, although in an examination, perhaps it would turn out to be only 5 percent. Nevertheless, I did have some impressions, and I want to express those impressions in the form of what will become a hypothesis, which perhaps you will challenge.

Dr. Sagüés gave two examples where he thought people would probably agree. One was on steel, and the other was on a noble metal in a Yucca Mountain type of oxidizing environment.

We've also heard from time to time about copper in a reducing environment, which is being proposed in Sweden, for example. And a nice thing about copper is it's thermodynamically stable and it exists in nature for periods in excess of a billion years.

During the conversation today, many, many questions and issues were raised about C-22. I did not see that there was a strong consensus that this is a material that passes a test as easily as the iron, noble metal and copper tests just mentioned. That didn't seem to be the case. Nor did I see clear guidelines for extrapolation. The kind of theoretical underpinnings that apply in copper didn't seem to emerge in the course of the conversation.

What did emerge was that issues, a number of, many different mechanisms, some proposed previously, some new ones that could cause problems, a clear statement that the chemical environment matters enormously, and the kinds of things that might build up on the surface might matter enormously. The cycling of various sorts might matter, and that there is an absolute necessity for consistent and superb manufacturing, both of the material itself and for the fabrication of the welds.

Now, scientists will, of course, disagree about almost anything. That's one of the things that makes science fun. What we're concerned about is when the differences really matter. And the hypothesis that I want to lay out is the differences that we heard about today are at a level of significance that it's not clear to me that the optimistic conclusions that Gerry Gordon laid out in the slide that he showed you, which was from a presentation to this Board a couple of months ago, that those observations and the confidence associated with those observations is consistent with the message which I'm hearing from this panel. My hypothesis is that in fact those conclusions are not consistent with the message that's coming out of this panel.

Perhaps I'm wrong in this, but in any event, this is a hypothesis that we can perhaps discuss at some point.

BULLEN: Thank you, Paul.

Any members of the panel want to respond to Paul's comments? Dr. Davenport?

DAVENPORT: Yes, you may be getting an overly pessimistic view from today's discussions, because effectively, what we've been charged with is coming up with possible ideas to suggest what could conceivably go wrong.

And so I think we're not--I mean, I think Roger made the point that he wouldn't mind having one in his back yard, but here are a few things that might go wrong. And I think that may sum up a lot of our attitudes here. So you may be getting an overly pessimistic view, because we're trying to be a bit creative in coming up with ideas about what might go wrong.

MACDONALD: And I'd just like to add that I think the prediction business is in better shape than what you probably would have concluded from today's discussion. I mean, we have been able to predict, you know, corrosion damage in nuclear reactors and the heat transport circuits quite accurately.

CRAIG: There have also been quite a few surprises in the nuclear reactor metals business.

MACDONALD: Yeah, that's because they don't use our methods.

BULLEN: Alberto, do you have a comment?

SAGÜÉS: Digby, I think that your statement that you have been able to predict the damage quite accurately is well substantiated. You have a verified prediction. What you indicated about being able to predict quite accurately the damage evolution in nuclear reactors is well substantiated. The difference between that and the task that we have, that the project has at hand, is I think one of time frames. We are talking in your case about predictions in a time frame which is in the order of years or decades, and a time frame that permits verification of the prediction, contrasting the predictions. We're talking here, however, about a time frame of unprecedented magnitude, and that I think is the part that demands more caution.

MACDONALD: Let me just put that up again. Okay? Where I see the greatest, probably the greatest problem at the moment, is specifying the future conditions.

I went out to Livermore and listened to some very fine scientists, geologists and geochemists talking about the conditions that will exist within Yucca Mountain. And, you know, those conditions are calculated on the basis of very large models, very sophisticated and complex models. But I'm just unsure as to how accurately you can actually predict the conditions.

Now, what is heartening in this whole thing is that the corrosion rate is only weakly dependent upon a number of parameters. Okay? Potential and pH, in particular, and temperature. So, provided that weakness in those dependencies remains, then we can probably withstand considerable uncertainty in the exact path that the repository is going to evolve along, and come out with a reasonable prediction.

So, that's where I see one of the major problems. It's in this one, the last bullet here, that the path to the future state is continuous and can be specified. That's an absolutely essential caveat on deterministic prediction of anything.

BULLEN: Roger?

NEWMAN: Are you sure you meant that corrosion is weakly dependent on different parameters? You're talking about general corrosion then?

MACDONALD: Yes, I'm sorry, I'm talking about general corrosion.

NEWMAN: Okay.

MACDONALD: But it's not even clear, and in fact in the NERI program, you know, we've been wrestling with the question how do we actually predict what form of corrosion is going to occur. And it's conceivable that over the lifetime of this repository, there might be various forms of corrosion occur at different times. And the question is how do you predict that path? That's a pretty tough thing to predict.

BULLEN: Do we have any more comments from the panel? And having no questions from the audience, I'd like to, before we close, express my appreciation to all the panel members for their patience and their preparation for this meeting. Some of you traveled great distances to get here, and I realize that we're in a time zone that's probably put you at about 3:00 in the morning, and I do appreciate your ability to stay focused and to address the issues.

We will reconvene. We're going to recess right now. We will reconvene tomorrow morning at 8:30 to address question number two.

I want to tell the panel members that we are going to reconvene our panel at the same room we had breakfast this morning at 6 o'clock tonight. So, the panel has about 40 minutes, and we will reconvene in the room we had breakfast this morning.

Thank you very much, and we'll see you tomorrow morning.

(Whereupon, the meeting was adjourned, to be reconvened at 8:30 a.m. on July 20, 2001.)