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Proceedings of the U.S. NRC/EPRI/ANL Heated Crevice Seminar

Held at
Argonne National Laboratory
October 7-11, 2002

U.S. Nuclear Regulatory Commission
Office of Nuclear Regulatory Research
Washington, DC 20555-0001

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J. Davis, NRC Project Manager

Abstract

An international Heated Crevice Seminar, sponsored by the Division of Engineering Technology, Office of Nuclear Regulatory Research, U.S. Nuclear Regulatory Commission, Argonne National Laboratory, and the Electric Power Research Institute, was held at Argonne National Laboratory on October 7-11, 2002. The objective of the seminar was to provide a working forum for the exchange of information by contributing experts on current issues related to corrosion in heated crevices, particularly as it relates to the integrity of PWR steam generator tubes. Forty-five persons from six countries attended the seminar, including representatives from government agencies, private industry and consultants, government research laboratories, nuclear vendors, and electrical utilities.

The seminar opened with keynote talks on secondary-side crevice environments associated with IGA and IGSCC of mill-annealed Alloy 600 steam generator tubes and the submodes of corrosion in heat transfer crevices. This was followed by technical sessions on (1) Corrosion in Crevice Geometries, (2) Experimental Methods, (3) Results from Experimental Studies, and (4) Modeling. The seminar concluded with a panel discussion on the present understanding of corrosive processes in heated crevices and future research needs.

FOREWORD

This seminar was co-sponsored by the Nuclear Regulatory Commission, Argonne National Laboratory, and the Electric Power Research Institute and was held at Argonne National Laboratory on October 7-11, 2002. This seminar provided an exchange of information on corrosion in heated crevices in steam generator tubes of pressurized water reactors. Much of the corrosion that occurs in steam generator tubes occurs in crevices created at the top of the tube sheet and at tube support plates on the secondary side of the steam generator.

The seminar started out with a keynote address on the environments found in heated crevices and how they contribute to intergranular corrosion and stress corrosion cracking of steam generator tubes. The keynote address was followed by four technical sessions: (1) Corrosion in Crevice Geometries; (2) Experimental Methods; (3) Results from Experimental Studies; and, (4) Modeling. Forty-five persons from six countries attended the seminar.

The Steam Generator Tube Integrity Program has been ongoing for the past several decades. The previous work concentrated on quantifying and improving in-service inspection reliability and on development of methods for predicting failure pressures and leak rates for degraded steam generator tubes under normal, accident, and severe accident conditions. The current program will continue the work on improved inspection techniques but will place more emphasis on the degradation of steam generator tubes on the secondary side of the steam generator in crevices. Key to the understanding of the degradation processes is better knowledge of the physical and chemical conditions within crevices. The purpose of this seminar was to gain an understanding of the state-of-the-art of crevice conditions and the corrosion that occurs as a result of those conditions. The long term goal is to use the results of the crevice studies to predict the behavior of steam generator tubes under field operating conditions.

Carl J Paperiello, Director
Office of Nuclear Regulatory Research
United States Nuclear Regulatory Commission

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The Heated Crevice Seminar was sponsored by the Division of Engineering Technology, Office of Nuclear Regulatory Research, U.S. Nuclear Regulatory Commission, Argonne National Laboratory, and the Electric Power Research Institute. and was hosted by Argonne National Laboratory. The seminar was organized by Jangyul Park of Argonne National Laboratory and Keith Fruzzetti of the Electric Power Research Institute. Roger W. Staehle of Staehle Consulting assisted with the program development.

Additional administrative assistance was provided by Denise Moores, Zhongquan Zhou, David Kupperman, Jonathan Meagher, Marianne Adair, and Joan Brunsvold, all of Argonne National Laboratory. Dwight Diercks of Argonne National Laboratory recorded the meeting minutes.

Meeting Agenda

October 7 (Monday) 6:00 pm – 8:00 pm Registration and Reception

Meeting for session chairmen and keynote speakers at 8:00 – 8:30 pm.

October 8 (Tuesday) 8:30 am – 5:30 pm Technical Session

Topic: Corrosion in Crevice Geometries Chairman: W. J. Shack

Presentations: 8:30 am – 10:30 am

An Overview of Recent French Studies of Possible Secondary Side Crevice Environments Causing IGA/IGSCC of Mill Annealed Alloy 600 PWR Steam Generator Tubes [Keynote Talk]	P. M. Scott [Framatome-ANP] F. Vaillant [EDF R&D]
Approach to Predicting Corrosion of SG Tubes Based on Quantifying Submodes of SCC in a Statistical Framework [Keynote Talk]	Roger W. Staehle [University of Mennesota]

Discussions: 10:30 am – 12:00 pm

Topic: Experimental Methods Chairman: K. Fruzzetti

Presentations: 1:00 pm – 3:30 pm

Heated Crevice—Design, Experimental Methods, and Data Interpretation [Keynote Talk]	Jesse B. Lumsden [Rockwell Scientific] Keith Fruzzetti [EPRI]
Experimental Simulation of Crevice Chemistry Evolution	C. B. Bahn [Seoul National Univ.] S. H. Oh [Seoul National Univ.] I.S. Hwang [Seoul National Univ.]
Experience of heated crevice experiments at Studsvik	H.-P. Hermansson [Studsvik Nuclear AB] A. Molander [Studsvik Nuclear AB] P.-O. Andersson [Ringhals AB]

High Temperature pH Probes for Crevice/Crack Tip Solution Chemistry Applications—A Preliminary Study [Not attending paper included in proceedings]	R. Srinivasan [Tohoku University, Japan] Y. Takeda [Tohoku University, Japan] T. Shoji [Tohoku University, Japan]

Discussions : 3:30 pm – 5:30 pm

October 9 (Wednesday) 8:30 am – 5:30 pm Technical Session

Topic: Results from Experimental Studies **Chairman: F. Vaillant**

Presentations: 8:30 am - 10:30 pm

Limits to Crevice Concentration Processes [Keynote Talk]	Allen Baum [Bechtel Bettis, Inc.]
My Conclusions after 25 Years of Model Boiler Testing [Not attending paper; presented by A. Baum]	Jacques Daret [CEA]
Inferences Regarding PWR SG Crevices from Model Boiler Results [Keynote Talk]	Jeff A. Gorman [Dominion Engineering, Inc.]

Discussions: 10:30 am - 12:00 noon

Presentations: 1:00 pm – 3:30 pm

Laboratory Experiments on Steam Generator Crevice Chemistry	P. V. Balakrishnan [AECL] G. L. Strati [AECL]
The Hideout and Return in a Sludged Ringhals TSP Crevice	P.-O. Andersson [Ringhals AB] A. Molander [Studsvik Nuclear AB] J. Chen [Studsvik Nuclear AB] P. Gillen [Studsvik Nuclear AB]

Experimental Study of Concentrated Solutions Containing Sodium and Chloride Pollutants in SG Flow Restricted Areas	D. You [CEA-Saclay] S. Lefevre [CEA-Saclay] D. Feron [CEA-Saclay] F. Vaillant [Electricite de France]
Some Effects of Steam Generator Deposits on Crevice Chemistry	Chuck Marks [Dominion Engineering, Inc.]
Evaluation of the Effect of Startup Oxidants on the ECP of a Crevice Filled with Deposits	Jesse B. Lumsden [Rockwell Scientific] Al McIlree [EPRI]

Discussion : 3:30 pm – 5:30 pm

October 10 (Thursday) 8:30 am – 5:30 pm Technical Session

Topic: Modeling **Chairman: Peter King**

Presentations: 8:30 am – 10:30 pm

Mechanisms for Concentrating Impurities at Line Contact Tube Support Crevices in PWR SG's [Keynote Talk]	Peter Millett [iSagacity] Dennis Hussey [iSagacity]
Hideout and Hideout Return in PWR Steam Generators: Predictions of Crevice Chemistry [Keynote Talk]	Steve Sawochka [NWT Corporation]

Discussions: 10:30 am - 12:00 noon

Presentations: 1:00 pm – 3:30 pm

Status of EPRI Software Tools for Evaluating Crevice Chemistry	Tina Gaudreau [EPRI]
Modeling and Analysis Supporting Argonne Model Boiler Facility Development	Kenneth E. Kasza et. al. [Argonne National Lab]
Numerical Modeling of Steam Generator Crevice Thermal-Hydraulics	Stephen Bajorek [USNRC] Donald Helton [USNRC]

Application of Chemical Equilibrium Model to the Evaluation of Magnetite-Packed Crevice Chemistry	C. B. Bahn [Seoul National University] I. H. Rhee [Soonchunhyang University] I. S. Hwang [Seoul National University]
The Conditions Known to Produce Crevice Corrosion by the *IR* Mechanism and Those Yet to Be Investigated [Not attending paper included in proceedings]	Howard W. Pickering [Univ. of Pennsylvania]

Discussion: 3:30 pm – 5:30 pm

October 11 (Friday) 8:30 am – 12:00 noon Technical Session

Panel Discussion **Chairman: Roger Staehle**

Panel : Session Chairmen, Keynote Speakers, and Others

Topic:

Integrated View of Prediction of Properties of Line Contact Crevices

Needed Research to Develop Predictive Methodologies for Heated Crevices and the Related Phenomena

What Useful Analyses should be Performed for Field Crevice Samples from SGs and How?

Summary and Integration, Conclusion and Future Direction

LIST OF PARTICIPANTS

Per-Olof	Andersson	Ringhals AB
Chi Bum	Bahn	Seoul National University
Stephen M.	Bajorek	U.S. Nuclear Regulatory Commission
Poyilath (Bala)	Balakrishnan	Atomic Energy of Canada Limited
Allen J.	Baum	Bechtel Bettis, Inc.
Stephen P.	Chambers	U.S. Department of Energy
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James A.	Davis	U.S. Nuclear Regulatory Commission
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Dan	Duncan	Lockheed-Martin/KAPL
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Tina	Gaudreau	EPRIsolutions
Jeffrey A.	Gorman	Dominion Engineering, Inc.
Donald M.	Helton	U.S. Nuclear Regulatory Commission
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Ken	Kasza	Argonne National Laboratory
Peter J.	King	Babcock & Wilcox Canada Ltd.
David S.	Kupperman	Argonne National Laboratory
William T.	Lindsay, Jr.	Lindsay and Associates
Jesse B.	Lumsden	Rockwell Scientific
Saurin	Majumdar	Argonne National Laboratory
Charles R.	Marks	Dominion Engineering, Inc.
Allan R.	McIlree	EPRI
Peter	Millett	iSagacity
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Denise	Moores	Argonne National Laboratory
Joseph	Muscara	U.S. Nuclear Regulatory Commission
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Michael A.	Switzer	U.S. Nuclear Regulatory Commission
Francois J.	Vaillant	Electricite de France
Glenn A.	White	Dominion Engineering, Inc.
Zhongquan	Zhou	Argonne National Laboratory

Location of Seminar:
Argonne National Laboratory, 9700 South Cass Avenue, Argonne, Illinois 60439 U.S.A.

Minutes from Heated Crevice Seminar by D. R. Diercks

Tuesday, Oct.8

Roger Poeppel (ANL): Welcomed attendees and gave a brief review of ANL involvement in nuclear energy and LWR work in particular.

Keith Fruzzetti (EPRI): Briefly reviewed goals and objectives of seminar and described seminar format and structure.

Joe Muscara (NRC): Reviewed NRC-sponsored programs on SG tube integrity. Noted that two previous programs did not consider mechanistic aspects of SCC in SG tubes. Stated that this is a goal of the present SGTIP-3, and we must therefore understand crevice conditions (both chemical and physical) in SGs. The principal objective of the current SGTIP-3 is to understand past problems in Alloy 600 and provide the knowledge base needed to avoid these problems in Alloy 690. Thanked ANL and EPRI for organizing seminar.

Roger Staehle (U. Minn.) Discussed structure and format of seminar. He noted that first crevice corrosion seminar was held in 1996 at Studsvik in Sweden, and a follow-on seminar was held there in 1998. Proceedings exist for both seminars but they have limited availability. Peter Millett (then of EPRI) had committed to organizing the next seminar in this series. At the same time, ANL was expanding its research work in this area. Therefore ANL and EPRI combined to organize the present meeting. Staehle felt that the ultimate objective of the present meeting is to outline the process for developing the bases needed to predict the corrosion performance of heated crevices, such as those in nuclear SGs.

Jangyul Park (ANL): Reviewed the meeting mechanics and, in particular, the use of the question and answer sheets,

Session 1: "Corrosion in Crevice Geometries" [W. J. Shack (ANL), Chair]

"An Overview of Recent French Studies of Possible Secondary Side Crevice Environments Causing IGA/IGSCC of Mill Annealed Alloy 600 PWR Steam Generator Tubes,"

by P. M. Scott F. Vaillant (Framatome-ANP) and F. Vaillant (EdF—R&D)

The first half of the paper was presented by Vaillant and the second half by Scott. [Note that Vaillant used several overheads that were not included in the handout. These overheads appear to be from May 8, 2002 SG Conf. in Canada.]

Following the Vaillant and Scott paper, there was a general discussion of the likelihood of "dry" crevices and the consequences of such crevices. Some questioned the ability of H to concentrate in such a crevice, in view of its high diffusivity. Note however, that the diffusion distance to the crevice is much shorter from the primary water than to the secondary water . It was argued that H must be produced at a very high rate in the crevice in order to maintain a meaningful H inventory there. Scott noted that, in view of the extremely fine porosity (1-2 nm) and smallness of the crack openings (≈100 nm), flow of liquid phase with impurities in and out of crevices and the associated cracks would appear highly unlikely. Scott asserted that detailed experimental studies are needed to define the nature of the crevice phase.

Bill Lindsay raised a point about Scott's use of the Kelvin equation correlating the vapor pressure of liquid droplets with droplet size. Lindsay stated that his recollection of this correlation was that the vapor pressure increases with increasing curvature for convex surfaces (as in a liquid droplet) but decreases with increasing curvature for concave surfaces (as for the meniscus of a liquid phase in a pore). [Lindsay later added that checking Adamson's text ("Physical Chemistry of Surfaces, Wiley, NY, 1997, pp. 53-54), the recollection is correct, but experimental evidence for the effect in capillaries is mixed. It is possible that surface tension itself may be affected for thin films in very small diameter capillaries.]

Scott closed the discussion by stating that there is a critical need for model boiler tests in which the H concentration in the vapor phase is measured particularly in plugged crevices, i.e., the potential is determined.

"Approach to Predicting Corrosion of SG Tubes Based on Quantifying Submodes of SCC in a Statistical Framework," by Roger Staehle

In the question and answer period, Joe Muscara asked what Roger's timeframe was for completing his predictive model for SCC in heated crevices. Staehle responded that he hoped to have the basic quantitative features of the model completed by the end of calendar year 2003.

Dan Duncan (KAPL) asked if the model would become more complicated if the various submodes of corrosion turned out to be not completely independent. Staehle responded that he believed the submodes to be independent, but if they were not, the model would have to deal with this complexity.

Bill Shack asked the effect on the model if the crevices are filled with steam rather than liquid phase, as most have assumed in the past. Staehle responded that that would mean that much of the existing laboratory data, most of which were obtained in liquid phase, may not be applicable. However, he had to use the data available in formulating the structure of the model. Ultimately, the model and its various components would have to be validated using the real field data, rather than simply fitting the existing laboratory aqueous data.

Jesse Lumsden (Rockwell) asked what the crack propagation mechanism was in the steam plus impurities phase. Staehle answered that this was uncertain and was a subject for ongoing research.

Bill Lindsay noted that if corrosion is assumed to be an electrochemical phenomenon, then ionic mobility was required. This would appear to require the presence of at least some liquid phase in the crevice. Staehle added that the electrochemical potential also appeared to be important in the corrosion process, and this again implied the presence of some liquid phase. However, Scott noted that SCC can occur by non-electrochemical processes, e.g., H cracking or in situ grain boundary oxidation.

Peter King (BWC) asked if we can determine whether the crevice phase was liquid or vapor by conducting laboratory experiments under both conditions and determining which results most closely reproduce reality.

After lunch, the discussion continued on the nature of the corrosive environment at the crevice and the evolution of that environment with time. Allen Baum (Bettis) stated that important processes with respect to corrosion are those that occur while the crevice is plugging. This, for example, is when Pb and other low soluble corrosive species are apparently introduced. Lindsay noted that in a model boiler test, the crevices are generally filled with sludge before the test is started.

Ken Natesan (ANL) noted that the Staehle modeling approach breaks the SCC process into various submodes. He asked if there was a hierarchy of submodes and whether beta in the Weibull statistical description varied with submode. Jeff Gorman (Dominion Engineering) stated that beta was typically 3 to 4 for field data, but could be higher for some specialized situations. Staehle responded that the value of beta varied somewhat with how you analyzed the data, and variations in beta were possible. He felt that the central problem was developing an understanding of the initiation process, what the dominant submode(s) were in complex environments, and the effect of sulfides and Pb, for example.

Baum asked that, assuming the local environment at the tube surface is superheated steam, how is that environment modified with time? Gorman responded that, based on the fact that cracks occur over long lengths of tube sheet and TSP crevices in plants, the introduction of impurity species appears to contaminate the entire crevice, and all the steam becomes doped steam, with cracking occurring more-or-less uniformly along the crevice length. Lindsay wondered whether impurity species might migrate into the crevice and replace the pure steam.

Peter Millett (iSagacity) stated that another critical point was whether the boiling point can be elevated sufficiently that steam can be present in equilibrium with liquid phase containing the concentrated corrosive species. King noted that even if the crevice is filled with steam, it is not necessarily dry steam, since it is probably in equilibrium with liquid phase whose boiling point has been raised by high levels of dissolved impurities. Scott was not sure this was true, since extremely high levels of dissolved impurities were required to raise the boiling point sufficiently.

Baum then proposed that, in general, the crevice probably contains superheated steam at the center of the crevice, steam in equilibrium with liquid near the edges, and liquid phase outside the crevice. The relative sizes of the various zones varies with the steam generator design and operating conditions.

Scott suggested that in situ oxidation generally precedes actual cracking. This process can occur without other impurities, but cracking is generally greatly accelerated by impurities.

Session 2: “Experimental Methods” [K. Fruzzetti (EPRI), Chair]

“Heated Crevice—Design, Experimental Methods, and Data Interpretation,” Jesse Lumsden (Rockwell Scientific)

In question and answer period, Jiaxing Chen (Studsvik) asked how the dissolved OH^- species was identified in the Raman spectrum. Lumsden responded that it was the only reasonable possibility, since there were no other impurities in the feedwater.

Lindsay asked whether Lumsden’s experiments were at sufficiently high temperatures that NaOH and water were completely miscible. Lumsden responded that he was not sure. [Lindsay later added that NaOH and water are completely miscible at temperatures at and above the melting point of pure NaOH, 318.4 C (605.1 F).]

“Experimental Simulation of Crevice Chemistry Evolution,” Chi Bum Bahn, Seoul National University

There were a few questions of clarification.

“Experience of Heated Crevice Experiments at Studsvik,” H-P Hermansson (Studsvik) and A, Molander (Ringhals AB)

In response to a question from Ken Kasza (ANL), Molander stated that the heat flux at the crevice was ≈40% of full power, or <20 watts/m^2. He also stated that the crevices were concentric.

In the second half of the talk presented by Hermansson, Baum asked if all the results presented were electrical heat input. Hermansson responded that they were, both for the unfilled and filled crevices.

Gorman proposed that, in a heated crevice, we would like to be able to predict the pH and potential relative to the H stability line and whether the crevice is dry or wet. Baum agreed, but noted that the crevice is, in his opinion, generally a two-phase environment. It can be difficult to characterize this environment in terms of a singe parameter with respect to pH and potential.

In the following general discussion, Staehle observed that the magnetite packing used in heated crevice experiments appears to be different from that in the plants. Lumsden agreed, noting that the packing in experiments is particles while the magnetite in the plant is a monolithic “brick.” However, he noted that packed particles in his experiments typically turns into a brick over the course of the experiment.

Staehle asked whether we should therefore reformulate the magnetite in these experiments, perhaps adding silica, for example. He asked how fast the porosity in the packed magnetite is filled up, since this relates to how fast the porosity is closed off.

Forrest Hundley (Southern Nuclear) observed that, in operating plants, consolidation of the deposit does occur, as evidenced by the loss of thermal performance. Staehle asked whether this would then imply that cracking should slow down and stop with time. Baum responded that this was not necessarily so, since the hostile environment in the crevice was sealed in by the non-porous deposits at the ends. Staehle then asked if the pH would be buffered by the magnetite, thereby again inhibiting cracking. Steve Sawochka (NWT) thought this would not be expected.

On the subject of deposit consolidation, Andersson observed that porosity data from Dampierre indicated deposit porosity in the range of ≈5-30% or more, depending upon location. Tube pulling forces were very high, indicating a solidified deposit.

King noted that the tubes in Lumsden's experiments cracked in times much shorter than those in observed in the field, even though the test conditions were ostensibly prototypic. Rich Eaker (Duke) responded that the conditions were not necessarily prototypic. Sawochka concurred and stated that field conditions were too variable to permit extrapolation of laboratory results like Lumsdens's with respect to the rate at which cracking would be expected to occur.

Staehle asked whether Lumsden should be considering more experiments in the mid-pH range and under more complex impurity conditions. Lumsden responded that he felt that the logical next step was to use more complex chemistries, but to add the impurity species one at a time to maintain a well-controlled experiment.

Shack suggested that the point of Lumsden's experiments was to get results for simple chemistries that agree with the models. The logical next step was to try somewhat more complex chemistries and see whether the results are still predictable. King agreed, observing that there was no need to go to line-contact experiments right away, for example.

Staehle expressed doubt that crevice chemistry was the same for line contact as for a drilled hole geometry. He noted that French work indicated that the hideout returns for drilled holes were significantly different than for line contact geometries. King again urged that the variables should be changed one at a time, and the line contact could be considered after more complex chemistries have been explored.

Allan McIlree (EPRI) inquired about correlating crack growth rates with electrochemical noise. Lumsden said that he had some limited success in doing this. Staehle then asked about correlating crack growth rates in plants with chemistry. Gorman stated that this had been tried to some extent, with little success, and Sawochka observed that, in general, crack growth rate data could not be obtained from operating plants. King felt that this was something that needed to be done.

With the objective of successfully predicting cracking behavior Staehle summarized by stating that the consensus of the group was that we should (1) look at mid-range pH conditions while slowly varying the chemistry to more complex environments, (2) defer the consideration of line-contact geometries to later, and that (3) we need crack growth rate data, especially for the mid-range pH situations.

The first-day's proceedings were adjourned.

Wednesday, October 9: Session 3: "Results from Experimental Studies" [F. Vaillant (EdF), Chair]

"Limits to Crevice Concentration Processes," A. Baum (Bettis)

"My Conclusions after 25 Years of Model Boiler Testing," Jacques Daret (CEA) [presented by A. Baum]

In the question and answer period, Staehle noted that in a number of experiments, Pb tended to end up at the metal-oxide interface. He asked where it ended up in the CEA AJAX tests that Baum described. The answer was that it was not clear, though it tended to not to be in the crevices.

"Inferences Regarding PWR SG Crevices from Plant Operating Experience," J. A. Gorman (Dominion Engineering)

Suat Odar (Framatome-ANP) corrected a point in Gorman's presentation, noting that, including four replacement steam generators and the Angra station, there are 22 PWRs with steam generators having Alloy 800 NG tubes, not 17 as stated by Gorman. He added that a total of two tubes in all of these steam generators had experienced damage. One of these tubes experienced IGA/IGSCC plus pitting and the second had pitting alone.

Steve Chambers (DOE-NR) asked whether the use of phosphate chemistry in the early operation of Japanese plants had any influence on subsequent cracking experience. Gorman responded that there was no obvious effect, but Baum observed that some of these plants experienced subsequent TSP corrosion, apparently associated with increased impurity ingress into the cleaner crevices resulting from the early phosphate water chemistry. (See the response by Gorman to Chamber's written question)

Gorman noted that the overall point of his first presentation was that a large plant experience data base exists that can and should be used to calibrate models developed for crevice corrosion.

"Inferences Regarding PWR Steam Generator Crevices from Model Boiler Results," J. A. Gorman (Dominion Engineering)

In the question and answer period, Baum observed that in tests with 2 ppm sulfates and 1 ppm Pb, for example, throughwall cracking was observed in ≈4 years. However, tests conducted with these levels of hydroxide to produced throughwall cracking in days. He noted that, as a practical matter, resins seem much less able to lead to cracking than caustic.

Kasza asked whether there was a quantitative process for determining whether a concentration process in the crevice was hydraulically or thermally driven. Baum responded that there was not; this must be determined from the details of the experiment. Millett added that there can be a transition from one mode to the other over time in a given crevice.

Kasza then asked for a clarification of Baum's statement that crevices are thermally driven. Baum responded that this statement applied to drilled holes on the hot side.

Chambers expressed surprise over an earlier statement by Baum that Pb was not responsible for much crevice ODSCC. Gorman stated that he did not put much faith in conclusions regarding the role of Pb, since laboratory techniques for detecting Pb have not been sufficiently sensitive until rather recently.

Staehle observed that Alloy 600 MA material usually cracks intergranularly, so the "fingerprint" for Pb-assisted SCC is not transgranular, as some have suggested. He noted that Pb typically ends up next to the metal at the OD interface with the oxide, and the oxide must be stripped away to see it. He added that Pb is seems to concentrate at the crack tip as $PbO_x^=$ in the alkaline state and as Pb^{+2} in acidic environments, in agreement with theory. The extent of Pb-induced cracking is very pH dependent, and it is most aggressive in the alkaline region. He asserted that, in the extreme case, virtually all cracking could, in principle, be associated at least in part with Pb. The reality is that Pb effects are not well understood, and more research is needed. No dedicated facilities for Pb-cracking studies exist, since no one is willing to contaminate their system with Pb.

Hundley noted that plant operators all know that Pb is bad and they work to keep it out of the plant. Why do research to confirm what plant operators already know? Staehle responded that the biggest question is why Pb is not causing everything to crack in the short term. We need to understand how it is tied up and thereby disabled by other impurities and under what circumstances it can be re-released.

Damien Feron (CEA) agreed that Pb must be reduced as much as possible. However, Millett noted that it will always be present at the ppt level in the bulk coolant, because it is introduced into the system as a tramp impurity in the other materials of fabrication. It cannot be reduced below this level as a practical matter.

Staehle then observed that chemical cleaning may be a potential problem in that one cannot be sure if it is removing Pb or instead removing the impurities that are tying the Pb up. However, Odar observed that chemical cleaning has been observed to remove the sources of Pb and to result in reduced levels of SCC in the tubes. His opinion is that chemical cleaning is beneficial in that it removes the sources of Pb.

"Laboratory Experiments on Steam Generator Crevice Chemistry," by P. V. Balakrishnan and G. L. Strati

In the question and answer period, Baum asked how the sludge is held in place in the AECL apparatus and what the crevice dimensions are. Strati responded that the sludge is held with a SS frit at the bottom and that the crevice dimensions are variable. In answer to a question from Sawochka, she stated that the Na/Cl ratio in the crevice was near unity. Sawochka wondered why $Mg(OH)_2$ was identified as a precipitate in AECL run no. 177, since the reported Na/Cl ratio suggests that the crevice is acidic.

"The Hideout and Return in a Sludged Ringhals TSP Crevice," by P.-O. Andersson (Ringhals) et al.

In the question and answer period, Andersson responded to a question from Gorman by stating that the Na^{24} tracer used was in the form of a carbonate. The pressure in the tubes was ≈200 bars. Feron noted that the French had reported similar results from the CLARINETTE loop at the Breckenridge Conference.

"Experimental Study of Concentrated Solutions Containing Sodium and Chloride Pollutants in SG Flow Restricted Areas," by D. Feron et al.

In the question and answer period, Gorman asked for a clarification of Feron's statement that " hideout return is not the opposite of hideout." Feron answered that the hideout/hideout return process is not completely reversible. Lindsay commented on this by noting that he had always been suspicious of attempts to calculate what was in the crevice by running MULTEQ backwards.

"Some Effects of Steam Generator Deposits on Crevice Chemistry," by C. R. Marks (Dominion Engineering)

"Evaluation of the Effect of Startup Oxidants on the ECP of a Crevice Filled with Deposits," by J. Lumsden (Rockwell Scientific)

Staehle asked whether Lumsden had considered the reduction of sulfates by hydrazine. Lumsden said that he was looking into that, but there was no evidence of reduction in the crevice so far.

Zhongquan Zhou (ANL) asked whether the ECP was stable at pH = 10 in deaerated water. Lumsden responded that it was stable.

In the general discussion of the papers from the afternoon session, Staehle reiterated that the biggest issue with Pb was immobilizing it. He said that we have identified many of the appropriate species, but we don't understand how they work or under what conditions the Pb is released. Gorman added that Pb levels in the deposits were typically in the range of 100-1000 ppm in the crevice, while the bulk water Pb level required to cause IGA/SCC is ≈0.1 ppm.

McIlree stated that the destructive examination of tubes from the Farley 1 SG may have characterized the crevice deposits with respect to Pb, but he was not sure of the details offhand. Marks stated that the Farley 1 results were included in the Dominion Engineering analysis, but he had no numbers for Pb. McIlree then added that Pb had also been found in the Thane 1 crevice samples in Belgium, and the researchers at Laborelec were very surprised.

Staehle noted that if Cu is added to a Pb-containing environment, cracking is enhanced according to some data. This appears to be an ECP effect, but it has not been well characterized. He also wondered why Pb usually ends up at the metal-oxide interface. Eaker noted that Duke had detected Pb at this interface in samples from Oconee through the use of EDF high resolution XRD analysis, since this technique penetrated the oxide film to the interface. Staehle noted that this segregation to the interface had been seen in several French plants as well as at Oconee.

Jeff Sarver (McDermott) noted that Pb appears to be reactive with Cr, based on C-ring tests. Staehle added that Pb also appears to be extremely aggressive in the steam phase over caustic solutions thereby producing severe SCC even in Alloy 690 TT in laboratory tests. It is not clear why, although we know that Pb has strong effect in breaking down the passive film.

McIlree noted EPRI-sponsored work by Lumsden on attempts to crack Alloy 600 with Pb additions. They found that 1.5 molal sodium sulfate solutions with silica, alumina, and magnetite additions and 50 ppm Pb did not crack Alloy 600. This may be because this Pb level is in balance with the sulfate additions. The next experiment will be to add excess Pb in an attempt to produce cracking.

Staehle noted that C. Laire at Laborelec has shown that phosphate ions can immobilize Pb very effectively. The important point is that Pb is one of the few species that can readily crack Alloy 690 TT. We need to understand why.

Gorman than brought up the effects of S species and their possible influence on cracking. He wondered whether we are wise or unwise in pushing for high hydrazine, since hydrazine appears to react with S species (i.e., it reduces sulfates). Vaillant agreed and noted that the French program was looking at the question of optimum hydrazine levels. Staehle added that in cracking involving Pb, sulfides are also commonly found in the cracks.

Andersson asked what is meant by high and low hydrazine. Gorman responded that anything above 100 ppb was high and 25 ppb or less was low. Andersson noted that these levels won't affect the potential, and Eaker agreed.

Eaker then asked which S specie or species should be tested. Staehle responded that several S species have similar deleterious effects, but those with +2.5, 2.0 and -2 valences appear to be the most aggressive. Species with the +4 and +6 valences are more benign. Eaker than asked about the relative volatilities of these species, and Staehle responded that he was not sure.

The second day's session adjourned.

Thursday, Oct. 10: Session 4: "Modeling" [P. King (BWC), Chair]

"Hideout and Hideout Return in PWR Steam Generators: Predictions of Crevice Chemistry," by S. Sawochka (NWT)

Following Sawochka's presentation, there was a general discussion of the uncertainties and limitations associated with the hideout return methodology.

Tina Gaudreau (EPRI Solutions) asked about the use of chloride additions (molar ratio control) to change crevice chemistry and pH. Sawochka responded that these additions are effective and have been used at Farley, for example, to achieve near-neutral pH values in the crevices, based on hideout return data.

Baum contended that we should not place too much importance on molar ratio control, since he is somewhat leery of the of hideout return data for predicting the chemistry in the hottest crevices in the steam generator. Sawochka responded that the industry believes in hideout return as a basis for determining crevice chemistry. Baum wondered whether it might introduce a false sense of security. Hundley stated that the utilities were not suffering from any false sense of security, since steam generators were so expensive and SG problems were so pervasive. The utilities feel that a sound basis exists for the hideout return methodology.

“Mechanisms for Concentrating Impurities at Line Contact Tube Support Plate Crevices in PWR SG’s,” by P. Millett (iSagacity)

Chen asked whether the parameters in equation for crevice chemistry can be verified from hideout data. Millett responded that the diffusion coefficients from hideout data are of the right order of magnitude, but they tend to be averaged values.

In the ensuing general discussion on the modeling of crevices, Duncan observed that one can successfully model the individual features of crevices, but it is very difficult to link them together in an overall model. On the other hand, one can validate the overall results of a model, but it is difficult to validate the individual components. For the case of the sludge deposits, one has the problem that in trying to accelerate the process of sludge buildup in an experiment, the deposits built up are typically not prototypic.

King stated that the utilities are asking what the applicability and practical significance of these models are to their situation, i.e., how can they be used at the operating plant? Sawochka concurred and added that, from the utility point of view, the primary objective is to keep the SGs operating. How does modeling help? Is it the most cost-effective approach, particularly in view of the difficulty in getting the required fundamental data? Hundley further commented that the utilities need to make the SGs last and keep them operating at 100% power. The utilities don’t want to repeat the mistakes that have destroyed SGs in the past. If modeling is to be relevant, it must help toward these objectives.

Millett felt that the evolution of the crevice chemistry is a very important consideration in modeling, and Feron added that, to accomplish this, one must couple chemistry, hydraulics, and heat transfer. There was general agreement that deposits, particularly at the point of line contact, are very important, and the deposition process is very difficult to model.

“Status of EPRI Software Tools for Evaluating Crevice Chemistry,” by Tina Gaudreau

Zhou asked what the advantage of MULTEQ was over competing softwares for determining water chemistry. Lindsay responded that MULTEQ is overseen and accredited by a distinguished committee of experts on water chemistry. The code is very widely used and has been shown to be quite stable. In a related question, Chen asked how useful MULTEQ was in a practical sense. Gaudreau responded that MULTEQ is built extensively on past experience and incorporates ongoing developments in the area of water chemistry,

Staehle asked whether MULTEQ considers the mixed Fe-Cr and Fe-Ni oxides in its analysis. Gaudreau replied that it does not at present. Lindsay added that MULTEQ does not treat solid phases of variable compositions, which would include the mixed oxides. He stated that the standard MULTEQ consists of three basic parts: (1) a data base, (2) a chemical equilibrium calculator, and (3) simulation programs. Staehle then asked how many Pb compounds were accounted for in MULTEQ and Gaudreau answered that ≈7-9 such compounds were included.

“Modeling and Analysis Supporting Argonne Model Boiler Facility Development,” by K. E. Kasza (ANL)

Lindsay suggested that a downcomer on the secondary side of the model boiler might be useful to define the circulation pattern in the boiler, but Kasza replied that it was not felt to be needed. Baum expressed further concern about adequate coolant mixing on the secondary side.

Staehle then asked whether the holes in the crevice simulators were to be broached or drilled, and Kasza replied drilled. Staehle then observed that the flow velocity on the secondary side has an important effect on the formation of deposits in the crevice region.

In response to a question from Molander, Kasza stated that model boiler incorporated features to permit control of ammonia and hydrazine levels on the secondary side. A number of questions were asked regarding the measurement of temperature, pH, potential, and chemistry in the crevice region.

With respect to the ANL modeling of the crevice heat transfer process, Sawochka and Duncan stated that in an actual SG crevice, one has multiple nucleation sites for bubbles in the crevice deposit. They wondered how relevant it was to model an idealized single-site nucleation process. Duncan added that under high-pressure, one gets very tiny bubbles with frequent departures. In addition, local temperature fluctuations are large and have a high cyclic frequency.

“Numerical Modeling of Steam Generator Crevice Thermal-Hydraulics,” by S. Bajorek (NRC)

Duncan observed that the CFD codes required to perform the desired modeling will require a very great amount of effort and time to adapt to this analysis. Baum added that the problem being solved was intellectually interesting, but the industry is much more interested in flow in a packed crevice. Eaker added that an eccentric crevice was of more interest than the concentric crevice being considered here. Bajorek responded that his approach was to start with a simplified and more tractable problem and then eventually extend it to more prototypic situations.

“Application of Chemical Equilibrium Model to the Evaluation of Magnetite-Packed Crevice Chemistry,” by C.-B. Bahn

Lindsay expressed reservations about using the HSC Chemistry Code for the analysis described. He suggested redoing the analysis with MULTEQ and comparing the results. Zhou added that her experience with HSC Chemistry Code has not been particularly good, and she recommended that the results be checked experimentally, if possible.

Feron questioned how applicable the modeling was, since the system described did not appear to be at thermodynamic equilibrium. Chen added that the mass transport in and out of the system also appeared to indicate non-equilibrium conditions. However, Lindsay stated that he felt that a code like MULTEQ could be used here, since the system appeared to be at ionic equilibrium. Complete thermodynamic equilibrium is not essential.

Odar stated that it was not possible to transform magnetite to hematite in the solid state, as the model had assumed, since the two phases have different crystallographic structures. One must instead dissolve the magnetite and then precipitate hematite. Finally, King observed that the results of the analysis do not appear to be consistent with the Pourbaix diagram for the system, and he expressed further doubts about the adequacy of the HSC Chemistry Code.

In the ensuing general discussion on the Modeling Session, Staehle began by asking just what problem we are trying to model. He stated that we should be primarily interested in the formation of the deposit and its properties. He suggested that there were two types of approaches, namely the heat-transfer, fluid dynamics approach and the morphological deposition approach. In view of our limited resources, and, in particular, the limited availability of model boilers, he questioned what our priorities are.

Baum broke the crevice attack problem down into three phases: (1) the buildup of the deposit, which is a thermal-hydraulic problem, (2) the development of the chemical environment in the pores of the crevice, which is a chemical problem, and (3) the impact of the local environment on the corrosion process, which is a metallurgical problem. He suggested that a multi-disciplinary approach was needed to attack the problem effectively.

Sawochka suggested that we think about what was achievable in a realistic time frame, since the industry needs guidance in the relatively near term. Their biggest question is how long they can operate before they form deposits at line contact point crevices. He stated that there was no interest in the drilled-hole geometry. He felt that we had a reasonable understanding of deposit formation, and he felt that we know how to perform the appropriate heated-crevice experiments. However, we must know more precisely what the corrosion people need to analyze or model the corrosion problem. He felt that the model boiler design proposed by ANL was not amenable to looking at the crevice deposition problem.

Lindsay stated that in past model boiler experiments, the deposition step was typically omitted by pre-packing the crevice with deposits. He didn't feel that line-contact crevices were all that different from drilled holes—we still expect to get deposits in either case.

Staehle observed that we see great variability in the cracking behavior of drilled-hole SGs in terms of time to cracking. For a line-contact crevice, which appears to be less constrained, he speculated that we might see even more variability. Lindsay speculated that perhaps there would be less variability, since the crevice has more exposure to the bulk water.

Staehle predicted that we would begin to see increased cracking of Alloy 690 TT tubes in the field in the future, and he felt that we must be more proactive in anticipating and dealing with these failures before they become a major problem.

King wondered about the critical depth of deposits required to lead to cracking and how long it takes to get to this depth. He felt that this was the critical question. Baum added that he felt that model boiler tests, as opposed to isothermal tests, are essential to obtaining a detailed understanding of the cracking problem.

Hundley stated that, from the utility's point of view, they need to know when and how often they should perform chemical cleanings to stay out of trouble. Millett added that the industry needs engineering solutions rather than rigorous scientific analyses, and the level of precision required by industry might well be attainable through modeling.

Baum suggested that Byron and Braidwood Units 1 versus Units 2 might be the ultimate model boiler experiment for quantifying the benefit of thermally treated tubing, since the tubes cracked in Units 1 while those in Units 2 did not under presumably similar operating environments.

Gorman suggested that it might be useful to consider the Alloy 800 operating experience. Many of these tubes have operated for more than 20 years. These crevices have surely built up substantial deposits by now, and yet cracking is virtually unknown. Why? Baum then suggested that we should compile the most relevant data from operating plants. Staehle added that we should look the deposits in operating SGs.

Muscara noted that the NRC was supporting modeling work to predict the onset of tube cracking. He suggested that operational assessment was the next step. We know that we cannot completely avoid cracking, so we must learn to minimize it and live with it. He asked how we could optimize the ANL model boiler.

Hundley wondered how one extrapolates model boiler results back to the conditions in an operating SG. He felt that the model boiler results were likely to be either far too conservative or much too optimistic. The past experience of the utilities in attempting to use model boiler data, e.g., on the use of inhibitors, has not been particularly successful.

The session adjourned.

Friday, Oct. 11: Panel Discussion (R. W. Staehle and A. Baum, Co-chairs)

Roger Staehle began by stating that the principal objective of the panel discussion was to “bring things back into focus.” He then handed out a proposed agenda for the discussions.

Alllen Baum then opened the first portion of the discussion with a short presentation.

Gorman began the discussion by inquiring about the nature of the cracking seen in the Alloy 600 TT tubes at Seabrook. McIlree replied that the cracks were short and separated by ligaments. He said that even if they were 99+% throughwall, they would not threaten the pressure integrity of the SGs.

McIlree then noted that if Alloy 600 or 690 TT tubes were properly processed at the mill, in principle there should be no residual stresses present to drive cracking. At Seabrook, however, they found that the tubes were re-straightened after the TT heat treatment, thereby introducing residual stresses. It seems likely that other TT tubing is out in the field with similar residual stresses. He wondered if we could develop NDE techniques to detect residual stresses in tubes in the field or to determine if the TSP lands were becoming active crevices.

Jim Davis (NRC) then commented that the Seabrook tubes appeared to have a MA metallurgical microstructure rather than a TT microstructure. McIlree observed that there is a great variation in TT microstructures, and some in fact resemble the MA microstructure. He stated that one cannot judge SCC resistance from the microstructure. The response of the microstructure to the heat treatment appeared to depend upon the C level. Gorman added that EDF experiments indicate that ≤ 0.033 wt. % C was needed to obtain the expected microstructural response to the TT heat treatment.

Davis noted that cracking had also been seen in Alloy 600 TT at a Korean plant, and Baum and Diercks (ANL) said that this was the Kori 2 plant. McIlree added that again the microstructure did not have the appearance normally associated with the TT heat treatment. McIlree said that we must assume that there are other "poor" TT microstructures in the field, and we must control residual stresses and environment in these plants to avoid cracking. He felt that most, but probably not all, of the plants with Alloy 600 TT tubes have low residual stresses.

Staehle observed that the highest stresses in SG tubes are typically at the top of the tube sheet. He suggested that perhaps our focus on chemistry at the line contact region of the tube sheets might therefore be somewhat misplaced. If we could somehow reduce the residual stresses from tube manufacture and SG fabrication, we might not have to worry so much about the operating environment. However, this does not seem likely. He agreed with McIlree that perhaps the use of NDE techniques to detect residual stresses in tubes in the field should be looked into further.

Duncan suggested that we should determine if there is a small population of high stress tubes in service that need to be followed more closely. Baum said that his earlier model boiler work focused on tube sheet joints, where the residual stresses were highest. Nevertheless, that one incident of ODSCC in Alloy 600 TT tubing was in a TSP crevice rather than a TS crevice.

Staehle then suggested that another important consideration is to figure out how to lengthen the time between inspections. He also noted that, in laboratory tests, both Alloy 600 TT and 690 TT can be cracked in environments not greatly different from those in service. He wondered why they are not cracking in service in significant numbers. Finally, he stated that we must be proactive in anticipating failures in Alloy 690 TT. We need to do the research now so that we are in a position to prevent failures in the field. As a part of this, we need to do research to enable us to conduct credible operational assessments.

Duncan stated that in addition to lengthening the time between inspections, we must make decisions about appropriate inspection intervals in the case where we have an existing crack. We therefore need crack growth rate data under the relevant conditions.

Muscara said that regulators must take the position that undetected cracks exist in the field, and these cracks must be properly dealt with. He also noted that should not totally shift our emphasis away from the TSP region, since conditions for mild denting exist there and even this mild denting can lead to cracking.

Gorman agreed that crack growth rate data are essential for doing a proper operational assessment. He also noted that the subject of mild denting at the top of the tube sheet was considered at a secondary side workshop in 1995. He expects to see more such denting in the future, leading to tube cracking.

Muscara noted that in terms of crack evolution and operational assessments, we must consider when to use ligament correlations for existing cracks and when to use a planar crack correlation.

Baum then offered one last comment on the Seabrook cracking, noting that while the greatest concern is on the mechanical aspects (i.e., residual stresses), there is also a chemical aspect to the problem. He noted that Seabrook had low silica (5-10 ppb) in the bulk water chemistry compared to other plants, and he wondered if this was significant.

Peter King then briefly reviewed ongoing SG research in Canada (Denise is typing up his handwritten overheads).

King noted that the precursors for cracking do not appear to form in Alloy 690 like they do in Alloy 600, at least not in reasonable times. He felt that the major questions to be answered were the time to critical crevice deposits and how to interpret and use the extensive available field data and relate it to our expectations for Alloy 690 TT.

Chambers then made several points. He first noted that residual stresses from manufacture are unavoidable. In addition, one would expect operating stresses in tubes from temperature cycling. He also suggested that *in situ* monitoring of autoclave and heated crevice test (e.g., Raman spectroscopy) could be very enlightening. Finally, he wondered how crevice chemistry might change under zero-power hot conditions.

King responded by first noting the work of Lumsden and others on monitoring crevice chemistry. With respect to the effect of zero-power hot conditions on crevice chemistry, he noted that people are working on this problem. He added that it is very difficult to get crack growth rate data under field conditions. He also agreed that we must assume that tubes, in general, have residual stresses from manufacture, and we must also assume that operations will produce aggressive environments somewhere in the SG. Therefore we must have the most crack resistant tube material possible, and this is why the industry is going with Alloy 690 TT at present. He stated that BWC is still interested in model boiler testing and crevice monitoring, but these tests are very expensive. He expressed the hope that future work at ANL can address these areas.

Per-Olaf Andersson then briefly reviewed ongoing SG research in Sweden. He noted that Sweden has only three PWRs, namely Ringhals 2, 3, and 4. Units 2 and 3 have replacement SGs, and there have been no problems with these. Unit 4 still has the original Westinghouse Model D-3 SG with Alloy 600 MA tubes from 1984, and this unit has experienced very little tube cracking.

Odar supplemented Andersson's presentation by showing results obtained from Na-24 hideout studies conducted in the Ringhals 3 plant simulator before SG replacement. Significant Na hideout was observed. The new KWU SG with grid tube supports showed virtually no hideout. Tests conducted three years later showed some hideout, indicating sludge buildup. The hydrazine concentration ratio in the SG feedwater for plants with higher Fe (1-2 ppb) decreased with time. For lower Fe (<1 ppb), the decrease was less rapid, thus suggesting increased sludge loading.

François Vaillant then summarized ongoing SG research in France. He reviewed work on life prediction and frequency of NDE inspections as well as on hydrazine requirements and SCC under plant shutdown and startup conditions.

Keith Fruzzetti reviewed EPRI-sponsored work on SGs.

Staehle then continued the discussion by noting that in order to predict cracking in a specific environment, we must have sufficient relevant data. However, almost no relevant data exist on cracking associated with reduced S species. With respect to silica effects, he cited a 1985 paper by Berman, who found a specific region in the silica-alumina system where cracking occurs in Alloy 690 MA. He felt that acid SCC had been pretty well characterized, as had alkaline SCC, though both remain issues. Cracking in complex environments has not been well defined, but relevant work is being conducted in France. Overall, he felt that there was much room for serious work to determine the dependencies for several of these submodes. He added that we cannot predict the behavior if we do not know the dependencies.

Gorman stated that, with respect to sulfate chemistry and complex environments, he has difficulty in understanding the process for attack since the species involved are not liquid at the superheats present in drilled hole crevices. He felt that further testing and/or modeling was needed.

Lindsay made an impromptu presentation on the subject of predicting the performance of line-contact crevice deposits, noting that, on the molecular scale, the tube surfaces and the TSP lands look flat. We must consider things on this scale. When things are considered on this scale, it is clear that chemical reactions in solution within the various types of crevices are not different from each other or from reactions that can take place in bulk water. The differences among crevice types are most likely due to their differing susceptibility to fouling. Lindsay added that he was not aware of any significant engineering science relating to crevice fouling under boiling heat transfer conditions. Good engineering science research is needed in this area. Staehle concluded that the important question is what remains to be done in this area and what resources are available to do it.

On the subject of critical experiments in model boilers, Staehle noted that there are only one or two model boilers available at present. How do we best use them and what alternative experimental techniques do we have? Duncan agreed that model boiler tests are needed, since codes and modeling cannot answer all of the questions that must be addressed. He said that model boiler experiments should emphasize multiple variable validation experiments. He felt that a different model boiler design from that being developed at ANL was needed to understand the fouling process at the crevices. Muscara noted that the ANL model boiler was not designed for such studies, but rather to study the evolution of crevice chemistry and how it leads to crack initiation.

Baum added that MULTEQ is a useful tool. But model boiler experiments were nonetheless needed to determine crevice chemistries with confidence. Duncan contended that model boiler results cannot reliably predict absolute cracking rates—they can only provide relative rates.

Staehle then stated that he felt that items 6-8 on the panel discussion agenda had already been thoroughly considered in the previous sessions, and, in view of the short time, they would not be further discussed here.

Muscara observed that, with respect to the data base, a tremendous amount of work was still needed. He suggested that perhaps an international group should be constituted to coordinate this work, and he suggested that perhaps the NRC and EPRI could pull this together.

Staehle suggested that discussions be ended on that note, and he thanked all of the participants.

Introductory Comments

Keith Fruzzetti

Electric Power Research Institute

It is my pleasure to welcome you all here to the Heated Crevice Seminar co-sponsored by the Electric Power Research Institute (EPRI), Argonne National Laboratory (ANL) and the U.S. Nuclear Regulatory Commission (NRC). As most of you are aware, both EPRI ANL, and the NRC were each planning a workshop to bring together international experts in the field of steam generator thermodynamics and chemistry in order to facilitate a technical exchange and discussion in this area. However, upon learning of each other's plans, we decided to combine forces in the spirit of partnership and cooperation. The result of this effort has come to fruition today and in the next few days with an exciting agenda of presentations and discussion topics.

We have a full agenda and many interesting presentations to hear. The purpose of the meeting, as I see it, is to present the work that is on-going with respect to crevice chemistry in order to develop an understanding of where we are as a community and then to identify those areas requiring further work. Hopefully, by the end of the seminar on Friday, we will have come to some consensus on the direction and areas requiring the most attention in the near term and in the long term going forward.

As you can tell from the agenda, there is plenty of time built into the seminar for discussion. Therefore, I encourage everyone to participate in open and frank dialogue as each presentation is given. The seminar has been divided into four sessions, each with a corresponding session chair, to focus the information presented and encourage technical exchange in a systematic manner. In addition, a panel discussion will take place following the fourth session, allowing for additional discussion.

So, I welcome you all to what I anticipate to be a very informative and fruitful seminar, and thank each of you for your support.

Introductory Comments

Joseph Muscara
US Nuclear Regulatory Commission

As many of you know, the NRC has completed two major Steam Generator tube Integrity research programs over the last two decades. We are now in the first year of another five-year program on SGTI. The first two programs concentrated on quantifying and improving in-service inspection reliability and on development of methods for predicting the failure pressures and leak rates of degraded steam generator tubes under normal operating, accident and severe accident conditions. Relatively little work was conducted in the previous two programs on developing an understanding of degradation mechanisms.

The new program will continue and complete work on improved inspection techniques and modeling of steam generator tube integrity. Much more attention will be placed in the new program in gaining a better understanding of degradation in steam generator tubes, particularly on the secondary side of the generator. We need this better understanding to be able to predict the future degradation of SG tubes in operating plants, including the behavior of Alloy 690 tubes. Key to understanding degradation on the secondary side is a better understanding of crevice chemical and physical conditions.

With knowledge of these conditions we can conduct realistic corrosion tests to develop correlations of crack initiation times and growth rates. I want to stress that we need a good understanding of both the chemical and physical conditions of crevices. Therefore understanding the thermal hydraulics and heat transfer across the crevices is also very important. Because conditions vary from location-to-location in a given generator and between generators, because crevices are not symmetric and there is a presence of line contact, it is important to know the crevice conditions axially and radially around the tube. Thus many varied situations are of interest, and we need to develop models to predict crevice physical and chemical conditions as a function of the surrounding conditions.

We intend to develop and evaluate such models. In addition to modeling efforts, we will be measuring physical and chemical conditions experimentally in a model boiler.

Information from the model boiler will be used to conduct corrosion tests of interest and to validate the crevice predictive models. Corrosion test results for both Alloys 600 and 690 will be used to develop correlations for crack initiation and growth. By coupling the laboratory behavior of 600 and 690, to the field experience of Alloy 600, we hope to develop a predictive capability for the behavior of 690 in the field. Gaining a good understanding of crevice conditions will be crucial to developing a predictive methodology for the behavior of steam generator tubing in operating plants, and hopefully we could avoid repeating the poor operating experience with Alloy 600 tubing.

From this seminar, we hope to gain a good understanding of the state-of-the-art of crevice conditions and of crevice corrosion. I look forward to obtaining your input and recommendations that will help us to effectively meet our objectives of developing a capability for predicting steam generator tube degradation under field operating conditions. I want to thank ANL and EPRI for organizing this seminar and you, the world experts, who are participating in the seminar.

Introduction

Roger W. Staehle
University of Minnesota

This meeting is the third in a series to consider in detail the properties of heated crevices in PWR steam generators. Such heated crevices include those associated with various support structures, deposits and top of tube sheet geometries.

The first two meetings were held in Studsvik, Sweden in 1996 and 1998 and were organized by Bo Rosberg and Andres Mollander and their colleagues. These were informal meetings and the proceedings were not intended for distribution but rather as records of the discussions. The present meeting resulted from two sources: one was a commitment by Peter Millett, who attended the Studsvik meetings, for EPRI to sponsor a third such a meeting in the US; the other was a strong interest at ANL to address critical problems in corrosion with the heat transfer crevice being the focus.

As a result of these prior commitments, EPRI and ANL agreed to sponsor jointly this meeting. Accordingly, Paul Frattini of EPRI and Jangyul Park of ANL organized the meeting.

I would like to thank all of you for attending and I would like to thank Roger Poppel, Division Director at ANL, for supporting the meeting at ANL.

The primary purpose of the considerations in this meeting is to develop a means for predicting the corrosion of steam generator tubes with respect to the secondary side of steam generators. Such a prediction requires specifically that the environment to which the tubes are exposed be specifically characterized. Prediction of any corrosion is not possible without a detailed characterization of the local environment that occurs specifically on surfaces. This meeting considers mainly environments that occur in heat transfer crevices. By this is meant those conditions were superheat occurs and where this superheat leads to the concentration of chemicals in the secondary water. Such geometries occur at tube suuports, antivibration bars, sludge piles, and top of tubesheet crevices. Concentration of chemicals also occurs on free spans and importantly on free spans in the upper bundle of OTSGs. These need to be considered.

This meeting has been organized to bring the world's experts together from the important disciplines that can contribute significantly to the discussion. To facilitate the interaction and synergy of these experts, extensive time has been allocated for discussions.

In order to facilitate preparing a record of the meeting, Dwight Diercks has agreed to prepare minutes of the meeting. Also, questions and answers from the audience will be included in the final proceedings. The operation of the meeting itself is being facilitated by Denise Moore and Zhou Zhongquan of ANL.

We hope that this meeting will: define the present state of understanding, define priorities for future work, and develop improved understandings through interactive discussions.

I would like to thank Paul Frattini and Jangyul Park especially for their extensive work in organizing this meeting. The quality of meetings is always proportional to the amount of work ahead of time.

An Overview of Recent French Studies of Possible Secondary Side Crevice Environments Causing IGA/IGSCC of Mill Annealed Alloy 600 PWR Steam Generator Tubes

P. M. Scott and F. Vaillant

Heated Crevice Seminar

October 7-11, 2002, ANL, Argonne, Illinois

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Overview of Possible Crevice Environments for IGA/IGSCC in Alloy 600MA

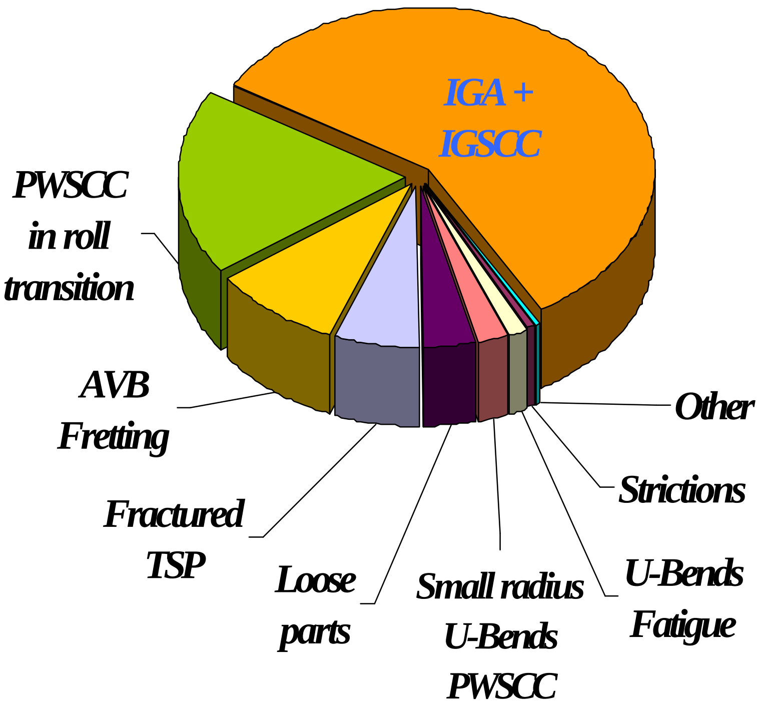
- > Introduction
- > Background : crevice environments
- > Background EDF caustic model
  EDF near-neutral sulfates
  EDF/FRA/CEA near-neutral complex environments
- > Summary
- > Discussion of liquid / steam environments
- > Future plans

Introduction : Causes of Steam Generator Tube Plugging in France in 1999

·Only Mill Annealed Alloy 600 tubes are affected so far in France but Thermally Treated Alloy 600 has started to crack in the USA

·Secondary water chemistry management is strongly influenced by the tube corrosion issue.

Plugged tubes in France in 1999



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IGA/IGSCC of Alloy 600 SG tubes: Analysis of operating experience 1

- In France, IGA/SCC in plants with 600 MA
  - drilled TSPs, one with broached TSPs in C-steel (axial cracks)
  - Above the tubesheet TS (small axial cracks) in the sludge pile
  - Under the top surface of the TS (circonf. cracks)
  - Very limited TGSCC (Pb identified)
- No cracking with 600 TT and 690 TT
- IGA/IGSCC related to hide-out of impurities in crevices under heat transfer conditions in flow-restricted areas

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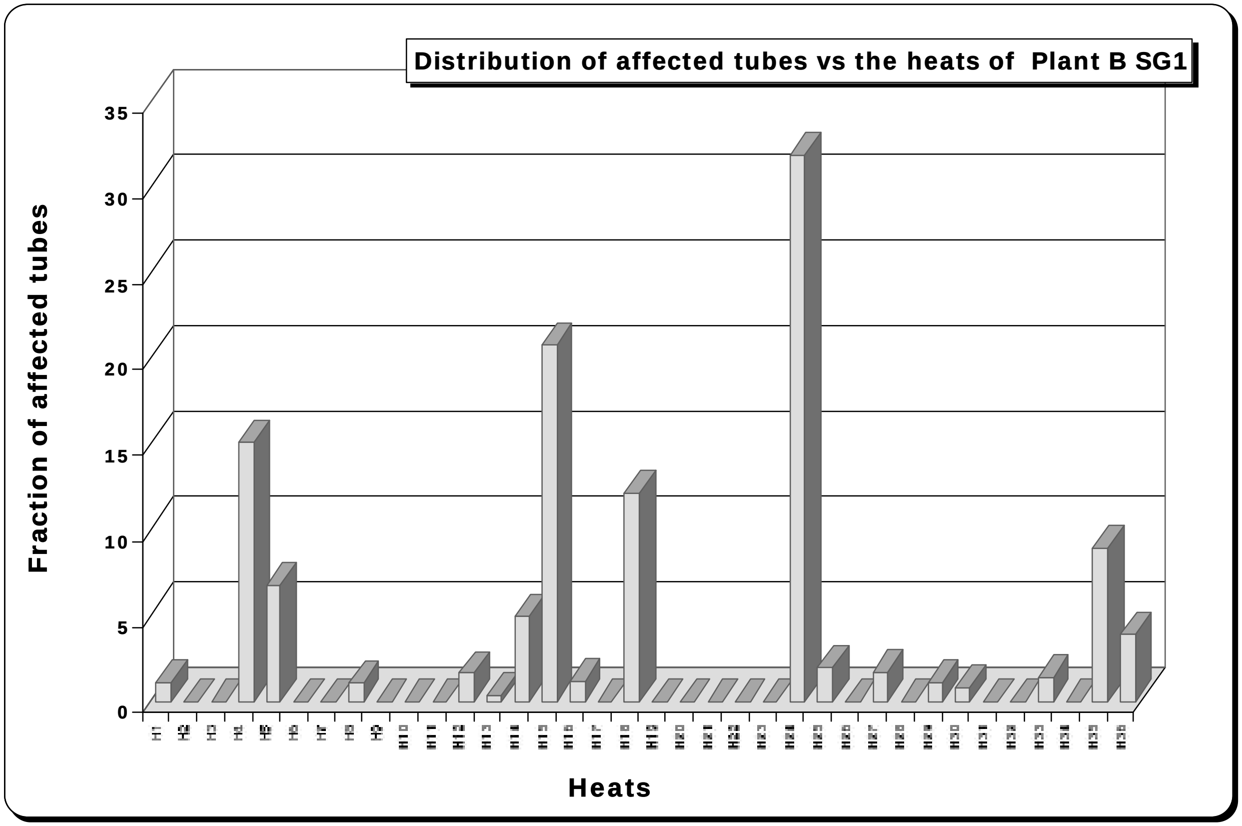
IGA/IGSCC of Alloy 600 SG tubes: Analysis of operating experience 2

- Inspections of large populations of tubes available for statistical analysis but rather few parametric trends can be discerned
- Strong heat to heat variability
- Some trends with strength and/or carbon content are observed for some tube bundle manufacturers with lower strength materials apparently more susceptible

IGA/IGSCC of Alloy 600 SG tubes : Analysis of operating experience 3

Heat to heat variability in a SG tube bundle after ~75,000 h in service



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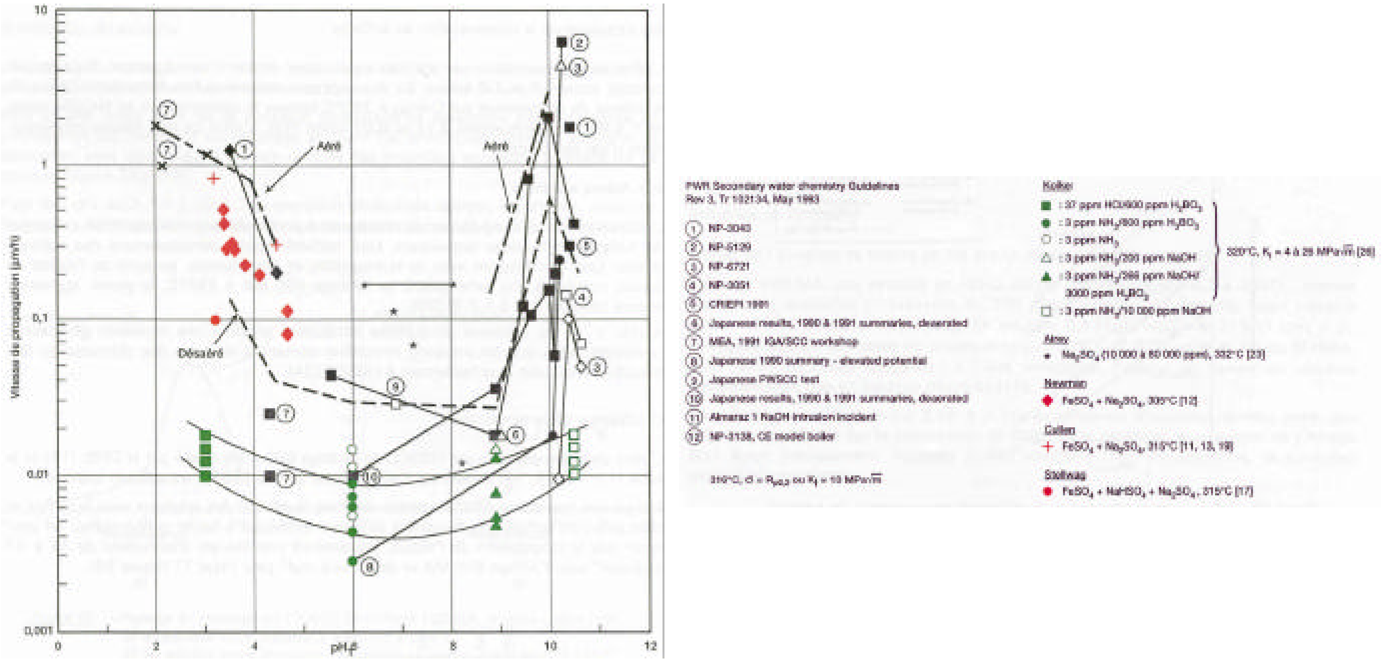
Background : crevice environments

- Crevice environments poorly characterized
- IGA/SCC traditionally linked to the formation of concentrated caustic or acid sulfate solutions whose boiling point is raised sufficiently to be in equilibrium with the available superheat of up to 30-35°C
- Many investigations in the past in caustic and acid sulfate

Background : Alloy 600 in Caustic and Acid Sulfate - Laboratory Data



> Only limited data in the range $5 < pH_T < 9.5$ in concentrated solutions (see Airey)

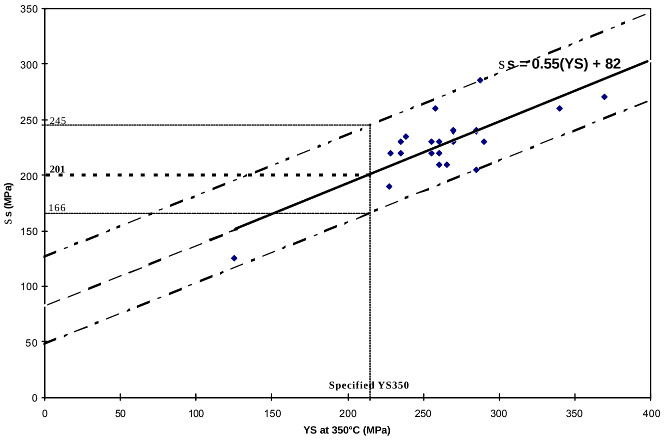
Background : EDF caustic model 1

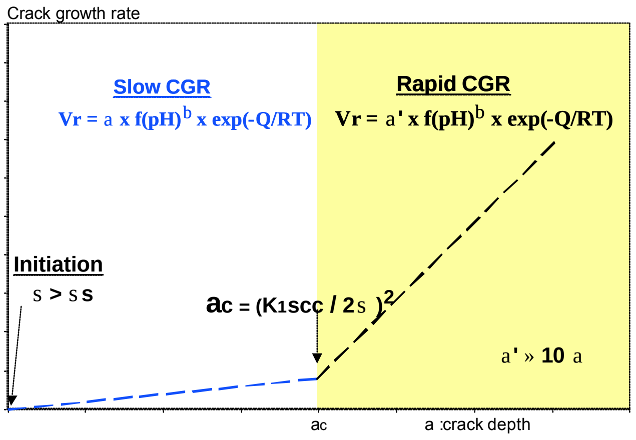
> IGSCC model in laboratory :

Stress threshold for initiation

Propagation

s **> 185 MPa**





Background : EDF caustic model 2

> 600 MA :

- the model explains the main features of the cracking (location, orientation)
- Slow propagation rate : see next slide
- No rapid propagation expected

> 600 TT : better behavior predicted, only circonf. cracking possible at the upper surface of the tubesheet

> 690 TT : no cracking expected

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Background : EDF caustic model 3

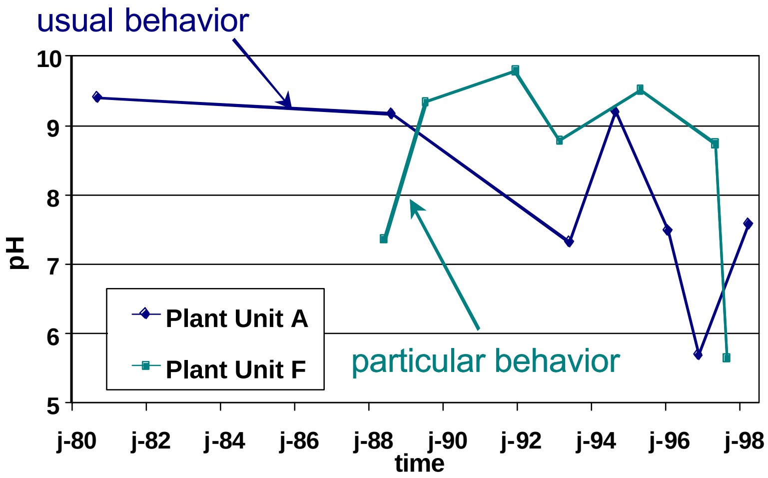
> **Coupling the corrosion model** with chemistry deduced from hideout return data

- **The calculated (slow) CGRs are consistent with average CGRs from pulled tubes on 8 of the oldest plants (river side) for the first decade of operation**
- **However, they are always lower than the CGRs measured in plants**
- **The model is not applicable to 3 other** (sea side) **plants**

To be improved (reassessment of T_{wall}, sludge porosity)

Background : EDF caustic model 4

> Coupling corrosion model (600 MA) with pH deduced with hideout return data

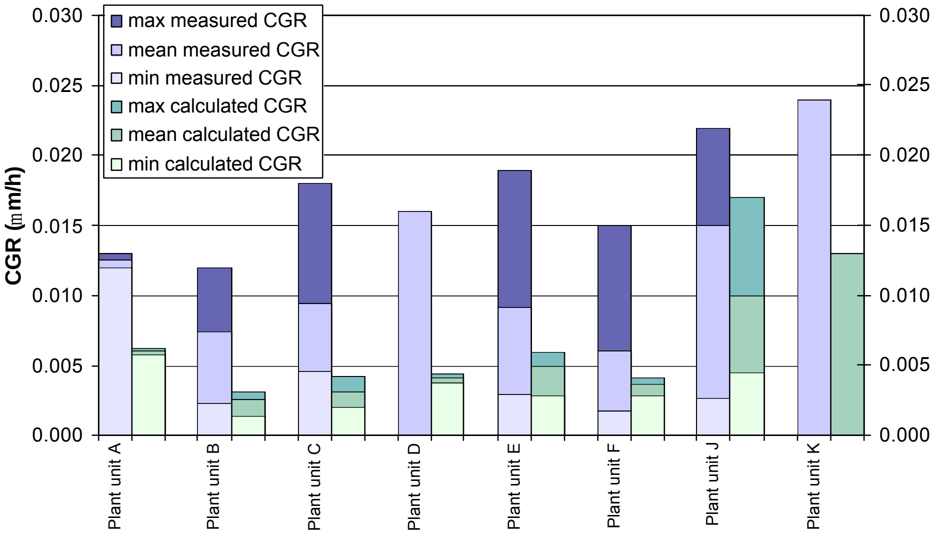


➔ Crevices less and less alkaline with time

Background : EDF caustic model 5

> Coupling corrosion model with pH deduced with hideout return data

- 8 river side plants



- 3 sea side plants : not alkaline

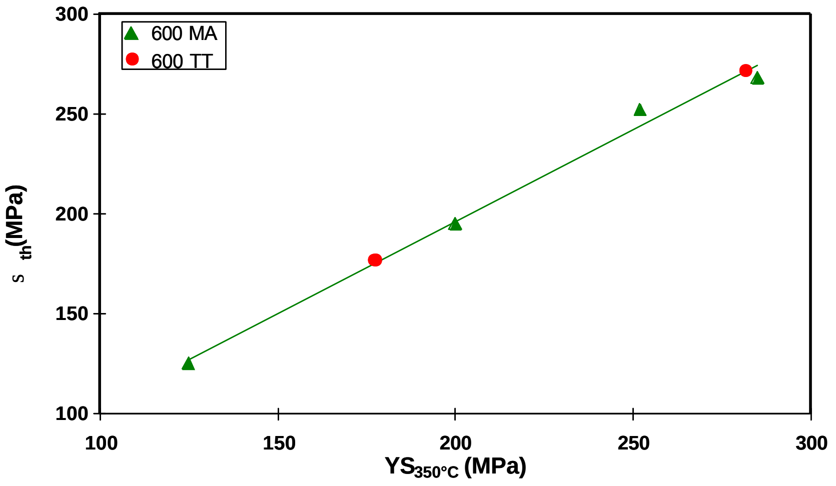
Neutral to slightly alkaline sulfates 1

- Hideout return data : sulfates are the main pollutants
- Surface analysis : Cr/Ni on pulled tubes consistent with slightly alkaline environment
- Laboratory investigation (EDF)

Neutral to slightly alkaline sulfates 2

- Initiation : $\sigma > 215$ MPa (required YS)

$[SO_4] = 0.05$ M, pH = 6.5, T = 320°C, C-rings, 2500 h

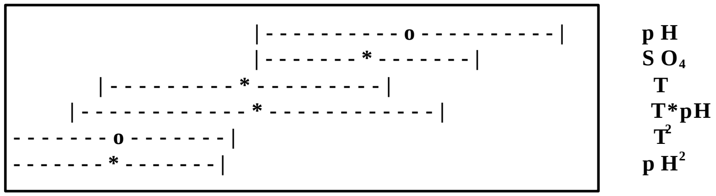


Neutral to slightly alkaline sulfates 3

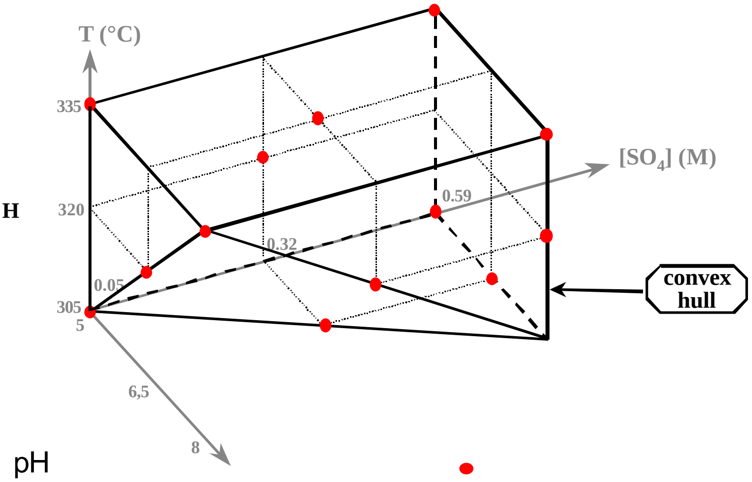
> Slow propagation Experimental Design

> **slow CGR (MA) = a + b.T + c.[SO$_4$] - d.pH +e.T.pH- f.T^2 + g.pH^2**

> Pareto diagram :

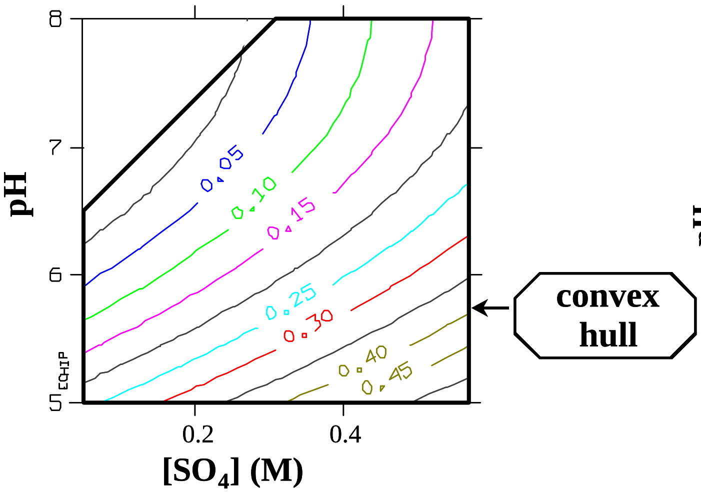


arbirtrary units
* : increasing effect on CGR
o : decreasing effect on CGR



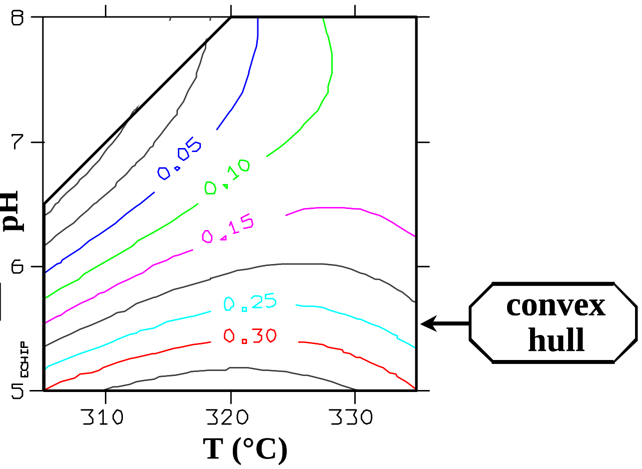
Neutral to slightly alkaline sulfates 4

Effects of pH and $[SO_4]$ for T = 320°C



convex hull

Effects of pH and T for $[SO_4]$ = 0.32 M



convex hull

Neutral to slightly alkaline sulfates 5

- 600 MA : the sulfate model
  - Consistent with some cracking in plants (location, orientation), but not all
  - Provides slow CGRs compatible with plant CGRs at [SO4] > 5000 ppm (pH = 6) or = 31 000 ppm (pH = 8) at 320°C
  - Reassessment of true T_{wall} and coupling of the model with HOR data in progress
- 600 TT predicted to be slightly better
- 690 TT immune

Complex environments 1

> Background :

> IGA/IGSCC of mill annealed alloy 600 tubes associated with the presence of **alumino-silicate deposits (zeolites) overlying brittle poorly protective chromium hydroxide films** instead of protective spinel.

> Recent high resolution ATEM work on IGA/IGSCC in alloy 600MA acid formed in acid sulfate or strong caustic do not show the same morphology as observed on those pulled tubes examined to date.

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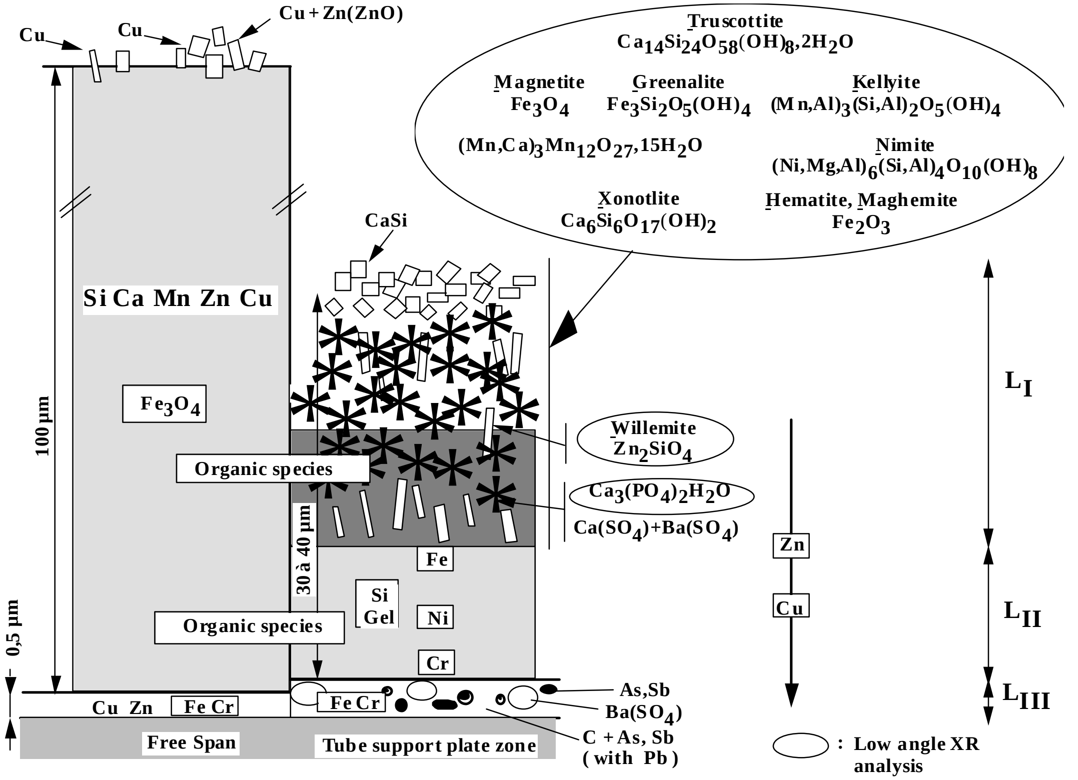
Complex environments 2

> Deposits at TSPs on pulled tubes :



Complex environments : 3

> **Specimens / examination**

- EDF : at least 2 C-rings/environment and metallurgical condition
- CEA : U-bend specimen
  - $\sigma > YS$ - surface state: as-received (AR)
  - Metallurgical examination on section (max Δa) + SEM / EDS
- Flat coupons, SEM/EDS, GDOS

> **Test facilities**

- EDF: Static SS autoclaves, 1 or 4 liters
- CEA : heated capsules (alloy 600TT) in an autoclave

> **Duration of the tests**

2500 h to 4000 h

Summary of Recent Results on IGA/IGSCC of Alloy 600 in Complex Mixtures of Impurities

Various combinations of impurities added to **pure water** studied using optimized experimental designs: NaOH, Na_2SO_4, Na_2S, CH_3CO_2H, CO_2, Fe_3O_4, SiO_2, Al_2O_3, CuO, $Ca_3(PO_4)_2$

pH range of the various mixtures at 325°C was 3.3 to 10.3

> Classical detrimental effects:

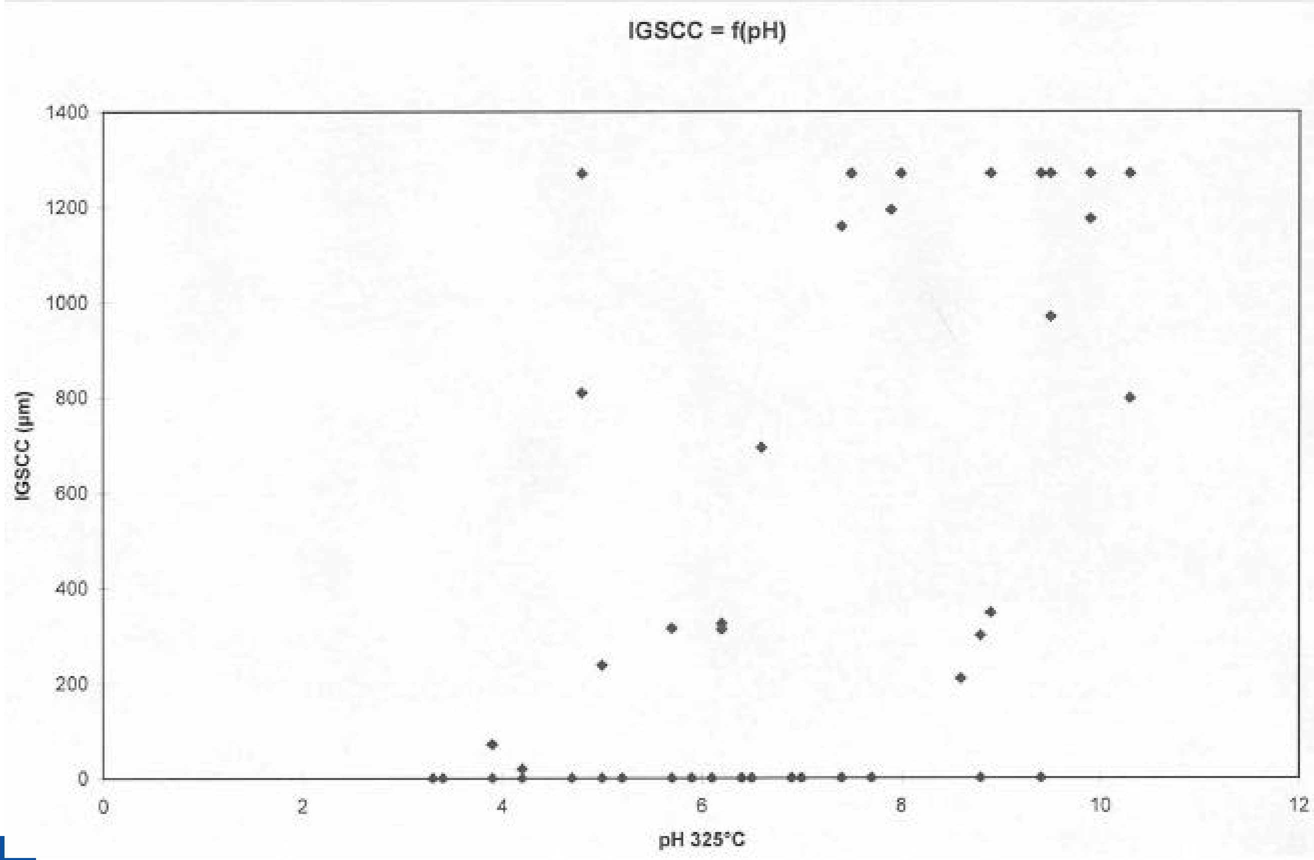
- pH<5 or pH>10 at temperature
- Presence of SO_4^{--} at pH<5 and HS^-/S^{--} at pH>10
- Presence of Fe_3O_4 & CuO

> Beneficial effects:

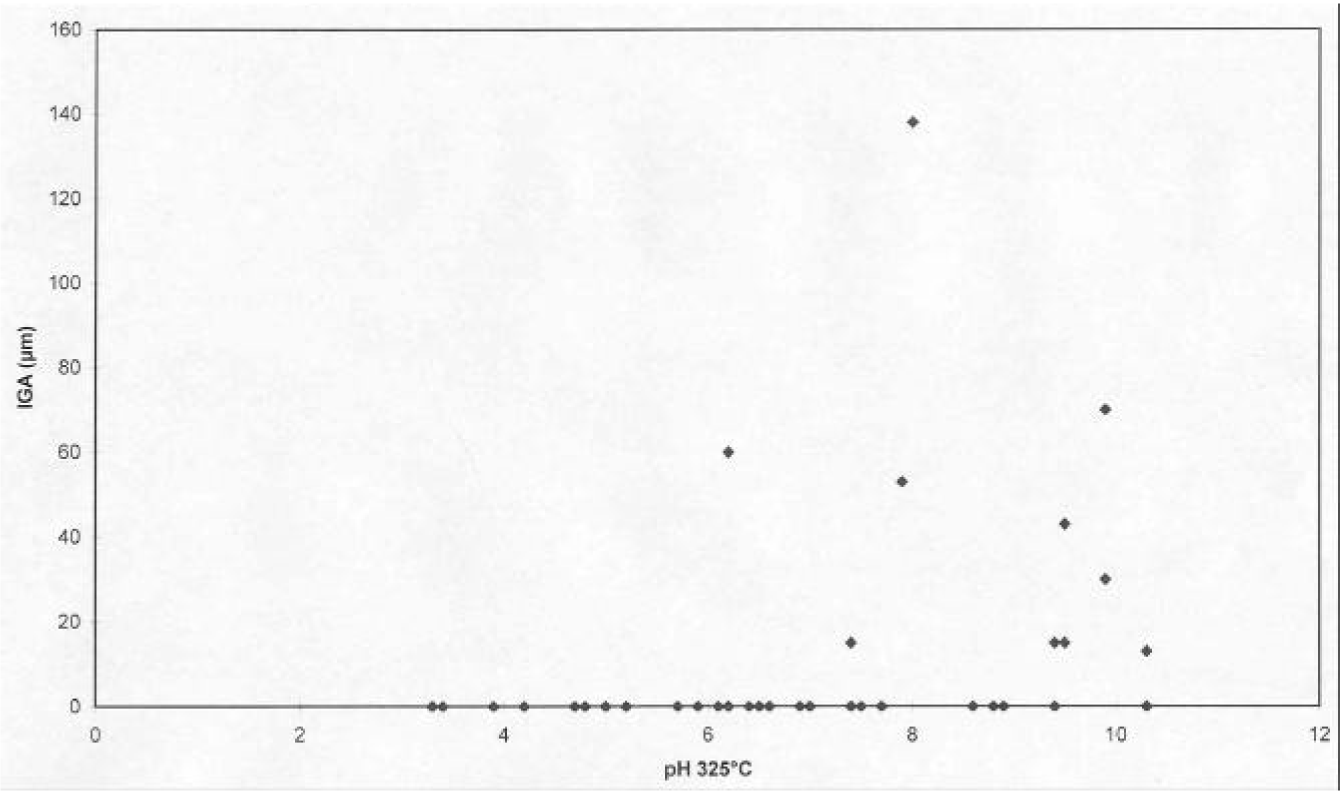
- SiO_2 and $Ca_3(PO_4)_2$ as chemical buffers or forming solid barrier deposits
- CuO only in presence of sulfides

One really surprising result where rapid (0.2µm/h) through-wall cracking was observed with CuO+SiO_2+Al_2O_3 but not with CuO alone

IGSCC of Alloy 600 as a Function of pH in Complex Mixtures of Impurities



IGA of Alloy 600 as a Function of pH in Complex Mixtures of Impurities



Experimental Plan and Results based on Pulled Tube Deposit Analyses

> Second Experimental Design in AVT environment

Run	Impurities in AVT Secondary Water			pH 325°C	Deepest crack, mm	
	$\frac{Al}{Si}$ (A) -1 level=0.1 +1 level=1.0	CuO (B) -1 level=0 +1 level=0.128M	$Ca_3(PO_4)_2$ + (100ppm CH_3COOH) (C) -1 level=0 +1 level=0.0064M +2 level=0.064M		Heat WF 422	Heat 9861
69*	-1	-1	-1	5.5	0	0
70	+1	-1	-1	5.5	100	150
71	-1	+1	-1	5.9	0	0
72	+1	+1	-1	5.9	0	635
73	-1	-1	+1	5.1	120	120
74	+1	-1	+1	5.1	70	200
75	-1	+1	+1	5.3	0	0
76	+1	+1	+1	5.3	0	0
77	-1	-1	+2	4.8	5	5
78	+1	-1	+2	4.8	100	100
79	-1	+1	+2	5.1	0	0
80	+1	+1	+2	5.1	0	0

* Note: repeated experiment by EDF →15 µm

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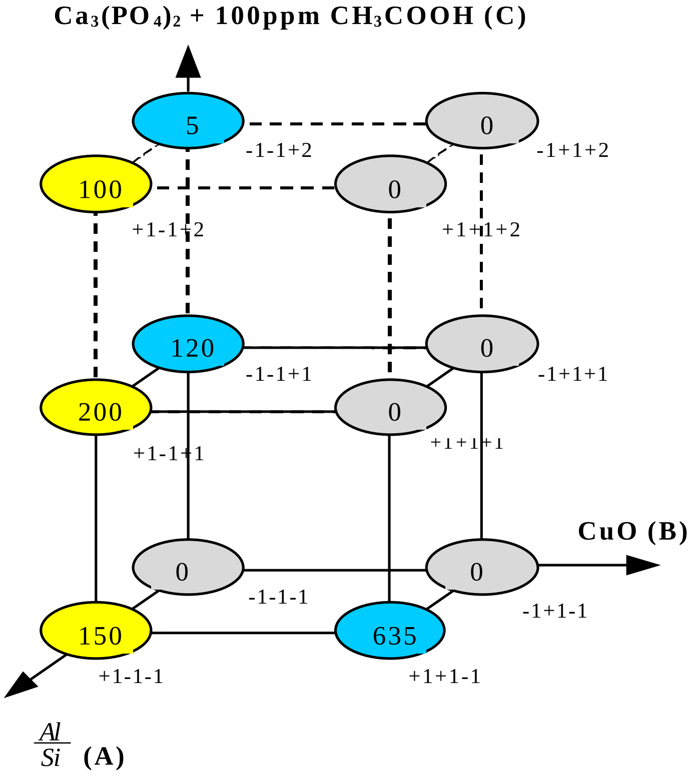
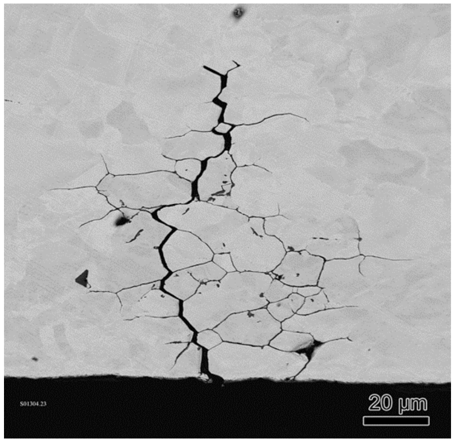
IGA/IGSCC of Alloy 600MA in the presence of alumino-silicates in AVT water



⬭	No cracking
depth (µm)	IGA/IGSCC
depth (µm)	IGSCC



Combination +1-1-1

Note: 1- IGA/IGSCC observed only in AVT water in the absence of CuO

2- Recent EDF tests show that organics are not a necessary condition for cracking

IGA/IGSCC of Alloy 600MA in the presence of alumino-silicates in AVT water

> Recent EDF data for polluted AVT (de-aerated ammonia solution + 2 ppm hydrazine, pH_{RT} 9.2)

environment parameter	simple	simple without silica		complex			
	Al/Si	w/o alumina	w/o phosph.	reference	amine	w/o organic	amine
Test Environ-ment	AVT + SiO_2 + Al_2O_3	AVT + $Ca_3(PO_4)_2$ + CH_3COOH	AVT + Al_2O_3 + CH_3COOH	AVT + SiO_2 + Al_2O_3 + $Ca_3(PO_4)_2$+ CH_3COOH	**idem** but **morpholine** instead of R	AVT + SiO_2 + Al_2O_3 + $Ca_3(PO_4)_2$	**idem** but **morpholine** instead of R
pH_{320} MulteQ*	5.9	5.2	4.1**	5.2	5.3	5.4	5.2
Test duration(h)	3000	2473	2500	3191	4000	4000	4000
SCC	0.005 µm/h	0.01 µm/h	No Cracking	0.01 µm/h	0.01 µm/h	0.03 µm/h	0.01 µm/h
Deposit	continuous AlSi	no	granular Al	continuous Si	-	-	-
Non protective Cr-rich layer	?	yes Fe, Cr	yes Cr, Fe	yes Cr, Si	-	-	-

* Al_2O_3 not in MulteQ data base : calculated with Al

** CH_3COOH concentration : 10 000 ppm instead of 10 ppm

Alumino-silicate deposits (Zeolites)

- Very wide range of compositions is possible in which the substitution of species such as aluminum, alkaline earths, phosphate and organic species such as glycols controls their structure and reactivity ('acidity')
- Observed to selectively absorb certain transition metal cations from the passive film on alloy 600 and leave a non-protective chromium hydroxide gel that allows IGA/IGSCC to develop
- Organic ligands can be synthesized in the alumino-silicate deposits and may play a role in the partial breakdown of passivity that is the precursor to IGA/SCC. However, recent EDF tests show that organics are not a necessary condition for cracking.
- Consequences for secondary water chemistry management?!

Summary 1

- IGA/IGSCC in some old plants can be explained with the EDF caustic model (reassessment of T_{wall} and influence of porosity in progress)
- However environmental chemistry associated with impurity hideout complex and still uncertain
- Local environments (hideout return data and surface analyses) are becoming less and less alkaline - neutral to slightly basic
- Neutral to slightly basic sulfate environments could be relevant (but can they exist in the liquid state?)

Summary 2

- Complex (liquid or wet steam) environments including SiO_2, Al_2O_3, organics and phosphate can reproduce IGA/IGSCC and deposits observed on pulled tubes (zeolites, formation of organic ligands to enhance dissolution of nickel)
- Thermally treated alloy 600 is more resistant than mill annealed alloy 600 in all the near neutral environments tested and thermally treated alloy 690 is immune.

IGA/IGSCC of Alloy 600 SG Tubes:
Do such concentrated liquids really form?

- **Concentrations of dissolved species must be ~ 8 M to ensure a liquid phase with up to 30-35°C of superheat**
  - Recent tests show that only NaOH is sufficiently soluble to ensure a liquid phase at the SG pressure and >25 °C superheat
  - Concentrated NaCl, for example, can only support 25°C of superheat before precipitating
  - Impurity concentrations in SGs are probably only sufficient to form droplets or a liquid film at most
- **Crevice mouths fouled with very low porosity (<10%) deposits**
  - Possibility of local steam blanketing (polluted and/or hydrogenated steam?)

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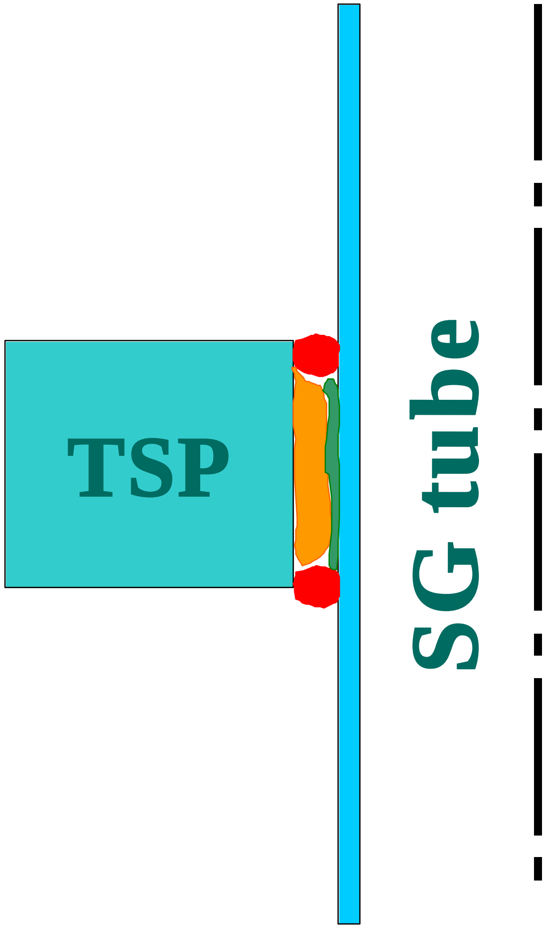
Typical Fouled Tube/Drilled Tube Support Plate Crevices

High density magnetite rich in silica.
High porosity magnetite and complex silicate deposits, which remain on pulled tubes



IGA/IGSCC in Steam or Aqueous Phase: Does it matter?

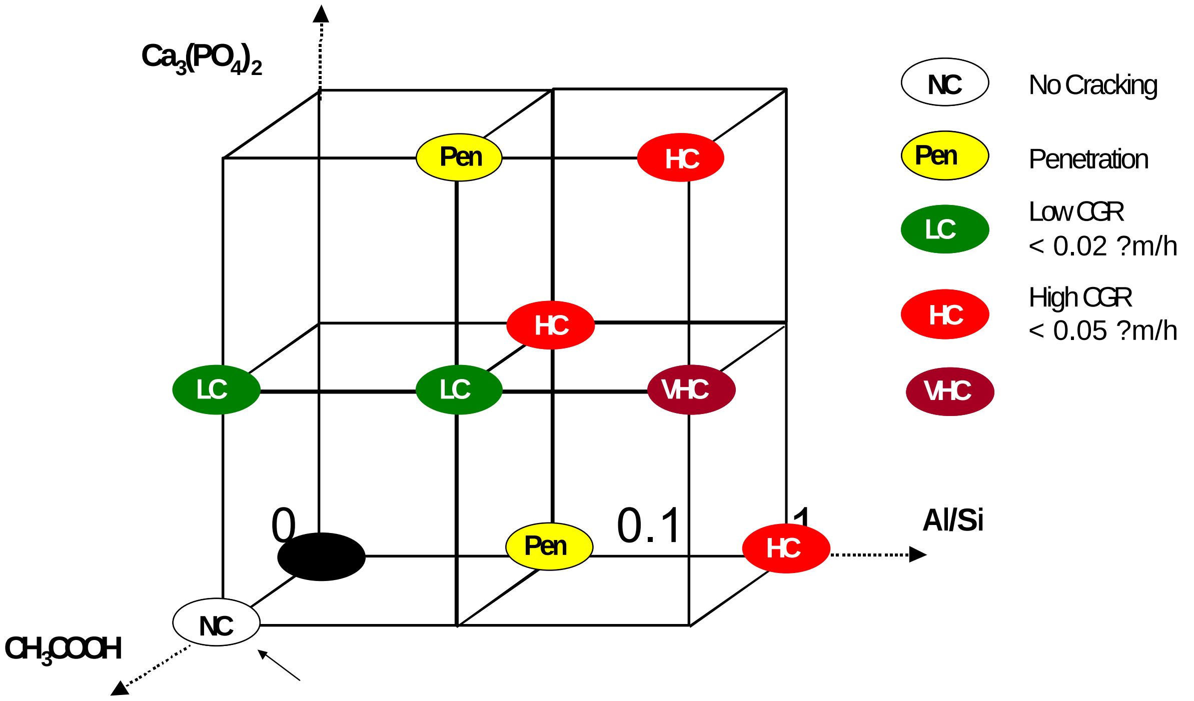
- Nano-porous (1 to 2 nm diameter with ATEM) deposits allow certain impurities, notably lead, copper and sulfur, to diffuse to the crack tip
- Liquid water and steam in a 2 nm diameter tube are unlikely to be distinguishable and transport to the crack tip is probably by surface diffusion
- Kelvin's equation (which allows the vapor pressure of extremely small droplets to be calculated) shows that the boiling point of pure water can be elevated by as much as 15°C (because of surface tension in very small diameter pores)

Current and future R&D

- Further assessments in (neutral) sulfates and complex environments

- Test program (FRA Owners' Group) in progress to test hypothesis of IGASCC in polluted superheated steam in plugged crevices

IGA/IGSCC of Alloy 600MA in the presence of alumino-silicates in AVT water



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  - E.M. PAVAGEAU (EDF-R&D)
  - P. COMBRADE (Framatome-ANP)
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APPROACH TO PREDICTING CORROSION OF SG TUBES BASED ON QUANTIFYING SUBMODES OF SCC IN A STATISTICAL FRAMEWORK

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Argonne National Laboratory

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PRIMARY OBJECTIVE OF THE MEETING:

Predict Corrosion of Tubes in Modern SGs.

REQUIRED TO PREDICT CORROSION

- **Dependencies of submodes of corrosion on primary variables: pH, potential, species, alloy composition, alloy structure, temperature, stress**

- **Definition of local environment immediately adjacent to tube surface.**

- **Statistical framework.**

MAIN COMPONENTS OF PREDICTING THE CORROSION BEHAVIOR OF STEAM GENERATOR TUBING IN MODERN PLANTS:

- **Alloys 600TT and 690TT**
- **Line contact crevices and TTS**
- **High purity water**

PROBLEMS IN PREDICTION FOR MODERN PLANTS

- Few failures of tubes
- No chemical, physical, nor phase definitions of line contact crevices: i.e. the environment that produces corrosion
- Lack of definition for possible serious SCC submodes including S^{-y}SCC, AcSCC, complex environments, and PbSCC
- Lack of data and theory for interaction of SCC species with immobilizing species, e.g. Pb with sulfate.

PROBLEMS IN CARRYING FORWARD DRILLED HOLE EXPERIENCE

- Little direct evidence for causative chemistries.
- Little agreement on the presence of steam phase.
- Few data on corrosion in steam phase
- Few data on corrosion in complex environments.
- Large variability of corrosion response for constant conditions, i.e. Scott study.
- No (semi)-quantitative theory for local chemistry.

MY APPROACH

- Objective: Predict first crack on secondary side before detection by NDE.

- Scope: Alloy 600MA, drilled hole,

- Basis: Use existing data from Alloy 600MA failures to calibrate and develop theory.

- Approach:

  - Integrate statistical framework with physical descriptions of the submodes from plant and laboratory data for describing SCC.

  - Evaluate integrated descriptions of submodes with chemistry of drilled hole crevices.

- Validation: Compare integrated theory with known behavior of Alloy 600MA in drilled hole crevices.

- Apply: Present plants still with drilled holes and Alloy 600.

- Modify: Apply methodology to modern plants

STEPWISE DEVELOPMENT

1. Assess the statistical nature of SCC in SGs and related applications and environments. [Done]. Conclude:

   - Weibull format models SG data well and provides a good format for prediction

   - Space parameter , θ, and location parameter, t_o, of Weibull follow same patterns as mean values of experimental data

   - Shape parameter, β, difficult to interpret and model.

2. Identify submodes of SCC (submodes depend differently on the primary variables of pH, potential, species, alloy composition, alloy structure, temperature, stress). [Done]. Conclude:

   - Sufficient data (more would be desirable) for modeling the primary variables for: AkSCC, LPSCC, AcSCC, PbSCC

   - Need data for S^{y-}SCC

   - Treating complex chemical environments not clear

   - Presence and signficance of steam phase not clear.

3. Survey dependencies of submodes on primary variables. [Done]

4. More detailed study of PbSCC. [One short report done. Detailed report almost done]

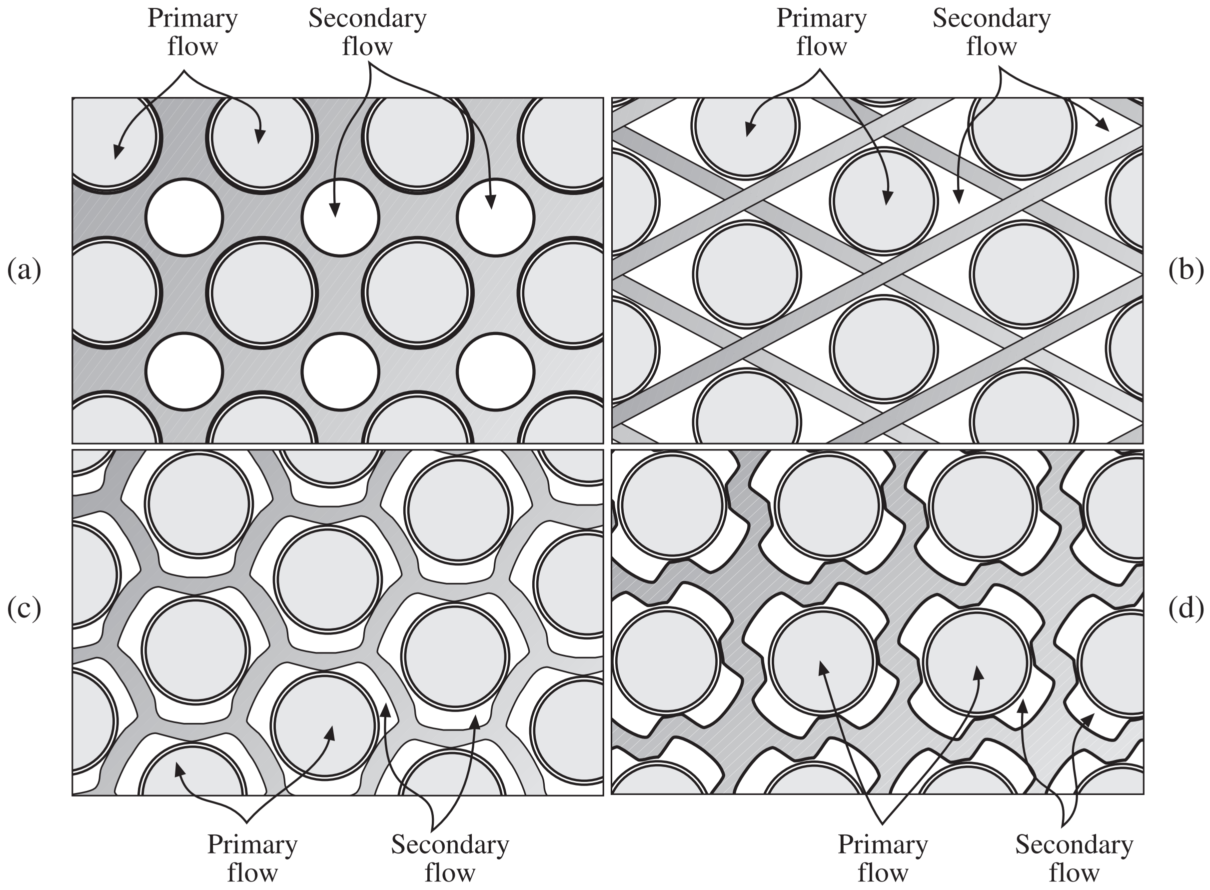
5. More detailed study of oxidized sulfur and other acidic species. [Next project]

6. More detailed study of reduced sulfur, S^{y-}SCC. [The next after #5.]

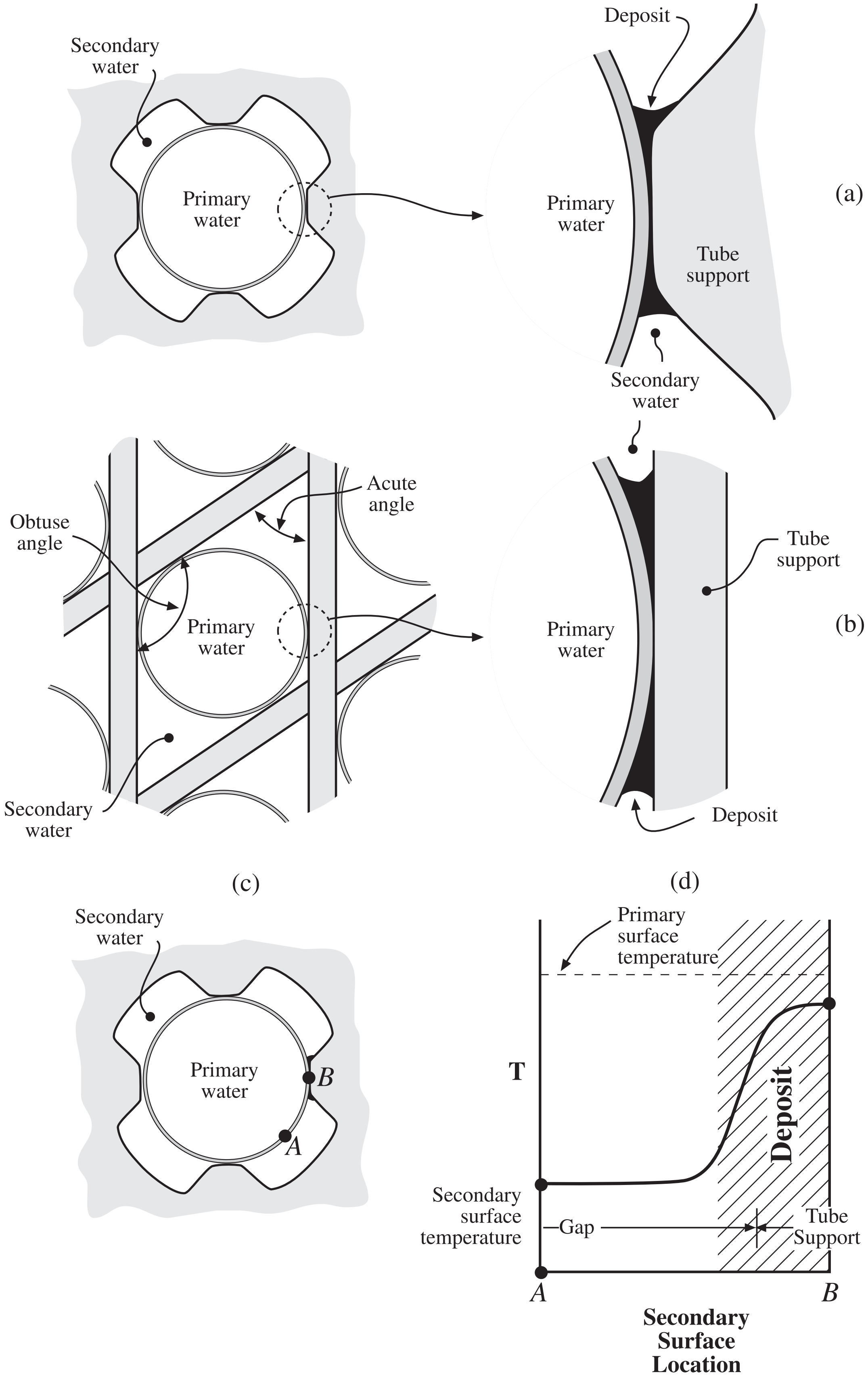
7. Detailed study of chemistry of crevices using data from: model boilers, pulled tubes, collars (pieces of deposit from intersection of tube and tube supports), hideout return. Use “machine thermodynamics” for analyzing data (evaluate MULTEQ, geochemist work bench, OLI) [Next]

8. Integrate all submodes using product of reliabilities. [Next]

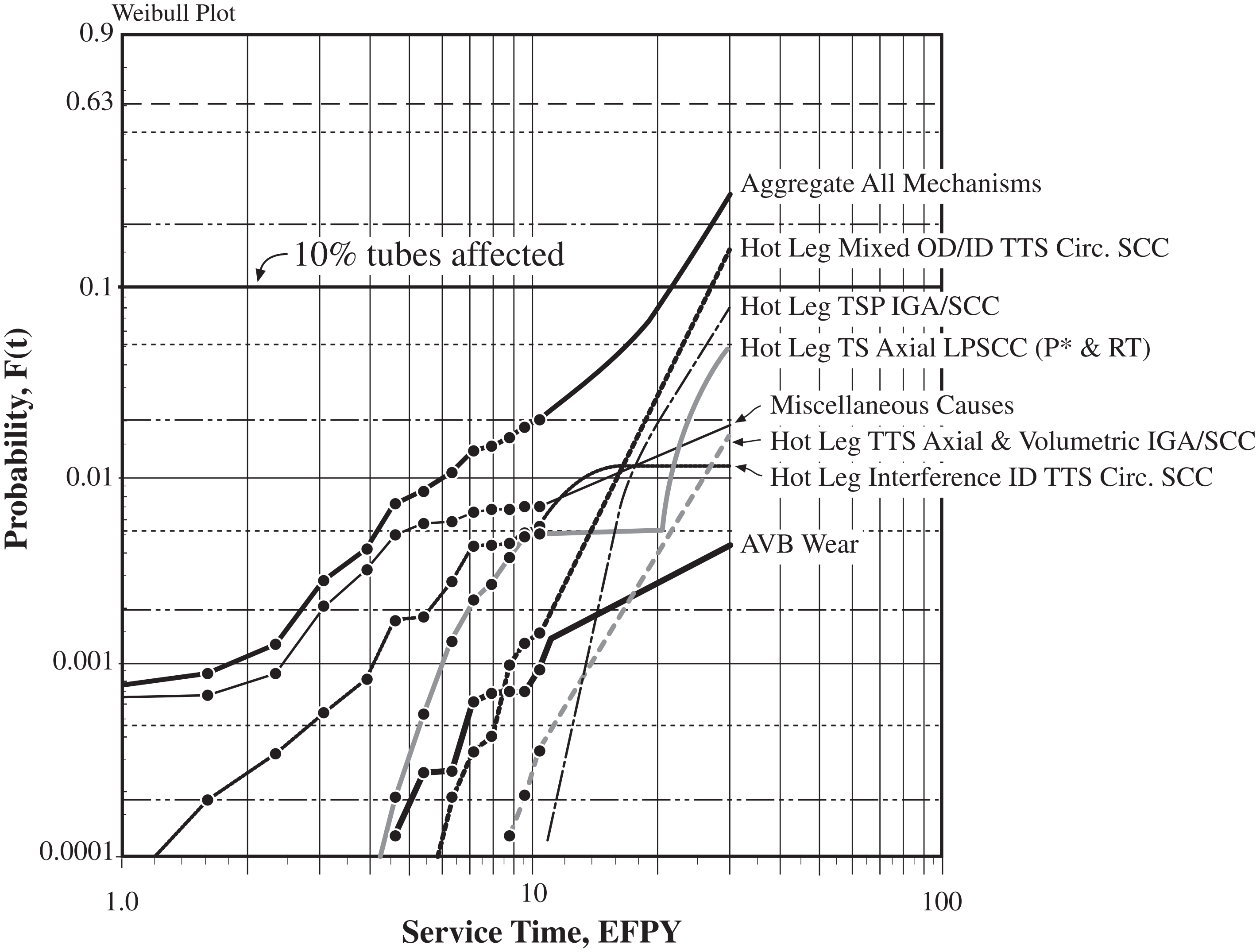
9. Integrate dependencies of submodes with chemistry of crevices. [Final]



Geometries of tube supports: (a) Drilled hole typical of early Westinghouse designs; (b) egg crate typical of siemens and Combustion Engineering; (c) broached trefoil typical of Babcock and Wilcox; (d) broached quatrefoil typical of later Westinghouse designs.



Schematic view of accumulation of deposits at line contact crevices associated with (a) broached holes and (b) egg crates. Example (c) of different temperatures (d) at open area and at deposit-filled contact area.



Probability vs. equivalent full power years (EFPY) for failures of tubing from a set of SGs in the Ringhals 4 PWR. Designations: TTS = "top of tube sheet." TS = "tubesheet." Circ. SCC = "circumferential SCC." P* = special location where SCC is not serious. RT = "roll transition." AVB = "antivibration bars." From Bjornkvist and Gorman.

$$f(t)=\left[\frac{\beta}{(\theta-t_o)^{\beta}}\right](t-t_o)^{\beta-1}\exp\left[-\left(\frac{t-t_o}{\theta-t_o}\right)^{\beta}\right],\ t>t_o \tag{1}$$

$$\ln\left[\ln\left(\frac{1}{1-F(t)}\right)\right]=\beta\left[\ln\left(t-t_o\right)-\ln\left(\theta-t_o\right)\right] \tag{2}$$

$$\begin{gathered} h(t)=\frac{f(t)}{1-F(t)} \\ h(t)=\left(\frac{\beta}{\theta-t_o}\right)\left(\frac{t-t_o}{\theta-t_o}\right)^{\beta-1}=\frac{\beta}{\left(\theta-t_o\right)^{\beta}}\left(t-t_o\right)^{\beta-1} \end{gathered} \tag{3}$$

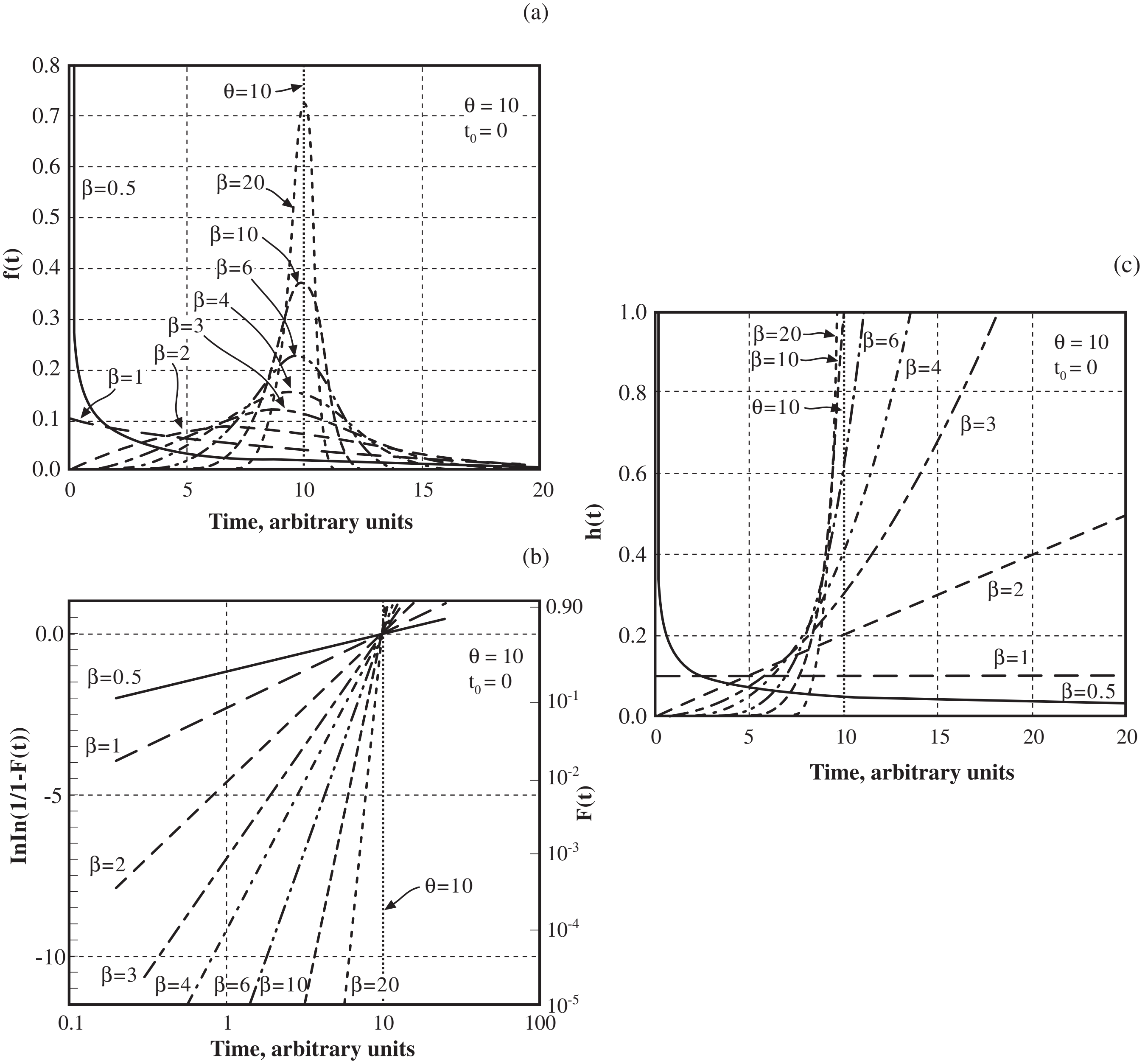
where:

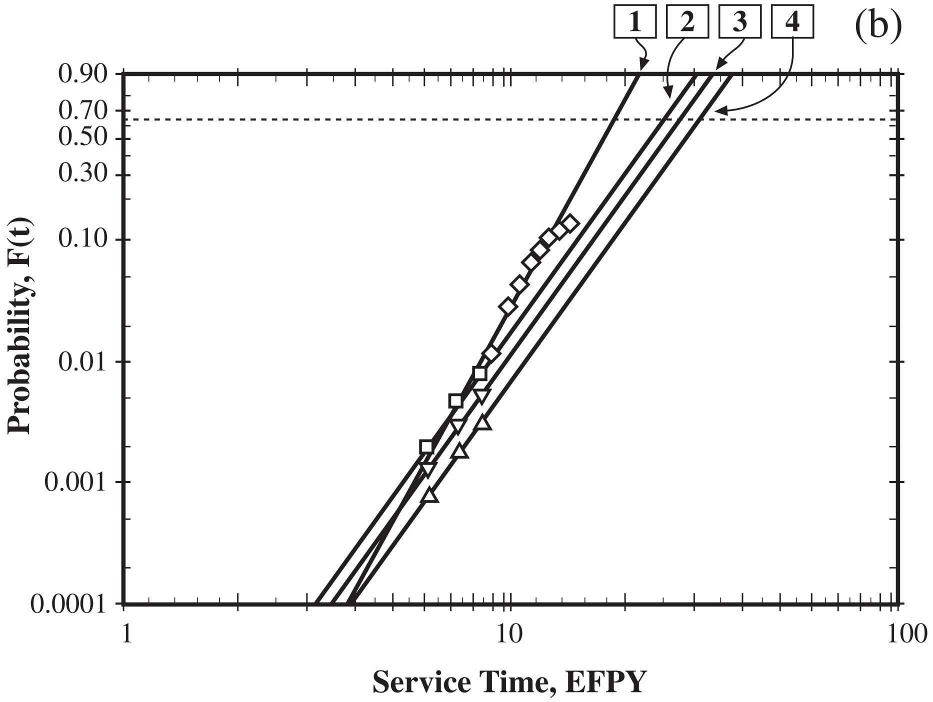
θ = Space parameter or Weibull characteristic

t_o = Location papameter

β = Shape parameter

t = Time


(a)
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
f(t)
θ=10
θ = 10
t_0 = 0
β=0.5
β=20
β=10
β=6
β=4
β=3
β=2
β=1
0
5
10
15
20
Time, arbitrary units
(b)
0.0
-5
-10
lnln(1/1-F(t))
0.90
10^{-1}
10^{-2}
10^{-3}
10^{-4}
10^{-5}
F(t)
θ = 10
t_0 = 0
β=0.5
β=1
β=2
β=3
β=4
β=6
β=10
β=20
θ=10
0.1
1
10
100
Time, arbitrary units
(c)
1.0
0.8
0.6
0.4
0.2
0.0
h(t)
β=20
β=10
θ=10
β=6
β=4
β=3
β=2
β=1
β=0.5
θ = 10
t_0 = 0
0
5
10
15
20
Time, arbitrary units

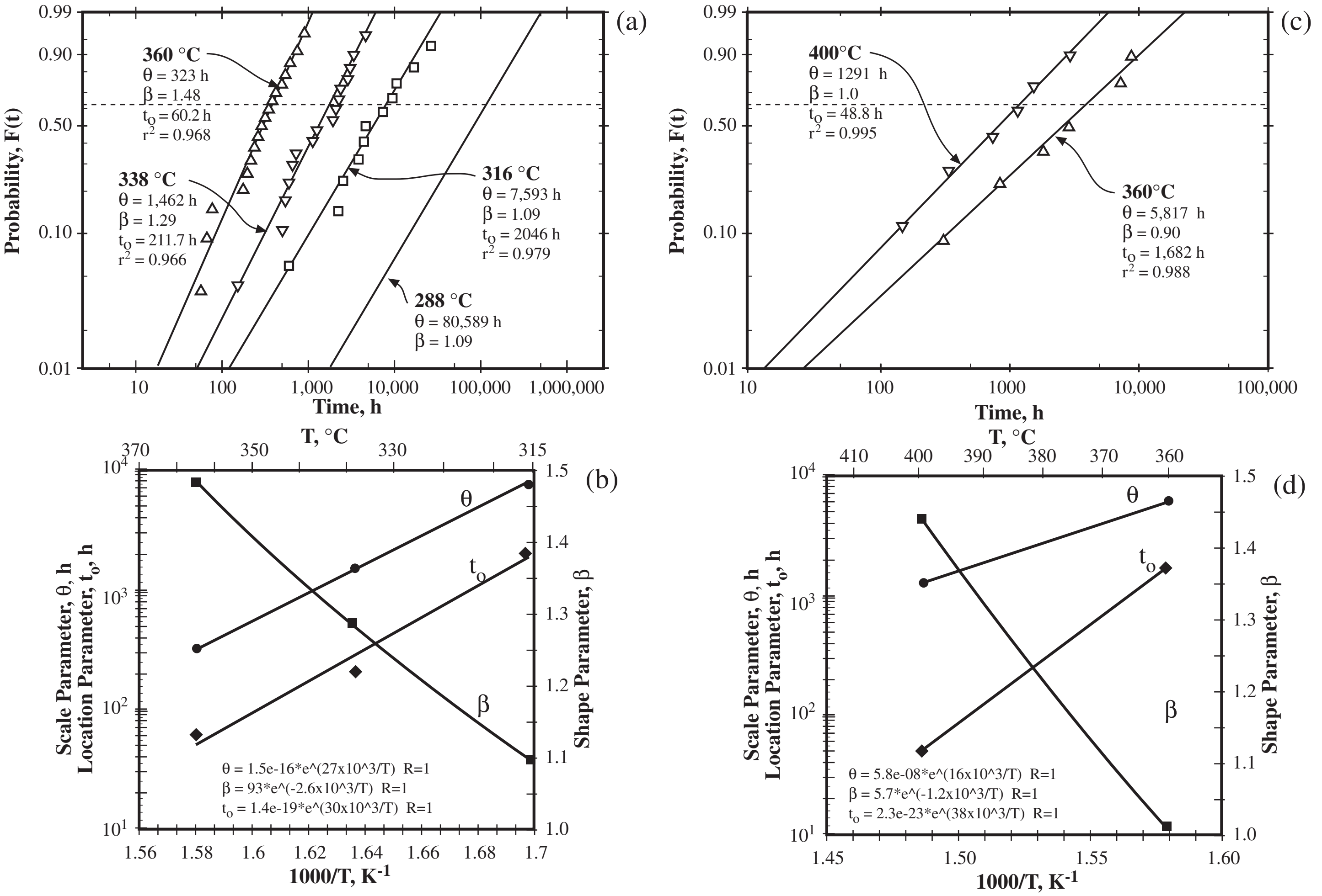


1. Cold Leg Sludge Pile, HTMA Tubing
θ = 30.24 EFPY
β = 4.49
r^2 = 0.975

2. Hot Leg Sludge Pile, HTMA Tubing
θ = 26.69 EFPY
β = 4.48
r^2 = 0.971

3. Hot Leg Eggcrate Tube Supports, HTMA Tubing
θ = 24.4 EFPY
β = 4.45
r^2 = 0.963

4. SCC and IGC on the Secondary Side in Tube Sheet Crevices
θ = 18.57 EFPY
β = 5.86
r^2 = 0.892

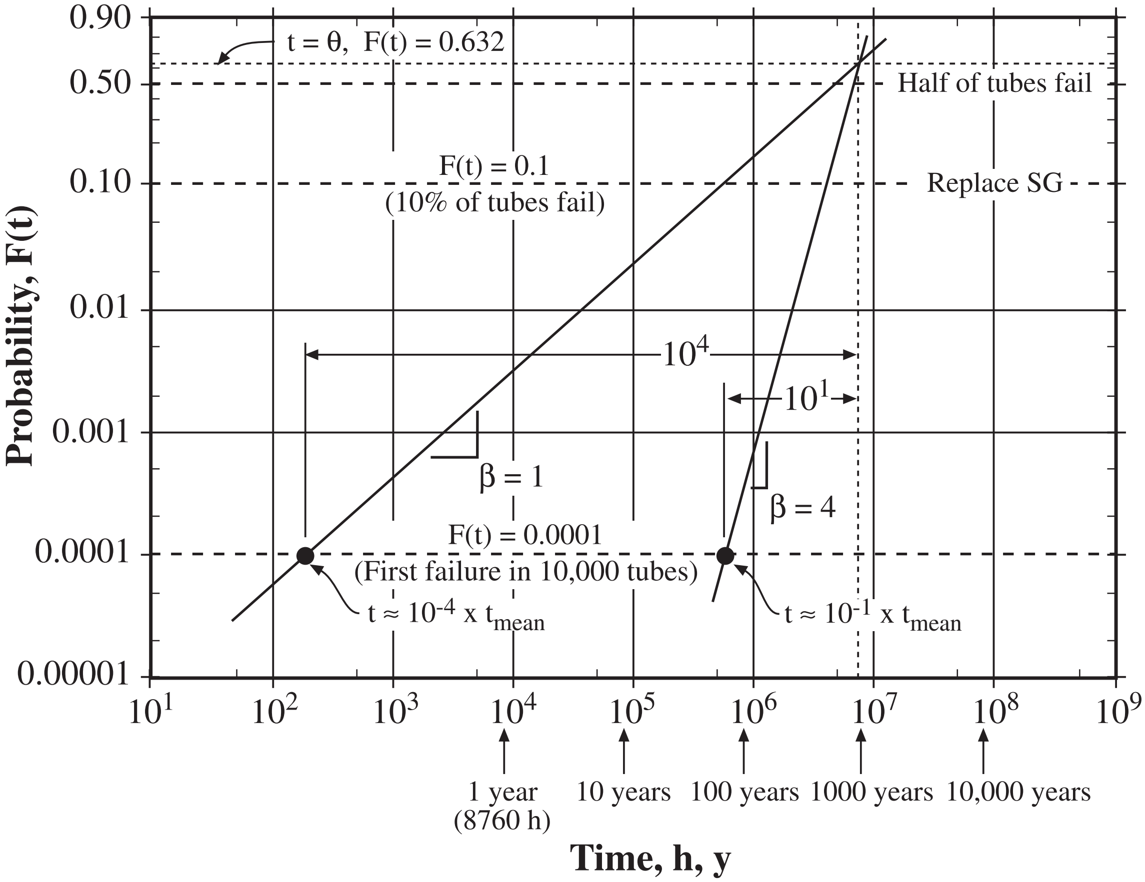


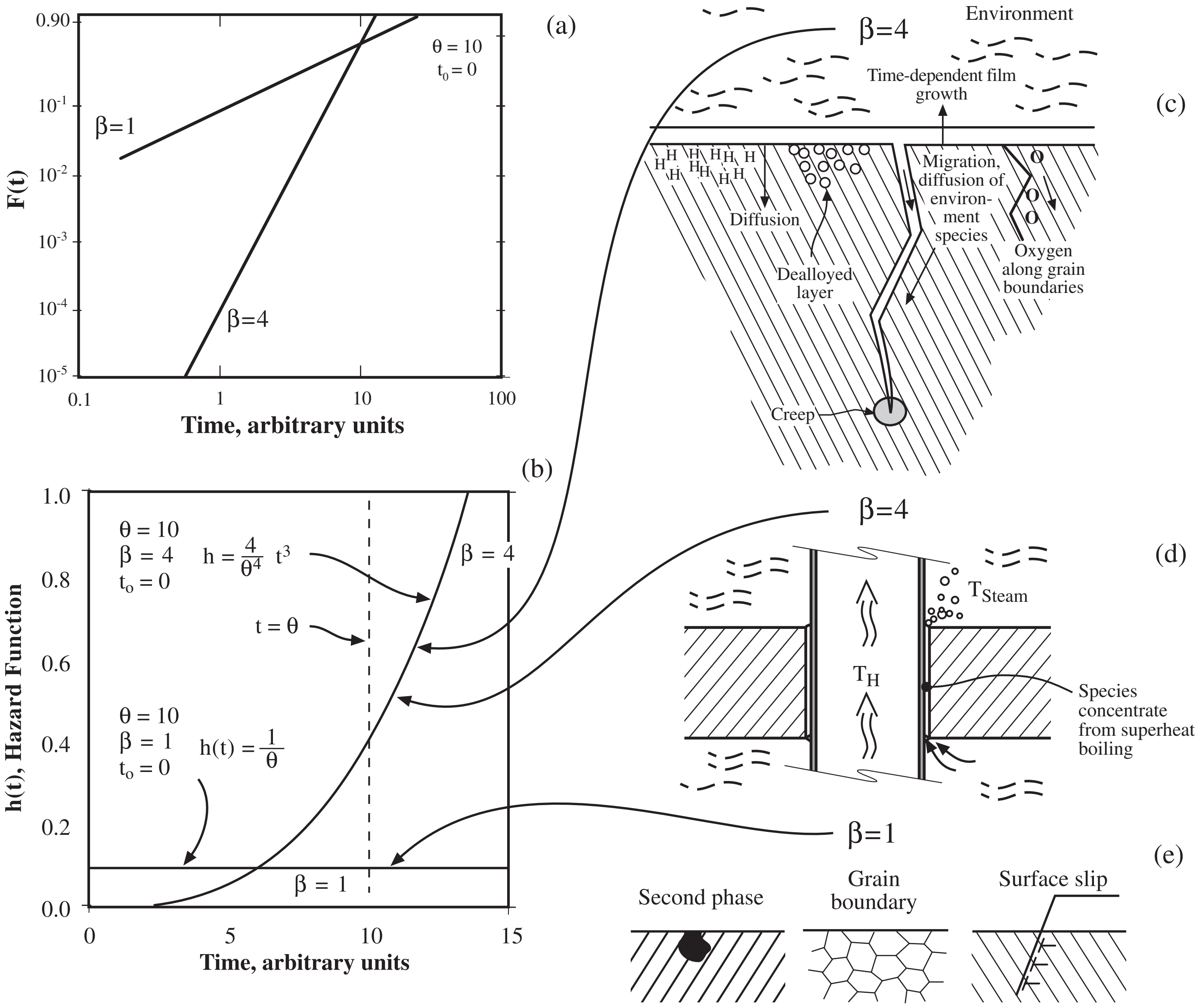
LPSCC of Alloy 600MA. (a) Probability vs. time to fail by LPSCC for a temperature range of 288 to 360°C for testing in high-purity deoxygenated water containing a hydrogen concentration of 10-60 cc H_2/kg H_2O. From Webb. (b) Correlation of data in (a) for θ, β, t_o vs. 1/T. (c) Probability vs. time to fail by LPSCC in high-purity water and steam for 360°C water and 400°C steam with 1 psia hydrogen in the former and 11 psia steam in the latter. From Jacko. (d) Correlation of data in (c) for θ, β, t_o vs. 1/T.

Cumulative Distribution Function (correlation without physical foundation)

$$F(t) = 1 - \exp\left[-\left(\frac{t - t_o}{\theta - t_o}\right)^{\beta}\right]$$

$$\ln\left[\ln\left(\frac{1}{1 - F(t)}\right)\right] = \beta\left[\ln(t - t_o) - \ln(\theta - t_o)\right]$$





(a) Probability vs. time for *b*=1.0 and *b*=4.0. (b) Hazard function vs. time for *b*=1.0 and 4.0. (c) Examples of physical processes that produce *b*=1.0. (d) Examples of a heated crevice where accumulation processes occur before SCC can initiate. (e) Examples of accumulation processes that occur within metals and inside SCC.

$\frac{\textbf{Problem with } \beta}{(\textbf{Dispersion } \alpha \frac{1}{\beta})}$

1. Stressor dependence

Stressors: T, σ, X, E, pH

- $\beta \; \alpha$ stressor

  or

- $\beta \; \alpha \; \frac{1}{\text{stressor}}$

2. Dependence on physical processes

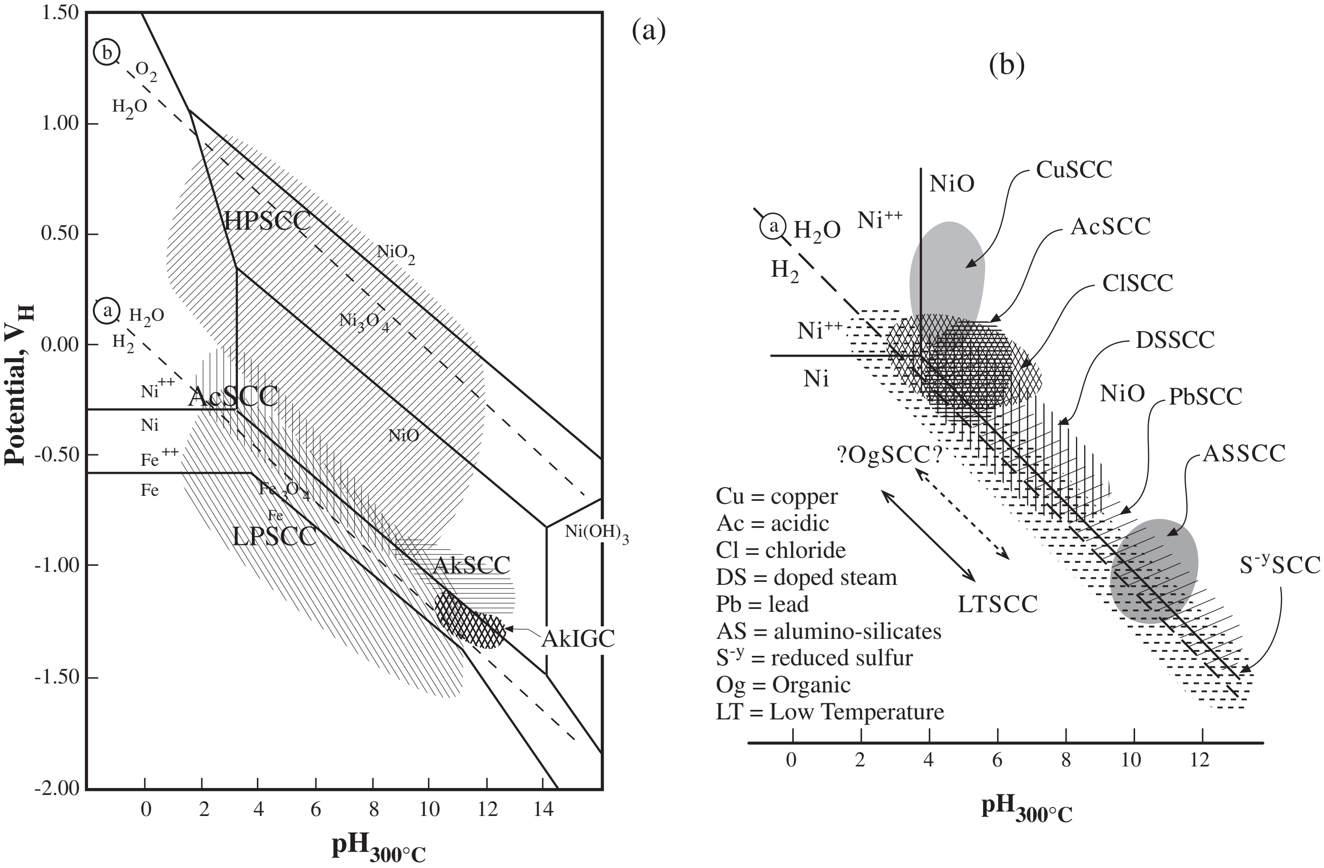
- $\beta = 1$ for surface processes (pitting, grain boundary, initiation of SCC)
- $\beta > 1$, e.g., $\beta = 4$ for accumulation at surface or inside metal

3. Initiation and propagation mixed

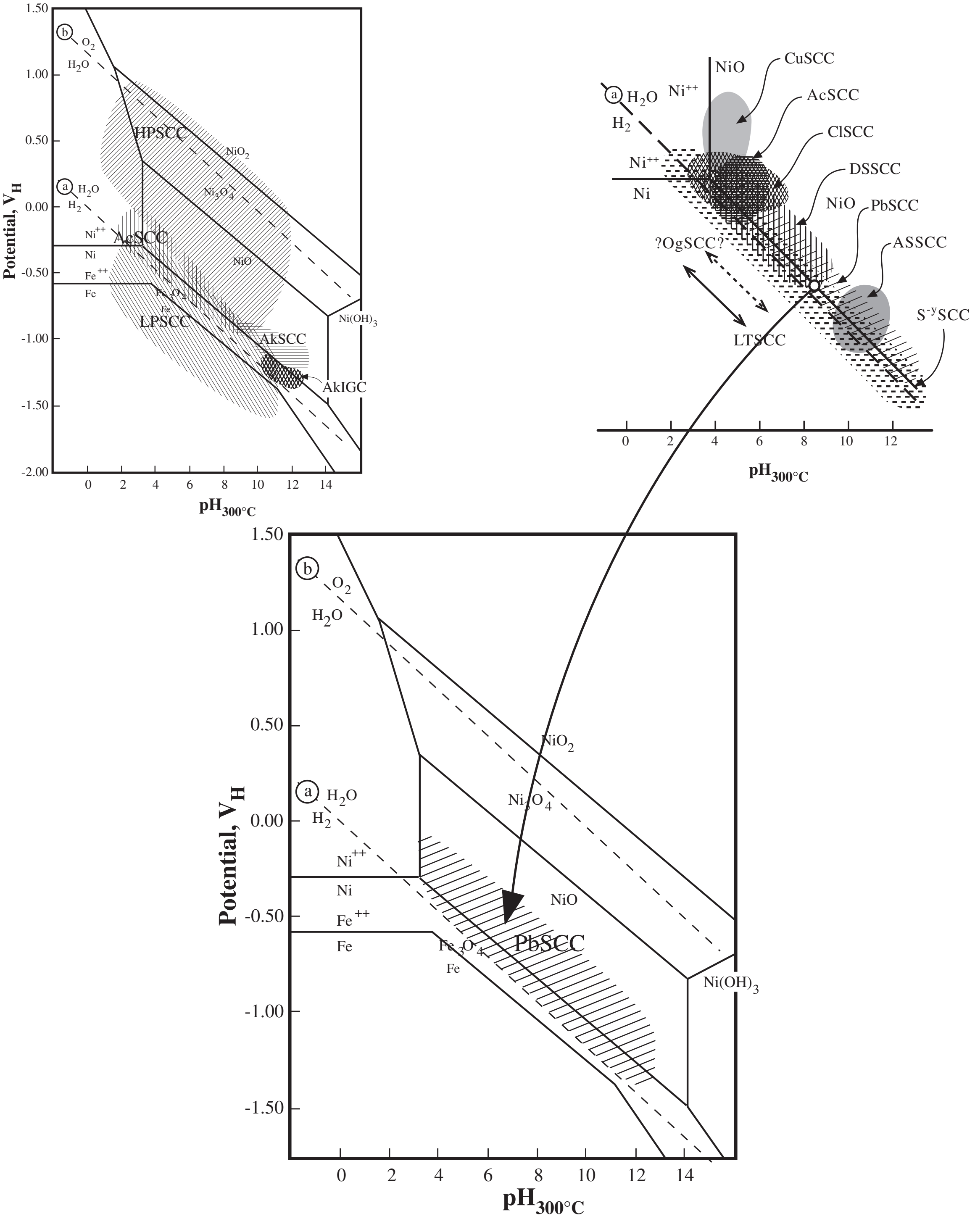
- $\beta = 1$ for initiation
- $\beta > 1$ for propagation

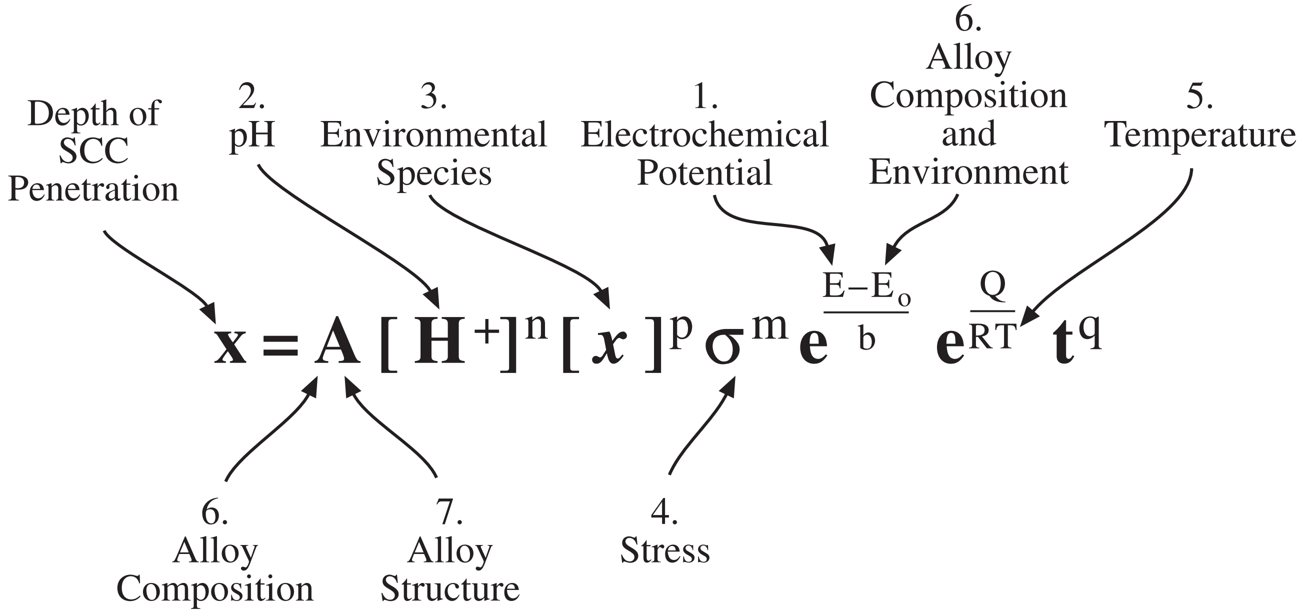
4. Aggregate data reduces β

5. Testing near boundaries of SCC submode reduces β

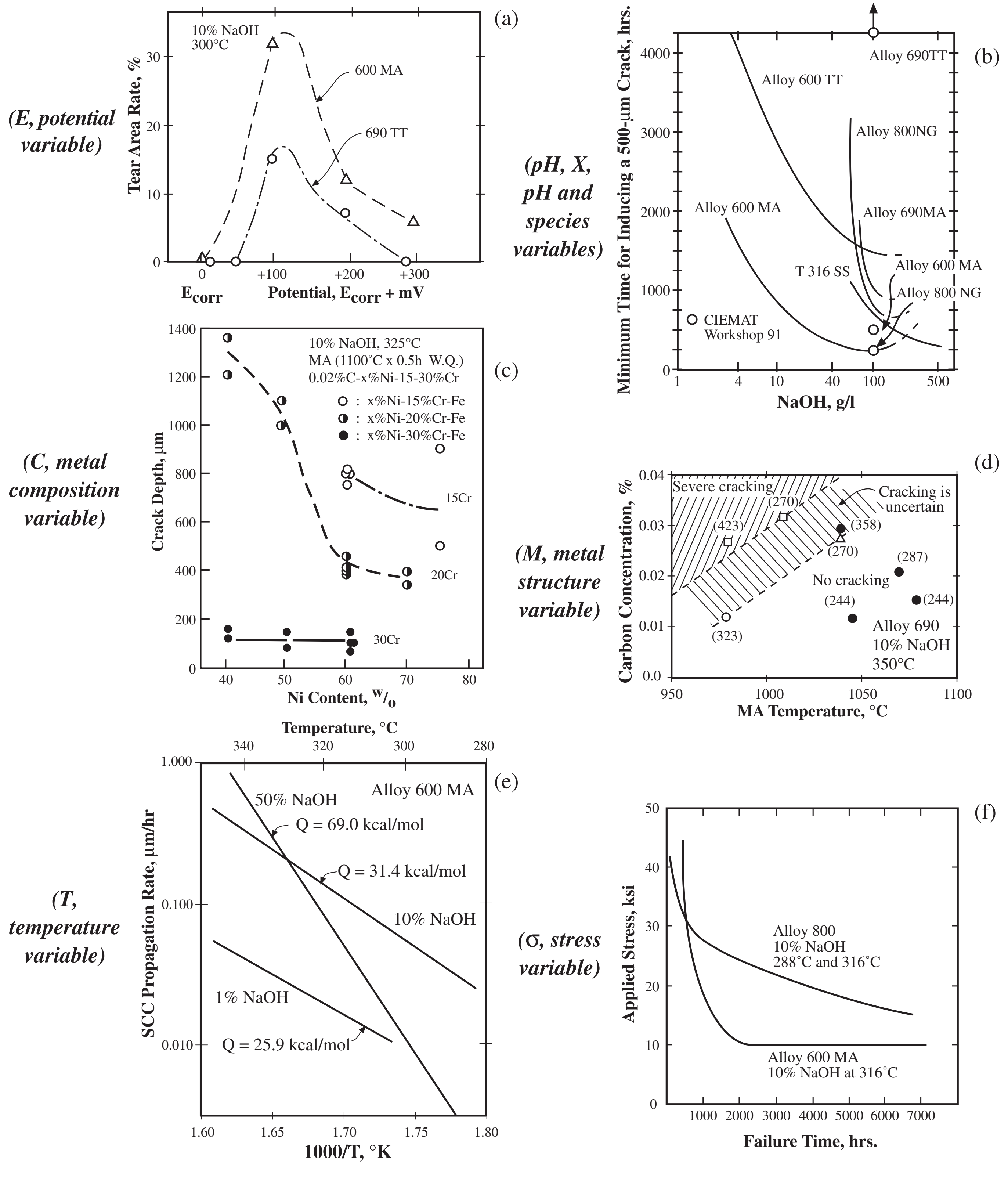


(a) Major submodes of SCC plotted with respect to coordinates of potential and pH for significant reactions of Ni and Fe at 350°C. Potential-pH relationships from Chen. Extent of the submodes based on experience from laboratory testing and reasonable interpolation and extrapolations. Submodes are applicable to Alloy 600 MA in the range of 300 to 350°C. (b) minor submodes of SCC for Alloy 600MA plotted with respect mainly to the NiO/Ni half-cell equilibrium at 300°C.

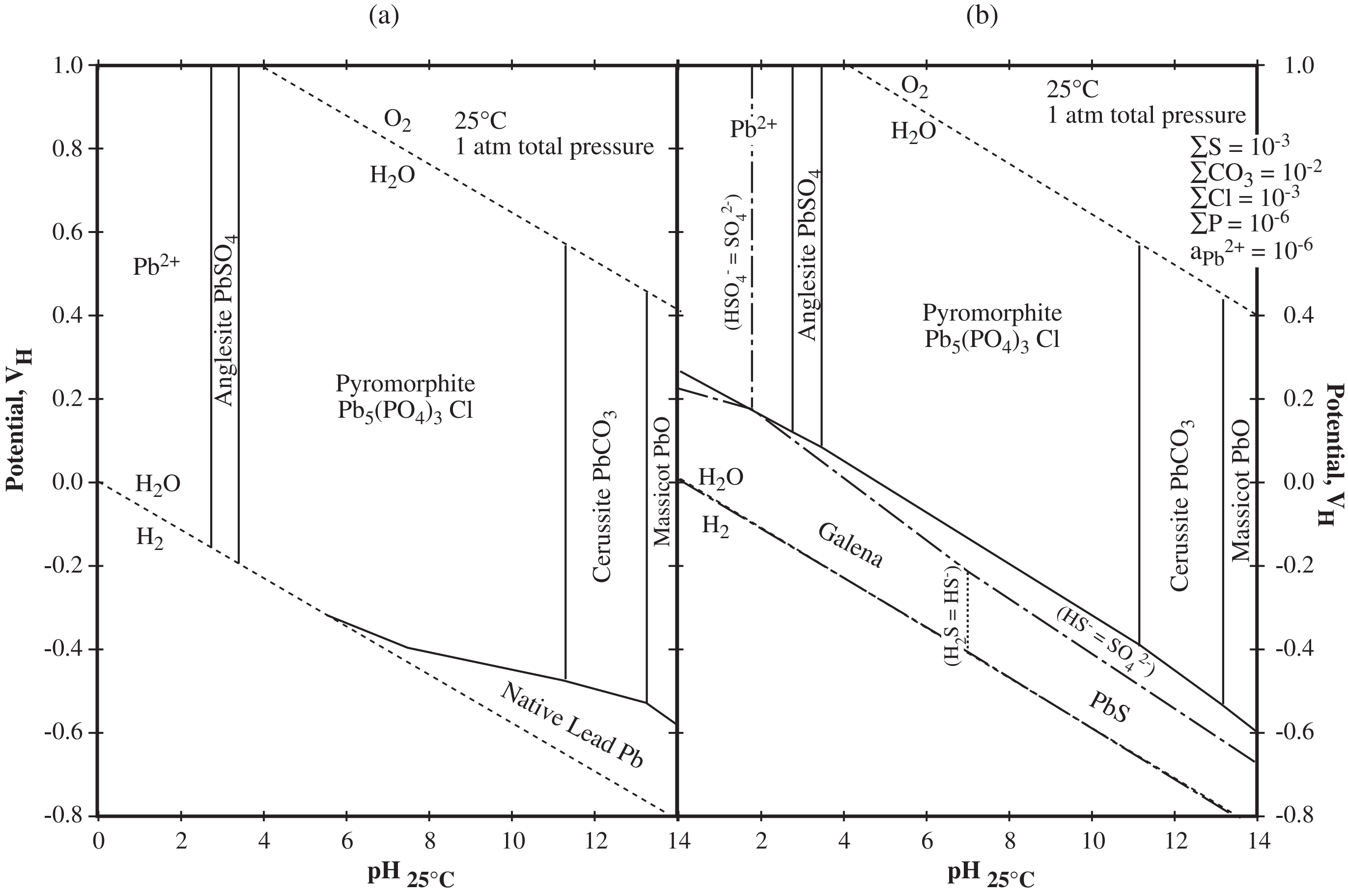

1.50
1.00
0.50
0.00
-0.50
-1.00
-1.50
-2.00
Potential, V_H
b
O_2
H_2O
a
H_2O
H_2
HPSCC
NiO_2
Ni_3O_4
Ni^{++}
Ni
AcSCC
Fe^{++}
Fe
Fe_3O_4
Fe
LPSCC
NiO
$Ni(OH)_3$
AkSCC
AkIGC
0 2 4 6 8 10 12 14
$pH_{300°C}$
NiO
CuSCC
a
H_2O
H_2
Ni^{++}
AcSCC
ClSCC
Ni^{++}
Ni
DSSCC
NiO
PbSCC
?OgSCC?
ASSCC
$S^{-y}SCC$
LTSCC
0 2 4 6 8 10 12
$pH_{300°C}$
1.50
1.00
0.50
0.00
-0.50
-1.00
-1.50
Potential, V_H
b
O_2
H_2O
a
H_2O
H_2
NiO_2
Ni_3O_4
Ni^{++}
Ni
Fe^{++}
Fe
Fe_3O_4
Fe
NiO
PbSCC
$Ni(OH)_3$
0 2 4 6 8 10 12 14
$pH_{300°C}$



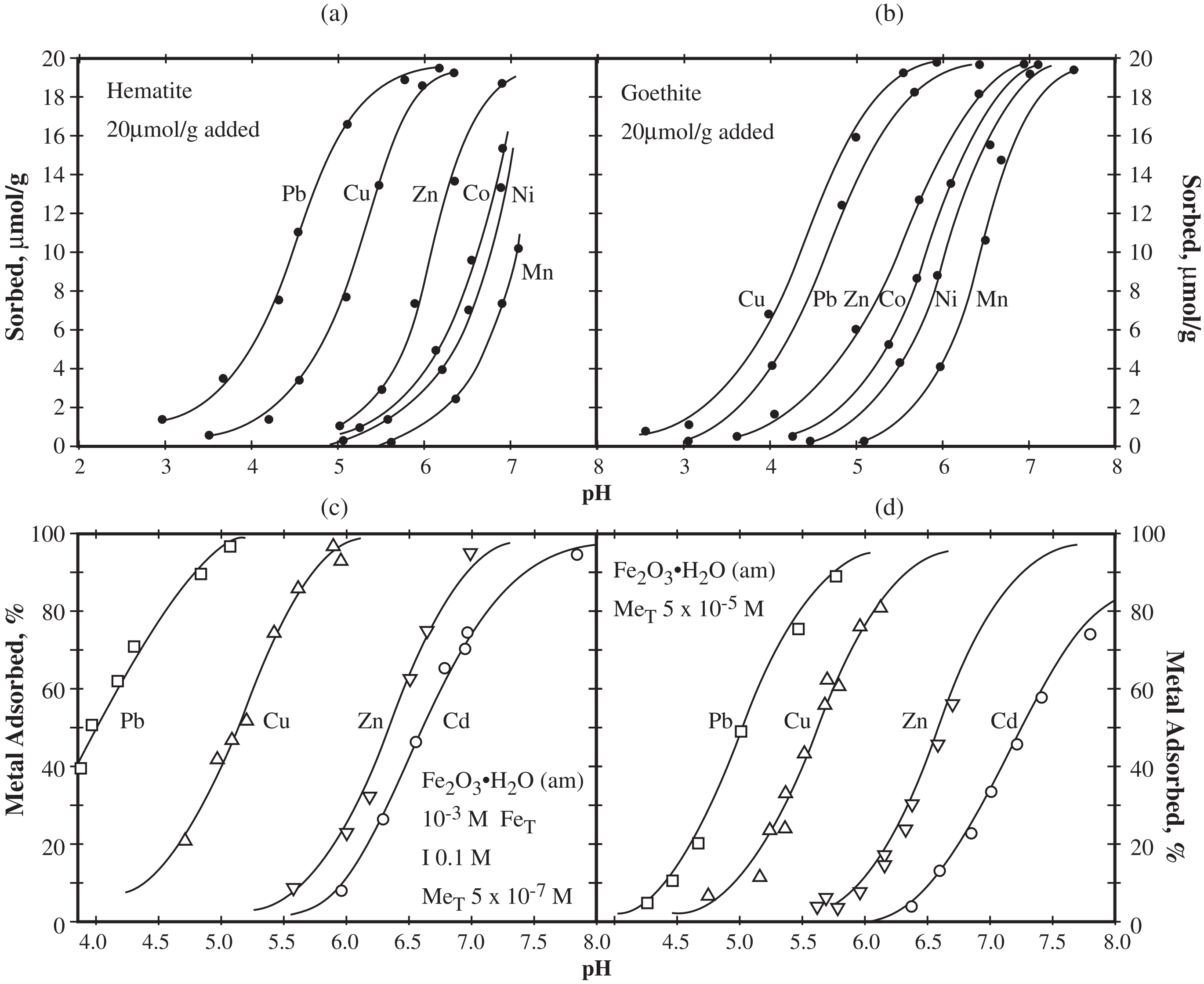
$$\mathbf{x} = \mathbf{A}\,[\,\mathbf{H}^{+}]^{n}\,[\,\boldsymbol{x}\,]^{p}\,\sigma^{m}\,\mathbf{e}^{\frac{E-E_{o}}{b}}\;\mathbf{e}^{\frac{Q}{RT}}\,\mathbf{t}^{q}$$



Dependencies of AkSCC on the primary variables. (a) Tear area ratio vs. potential for Alloy 600MA and 690TT on 10% NaOH at 300°C. From Suzuki. (b) Minimum time for inducing a crack in smooth surface specimens vs. concentration of NaOH for various Fe-Cr-Ni alloys. Specimens are C-rings stressed to approximately the yield stress. The original curves of Berge and Donati were redrawn, and data were added by McIlree. Data points added by McIlree were C-rings with 2% strain tested at 10% NaOH. testing at 350°C. (c) Crack depth vs. Ni concentration for Ni-Cr-Fe alloys +0.02%C exposed to deaerated 10% NaOH solution at 325°C for 200 hours as single U-bends. Speciments are mill annealed. From Nagano et al. (d) IGSCC sensitivity of TT (700°C) Alloy 690 vs. MA, temperature and C constant in 10% NaOH, 350°C. From Valliant et al. (e) SCC propagation rate vs. 1000/T for Alloy 600 MA in various concentrations of NaOH. From Jacko. (f) Stress vs. time for Alloy 600 in 10% NaOH at 288 and 316°C for Alloys 600 and 800. From Wilson et al.



Potential vs. pH at 25°C for the H_2O, S, C, P, Cl system (a) without galena and (b) with galena. From Nriagu. [NRI-74]

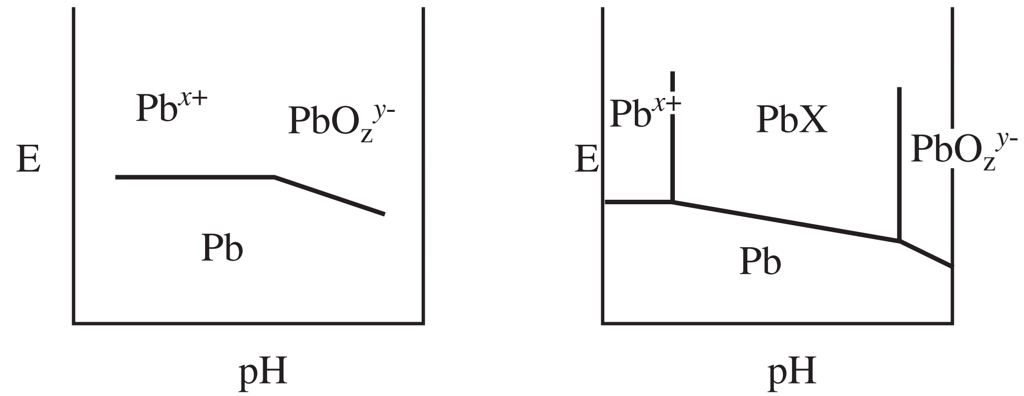


Quantity absorbed vs. pH at RT of Pb, Cu, Zn, Co, Ni and MN on (a) menatite and (b) goethite. From McKenzie. [McK-80] (c) Precent metal, Pb, Cu, Zn, Cd, adsorbed vs. pH at RT on amorphous $Fe_2O_3 \bullet H_2O$. (c) added metal 5x10^{-7} M. (d) added metal 5x10^{-5} M. From Benjamin and Leckie3. [BEN-81]

The Immobilization of Pb

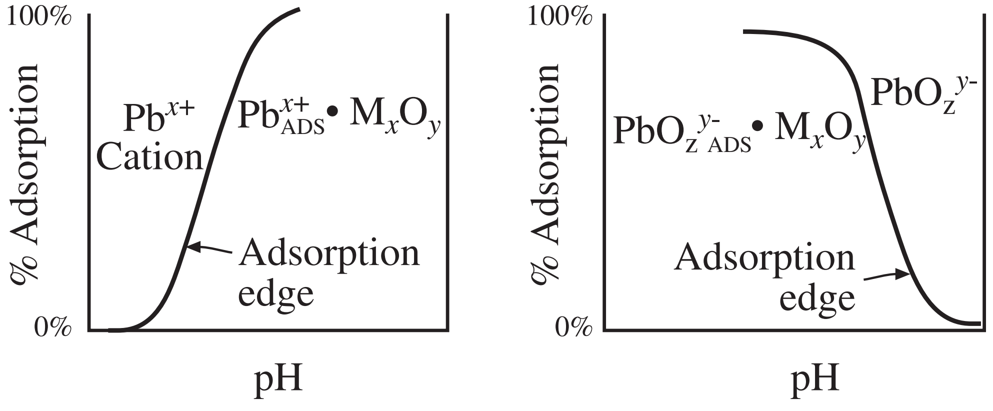
Formation of Soluble Compounds

$$Pb + X \Rightarrow PbX$$



Adsorption

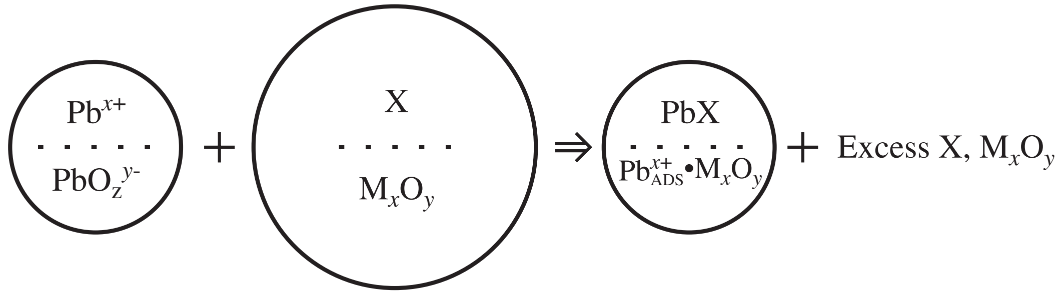
$$\left.\begin{matrix}Pb^{x+}\\PbO_z^{y-}\end{matrix}\right\} + M_xO_y \Rightarrow \left.\begin{matrix}Pb^{x+}_{ADS}\\PbO_{z\,ADS}^{y-}\end{matrix}\right\} \bullet M_xO_y$$



Schematic view of options for immobilizing and mobilizing Pb in SG deposits. Roles of compound formation and adsorption in immobilizing Pb.

The Immobilization of Pb (cont.)

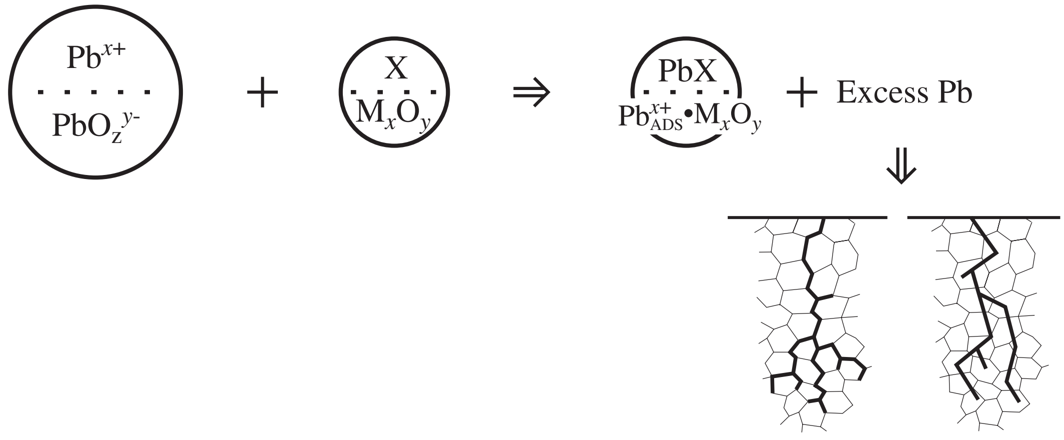
Condition for No PbSCC



⇓ Reduce Immobilzation

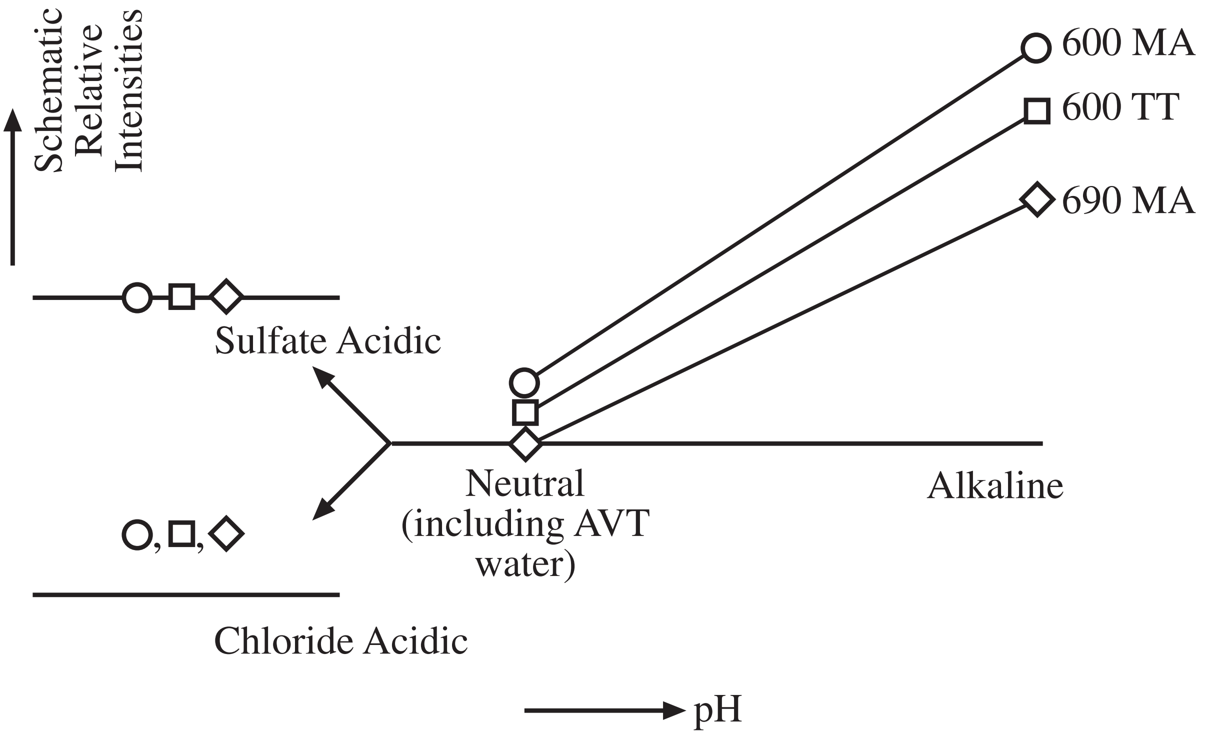
- Increase Water Purity
- Chemical Cleaning
- Soaks

Condition for PbSCC



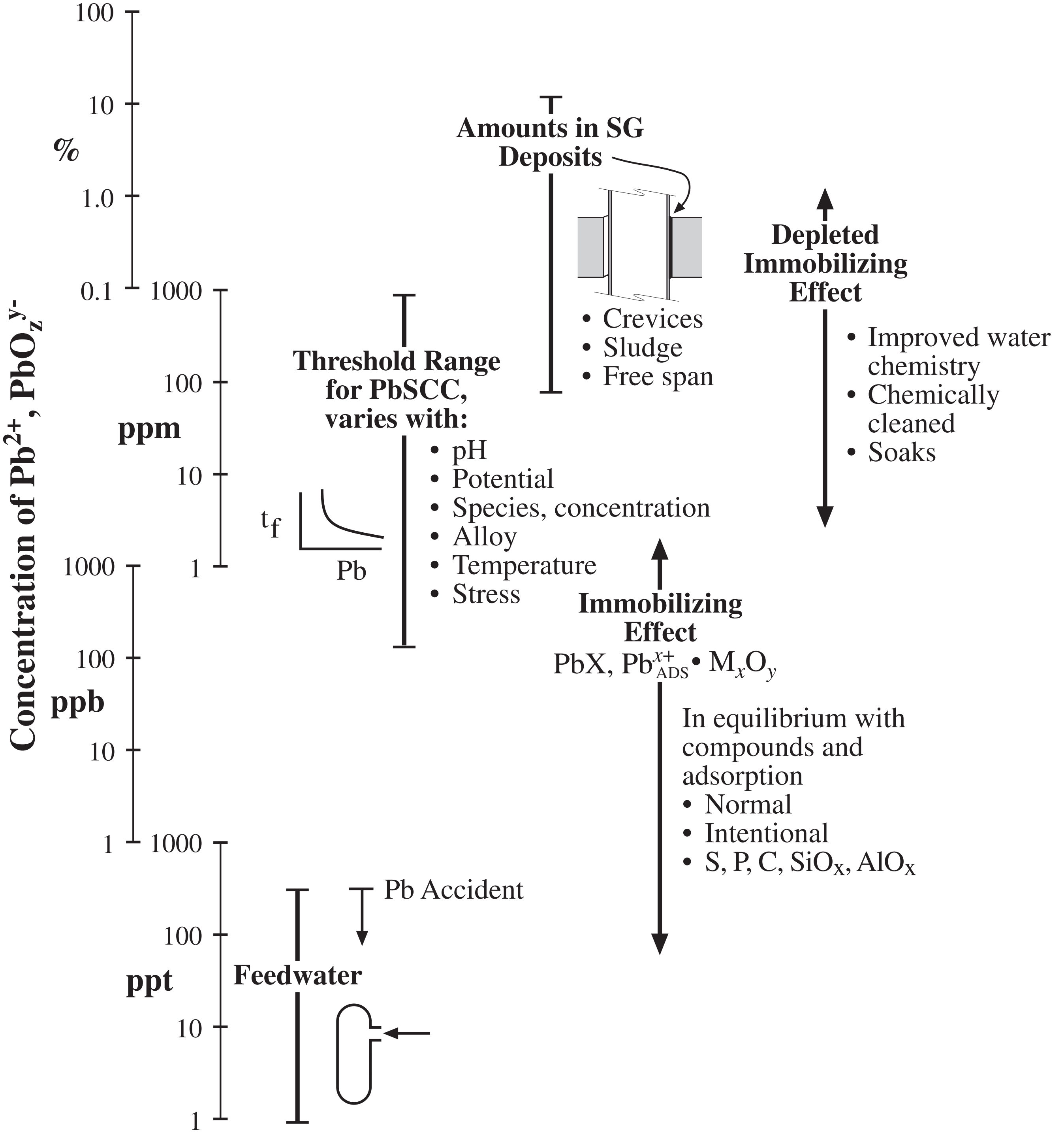
Schematic view of options for immobilizing and mobilizing Pb in SG deposits. Conditions for avoiding PbSCC.

Schematic Relative Intensity of PbSCC in SG Temperature Range



Schematic view of dependence of PbSCC for Alloys 600MA, 600TT, and 690TT on pH in the alkaline, neutral and acidic regions. Horizontal reference lines are for zero PbSCC.

Schematic Effect of Pb Concentrations as They Affect SGs



Amounts in SG Deposits

- Crevices
- Sludge
- Free span

Depleted Immobilizing Effect

- Improved water chemistry
- Chemically cleaned
- Soaks

Threshold Range for PbSCC, varies with:

- pH
- Potential
- Species, concentration
- Alloy
- Temperature
- Stress

Immobilizing Effect

PbX, Pb^{x+}_{ADS} • M_xO_y

In equilibrium with compounds and adsorption

- Normal
- Intentional
- S, P, C, SiO_X, AlO_X

Pb Accident

Feedwater

$$\left.\begin{array}{ll} \text{pH} & \text{pH} \\ \text{Potential} & E \\ \text{Identity and concentration of species} & X \\ \text{Alloy composition} & C \\ \text{Alloy structure} & M \\ \text{Temperature} & T \\ \text{Stress} & \sigma \end{array}\right\} \longrightarrow \left\{\begin{array}{l} \theta \\ \beta \\ t_o \end{array}\right.$$

$$F_i(t) = F_i(\theta, \beta, t_o)$$

$$\theta_i, \beta_i, t_{o_i} = \theta_i, \beta_i, t_{o_i}(E, \text{pH}, X, C, M, T, \sigma)$$

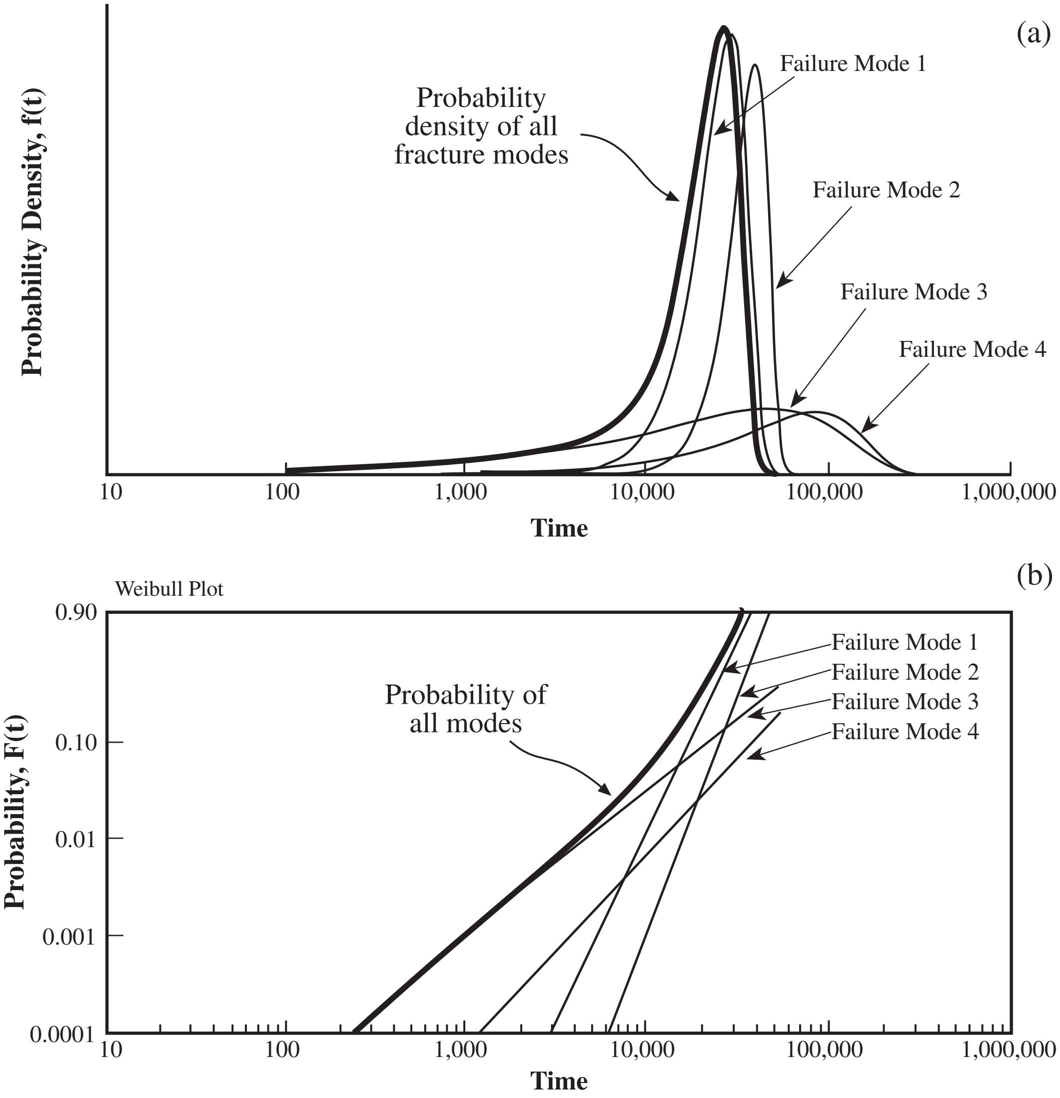
where i = AkSCC, LPSCC, AcSCC, PbSCC, S^{y-}SCC

Application of primary variables to statistical parameters.

$$F_T(t) = 1 - [1 - F_1(t)][1 - F_2(t)] \bullet\bullet\bullet [1 - F_n(t)]$$

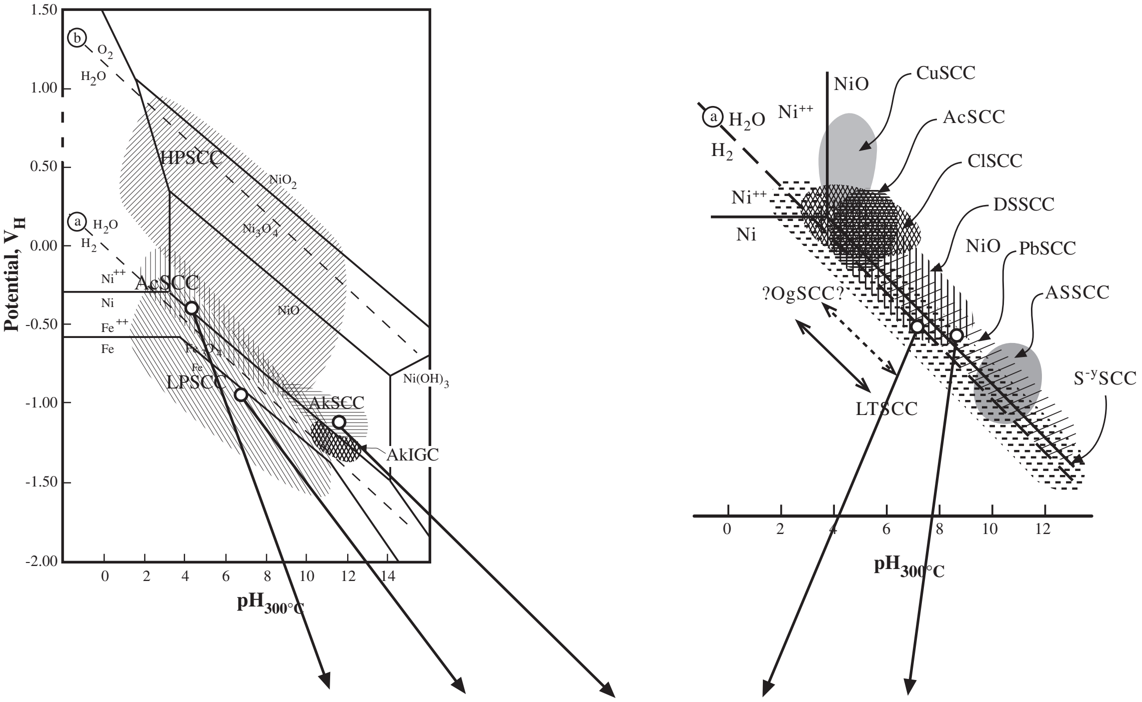
Where:

F_T = Total probability, and where the subscripts refer respectively to AkSCC, LPSCC, PbSCC and S^{y-}SCC

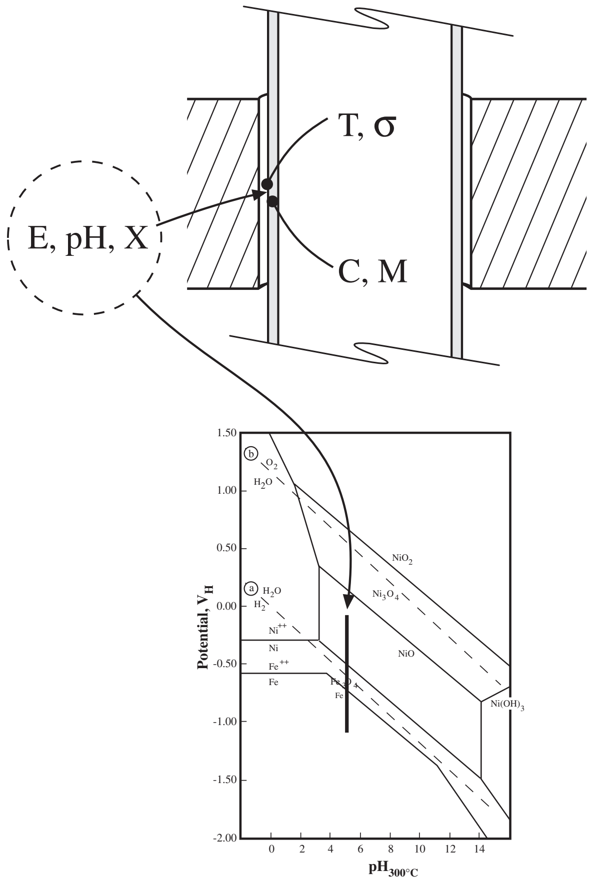


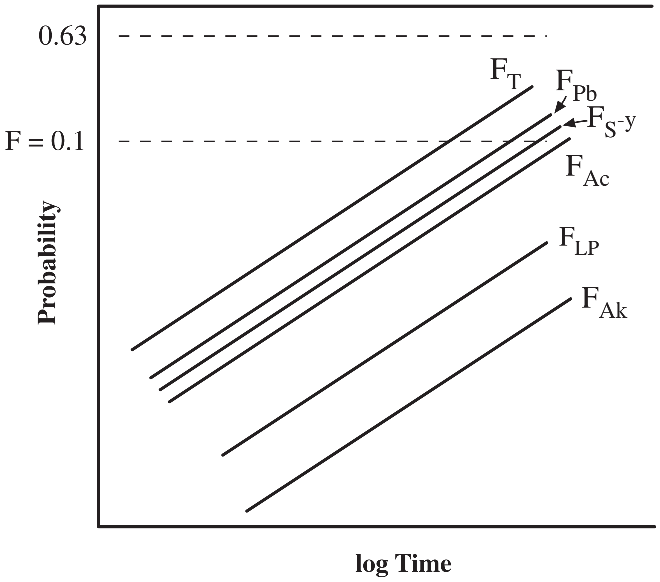
(a) pdfs for four separate failure modes occurring in the same subcomponent. Total pdf shown aggregating data from four. (b) cdf for the four cases in (a) and the aggregate distribution is shown based on Eqn. (36).

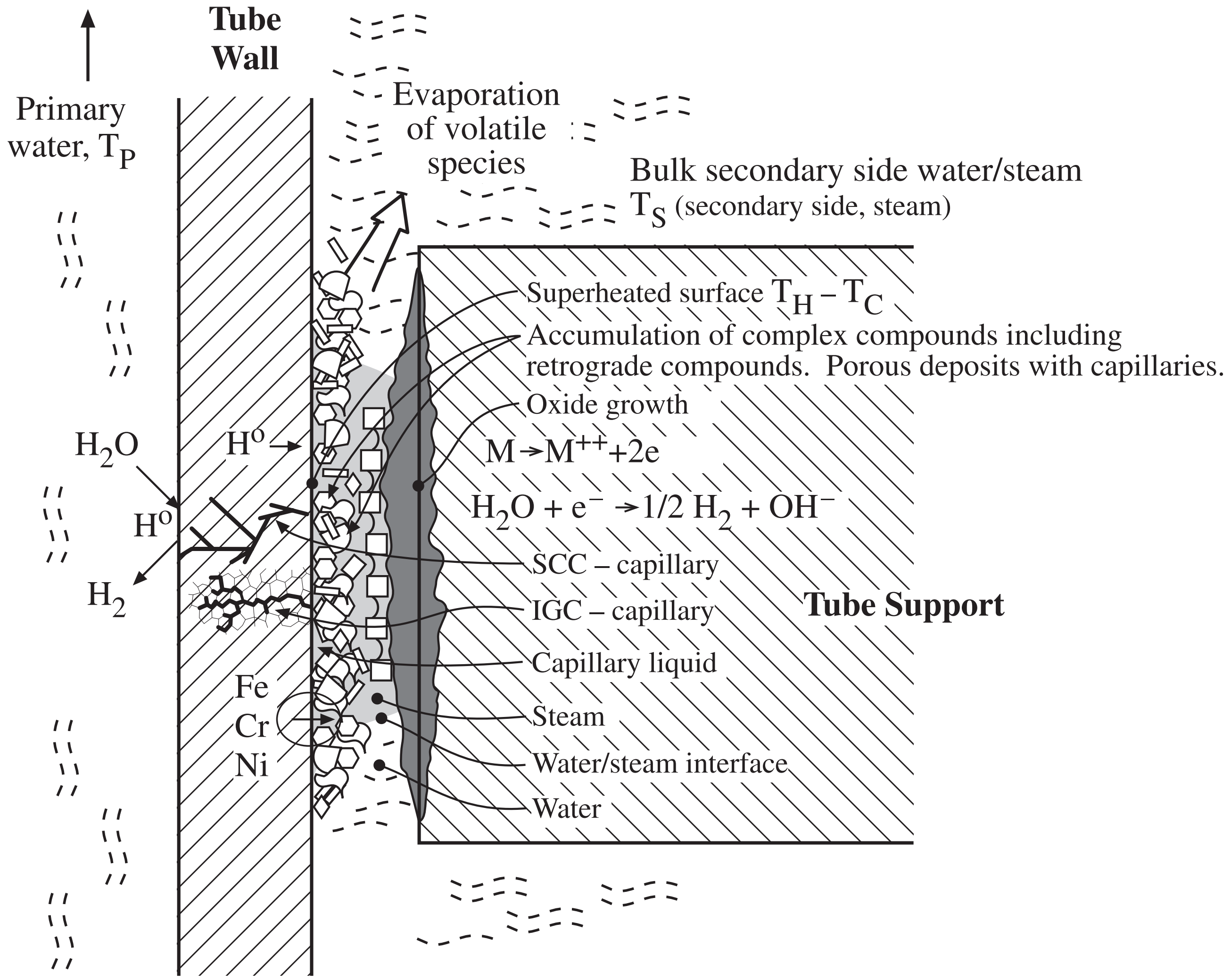
Overall Expression



$$F_T(t) = 1 - (1-F_{Ac})(1-F_{LP})(1-F_{Ak})(1-F_{S^{-y}})(1-F_{Pb})]$$

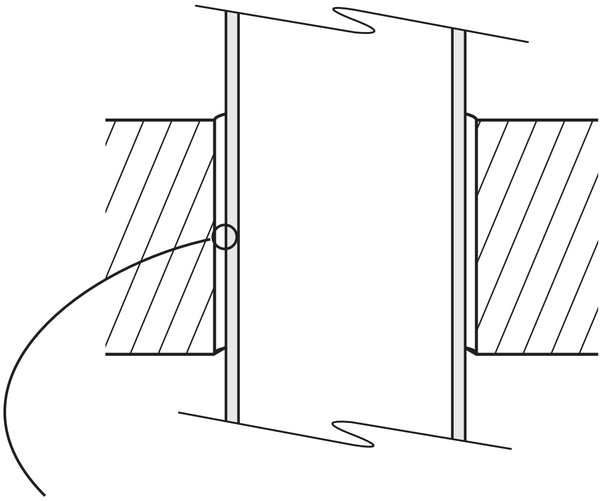






Schematic view of heat transfer crevice at a tube support.

Defining the Local Environment



Need: E, pH, X

Sources:

- Morphology of deposits
- Chemistry of deposits
- Hideout return
- Blowdown chemistry
- Concentration relative to bulk
- Analysis
- Laboratory experiments

Data from:

- EPRI Reports
- Direct measurements of collars
- Utility reports
- Published literature
- Experiments

Heated Crevice - Design, Experimental Methods, and Data Interpretation

Jesse Lumsden
Rockwell Science Center

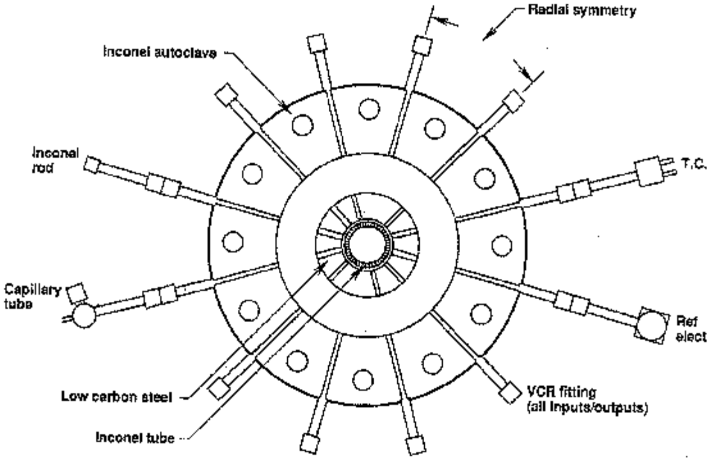
Keith Fruzzetti
EPRI

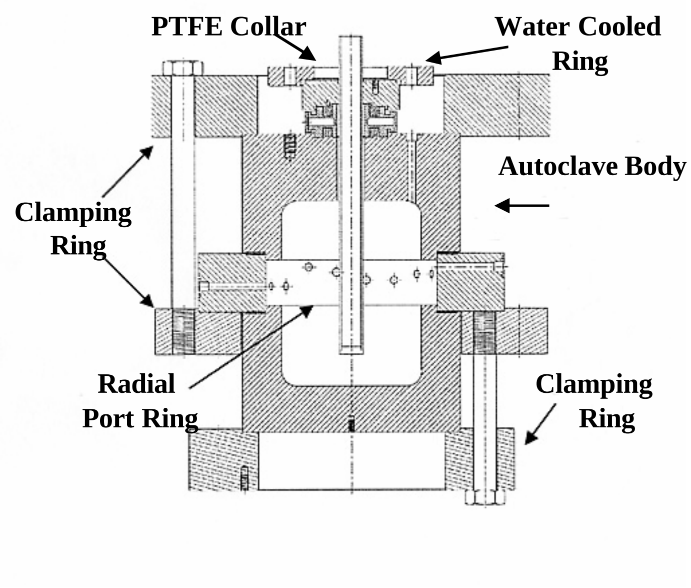
Heated Crevice Seminar
Argonne National Laboratory

Heated Crevice - Design

- Desired Flexibility
  - Easily Change Geometric Configuration/ Crevice Dimensions
  - Open Crevice, Packed Crevice, Closed Bottom Options
  - Disassemble & Tube Inspection Easy
- Clam Shell Design for Autoclave Body
- Tube Assembly Detachable from Autoclave
- Ring (Support Plate) Mounted Using Support Rods from the Side

Heated Crevice - Design





PTFE Collar

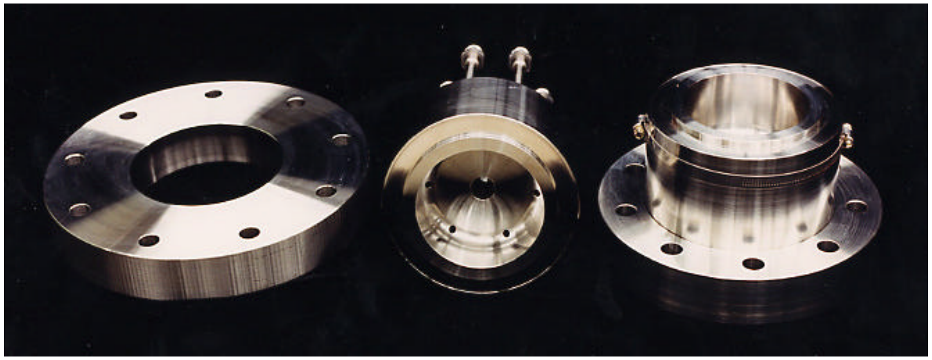
Water Cooled Ring

Autoclave Body

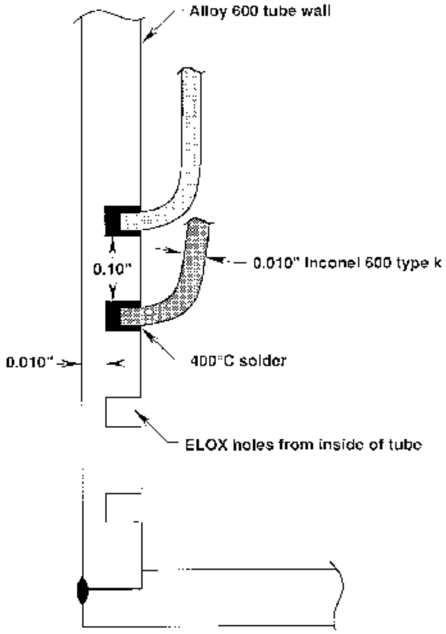
Clamping Ring

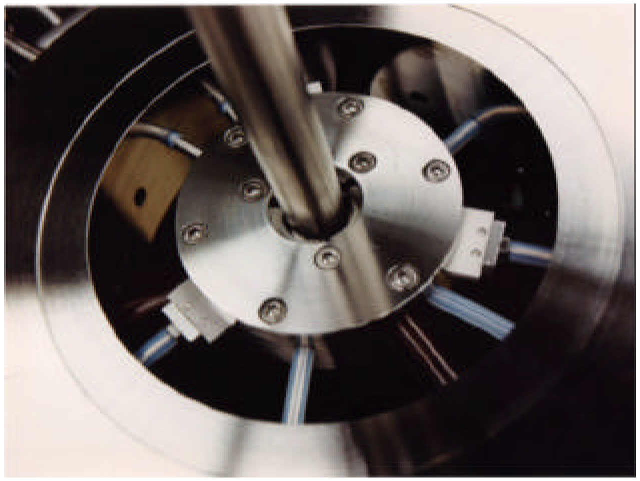
Radial Port Ring

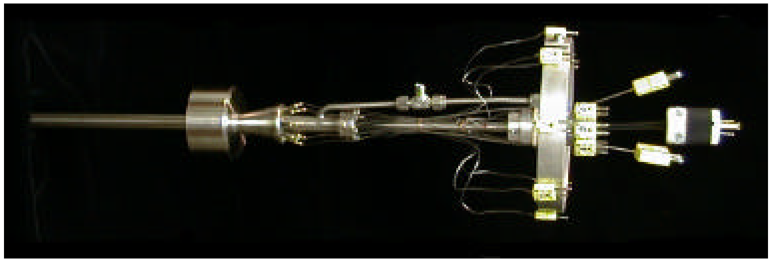
Clamping Ring



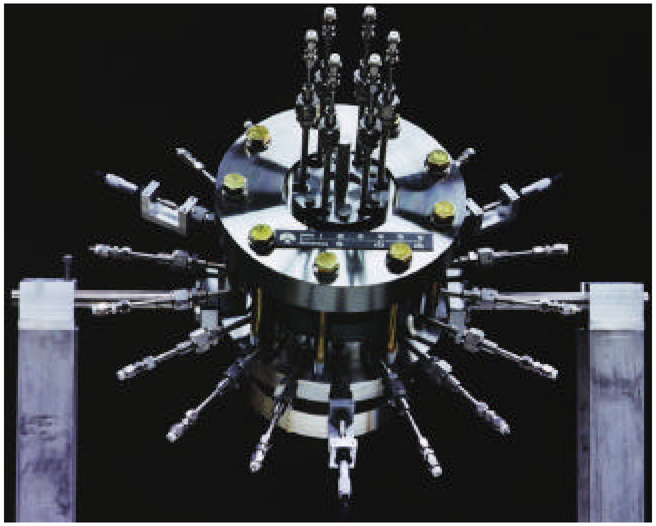
Heated Crevice - Design

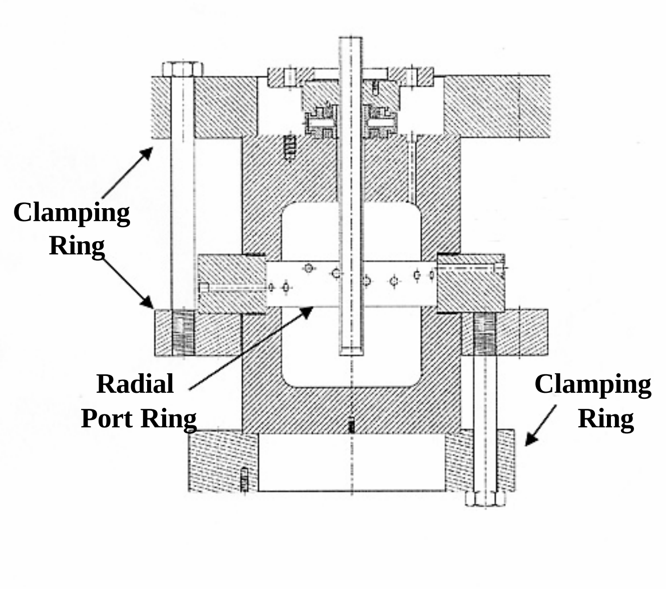






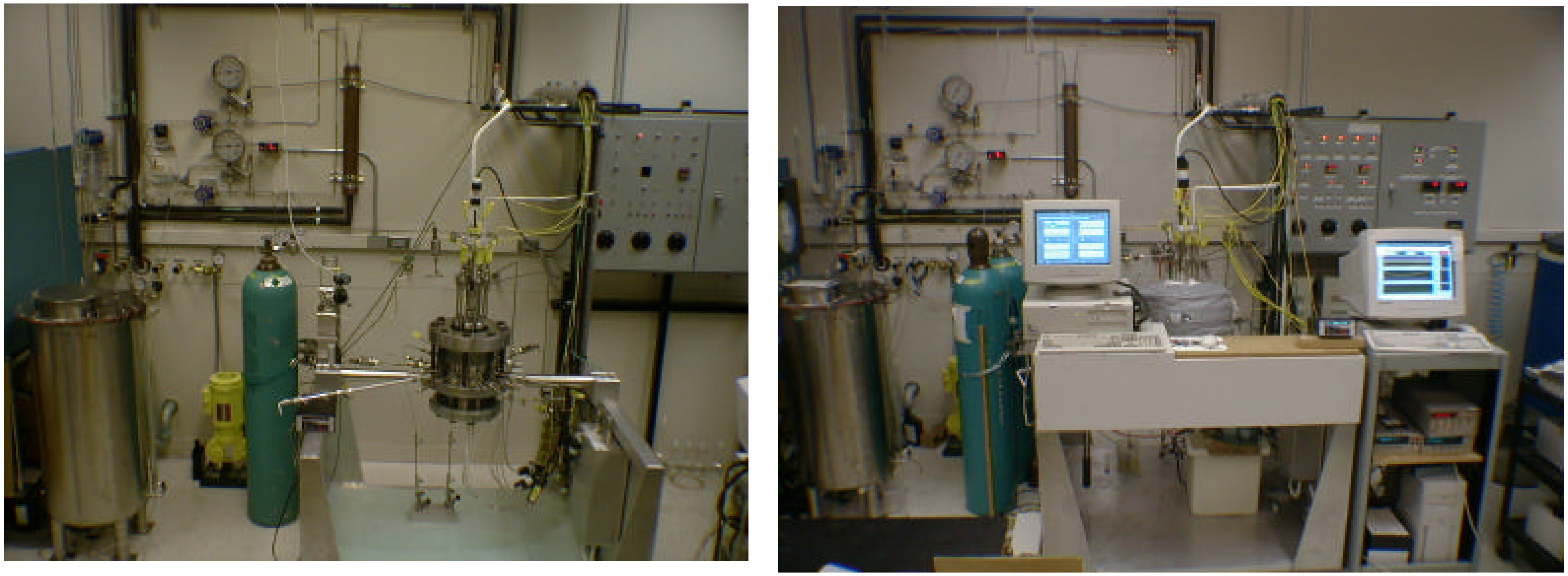
Heated Crevice - Design





- Temperature of tube wall in crevice
- Bulk solution extraction for analysis
- Crevice solution extraction for analysis
- ECP of Freespan (NWT- Ag/AgCl)
- ECP of Alloy 600 Tube in crevice (NWT- Ag/AgCl)
- Temperature vs. elevation in crevice
- Electrochemical Noise
- AC Impedance
- pH Electrode
- Raman Spectroscopy

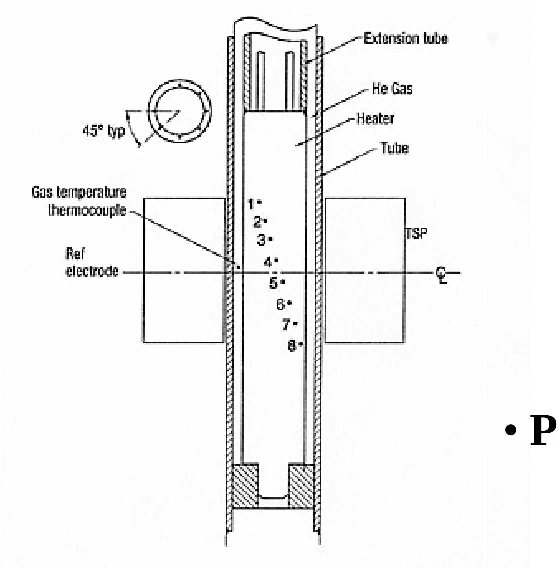
Heated Crevice - Design



Secondary Water System

- **Once through or recirculating**
- **Deaerated**
- **Adjustable Saturation Temperature – 280 C Typical**

Heated Crevice - Design



Options for Heat Input to the Crevice

- **Cartridge Heater**
    - **Constant Heat Flux**
    - **Maximum rate of hideout accumulation**

$dm/dt = QC/L$ (100% efficiency)

m = mass of salt
Q = Heat Flux,
C = Concentration of impurity in Bulk
L = Heat of Evaporation

$m = (QC/L)t$

- **Primary Circulating Loop**
    - **Constant Temperature**
    - **Maximum rate of hide accumulation**

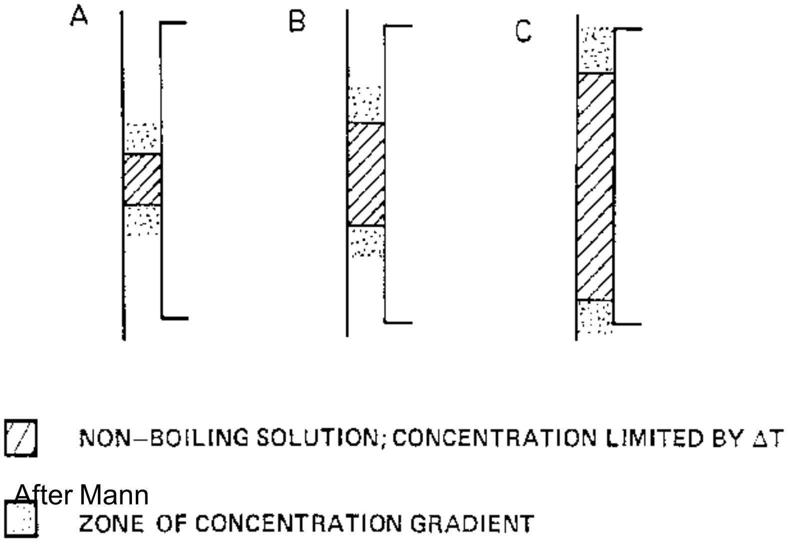
$dm/dt = QxC/SL$ (100% efficiency)

x = length of crevice not fully wetted
L = total length of crevice

$m = m_0[1 - \exp(-QCt/Lm_o)]$

m = mass of hideout at equilibrium

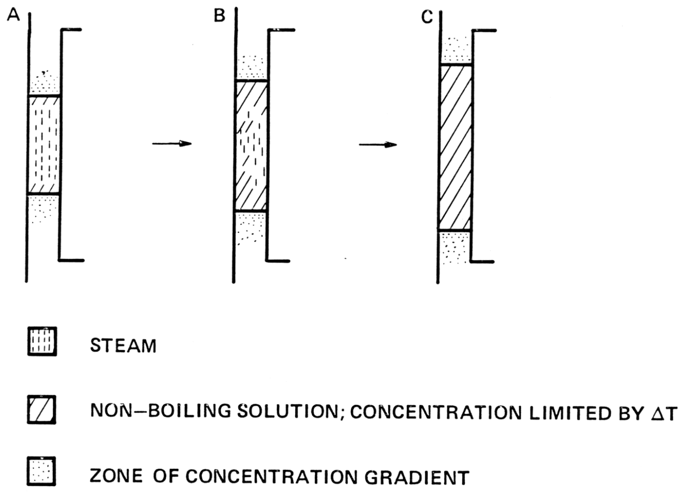
Hideout Model For Loosely Packed Crevice



After Mann

- Salt Initially Concentrates Deep in Crevice
- Boiling Point of Concentrated Solution Equals Superheat
- Boundary of Liquid Region Moves Toward Open End(s) of Crevice
- At Constant Heat Flux
  - Transition from Boiling to Fully Wetted Condition Marked by Increase in Temperate
  - Liquid has lower heat transfer coefficient

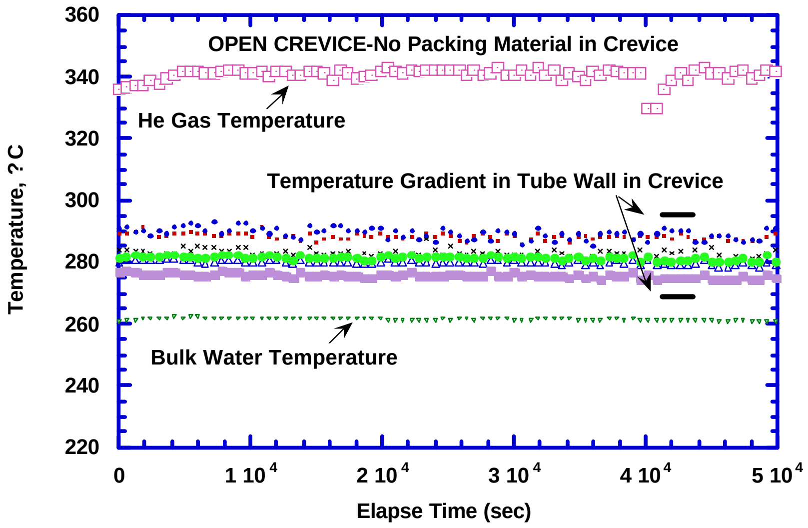
System Test
Hypothesized Hideout Model For Tightly Packed Crevice
Simple systems - NaOH, NaCl



- Most of Crevice Initially Steam Blanketed
- Hideout Begins at Top & Bottom Of Steam Blanket
- Concentrated Solution Penetrates into Steam Filled Region By Capillary Action
- Boiling Point of Concentrated Solution Equals Superheat
- At Constant Heat Flux
  - Transition from Steam Blanket to Boiling Marked by Temperature Decrease
  - Steam poorly conducting
- Successfully Quantitatively Modeled
- Multi-component Feedwater Chemistries & Precipitation not Yet Investigated

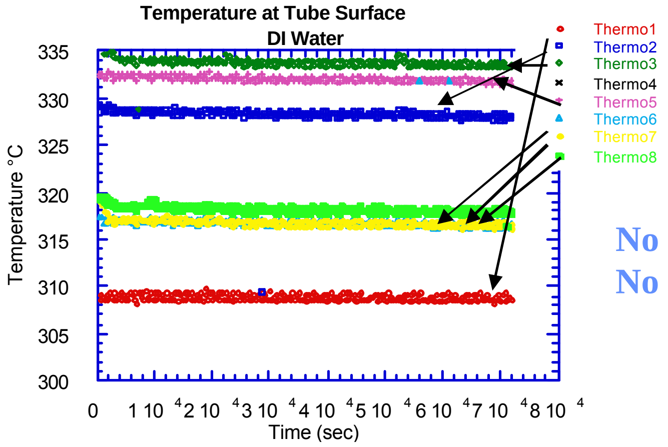
Heat Transfer Crevice/Thermo-Hydraulics

- **Open T/TSP Crevice**
- **Unrestricted flow**
- **Boiling heat transfer in crevice**
- **No hideout - no temperature gradient**

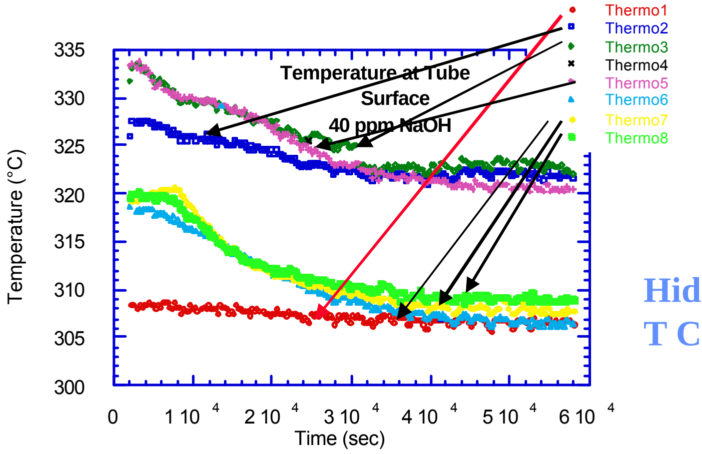


40 ppm NaOH Feedwater

Effects of Hideout on Crevice Wall Temperature

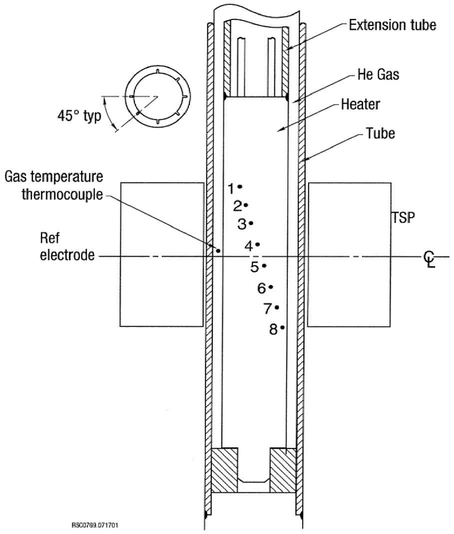


No Hideout
No Change in T



Hideout
T Changes with time

- **Crevice packed with diamond dust**
  - **52% porosity**
- **Feedwater at 2l/hr**
- **Constant heat flux**
- **T_{SAT} = 280°C**

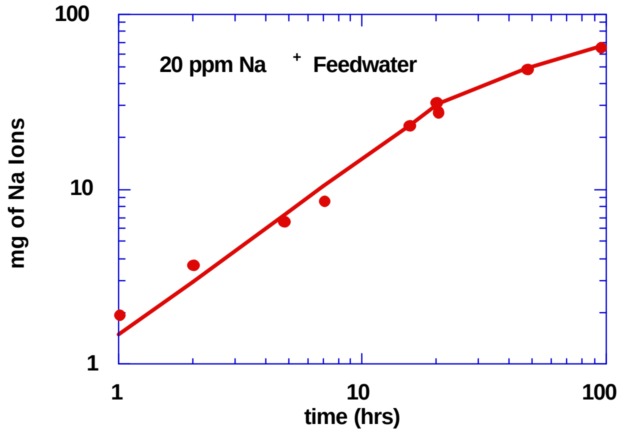


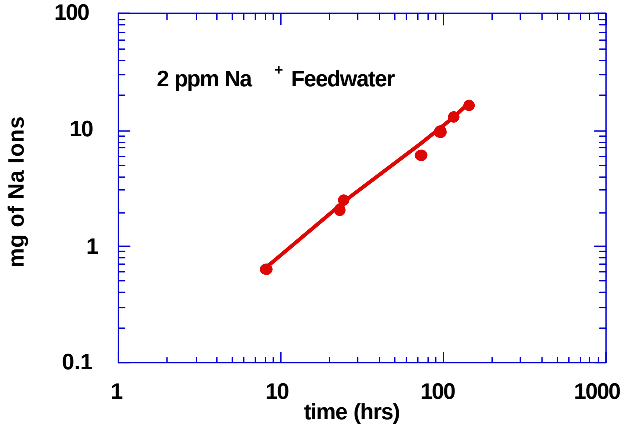
Extraction Results TSP- Type Crevice : Na Concentration

Time of Superheat Crevice(Open)	Feedwater	Bulk	Crevice
Open Crevice--No Significant Hideout			
2 hours	19.2 ppm	22.5 ppm	860 ppm
Packed Crevice (25% Porosity)			
2 hours	19.5 ppm	19.5 ppm	8.23 X 10^4 ppm
6	19.4	19.6	1.15 X 10^5
14	19.6	23.0	3.31 X 10^5
25	18.2	21.7	3.60 X 10^5

Effect of Packing Density on Hideout

Extraction Results - 52% Porosity Crevice - Constant Heat Flux





- Initial Slope Equals One Implies Linear Hideout Rate
- Maximum possible Hideout Rate

$$dm/dt = QC/L$$

Q = Heat Flux From Section of Heater in Crevice

C = Bulk Concentration of Sodium Ions

L= Heat of Vaporization

Efficiency of Hideout Approx. 67% in Linear Region

- Higher Na^+ than for 36% porosity

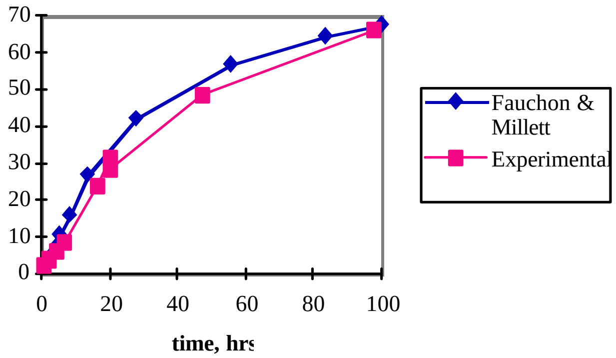
Max hideout rate = 2.17 mg/hr @ 20 ppm
Hideout rate, 20 ppm = 1.46 mg/hr
Hideout rate, 2 ppm = 0.126 mg/hr

Tightly Packed Crevice - Model Calculations

Computer Code Results

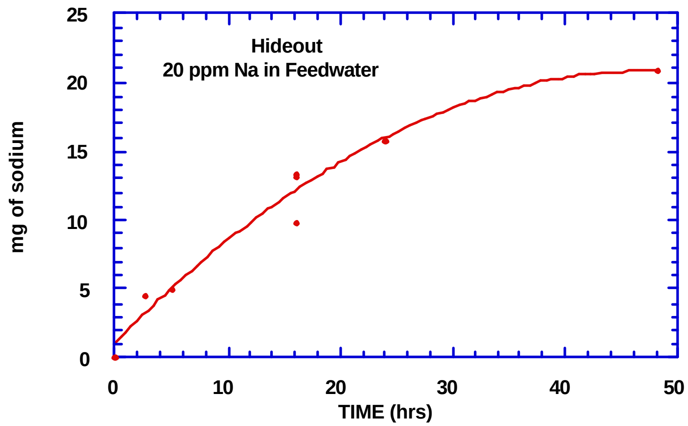
23 ppm Na^+ in Feedwater

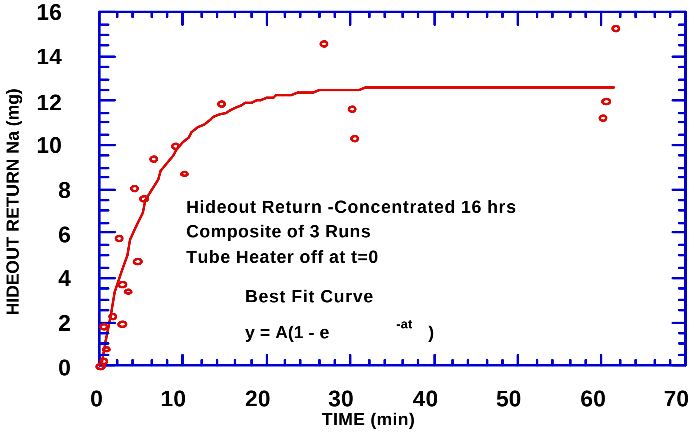
- Hideout in good agreement with Millett model for a single concentrating specie in a packed crevice
  - – Water drawn into crevice by capillary action
  - – When water boils all salt drawn into crevice remains
  - – Saturation concentration occurs when boiling point reaches available superheat
  - – Applies conservation of energy, mass & momentum to transport within pores
  - – Code solves set of differential equations



- Experimental Results in Excellent Agreement with Model Predictions
  - \- Model Predicts 14% of Crevice Initially Wetted
  - \- Predicts Initial Linear Rate of Accumulation
  - \- Predicts Steam Blanket Gradually Replaced with Concentrated Solution

Hideout and Hideout Return Kinetics





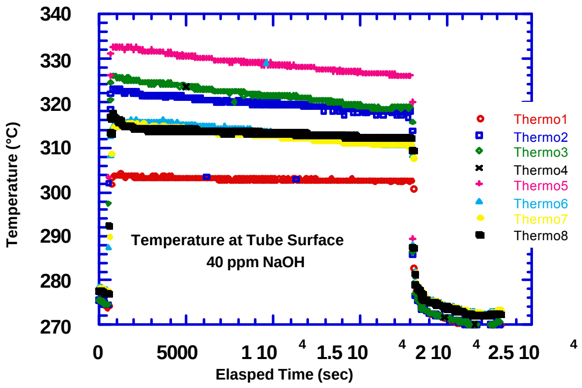
- Hideout in good agreement with Millett model for a single concentrating specie in a packed crevice
  - Water drawn into crevice by capillary action
  - When water boils all salt drawn into crevice remain
  - Saturation concentration occurs when boiling point reaches available superheat

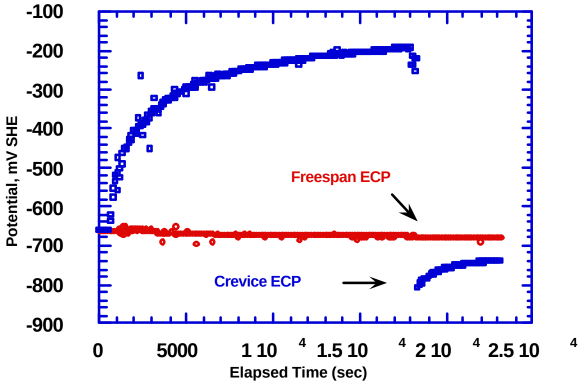
- Cumulative hideout return of Na from a single crevice follows exponential model
- Mass balance for hideout and hideout return in good agreement

$$D = aS^2/p^2 \longrightarrow 1.47 \text{ X } 10^{-7} \text{ m}^2/\text{sec}$$

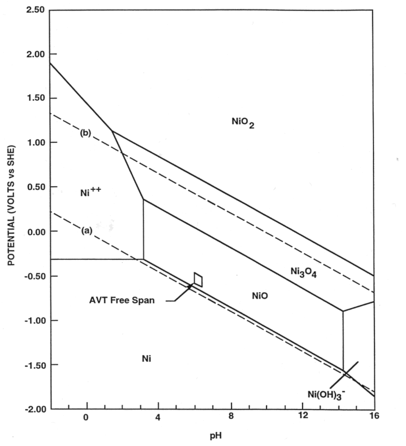
Electrochemical Potential Measurement

- ECP not measurable during heat flux
    - Steam in Crevice if packed with diamond powder
- ECP measurable after tube heater turned off
    - Fully liquid path 1- 2 min after tube off
- Crevice less than free span ECP with NaOH
    - Indicates caustic crevice
    - Approx. 110mV per pH unit





Electrochemical Potential Measurement



- Assuming Corrosion Kinetics of alloy 600 Under Cathodic Control ECP is the reversible hydrogen electrode

  $E_{H2/H+}$ = 2.303 RT/F (log a_{H+}) – 2.303 RT/2F (log p_{H2})
  Or
  $E_{H2/H+}$ = -0.110 pH – 0.056 log p_{H2}

  p_{H2} = 0.0025 atm, calculated from the bulk ECP

- Crevice ECP < Bulk ECP if the crevice is caustic
- Crevice ECP > Bulk ECP if the crevice is acidic

BENCHMARKING ECP MEASUREMENT METHODOLOGY

- Crevice pH calculated from potential measurement and by MULTEQ using results from extraction as input

Feedwater with 40 ppm NaOH

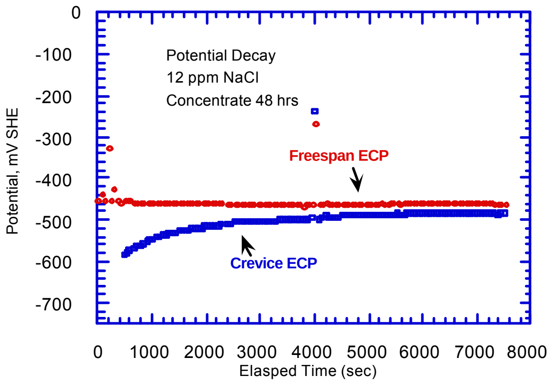
Time	E_{crv} (SHE)	E_{bulk}(SHE)	DE	pH (MULTEQ)	pH (ECP)
2.5 hrs	-780 mV	- 690 mV	90 mV	10.1	9.1
5	- 820	- 680	140	10.15	9.6
16	- 830	- 640	190	10.4	10.0

Results

1. Crevice ECP Decreases with Concentrating Time
    - Suggests Increase in pH
2. Difference between pH values calculated by MULTEQ (extraction results) & from ECP decrease as concentration time increases
    - Volume occupied by steam decreases as hideout increases
    - Volume of bulk liquid drawn into crevice after heat flux removed is greater

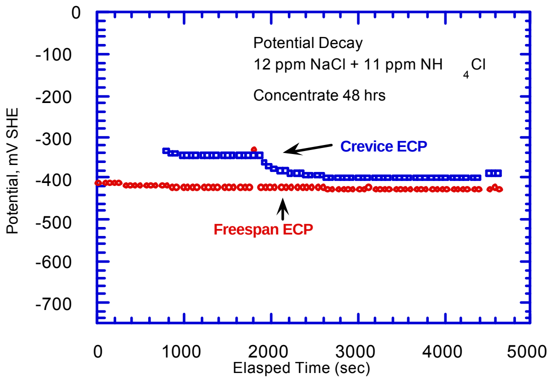
BENCHMARKING ECP MEASUREMENT METHODOLOGY

Molar Ratio



- Na/Cl Molar Ratio = 1
  - Crevice ECP > Bulk ECP
  - Implies Crevice pH > Bulk pH
  - Implies Hideout Efficiency Cl^- < Na^+
  - Na = 0.34 Cl = 0.36
    Na/Cl Molar Ratio = approx 1
  - Implies Hideout efficiency Cl^- & Na^+ same

Reference electrode in the center of the crevice.
Is there a Na/Cl concentration gradient in the crevice?

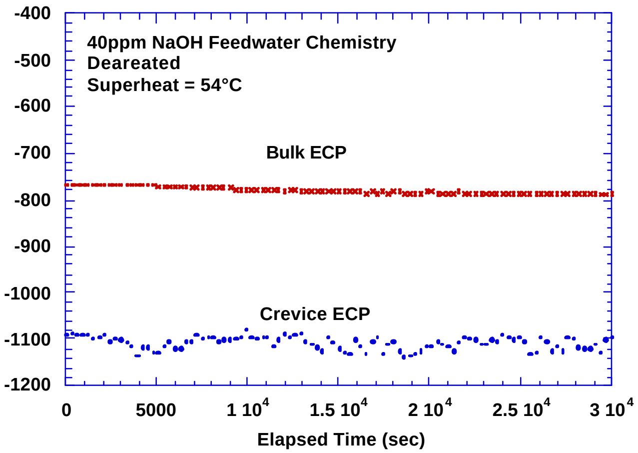


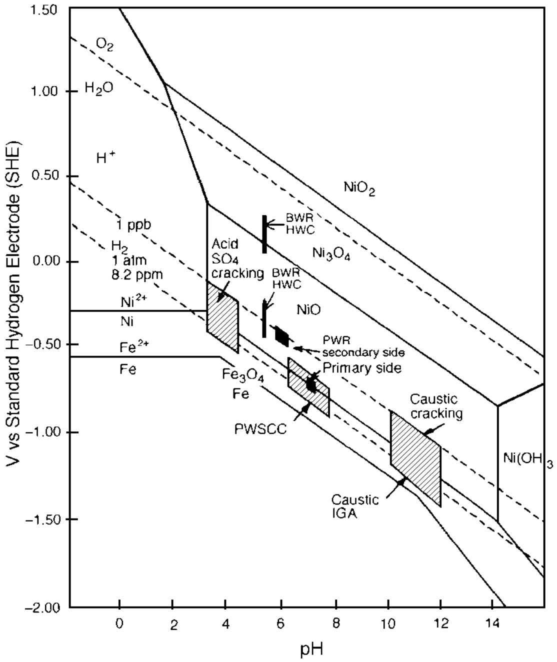
- Na/Cl Molar Ratio = 0.2
  - Crevice ECP< Bulk ECP
  - Implies Crevice pH< Bulk pH
  - HOR Results not yet available

BENCHMARKING ECP MEASUREMENT METHODOLOGY

Magnetite Packed Crevice

- Feedwater: Deaerated with 40 ppm NaOH
- Thermal Conditions: 340°C tube/280°C bulk
- Crevice packed with magnetite: 78% density
  - * Apparently becomes “mud”
- Once through flow, 2l/min

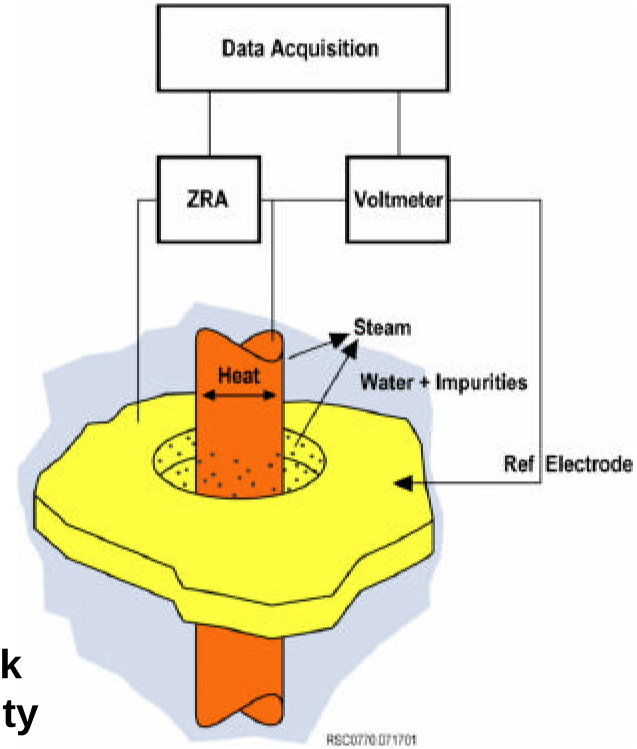




- Bulk pH = 8.2 EPRI for 40 ppm NaOH
  - From EPRI Computer code, MULTEQ
- Crevice ECP is 320 mV less than bulk ECP
  - Implies crevice pH = 10.9 since 118mV/pH unit
- Places tube section in crevice in caustic cracking zone

Heat Transfer Crevice Program / Electrochemical Noise

- Current fluctuations measured
  - Between Alloy 600 tube and Alloy 600 TSP
  - Use zero resistance ammeter
- Measure potential fluctuations
  - Between Alloy 600 tube and Ag/AgCl reference electrode Or Ni wire reference electrode



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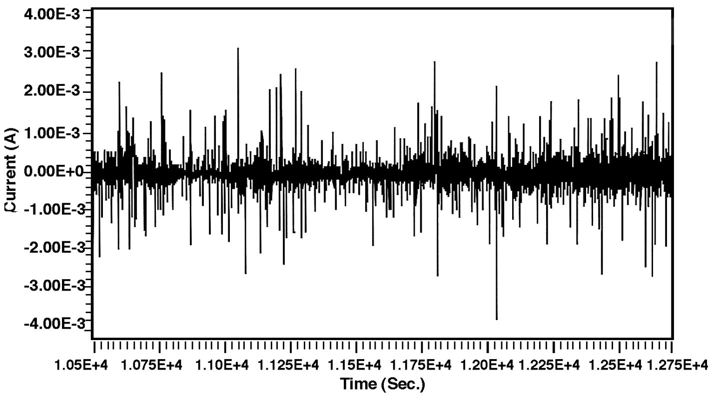
- Thermal Conditions: 340°C tube/280°C bulk
- Crevice packed with magnetite: 78% density
  - * Apparently becomes “mud”
- Once through flow, 2l/min

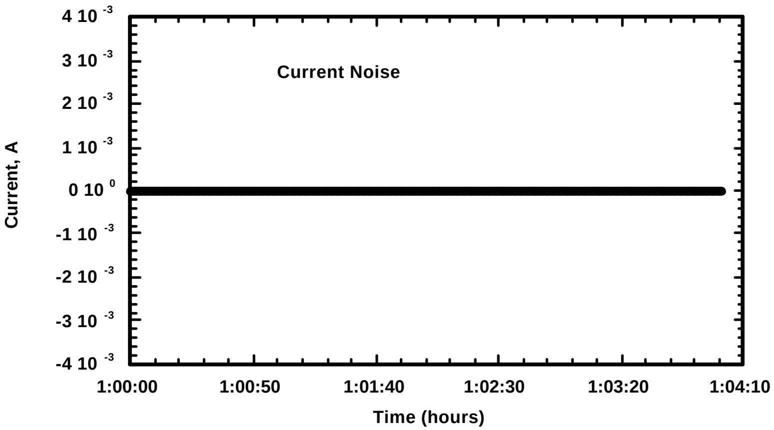
Heat Transfer Crevice Program / Electrochemical Noise

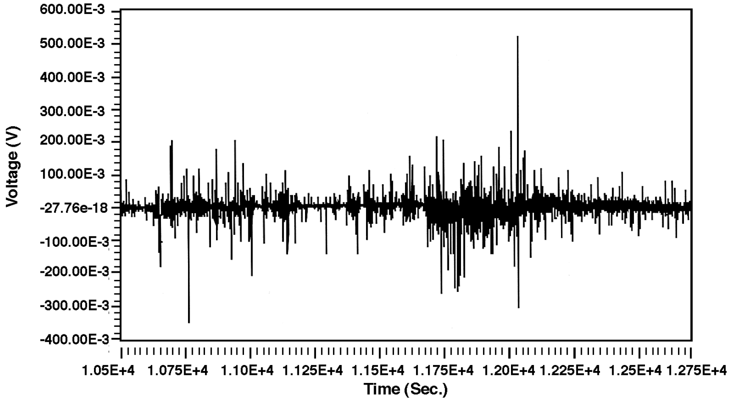
Noise intensity related to pressure (SCC?)

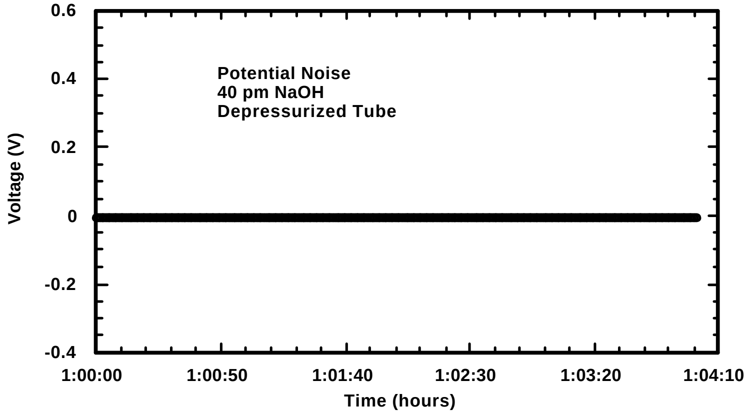
Tube Pressurized @ 3000 psia

Tube Depressurized



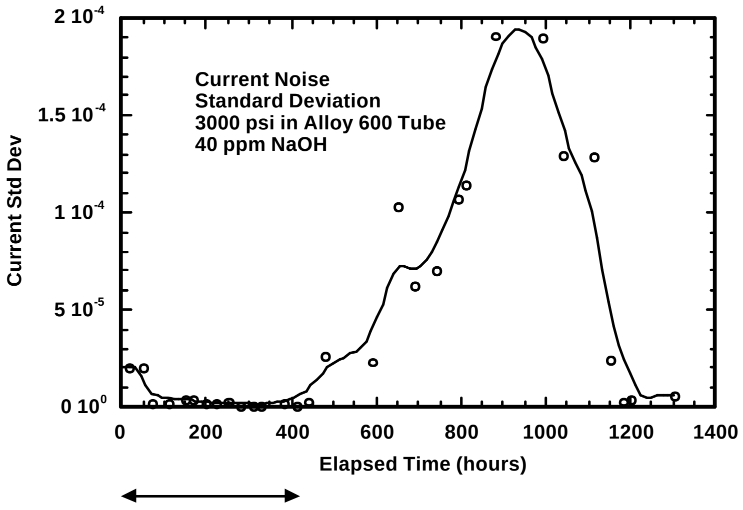




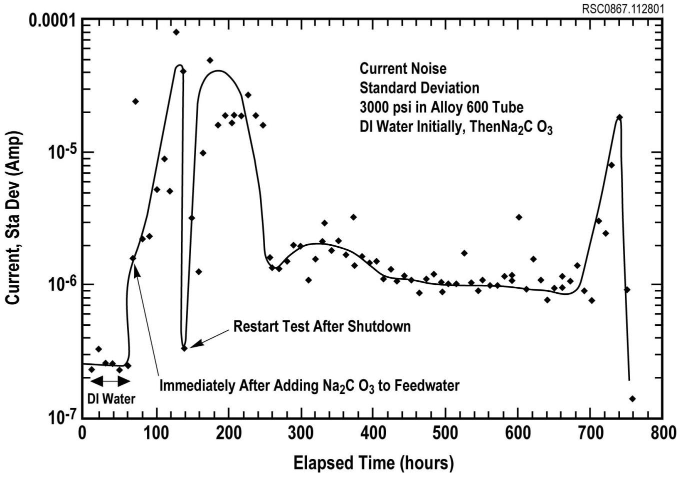


Heat Transfer Crevice/Electrochemical Noise

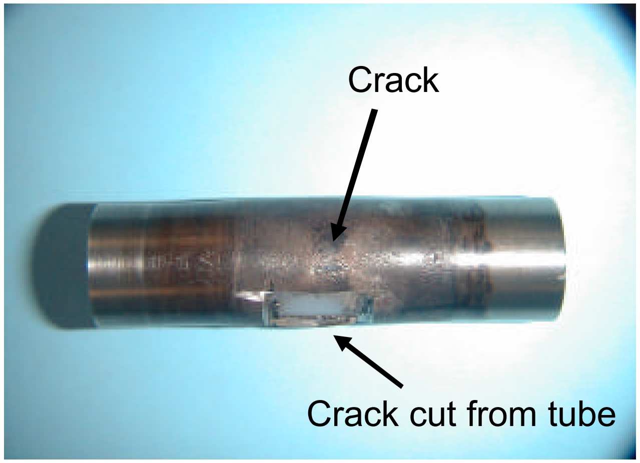
Effect of Chemistry on Crack Initiation

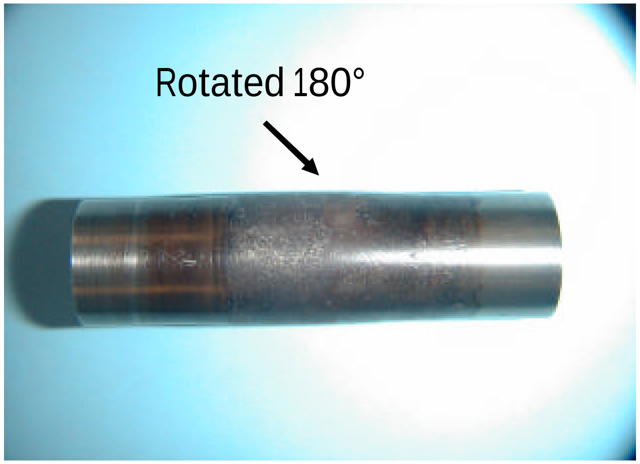


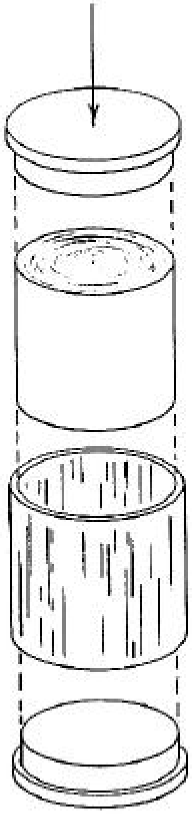
Initiation Time



Heat Transfer Crevice Program/ baseline



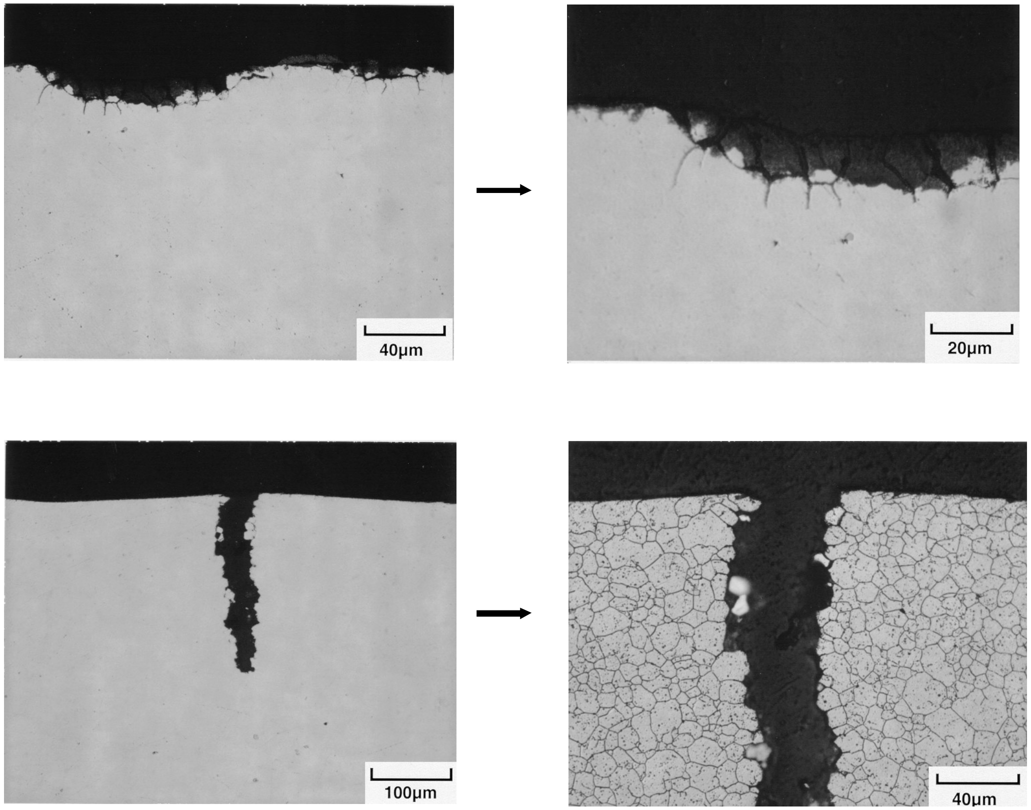




- **Crevice Section Expanded**
- **Compressed polymer Plug**
- **Opened cracks for observation**

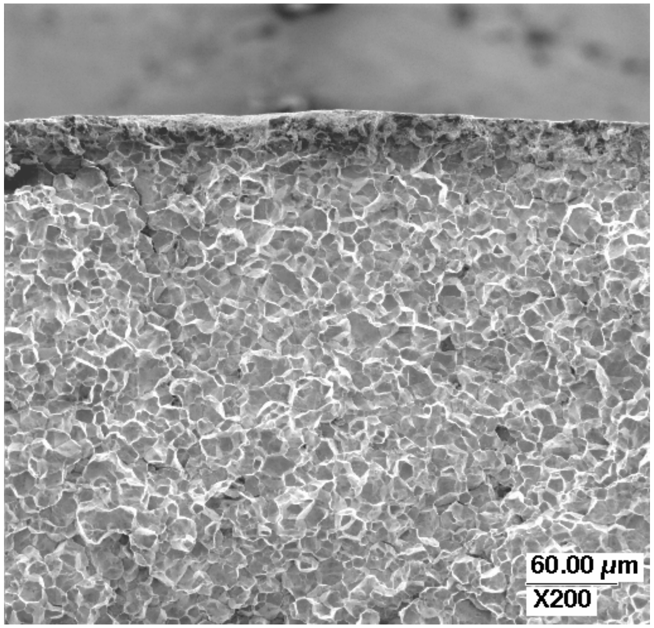
Heat Transfer Crevice Program

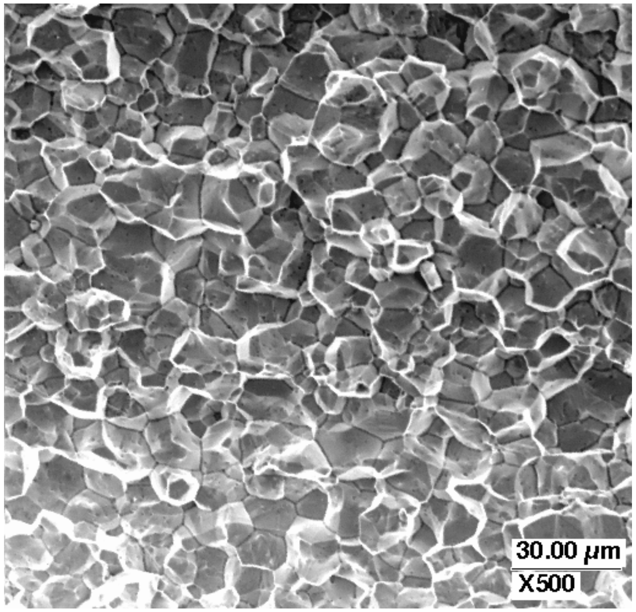
- **Regions of IGA**
  - **Uniform**
  - **Shallow**
- **Localized SCC**
  - **Deep penetrations**
  - **Intergranular**



Heat Transfer Crevice Program

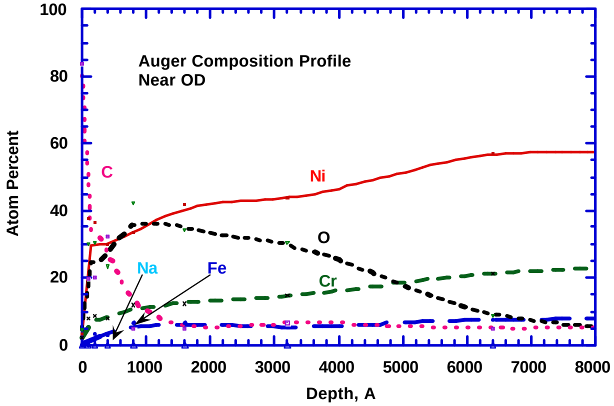
- **Scanning electron microscopy view of fracture face**
  - **Intergranular with secondary cracks**

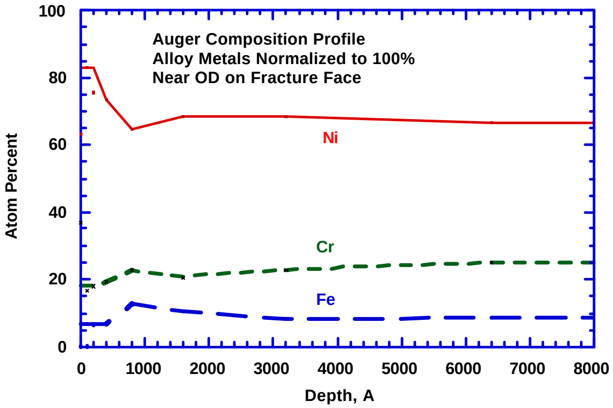


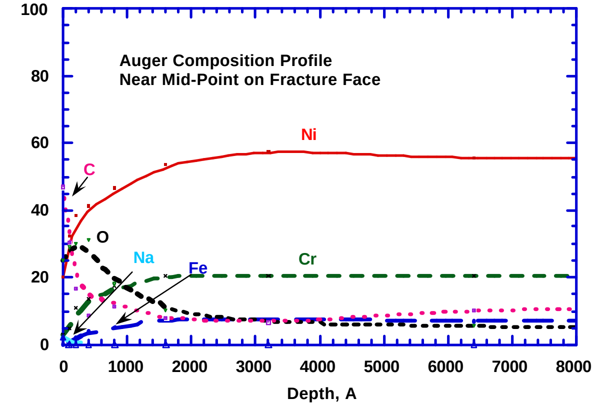


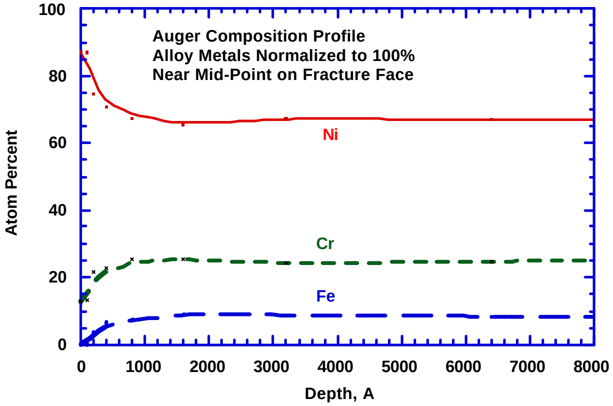
Heat Transfer Crevice Program

- **Oxide film decreases in thickness as crack tip approached**
- **Ni enriched on surface, Negligible Na on fracture face**



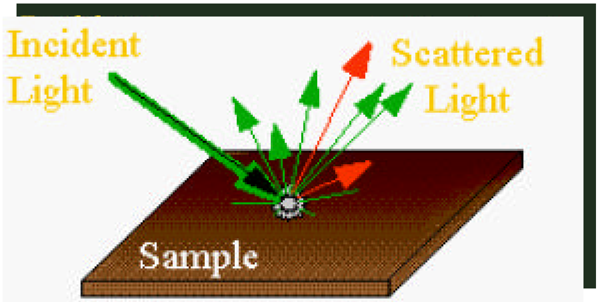






Raman Spectroscopy

Laser



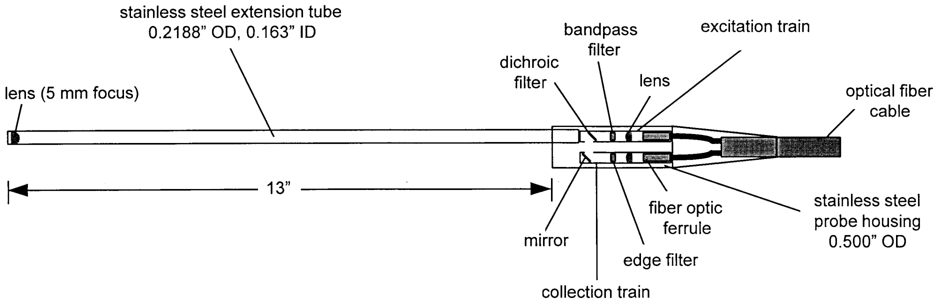
Liquid or solid

Two Types of Scattered Light

- **Same wavelength as incident light**
- **Different wavelength as incident light (Raman Scatter)**

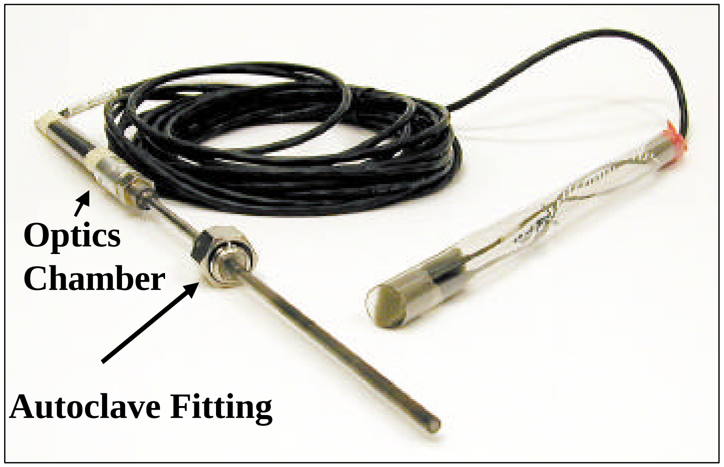
E_i energy of incident light
E_s energy of Raman scattered light
E_v energy of molecular vibration state
$E_s = E_i - E_v$ (visible range)

Raman Spectroscopy



- Designed uniquely for the heated crevice
- Stainless steel tube for light path
- Variable focal point for the laser exciting light and coincident collection point for the signal
- Filters at end of probe to remove "stray" light scattered from the incident laser beam
- Fiber optics from probe to spectrometer

Raman Spectroscopy

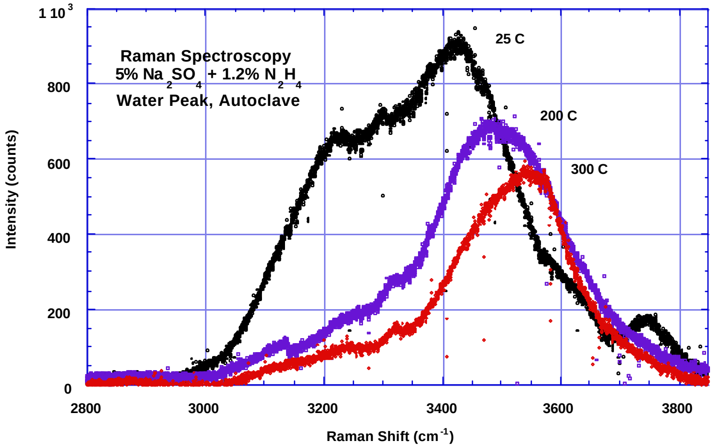


Diamond Window

Probe/Fiber Optic Cable

Raman Spectroscopy

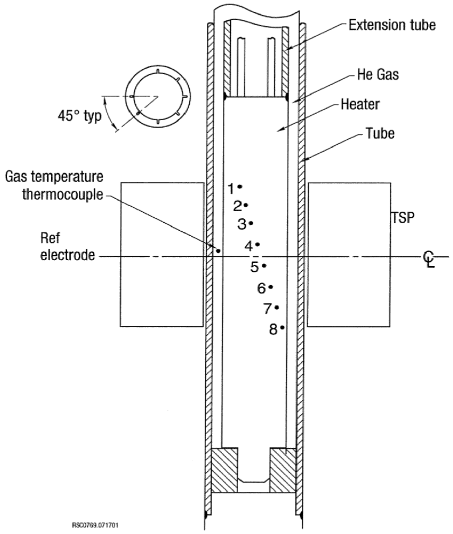
Effects of Temperature on the Water Line



- **H-bonding causes a distribution of O-H bond strengths and vibration freq.**
  - **Causes broadening at room temperature**
- **Increase in temperature decreases H-bonding**
  - **Causes line to narrow**
  - **Increases O-H bond strength leading to shift to higher frequencies**
- **Decrease in density of water at high temperatures leads to intensity decrease**

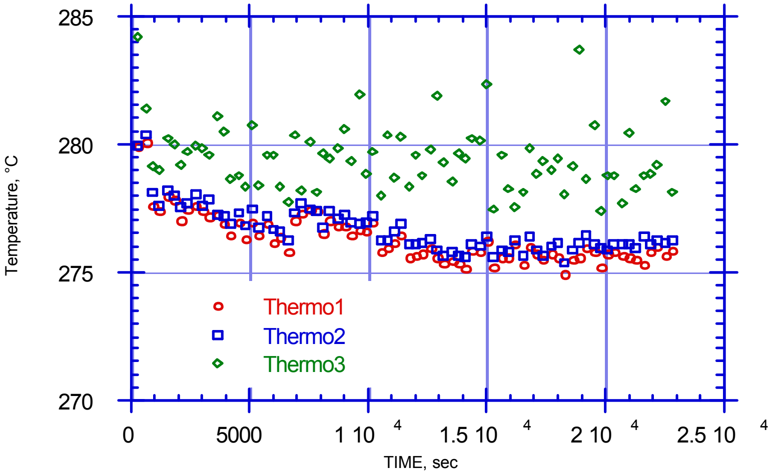
Raman Spectroscopy

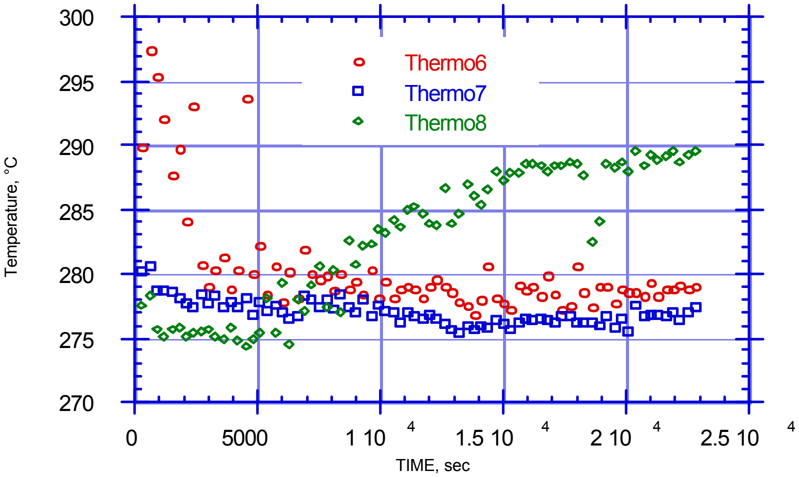
- **Development work uses closed bottom crevice**
  - **No deposits needed for hideout**
  - **Hideout is the same, kinetics are different**
- **Next step will use packed Tube/TSP-type crevice**



Closed Bottom Heated Crevice/Thermal- Hydraulics

Temperature of Tube Wall at Various Elevations in the Crevice During Hideout





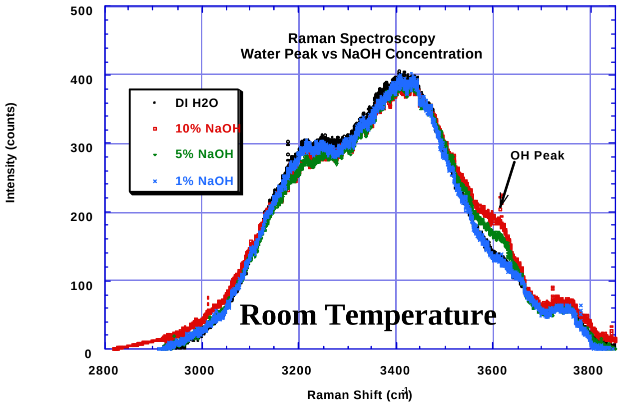
- Boiling at locations 1, 2, & 3

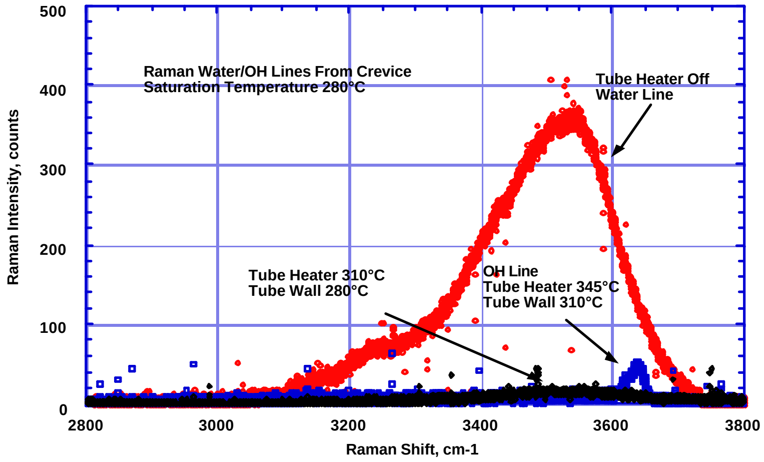
- Steam blanketed to boiling at 6
- Boiling to fully wetted at location 8
  - Indicated by increase in temp

Extraction Results--25.2 w/o
MULTEQ gives 27°C BPE
Measured BPE - 22°C T_{SAT} = 270°C

Raman Results-Caustic

First Raman Results from the Heated Crevice (closed bottom)

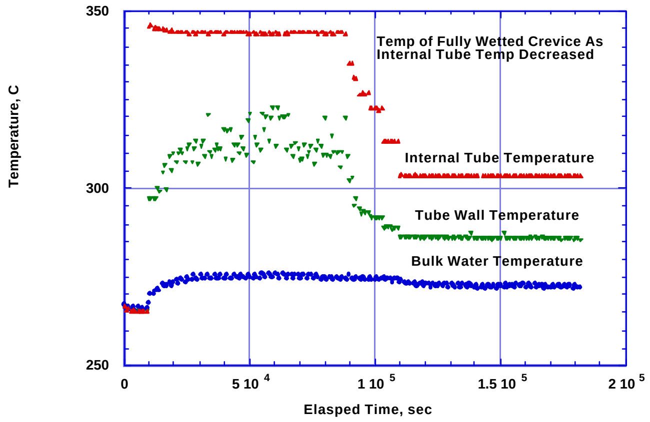




- At a saturation temperature of 280°C with tube heater off
  - Water line same as static autoclave results
- At low super heats, no Raman lines from the crevice
  - Steam blanketed
- He heat transfer gas at 345°C, average wall temperature at 310°C
  - Hydroxide line, no water line
  - MULTEQ gives 25w/o NaOH for a boiling pt. Elevation of 30°C
- Every water bound to NaOH

Raman Spectroscopy

Is NaOH Molten?



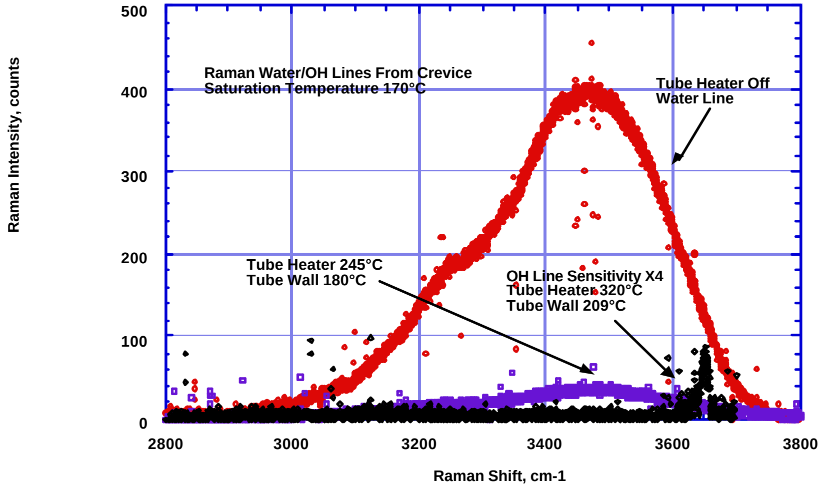
OH line
No water line

No OH line
Water line

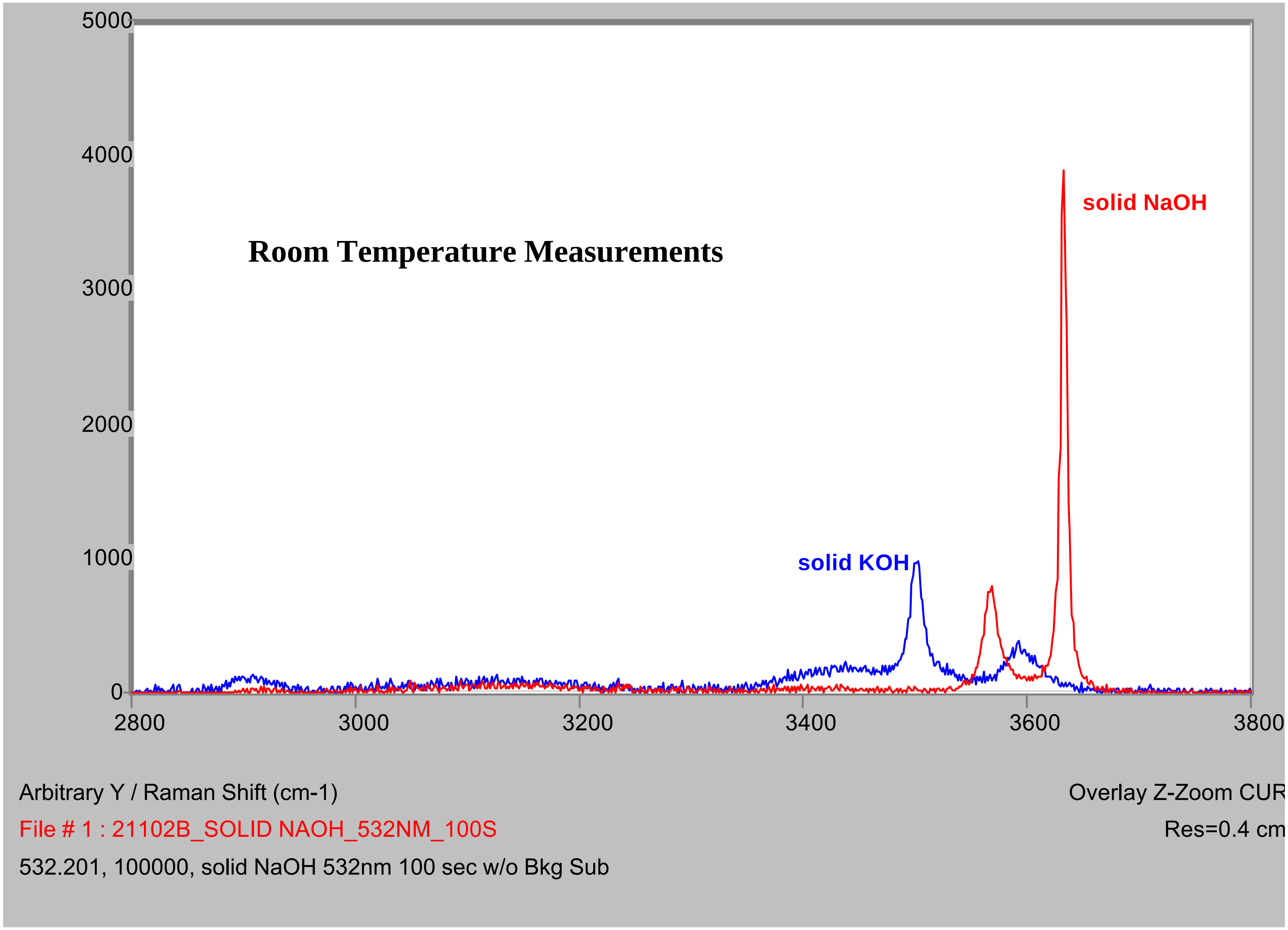
- **Temperature of He decreased in steps, 335°C, 330°C, 325°C, 320°C, 315°C, 305°C**
  - **Raman spectrum OH line until 305°C**
- **Wall temperature did not change until interior temperature was 305°C**
- **Water line appeared at 305°C**
- **Suggests region of Raman probe fully wetted**

Raman Spectroscopy

Is NaOH Molten, melting point is 318°C?



- Pressure lowered to give a saturation temperature of 170°C
- At 170°C with tube heater off, water line
- When He temp below 209°C, no Raman signal from the crevice
- At a He temp. of 209°C, hydroxide line appeared, same as 280° C T_{sat}
- Suggests OH line from concentrated NaOH solution, not molten

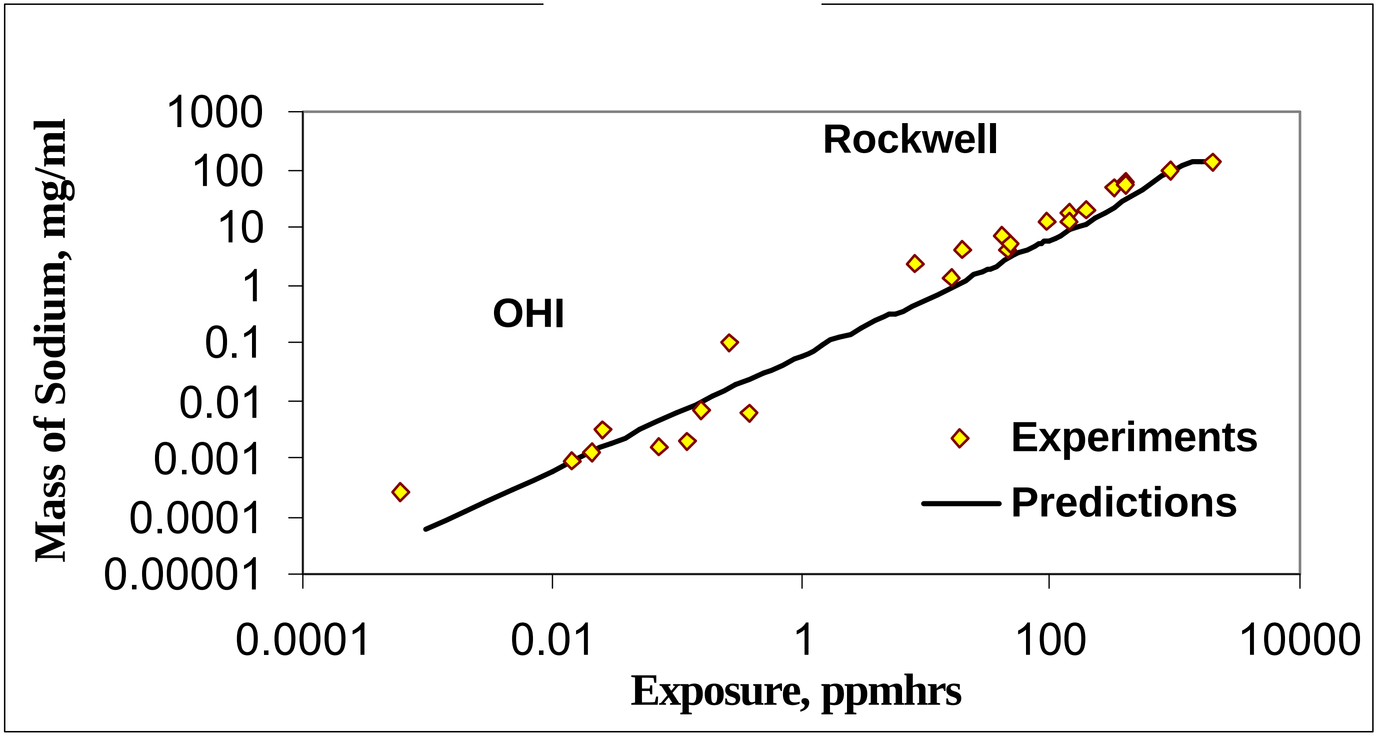

Room Temperature Measurements
solid NaOH
solid KOH
5000
4000
3000
2000
1000
0
2800
3000
3200
3400
3600
3800
Arbitrary Y / Raman Shift (cm-1)
Overlay Z-Zoom CUR
File # 1 : 21102B_SOLID NAOH_532NM_100S
Res=0.4 cm
532.201, 100000, solid NaOH 532nm 100 sec w/o Bkg Sub

Raman Spectroscopy

Raman spectroscopy ideally suited to investigating build up of deposits and precipitates in crevices

Do the high impurity concentrations in the feedwater of a heated crevice correctly accelerate processes occurring in plants?

- **Sodium hideout results in lab experiments linearly extrapolate to results from identical system installed in Ohi Nuclear Power Station**
- **IGA/SCC pattern, chemistry of OD film and fracture face are similar to observations from examinations in pulled tubes**



Heated Crevice Seminar

Experimental Simulation of Crevice Chemistry Evolution

Chi Bum Bahn, Si Hyoung Oh, and Il Soon Hwang
Seoul National University

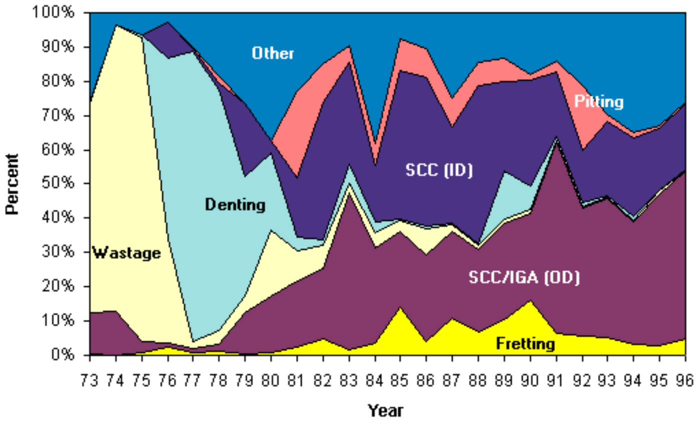
October 7-11, 2002
Argonne Guest House, ANL

Outline

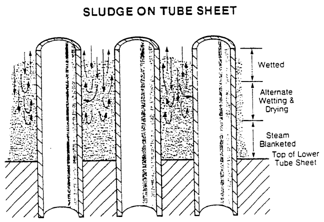
- Introduction
- Literature Review
- Goals & Approach
- Experimental System
- Results & Discussion
    - Open Crevice Test
    - Packed Crevice Test
- Summary & Conclusions

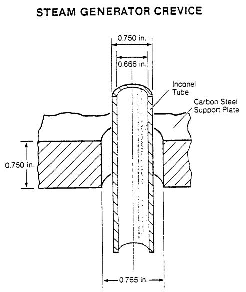
Introduction

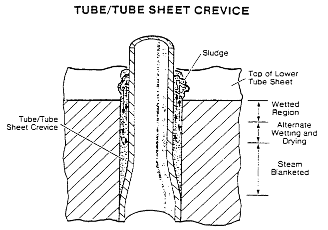
- In a locally restricted SG geometry, such as tube/TSP crevice, tubesheet crevice, or sludge pile, trace impurities in the bulk water can be concentrated by boiling processes to extreme pH.
- These concentrated solutions may then cause ODSCC/IGA, which is the one of the primary degradation mechanisms.
- In order to find the mitigation method for tube degradation in crevice, the understanding of boiling crevice phenomena must be advanced.



Worldwide Causes of Tube Plugging







(From P. Millett's Thesis)

Literature Review

Thermal-hydraulic Aspects

Author	Year	Experiment	Pressure Condition	Crevice Geometry	Packing	Heating Method	Control Method
M. K. Jensen	1977	Boiling heat transfer and CHF in annular geometries	Atmospheric	Horizontal TSP	Open	Electrically heated tube	q”
A. Baum	1980	Dryout and chemical concentration in confined geometries	High (5.5 MPa)	TSP	Open	Electric heater	q”
A. Baum	1981	Boiling heat transfer in porous bodies	High (5.5-7.6 MPa)	Tubesheet	Sludge Packed	Flowing water	ΔT
Y. Kozawa	1982	Alternate drying and rewetting of heat transfer surface	Atmospheric	Planar Tubesheet	Open	Flowing water	ΔT
S. Aoki	1982	Boiling phenomena within a narrow gap	Atmospheric	TSP & Tubesheet	Open	Electric heater	q”
S.-C. Yao	1983	Boiling heat transfer Boiling regimes thru visual observation	Atmospheric	Tubesheet	Open	Electrically heated tube	q”
Y. Chang	1983	CHF of narrow vertical annuli	Atmospheric	Tubesheet	Open	Electrically heated tube	q”
S. Tieszen	1986	Boiling regimes thru visual observation	Atmospheric High(1.5 MPa)	TSP	Open	Flowing water	ΔT
G. M. W. Mann	1987	NaCl hideout and return in heated crevices	High(6.4 MPa)	TSP	Carbon fiber packed	Electric Heater	q” & ΔT
J.-L. Campan	1988	Na hideout studies as a function of various parameters	High (~5.5 MPa)	TSP & Tubesheet	Magnetite packed	Flowing water	ΔT

Literature Review

Electrochemical Aspects

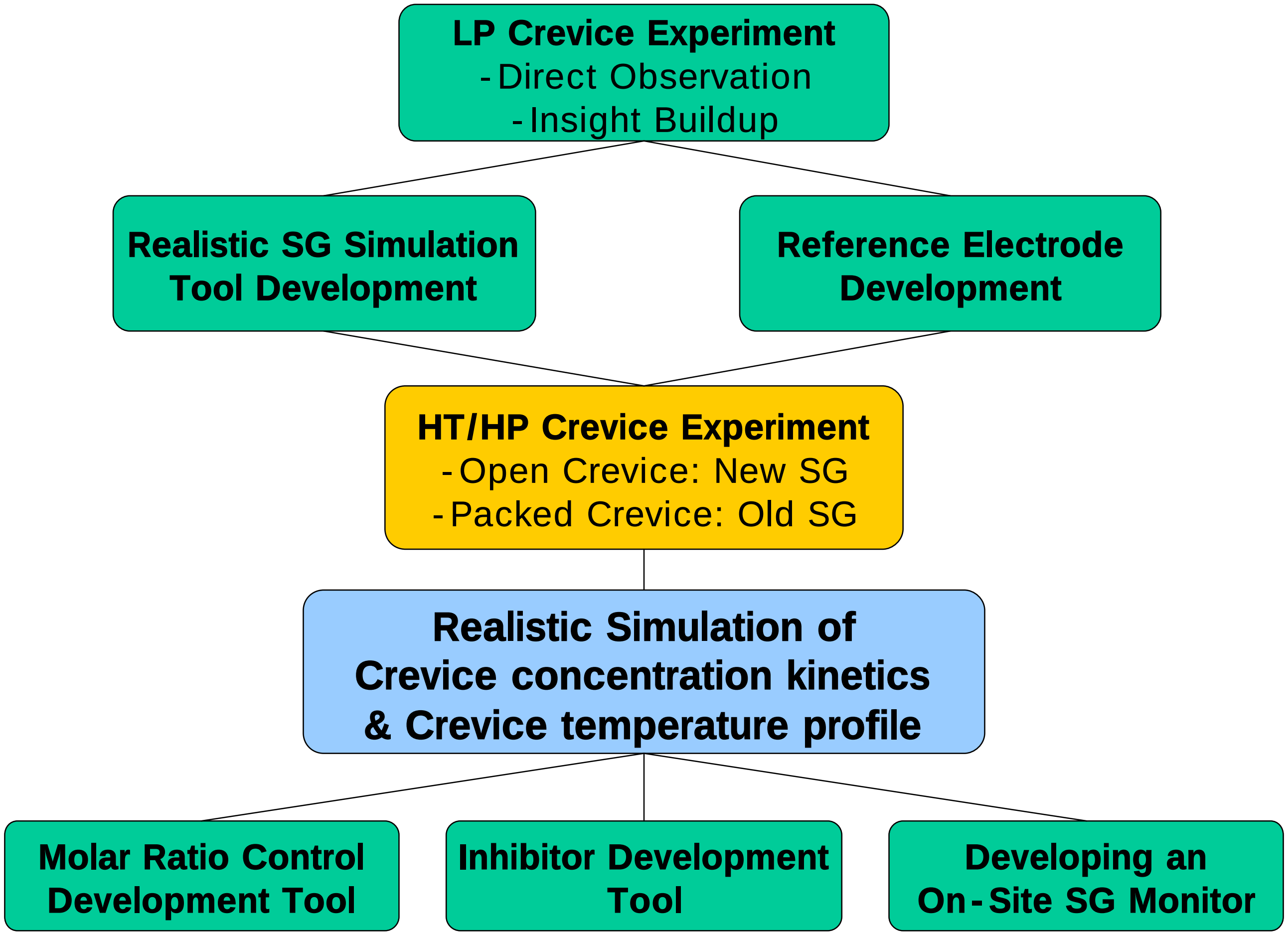
Author	Year	Experiment	Pressure Condition	Crevice Geometry	Packing	Heating Method	Control Method
R. E. Hermer	1988	A600 ECP measurement by using 0.01 M KCl Ag/AgCl	High (5.5 MPa)	TSP	Sludge packed	Flowing water	ΔT
F. Damien	1991	Sodium & boric acid hideout with electrochemical impedance spectroscopy	High (6.4 MPa)	TSP	Open	Flowing water	ΔT
A. M. Brennenstuhl	1997	Electrochemical noise measurement to monitor the effects of chemical excursions on the corrosion response of A 800	High (5.5 MPa)	Tubesheet	Magnetite packed	Electric heater	ΔT
J. Lumsden	1997 1999	NaCl hideout studies with ECP & temperature measurement	High (5.5 MPa)	TSP	Diamond Packed	Electric heater	ΔT & q”
H. Kawamura	1999	Na concentration factor measurement with high temperature conductivity cell	High (5.5-6.4 MPa)	TSP	Open	Flowing water	ΔT
A. Baum	2001	Crevice chemistry evaluation by measuring temperature, impedance, and pH difference	High (3.3 MPa)	TSP	Magnetite packed	Flowing water	ΔT
On-Site Model Boiler Test							
H. Takamatsu	1991	Direct solution sampling from crevice by using on-site model boiler	High (5.5 MPa)	Tubesheet	Open	Electric Heater	q”

Problem Statements

- Experimental Technique
  - Constant heat flux experiment may cause a overheated dryout area in crevice, which cannot be occurred in a real SG condition.
  - Constant temperature experiments using stagnant molten salt with an electric heater have a concern about axial temperature uniformity inside primary tubing.

- Water Chemistry Management
  - On-line crevice monitor that simulates a realistic SG crevice thermal condition and equipped with various probes, needs to be developed.

Goals & Approach



LP Crevice Experiment
- Direct Observation
- Insight Buildup

Realistic SG Simulation Tool Development

Reference Electrode Development

HT/HP Crevice Experiment
- Open Crevice: New SG
- Packed Crevice: Old SG

Realistic Simulation of Crevice concentration kinetics & Crevice temperature profile

Molar Ratio Control Development Tool

Inhibitor Development Tool

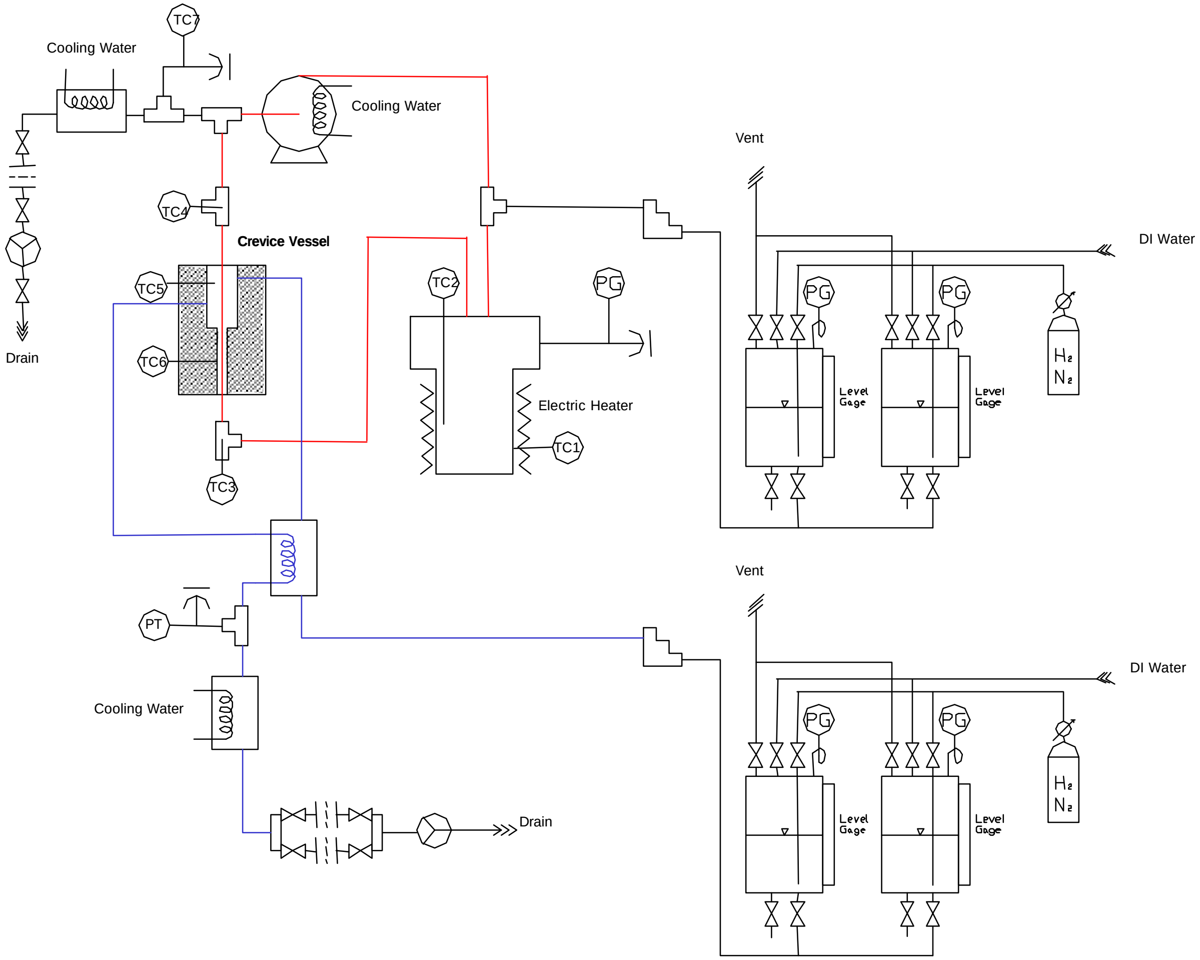
Developing an On-Site SG Monitor

High Temperature/High Pressure SG Crevice Simulation Experiment

- Experimental Systems
  - Two-Loop System Design for Constant $T_{primary}$ control
  - Electrode Development
- Results
  - Open Crevice Test
    - Temperature & Potential Data
    - Measured and Predicted Results
  - Packed Crevice Test
    - Temperature & Potential Data
    - Measured and Predicted Results

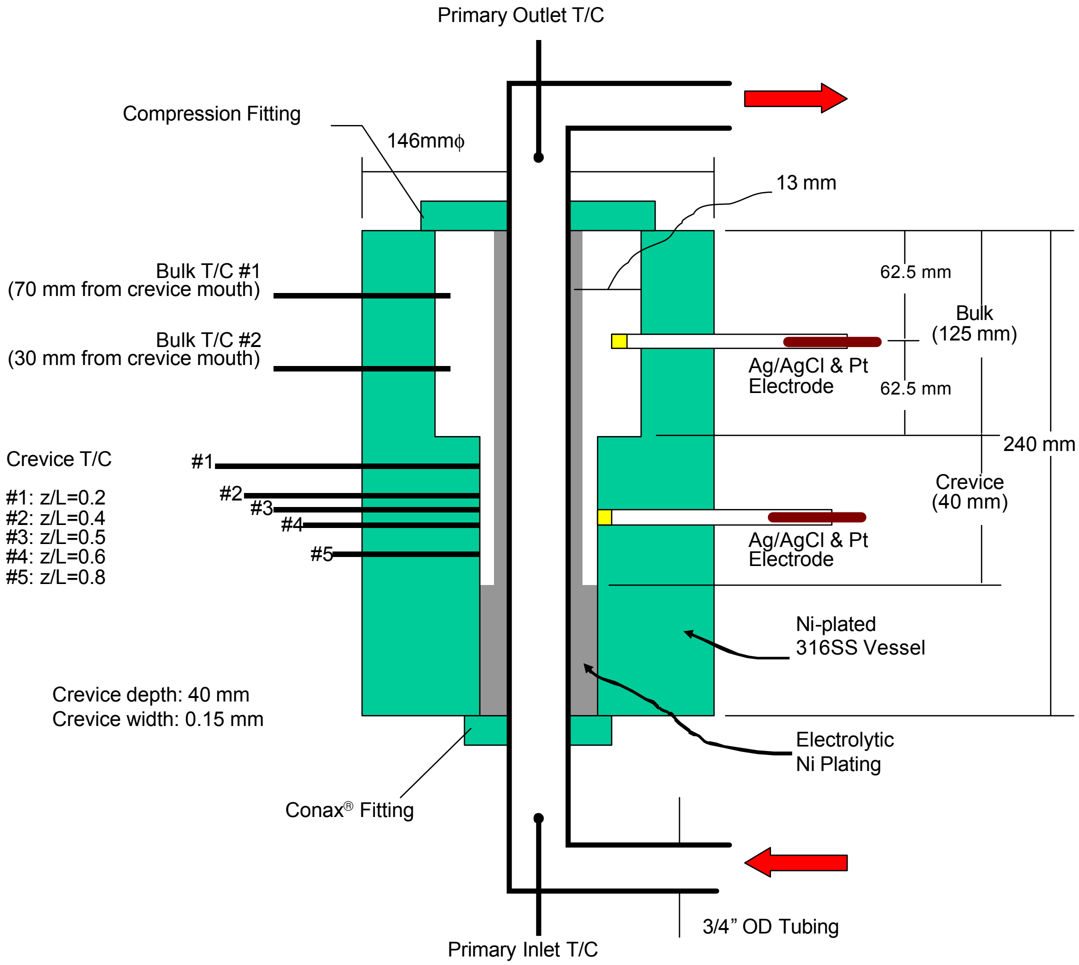
Experimental

Schematic View of Experimental System



Experimental

Schematic View of Test Cell



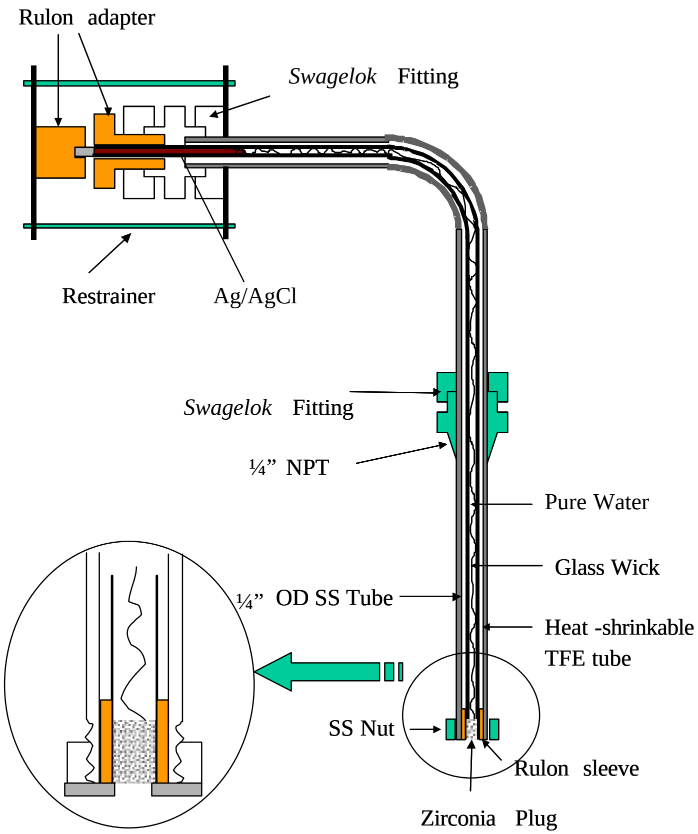
Experimental

Monitoring Parameters

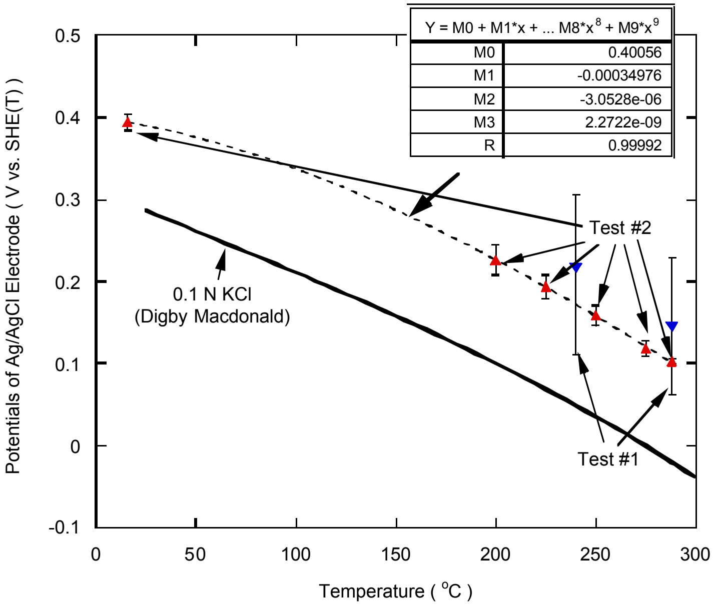
- Chemical & Electrochemical Parameters
  - pH monitoring
    - Pt electrode
    - Ni-plated Tubing & Autoclave
    - Reference electrode: Ext. Ag/AgCl (Pure Water) electrode
    - Measurement of Pt electrode and Ni potential vs. Reference electrode
  - Crevice solution monitoring
    - Conductivity measurement by AC impedance (failed)
    - *Crevice solution sampling: 1/16” OD Teflon tube (future work)*
- Thermal-hydraulic Parameters
  - temperature profile with crevice depth
  - local crevice temperature variation as a function of time

Experimental

Ag/AgCl (Water) Ref. Electrode Development



Calibration Results
as a Function of Temperature



$Y = M0 + M1*x + ... M8*x^8 + M9*x^9$	
M0	0.40056
M1	-0.00034976
M2	-3.0528e-06
M3	2.2722e-09
R	0.99992

Experimental

Experimental Conditions

- Primary Side: Recirculating High Purity Water
- Secondary Side: Refreshed Water

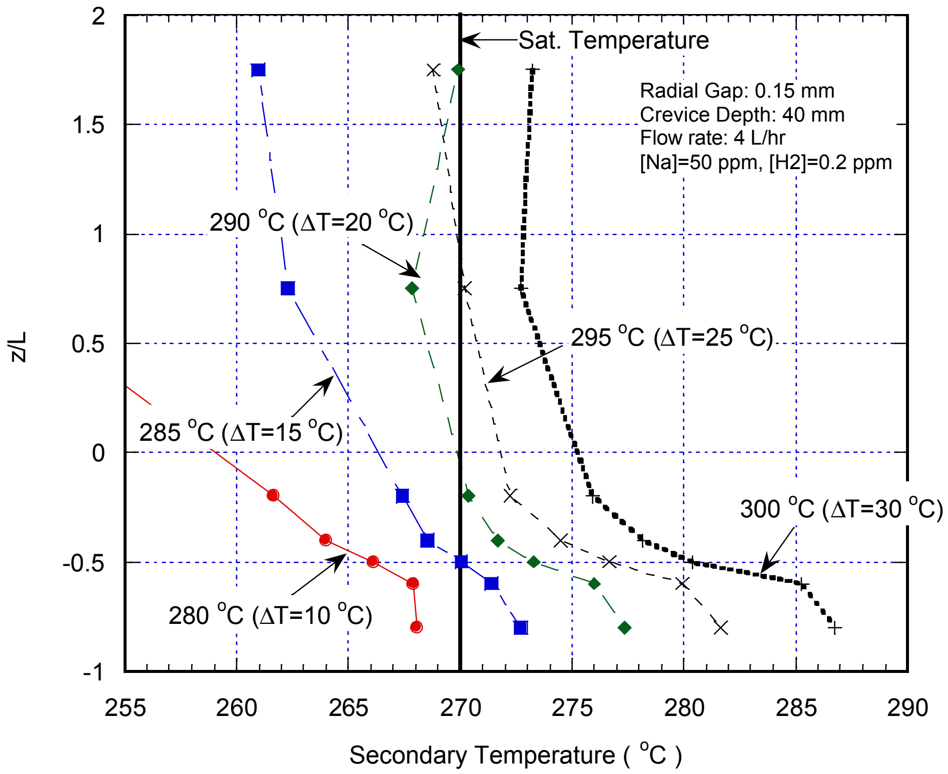
	Primary	Secondary
Temperature (^oC):	max. 300	270
Pressure (MPa):	13-14	5.6
Flow Rate (L/hr):	~2000	~4
Water Chemistry:	H_2O	H_2O/NaOH
ECP:	reducing(H_2)	reducing(H_2)
Crevice Materials:	NA	open/packed(magnetite)

Experiment & Control: Fully Computerized System

Results

Open Crevice Test

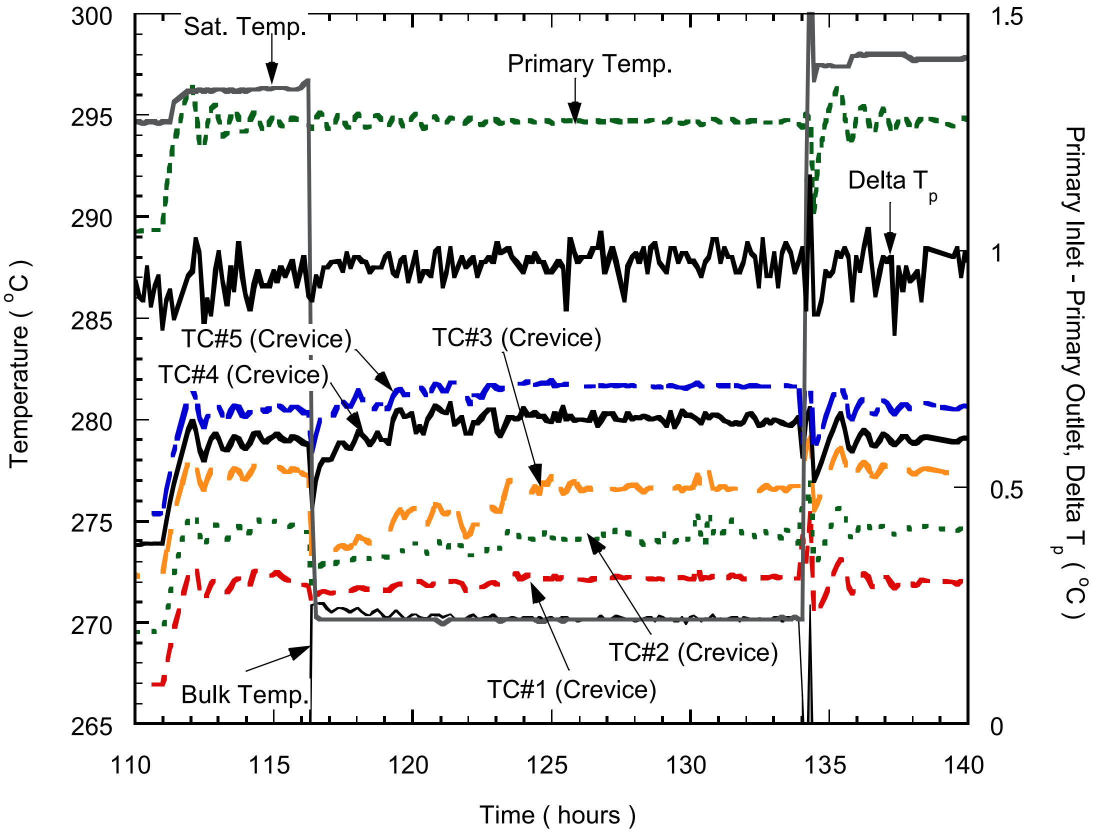
Axial Temperature Profile at a Steady States



Results

Open Crevice Test

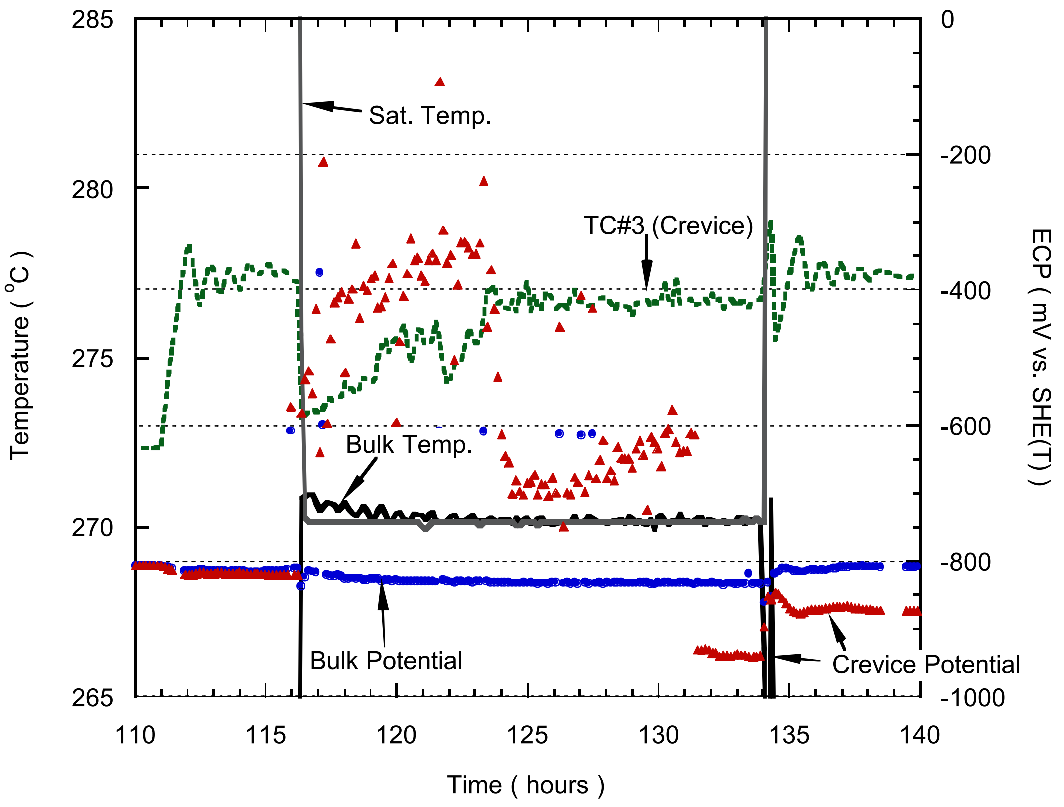
Local Temperature Variation with Time (ΔT=25 °C)



Results

Open Crevice Test

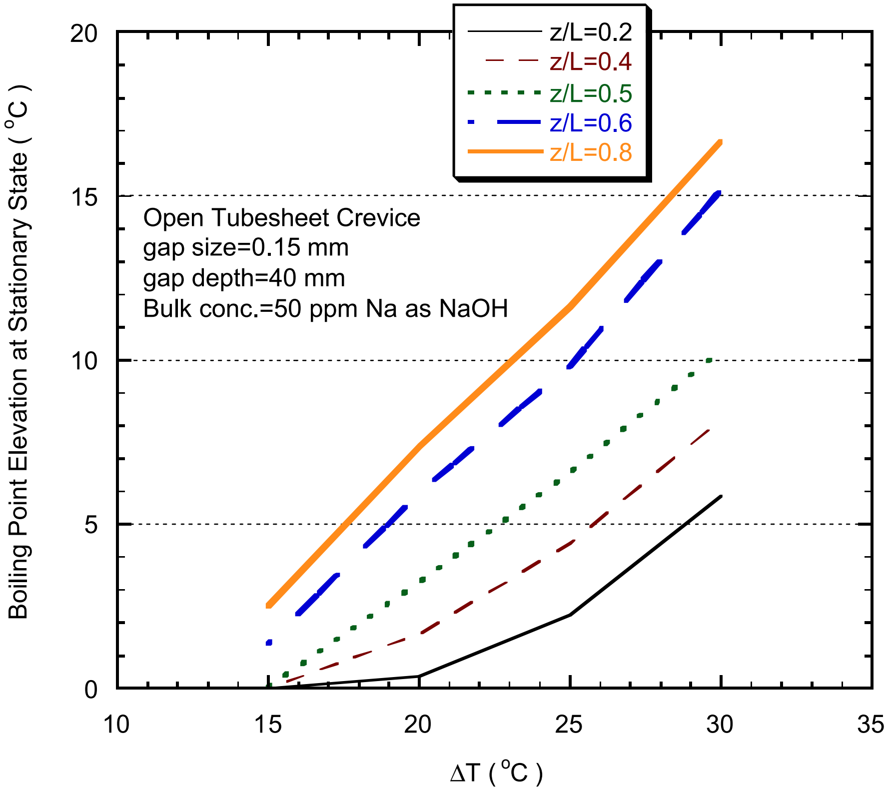
Bulk & Crevice Potential Variation with Time (ΔT=25 °C)



Results & Discussion

Open Crevice Test

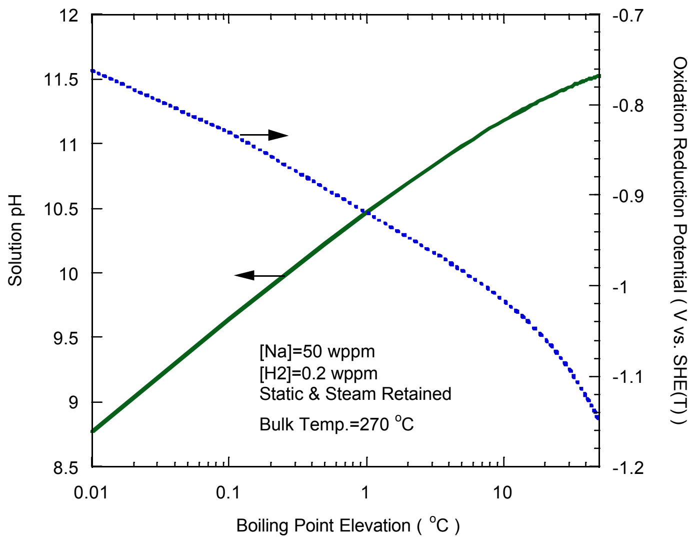
Boiling point elevation as a function of DT



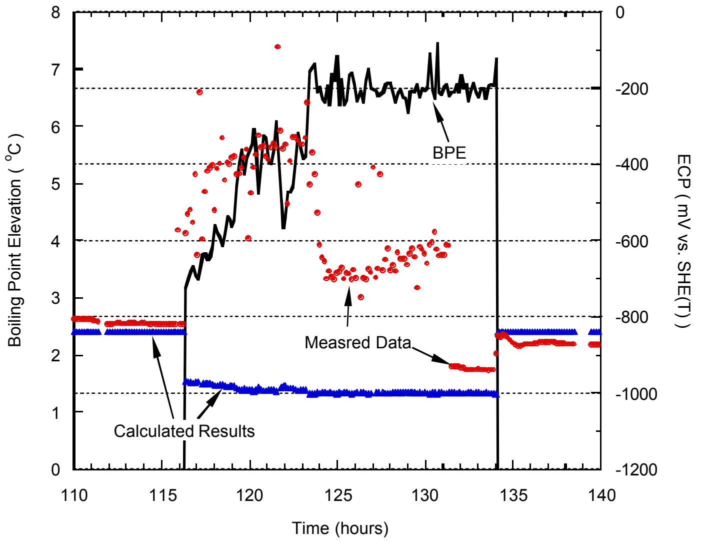
Results & Discussion

Open Crevice Test

Predicted solution pH and oxidation reduction potential as a function of boiling point elevation



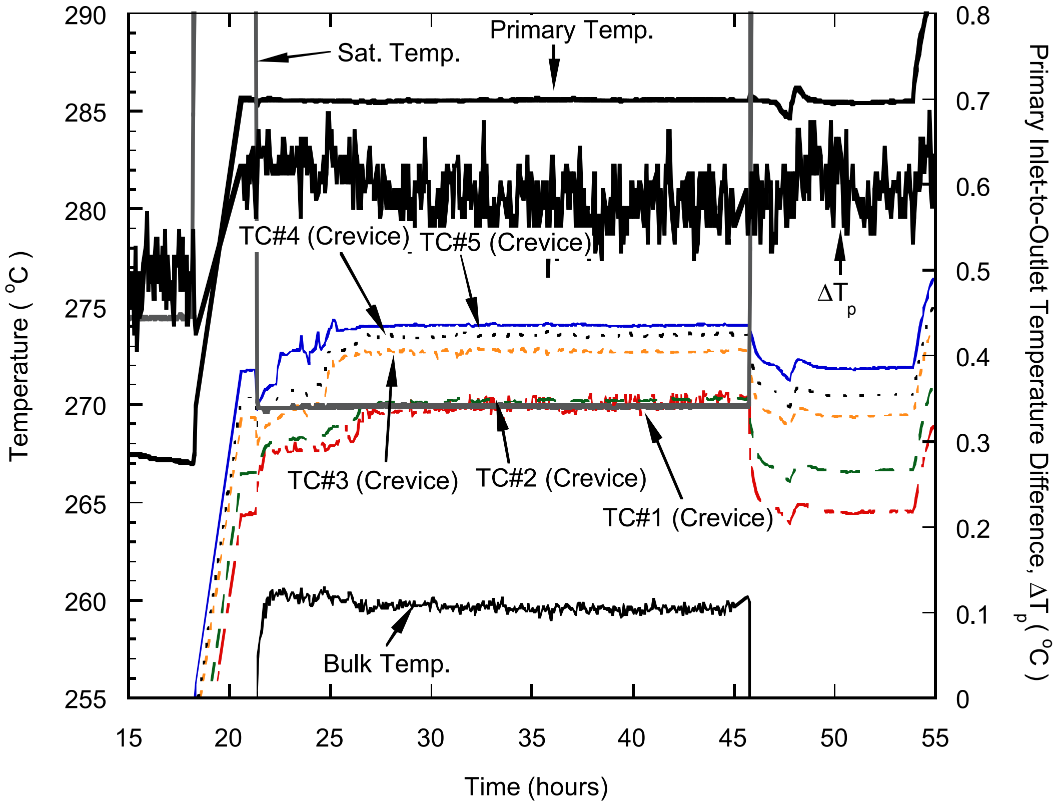
Comparison of Predicted Data with Measured Data



Results

Packed Crevice Test

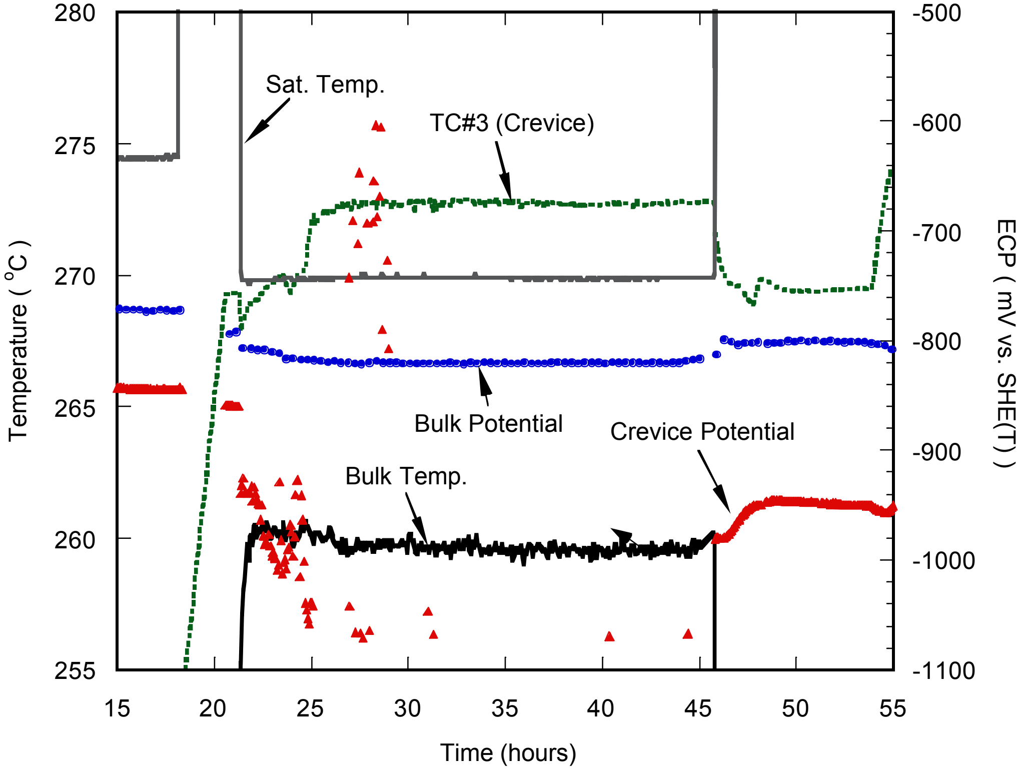
Local Temperature Variation with Time (ΔT=15 °C)



Results

Packed Crevice Test

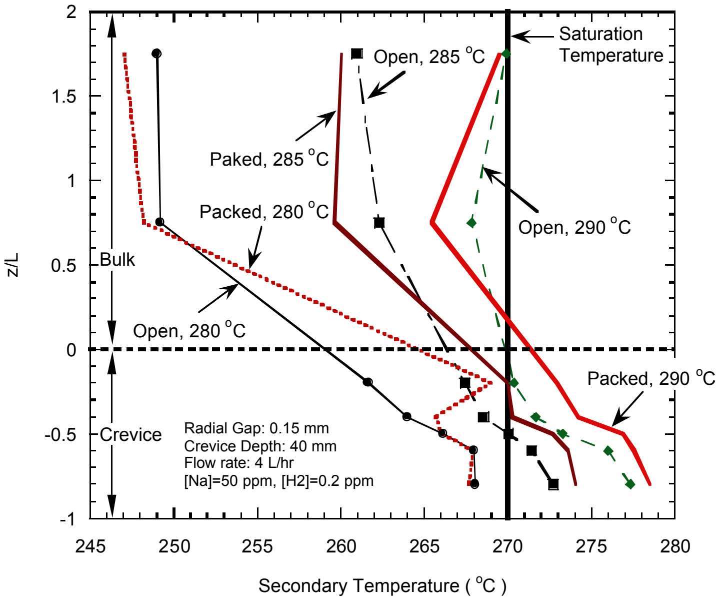
Bulk & Crevice Potential Variation with Time (ΔT=15 ^{o}C)



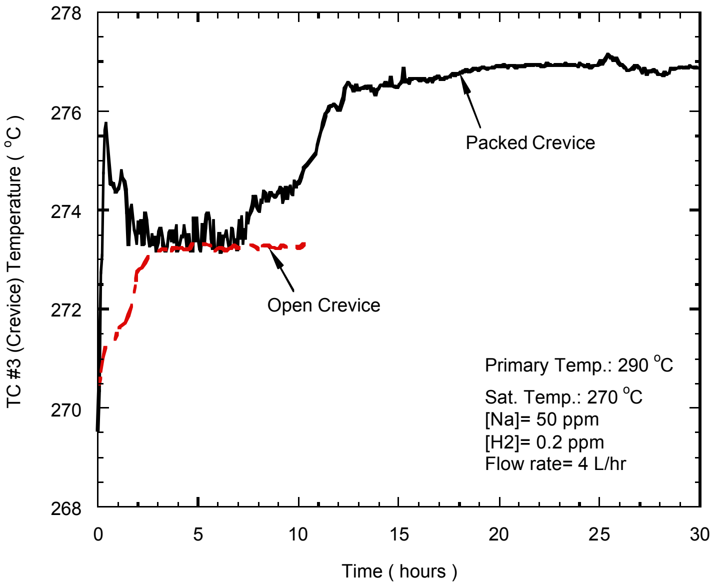
Results & Discussion

Comparison of Packed Crevice with Open Crevice

Axial Temperature Profiles



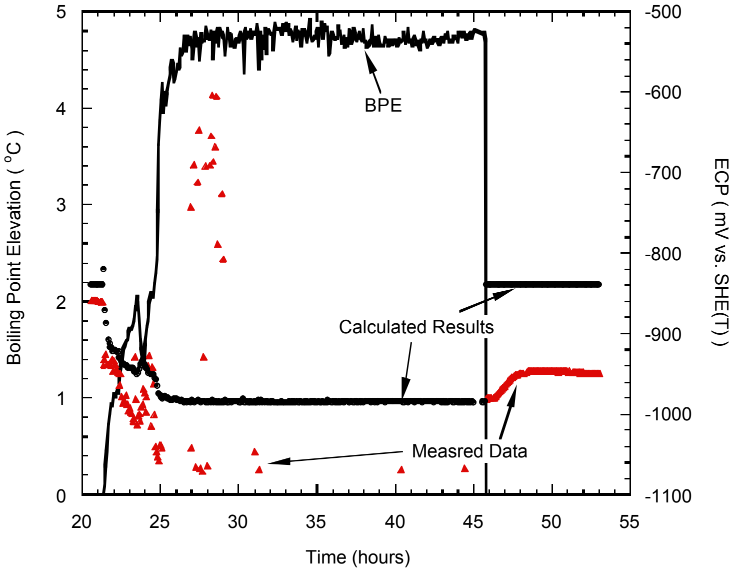
Concentration Behaviors As a Function of Time



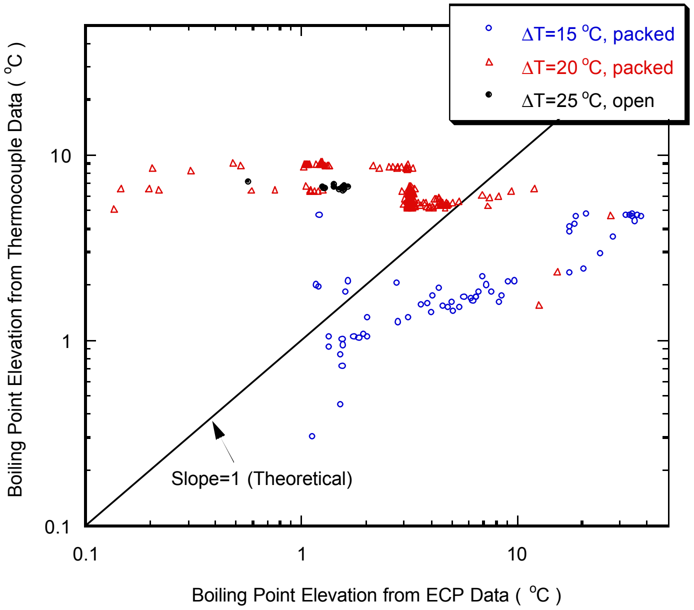
Results & Discussion

Measured and Predicted Potential

Comparison of Predicted Data with Measured Data



Boiling Point Elevation from Temperature Data vs. Boiling Point Elevation from Potential Data



Summary & Conclusions

- Heated crevice chemistry was studied by high temperature tests using a simulated PWR steam generator.
- Ag/AgCl reference electrode was developed for monitoring chemical concentration in the simulated SG tubesheet crevice, by using pure water as filling solution in order to solve potential drift problem.
- NaOH concentration process was confirmed in the tubesheet crevice with 0.15 mm radial gap based on temperature and electrochemical potential measurement data.
- As ∆T across the tube wall increased, the axial temperature gradient in crevice and time constant for concentration transient increased.
- A reasonable agreement was found between the measured and predicted data on the crevice potential.
- When the crevice was filled with magnetite particles, it showed the longer time constant for Na concentration and the severer concentration behavior compared with the case of open crevice.

Experience of Heated Crevice Experiments at Studsvik

H-P Hermansson*), A. Molander*)
P-O. Andersson) and H. Takiguchi ***)**

*) Studsvik Nuclear AB, SE-611 82 Nyköping, Sweden
**) Ringhals AB, SE-430 22 Väröbacka, Sweden
***) Japan Atomic Power Company, Mitoshiro Building, 1-1 Kanda-Mitoshiro-cho, Chiyoda-ku, Tokyo 101-0053, Japan

Introduction

A facility was designed and constructed for characterization of crevice environments during realistic conditions. TSP intersections has been simulated. Crevices were open both at top and bottom.

The equipment has been used to study hideout of impurities relevant to the Ringhals 4 PWR and oxygenated conditions in PWR secondary systems, so called OWC.

A variety of testing conditions has been used. Different crevice gap and different crevice geometry have been used. The tests were carried out with or without crevice filling. The heat transfer conditions and the hydrodynamic conditions have also been varied within relatively wide conditions.

This presentation summarizes some of the results.

Features of the equipment

Steam generator tube heated electrically or by pressurized high temperature water.

Measurements of corrosion potential, redox potential, pH and conductivity in bulk phase and in the crevice region.

Pressure drop over crevice simulated in some test by high flow recirc pump.

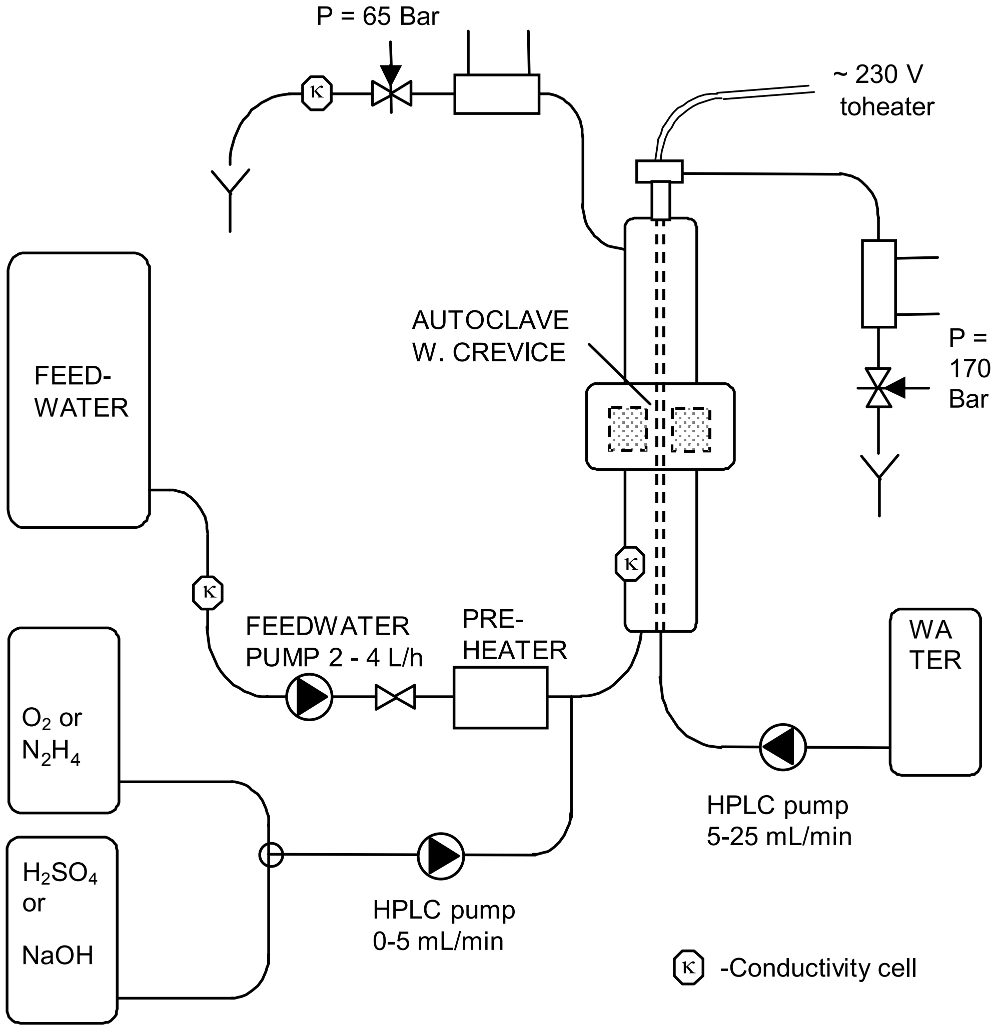
Temperature measurements in the SG tubing.

Crevice section easy to replace.

Different SG material has been used and TSP simulating part of both carbon and stainless steel have been used.

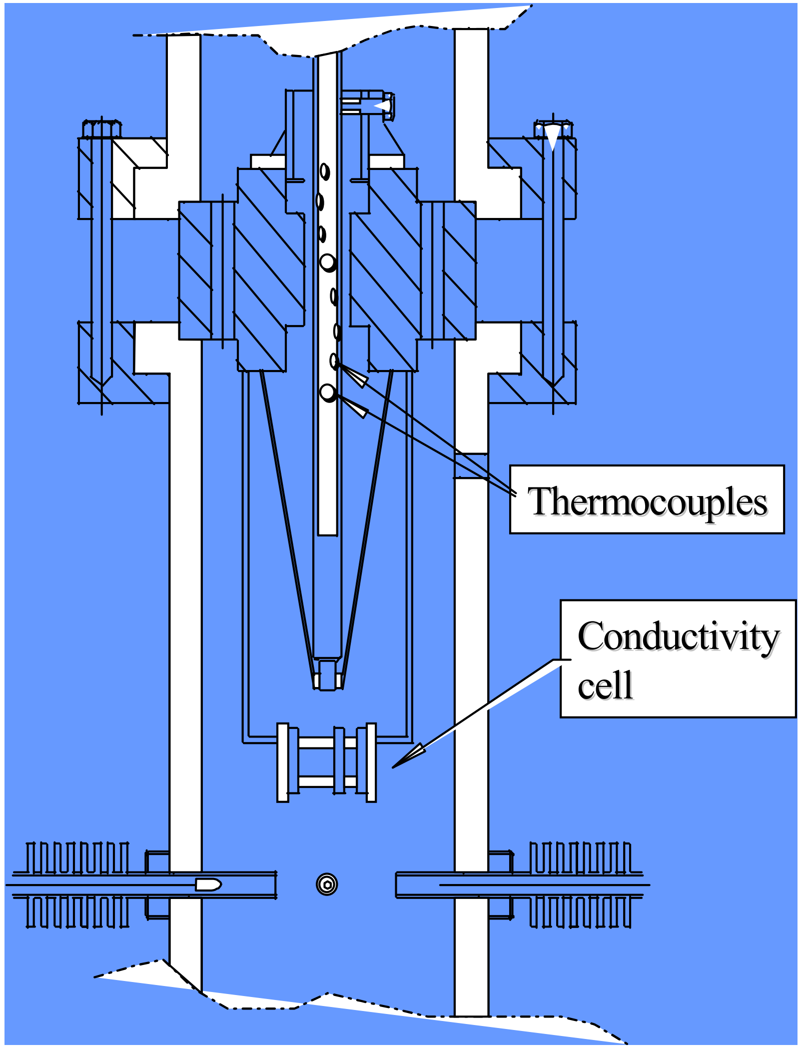
No crevice sampling.

The Studsvik Loop for Heated Crevice Studies



Water heated version without high flow recirc.

Monitoring outside the crevice region



Thermocouples

Conductivity cell

Experimental

Steady autoclave conditions were established by boiling and decrease of the water level in the autoclave.

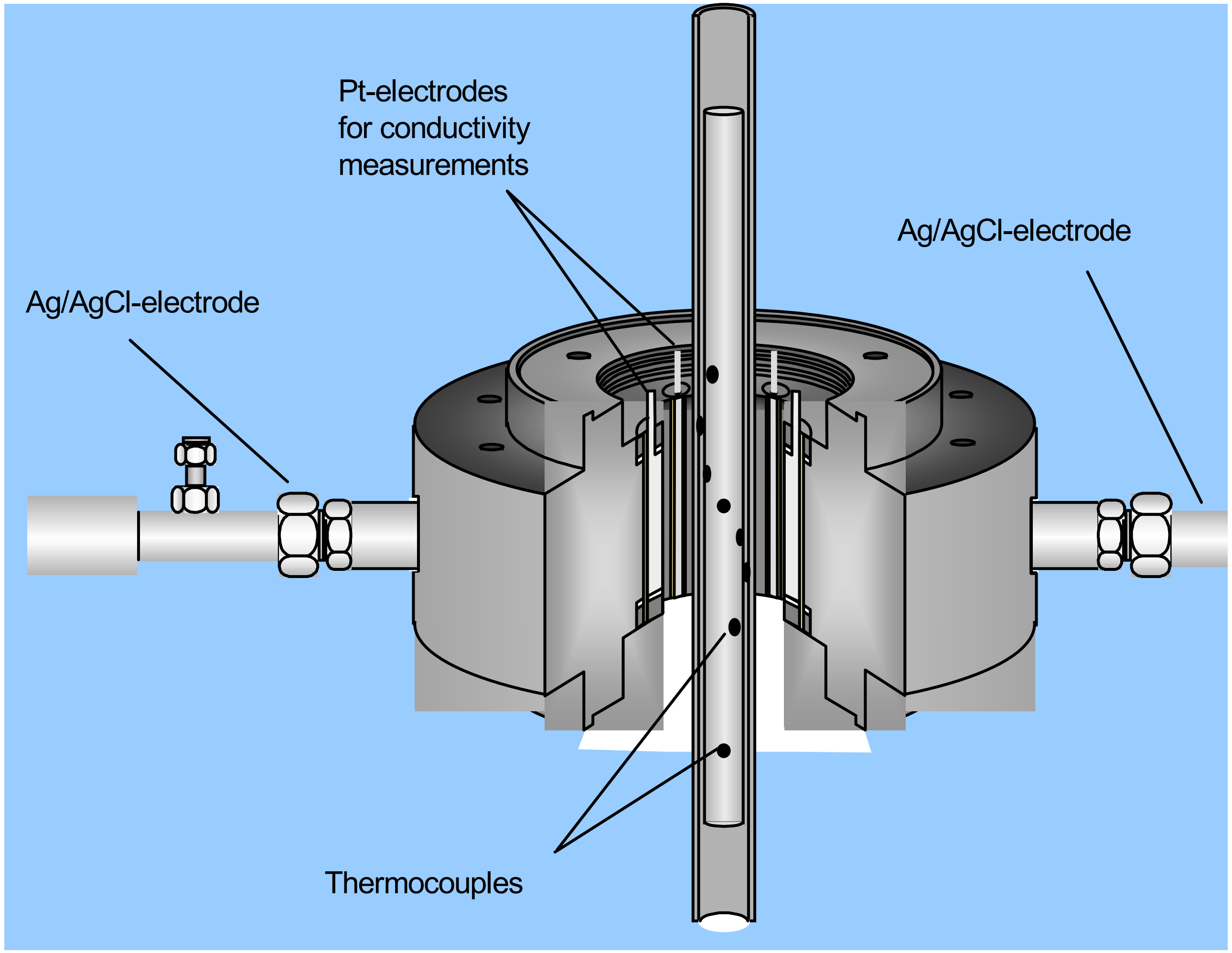
The water level was kept constant with a “feedwater pump” controlled by the signal from a differential pressure meter keeping the water level in the autoclave constant.

Controlled small amounts of impurities were added to the bulk phase.

Hideout was measured by a conductivity decrease and potential change in the bulk phase.

Simultaneous monitoring was made in the crevice to try to follow the hideout in-situ.

Heated Crevice Arrangement



Asymmetric filled crevice design

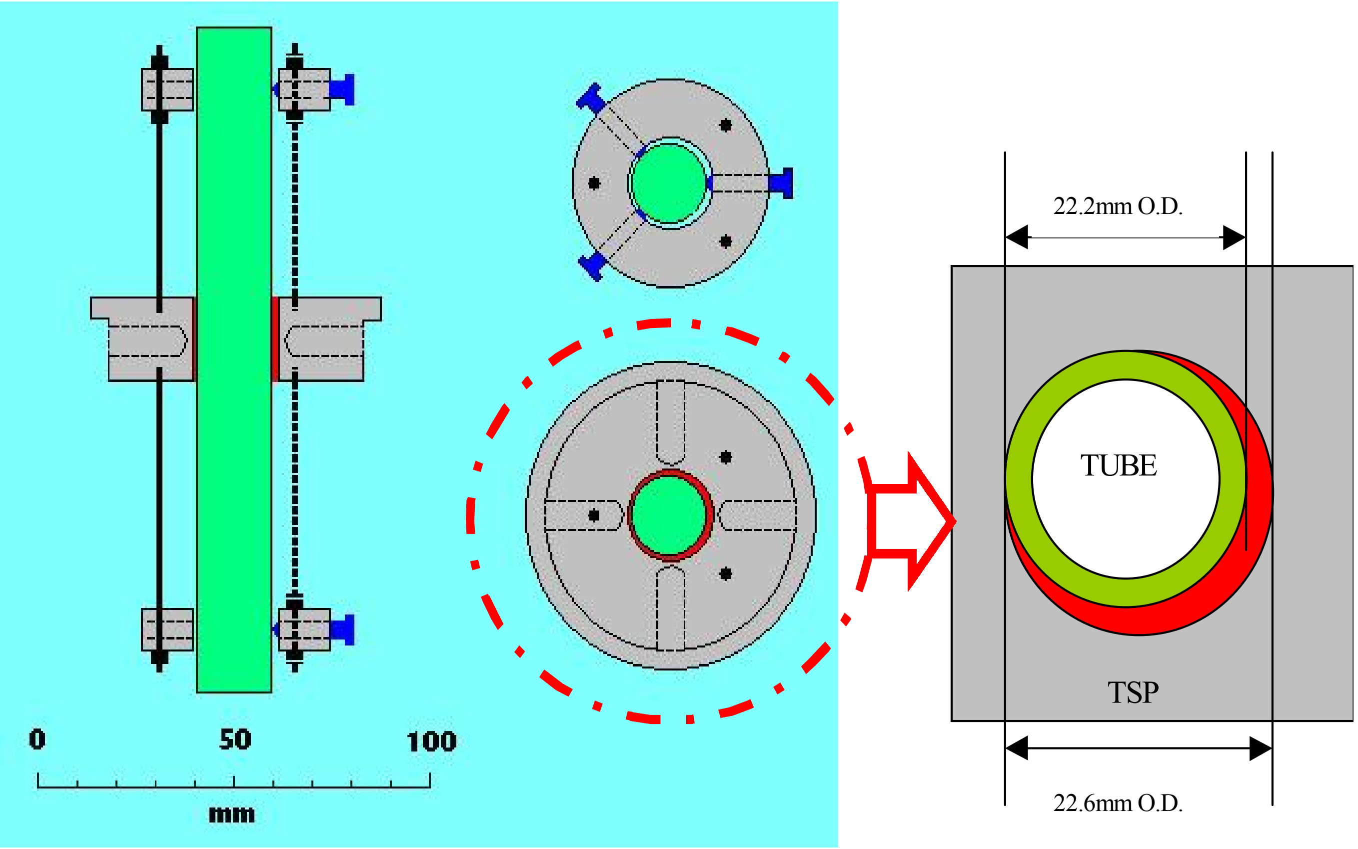


Figure 1
Schematic drawing of asymmetric crevice design.
<u>Legend</u>: Red is asymmetric crevice. Green is tube. Large gray part is TSP.

Typical primary results

After the controlled amounts of impurities were added to the bulk phase hideout was easily measured by a conductivity decrease and potential change in the bulk phase.

Simultaneous monitoring was made in the crevice to try to follow the hideout in-situ. However, the crevice measurements were often hard to evaluate and understand. Results were often difficult (or impossible) to reproduce.

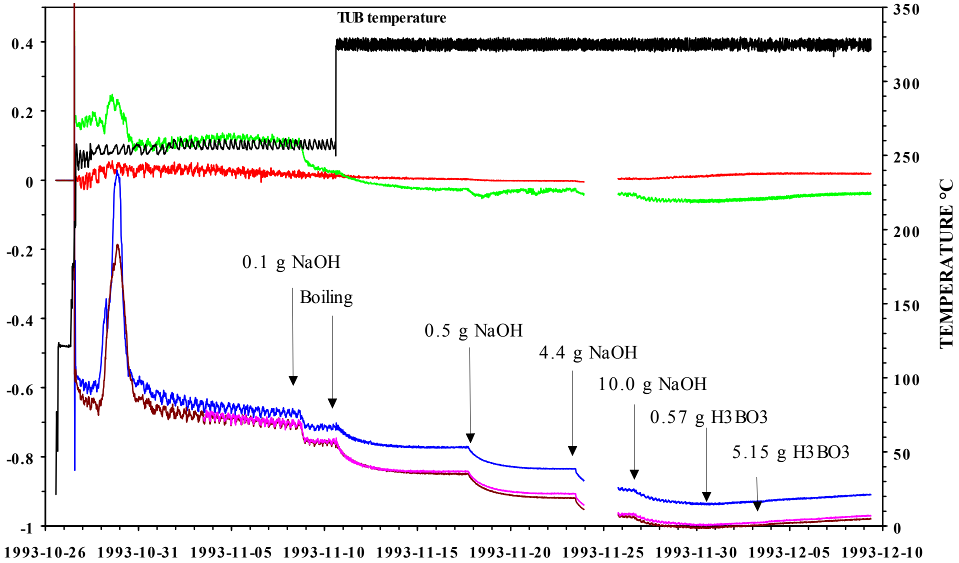
By interrupting the heating, return could be demonstrated.

The hideout/return was heavily dependent on the crevice gap and the crevice filling.

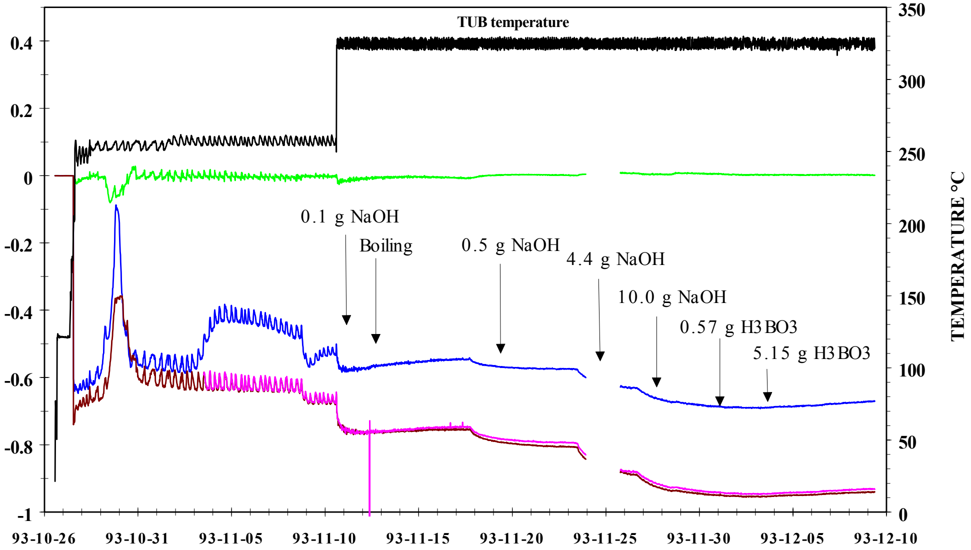
A pressure drop over the TSP significantly decreases the obtained hideout.

Example: Crevice gap: 1 mm, unpacked

Bulk



Crevice



Crevice and bulk reading are essentially the same at 1 mm crevice gap.

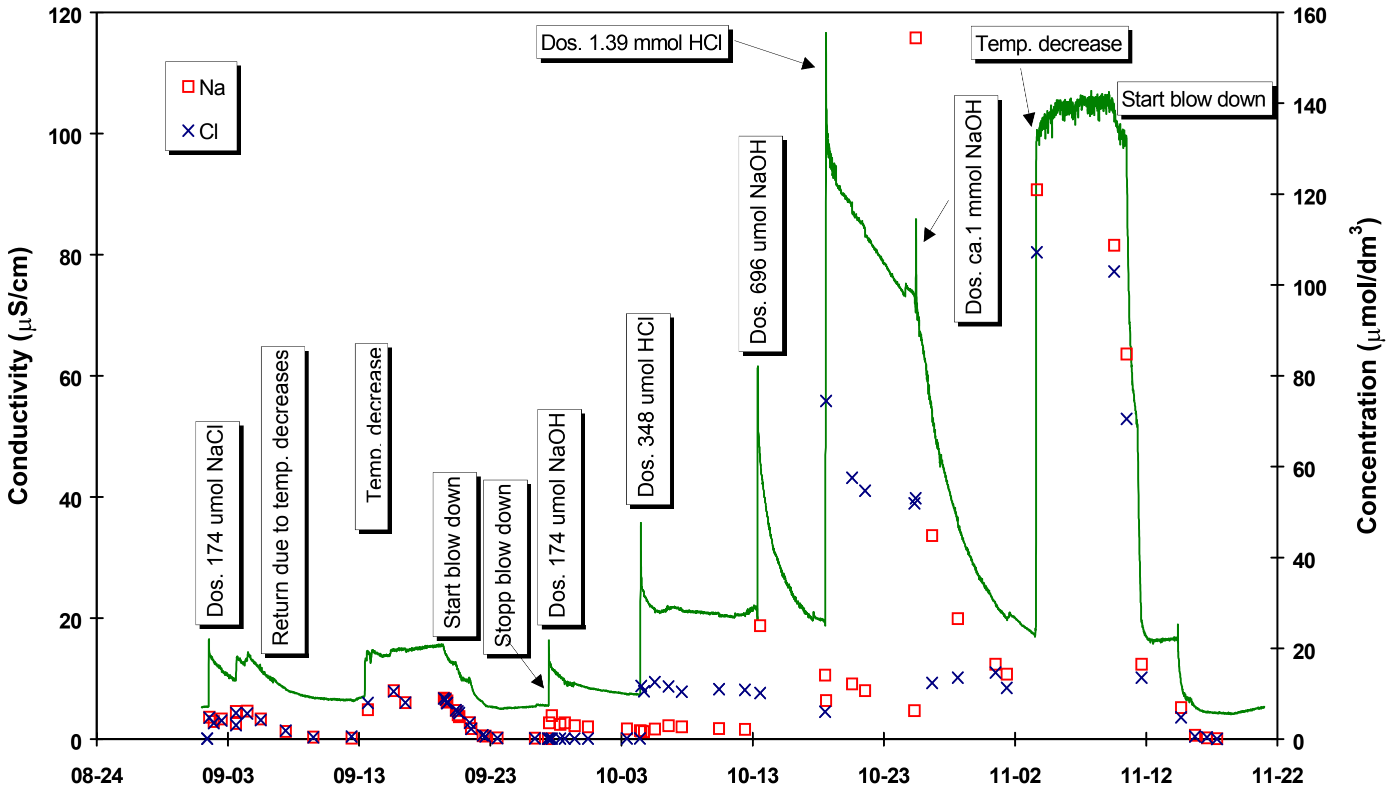
Ringhals
INGÅR I VATTENFALL

Studsvik™ Nuclear

JAPC

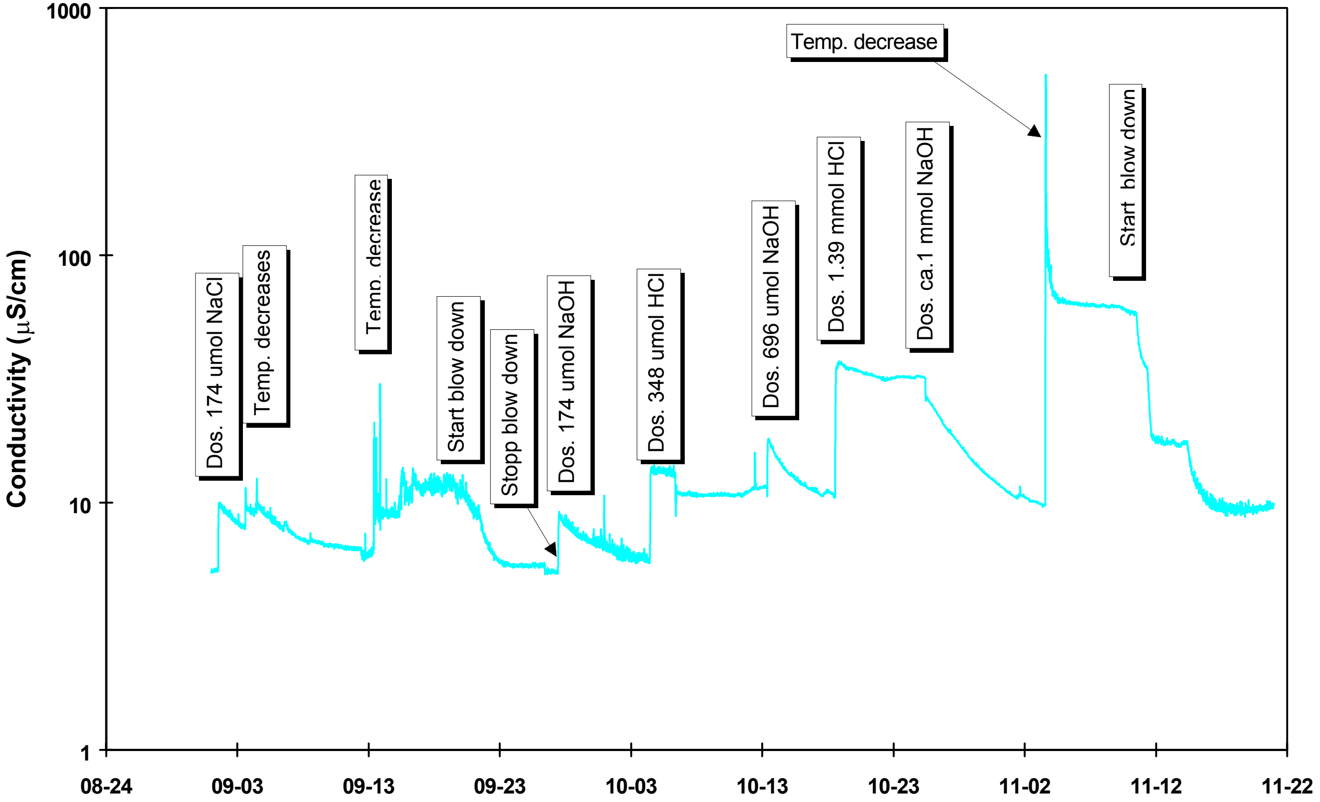
Example: Crevice gap: 0.2 mm, unpacked

Bulk measurements



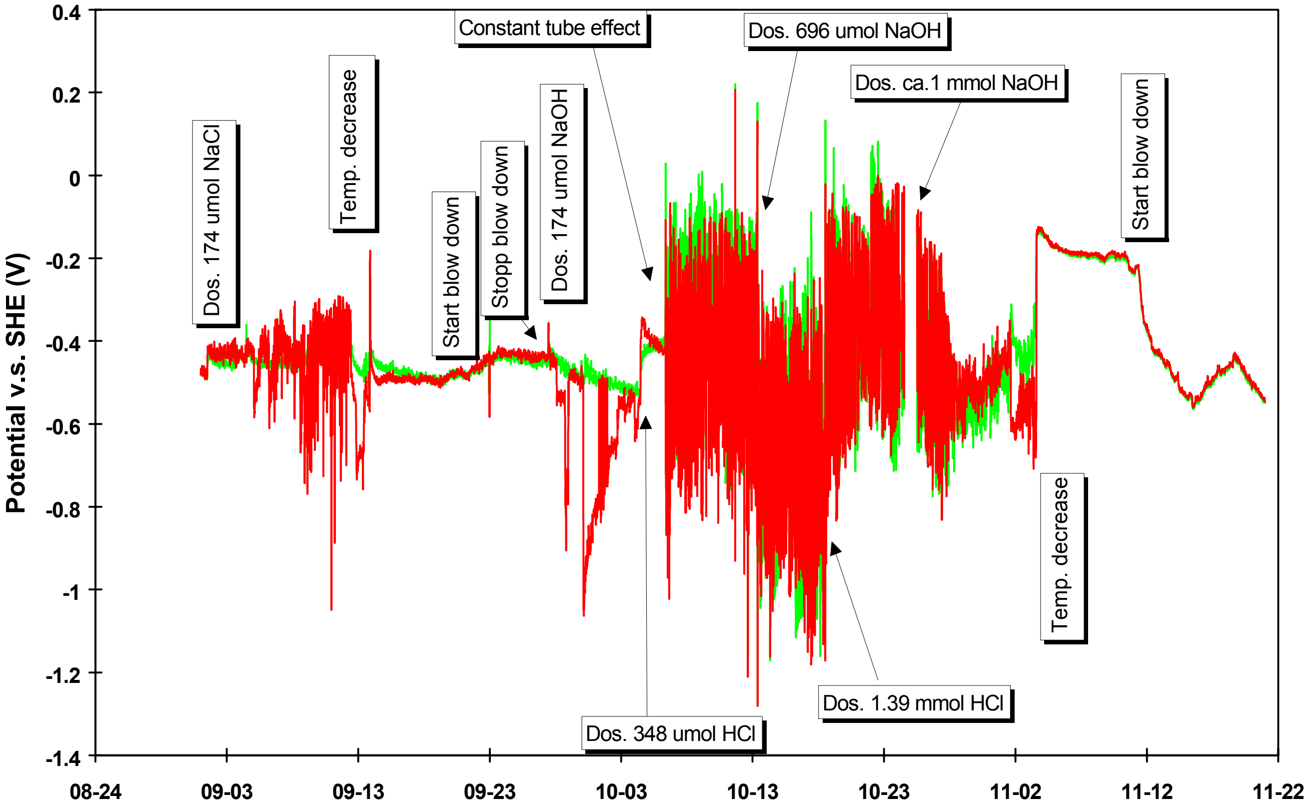
Example: Crevice gap: 0.2 mm, unpacked

Crevice conductivity



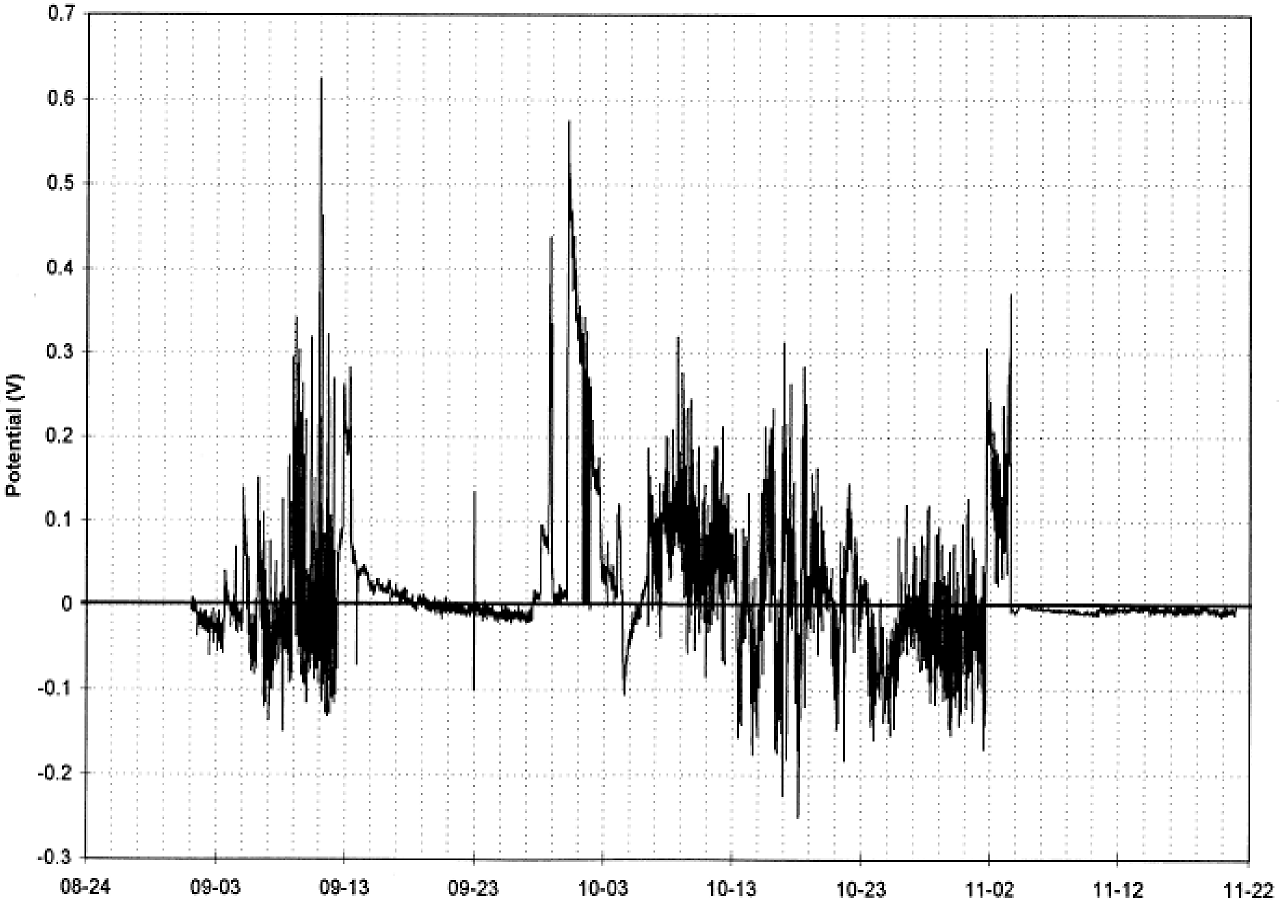
Example: Crevice gap: 0.2 mm, unpacked

Potential of PT inside crevice vs two reference electrodes



Example: Crevice gap: 0.2 mm, unpacked

Potential between two reference electrodes in the crevice



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Discussion

Hideout and return occur in the crevice of the loop if the crevice gap is small or filled with a porous filling.

Hideout is easily measured by bulk conductivity and corrosion/redox potentials.

Crevice measurements often confirm the hideout process but the measurements show large variations inside the crevice.

This means that just beside the measuring locations an even more aggressive solution can exist (which determines the corrosion attack).

So how shall we use data from heated crevice experiments?

Discussion (cont.)

By modeling crevice concentrations can be calculated. The nominal crevice volume is used and the chemicals that ”disappear” from the bulk are assumed to go into the crevice.

However:

Crevice volume is undefined (the void ratio inside the crevice is unknown).

The concentration of chemicals inside the crevice show a huge variation.

Calculated concentrations and concentration factors are not valid in these short term experiments and corrosion predictions are uncertain.

Can long term exposures help the situation?

Filled crevices

Asymmetric crevices with a filling of about 25 % porosity.

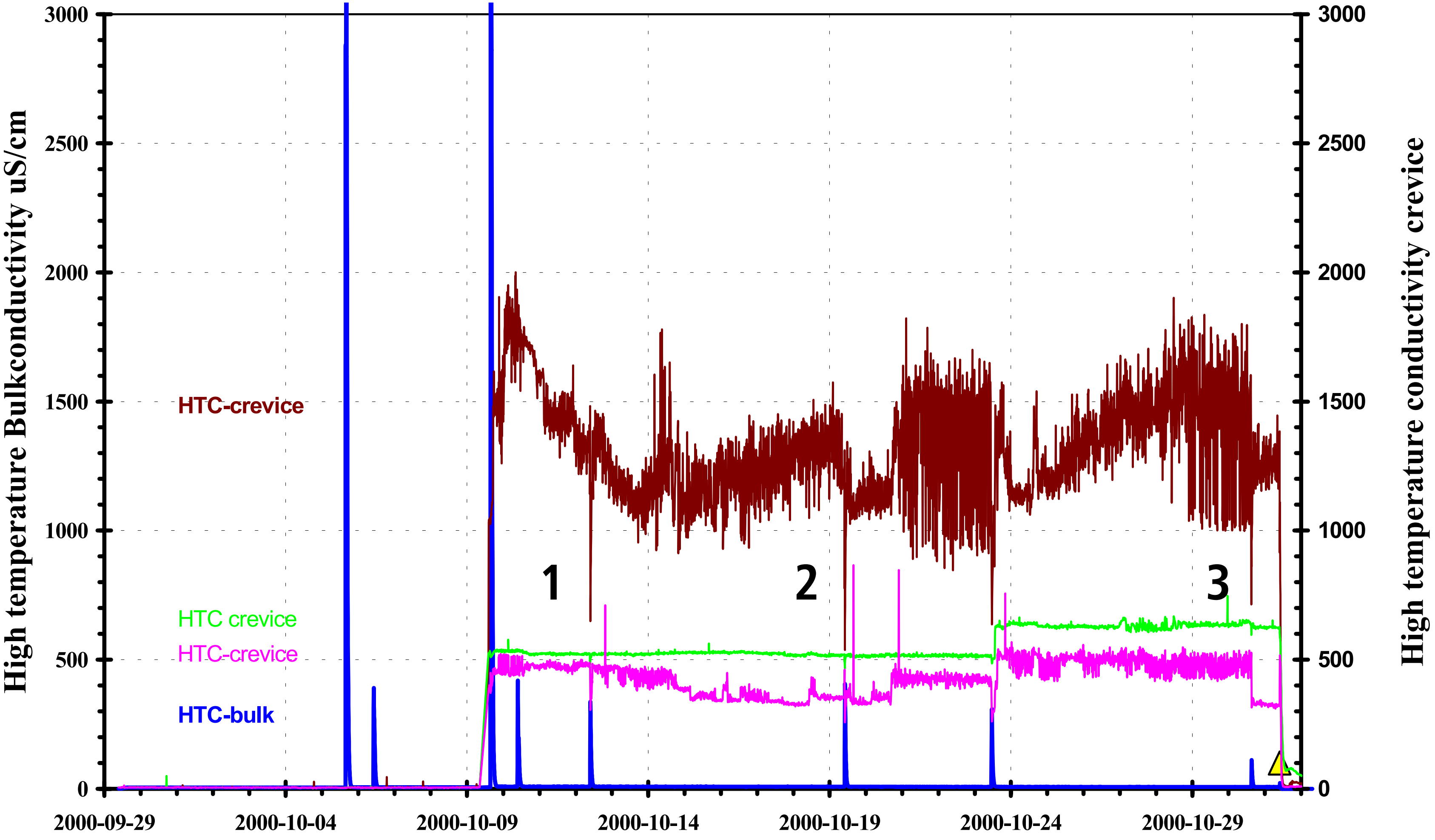
Hematite in oxidizing (O_2) and magnetite in reducing (N_2H_4) environment.

Alkaline and acidic environment.

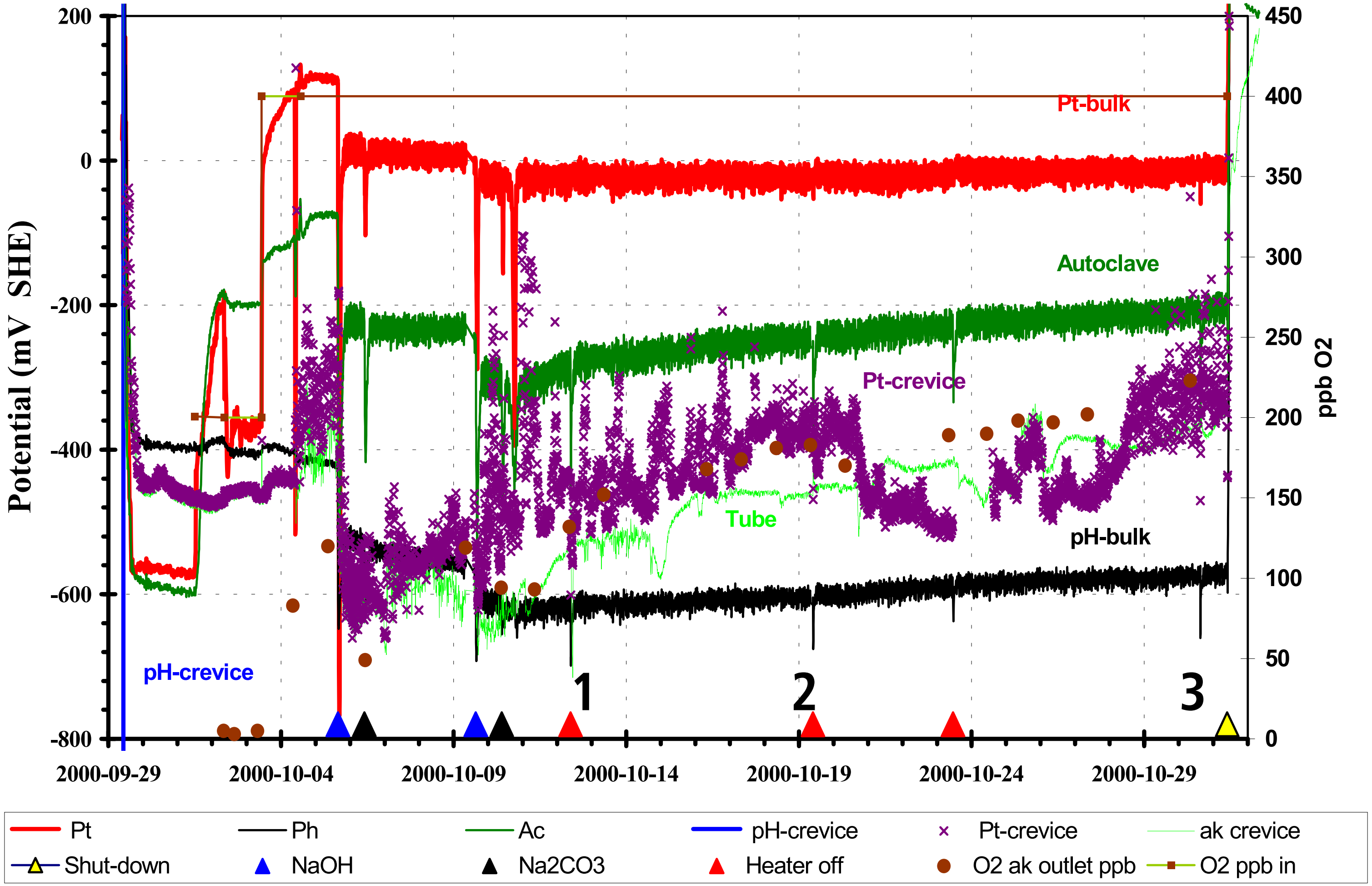
Temperature (°C), pH_t, and different E_{SHE}, were monitored in bulk and crevice.

The recordings were analyzed for hideout/return (amplitudes and time dependencies).

Example of alkaline/ox. HTC



Example of alkaline/ox. E_{SHE}



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Results for alkaline/ox/red. crevice

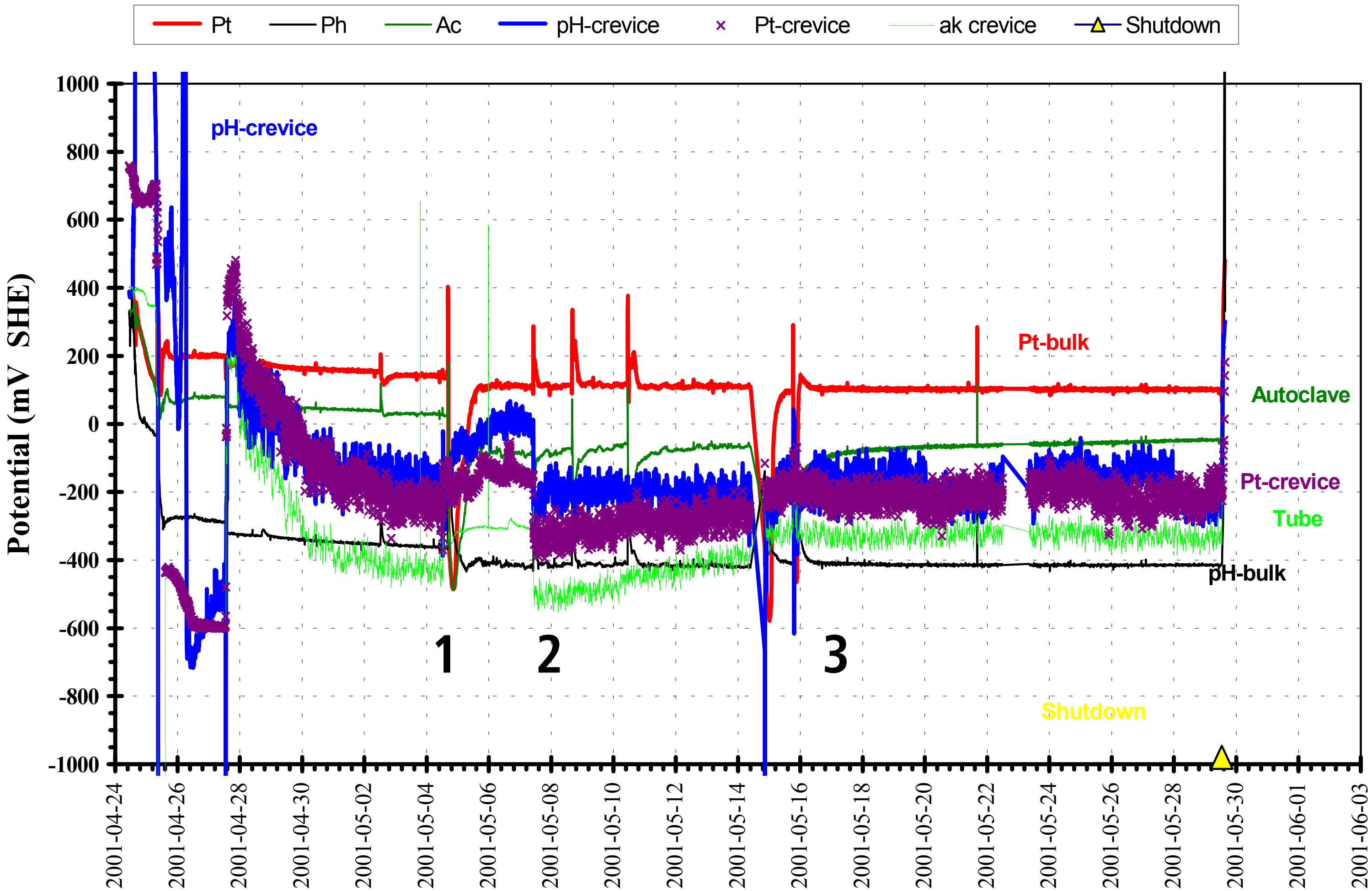
Simultaneous observations were made of decrease in the crevice HTC and increase of the bulk HTC indicating Hideout/return at temp. dips.

In between temperature dips, crevice HTC slowly increases again and bulk HTC falls back to very low values, indicating hideout.

Simultaneous temp and bulk potential dips verify a return effect.

An ongoing increase of the Pt(crevice) potential in oxidizing and decrease in reducing environment indicates a slow reaction on the redox environment in the bulk.

Example of acidic/ox. E_{SHE}



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Results for acidic/ox. crevice (8)

Simultaneous decrease in crevice HTC and increase of bulk HTC, but crevice HTC signals different from alkaline cases at temp. dips.

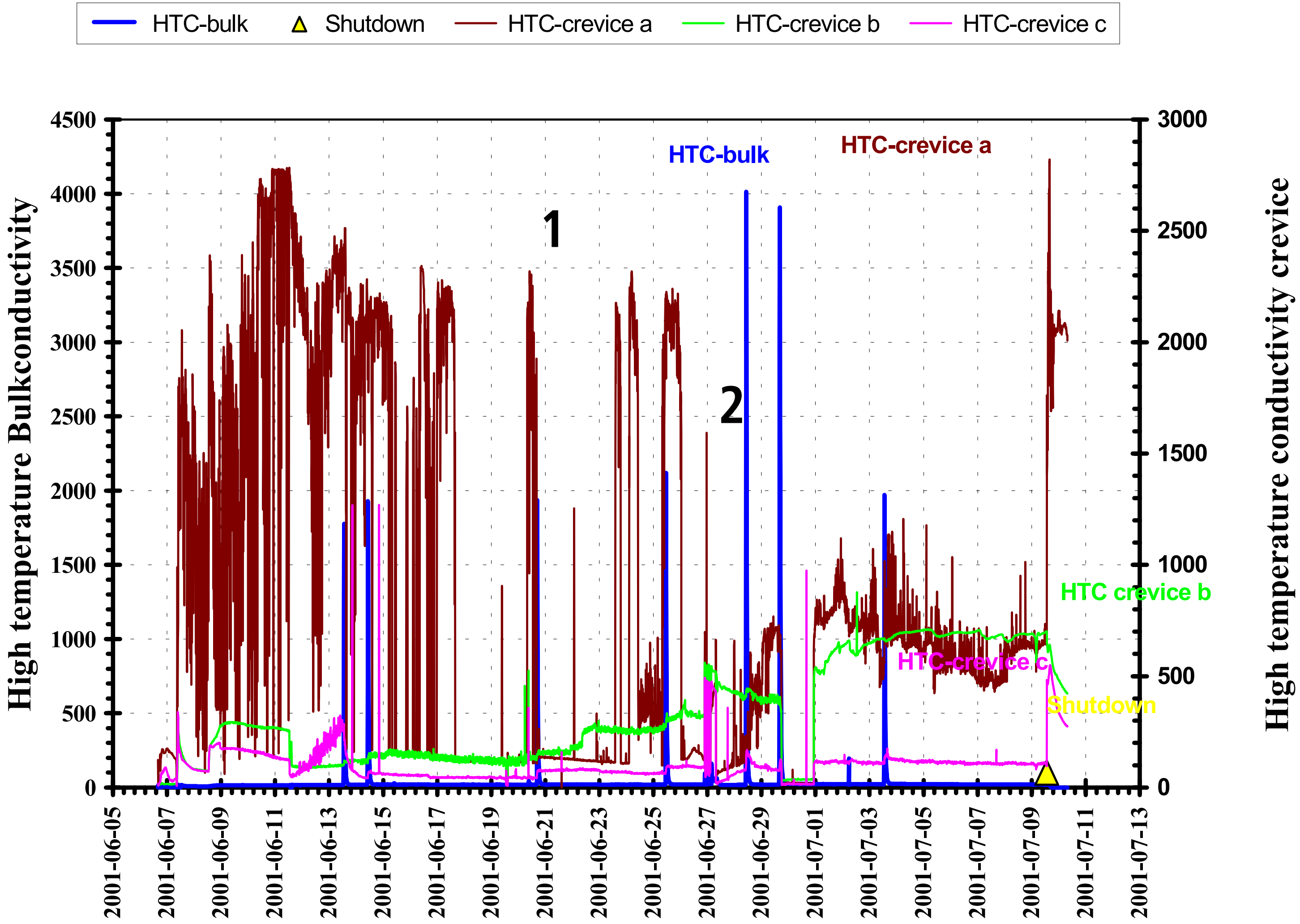
Crevice HTC did not change between temp. dips, but bulk HTC falls back to very low values. Main hideout level established very early?

The Pt(crevice) potential responds with dips on temperature dips, indicating an acidic return process.

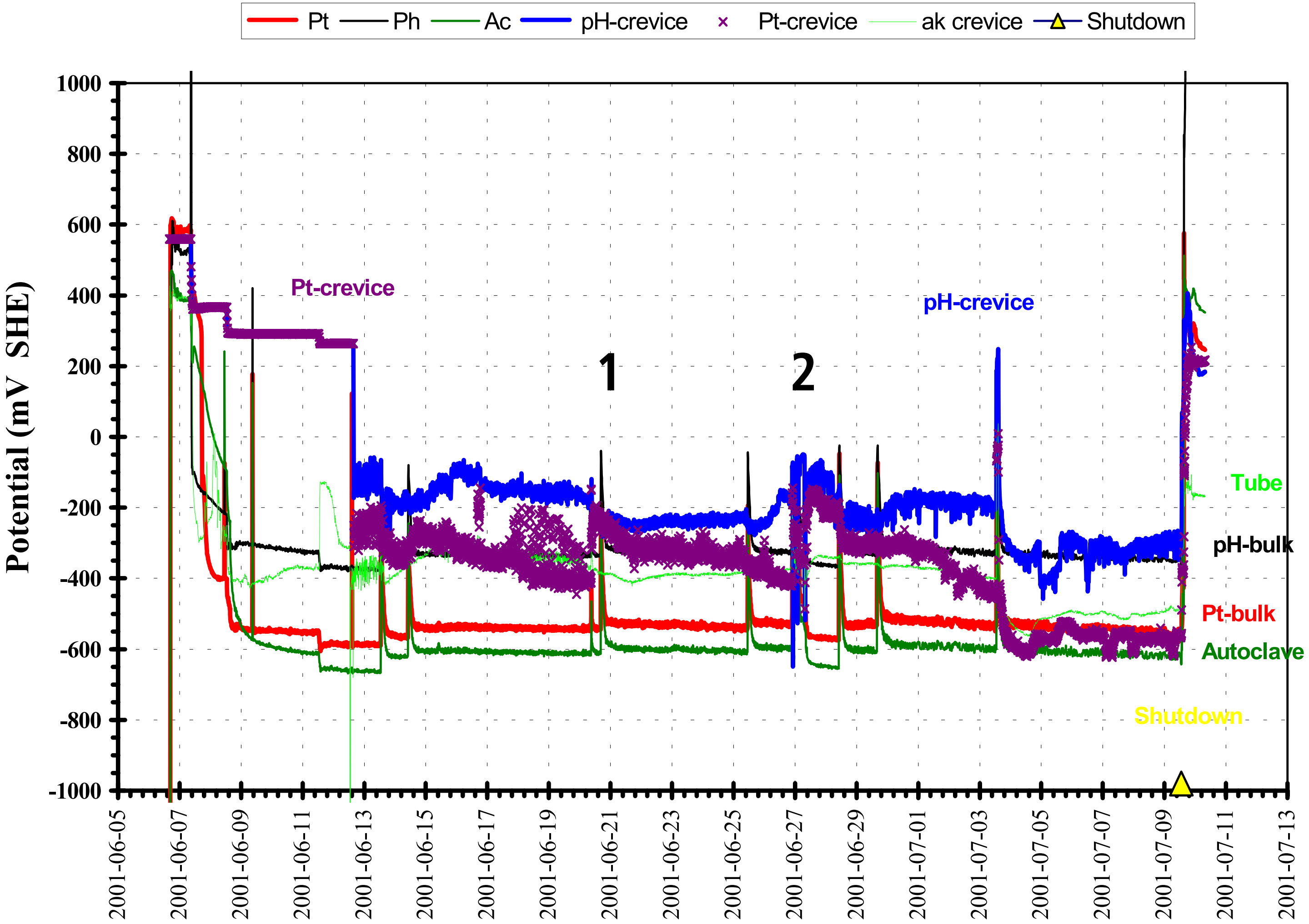
The temperature dips also generate simultaneous increase in most bulk potentials, indicating an acidic return effect.

The crevice related potentials equilibrate more rapidly than in alkaline environment.

Example of acidic/red. HTC (9)



Example of acidic/red. E_{SHE} (9)



Results for acidic/red. crevice (9)

One crevice HTC very scattered. Equals other after 2nd heater trip.

Bulk HTC always falls back to very low values, indicating hideout.

All E(bulk) increase at the heater trip, indicating return.

The pH(crevice) potential decreases, confirming the return.

The Pt(crevice) potential seems to be more dependent on hide-out and return of hydrazine than of acid as it goes in opposite direction.

After 0703 HTC(crevice)=HTC(bulk), E(crevice)=E(bulk) indicating total loss of the magnetite filling. The loss was confirmed at shut down.

Discussion, Filled Crevices

HTC and pot. values indicate hideout and normally confirm each other.

Hideout/return observed in all alk./acidic - ox./red. conditions.

Acidic hideout/return more rapid than alkaline?

Protolythic hideout/return more rapid than redox hideout/return?

Final response stronger in a porous filling compared with no filling?

The wider and outer parts of the filled crevices seems to communicate with the bulk in the hideout/return process. The outer parts rapidly.

Conclusions

It is difficult to draw firm conclusions about the crevice chemistry through heated crevice experiments.

The exposure times may not be enough to reach a steady state inside the crevice.

Results difficult to reproduce.

Improvements of the heated crevice technique may be possible but alternative methods would be attractive to improve corrosion/hideout predictions.

Combined radiotracer and chemical in-crevice monitoring may be such a possibility.

High Temperature pH probes for crevice/ crack tip solution chemistry applications - A preliminary study

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Abstract

The importance of water chemistry for economic, reliable and safe operation of water cooled power plants is well known. Among the various water chemistry parameters, pH plays an important role as it controls the local environmental chemistry through acid/ base equilibria of the dissolved electrolytes and various corrosion reactions of the structural materials with high temperature water. The pH of the crevice / crack tip solution rapidly changes due to occluded geometry and other associated phenomena like mass transport, thermal / potential gradients and boiling etc. This paper describes the fabrication of a few miniature pH probes based on YSZ membrane (with Cu/Cu_2O and Ni/NiO internals) and normal W/W_xO_y systems by employing conventional, special electrochemical procedures and advanced methods like plasma spray techniques. The results on surface morphology and electrode interphases by Back scattered electron microscopy (BSM), EDAX and ESCA measurements were reported. Thermodynamic calculations are presented for arriving at the standard potential (E^o) values of these probes at different temperatures and the theoretical potential values (vs SHE) for various pH values of the solution were calculated. The pH measurements were carried out in bulk PWR water with hydrogenated conditions (1200 ppm Boric acid and 2 ppm LiOH; DO < 5 ppb; 0-2 ppm DH) in the temperature range of 250-300 ^oC by monitoring the potential of the pH probes with an external Ag/AgCl reference electrode. The results show that the electrode potentials are very stable at a constant temperature and change with temperature as the pH changes. The electrodes are also unaffected by the presence hydrogen in the solution. However, the electrodes performance were found to decrease beyond 200 hours and after repeated hydrogen cycling. The experimentally measured and theoretically calculated values are compared and discussed.

Key words: crevice chemistry, crack tip, pH, YSZ, high temperature

Introduction

The operational safety of a power plant mainly depends on the structural materials and the environmental chemistry. The plant life can be extended by switching over to improved engineering materials and practicing a controlled environmental chemistry. However, for the operating power plants, changing of material is not only economical but also very difficult. On the other hand, controlling the environment is relatively easy and hence most of the plant utilities adopt to this procedure for economical operation of their power plants. For water cooled power plants, the environment is nothing but water chemistry with deliberately added chemical components to minimize the corrosion damage of the structural materials. Of the various water chemistry parameters viz., dissolved oxygen, specific conductivity etc., pH plays an important role as it controls the local chemistry through acid/ base equilibria of the dissolved electrolytes and various corrosion reactions of the structural materials with high temperature water. The bulk water pH for a given composition of electrolytes does not change rapidly, but the crevice pH or the pH at the crack tip solution changes dynamically due to occluded geometry and other associated phenomena like mass transport, thermal / potential gradients and boiling etc. This leads to an aggressive chemistry in crevice or crack tip regions and influences the local corrosion reactions. Many studies have shown that the pH of crack tip solution is a function of the crack growth behavior of the material tested and in-situ pH measurements are always essential for validating the theoretical models of crack tip solution chemistry and hence the mechanism of environmentally assisted cracking (EAC) of the structural materials. This paper describes the fabrication of a few miniature pH probes based on YSZ membrane (with Cu/Cu_2O and Ni/NiO internals) and normal W/W_xO_y systems by employing conventional, special electrochemical procedures and advanced methods like plasma spray techniques. Apart from surface morphology of the pH probes, the preliminary results of pH measurements in bulk PWR water with hydrogenated conditions (1200 ppm Boric acid and 2 ppm LiOH; DO < 5 ppb; 0-2 ppm DH) in the temperature range of 250-300 ^{o}C) are reported. The experimentally measured and theoretically calculated values are compared and discussed.

Experimental

Design and Fabrication of pH probes

Earlier, standard hydrogen electrodes (SHE) based on Pt, Pd-H and Pd-Ag-H systems were used for high temperature pH measurements. However, these electrodes lost their popularity due to various problems viz., H_2 gas handling, difficulty in maintaining a particular partial pressure of hydrogen and their sensitivity to red-ox species. Later, pH electrodes based on yttria-stabilised zirconia (YSZ) with various internal metal / metal oxide systems gained importance as they don't have problems that are faced with standard hydrogen electrodes and since they are chemically inert to high temperature water [1-6]. The high temperature pH probes for bulk water applications can be prepared by filling a commercially available YSZ tubes (usually ¼ in. OD) with a suitable metal/ metal oxide powder and using a metallic wire as the contact and lead from the sensor. However, the crevice / crack tip solution chemistry applications require miniature probes.

In this study, three different miniature pH probes were prepared based on **Cu/Cu_2O, Ni/NiO and W/W_xO_y** systems by using a 0.5 mm metallic wire and sequentially forming the corresponding metal oxide and YSZ coating (only for Cu and Ni based systems) by various methods. The wire was then covered with heat shrinkage polytetrafluoroethylene (PTFE) tubing, leaving the sensor portion exposed to test solution. For copper, the oxide coating was obtained either by heating with a propane gas torch or at 1000 ^{o}C in a muffle furnace under normal condition or at 800 ^{0}C in Argon atmosphere. The upper layer of cupric oxide was naturally flacked off by slowly cooling the furnace and the remaining cupric oxide, if any, was brushed off to expose the inner cuprous oxide film. In another procedure, a thin composite film of copper / cuprous oxide was formed by employing an electrodeposition method with a 0.6 M copper lactate solution (pH 9.0) using a current density of 1.5 mA/cm^2. For Ni/NiO and W/W_xO_y, the oxide coating was obtained by heating in air to a red heat for 3-5 minutes using a propane gas torch. Since the bonding characteristics of the YSZ depends on the substrate surface as well as the method of coating technique, different methods viz., Plasma Spray, Chemical Vapor Deposition (CVD) and Electrophoretic Deposition (ED) were proposed. However, for this study, only the electrodes coated with Plasma Spray technique were used for the pH measurements. The latter procedures are supposed to give more compact layer of YSZ and hence are now under way.

Theoretical Calculation of Standard Potentials of the sensors

Fig.1. gives the basic mechanism of potential development across the YSZ membrane. Based on the interphase potentials of the reactions at the various interfaces, one can show that the potential of these electrodes can be calculated from the free energy of the reaction,

$$xM + yH_2O \Leftrightarrow M_xO_y + 2yH^+ + 2ye^- \qquad \ldots.(1)$$

and the potentials with respect to SHE can be obtained by coupling this half-reaction with that of hydrogen reduction,

$$yH_2 \Leftrightarrow 2yH^+ + 2ye^- \qquad \ldots.(2)$$

Hence, the standard potential of these electrodes in a solution containing unit activity of hydrogen ion can be calculated from the free energy change for the overall reaction,

$$xM + yH_2O \Leftrightarrow M_xO_y + yH_2 \qquad \ldots.(3)$$

For the above reaction, the metal oxides viz., Cu_2O, NiO and W_4O_{12} [7] were used for the copper, Nickel and Tungston based systems respectively. Once the standard potential of these electrodes are known at a given temperature, the pH_T of the solution can be calculated from the measured potential of the YSZ probe according to the expression:

$$E_{(YSZ\ VS\ SHE)} = E^o_{(M/MO)} - (2.303*RT/F)*pH_T \qquad \ldots.(4)$$

where the symbols R, T, and F represent the usual meaning. However, if the YSZ probe potential is monitored with respect to an external Ag/AgCl reference electrode, the pH_T of the solution can be given by the expression,

$$pH_T = [E^o_{(M/MO)} - \{E_{(YSZ\ VS\ Ag/AgCl)} + A\}] * [F/(2.303*RT)] \qquad \ldots.(5)$$

where A is the correction term to convert the potentials from Ag/AgCl to SHE scale [8,9].

Measurement system

A recirculating, high temperature and high pressure water loop with an autoclave facility having ports for introducing the pH probes and external Ag/AgCl reference electrode was used for this study. The measurements were carried out in simulated PWR water with hydrogenated conditions (1200 ppm Boric acid and 2 ppm LiOH; DO < 5 ppb; 0-2 ppm DH) in the temperature range of 250-300 ^{o}C. Electrodes of each kind were tested for a total duration more than 240 hours and the potentials were measured with a Keithley 6515 system electrometer and recorded in the computer for subsequent calculations.

Results and Discussion

Electrode surface morphology and characterisation studies

The photographs of copper based pH probe with cuprous oxide and YSZ films by various methods are given in Figure 2. A good adherent film of cuprous oxide was obtained by all the heating procedures. The electrolytic method gave a composite film of the cuprous oxide and metallic copper. Figure 2 (e) shows the YSZ coated Cu/Cu2O wire by Plasma Spray method while figure 2 (f) shows the outer and interior surfaces of the copper based pH probe. Figure 3. shows the XPS spectrum of the oxide coated copper wire. The cross-section of the coated film electrodes were studied by Back scattered electron microscopy (BSM) to identify the surface morphology and to evaluate the relative thickness of the films. Figure 4. gives the SEM pictures of the cross-section of the coated electrodes. It can be seen that for copper, the cuprous oxide film prepared in Argon atmosphere was not very uniform as compared to that prepared by propane gas torch. Of all the methods, the electrolytic method gave the thinner-most film. For nickel and Tungsten, the oxide films were quite uniform and very adherent. From the fabrication point of view, nickel and tungsten based electrodes are better than copper based electrodes. The tungsten based electrode has an additional advantage that it need not be coated with YSZ film for the pH measurements. Figure 5. gives the SEM images of YSZ coated Cu/Cu2O based pH probes. It can be observed that some delamination had occurred near the oxide/YSZ interface and this could have happened during the molding process used for sample preparation for SEM. This was clarified by EDAX measurements (not given here) which showed various interfaces. Figure 6. gives the photograph of Nickel & Tungsten probes after use. It shows the micro-crack that had developed on YSZ coating on nickel electrode towards the end of the test.

Expressions for Standard Potential of the Electrodes:

A computer program was written in BASIC language to calculate the standard potential of the sensor from the free energy changes of the overall reaction (3) at various temperatures and to calculate the pH of the solution according to equation (5). The following expressions were derived from the results of the computer program to obtain the standard potentials, E^{o} vs SHE in Volts for different pH probes.

$$E^{o}_{(Cu/Cu2O)} = 0.48381 - 0.462513.10^{-3}.T + 2.14013.10^{-7}.T^{2} - 1.36749.10^{-10}.T^{3}$$

$$E^{o}_{(Ni/NiO)} = 0.14099 - 0.363071.10^{-3}.T + 1.3041.10^{-7}.T^{2} - 0.253191.10^{-10}.T^{3}$$

$E^o_{(W/W4O12)} = 0.08149 - 0.390169.10^{-3}.T + 1.62278.10^{-7}.T^2 + 0.395135.10^{-10}.T^3$

For converting the measured potentials of the pH probes to SHE scale from that of the Ag/AgCl/(0.1M KCl) reference electrode, the correction term, A is given by the expression

$$A = 0.286637-1.003217.10^{-3}.(T-25) + 0.017447.10^{-5}.(T-25)^2 -0.303004.10^{-8}.(T-25)^3$$

where T is the temperature in °C.

pH measurements:

Electrodes of each kind were tested for a total duration more than 240 hours and the potentials were measured with a Keithley 6515 system electrometer and recorded in the computer for subsequent calculations.

Figure 7. (a-c), gives the potential measurements of the $Cu/Cu_2O/YSZ$ pH probe monitored over a period 12 days. All the potentials were measured with respect to autoclave frame and converted to SHE scale for pH calculations. The red-ox potential of the autoclave solution was also monitored by Pt electrode and were presented in some of the graphs for identifying the reason for the change in the potential values. For example, the change in potential in the first figure (labeled as 16th) of 7 (a) can be reasoned out to change in temperature while the same in figure (labeled as 23rd) of 7 (b) to introduction of hydrogen into the system. It can be seen that the potential of the pH probe and the Ag/AgCl reference electrode changed uniformly and the differences between the two potentials were almost constant. This behaviour is expected because at a given temperature the pH of the solution is constant and hence the potential of the pH probe should also remain constant. At this stage, both Ag/AgCl and pH probe function as a reference electrode. The potential of the pH probe did not change with the addition of hydrogen showing thereby its insensitivity to hydrogen or any redox changes to the system. However, after 24 hours of hydrogen addition the potential drifted to more negative value and remained constant and again after 36 hours the potential changed drastically and reached value of zero. The electrode was inspected after the test and was found to have micro-cracks. The rapid changes in potential could be due to development of the cracks which exposes the interior oxide phase to the test solution.

Figure 7. (d-f), gives the potential of the nickel and tungsten based pH probes with time. It can be seen that as the temperature is increased the potential of both the pH probes change to more negative values and become steady when the temperature remains steady. When the temperature was maintained for a number of days, the potentials were also remarkably constant. After a few days, when the temperature was decreased the potentials of both the probes moved in positive direction. It also was observed that the potential of the tungsten probe was more positive than that of nickel probe below 250 °C and became more negative at higher temperature. The reverse trend was observed when the temperature was decreased from 300 °C to 200 °C and hence this change was found to be reversible. Similar to the copper based pH probe, the potential of the nickel and tungsten based pH probes also did not change when hydrogen was introduced into the system. This can be seen in the figure (labeled 06/12/02) of 7 (e) where the potential of a Pt

electrode is changing due to hydrogen addition while that of the pH probes remain at a constant value. However, while hydrogen was removed from the system, all the electrodes showed a change in potential. The nickel based YSZ probe showed a crack on the electrode surface (see figure. 6) and this could be a reason for the changes in potential of this probe. But the reason for the potential shift of tungsten probe was not clear. The estimated pH values calculated from the potentials after the system had stabilized was found to be within two pH units from the theoretically calculated values for the copper and nickel based electrodes. But this deviation can be minimized by improving the YSZ coating and by calibrating the electrode over a wide range of pH. However, for the tungsten electrode, the deviation was more which could be due to the uncertainty in the calculated standard potential because of a mixed oxide phase.

Conclusion

The copper and nickel based YSZ probes seem to work in the expected way. But needs to be calibrated for a wide range of pH. The standard potential, E^o vs SHE for the various sensors were calculated from the free energy changes of the electrode reactions and expressions were derived to obtain the same at various temperatures. The estimated pH values (using the theoretically calculated standard potential) differed by two pH units from the theoretical pH values of the solution. However, the results can be improved by better fabrication procedures using Chemical Vapor Deposition (CVD) and Electrophoretic Deposition (ED) techniques to minimize the development of minor cracks and by calibration of the probes and using experimental E^o values. Ni/NiO system seems to be better than Cu/Cu_2O, because NiO coating was more uniform, the deviation in pH values was relatively less and also doesn't pose any problem if nickel ions are released to the solution. Tungsten based electrode does not need YSZ coating and it is advantageous from the construction point of view. But the main draw back is the uncertainty in the theoretical E^o value due to the mixed oxide phase. However, with proper calibration it can also be used as it is very simple in design and electrode dimension can be very small to suit Crevice / crack tip solution measurements.

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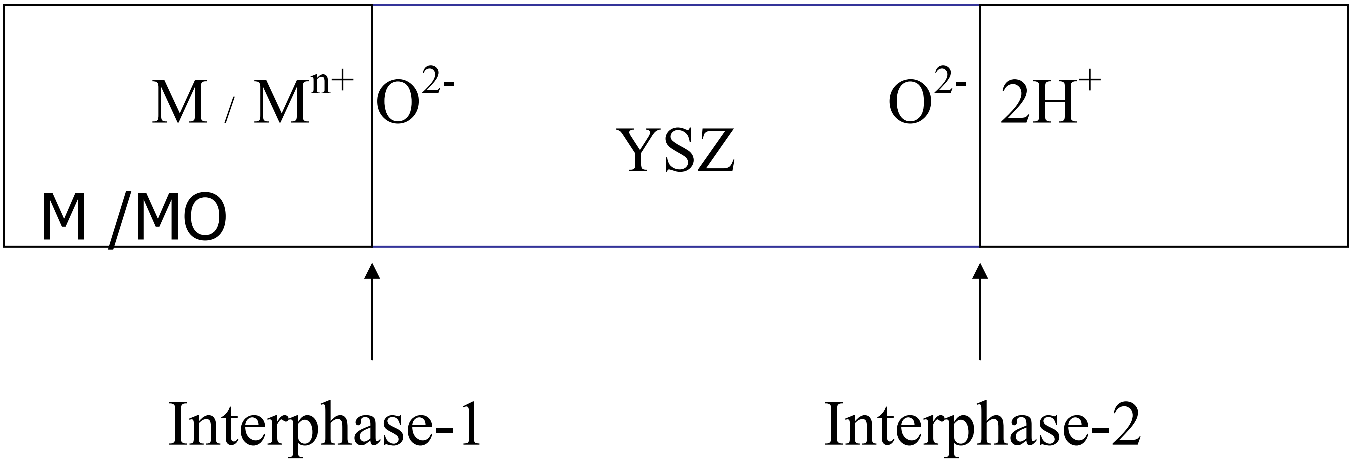


FIGURE 1. Basic mechanism of potential development across the YSZ membrane probe

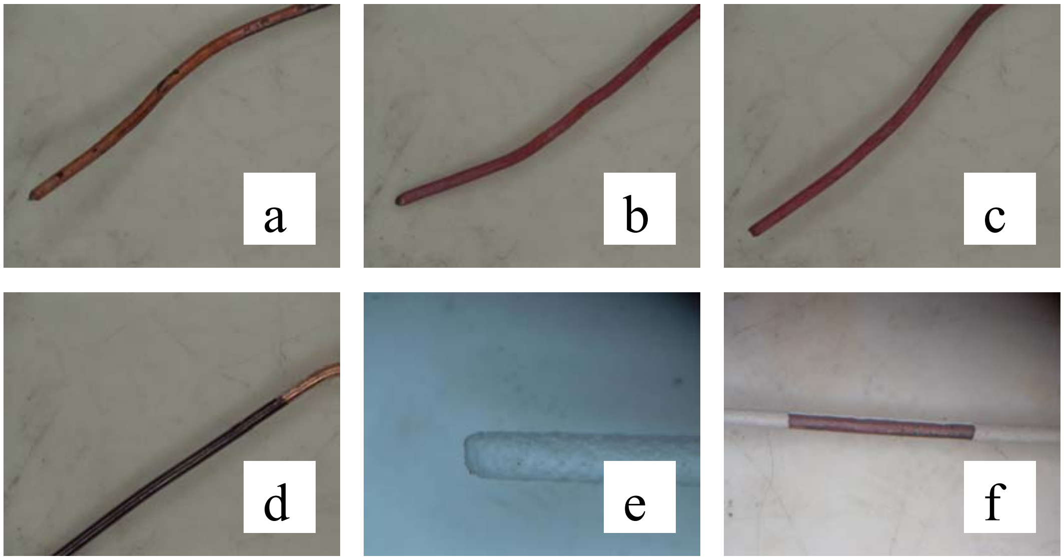


FIGURE 2. Photograph of Copper wire coated with Cu_2O and YSZ: (a-c) Cu_2O coating by heating in Argon atmosphere at 800 °C for 2, 8, 16 minutes respectively (d) Cu_2O coating by electrolytic method (e) YSZ coated, (f) YSZ partially removed to show inner oxide layer

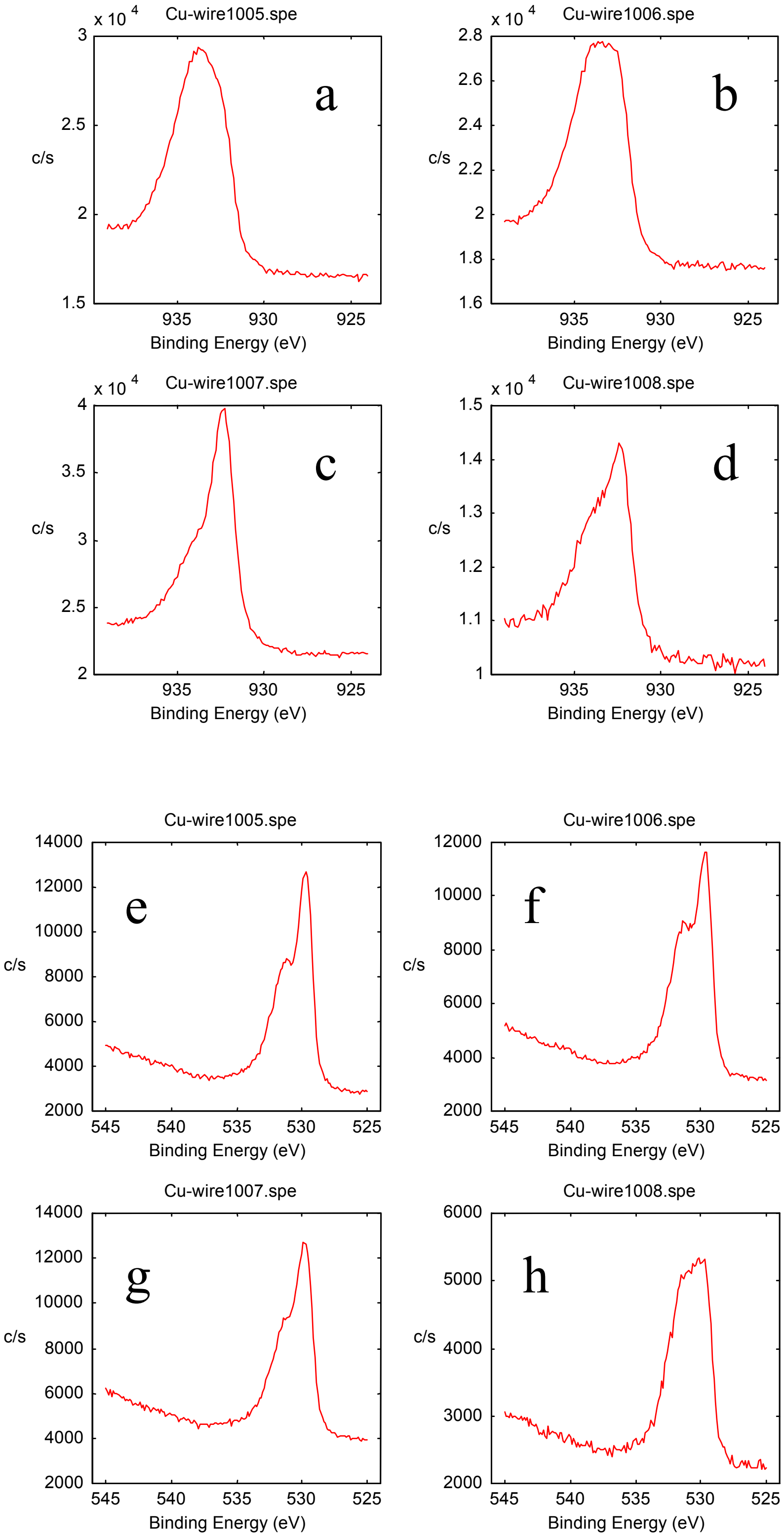


FIGURE 3. XPS spectrum of the oxide coated copper wire: (a-d) copper peaks (e-h) oxygen peaks (a,,b, e & f - with top CuO layer; c,d,g & h – without top CuO layer)

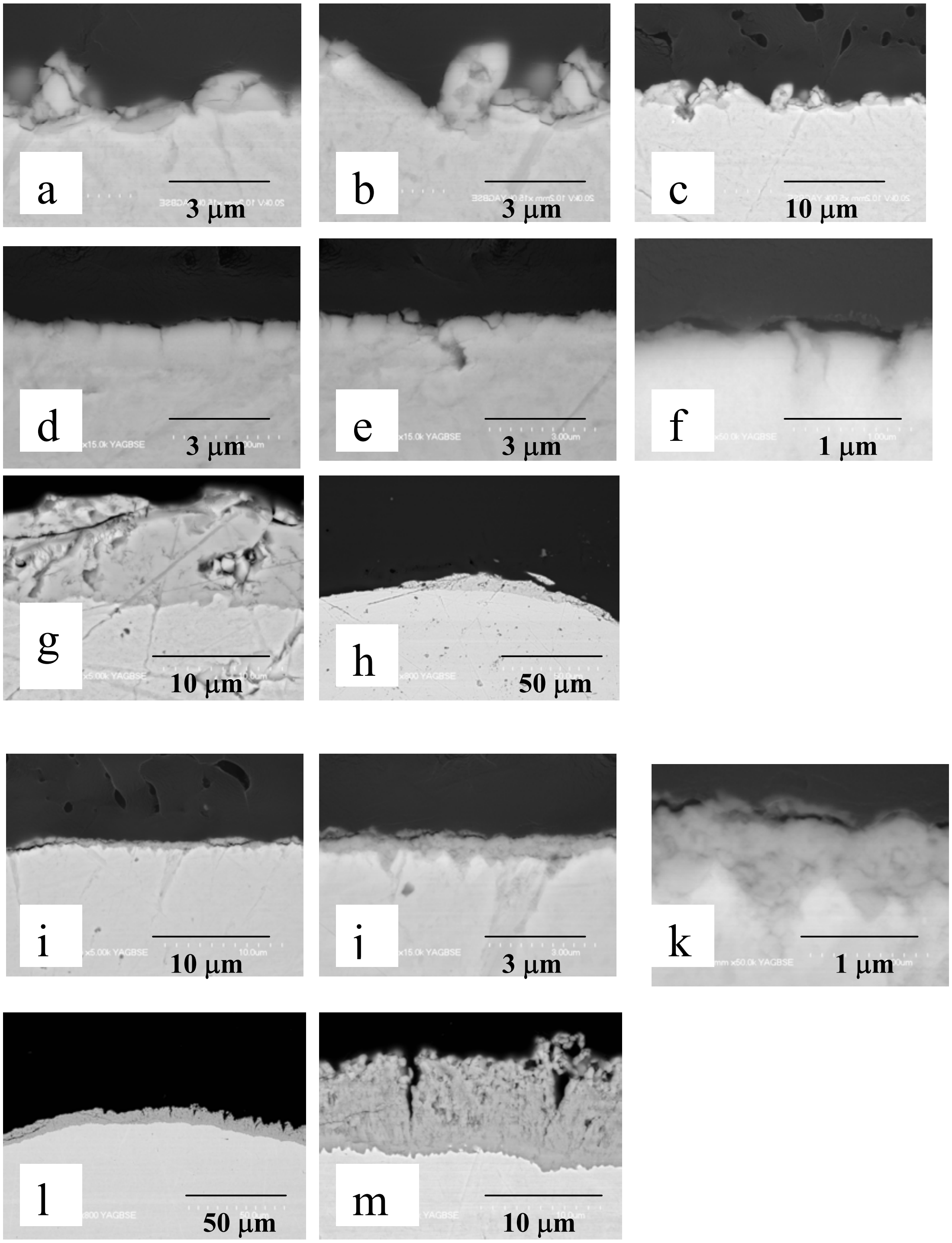


FIGURE 4. SEM Photographs of metal/metal oxide coating: (a-c) Cu_2O prepared in Argon atmosphere at 800 ^{0}C, (d-f) Cu_2O prepared by Electrolytic method, (g-h) Cu_2O prepared by Propane gas torch, (i-k) NiO prepared by Propane gas torch, (l-m) W_xO_y prepared by Propane gas torch

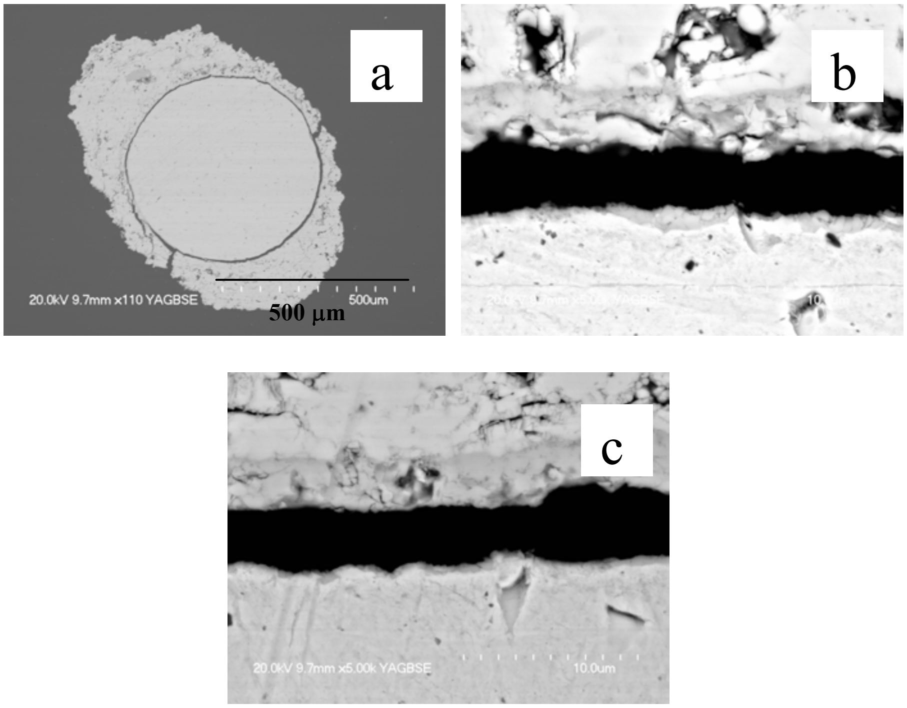


FIGURE 5. SEM images of YSZ coated Cu/Cu2O based pH probes: (a) Full cross-section (b) surface boundary on thickly coated side (c) surface boundary on thinly coated side

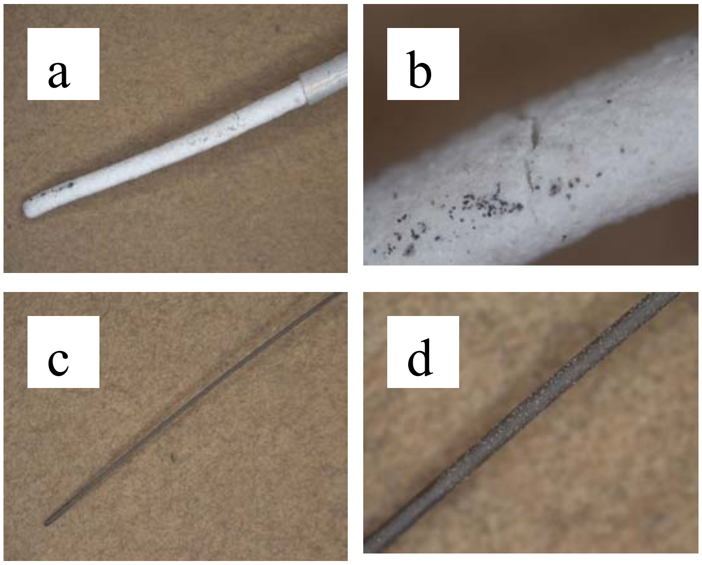


FIGURE 6. Photograph of Nickel & Tungsten probes after usage: (a) Ni/NiO/YSZ (b) same as (a), but enlarged for showing the micro- crack(c) W/W_xO_y coating (d) same as (c), but enlarged

FIGURE 7. (a) Potential Measurements with Cu/Cu$_2$O/YSZ pH probe (Simulated PWR water, 1200 ppm Boric acid and 2 ppm LiOH; DO < 5 ppb; 0-2 ppm DH)

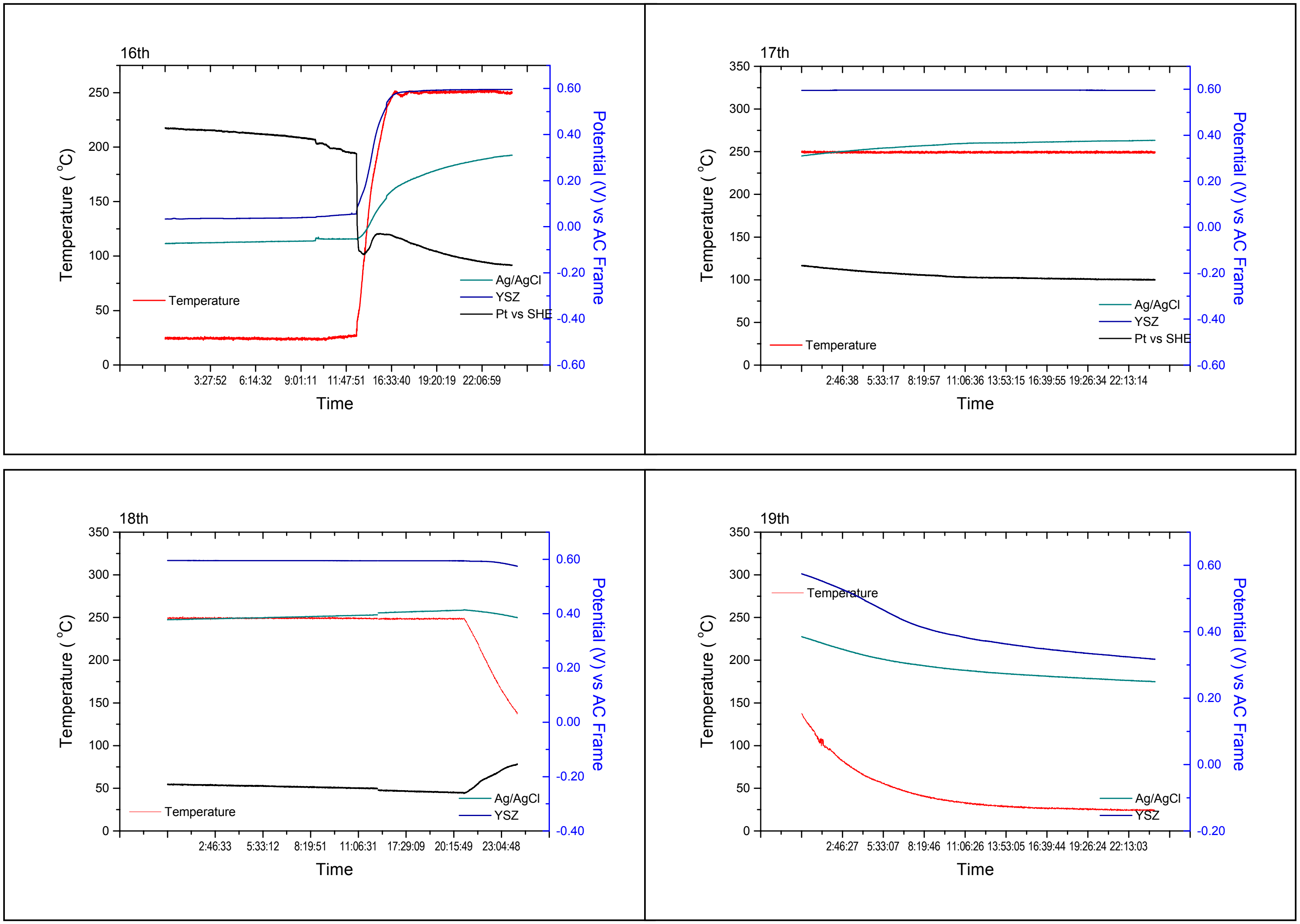


FIGURE 7. (b) Potential Measurements with Cu/Cu$_2$O/YSZ pH probe (Con’td)

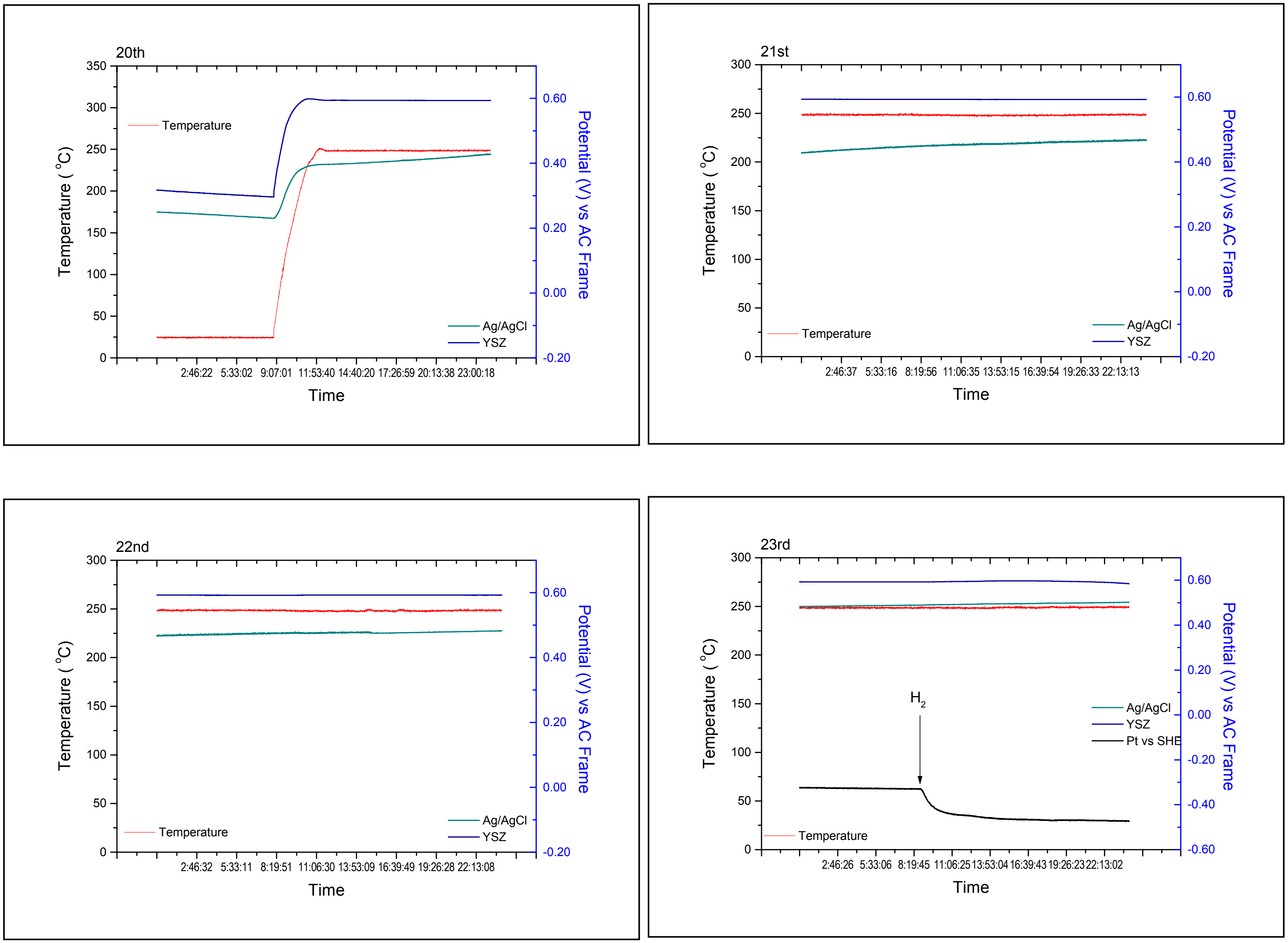


FIGURE 7. (c) Potential Measurements with Cu/Cu_2O/YSZ pH probe
(Con'td)

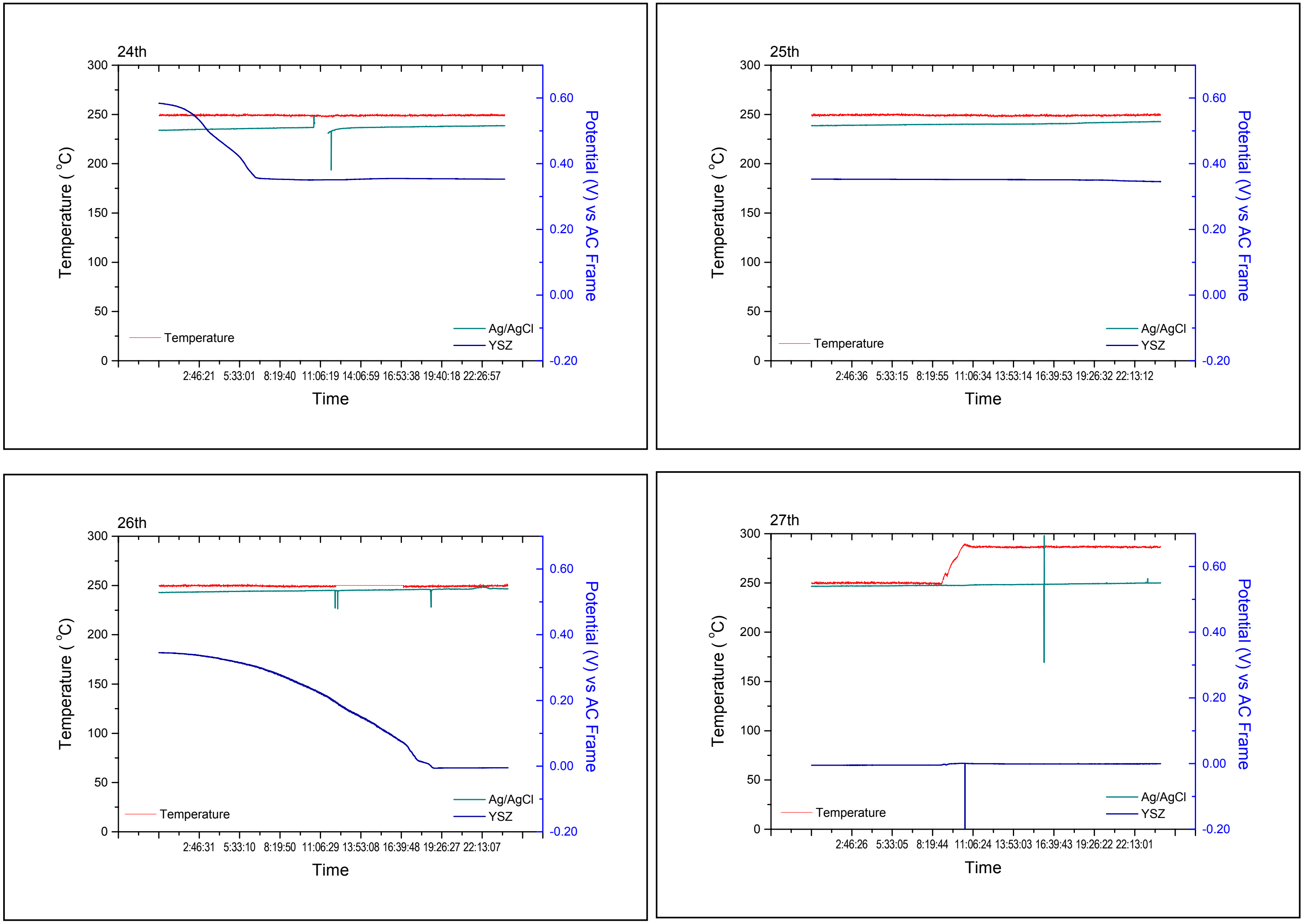


FIGURE 7. (d) Potential Measurements with Ni/NiO/YSZ and W/W$_x$O$_y$ pH probes (Simulated PWR water (1200 ppm Boric acid and 2 ppm LiOH; DO < 5 ppb; 0-2 ppm DH)

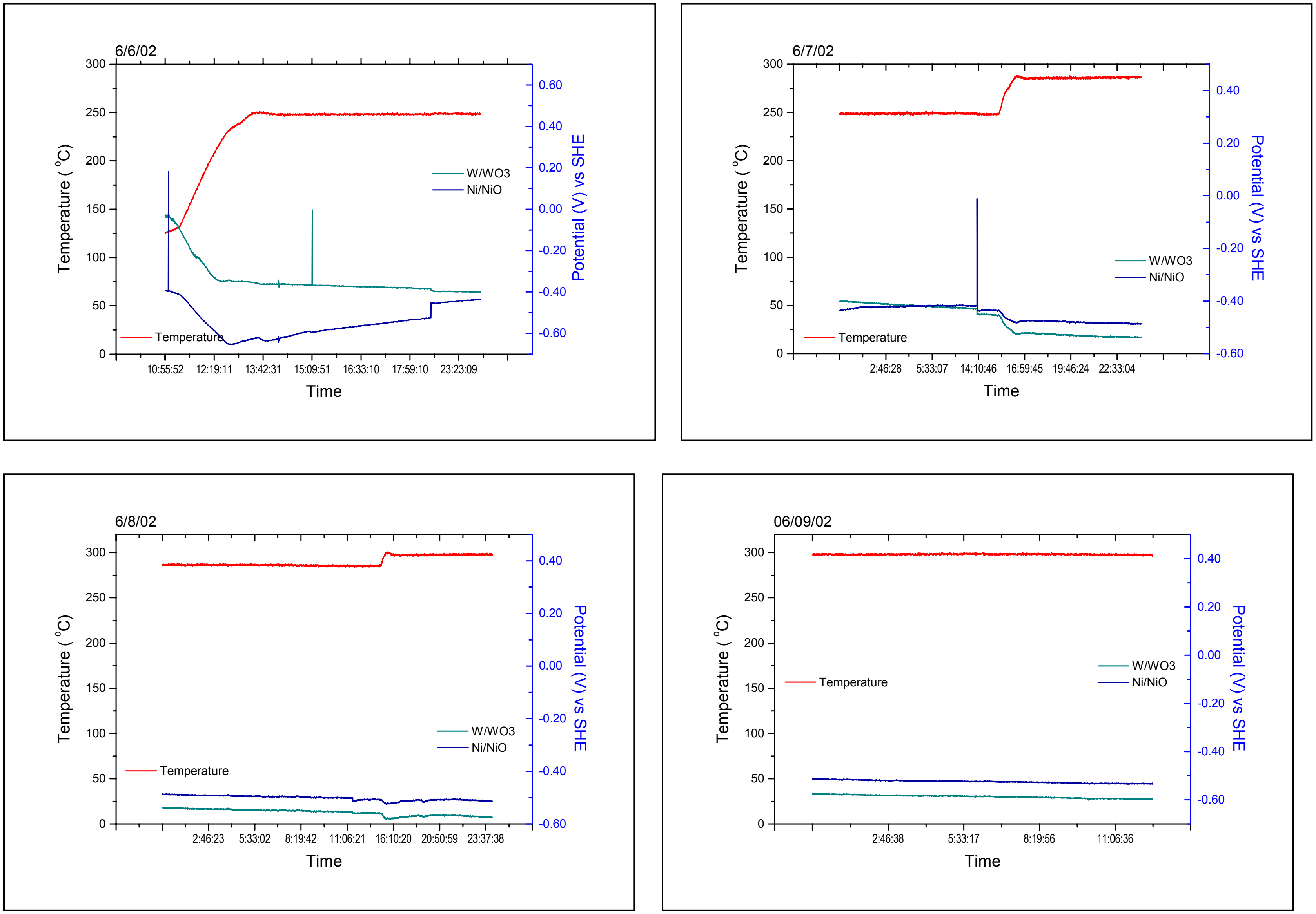


FIGURE. 7 (e) Potential Measurements with Ni/NiO/YSZ and W/W_xO_y pH probes (Con'td)

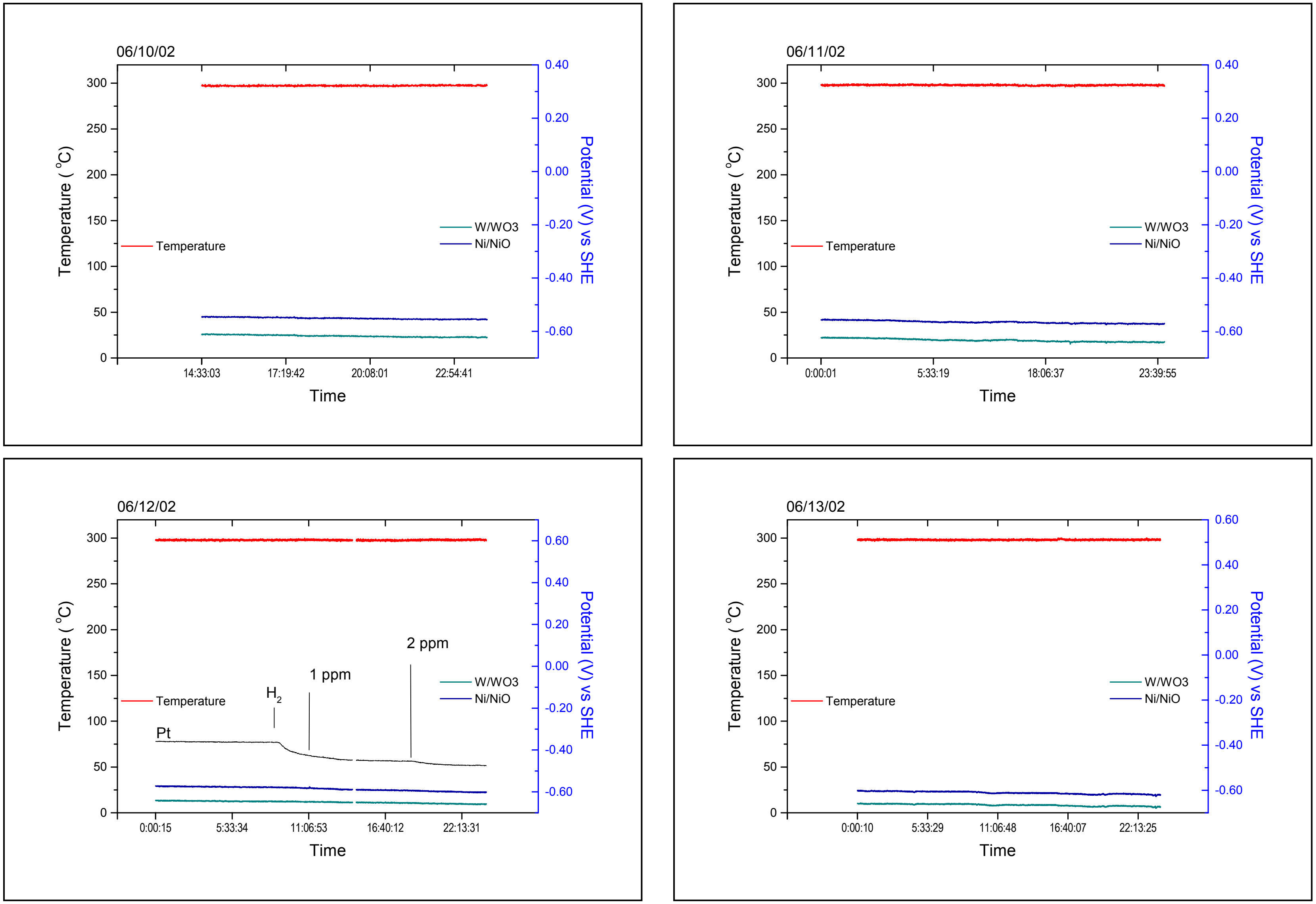
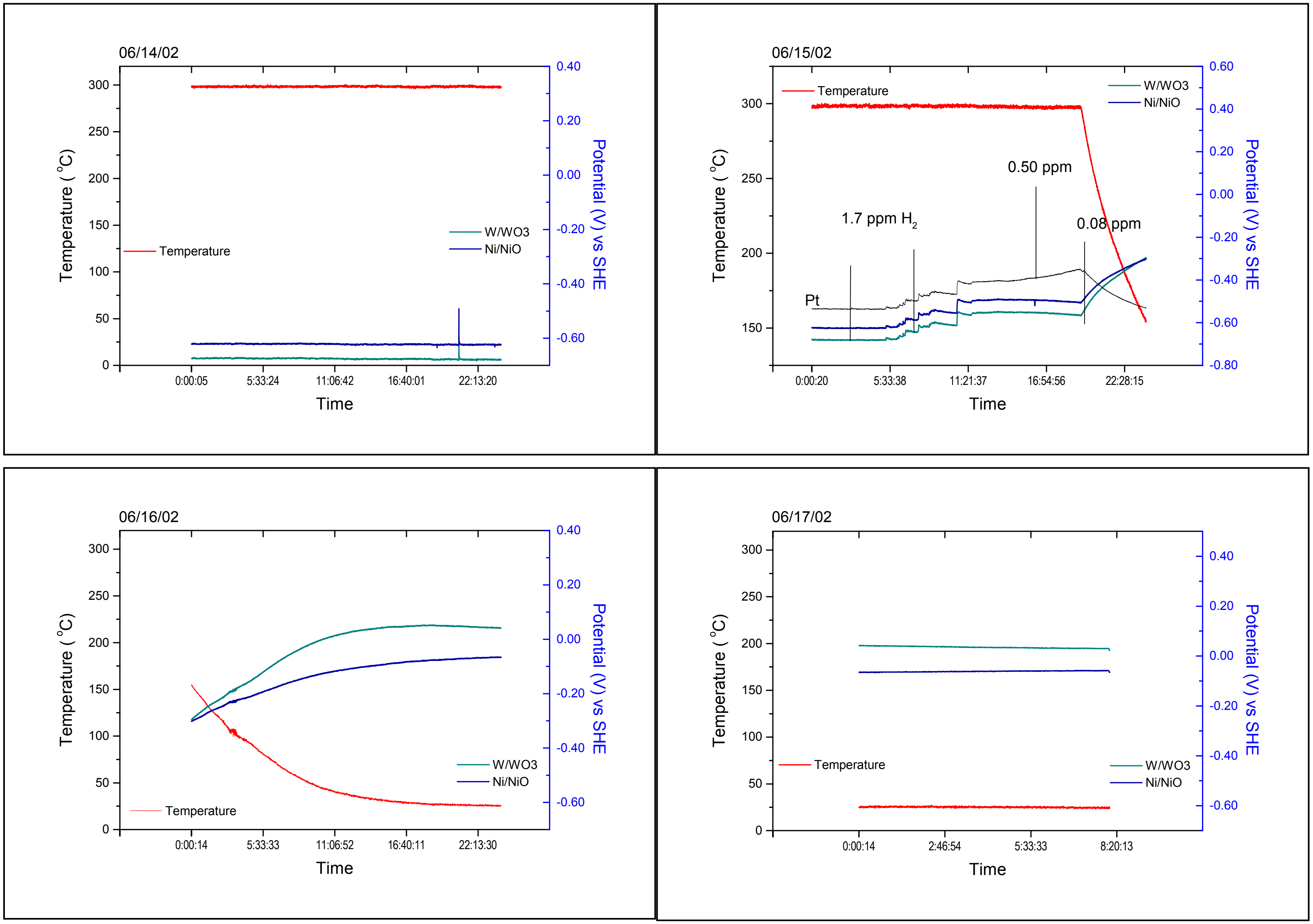


FIGURE. 7 (f) Potential Measurements with Ni/NiO/YSZ and W/W_xO_y pH probes (Con’td)



B-T-3470

LIMITS TO CREVICE CONCENTRATION PROCESSES

Allen Baum

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Presentation to:

EPRI/Argonne Crevice Workshop

October 9, 2002

Presentation Outline

- Concentration process summary
- Historical review of selected heat transfer tests
- Crevice chemistry testing

Heat Transfer, Concentration, and Corrosion Relationships

Crevice:	***Open***		***Packed***	
Heat Transfer Regime	**Nucleate Boiling**	**Dryout**	**Nucleate Boiling**	**Dryout**
Concentration Mechanism	Beneath bubble sublayer	Alternate wetting and drying	Hydraulically driven	Thermally driven
Extent of Concentration	Limited	Modest	Modest	Extensive
dT/dt	= 0	≠ 0	> 0	< 0
Corrosion Form	None	Cold leg thinning	Wastage	SCC

Limits to Packed Crevice Concentration Processes

Process:	***Hydraulic***	***Thermal***
Heat Transfer Regime	Nucleate Boiling	Dryout
Independent Variable	Concentration	Liquid Fraction
dT/dt	> 0	< 0
Limits to Concentration	Kinetic: concentration factor =f(position) Convection (low cf) Diffusion (low cf) Solubility (high cf) Superheat (high cf)	Thermodynamic Superheat Adsorptivity Volatility Solubility

Mass Transport and Thermodynamic Criteria Determine if Corrosion Occurs at Crevice Periphery or Interior

Crevice Location:	***Periphery***	***Interior***
Concentration Process	Hydraulic	Thermal
Mass transport criterion	$m_{in} > m_{out}$ **or**	$m_{in} < m_{out}$ **and**
Thermodynamic criterion	BPE < –T	BPE > –T

Definitions:

m_{in} = rate of accumulation = f (bulk concentration)

m_{out} = rate of transport to crevice interior = f(permeability)

BPE = boiling point elevation at solute solubility limit

-T = available superheat

Summary of Supporting Laboratory Testing

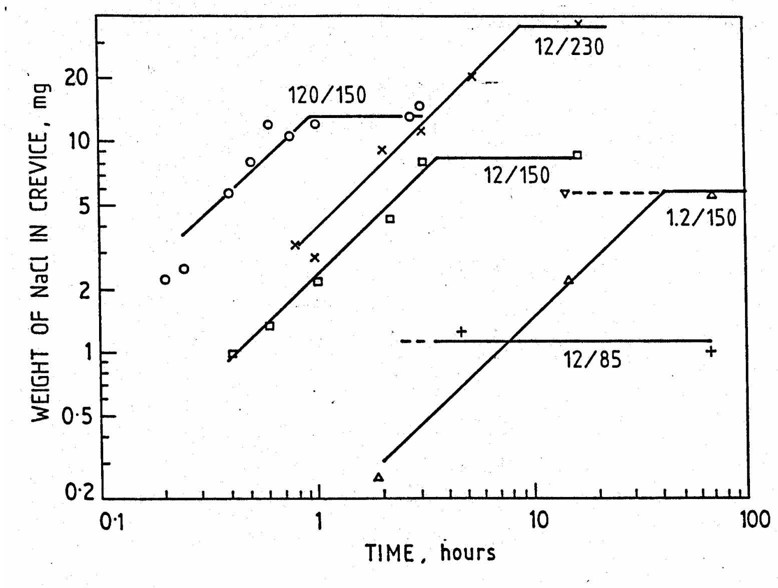
- Early thermal-hydraulic testing
- Concentration testing
  - CERL (cartridge heat)
  - Rockwell (cartridge heat)
- Crevice ECP test - Westinghouse (temperature controlled)
- Corrosion tests
  - Westinghouse sodium carbonate tests
  - CEA sodium hydroxide tests
  - CEA, CE, Ciemat, and Westinghouse acid addition tests
  - A600MA - A600TT Comparison Tests

Early Thermal-Hydraulic Testing Laid Foundation for Later Work

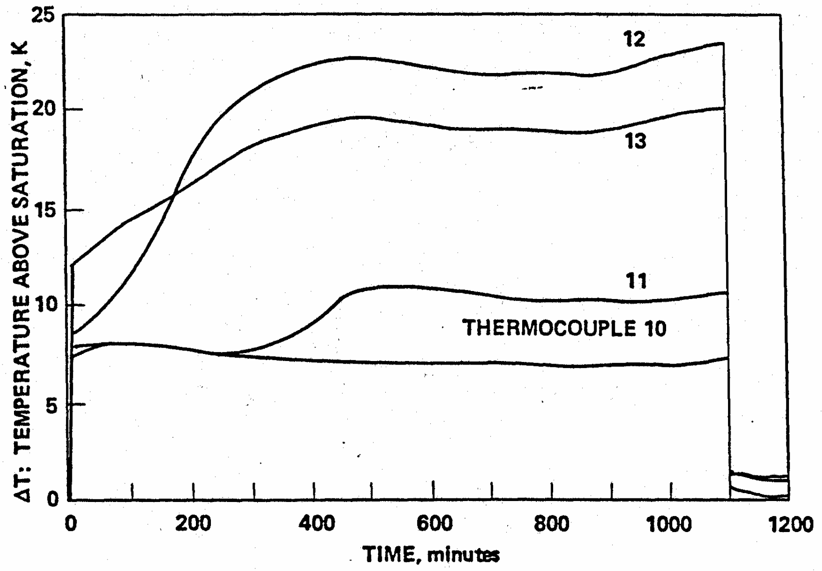
Researchers	Experimental	Contributions
Ishibashi & Nishikawa, Kyushu U., 1968	Cylindrical crevice, large diameter tube, atmospheric pressure	Crevice boiling regimes, nucleate boiling effectiveness increases with decreasing gap
Jensen, Cooper, & Bergles, Iowa State, 1976	Cylindrical and chamfered, horizontal	Minimal effect of tube misalignment; "Dryout is unlikely to be a problem in commercial equipment"
Ono & Hukada, Electric Power Central Research Center, 1979	Cylindrical, chamfered, low pressure; cartridge heat	CHF decreases with gap; Order of magnitude decrease in CHF due to deposit formed by alternate wetting & drying
Vroom, Babcock, & Cassell, CE,1982	Cylindrical, trefoil, and eggcrate, vertical	Dryout at all heat fluxes in cylindrical hole; no dryout in trefoil or eggcrate
Johnston, Sharon, et al, Northwestern, 1982	Cylindrical, low pressure	Dryout disappears with gaps greater than 25 microns

Early CERL Tests Demonstrated Concentration in Hydraulically Driven Crevice

NaCl Hideout as Functions of Concentration (ppm) and Heat Flux (kw/m²)

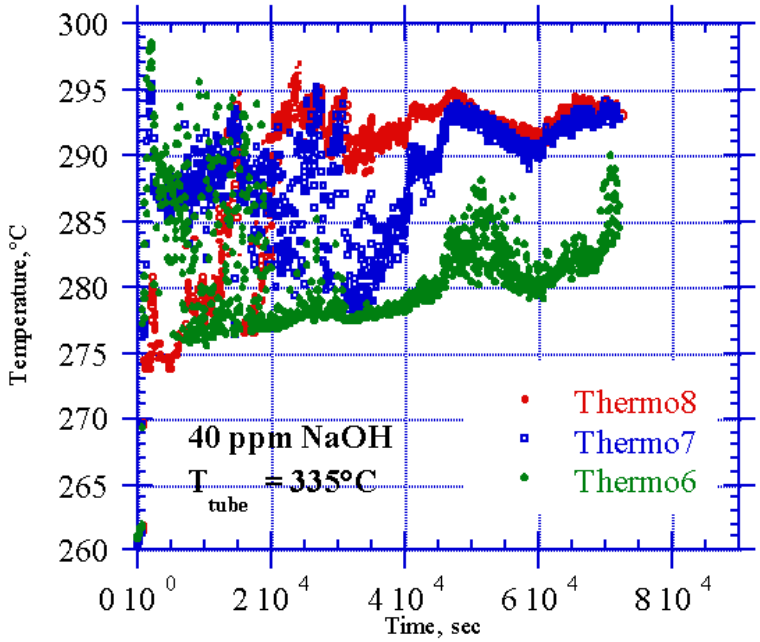


Superheat Response for 12 ppm NaCl and 120 kw/m² (45°K)



Mann and Castle, Kinetics and Processes of Solute Concentration at Crevices in Steam Generators, Central Electricity Research Laboratories, Leatherhead, 1984.

Rockwell Testing Shows Both Thermally and Hydraulically Driven Concentration Processes



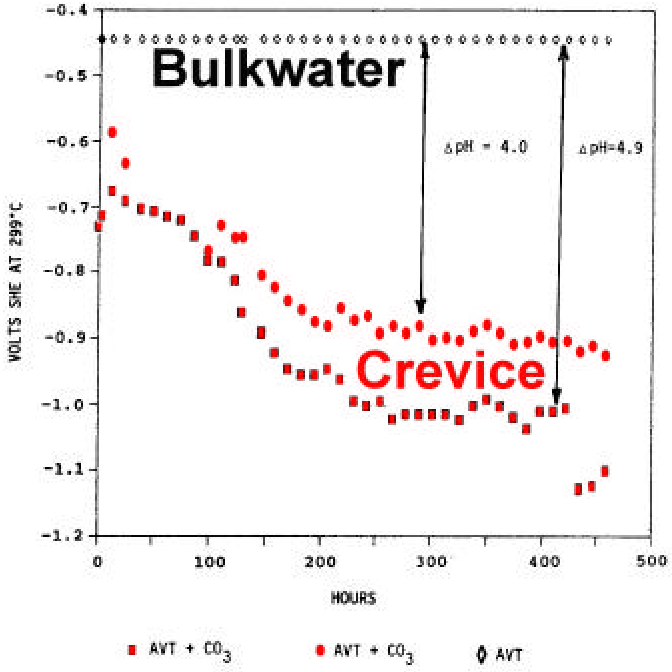
TC 8 at z/L = 0.71
TC 7 at z/L = 0.86
TC 6 at z/L = 1.0 (bottom)

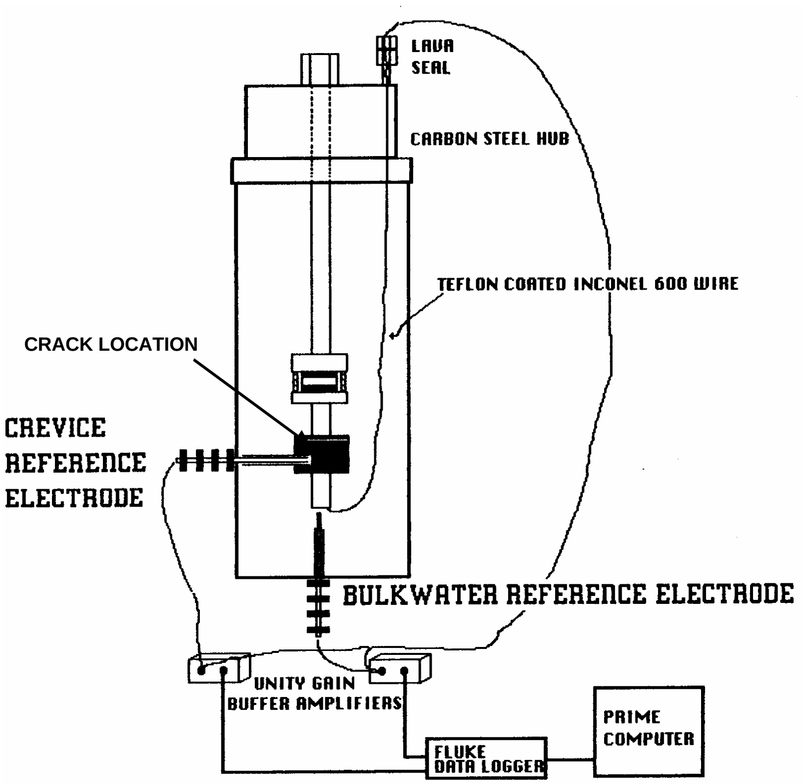
J. B. Lumsden, et al, "Hideout in Prototypic Tube/Tube Support Plate Heated Crevices," Eighth Int. Sym. on Env. Deg., 1997. Copyright 1997 by the American Nuclear Society, La Grange Park, Illinois. Reprinted with permission from ANS and Jesse Lumsden

Westinghouse Heat Transfer Electrode (HTE) Measured Change in Crevice ECP

0.3 ppm Sodium Carbonate

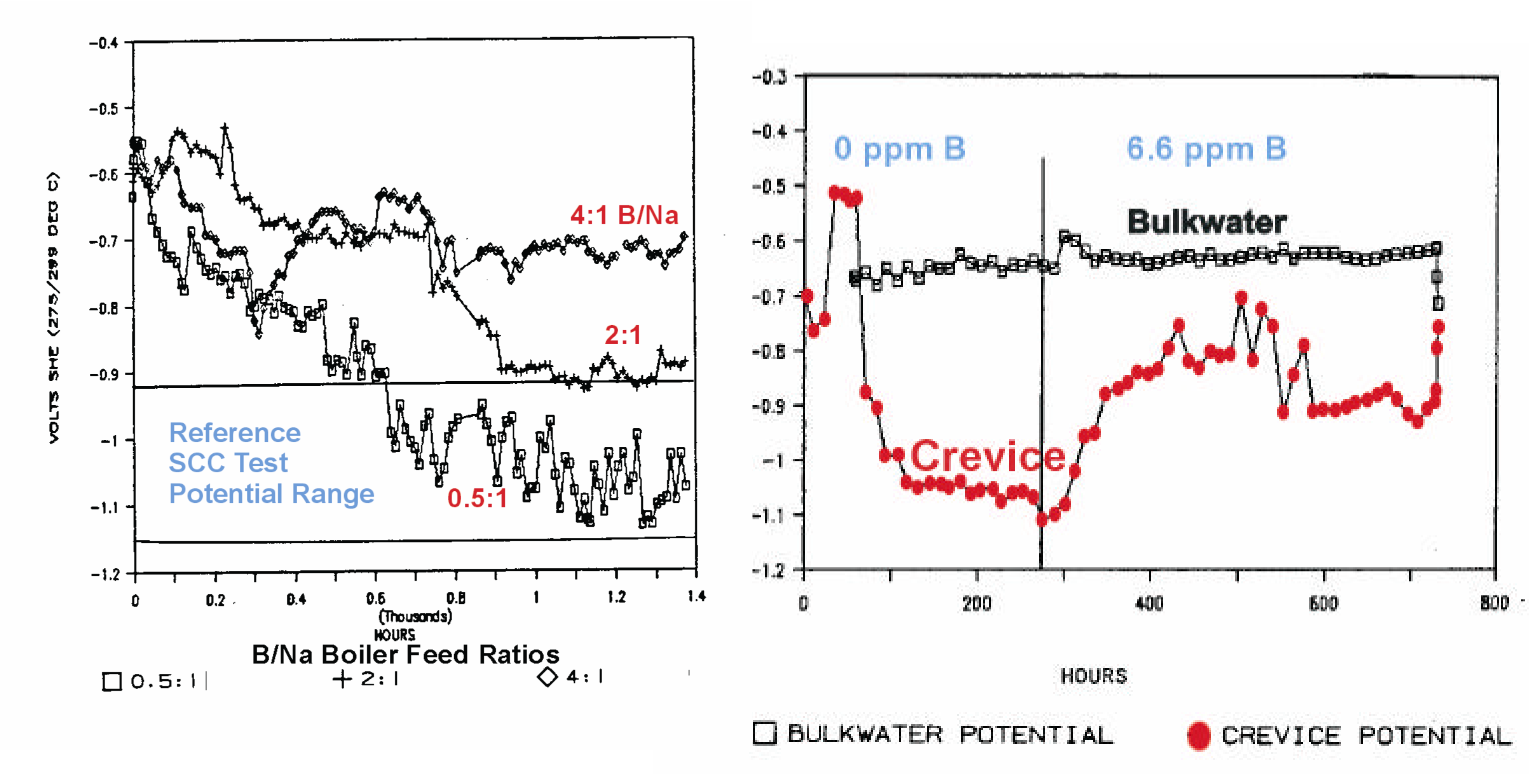
(~ 500 ppb Na^+ in boiler)





R. E. Hermer, et al, "The Effect of Morpholine/Boric Acid/ Hydrazine Chemistry on Alloy 600 Steam Generator Crevice Corrosion," CORROSION89, 1989. [Reprinted with Permission from NACE, 2002]

HTE Testing Found Strong Effect of Boric Acid



R. E. Hermer, et al, "The Effect of Boric Acid on Alloy 600 Electrochemical Potentials in Steam Generator Crevice Environments", 1988 JAIF Int. Conf. on Water Chem. in Nuclear Power Plants

Westinghouse A600 MA SCC Testing May Have Shown Importance of Mass Transport Criterion

Sodium Carbonate Concentration (ppm)	***Test Time (days)***	***Corrosion***	***Depth***	***Location***
3.0	6 - 7	SCC	100%	Below frit
0.3	15 - 17	SCC	100%	Below frit
0.11	51	IGP	A few grains	Distributed in sludge

C. R. Wolfe and J. B. Prestegiacomo, "Effects of Calcium Hydroxide and Carbonates on IGA and SCC of Alloy 600, Background Report," 1983

CEA AJAX A600MA Testing Also Found Strong Concentration Dependence

Na^+ Concentration (ppm)	***Test Duration (days)***	***Depth (%)***	***Rate (µm/hr)***
2.3	6 – 27	100	2.0 – 8.8
0.6	8 - 21	100	2.2 – 5.7
0.06	185	6	.016

J. Daret, "Secondary Side Degradation of Steam Generator, Which Inhibitor for Which Causes? A Review of Model Boiler Test Results," Proc. 8th Int. Sym. on Environmental Degradation of Materials, 1997

CEA AJAX A600MA Testing Found that Acidic Chemistries Produced Lower SCC Rates

Chemistry	***Concentration***	***Test Duration (days)***	***Depth (%)***	***Rate (μm/hr)***
Na_2, Fe, H_2, SO_4; O_2	10.7 ppm SO_4^{-2}	240	0.9	0.003
Acetic + formic	0.5 ppm acetic, 0.2 ppm formic	465	0.	0.
Acetic + formic + sulfuric	0.5 ppm A & F, 1 ppm SO_4^{-2}	160	1.3	0.008
Resin fines	1 gm/day ♉7 ppm SO_4^{-2}	357	23.6	0.03
Resin extract + sludge + 1% PbO	1 ppm SO_4^{-2}	189	55.1	0.15

J. Daret, "Secondary Side Degradation of Steam Generator, Which Inhibitor for Which Causes? A Review of Model Boiler Test Results," Proc. 8th Int. Sym. on Environmental Degradation of Materials, 1997

CE and W A600MA Boiler Testing Found Acid Sulfates Produced Aggressive SCC only at High Concentrations

Test	*Duration (Days)*	*Na^+/SO_4^{-2} (MR)*	*$[SO_4^{-2}]$ (ppm)*	*Depth (%)*	*Rate (µm/hr)*
CE OH^- Resin	462	~0.	0.2	2	0.002
CE Pot Blr	130	0.	0.3	3	0.01
CE Cl^- Resin	276	0.9	5.3	20	0.03
CE, L I Sound	114	1.	30.	80	0.33
CE Tenn. River	219	varied	~90.	95	0.21
<u>W</u> STMB #1	90	0.5	~14.	9	0.05
<u>W</u> STMB #2 (5)	58 - 116	0. - 1.8	29 - 60	0 - 12	0.02 – 0.08

EPRI NP-7346-SD, EPRI TR101105

Ciemat Testing of A800SP Tube Produced Modest SCC in Acid Sulfates

Chemistry	*Amount*	*Duration (Days)*	*Depth (%)*	*Rate (µm/hr)*	*Crack Location*
Na_2SO_4	1. ppm	396	23 5	0.02 0.005	Roll-transition region TSP crevice
$FeSO_4$	0.4 ppm				
H_2SO_4	pH = 4				

- **~40% Wastage in roll transition region**

D. Gómez-Briceño, et al, “Effect of Secondary Cycle Sulphuric Acid Injection on Steam Generator Tubes,” 1994 Fontevraud Conference

CEA Reduced Sulfate Testing Produced Some SCC Acceleration at Deposit Periphery

Chemistry	*Amount*	*Duration (Days)*	*Depth (%)*	*Rate (µm/hr)*	*Crack Location*
Paluel sludge **Resin extract** **Hydrazine**	0.2 gm/day 1. ppm SO_4^{-2} ~3. ppm	215	33%	0.07	Deposit Periphery

- **Order of magnitude higher reduced sulfate concentration in steam bleed than in blowdown and suggests that concentration in crevice interior is unlikely**

J. Daret et al, “Evidence for the Reduction of Sulfates Under Representative SG Secondary Side Conditions, and for the Role of Reduced Sulfates on Alloy 600 Tubing Degradation,” Proc. 9th Int. Conf on Env. Deg. Of Mat’ls in Nuclear Power Systems

Model Boiler Testing of A600TT Tubing Showed Large Variability

Facility	*Tube - Material*	*Corrosion (Depth)*	*Ave. Boiler Sodium (ppm)*	*Duration (days)*
W Modular Model Boiler	1 - A600MA 2 - A600TT 3 - A600TT	SCC (100%) SCC (100%) IGP (2 grains)	3	317
W Multi-Tube Model Boiler #1	A600MA (2/3) A600TT (4/4)	SCC (100%) IGP	0.19 1.5	25 228
W Multi-Tube Model Boiler #2	A600MA A600TT (1/1 TSP) A600TT (2/2 Hyd)	SCC (100%) SCC (100%) NDD	0.14 0.60 1.0	18 100 132

EPRI NP-6997-LD, October 1990; EPRI TR-104064, May 1995

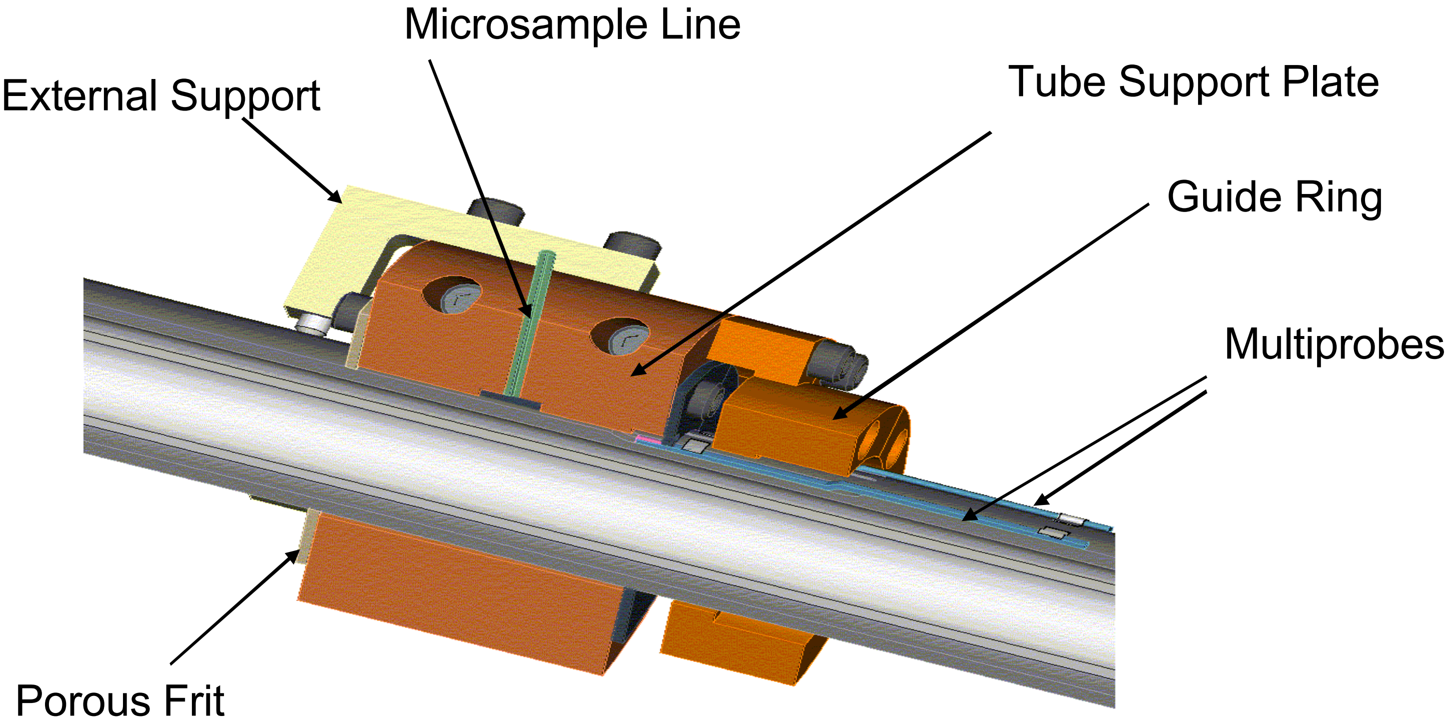
Summary

- Hydraulically and thermally driven concentration processes have different responses and limits
- Location of corrosion is a function of satisfying mass transport and thermodynamic criteria
  - Caustic model boiler testing indicated a binary concentration dependence, depending upon mass transport criterion
- Model boiler testing with acidic chemistries has produced less aggressive SCC than alkaline chemistries
- 600TT model boiler testing indicated high degree of variability in straight tubing sections

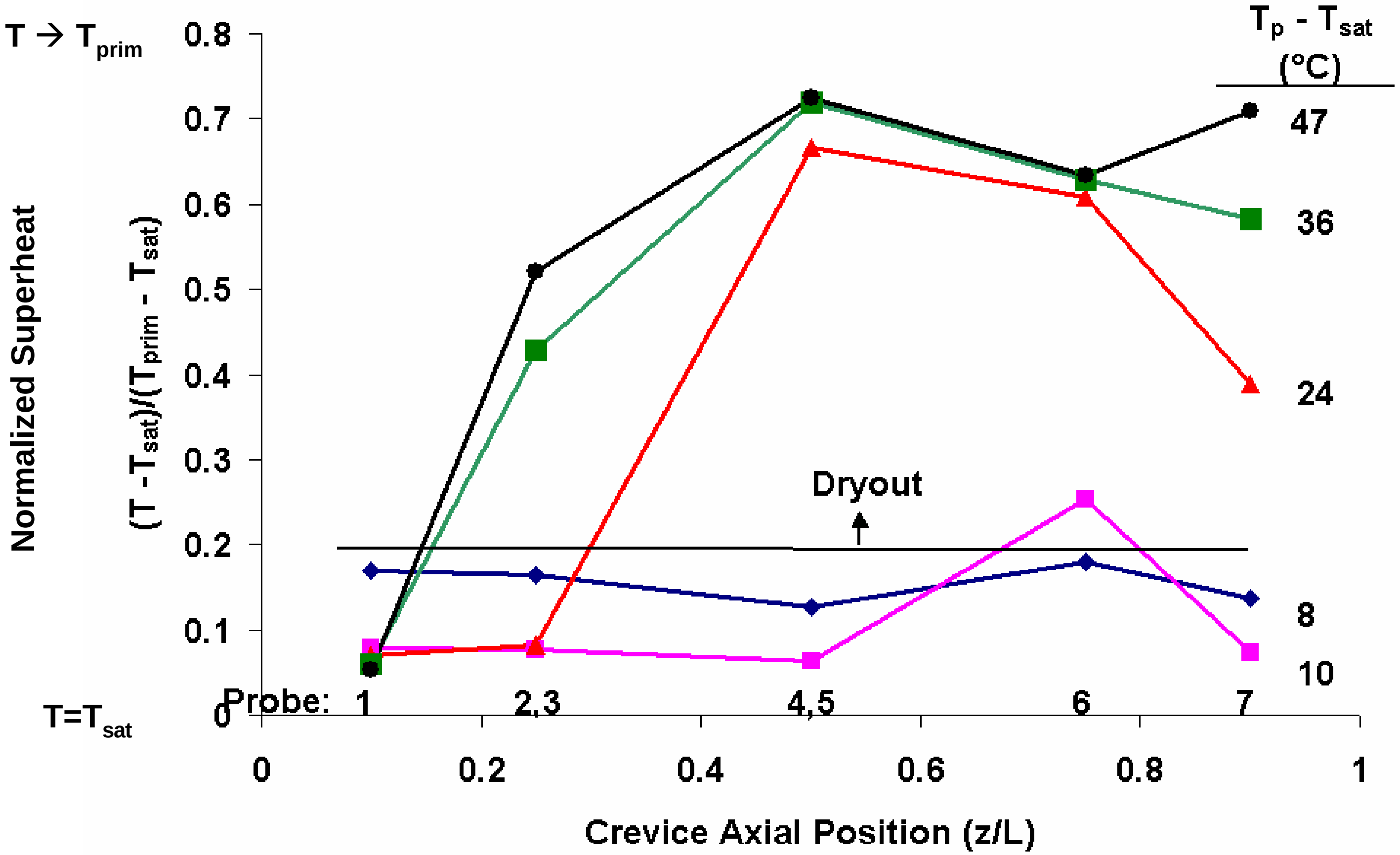
Crevice Chemistry Testing and Applications

- Review factors promoting and limiting concentration
  - Volatility
  - Solubility
  - Adsorptivity
- Application to lead
  - Model boiler testing
  - Degradation comparisons
- Generalized model for relating plant chemistry to ODSCC

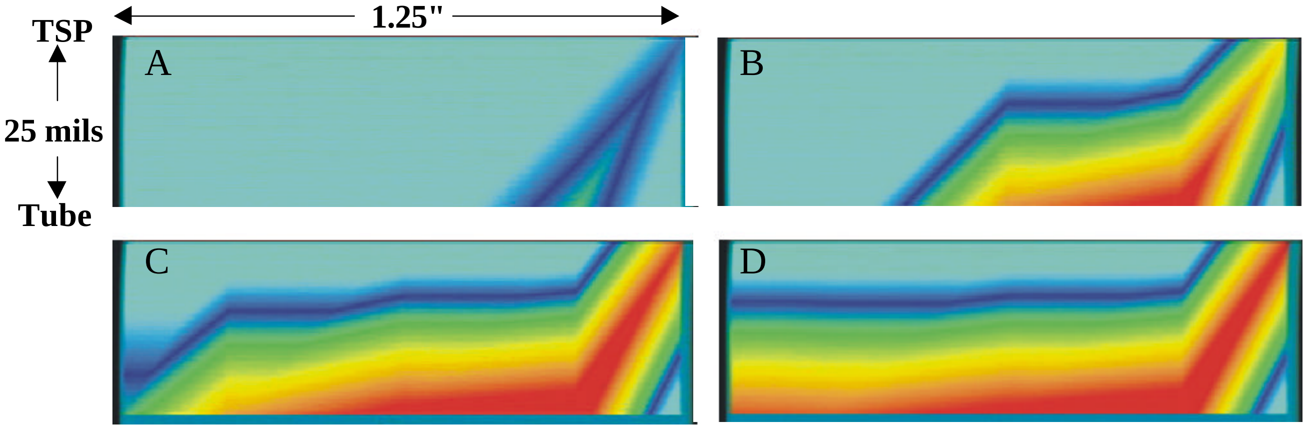
Cross-section of Instrumented Test Piece



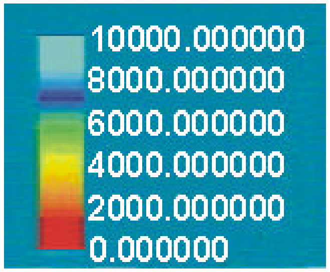
Dryout Initiated at About 10°C ΔT

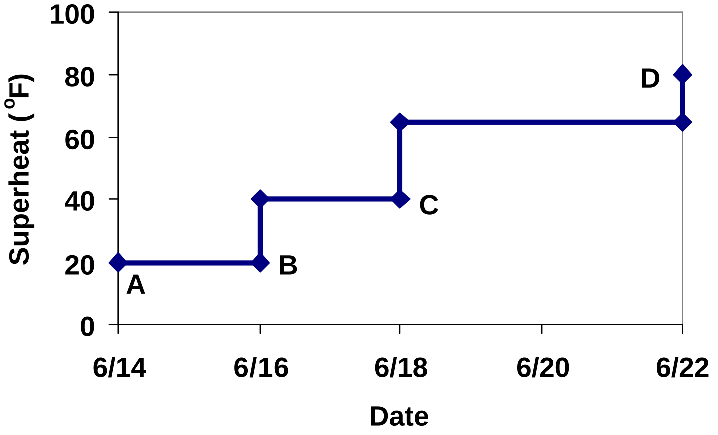


Impedance Response of 300 ppb Cl^- as Seawater Showed Local Concentration at Tube Surface

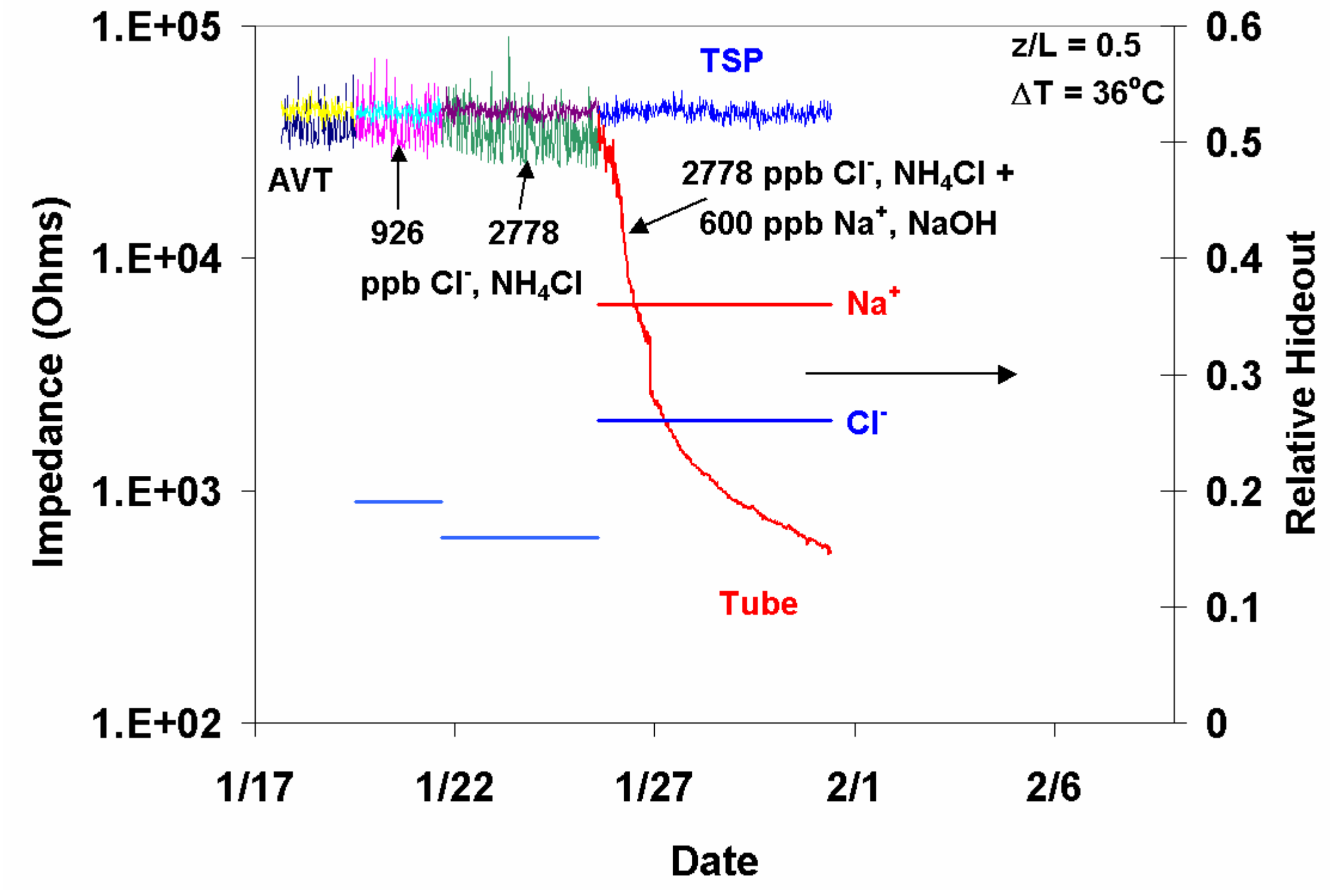


Color Key

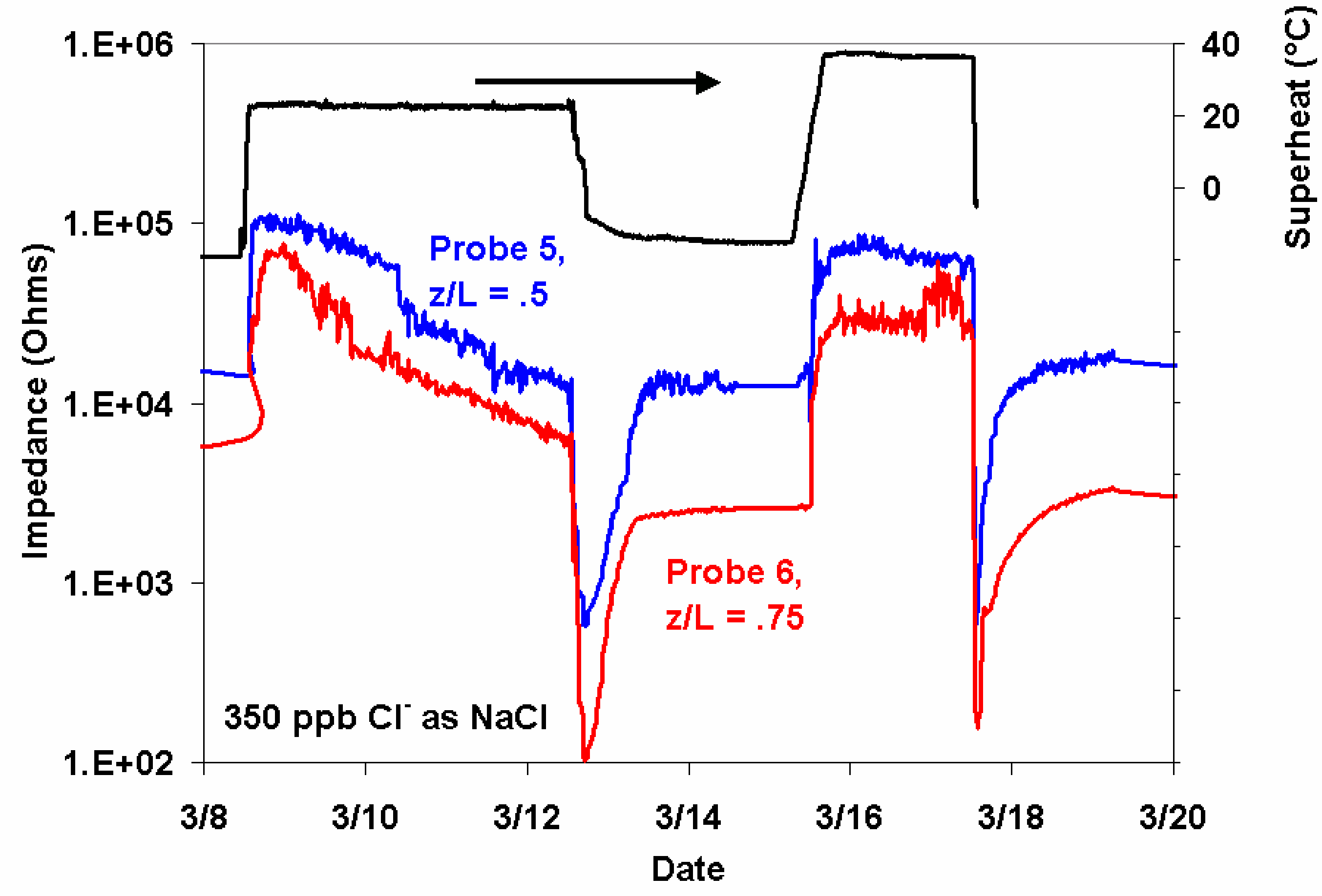




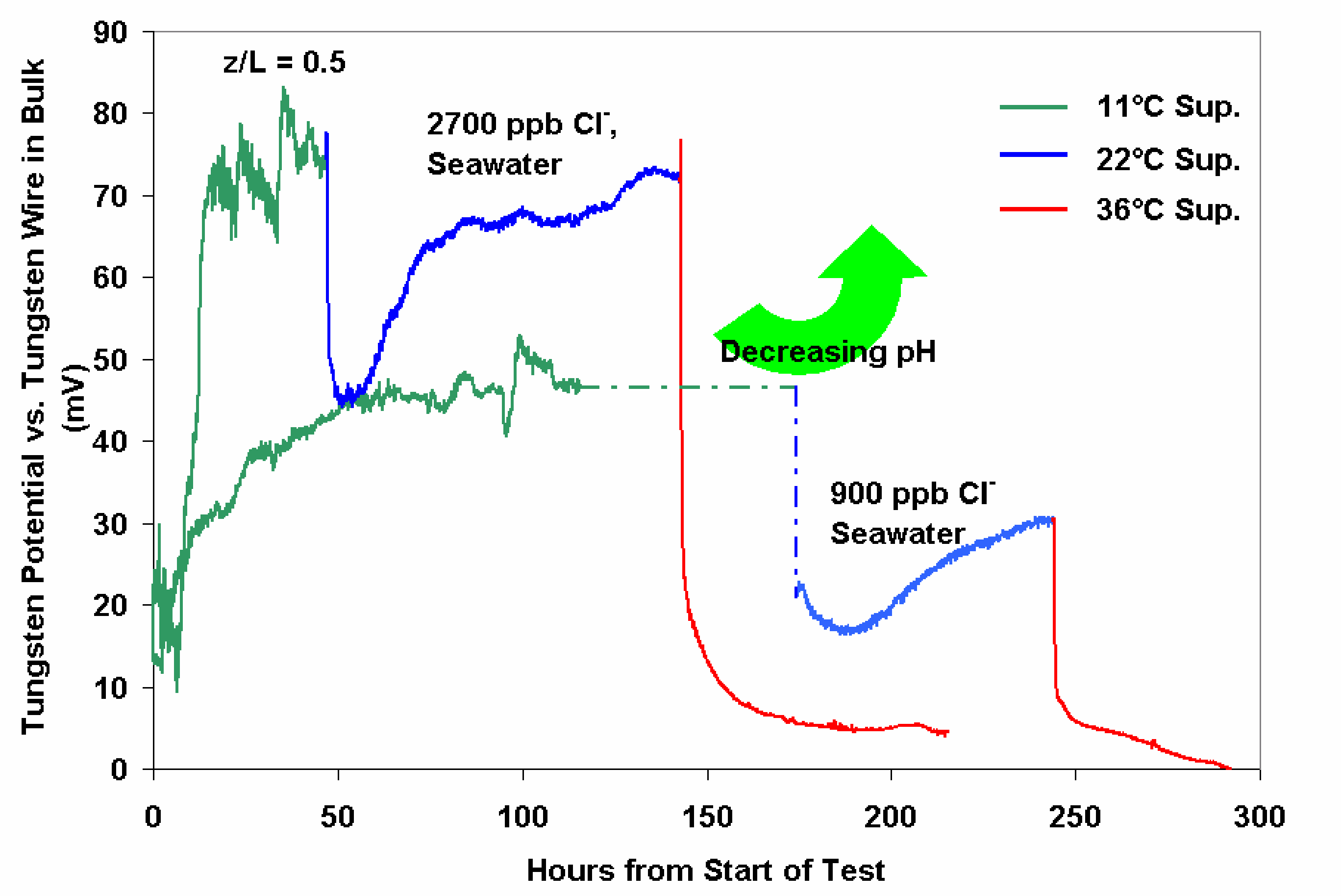
Chloride Concentration Limited Both by Volatility and Adsorptivity



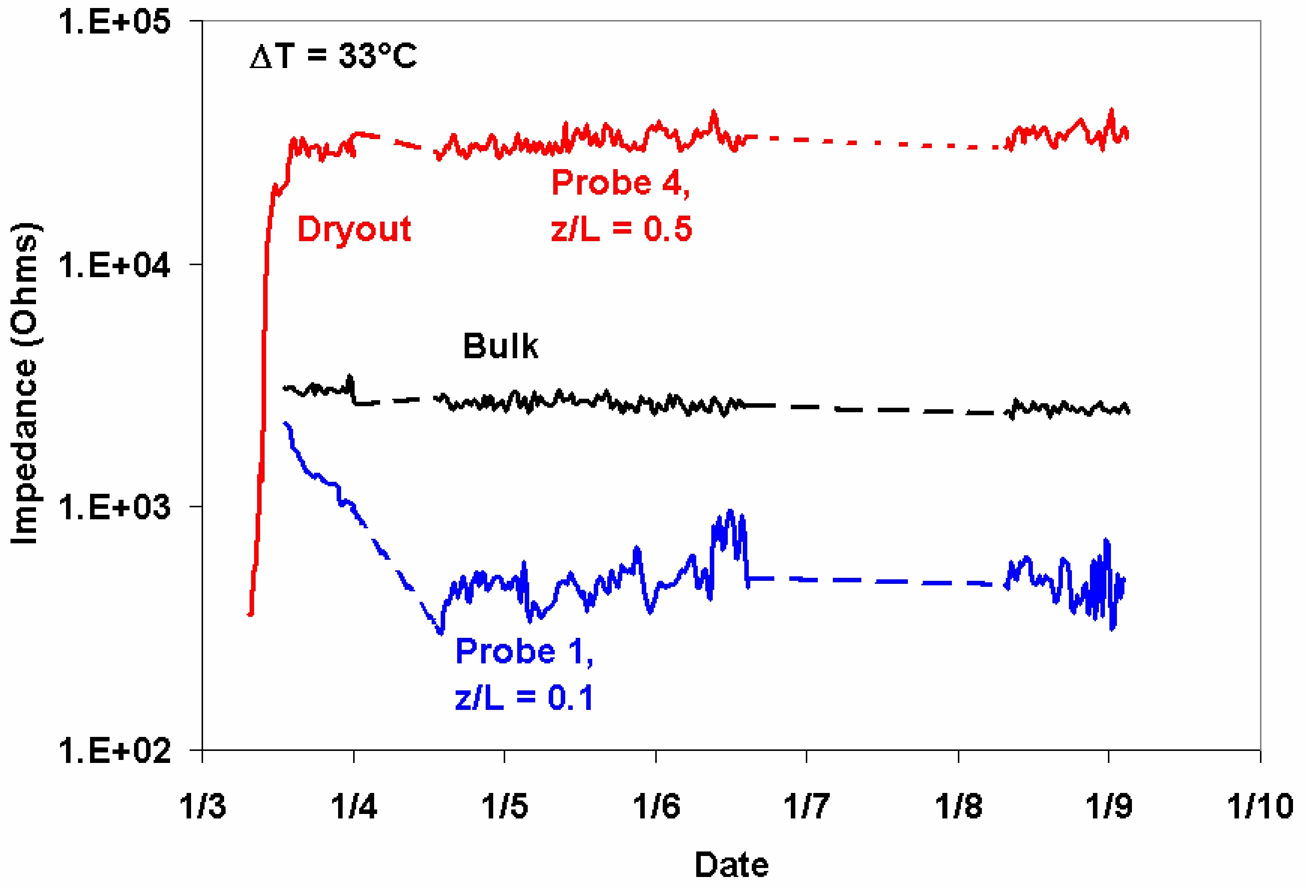
NaCl Precipitated at Highest Superheats



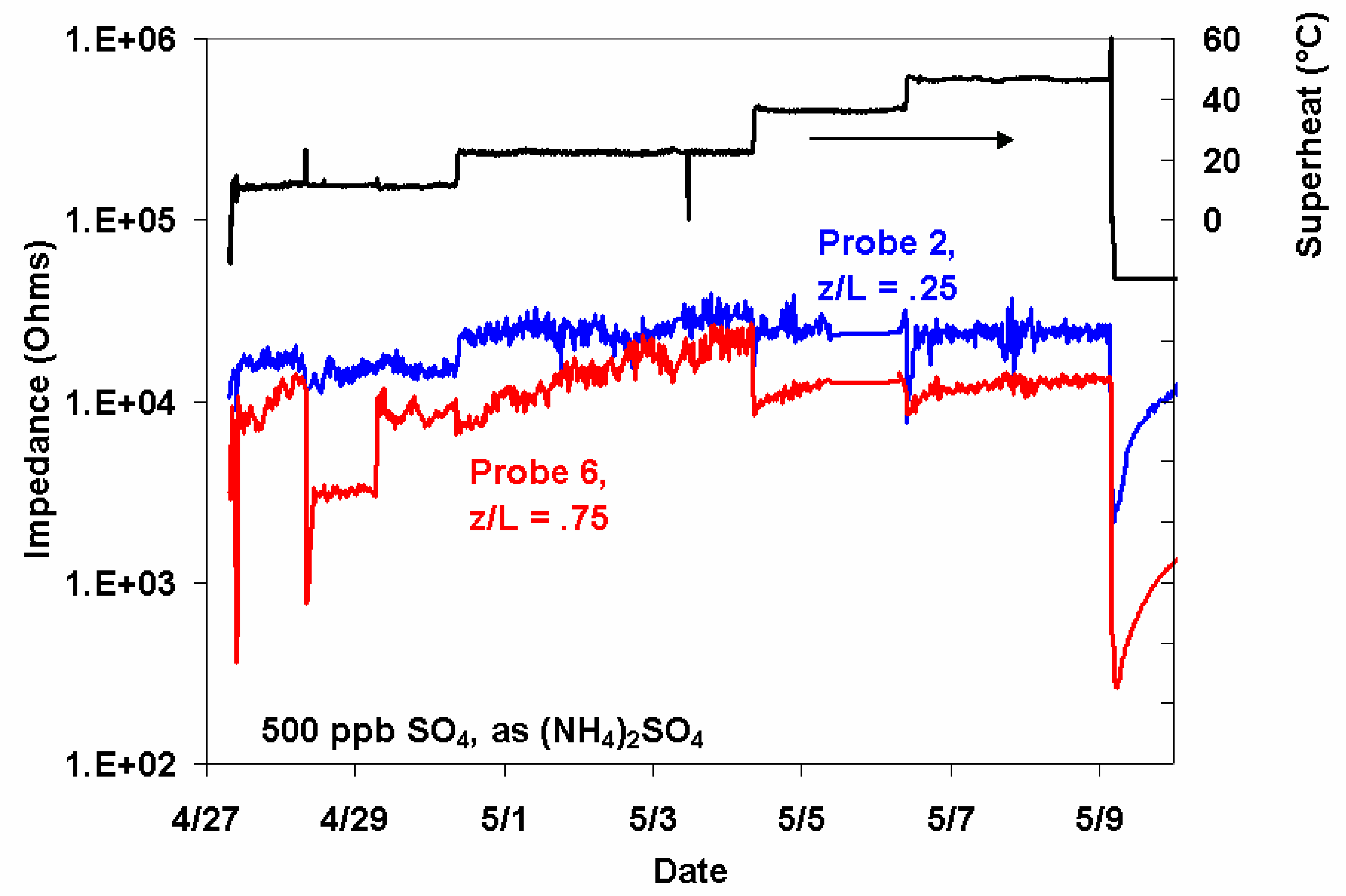
Seawater Concentrate Lost Acidity with Increasing Superheat



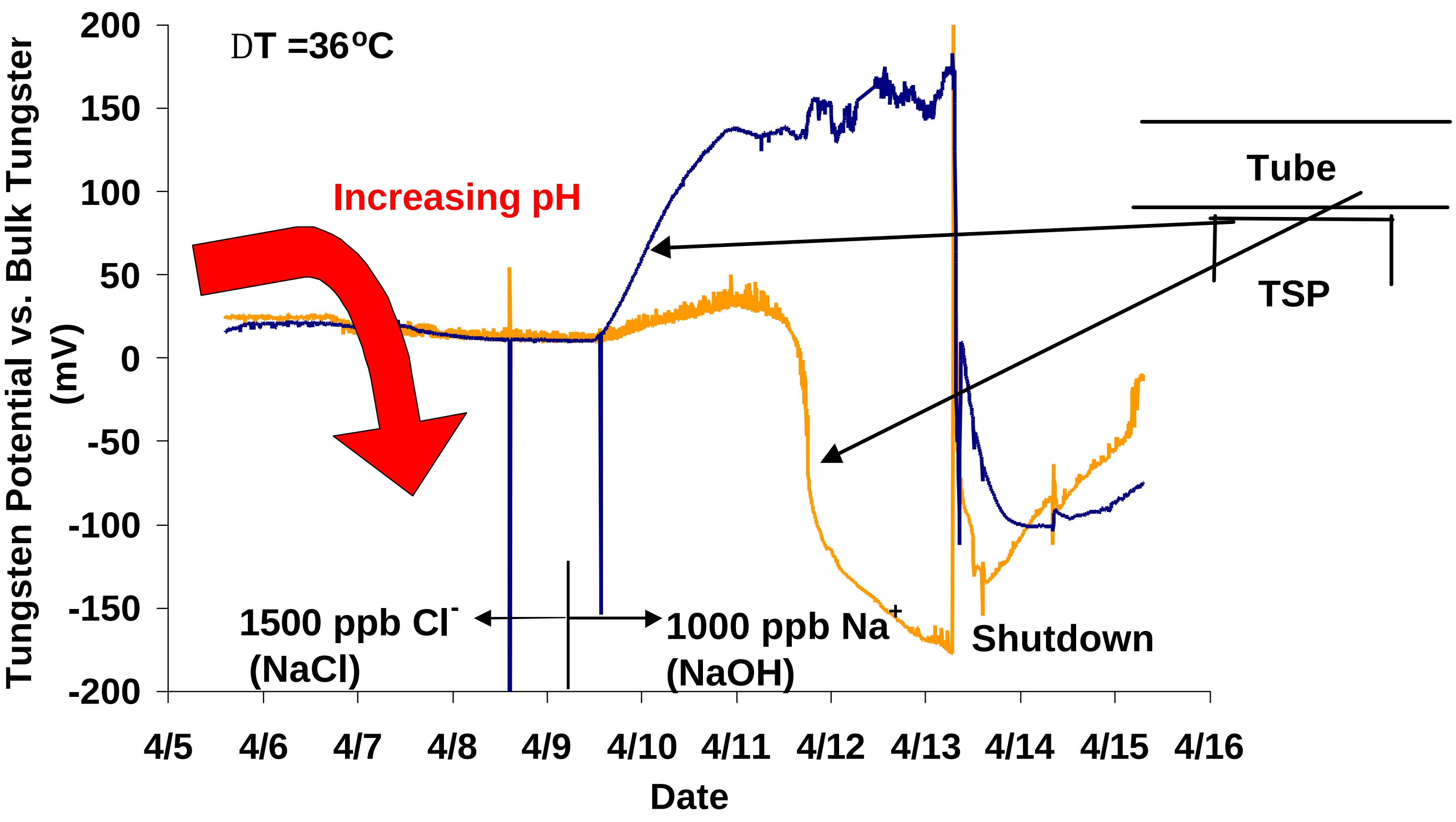
Sodium Phosphate, Indicative of Less Soluble Salts, Precipitated in Crevice Interior



Ammonium Sulfate Testing Produced Little Impedance (or pH) Response, Indicative of Solute Adsorption



Large Radial pH Gradients in Caustic Test may have Resulted from Chloride Desorption



Bettis Atomic Power Laboratory
Bechtel Bettis, Inc.

Crevice Chemistry Testing Indicates Few Species Can Concentrate on Tube Side of Crevice at High Superheats

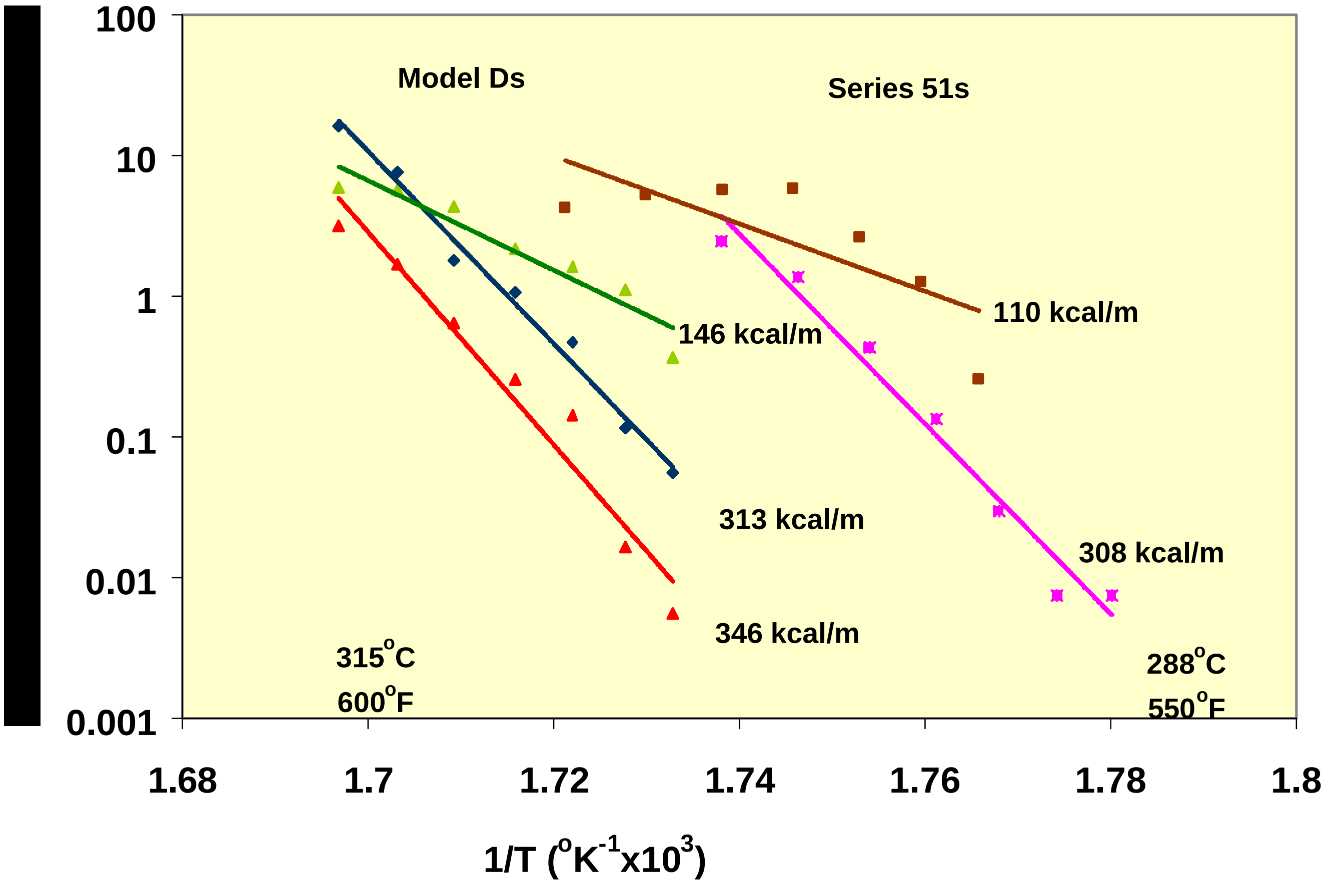
- Phosphate precipitated
  - As would less soluble species

- Chlorides volatilized, adsorbed, and precipitated

- Sulfates adsorbed

- Sodium was only ion tested that was not subject to volatilization, adsorption, or precipitation

Progressive Loss of Other Species is Consistent with High SG ODSCC Activation Energies

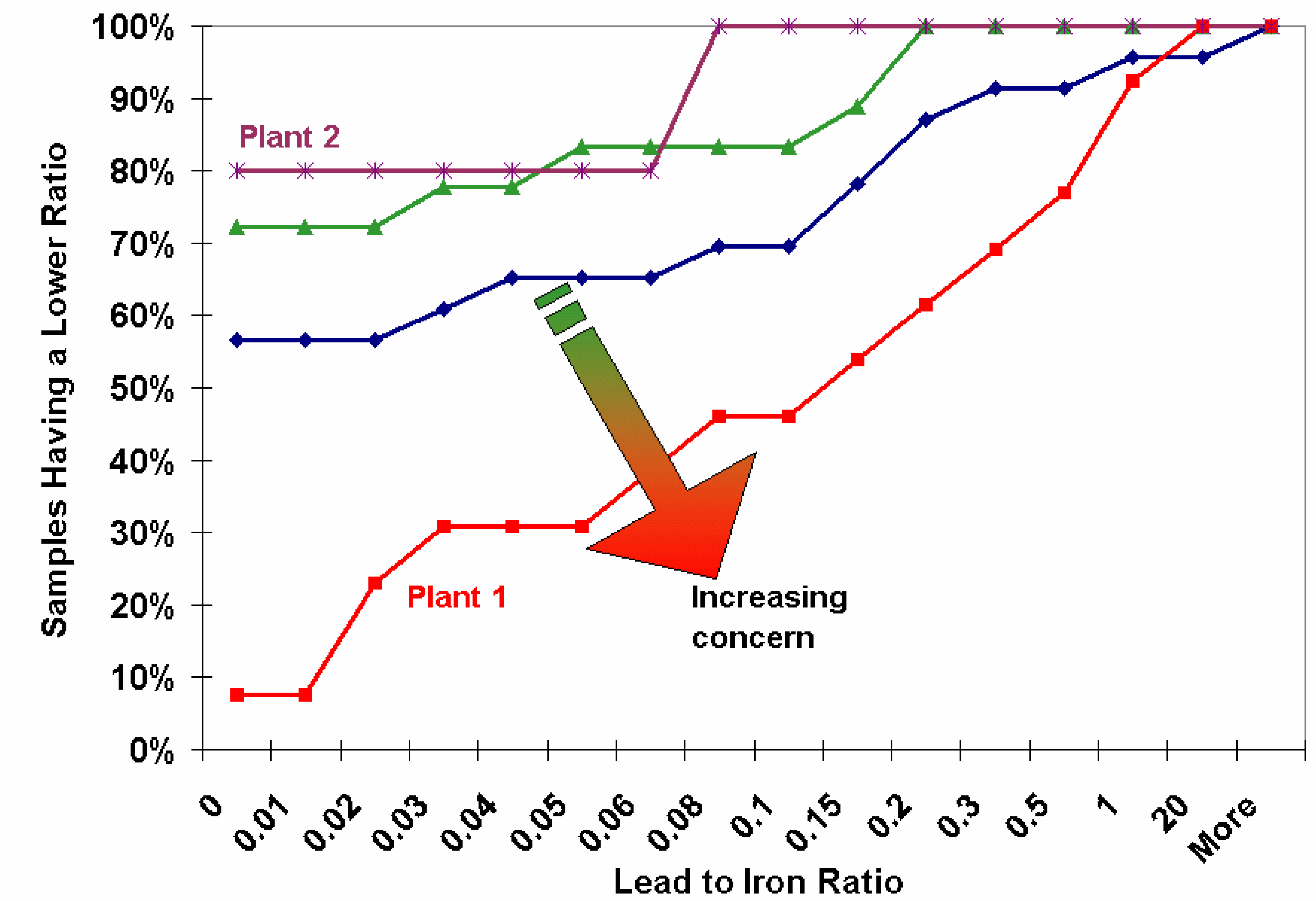


CEA Model Boiler Test Found that Lead Produced Little SCC, Consistent with Low Solubility

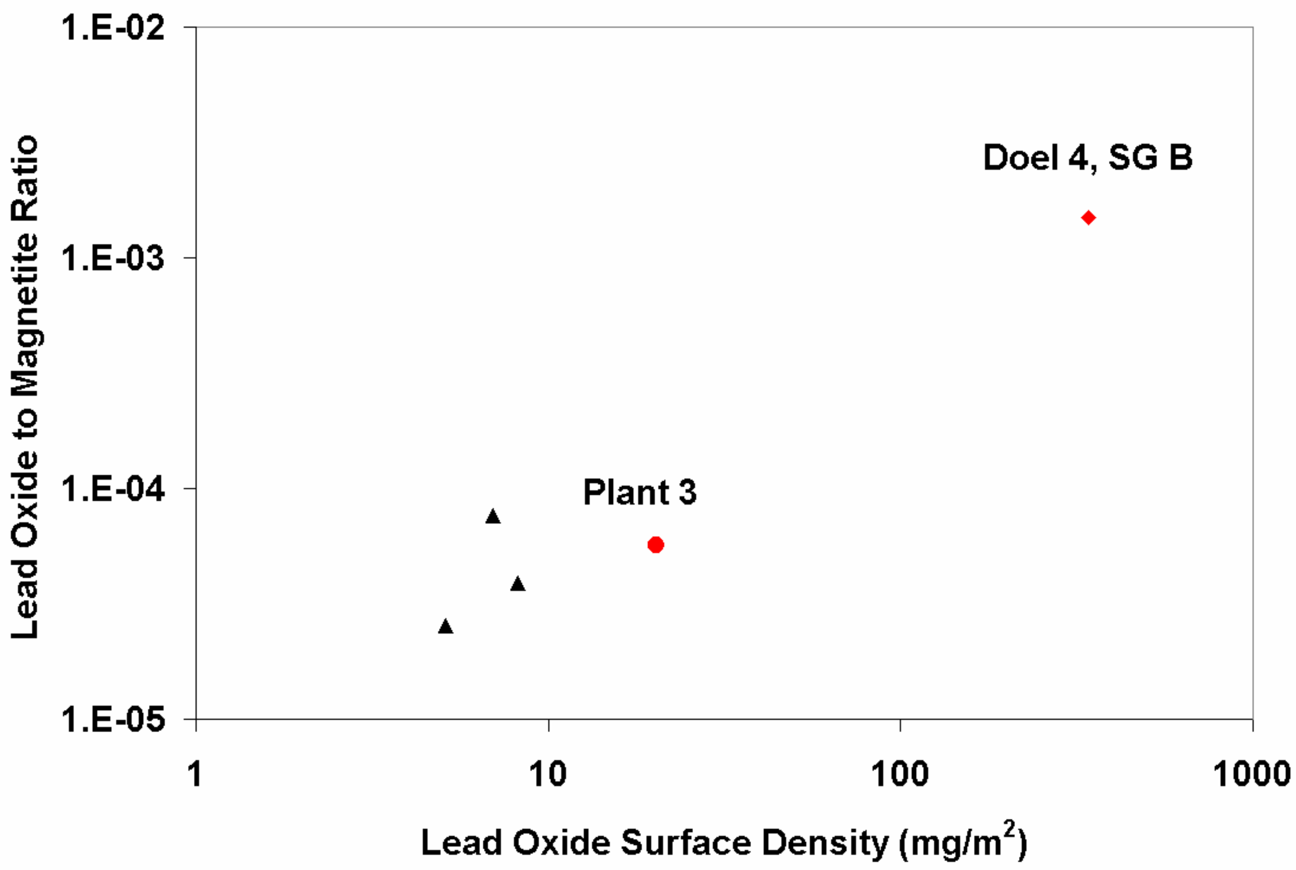
	AJAX Test 14-10 (LETC/292/92, 12/92)	CEA and W NaOH Model Boiler Tests
Concentration (ppb) Makeup Tank Blowdown	(Pb) 1000 59	(Na+) 600 500
Test Duration (days)	209	19
SCC Depth (%)	11	100
SCC Location	Deposit Periphery	Deposit Interior

- **A600 mill annealed tubing**

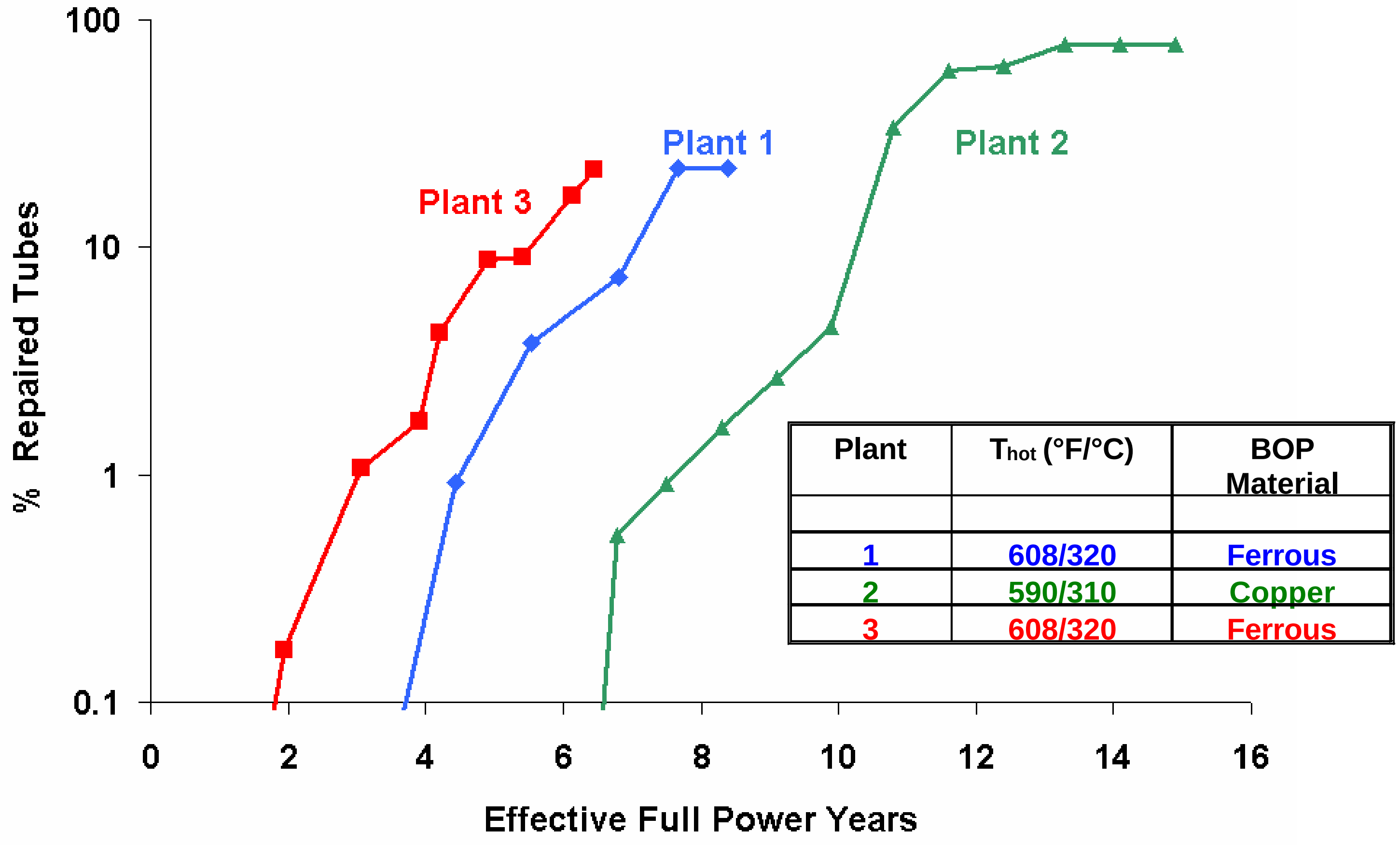
Cumulative Histograms Provide Convenient Means for Comparing Lead Content Identified in Tube Exams



Two Measures for Comparing Lead Removed by Chemical Cleaning

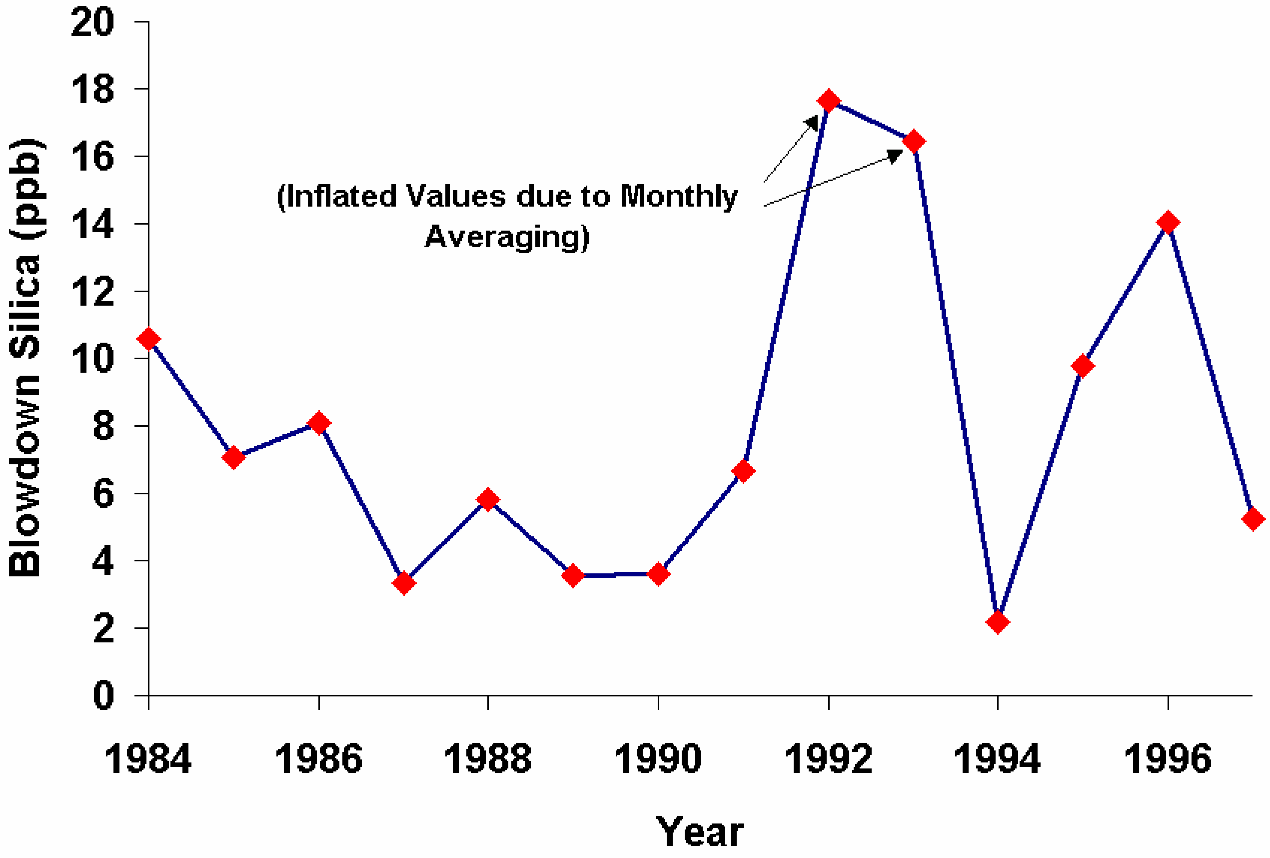


All Three Plants Experienced Extensive SCC in Crevice Interior



Plant	T_{hot} (°F/°C)	BOP Material
1	608/320	Ferrous
2	590/310	Copper
3	608/320	Ferrous

Plant 2, with Low Lead to Iron Ratio in Crevice, Operated with Exceptionally Low Blowdown Silica



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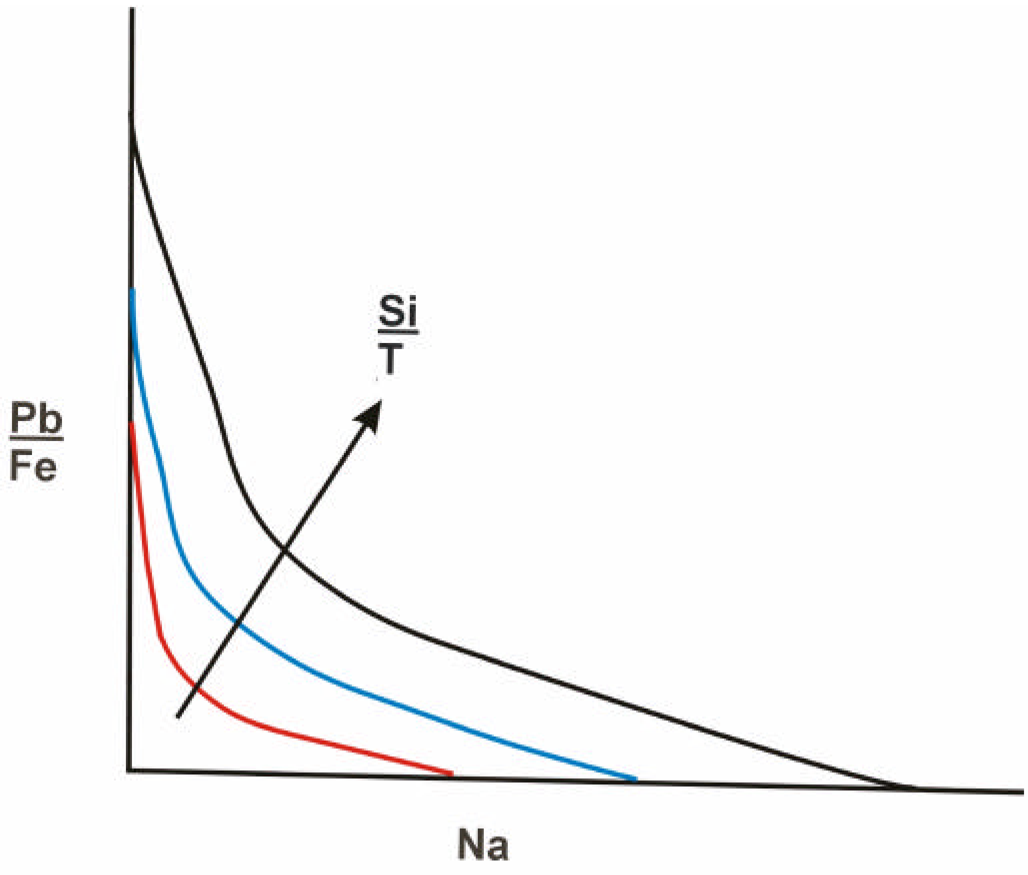
First Order ODSCC Variables Show Plane Having Equal Corrosion



Conclusions

- Concentration in packed crevices on tube surfaces having elevated superheats may be limited by solute:
  - Solubility (NaCl and Na_xPO_4; → Pb)
  - Volatility (Cl^-; → Organic acids)
  - Adsorptivity (Cl^-, SO_4^{-2})
- Concentration at high superheats may be largely limited to highly soluble, non-volatile, alkaline forming species
- Low lead solubility limits its crevice ODSCC capability
  - May be responsible for free-span ODSCC
- Lead, in combination with caustic, may be responsible for much of crevice ODSCC
  - SCC almost invariably occurs in crevice interior

MY CONCLUSIONS AFTER 25 YEARS OF MODEL BOILER TESTING

Jacques Daret
CEA, Cherbourg

Heat transfer vs isothermal testing, actual tubes vs RUB or U-bend specimens

- A SG crevice cannot be considered as an isothermal medium, and a SG tube is not a RUB or a U-bend
- Isothermal tests on non-representative specimens can produce results which are not obtained under representative conditions.
  - It is impossible to reach, in representative SG crevices, the concentrations of organic species that have been used in some hoaxing isothermal tests.
  - Under representative SG mechanical and chemical conditions, it is impossible to get the severe IGSCC which was obtained on TT alloy 690 using abusively stressed specimens in autoclave.

Chemical causes of secondary side degradation

- Realistic kinetics and significative extension of tubing degradation under heat transfer conditions were only obtained using the following pollutions:
  - decomposition products of ion exchange resins, essentially containing mildly acidic sulfur species
  - sodium hydroxide at very low concentration, i.e. in midly caustic medium
  - lead oxide in neutral medium (AVT)

Chemical causes of secondary side degradation (cont'd)

- The important experimental effort devoted at checking the nocivity of complex pollutions, made of organic species, silica, alumina, calcium phosphate and magnetite was wasted time. Though producing a fragile film at the tube surface, these pollutions are able to induce tubing degradation <u>only in the presence of reduced sulfates (such as sulfides and sulfites)</u>

- There is still a doubt on the phase (liquid or vapor) at the location where degradation occurs. It might be in fact at the liquid/vapor interface

Remedial actions

- If the cause of degradation is a caustic pollution, boric acid addition is the best remedy
- If the cause of degadation is an acidic pollution, boric acid is no longer efficient; only cerium acetate addition seems able to prevent tubing degradation
- Whatever the cause of degradation, limiting sludge ingress an/or avoiding accumulation is absolutely necessary

New tubing materials & TSP designs

- Alloy 800 is more resistant than Alloy 600 in the case of caustic pollution, but not that much in the case of acidic pollution
- Alloy 690 is also more resistant than Alloy 600 in the case of caustic pollution, and furthermore <u>it is practically immune to IGA/IGSCC under acidic pollution</u>
- Combination of Alloy 690 or 800 tubing with tri or quatrefoiled, convex lands TSP, or with egg-crate TSP, offers an undeniable benefit

Inferences Regarding PWR SG Crevices from Plant Operating Experience

Jeff Gorman, Dominion Engineering, Inc.

Heated Crevice Seminar

Argonne, Illinois, Oct. 8-11, 2002

Objectives

- Present some preliminary observations and conclusions regarding conditions in PWR SG crevices based on reviews of plant operating experience

- Hopefully, help inspire future performance of a more thorough and disciplined review, leading to development of industry consensus on lessons learned

Methodology

- Case studies, considering
  - SG and plant design
  - Water chemistry history
  - Tube corrosion experience
  - Likely crevice environments
  - Lessons learned re crevice environments
- Summary

Acronyms

AVT	All volatile treatment	IGSCC	Intergranular stress corrosion cracking
BA	Boric acid	LAS	Low alloy steel
BD	Blowdown	MR	Molar ratio
CDO	Condensate dissolved oxygen	PDR	Part depth roll
CP	Condensate polishers	RMO	Reducible metal oxide
CS	Carbon steel	SCC	Stress corrosion cracking
FDB	Flow distribution baffle	SG	Steam generator
FDR	Full depth roll	TS	Tube sheet
FWH	Feedwater heater	TSP	Tube support plate
IGA	Intergranular attack	TTS	Top of tube sheet
IGA/SCC	Intergranular attack/stress corrosion cracking		

Case 1 - Early Westinghouse Units on Phosphates

- SG and Plant Description
  - Feedring, 600 MA tubes, CS drilled hole TSPs
  - Frequent condenser leaks, air inleakage, no CPs

- Water Chemistry History
  - Initially on coordinated chemistry, Na/PO_4 MR < 2.6.
  - Next, congruent chemistry, Na/PO_4 MR 2.0 - 2.6.
  - Finally, congruent chemistry, Na/PO_4 MR 2.3 - 2.6.

Case 1 - Early Westinghouse Units on Phosphates (Cont.)

- Tube Corrosion Experience
  - First, rapid IGA/SCC above TTS (~1970-1971)
  - When change to congruent chemistry, get wastage, mainly at TTS, but also some elsewhere (~1972-1973)
  - With tighter congruent chemistry, wastage continues (~1973-1974)
- Likely Crevice Environments
  - High MR: caustic conditions
  - Low MR: acidic phosphate compounds

Case 1 - Early Westinghouse Units on Phosphates (Cont.)

- Lessons Related to Crevice Environments
  - ppm levels of cations and anions can concentrate in sludge piles and similar occluded areas to aggressive levels
  - High MR with non-volatile cation can lead to caustics and IGA/SCC
  - Low MR with non-volatile anions can lead to strong acids and wastage
  - Caustics and acids from phosphates attack tubes in TTS sludge piles in preference to inside deep crevices

Case 2 - Experience of Early Westinghouse Units After Switch to AVT

- SG and Plant Description
  - Feedring, 600 MA tubes, CS drilled hole TSPs
  - Frequent condenser leaks, air inleakage, no CPs
- Water Chemistry History
  - After switch to AVT in ~1974-1975, relatively high impurities allowed, e.g., BD cation conductivity < 2 μS/cm (Cl- ~ 170 ppb)
  - After denting detected, water chemistry progressively tightened (lower impurity & oxidant ingress)
  - Beznau 1 started up on AVT, switched to phosphates after IGA/SCC occurred in tube sheet crevice, returned to AVT after wastage at TTS

Case 2 - Experience of Early Westinghouse Units After Switch to AVT (Cont.)

- Tube Corrosion Experience
  - Rapid denting at salt water cooled plants
  - Denting rate reduced in some plants by reductions in impurity and oxidant ingress
  - Serious IGA/SCC in deep tube sheet crevices of fresh water cooled plants and sea water cooled plants with tight condensers

Case 2 - Experience of Early Westinghouse Units After Switch to AVT (Cont.)

- Likely Crevice Environments
  - Acidic environments in TSP and deep TS crevices of salt water cooled plants. Potentials elevated by ingress of oxygen and RMOs. Leads to denting of TSPs, little denting at TS.
  - Alkaline TS and TSP crevices in freshwater cooled plants. Potential elevated by ingress of oxygen and RMOs. Leads to rapid IGA/SCC at TS crevices, little attack at TSPs.

Case 2 - Experience of Early Westinghouse Units After Switch to AVT (Cont.)

- Lessons Related to Crevice Environments
  - With bulk water impurities in the ppm range, TSP crevices can quickly accumulate sufficient impurities to corrode TSPs
  - Tubes in deep TS crevices are much more susceptible to IGA/SCC than in TSP crevices. Reasons not clear: higher superheat? More hydrogen? More reducing conditions?
  - TSPs much more susceptible to denting than TTS region. Reasons not clear: Increased corrosion resistance of LAS vs. CS? Less access of oxidants to TS crevices (no delta P to force entry of liquid)? ΔT across crevice causes increased acidity at CS surface?

Case 2 - Experience of Early Westinghouse Units After Switch to AVT (Cont.)

- Lessons Related to Crevice Environments (Cont.)
  - TSP crevices in salt water plants can quickly develop aggressive acidic conditions conducive to denting
  - Deep TS crevices develop aggressive IGA/SCC conditions quickly over full height, implying that attack occurs in steam filled areas
  - Acidic conditions that lead to denting are not especially conducive to IGA/SCC (low IGA/SCC in severely dented salt water cooled plants)

Case 3 - Ringhals 2 Experience

- SG and Plant Description
  - Model 51 SGs with part depth rolls, CS drilled hole TSPs, no CPs
  - Original condensers had copper alloy tubes, leaked
  - Seawater cooled
- Water Chemistry History
  - Started up on phosphates, used only at low power
  - Sept. 1974 switched to AVT
  - After denting discovered in 1977, plant and water chemistry improvements made, including replacing copper alloy condenser tubes with seal welded titanium tubes

Case 3 - Ringhals 2 Experience (Cont.)

- Tube Corrosion Experience
  - Denting discovered in 1977
  - PWSCC at U-bends (1979) and roll transitions (1981)
  - Starting in ~1980, IGA/SCC in deep TS crevices occurs, worsens, leads to temperature reductions, power decrease, sleeving, replacement
  - Never plugged tubes due to IGA/SCC at TSPs

Case 3 - Ringhals 2 Experience (Cont.)

- Likely Crevice Environment
  - Detailed investigation, including hideout return studies and leaching evaluations of pulled tube deposits, indicate TS crevices were strongly alkaline (pH_T ~ 10)
  - Because of large volume of crevices and small amounts of impurities, crevices probably steam dominated

Case 3 - Ringhals 2 Experience (Cont.)

- Lessons Related to Crevice Environments
  - IGA/SCC can occur in steam filled spaces
  - Cracking more severe in tubes with intragranular carbides, few grain boundary carbides
  - Cracking due to caustic in a steam filled space seems likely mechanism
  - Reasons for lack of IGA/SCC at TSPs never established - Stress patterns changed by denting? Crevices sealed by denting? Residual salts buffer pH?

Case 4 - Operation with Low Hydrazine

- SG and Plant Description
  - Model D3 SGs with full depth rolled 600MA tubes and CS drilled hole TSPs
  - Seawater plant, no CPs
  - Initially, copper alloy condensers and FW heaters, many condenser leaks and air ingress problems
- Water Chemistry History
  - Always on AVT. During first cycle, many condenser leaks, lots of air inleakage
  - AT EOC1, replaced condenser tubes with titanium and on-line boric acid initiated
  - 2nd cycle - purity good, pH about 9.4, hydrazine about 30 ppb

Case 4 - Operation with Low Hydrazine (Cont.)

- Water Chemistry History (Cont.)
  - 3rd cycle - BA continued, but hydrazine reduced to CDO + 5 ppb, pH reduced to ~8.9 (to reduce copper transport)
  - 4th cycle - BA continued, pH increased to ~ 9.0, hydrazine to about 25 ppb
- Tube Corrosion Experience
  - EOC 1 - Widespread denting. Leads to condenser replacement, use of BA
  - EOC 2 - some pits, IGA/SCC, significant amount of copper deposits. Concerns re copper lead to reduction of hydrazine during next cycle

Case 4 - Operation with Low Hydrazine (Cont.)

- Tube Corrosion Experience (Cont.)
  - EOC 3 - Large increase in IGA/SCC at TSPs (364 tubes plugged). Leads to increase in hydrazine in future cycles
  - After Cycle 3, rate of IGA/SCC at TSPs strongly reduced
- Likely Crevice Environments
  - Denting in first cycle due to acidic TSP crevices, oxidant ingress
  - Rapid IGA/SCC during third cycle likely aggravated by oxidizing conditions associated with use of low hydrazine, coupled with high stresses from denting. No info re pH in crevices

Case 5 - Japanese Plant Experience

- SG and Plant Description
  - Westinghouse type with 600MA tubes, CS drilled hole TSPs
  - Early units with PDR, deep tube sheet crevices. Later units with FDR
  - Early units initially no CPs (added later), later units with CPs from start up
  - Copper alloy condensers and FWH

Case 5 - Japanese Plant Experience (Cont.)

- Water Chemistry History
  - Most plants always used AVT
  - After detection of denting and IGA/SCC, some units used BA
  - Hydrazine initially about 10 - 20 ppb in early units, raised to 100 - 600 ppb about 1982
  - Units with polishers always operated with low MR
  - By mid 1980s, all units had high purity, low MR, high hydrazine. Units affected by IGA/SCC initiated use of BA as a counter measure

Case 5 - Japanese Plant Experience (Cont.)

- Tube Corrosion Experience
  - About 1981 - IGA/SCC detected in deep TS crevices
  - About 1982 - IGA/SCC detected at TSP crevices
  - Minimal denting at TSPs
  - IGA/SCC continues in deep TS crevices and at TSPs despite high hydrazine, low molar ratio, high purity, use of boric acid
  - No IGA/SCC reported for TTS of FDR plants, even at plants with large scale attack at TSPs
  - Several FDR plants never detected secondary side IGA/SCC, despite > 20 years operation with 600MA. These started up with CP, high hydrazine, low MR

Case 5 - Japanese Plant Experience (Cont.)

- Likely Crevice Environments
  - Japanese concluded that initiation of IGA/SCC was due to caustics from secondary system (e.g., from welding deposits), coupled with oxidizing conditions during early cycles
  - Crack propagation continued with near neutral crevices

Case 5 - Japanese Plant Experience (Cont.)

- Lessons Related to Crevice Environments
  - Maintenance from beginning of operation of low impurity ingress, highly reducing conditions, low MR can prevent or strongly retard development of IGA/SCC in 600MA. Appears to be associated with near neutral fully reduced conditions
  - Application of above conditions after IGA/SCC initiation does not prevent continued growth of already initiated cracks. Possible reasons:
    - ? High stress intensity at crack tip causes threshold conditions to be exceeded
    - ? Establishment of protective oxides on surfaces under benign chemistry required to prevent initiation - not possible at crack tip

Case 5 - Japanese Plant Experience (Cont.)

- Lessons Related to Crevice Environments (Cont.)
      - ? Once non-protective oxide formed, it can't be repaired
  - Use of BA may slow IGA/SCC, but does not prevent continued growth of IGA/SCC - caustic not required for IGA/SCC growth
  - Crevices in clean TTS areas significantly less susceptible to IGA/SCC than TSPs in feedring units - possibly due to lower temperature due to subcooled water in downcomer?
  - Use of high hydrazine, by itself, does not cause IGA/SCC

Case 6 - Ratio of IGA/SCC at TSPs to TTS for Feedring vs. Preheater Units

- SG and Plant Description
  - 600MA tubes, CS drilled hole TSPs, full depth roll expansions and FDBs
  - Feedring group includes 1 domestic unit and 12 French units (with kiss rolls)
  - Preheater group includes 8 domestic units
- Water Chemistry History
  - All AVT water chemistry to modern standards

Case 6 - Ratio of IGA/SCC at TSPs to TTS for Feedring vs. Preheater Units (Cont.)

- Tube Corrosion Experience
  - Feedring Units: Ratio of IGA/SCC at TTS to that at TSPs: median of 0.05
  - Preheater Units: Ratio of IGA/SCC at TTS to that at TSPs: median of 0.95
  - Attack at TTS of feedring units is much less important than attack at TSPs, while it is about of equal importance at preheater units

Case 6 - Ratio of IGA/SCC at TSPs to TTS for Feedring vs. Preheater Units (Cont.)

- Likely Crevice Environments
  - TTS crevice depths typically ~3 mm - less severe than in TSPs (assuming minimal sludge) - supports lower superheat than in TSPs
  - In feedring units, lower temperature at TTS than at lower TSPs due to subcooled downcomer water at TTS
  - In preheater units, lack of subcooling results in bulk temperature at TTS similar to that at lower TSPs
  - Stresses at TTS higher and more uniform than in TSPs in both feedring and preheater units

Case 6 - Ratio of IGA/SCC at TSPs to TTS for Feedring vs. Preheater Units (Cont.)

- Lessons Related to Crevice Environments
  - In feedring units, lower temperature at TTS due to subcooled downcomer water, coupled with less severe crevice at TTS vs. TSP, leads to reduced relative rate of IGA/SCC at TTS, despite higher stresses
  - In preheater units, lack of subcooling results in higher relative rate of attack for TTS vs. TSPs than for feedring units, despite less severe crevice (lower superheat)

Case 7 - Alloy 800NG Siemens SGs

- SG and Plant Description
  - 17 PWR plants with 800NG tubes
  - One of 17, Doel 3, originally had 600MA
  - Closed TS crevices, SS lattice supports
  - All except Doel 3 have large deaerating FWHs
  - Early units had copper alloy condensers, collected significant sludge. Copper now eliminated
  - Startup dates range from 1972 to 1993 (Doel 3)
  - Hot leg temperatures 596 - 620°F; 12 between 617 - 620°F - among hottest in world
  - Later units have FDB and preheaters
  - 6 of 17 have been chemically cleaned

Case 7 - Alloy 800NG Siemens SGs (Cont.)

- Water Chemistry History
  - – 8 early units started up with phosphate water chemistry
    - ? Used lower MR of Na to PO_4 than in US (~2 to 2.2 vs. 2 - 2.6), and lower concentration (2-6 vs. 10-80 ppm)
    - ? Because of wastage problems, first increased pH of secondary system while still on phosphates, then converted to high AVT ($pH_{25^\circ C} > 9.8$) in 1980s
  - – First unit to startup on high AVT was Grafenrheinfeld in 1982
  - – High AVT involves high hydrazine, e.g., 80 - 200 ppb
  - – Low iron ingress due to high pH, material changes

Case 7 - Alloy 800NG Siemens SGs (Cont.)

- Tube Corrosion Experience
  - Units that started up with phosphate water chemistry experienced wastage, mostly in TTS sludge piles
    - ? Wastage brought under control by sludge lancing, iron ingress reduction (higher system pH, material replacement)
    - ? Because of wastage problems, converted to high AVT ($pH_{25°C} > 9.8$) in 1980s
  - Have had 1 tube with identified IGA/SCC, 2 tubes with pitting - essentially no corrosion other than early wastage problems

Case 7 - Alloy 800NG Siemens SGs (Cont.)

- Likely Crevice Environments
  - During period with phosphate chemistry, crevices likely had concentrated acidic phosphate compounds
  - During high AVT period, crevice environments probably have had similar ranges of pH, potential, and aggressive species as in 600MA plants, especially for TTS crevices and for crevices at SS lattice bar supports
    - Water chemistry specifications less stringent than those of EPRI
    - Large number of plants, many years, undoubtedly have had many chemistry upsets
    - Large FWHs may result in lower exposure to oxidants

Case 7 - Alloy 800NG Siemens SGs (Cont.)

- Lessons Related to Crevice Environments (Applies only to TTS and SS lattice bar crevices)
  - Absence of Pitting: Based on Siemens tests (1983 symp.), indicates that potentials in crevices have not exceeded -250 mV_{SHE} for rest potential of -600 mV_{SHE}
  - Absence of IGA/SCC:
    - ? NaOH concentrations must generally be < 4% since > 4% attacks 800NG - sodium generally tied up by other species? $pH_T < 10.4$
    - ? pH_T <5 generally does not occur in crevices since 800NG experiences IGA/SCC at pH_T 5 and below (Pierson 1996, de Bouvier 1999)

Case 7 - Alloy 800NG Siemens SGs (Cont.)

- Lessons Related to Crevice Environments (Applies only to TTS and SS lattice bar crevices) (Cont.)
  - Absence of IGA/SCC (Cont.):
    - ? 800NG not particularly sensitive to lead (Helie, 1993, Castaño Marín 1993), so absence of IGA/SCC provides little guidance
    - ? Concentrated chlorides and potentials over +290 mV_{SHE} do not occur simultaneously (Stellwag 1991 symp. - TGSCC occurs for pot. > 290 mV_{SHE})
    - ? Acidic environments with significant amounts of reduced sulfur do not occur (Daret 1999 - IGSCC occurs in MB with 800NG under these conditions)

Summary of Lessons from Plant Operating Experience

- High MR with non-volatile cation can lead to caustics and IGA/SCC
- Low MR with non-volatile anions can lead to strong acids and wastage
- Caustics and acids from phosphates attack tubes in TTS sludge piles in preference to inside deep crevices
- With AVT, TS crevices can rapidly develop conditions that cause IGA/SCC. Attack probably occurs in steam. Evidence indicates caustic pH involved

Summary of Lessons from Plant Operating Experience (Cont.)

- TSP crevices are more efficient than TS crevices at accumulating corrodents that cause denting, but are less efficient re corrodents that cause IGA/SCC. Understanding mechanistic reasons for these differences important to understanding crevice behavior
- Acidic conditions that lead to denting are not especially conducive to IGA/SCC (low IGA/SCC in severely dented salt water cooled plants). Understanding mechanistic reasons important to understanding crevice behavior
- Oxidizing conditions associated with low levels of hydrazine can raise crevice potentials and accelerate IGA/SCC. Use of high hydrazine does not appear to have caused IGA/SCC

Summary of Lessons from Plant Operating Experience (Cont.)

- Maintenance from beginning of operation of low impurity ingress, highly reducing conditions, low MR can prevent or strongly retard development of IGA/SCC in 600MA. Appears to be associated with near neutral condition
- Application of above conditions after IGA/SCC initiation does not prevent continued growth of already initiated cracks. Possible reasons:
  - High stress intensity at crack tip causes threshold conditions to be exceeded
  - Establishment of protective oxides on surfaces under benign chemistry required to prevent initiation - not possible at crack tip
  - Once non-protective oxide formed, it can't be repaired

Summary of Lessons from Plant Operating Experience (Cont.)

- In feedring units, lower temperature at TTS due to subcooled downcomer water, coupled with less severe crevice at TTS vs. TSP, leads to reduced relative rate of IGA/SCC at TTS, despite higher stresses
- In preheater units, lack of subcooling results in higher relative rate of attack for TTS vs. TSPs than for feedring units, despite less severe crevice (lower superheat)
- pH_T in TTS and SS lattice bar crevices rarely < 5, rarely >10.4
- Acidic environments with significant amounts of reduced sulfur rarely occur in TTS and SS lattice bar crevices

Inferences Regarding PWR SG Crevices from Model Boiler Results

Jeff Gorman, Dominion Engineering, Inc.

Heated Crevice Seminar

Argonne, Illinois, Oct. 8-11, 2002

Objectives

- Present some preliminary observations and conclusions regarding conditions in PWR SG crevices based on reviews of model boiler test results, especially with regard to identifying the species, pH and potentials involved in IGA/SCC

- Hopefully, help inspire future performance of a more thorough and disciplined review, leading to development of industry consensus on lessons learned

Methodology

- Assemble data on crack growth rates in different environments (starting with results assembled by Daret at the Eighth International Symposium on Degradation of Materials in Nuclear Reactor Systems - Water Reactors (1997).
- Evaluate the results in light of plant experience
- Reach tentative conclusions regarding environments that seem representative of plant conditions

Acronyms

AVT	All volatile treatment	PB	Pot boiler
BA	Boric acid	SCC	Stress corrosion cracking
CS	Carbon steel	SG	Steam generator
IGA	Intergranular attack	SPS	Simulated Plant Sludge
IGA/SCC	Intergranular attack/stress corrosion cracking	STMB	Single tube model boiler
IGSCC	Intergranular stress corrosion cracking	TCSA	Tubesheet crevice simulation apparatus
ISTMB	Inverted single tube model boiler	TS	Tube sheet
LAS	Low alloy steel	TSP	Tube support plate
MB	Model boiler	TTS	Top of tube sheet
MR	Molar ratio	TW	Through wall
MUT	Makeup Tank		

Model Boiler Methodology

- General Approach (see Figures 1-3)
  - Use realistic or somewhat elevated primary and secondary temperatures and heat fluxes
  - Use realistic primary coolant chemistry
  - Use AVT chemistry plus selected additive(s)
  - Use realistic tubes, crevices
  - Add sludges of various compositions (often oxidizing)
  - Often use sludge cups and porous frits to hold sludge in place
  - Often use periodic power and pressure cycling to introduce solutions into crevices

Westinghouse Model Boiler System (from WCAP-10273)

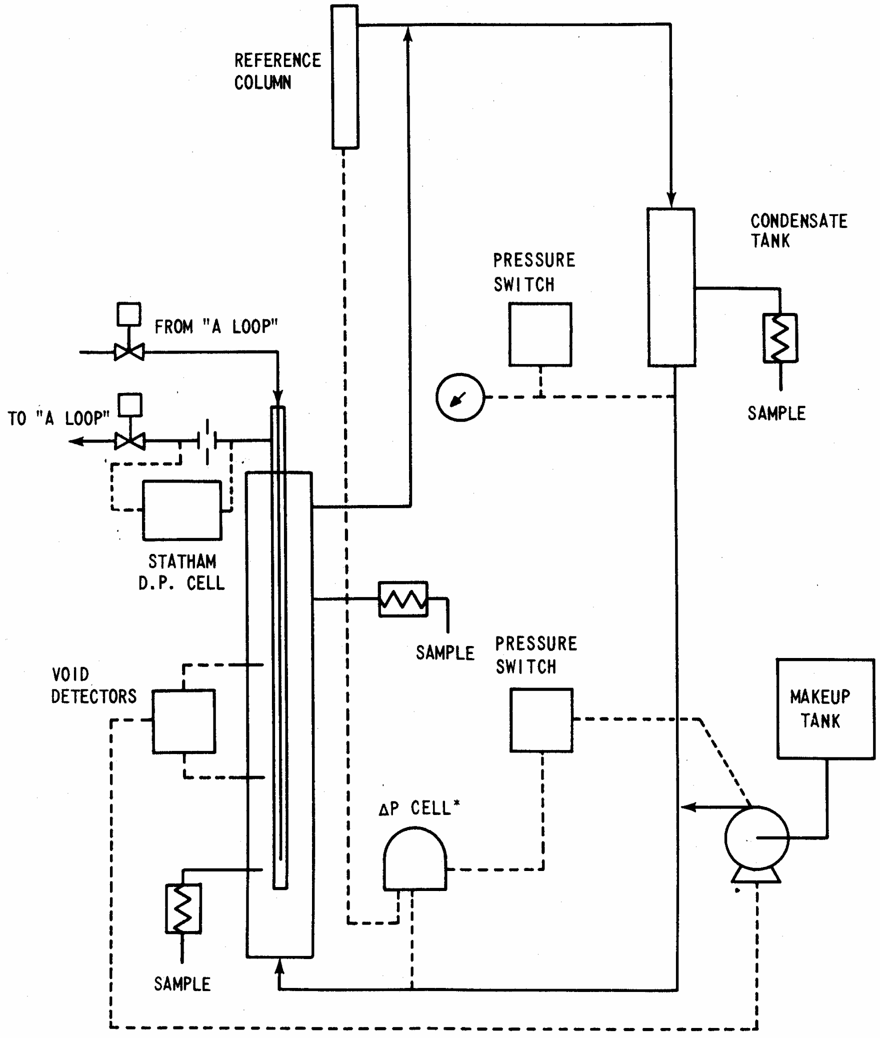


Figure 3-1. Schematic Diagram of Forest Hills Model Boiler System

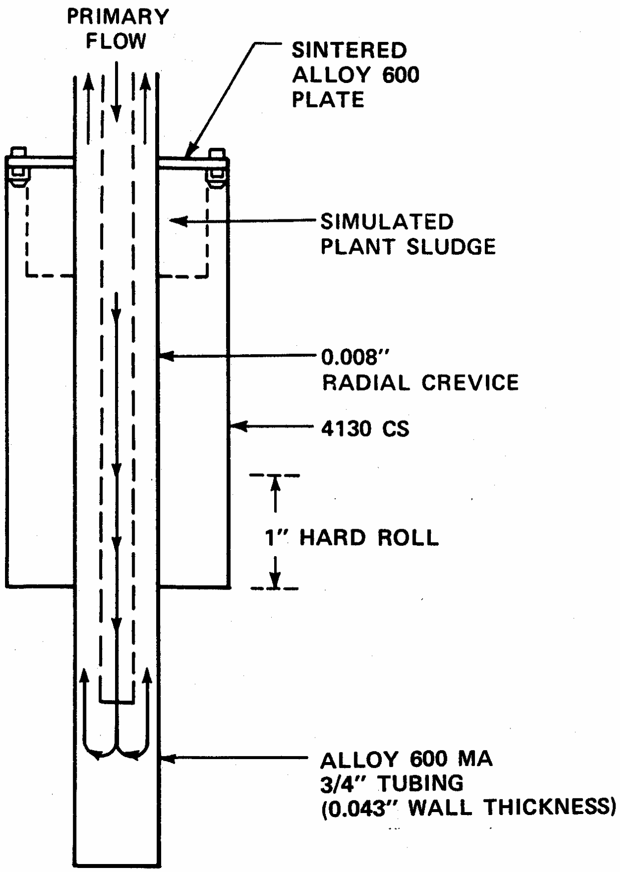


Figure 3-2. Schematic Diagram of Tubesheet Simulant

Tube Sheet Simulant (from WCAP-10273)

CEA's AJAX MB (from Daret, 1997)

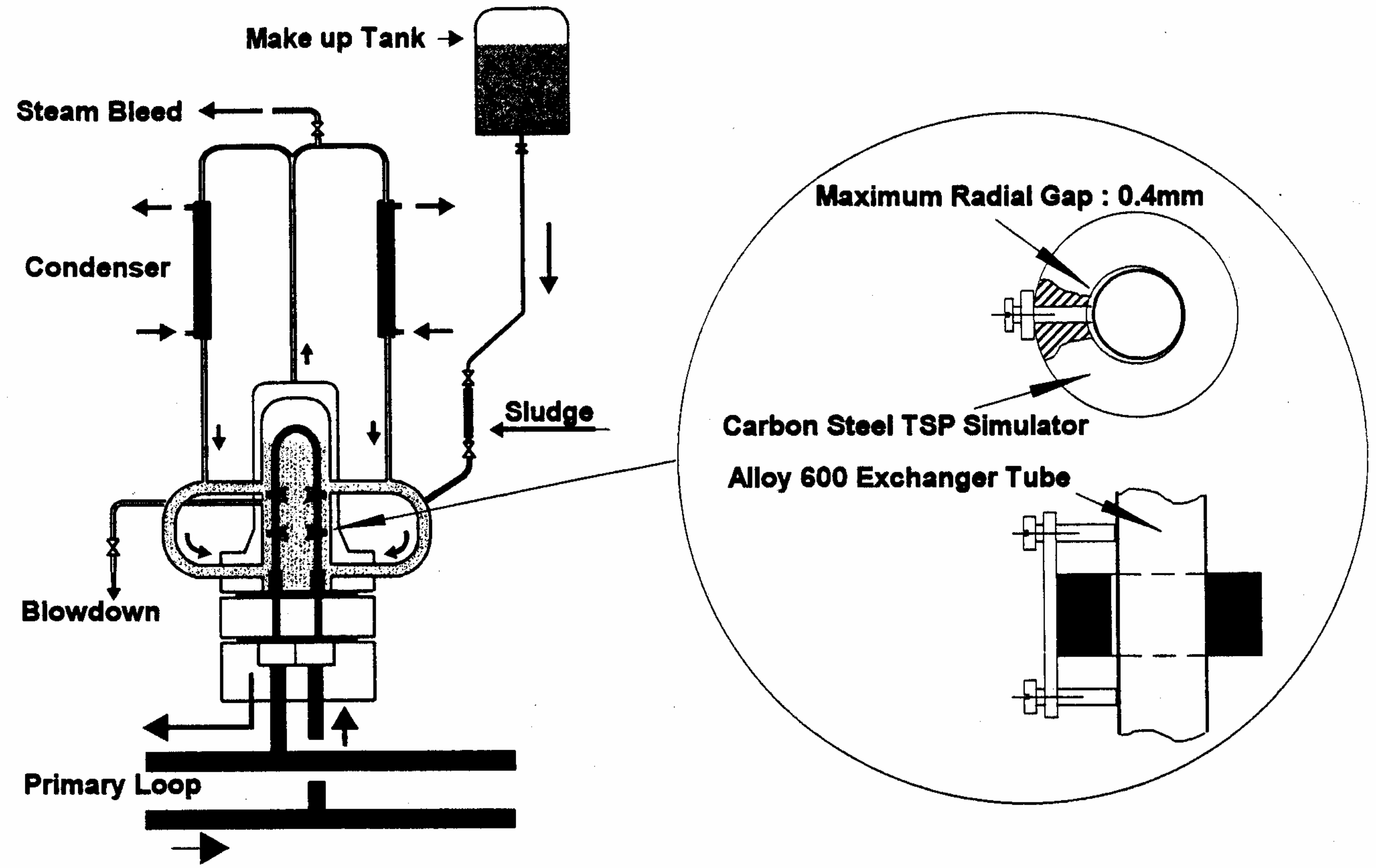


Figure 1. Schematic flow sheet of an AJAX model boiler, with a close view of a simulated tube-tube support plate intersection

Model Boiler Methodology (Cont.)

- Typical Objectives of Model Boiler Tests
  - Test effects of different pollutants
  - Test effects of different crevice, support, and expansion designs
  - Rank resistance of different materials
  - Evaluate remedial measures such as use of buffers and inhibitors

Model Boiler Methodology (Cont.)

- Advantages of Model Boilers
  - Realistically duplicate effects of heat flux and heat transfer conditions on establishing chemistry and potential in crevice areas
  - Provide realistic simulation of effects of chemistry on actual tubes (realistic material condition, surface condition, stresses, geometry)

Model Boiler Methodology (Cont.)

- Limitations of Model Boilers
  - Because of time limitations, concentrations of additives often much higher than in plants - can lead to unrealistic results
  - Water chemistry in MB system not necessarily representative of complex and varied chemistries of real plants
  - Because of different surface to volume ratio (vs. real SG), difficult to realistically model hydrazine concentrations
  - Sludge and frits have a strong effect on results - difficult to assess realism involved

Model Boiler Methodology (Cont.)

- Simulated Plant Sludge (SPS)
  - Widely used
  - Oxidizing - raises potential
  - Based on early plant sludge with relatively high copper
  - Composition (from WCAP-10273):

? Cu	32.5%
? CuO	4.5%
? Fe_3O_4	59.7%
? NiO	2.1%
? Cr_2O_3	1.2%

Results for Different Pollutants

- Results of MB tests with each of the main pollutants that have been used are reviewed in the next slides
- Pollutants include
  - Caustics (mainly sodium carbonate and sodium hydroxide)
  - Sodium sulfate
  - Resins and resin liquor
  - Acid sulfate
  - Lead
  - Organics
  - Lake and river water
  - Mixes of the above

Caustic Dominated Environments

Pollutant	Sludge	MB	Ref	Duration of Test, h	Maximum CGR μm/h	Location of IGA/SCC	Comments
3 ppm Na_2CO_3	Oxidizing	W STMB	13	~400	2.7	In sludge at TTS	
3 ppm Na_2CO_3	Non-oxidizing	W STMB	14	2,904	0.38	In sludge at TTS	No IGA
0.3 ppm Na_2CO_3	Non-oxidizing	W STMB	14	4,320	0.056	In sludge at TTS	IGA in crevice about 10x slower
0.3 ppm Na_2CO_3 + BA	Non-oxidizing	W STMB	15	4,320	0.0019		
0.3 ppm Na_2CO_3 + BA after crack initiation	Non-oxidizing	W STMB	15	1,584	~0.2		BA applied after 10 days
Na_2CO_3	PbO after 8000 h	Ciemat MB	7	10,300		TSP crevices w/o PbO	IGC observed (detected by ECT, >25% of wall)
Na_2CO_3 + caustic	Magnetite	CE TCSA2	4	3,624	1.45	1/2" below TTS	TW in 35 days, slight denting, shallow IGA in crevice
Sodium, =0.6 ppm	Oxidizing	CEA AJAX	1		2 - 9	open TSP crevice, eccentric	
Sodium, 0.06 ppm	Oxidizing	CEA AJAX	1		0.016	open TSP crevice, eccentric	
Sodium, 1.35 ppm	Oxidizing	W STMB	16	1,872	0		wastage
Na+SO_4, MR=16, 0.77 ppm Na	Oxidizing	W STMB	16	648	1.7	In sludge at TTS	
Na+SO_4, MR=16, 0.77 ppm Na	Non-oxidizing	W STMB	16	2,088	0.9	In rolled region	
Na+SO_4, MR=19.6, 0.75 ppm Na	Oxidizing	W STMB	16	384	2.8	In sludge at TTS	
Sodium, 0.01 ppm	None	Tokyo U MB	19	15,181	0.0066	In DH TSP	

Note: Through wall in 4 years = 0.03 μm/h

Comments re Caustic Environments

- Widely used in MB testing
- With ppm level Na_2CO_3 + oxidizing sludge, reproducibly causes rapid IGSCC (~2 - 3 weeks thru wall)
- Crack morphology similar to that in plants
- At lower levels and with non oxidizing sludge, often results in realistic appearing IGA
- CGR often much higher than seen in plants
  - MB: ~3 μm/h
  - Plant ~0.03 μm/h
- With ppm level caustic, IGA/SCC often occurs in sludge, not in crevice. With lower levels of caustic, less oxidizing sludge, IGA/SCC occurs in crevice areas

Comments re Caustic Environments (Cont.)

- MB tests with ppm level caustics useful for ranking materials, configurations, remedial measures, etc., but some doubt thrown on these results as a result of unrealistic CGR, and lack of complexity in environments
- Caustics at lower concentrations result in realistic IGA/SCC - demonstrates that caustics need to be avoided in plants
- Tests with BA indicate big benefit from BA. Lack of similar effect in plants indicates that caustic is not the main cause of continuing IGA/SCC growth in plants
- Some tests indicated that sulfates combined with caustic significantly increase aggressiveness. However, other tests indicated that sulfur has little or beneficial effect

Seawater Polluted Environments

Pollutant	Sludge	MB	Ref	Duration of Test, h	Maximum CGR μm/h	Location of IGA/SCC	Comments
Seawater	??	CEA AJAX	1		0	??	No IGA/SCC - some pitting
Seawater	Oxidizing	CE MB7	5	8,016	0	None	No IGA/SCC - pitting
Seawater + morpholine	Oxidizing	CE PB6D	5	2,016	0	None	Extensive pitting
Seawater + cyclohexamine	Oxidizing	CE PB7C	5	2,016	0	None	Extensive pitting
Seawater+phos, seawater+AVT	Oxidizing	CE PB8	5	2,880	0	None	Pitting and wastage
Seawater	Oxidizing	CE PB6E	5	3,192	0	None	Denting and pitting
Seawater+phos, seawater+AVT	Oxidizing	CE MB5A	5	6,576	0	None	Extensive denting (TSP cracking), pitting
Periodic seawater	Oxidizing	CE MB7A	5	4,104	0	None	Minor pitting (3.7 mils max)
Periodic seawater	Hematite	CE PB4I	5	3,336	0	None	Pitting
Seawater	Oxidizing	CE MB5B	6	12,720	0.096	In dented TSPs	Systematic IGA + SCC in DH TSPs, none in eggcrates
Seawater	None	MHI MB	17	3,000	0	None	Pitting
AVT+Na+Cl	Oxidizing	CE MB3	5	8,256	0	None	Widespread pitting

Comments re Seawater Pollution

- Only one MB test with seawater pollution resulted in IGA/SCC
- Main damage forms with seawater are denting and pitting
- Consistent with plant experience - plants with significant seawater inleakage experienced mostly denting and pitting, with IGA/SCC only after seawater ingress was largely stopped

Fresh Water Pollution

Pollutant	Sludge	MB	Ref	Duration of Test, h	Maximum CGR μm/h	Location of IGA/SCC	Comments
Fresh water	??	CEA AJAX	1,2	7,800	0.001	Deep in deep TS crevice	10 micron IGA at roll transition
Fresh water	Oxidizing	W STMB	3	1,580	0.006	In sludge at TTS	10 micron IGA
Phosphate, then fresh water	Oxidizing	CE TCSA1	4	7,870	0	None	Denting at TS, minor pitting
Fresh water	Oxidizing	CE MB1	5	6,888	0	None	Minor pitting

Comments re Fresh Water Pollution

- Only very shallow IGA experienced in long tests
- Investigators concluded that fresh water pollution from rivers and lakes unlikely to cause serious IGA/SCC
- Since fresh water cooled plants have experienced a great deal of IGA/SCC, the lack of IGA/SCC in MB tests needs explanation. Possibilities:
  - Tests not carried out long enough
  - Plants have more impurities, e.g., resin degradation products.

Resin and Lead Pollution

Pollutant	Sludge	MB	Ref	Duration of Test, h	Maximum CGR mm/h	Location of IGA/SCC	Comments
Resin Pollution							
Resin fines	Oxidizing	CE MB8	5	6,624	0.018	Dented CS TSP	Severe denting, some wastage, IGA only-no IGSCC
Resin fines	None	CEA AJAX	1		0.03	TSP	
Resin extract + high hydrazine	Non-oxidizing	CEA AJAX	10	5,000	0.07	Open TSP crevice, eccentric	Reduced sulfur species detected
Resin extract + high hydrazine	Oxidizing	CEA AJAX	10	6,000	0.065	Open TSP crevice, eccentric	Reduced sulfur species detected
Lead Pollution							
Soluble lead		CEA AJAX	1		0.03	TSP crevice	
sodium+lead	Oxidizing + 1% PbO	CEA AJAX	1		0.039	Open TSP crevice, eccentric	
Resin + Lead Pollution							
Resin extract	Magnetite + PbO	CEA AJAX	1		0.15	TSP	
Resin extract	Plant sludge + PbO	CEA AJAX	1		0.06	TSP	
Resin extract	Plant sludge + PbO	CEA AJAX	1		0.15	TSP	
Resin extract + BA	Plant sludge + PbO	CEA AJAX	1		0.11	TSP	
Resin extract+Ti Lactate	Plant sludge + PbO	CEA AJAX	1		0.12	TSP	
Resin extract+Ce Acetate	Plant sludge + PbO	CEA AJAX	1		0.004	TSP	
Resin extract+high hydrazine+PbO	Oxidizing	CEA AJAX	10	6,000	0.03	Open TSP crevice, eccentric	Reduced sulfur species detected

Comments re Resin and Lead Pollution

- Low levels of resin and/or lead pollution cause realistic CGR and morphology. Either resin or lead alone, or the two together, can lead to realistic IGA/SCC
- Resin and lead test results indicate a need for limiting resin and lead ingress, and a need to test materials and configurations for resistance to these environments
- Aggressiveness of resin pollution likely associated with reduced sulfur species

Sulfate Dominated Environments

Pollutant	Sludge	MB	Ref	Duration of Test, h	Maximum CGR μm/h	Location of IGA/SCC	Comments
H_2SO_4		CE PB	11	3,120	0.01		
$NaHSO_4$+ oxygen		CE PB	11	2,976	0.29		
Na_2SO_4 + $(NH_4)_2SO_4$+NH_4Cl		CE PB	11	5,256	0.19		
H_2SO_4	Oxidizing	CE MB10	11	8,592	>0.12	At edges of TS and TSP	7 tubes cracked through wall at end of test
H_2SO_4+NaHSO4		W STMB	11	2,160	0.05	In eccentric TSP	IGA, not IGSCC
$Ca(SO)_4$+$Ca(OH)_2$		Ciemat MB	7	9,000	0	None	600TT and 690TT tested
Na_2SO_4 + low hydrazine	Non-oxidizing	CEA AJAX	10	8,000	0	None	Reduced sulfur species detected
Na_2SO_4 + high hydrazine	Non-oxidizing	CEA AJAX	10	8,000	0.04	TSP crevice (steam filled)	Reduced sulfur species detected
Various mixes of $(NH_4)_2SO_4$, Na_2SO_4, & NH_4Cl	Non-oxidizing & oxidizing	W STMB	12	1392-2784	0.007	Associated with wastage	Not typical of plant IGA/SCC
Na_2SO_4 + low hydrazine	Oxidizing	W STMB	16	1,584	0.01	In sludge at TTS	0.24 ppm Na in MUT, 1 grain IGP

Comments re Sulfate Dominated Environments

- Tests in acidic sulfates have caused some IGA/SCC, but often resulted in wastage rather than IGA/SCC
- Neutral sulfates with high hydrazine have caused realistic appearing IGA/SCC, especially at edges of steam blanketed areas in crevices
- Suspicion is that sulfates by themselves are not especially aggressive re IGA/SCC, and that main concern is reduced sulfur species
- Further definition of conditions under which sulfates + hydrazine lead to aggressive situations under heat transfer conditions seems needed
- Further definition of pHT at which sulfates cause IGA/SCC under heat transfer conditions seems needed

Halide and Organic Pollution

Pollutant	Sludge	MB	Ref	Duration of Test, h	Maximum CGR μm/h	Location of IGA/SCC	Comments
Halide Environments							
NaCl, $FeCl_2$, $FeCl_3$, HCl, NaF, NH_4F individually		CEA AJAX	1		0		
Organics							
Acetic+formic acids		CEA AJAX	1		0		
Acetic+formic acids+0.06 ppm Na		CEA AJAX	1		0		
Acetic+formic acids+ 1 ppm SO_4		CEA AJAX	1	3,840	0.008		

Comments re Halide and Organic Pollution

- Tests with halides are consistent with most seawater tests - no IGA/SCC
- Tests with organics indicate that they do not by themselves cause IGA/SCC
- Only when combined with sulfates did organics result in IGA/SCC

Tests with AVT or AVT + BA

Pollutant	Sludge	MB	Ref	Duration of Test, h	Maximum CGR μm/h	Location of IGA/SCC	Comments
None (AVT)	Oxidizing	CE MB5	5	8,328	0	None	No IGA/SCC - some minor pitting
AVT+BA	None	Ohi MB	9	11,408	0.014	Pre-crack in TSP	pH_T ~ 6 in crevice
AVT+BA	Various	Ohi MB & MHI MB	18	up to 8342	0.06	Pre-crack in TSP	pH_T ~ 6 in crevice, CGR decreased for high B/O ratio in the crack tip oxide

Comments re Tests with AVT and AVT + BA

- Tests have not been able to duplicate crack initiation
- Tests indicate that cracks, once initiated, continue to grow in near neutral crevices
    - Max growth rates - through wall in about 2 years
    - Min growth rates - through wall in about 12 years

Summary Comments

- MB tests show that several environments can cause realistic IGA/SCC of 600MA, e.g.,
  - Dilute caustic
  - Resins and resin extracts
  - Lead
  - Reduced sulfur from sulfate + hydrazine
  - Possibly, acidic sulfates
- MB tests show that oxidizing sludges have a strong effect on rate of wall penetration and on mode of attack (IGSCC vs. IGA)

Summary Comments (Cont.)

- This survey has barely scratched the surface - there is a wealth of information in the MB test results re influence of:
  - Tube material
  - Material condition
  - Sludge composition
  - Joint geometry
  - Etc.

Summary Comments (Cont.)

- Possible additional tasks include, for example:
  - Studying how 800NG compares to 600MA in all tests, to help evaluate which environments are most representative of real plant environments (i.e., exclude those that crack 800NG)
  - Developing and benchmarking crevice and IGA/SCC models using MB data. In this regard, conditions in MB tests are generally better defined and more amenable to quantification than in plants

Model Boiler Data

Name	**Organization**	**Ref.**	**Thot**	**Tcold**	**Tsat**	**Heat Flux**
			°F	**°F**	**°F**	**Btu/h-ft^2**
AJAX	CEA	1	626-635	622-631	554-563	95,200
STMB	W	12	615	595	532	60,000
Pot Boiler	CE	6	600	575	520-545	15,000
Model Boiler	CE	6	600-621		540-550	50,000-80,000
TSCA	CE	4	600		525	100,000
MB	Ciemat	8	617	563	535	
Sidesteam MB	Japan	9	608		522	92,000
Model Boiler	MHI	17	592	579	514	78,000
Model Boiler	Tokyo Univ.	19	644		554	92,000

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17	K. Onimura, et al., "Corrosion Resistance of Inconel 600 Under AVT Conditions," Mitsubishi Technical Bulletin No. 136, Nov. 1979
18	H. Takamatsu, et al., "IGA/SCC Crack Propagation Rate Measurements on Alloy 600 Steam Generator Tubing Using a Side Stream Model Boiler," 6th Symposium," Sixth Intl. Symp. on Env. Degr. of Mat. in Nuclear Power Systems - Water Reactors, p81, TMS, 1993
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Laboratory Experiments on Steam Generator Crevice Chemistry

P.V. Balakrishnan and Gina L. Strati

Component Life Technology

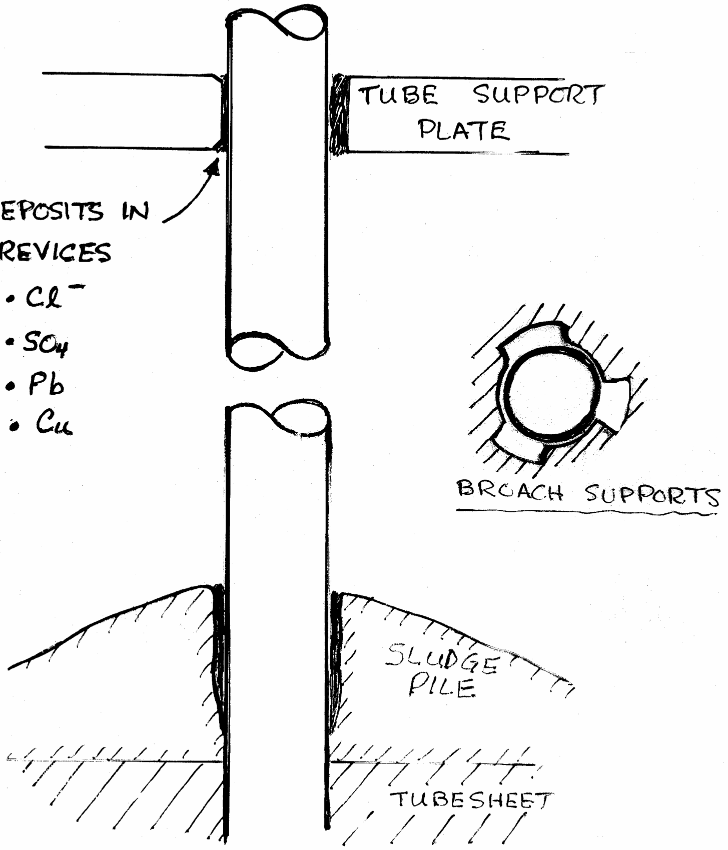
Atomic Energy of Canada Limited

Chalk River Laboratories, Chalk River, Ontario

- **To understand how crevice chemistry affects the performance and health of steam generators by relating corrosion behavior with crevice chemistry.**

Crevice Chemistry

- Crevices formed by tube-to-support gaps (~ 10's of m meters) and by tube-to-sludge pile, or tube-to-deposit gaps
- Can concentrate impurities in feedwater by factors up to 10^6 (from ppb to % levels)



Processes Affecting Crevice Chemistry

- ***Redox*** **conditions**
- ***Adsorption*** **behavior**
- ***Volatilization***

Hideout and Hideout Return

- **Chemistry in the crevice is determined from "hideout return" data.**
- **"Hideout" – concentration of solute species with boiling in a flow restricted location ⬇ heat flux driven**
- **"Hideout Return" – release of these concentrated solutes ⬇ diffusion controlled**

Objectives

- To study hideout and hideout return behavior of representative simple and complex solutes and the effect of these processes on the chemistry in the crevice.

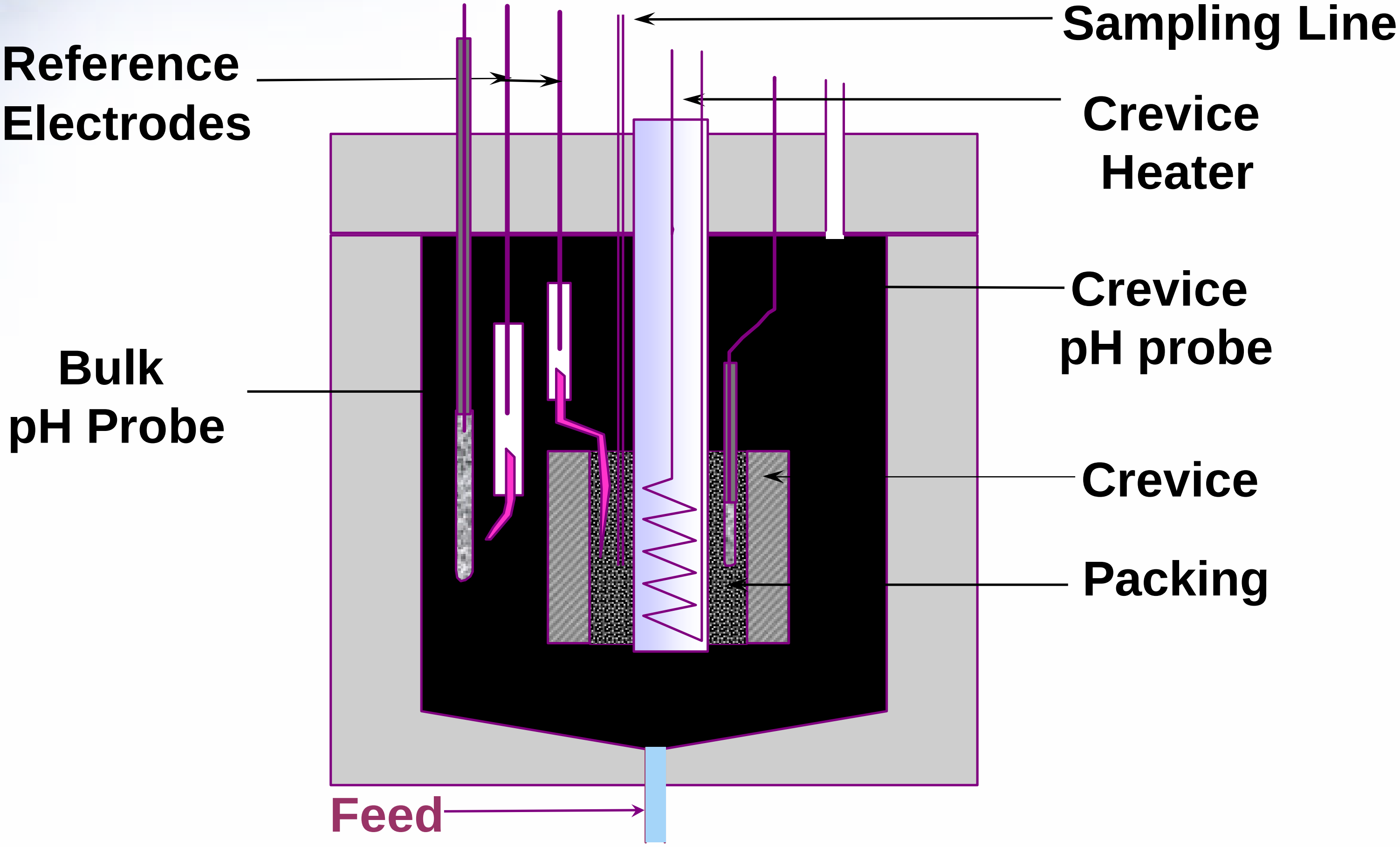
Experiments

- **Hideout/Hideout Return**
  - **Hideout – concentration of solute species with boiling in a flow restricted location.**
    - **⇒ Simulate operational conditions.**
  - **Hideout Return – release of these concentrated solutes on “turning off” heat flux**
    - **⇒ Simulate shut down and layup conditions.**
- **Crevice sampling**
  - **Samples withdrawn directly from the heated crevice.**

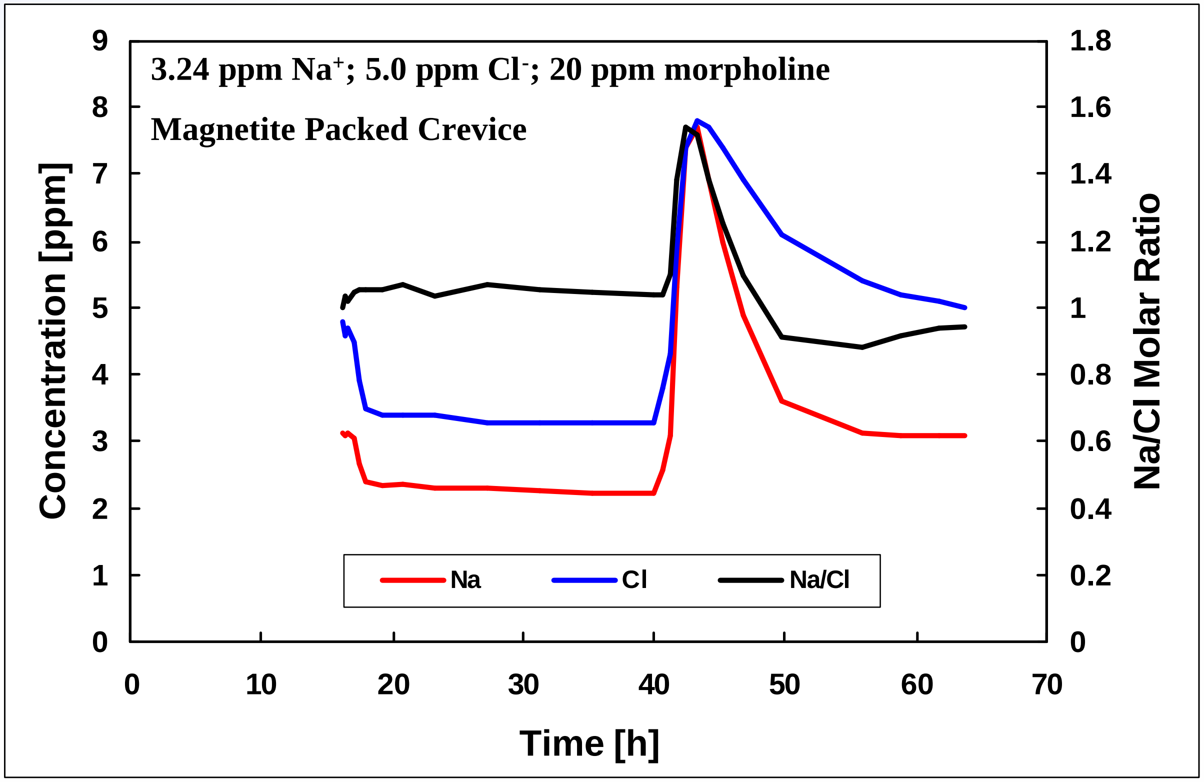
Systems

- Common solute species found in SG such as Na^+ and Cl^- as well as more complex chemical species including Ca^{+2}, Mg^{+2} and SO_4^{2-} .
- Replenished autoclave system:
  - Secondary Side T: 265 °C (509°F) (CANDU 6)
    281 °C (538°F) (ACR)
  - Crevice: packed with magnetite, diamond powder, or carbon cloth and sized to accommodate probes.

Replenished Autoclave System



Typical Hideout/Hideout Return Profile



- Non-deaerated conditions to simulate shutdown conditions with ingress of oxygen from make-up water.

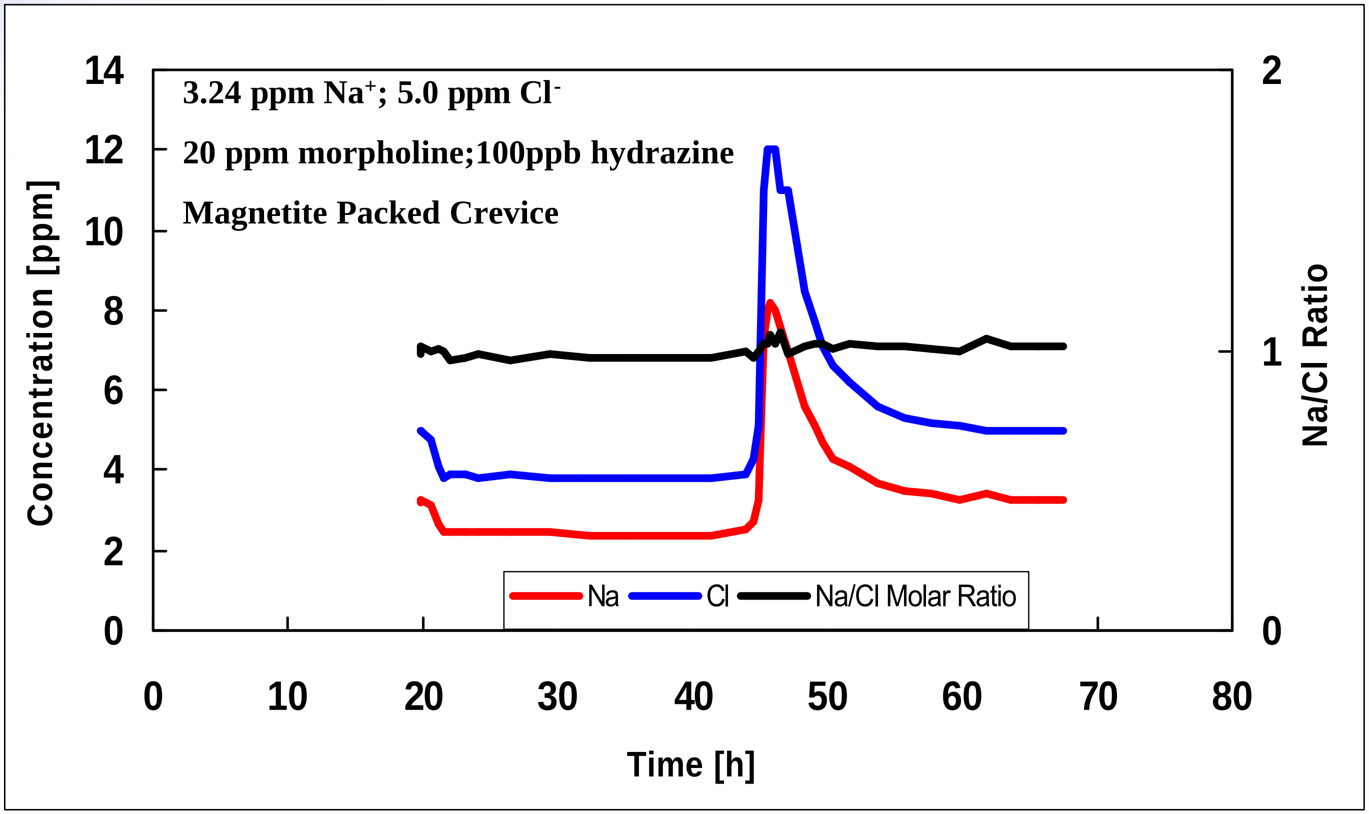
Hideout/Hideout Return

- **SG Crevice chemistry is usually inferred from hideout return data.**
- **Possibility of determining incorrect crevice chemistry conditions:**
  - **Ex: Na:Cl > 1 ⬇ alkaline crevice**

    As Cl returns (Na:Cl < 1) ⬇ acidic crevice

    Reality may be overall neutral

Hideout Return Profile w/ Hydrazine



- De-Aerated Conditions → non-oxidizing

Hideout/Return with Hydrazine

- With Hydrazine addition, Na^+ and Cl^- return together.
- Under non-deaerated conditions, Na^+ and Cl^- return at different rates due to segregation of anodic and cathodic reaction sites.
- Determined need to add hydrazine in excess of O_2
- To use hideout return as basis for molar ratio control in SG, the bulk H_2O must be non-oxidizing

Processes Affecting Crevice Chemistry

- Redox conditions
- Volatilization ↓ Cl^-
- Adsorption behavior ↓ SO_4^{2-}

Chloride Volatility Experiments

Run #	Feed (Na/Cl)	Hideout (Na/Cl)	Hideout Return (Na/Cl)
161	1	0.798	1.23
165	1	0.788	1.20
167	0.5	0.257	0.73
168	1	0.882	1.21
170	1	0.944	1.17
172	1	0.762	1.46

- NaCl with addition of morpholine and hydrazine
- Low concentrations, high heat flux, smaller crevice

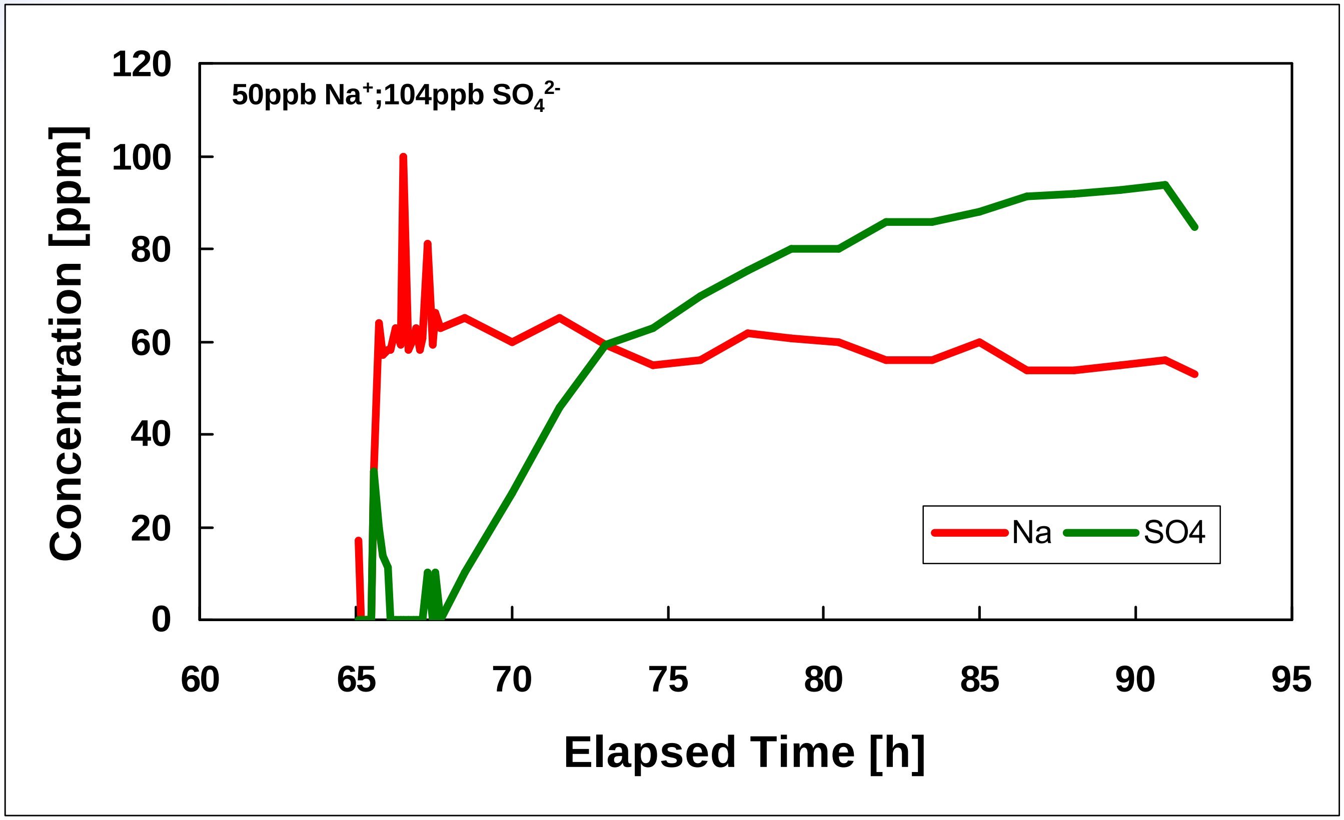
Characteristics of Chloride Volatility

- an excess of Cl^- in the hideout portion of the profile (Na/Cl < Feed)
- an excess of Na^+ in the hideout return portion of the profile (Na/Cl > Feed)
- a distinct peak in the Na/Cl ratio profile during hideout return even with addition of hydrazine to the chemistry.

Processes Affecting Crevice Chemistry

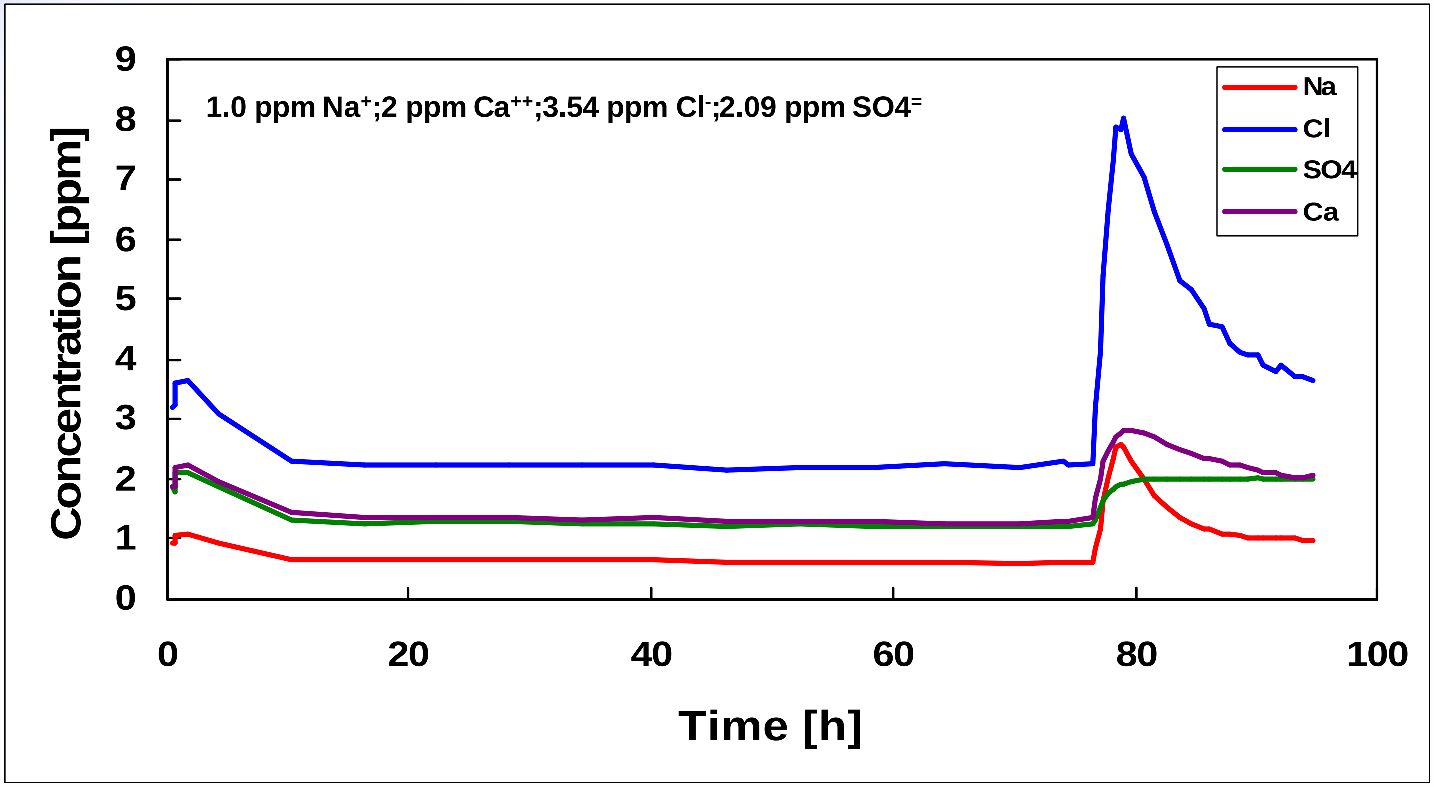
- **Redox conditions**
- **Volatilization ⬇ Cl^-**
- **Adsorption behavior ⬇ SO_4^{2-}**

Sulphate Adsorption on Magnetite



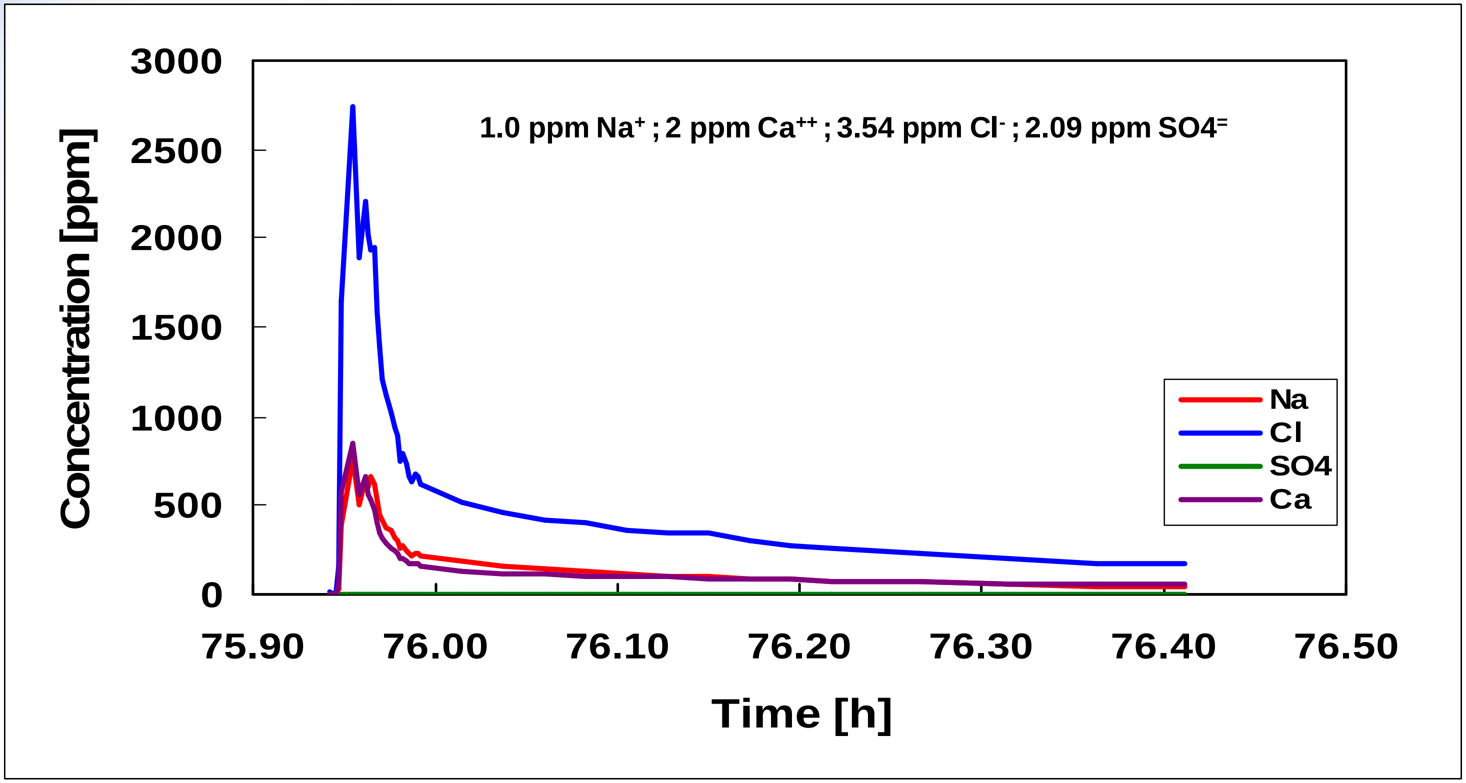
- Solution pumped through a magnetite column (270°C)

Hideout/Return of Complex Solutes



- Indicates incomplete return of Ca^{2+} and SO_4^{2-}

Crevice Sampling



- Lower than expected concentrations of SO_4^{2-} and Ca^{2+}

Crevice Sampling Results

Run #	Na^+[ppm]		Ca^{2+}[ppm]		Cl^- [ppm]		SO_4^{2-} [ppm]	
	Peak	Lost	Peak	Lost	Peak	Lost	Peak	Lost
166	2208 *2208	N/A	—	—	1760 *1700	N/A	2200 *2318	N/A
171	—	—	569 *569	N/A	928 *1007	N/A	—	—

*Expected concentrations [ppm] normalized to Na^+ or Ca^{2+}

- All species are recovered during crevice sampling

Crevice Sampling Results

Run #	Na^+[ppm]		Ca^{2+}[ppm]		Cl^- [ppm]		SO_4^{2-} [ppm]	
	Peak	Lost	Peak	Lost	Peak	Lost	Peak	Lost
169	8152 *8152	N/A	9.96 *6114	6104 †304	10,000 *10,820	N/A	1840 *17,038	15,198 †316
1	263 *263	N/A	276 *526	250 †12.45	939 *931	N/A	2.0 *550	548 †13.67
9	766 *766	N/A	858 *1532	674 †33.6	2737 *2712	N/A	4.6 *1601	1596 †33.2
11	914 *914	N/A	121 *914	793 †39.5	1690 *1618	N/A	17 *1910	1893 †39.4

*Expected concentrations [ppm] normalized to Na^+

†Number of equivalents lost based on expected value

- Ca^{2+} and SO_4^{2-} “missing” in equivalent amounts ⇒ precipitation

Crevice Sampling Results

Run	Na^+ [ppm]		Ca^{2+} [ppm]		Mg^{2+} [ppm]		Cl^- [ppm]		SO_4^{2-} [ppm]	
	Peak	Lost	Peak	Lost	Peak	Lost	Peak	Lost	Peak	Lost
177	300 *300	N/A	-	-	11.6 *300	288 †23.7	1320 *1362	N/A	-	-
2	122 *122	N/A	119 *122	N/A	2.9 *122	119 †9.8	398 *404	N/A	16 *482	466 †9.7
10	327 *327	N/A	259 *259	N/A	6.4 *359	352 †29	1140 *1082	N/A	20 *1292	1272 †26.5
4	384 *384	N/A	7.82 *192	184 †9.2	7.07 *192	185 †15.2	359 *338	N/A	404 *1554	1150 †24

*Expected concentrations [ppm] normalized to Na^+

†Number of equivalents lost based on expected value

- •Evidence for $Mg(OH)_2$ precipitation in run 177
- •Mg^{2+} and SO_4^{2-} “missing” in equivalent amounts ⬇ precipitation

Crevice Chemistry

- Simple solute combinations like NaCl or $CaCl_2$ are completely recovered during crevice sampling ⇒ no precipitation
- Surprisingly, in presence of Ca^{2+}, Mg^{2+} and SO_4^{2-} are absent in equivalent amounts which is suggestive of $MgSO_4$ precipitation.
- With excess SO_4^{2-}, both Ca^{2+} and Mg^{2+} are “missing”
  - $CaSO_4$ and $MgSO_4$ precipitation occurs
- Models predict $CaSO_4$ and $Mg(OH)_2$ precipitation
  - Propose Mg^{2+} and SO_4^{2-} co-precipitate as part of another complex

Conclusions

- **Crevice sampling experiments show:**
  - **precipitation of $Mg(OH)_2$, $CaSO_4$**
  - **$Mg_x(SO_4)_y$ complex precipitates preferentially over $CaSO_4$ unless there is sufficient SO_4^{2-} for both to precipitate**
- **Hideout return data suggests:**
  - **chloride volatility occurs in the crevice**
  - **sulphate adsorption to magnetite occurs**

Conclusions

- Crevice sampling gives a good approximation of crevice solution composition.
- Crevice chemistry predictions from hideout/return data depend on the chosen model ⬇ verify thermodynamic database and update models
- Caution advised in deducing crevice chemistry from hideout/return data ⬇ analysis should be done carefully and under reducing conditions.

Acknowledgements

- Henry Searle and Seanna Hoendermis for their technical assistance
- R. L. Tapping, Manager

AECL

The hideout and return in a sludged Ringhals TSP crevice

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J. Chen, Studsvik Nuclear AB
P. Gillén, Studsvik Nuclear AB

Studsvik®Nuclear

Ringhals

Background

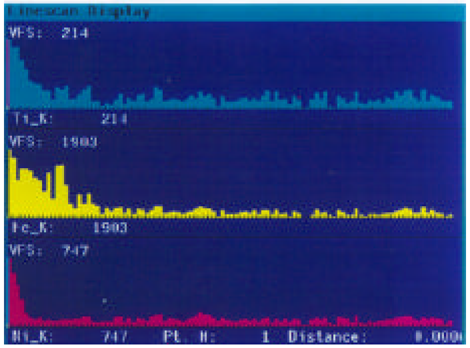
Data from two tests performed with TiO_2 addition:

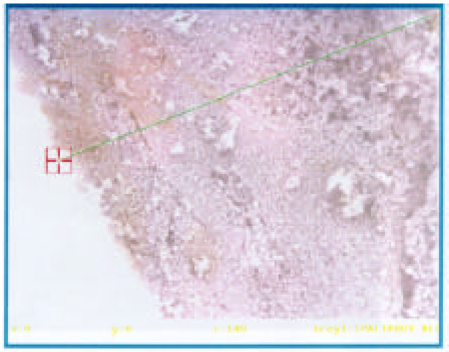
1) In lab test on retired tube/tubesheet intersections from EDF
2) In field test on Ringhals unit 3 (now retired SG's) gave similar information: Little penetration of Ti^{4+} into the packed crevices.

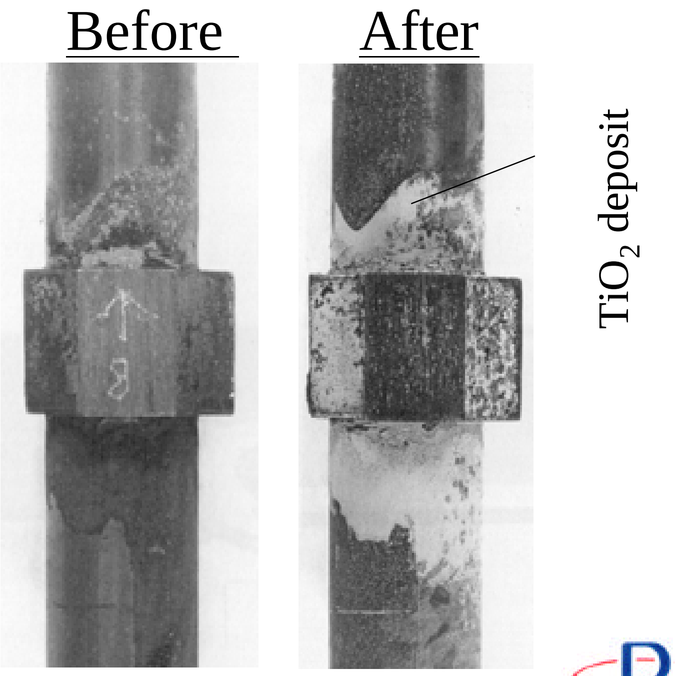
Question:

No impurities are capable to penetrate the tube/tube sheet intersection in sister unit 4?

Ti penetration tests on a sludged TSP crevice



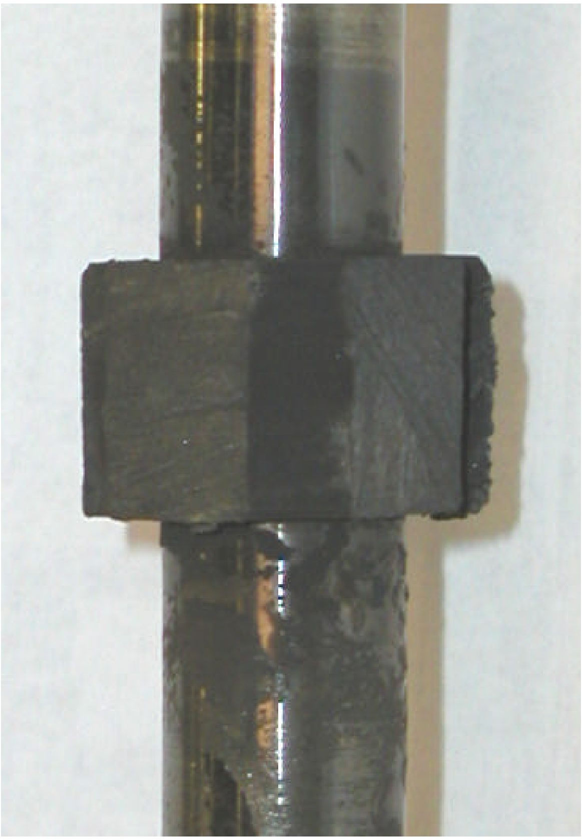




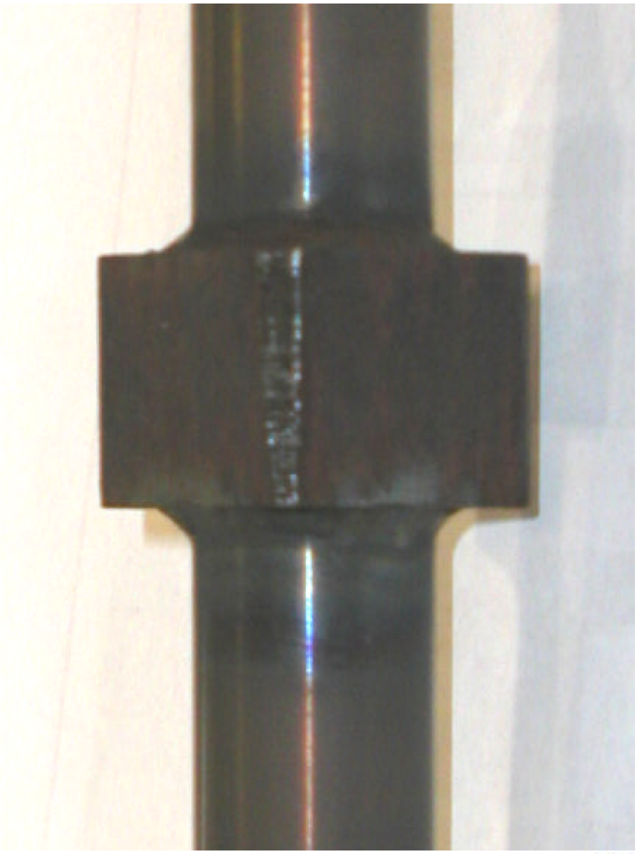
This presentation

- To show if/how sodium penetration occurs in a sludged TSP crevice
- To show the differences in penetration behavior among a real sludged TSP crevice and a fully sealed TSP crevice and metal-net packed TSP crevice
- To give a quantitative estimation, if possible.

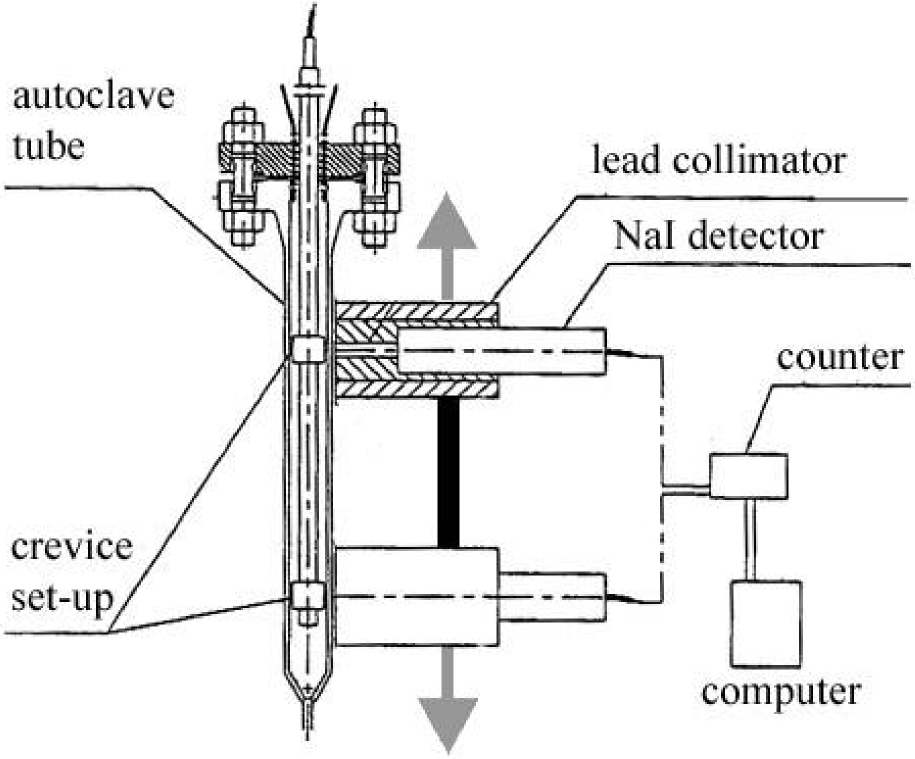
Ringhals 3



Dummy

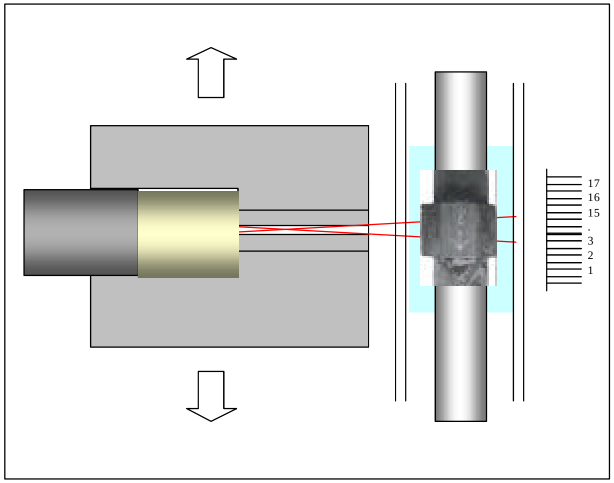


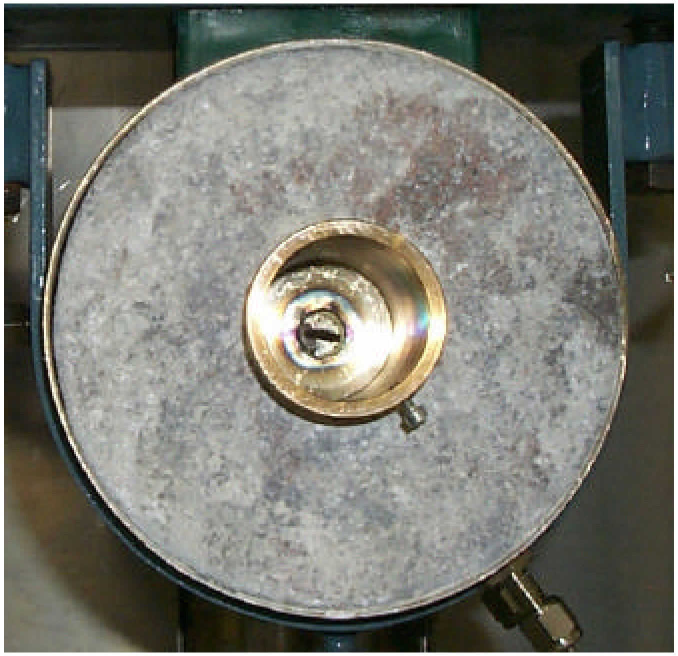
Autoclave setup



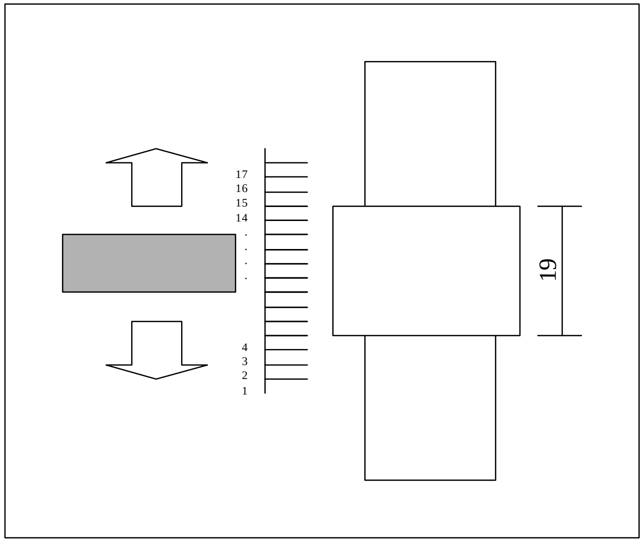
Slit

Dimension: 2 x 10 mm



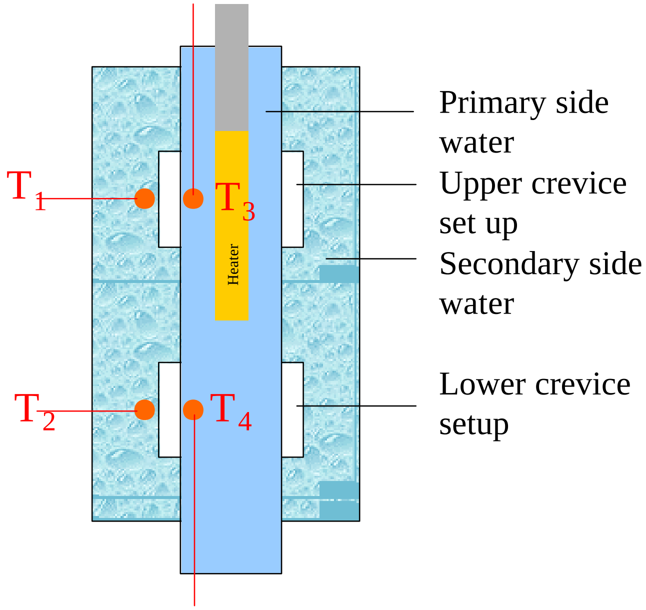


γ-scanner



Control systems

- Accurate control over heat transfer over crevices
- Computerized γ-scanning over crevices
- Water conductivity monitoring



Examination on

Sludged Ringhals TSP

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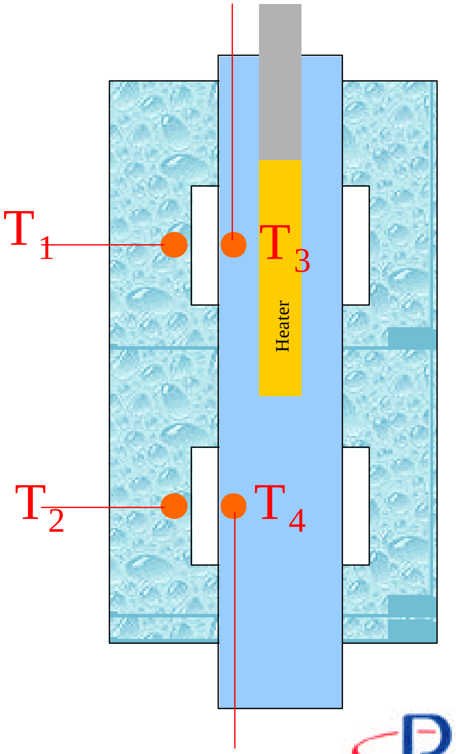
Ringhals

Test conditions

- [Na]: 3.37 ppm (by weight)
- Activity at start: 55 MBq
- Heating: 1.3 kW at 100% FHP
- Temp. at TSP:

Heating power (%)	T_3 (°C)	T_1 (°C)	T_3-T_1 (°C)
0	249.6	245.8	3.8
25	307.8	286.0	21.7
30	311.3	286.0	25.4
35	315.6	285.8	29.8
40	318.6	285.8	32.8



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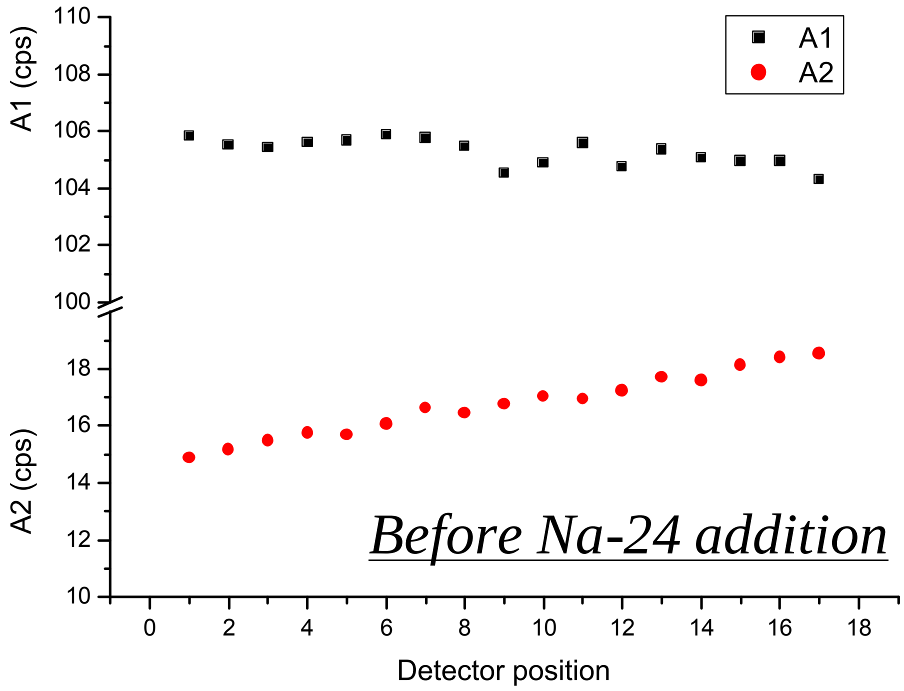
Activity of as-received Ringhals TSP sample

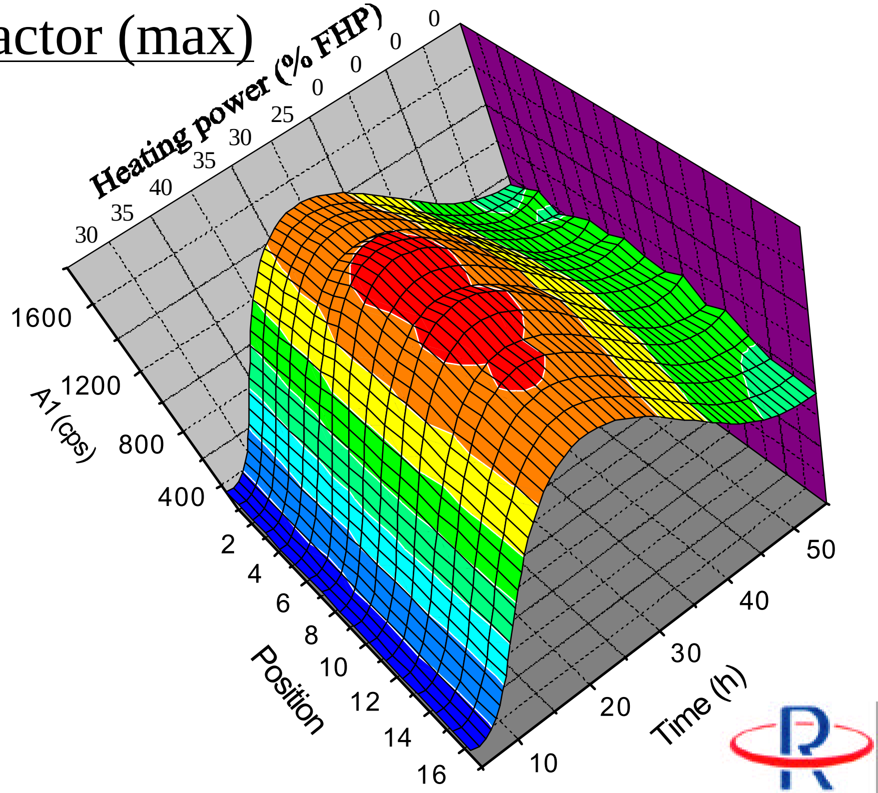


Before Na-24 addition

Hideout and return at the crevice

<u>Estimated concentration factor (max)</u>

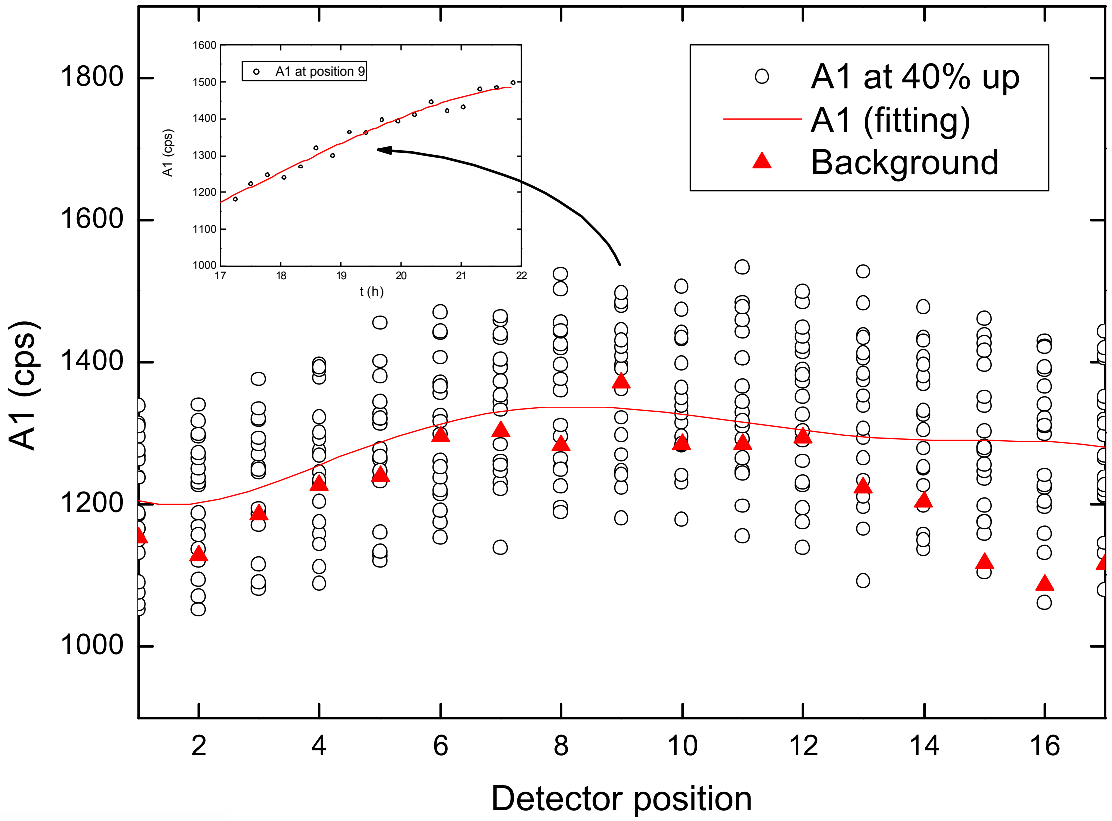
~3000x or [10 g$_{(Na)}$/L]*



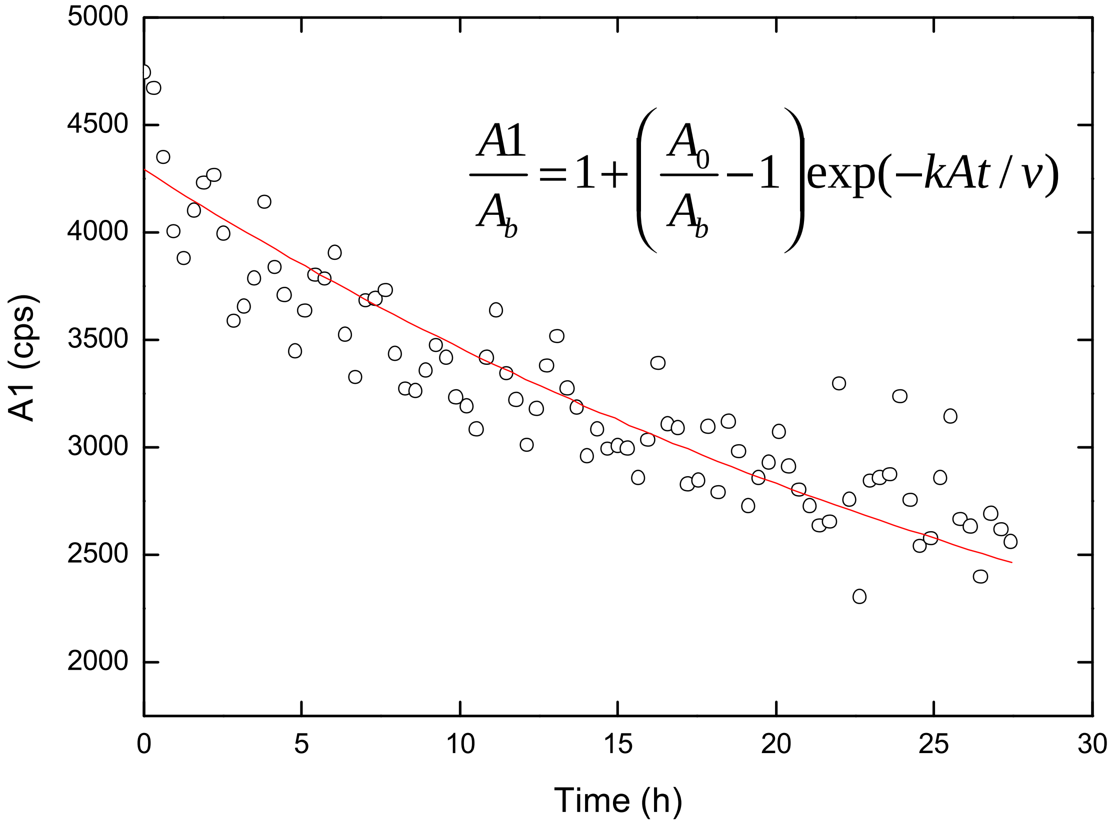
* assuming $V_1/V_c = 1000$

$$C_c = \frac{m_c}{V_c} = C_1 \frac{V_1}{V_c} \left(\frac{I_2}{I_1} - \frac{k_2}{k_1}\right)$$

Activity build-up in the crevice



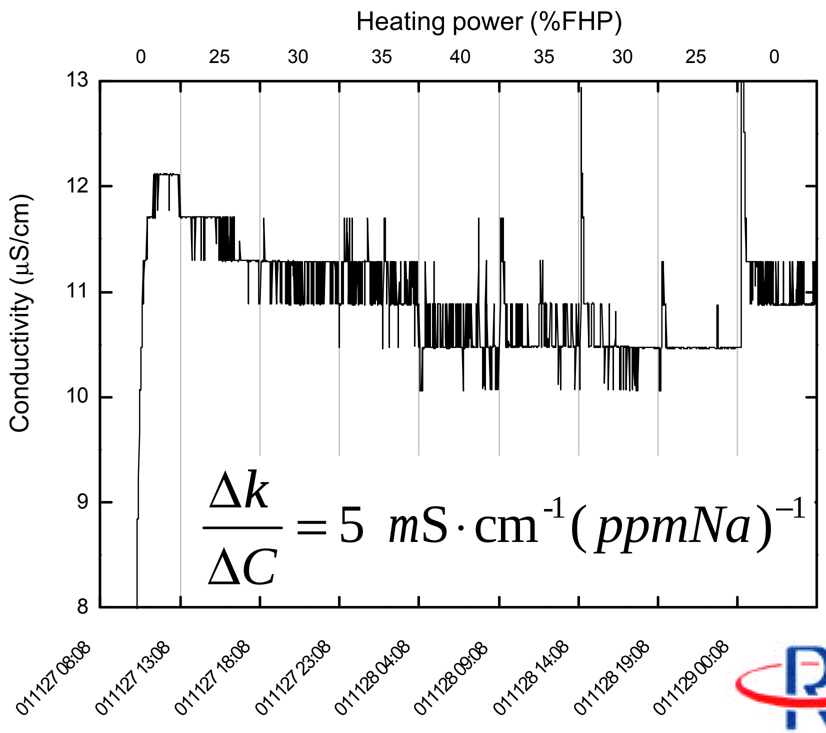
The return



$$\frac{A1}{A_b} = 1 + \left(\frac{A_0}{A_b} - 1 \right) \exp(-kAt / v)$$

Water conductivity change during hideout and return

- It decreases with increasing heating
- It increases when the heating is off.



$$\frac{\Delta k}{\Delta C} = 5\ m\mathrm{S} \cdot \mathrm{cm}^{-1} (ppmNa)^{-1}$$

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Estimation of Na concentration in the crevice

$$C_c = \frac{m_c}{V_c} = C_1 \frac{V_1}{V_c} \left(\frac{I_2}{I_1} - \frac{k_2}{k_1} \right)$$

C_1	the original bulk concentration of Na (together with Na-24)
V_1/V_c	the ratio of the volume detected by the γ-detector and the liquid volume in the crevice, from where Na-24 nuclides contribute to the intensity as measured by the γ-detector
I_2/I_1	the ratio of the intensities, as measured after and before boiling, by the γ-detector
k_2/k_1	the conductivity ratio, as measured after and before boiling, of the bulk water

Conclusions

- Na-24 nuclides were seen to enter the sludged Ringhals TSP crevice and to accumulate in the crevice under boiling
- The Na-24 accumulation increases with increasing heating power on the crevice

Conclusions (cont.)

- A slow return of the Na-24 tracer to the water was seen when the heating on the sludged Ringhals TSP crevice sample was turned off.

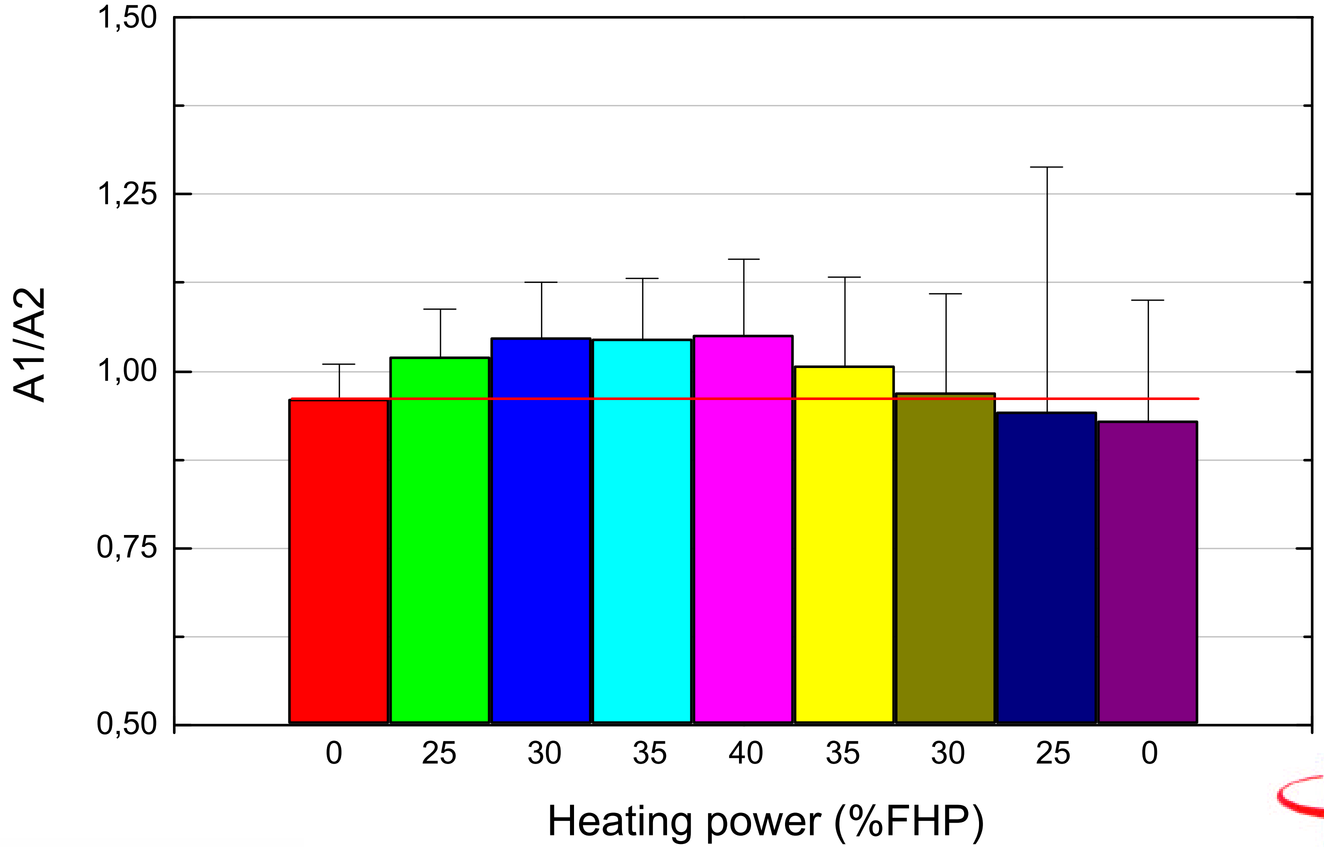
Conclusions (cont.)

- Additional amount of Na-24 nuclides were seen in the regions immediately outside of the sludged Ringhals TSP crevice, especially in the upper region of the crevice.

Examination on

A dummy TSP

Dummy crevice test



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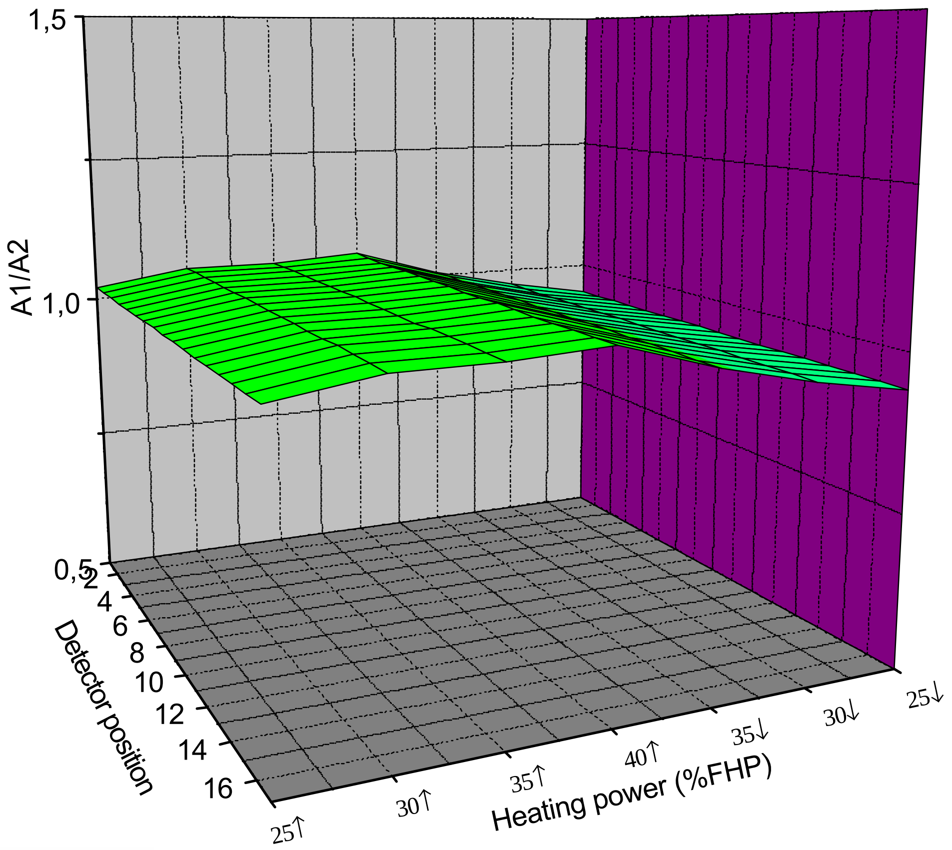
Axial profile of the activity ratio



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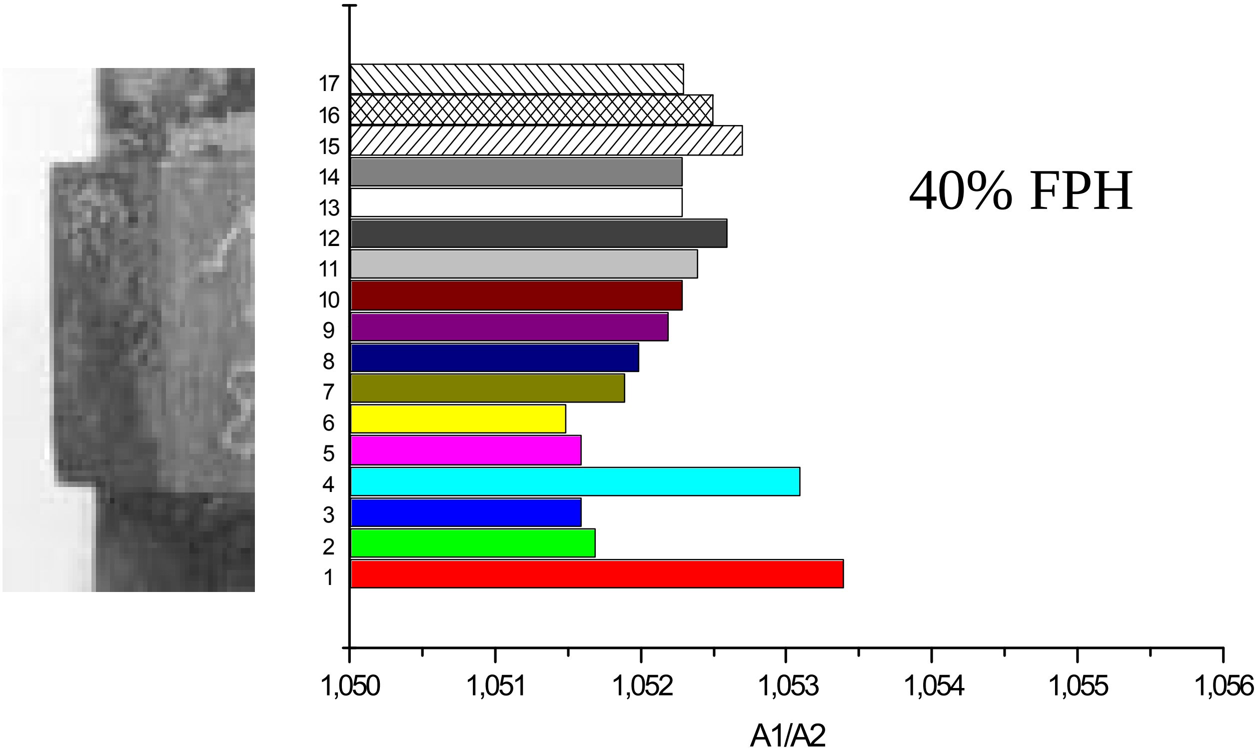
Ringhals

Axial profile of the activity ratio



40% FPH

Studsvik® Nuclear

Ringhals

Conclusions for the dummy crevice

- There is a slight activity buildup around the dummy crevice when heated (the amount is negligibly small)
- At the upper mouth location, there is a slightly increased activity (the amount is negligibly small)

Examination on

A metal-net filled TSP crevice

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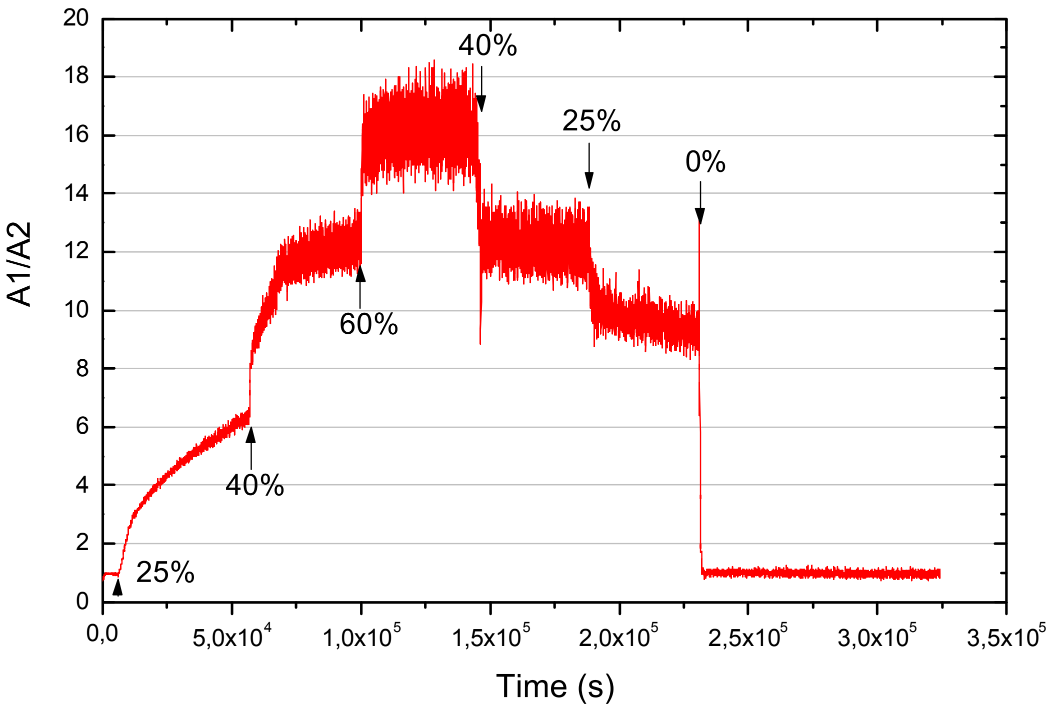
Hideout and return of a metal-net filled TSP crevice



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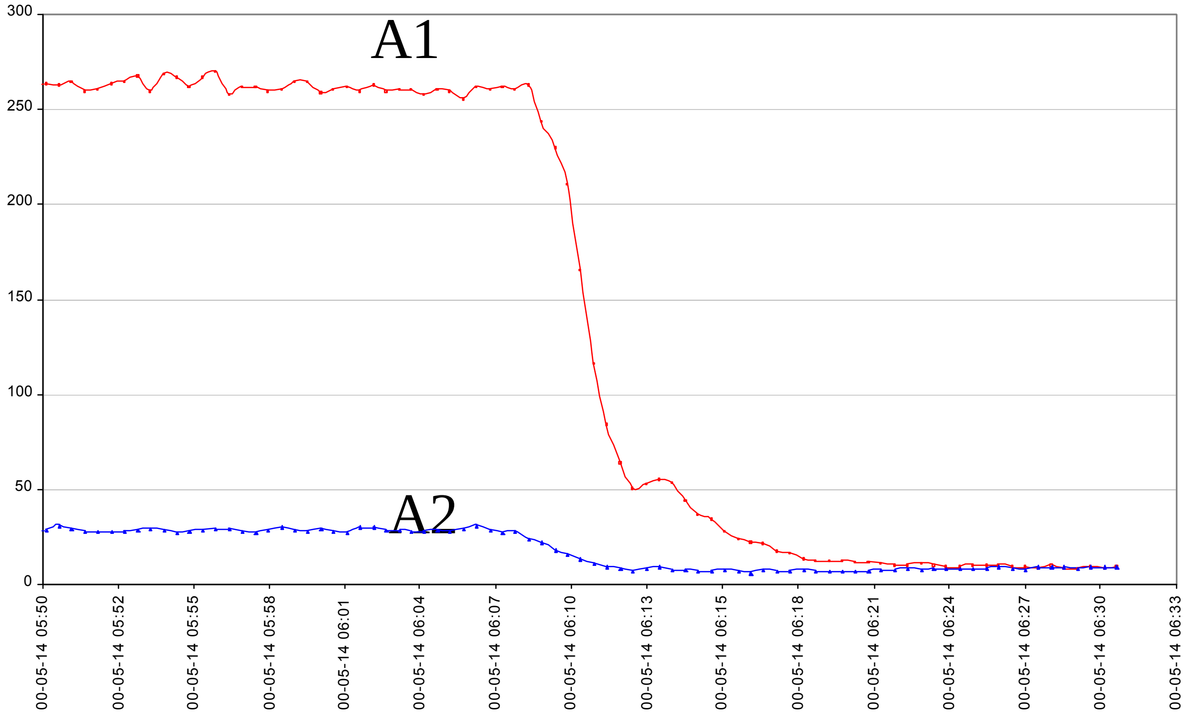
Rapid return at zero power



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Sludged TSP crevice
vs.
metal-net filled crevice

- Much slower activity buildup and return in the sludged crevice

Experimental study of concentrated solutions containing sodium and chloride pollutants in SG flow restricted areas

D. You, S. Lefèvre, D. Féron, F. Vaillant*

CEA-Saclay, Laboratoire d'Étude de la Corrosion Aqueuse, France
* EDF-Les Renardières, DRD/EMA, France

Heated crevice seminar, Argonne Guest House, Argonne, Illinois, USA
October 7 – 11, 2002

Heated crevice seminar, Argonne Guest House, Argonne, Illinois, USA
October 7 – 11, 2002

Content

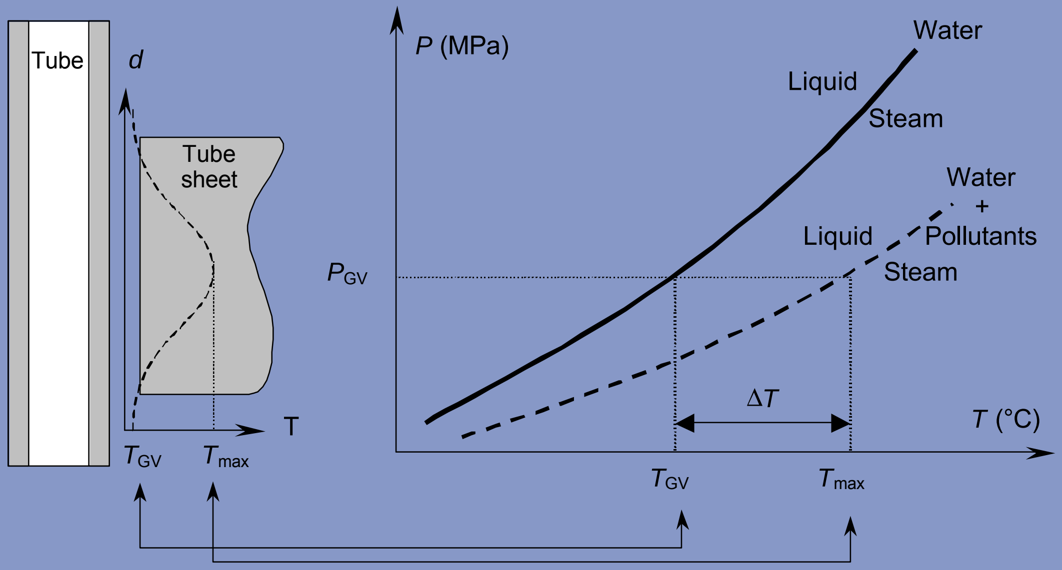
- Background & Methodology
- Description of the EVA device and experiments
- Results: simple aqueous solutions (results with more complex aqueous phases have been presented at Water Chemistry'98)
  - NaOH
  - NaCl
- Conclusive comments

Background

- S.G. tube degradations are mainly associated with IGA/IGSCC in restricted areas where hideout occurs
- Caustic has been considered as the “only” corrosive pollution
  - Plant experience with boric acid
  - Hideout return data

- Crevice chemistry appears more and more complex
  - Tube examinations : Si, Al, Ca, Mg, Fe, ... are the predominant species
  - Plant “experiences” with other corrosive species (lead, resins, ...)

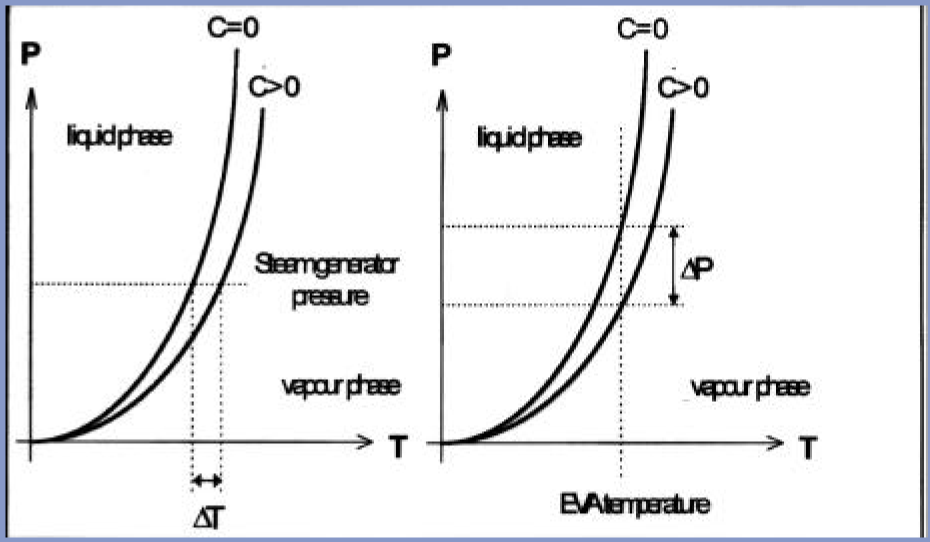
Liquid/vapor equilibrium in crevices



In S.G., a concentrated liquid phase is stable when its vapour pressure is equal to the secondary pressure.

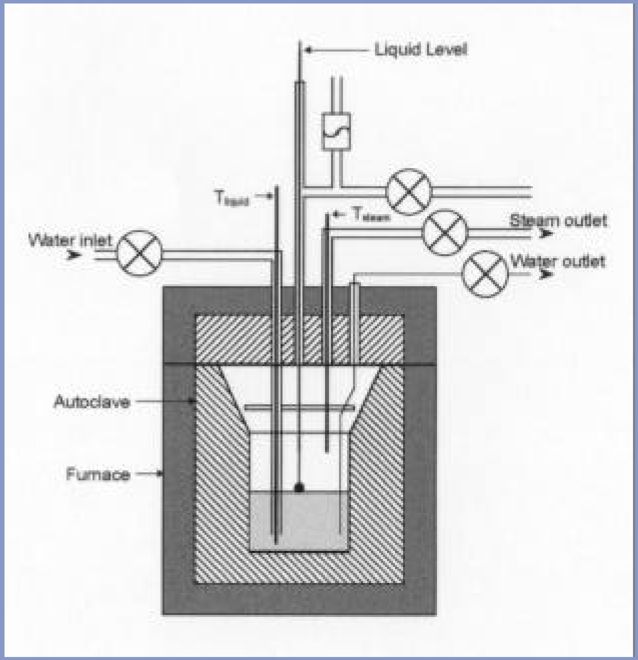
Methodology

- Hideout processes at constant pressure and temperature
  - Constant pressure: steam generator
  - Constant temperature: easier to investigate chemical and phase equilibrium
  - Thermodynamically, results are the same

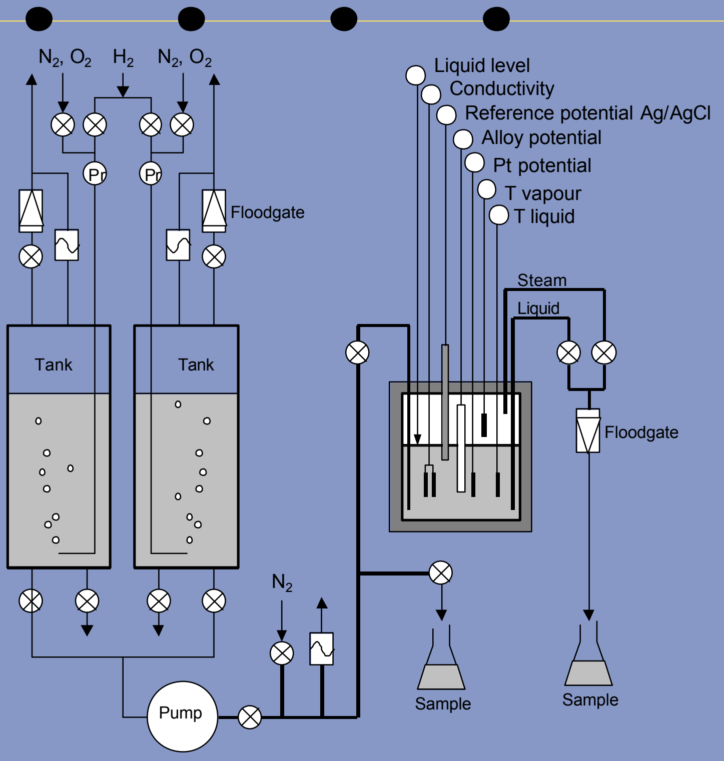


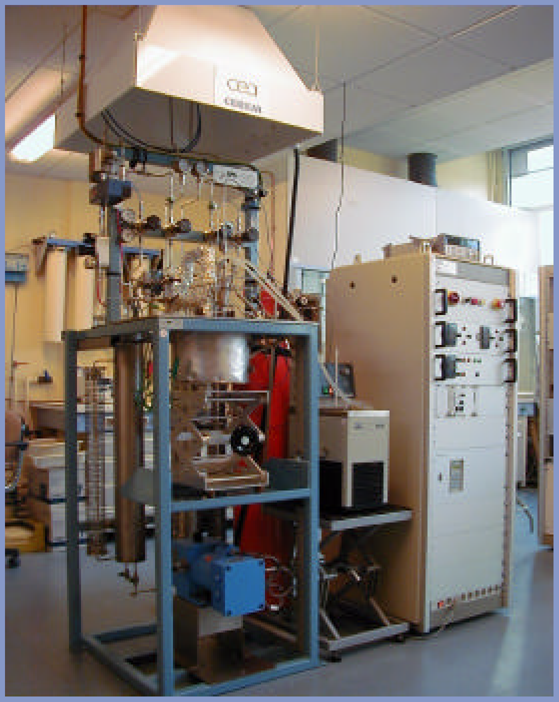
EVA facility

- Device made to study isochoric and isotherm concentration processes by evaporation of an homogeneous aqueous solution in pseudo-equilibrium conditions with its vapour phase
    - Constant liquid phase volume
    - Maximum temperature: 320°C
    - Feed flow rate: 30g.h^{-1}
    - Maximum pressure: 15 MPa

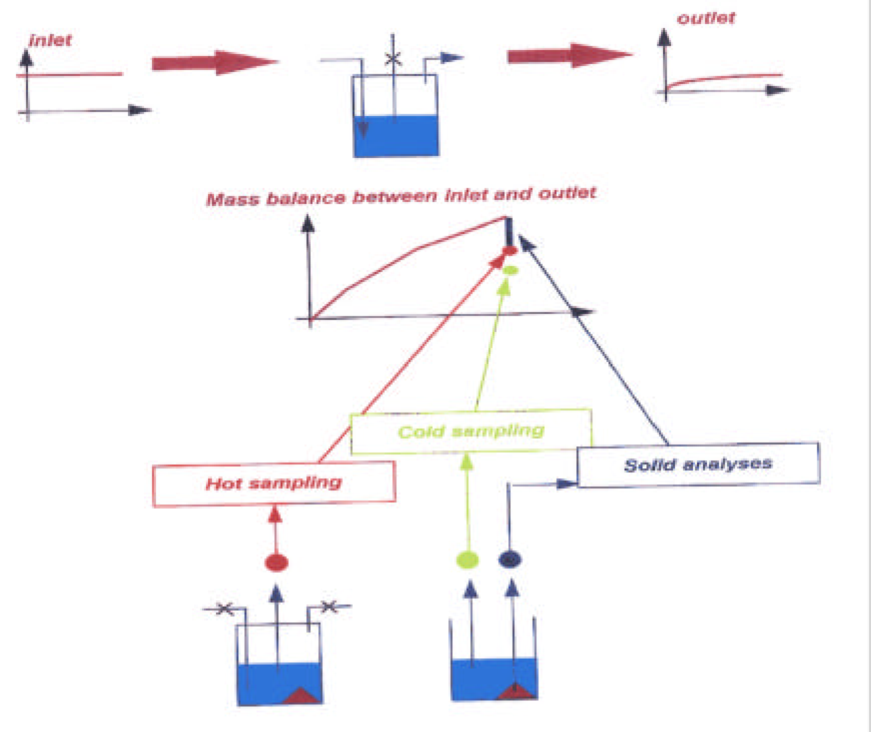


EVA facility (cont'n)





Test methodology



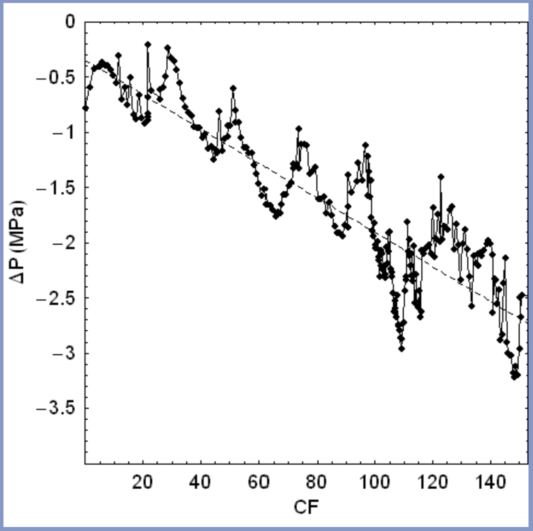
1- Inlet and outlet analyses

2- Mass balance calculations

3- Sampling at the end of
   1. Hot liquid phase (or a hideout return phase)
   2. Cold liquid phase
   3. Solid phases

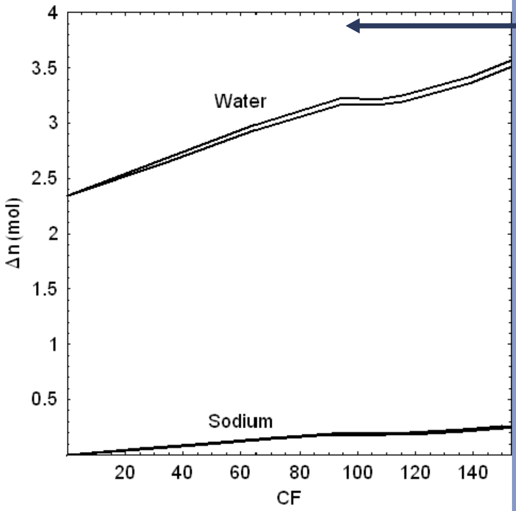
NaOH results (1)

- 0.05 mol.Kg^{-1} in the feed water
- 310°C
- Decrease of the internal pressure during the hideout test (2.5 to 3.0 MPa)
- Hideout return phase by pure feed water and continuous sampling of the liquid water phase at 310°C (return to the initial internal pressure after renewing 0.4 the EVA cell volume)

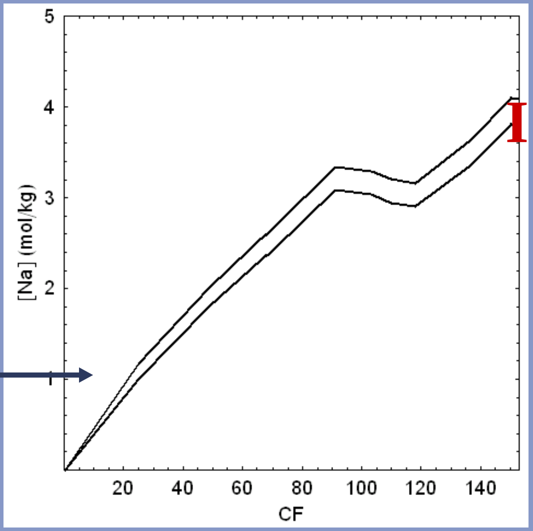


Decrease of the internal pressure during the caustic EVA hideout test

NaOH results (2)



Increase of caustic and water masses means that the density of the liquid caustic phase increases (up to 70%)

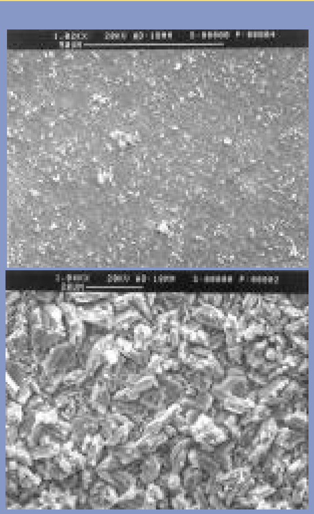


Evolution of the caustic concentration inside the EVA device during the caustic hideout test: good agreement with the sampling of the liquid phase at the end of the hideout period

NaOH results (3): after test examinations

Vapour phase

Liquid phase



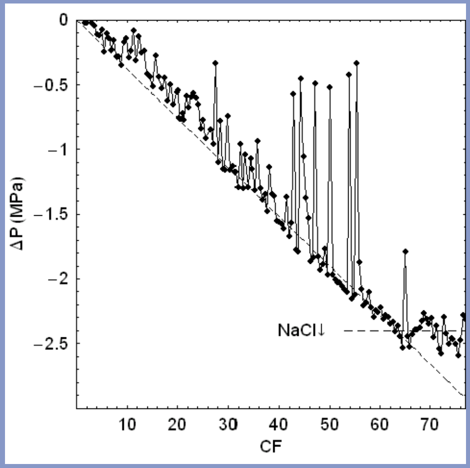
Hydrated iron and nickel silicate
$(Ni,Fe)_3Si_2O_5(OH)_4$

Hydrated iron and nickel silicate
$(Ni,Fe)_3Si_2O_5(OH)_4$

View of the alloy 600 coupon exposed during the caustic tests in EVA device

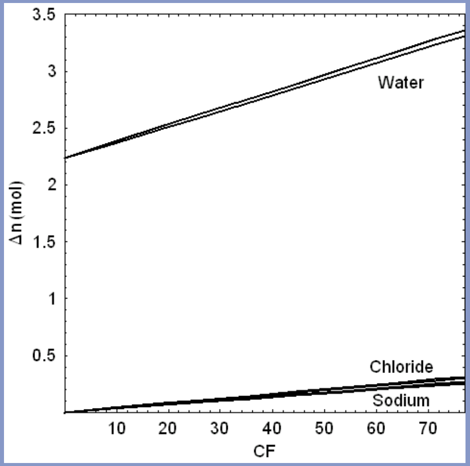
« NaCl » results (1)

- 0.09 mol.Kg^{-1} of sodium and 0.10 mol.Kg^{-1} of chloride in the feed water
- 310°C
- Decrease of the internal pressure during the hideout test to 2.5 Mpa and then constant
- No hideout return phase, neither hot sampling (precipitation of NaCl in the sampling line).



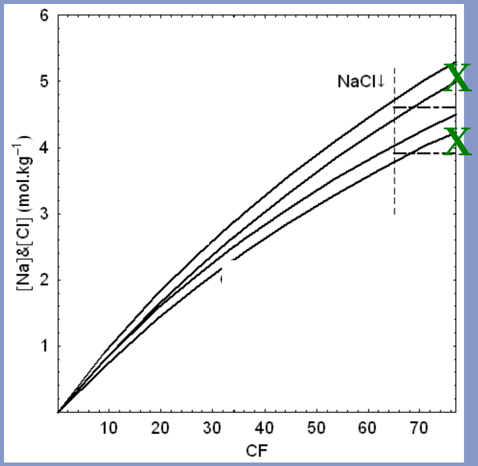
Evolution of the internal pressure during the NaCl pollution test

NaCl results (2)



Increase of water and sodium masses during the "NaCl" hideout test (density of the liquid phase: +85%)

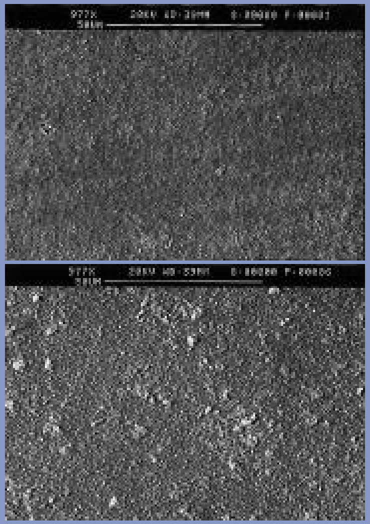
Evolution of the chloride and sodium concentrations inside the EVA device during the "NaCl" hideout test.
Agreement between the mass balances



NaCl results (3):
after test examinations

Vapour phase

Liquid phase



Hydrated iron and
nickel silicate
$(Ni,Fe)_3Si_2O_5(OH)_4$

Hydrated iron and
nickel silicate
$(Ni,Fe)_3Si_2O_5(OH)_4$

View of the alloy 600 coupon exposed during the NaCl tests in EVA device

Comments (1)

- Thermodynamic properties of not only soluble species but also of the solvent as to be considered (increase of the density with hideout)

- Stable aqueous phases with a 40°C superheat (4.4 MPa decrease of boiling pressure):
  - Not “NaCl”: only 2.5 MPa (25°C superheat)
  - Pollutants presented at Water Chemistry’98 presented even lower pressure decrease (lower superheat)
  - Only NaOH aqueous phase leads to 4.4 MPa decrease of the boiling pressure

Comments (2)

- Deposits
  - Liquid and vapour phases
  - Same hydrated iron and nickel silicate with caustic and sodium chloride, which focus on the interactions with impurities (Si) and nickel base alloy
- Hideout return
  - Complete return when aqueous solution (caustic)
  - *Not related with pollutants when deposits (results presented at Water Chemistry'98)*
  - Hideout return is not the opposite of hideout

Conclusion

- EVA facility is a powerful and simple device to study crevice chemistry (hideout and hideout return)
- During the performed hideout tests and up to now, only caustic solution is thermodynamically stable under high superheat (40°C)
- With other pollutants as NaCl, *boron, silicate or aluminium (Water chemistry'98),* maximum super heat of 25°C has been obtained.
- Hideout return is not the opposite of hideout when a solid phase has precipated during hideout.

Some Effects of Steam Generator Deposits on Crevice Chemistry

Heated Crevice Seminar
Argonne IL
October 2002

C.R. Marks
Dominion Engineering, Inc.

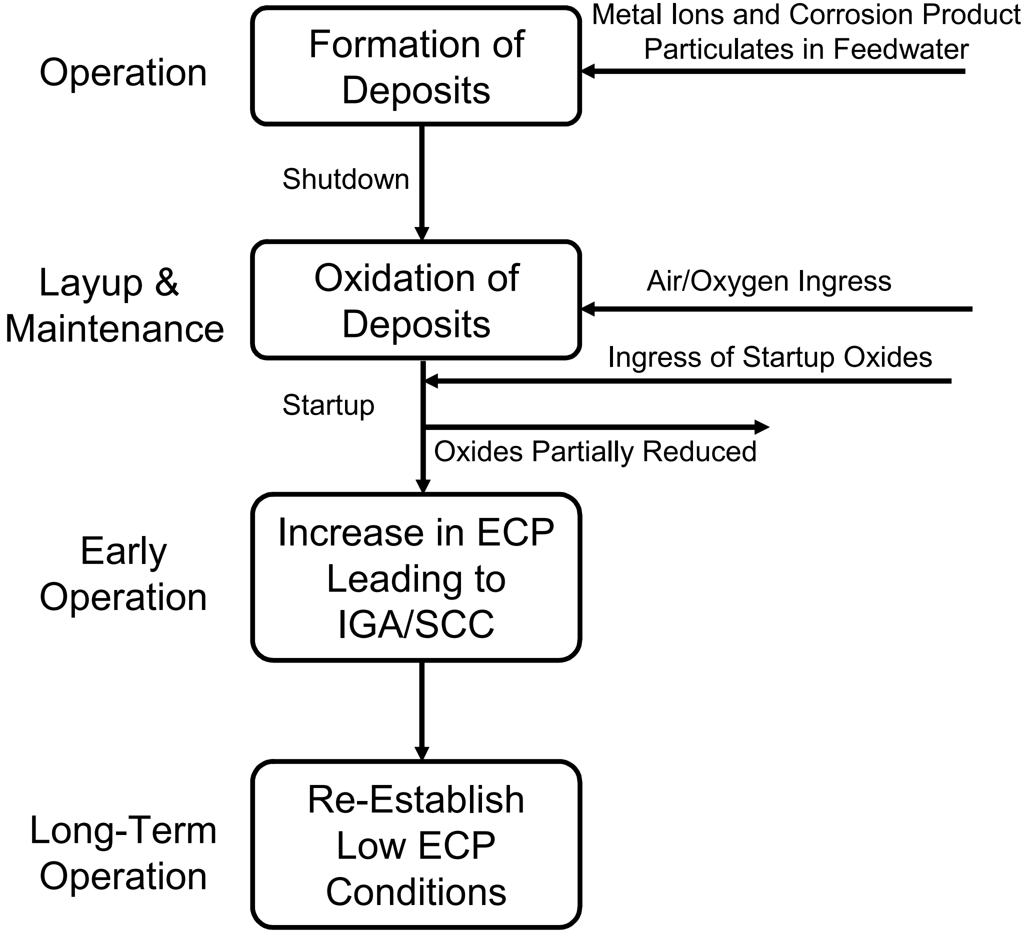
Dominion Engineering, Inc.
11730 Plaza America Drive
Reston, Virginia 20190

Overview of Presentation

- Project Background
- Deposit Characterization
- Deposit Oxidation Rates
- Oxygen Scavenger Decomposition
- Reduction During Startup

Project Background

Startup Oxide Theory



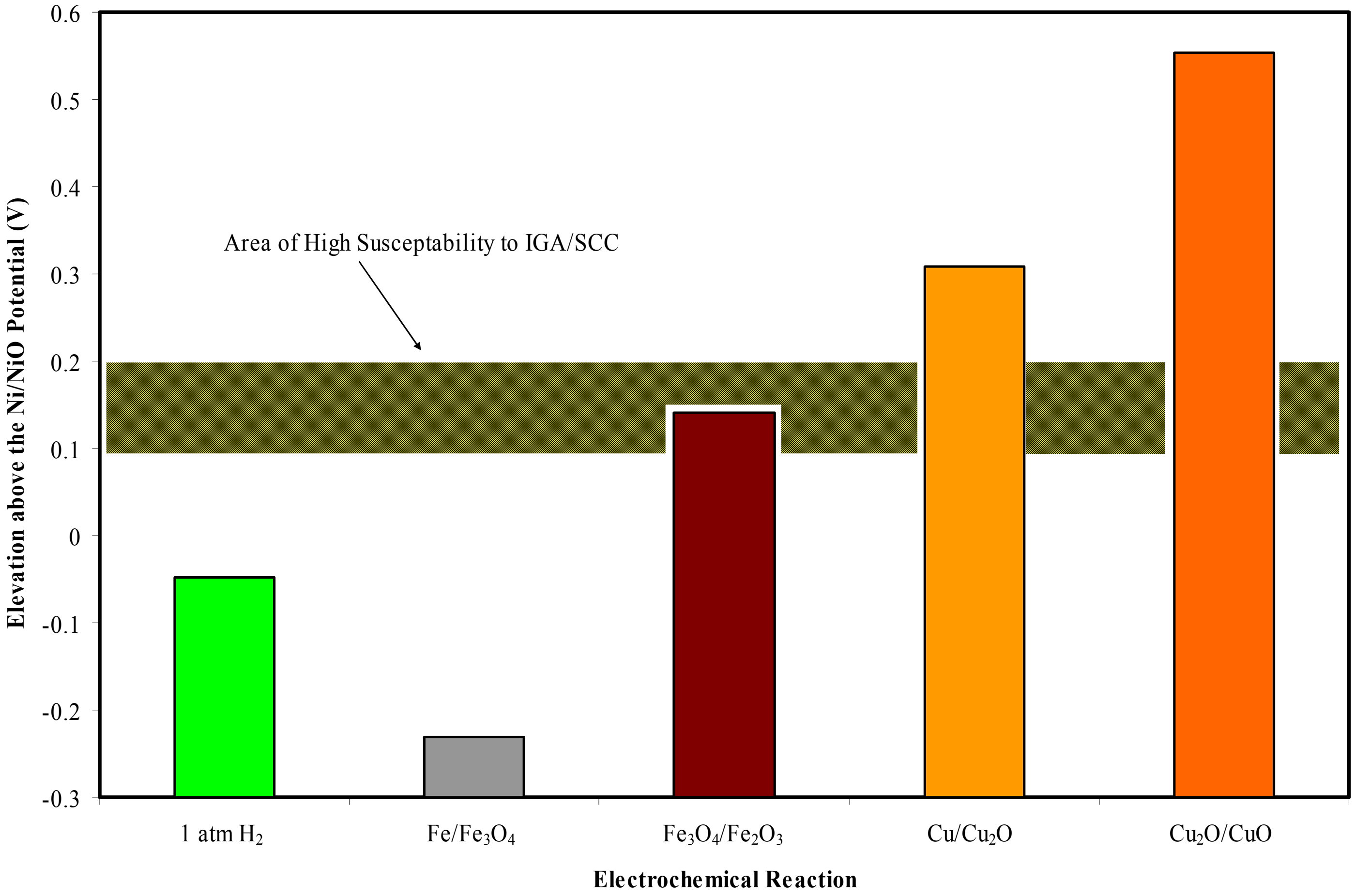
Project Background

Evidence for the Influence of Oxidized Species on IGA/SCC

- Low IGA/SCC rates at Swedish and Japanese plants where strict controls on shutdown/startup oxidants were in place during the plants' entire life
- An evaluation of Belgian plants indicating that IGA/SCC is related to the number of shutdowns and startups rather than operating life
- A rapid increase in circumferential cracking at a plant after a chemical cleaning that may have left oxidized copper in the TTS area of the SGs
- The absence of accelerated IGA/SCC after chemical cleanings that included a high-temperature oxide reduction step
- The successful amelioration of severe IGA/SCC when strict controls over startup oxides (along with other measures) were imposed

Project Background

Electrochemical Potentials of Deposit Constituents



Project Background

Project History—EPRI Project WO S515-03

- Literature review of deposit oxidation kinetics
  - EPRI Report 1001204
- Experimental determination of deposit oxidation rates under prototypical layup conditions
  - EPRI Report 1001204
- Determination of oxygen scavenger decomposition rates
  - EPRI Report 1003591
- Experimental determination of deposit oxide reduction kinetics
  - EPRI Report 1003591
- Development of analysis techniques for assessing the deposit condition at startup
  - EPRI Report 1003591

Deposit Characterization

Types of Deposits Recovered during Sludge Lancing

- Loose powder
  - Mostly from top-of-tubesheet and other horizontal settling surfaces
  - Generally composed mostly of magnetite (Fe_3O_4)
  - Particle size on the order of 1μm (from specific surface area measurement)
- Tube scale
  - Originates from tube freespan areas
  - Generally composed mostly of magnetite (Fe_3O_4)
  - Relatively thin (50 to 250 μm, depending on plant history)
  - Typically porous (depending on plant history)
  - Copper inclusions are common
- Sludge collars
  - Originates from support intersections or hardened sludge piles
  - Highly heterogeneous composition (typically contain inclusions)
  - Can have low porosity

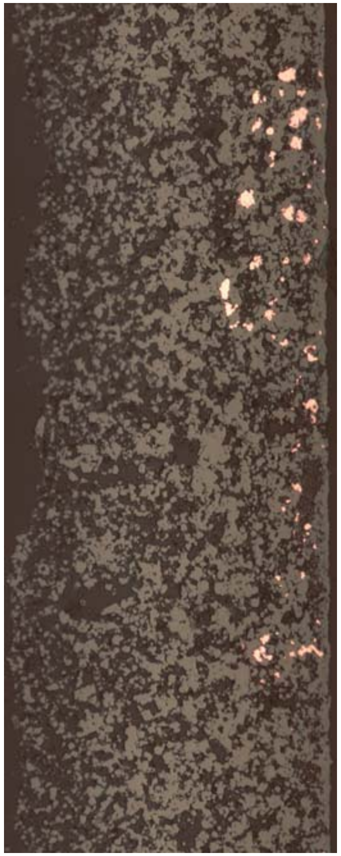
Deposit Characterization

Copper Inclusions

- Copper is an easily oxidized constituent of most deposits
  - 0.3% to 1% for plants with nominally “copper free” feedtrains
  - 2% to 20% for plants with copper bearing feedtrains
- Typically present as discrete inclusions
  - Pure copper (>90% Cu by microprobe analysis)
  - Generally located near the tube/scale interface
  - On the order of 1 to 100 μm
- Copper content can vary within SG depending on location
  - Especially sensitive to chemical cleaning history

Deposit Characterization

Typical Flake with Copper Inclusions



- SG Tube Flake
- Tube side on right
- Flake ~140 μm thick
- Average flake copper content: ~3%
- Typical inclusion diameter ~4 μm
- Remainder of flake magnetite (Fe_3O_4)
- Porosity ~50%

Copper is Easy to Oxidize, Hard to Reduce and Close to the Tube

Deposit Characterization

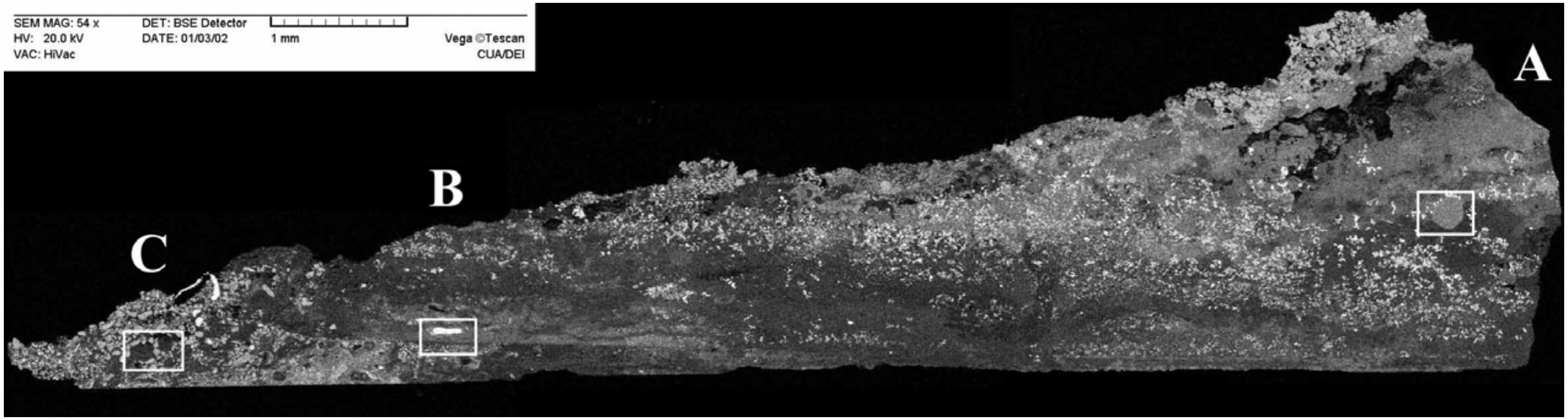
Collar (Deposits Adjacent to Crevices) Compositions

- 22 Samples from 10 Plants analyzed by ICP
- Five most common elements are Fe, Al, Cu, Si and Zn
- These elements make up 91±9% of sampled mass (min 58%, max 98%)
- 8 Collars from one plant analyzed—variability still large

Element	Assumed Oxide	10 Plants (22 Collars)		Plant A (8 Collars)	
		Average Concentration (%)	Standard Deviation	Average Concentration (%)	Standard Deviation
Fe	Fe_3O_4	46.4	23.5	28.36	16.99
Al	AlOOH	23.1	18.7	42.60	16.61
Cu	Cu	12.5	6.5	17.61	3.97
Si	SiO_2	6.9	3.4	7.60	1.52
Zn	ZnO	2.5	5.0	0.44	0.15
Pb	Pb	0.084	0.056	0.132	0.047

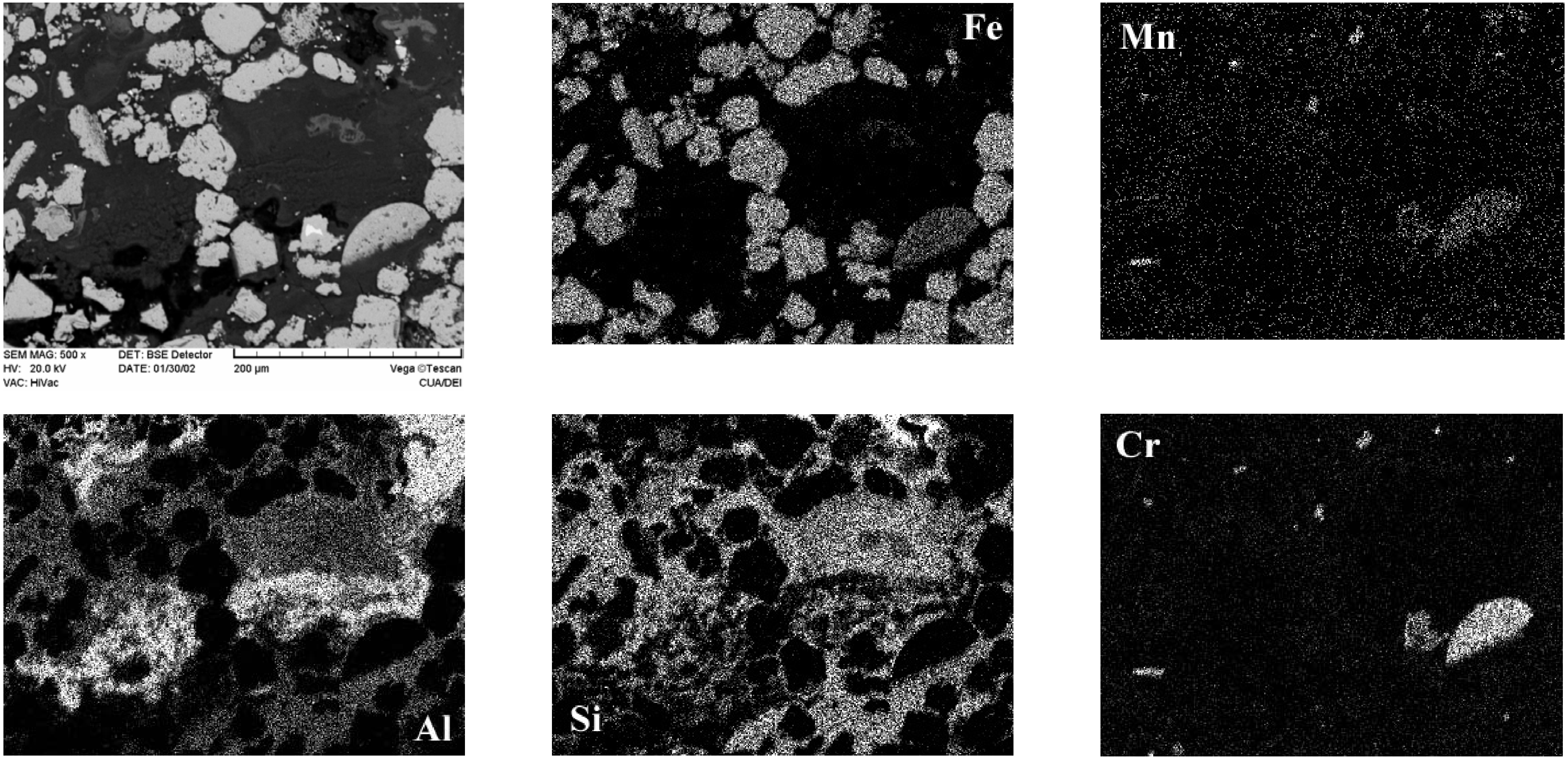
Deposit Characterization

“Typical” Collar



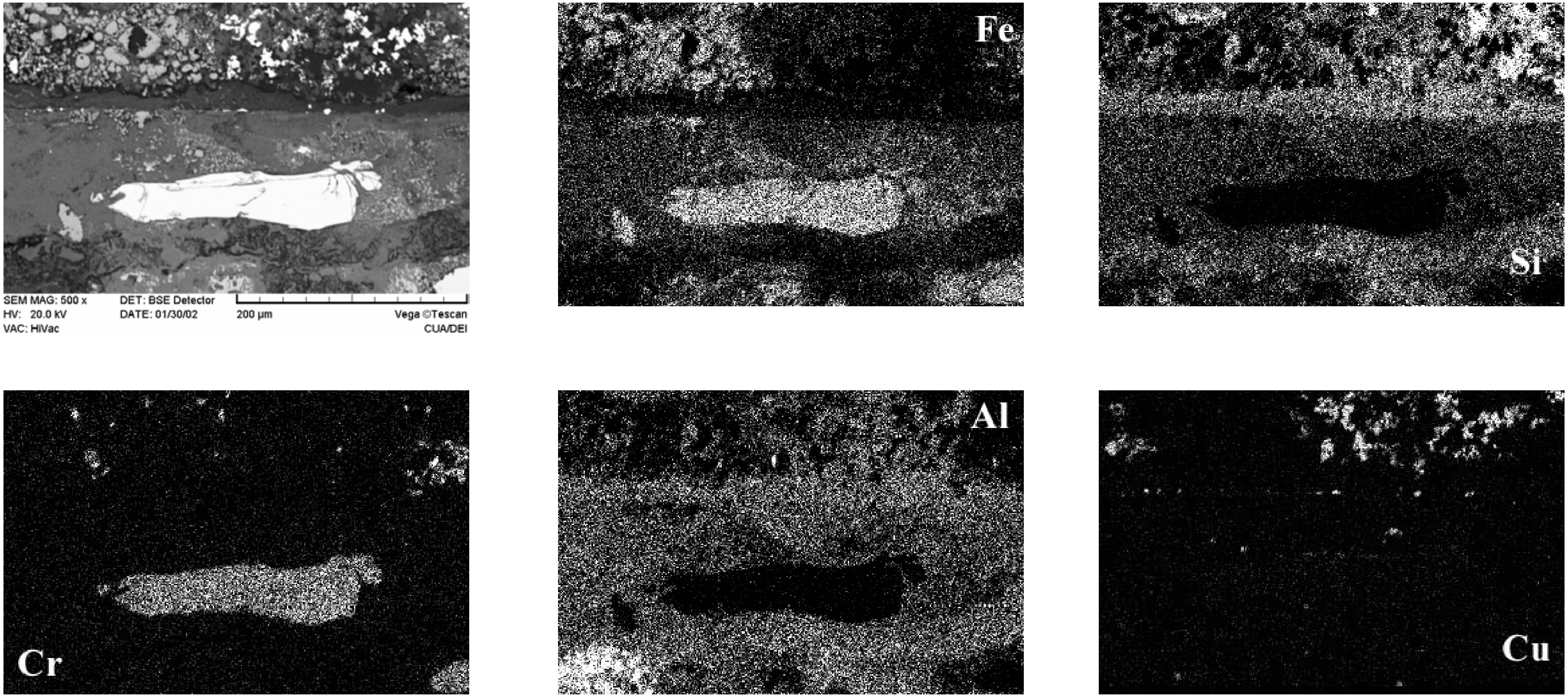
Deposit Characterization

Heterogeneous Morphology—Area A



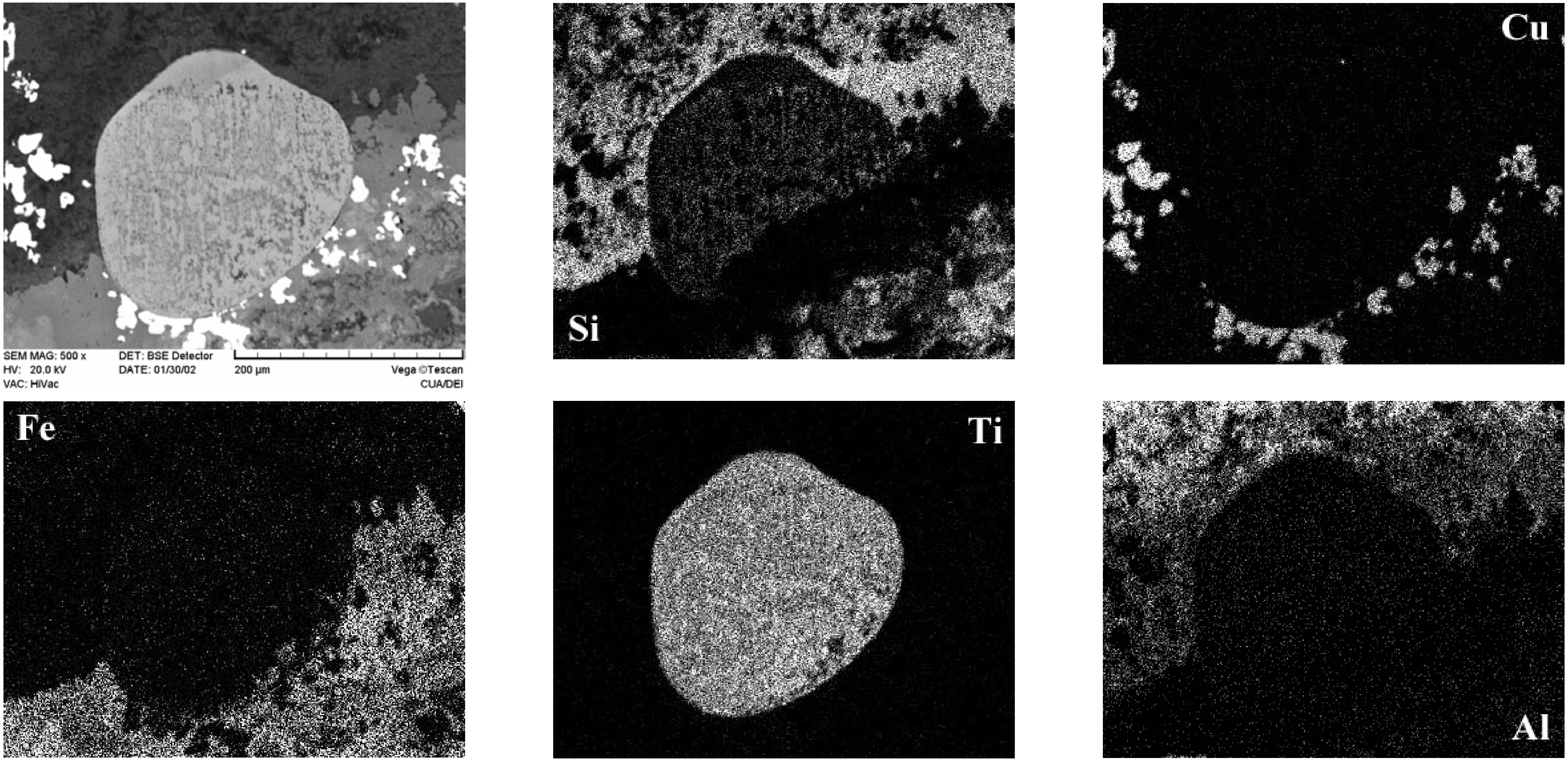
Deposit Characterization

Heterogeneous Morphology—Area B



Deposit Characterization

Heterogeneous Morphology—Area C



Deposit Characterization

Implications for Crevice Chemistry

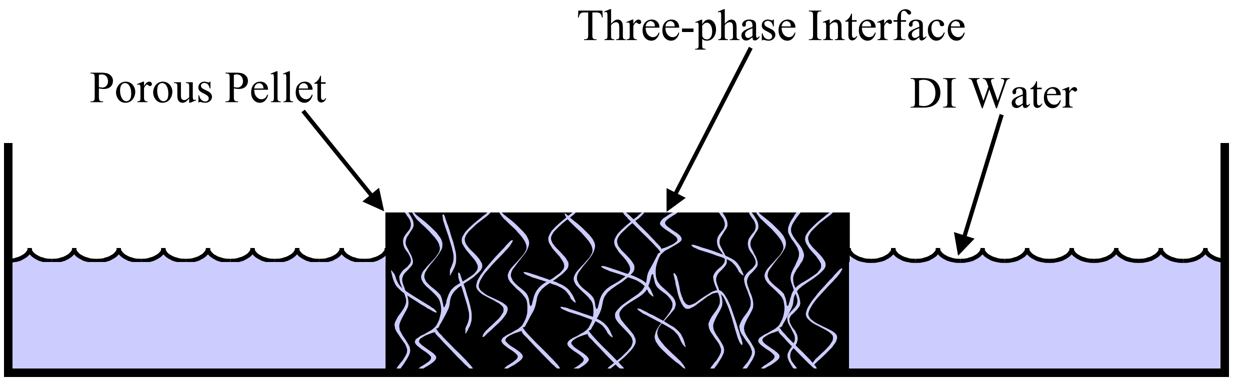
- Variations in crevice chemistry
  - Plant to plant variability
  - Crevice to crevice variability
  - Magnetite packing is not necessarily realistic
- May need to consider plant history
  - Collars may contain residual chemicals from early operation
- Deposit variability may be mitigated by consolidation of deposits
  - Porosity in collars can be very low
  - Magnetite coatings may isolate older chemicals
- Need to consider whether crevice chemistries (extreme acid or caustic) can redisolve collar species
  - Some species might buffer crevice chemistry (silica)
  - Some species might accelerate IGA/SCC (lead)

Deposit Oxidation Rates During Layup/Shutdown

- Experimental determination of oxidation rates
- Main constituents of powders and flakes studied
  - Magnetite (Fe_3O_4)
  - Copper (Cu)
- Different environments tested
  - Aqueous
    - With and without oxygen scavengers
    - Multiple pH levels and temperatures
    - With various amines
  - Atmospheric
    - Multiple humidities
    - As a function of temperature

Deposit Oxidation Rates During Layup/Shutdown

Magnetite—Pellet Experiment

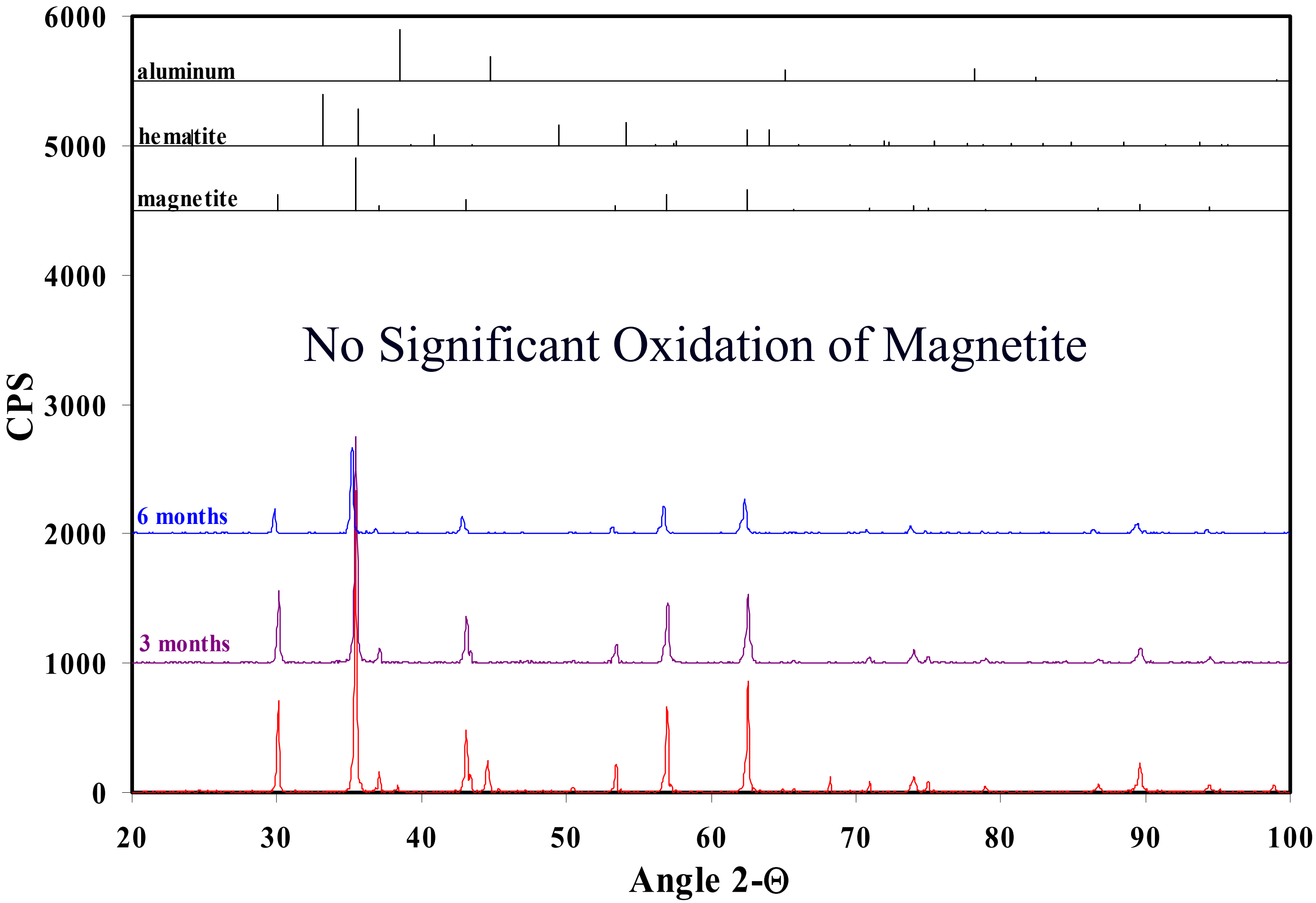


Room Temperature
Untreated DI water
6 month exposure
Pellets of SG Powder, Crushed SG Flakes or Synthetic Magnetite

Oxidation determined by XRD of Pellet

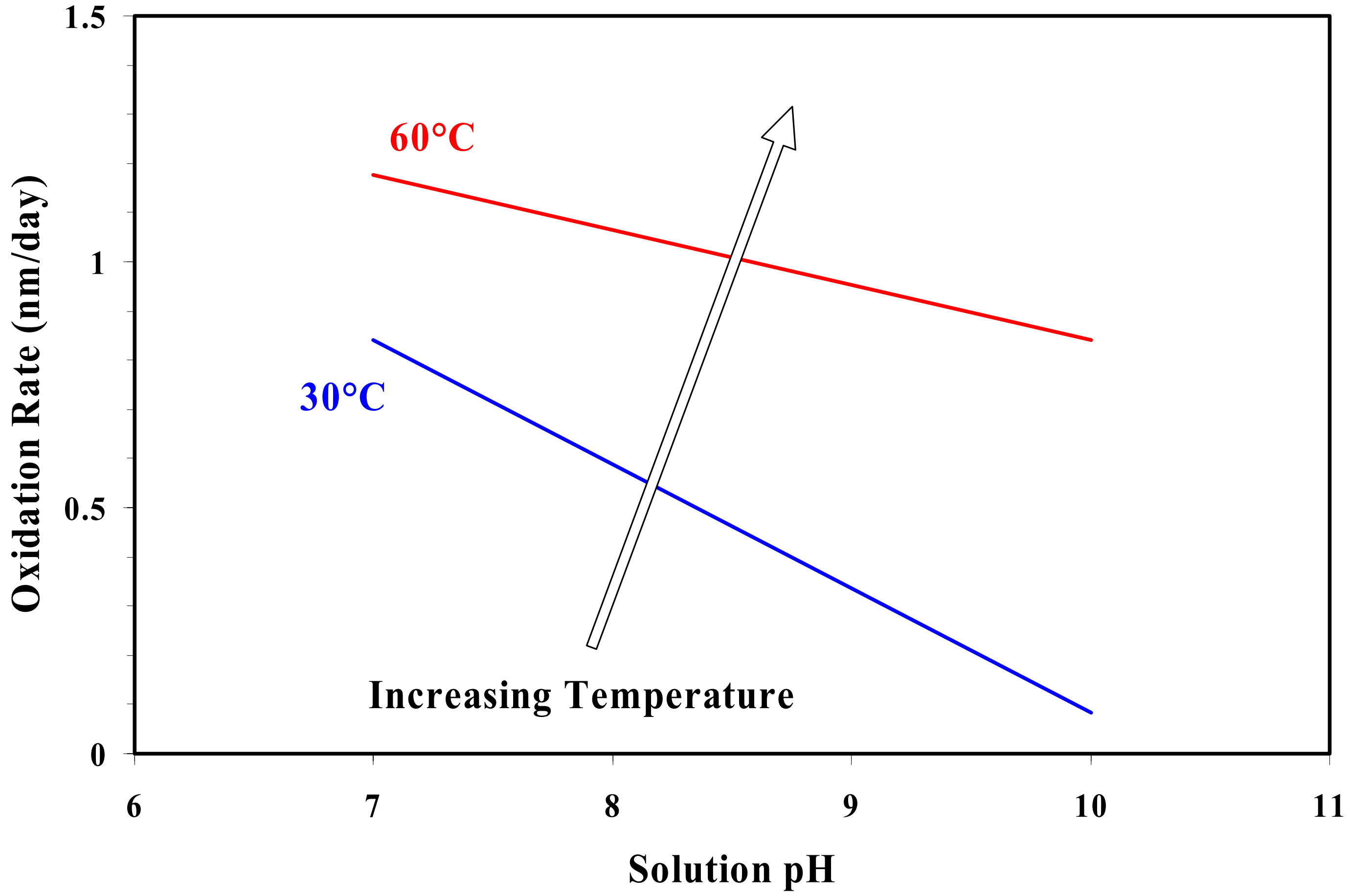
Deposit Oxidation Rates During Layup/Shutdown

Magnetite—Pellet Experiment Results



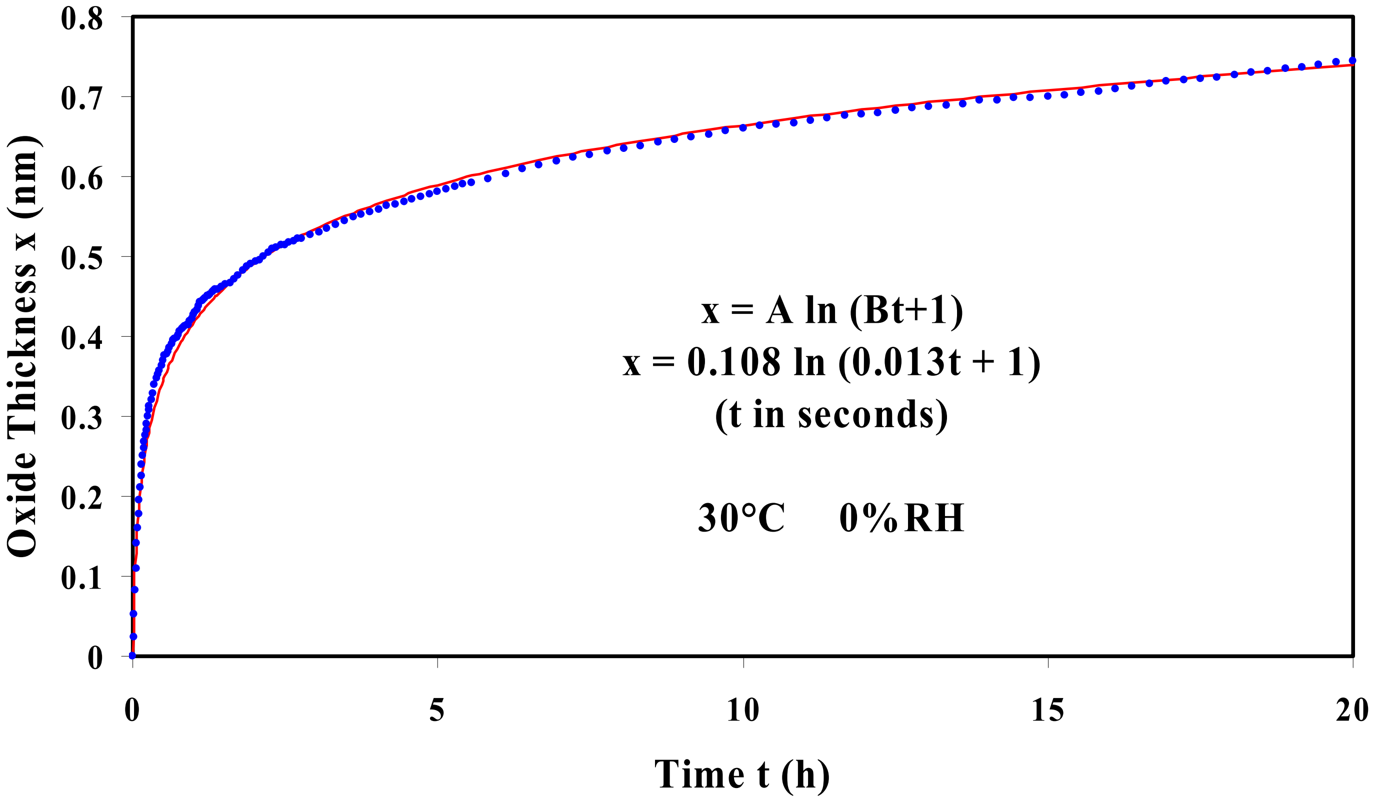
Deposit Oxidation Rates During Layup/Shutdown

Copper—Aqueous Oxidation



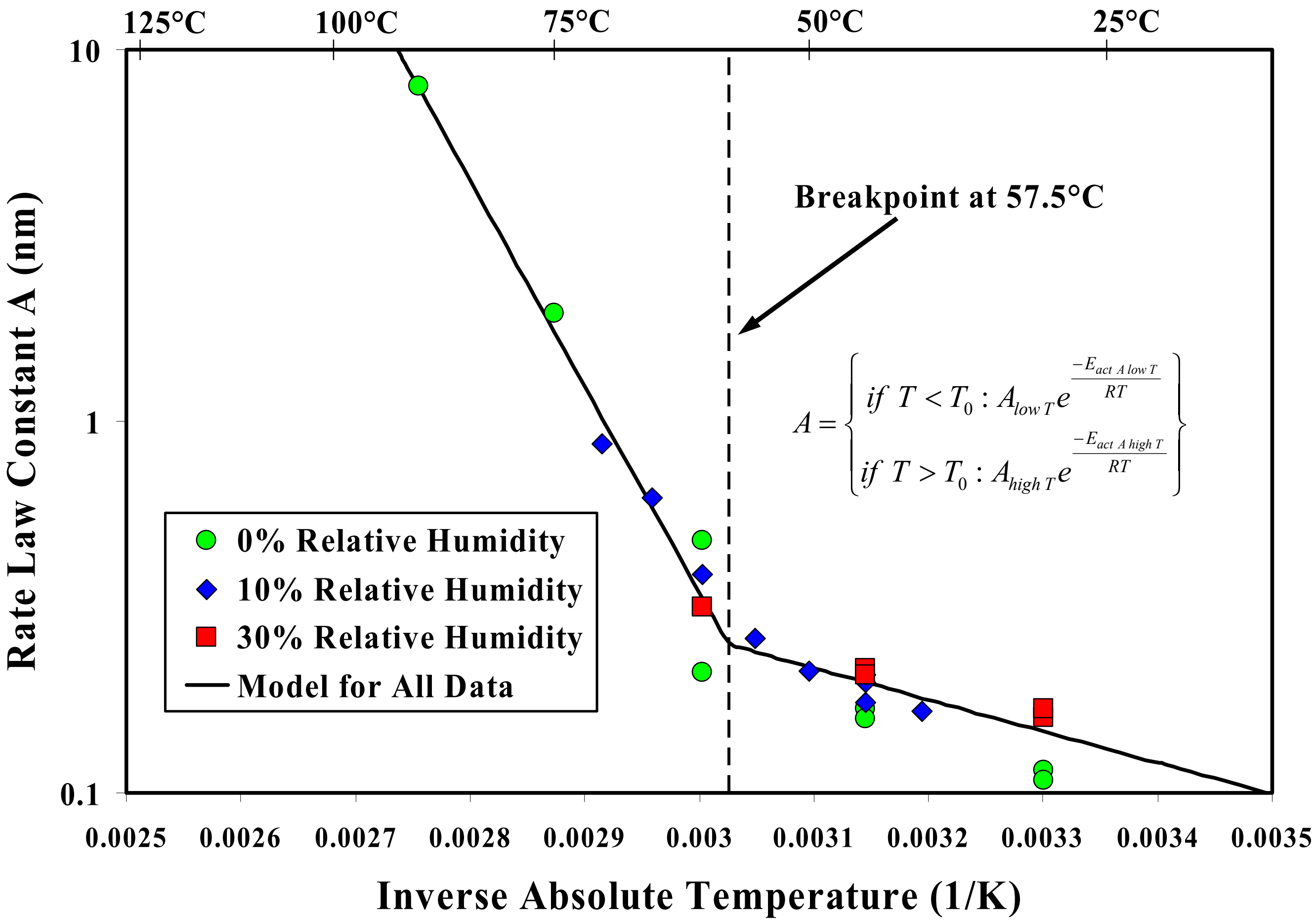
Deposit Oxidation Rates During Layup/Shutdown

Copper—Atmospheric Oxidation



Deposit Oxidation Rates During Layup/Shutdown

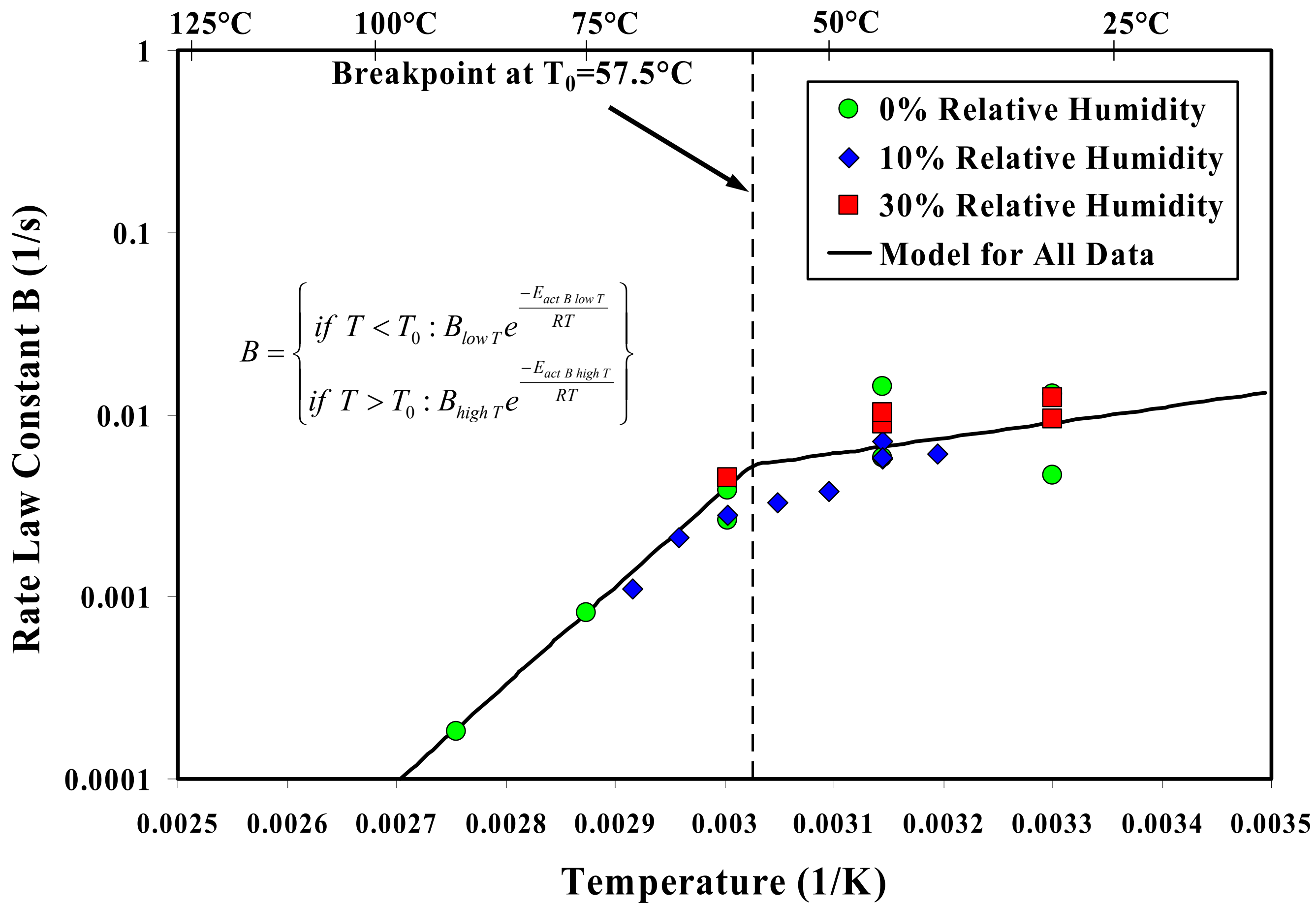
Copper—Atmospheric Oxidation Parameters



$$A = \left\{ \begin{array}{l} if\ \ T < T_0 : A_{low\ T} e^{\frac{-E_{act\ A\ low\ T}}{RT}} \\ if\ \ T > T_0 : A_{high\ T} e^{\frac{-E_{act\ A\ high\ T}}{RT}} \end{array} \right\}$$

Deposit Oxidation Rates During Layup/Shutdown

Copper—Atmospheric Oxidation Parameters



$$B = \left\{ \begin{array}{l} if\ T < T_0 : B_{low\,T} e^{\frac{-E_{act\,B\,low\,T}}{RT}} \\ if\ T > T_0 : B_{high\,T} e^{\frac{-E_{act\,B\,high\,T}}{RT}} \end{array} \right\}$$

Deposit Oxidation Rates During Layup/Shutdown

Conclusions

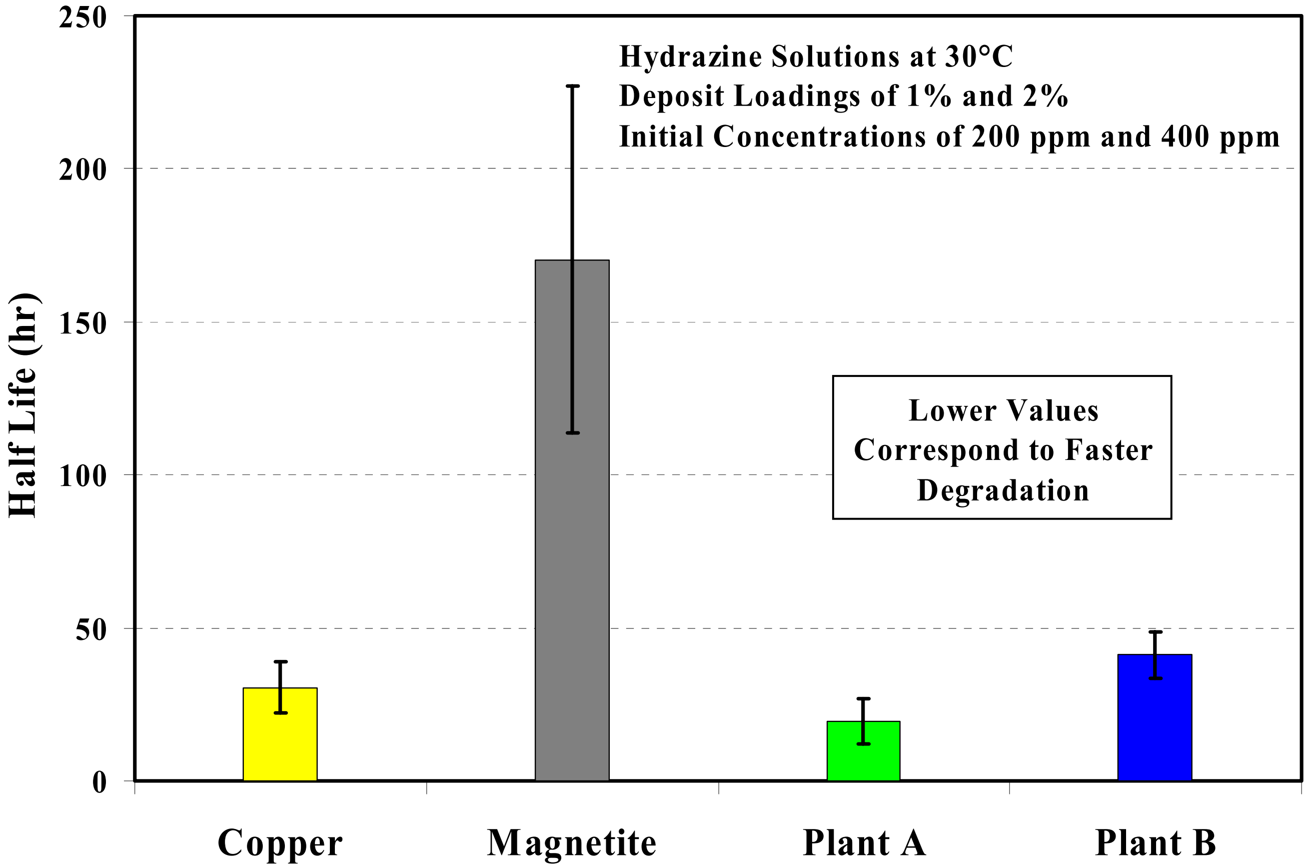
- No significant oxidation of magnetite
- Copper is easily oxidized
- Copper oxidation rates characterized
  - Atmospheric oxidation
  - Aqueous oxidation
- Can determine the extent of oxidation (oxide thickness) from outage schedule
  - Necessary component to assessing degree of oxidation at operating temperature

Oxygen Scavenger Decomposition

- Deposits accelerate oxygen scavenger decomposition
- Possible that deposits prevent oxygen scavengers from reaching deep into crevices or into porous deposits
  - Scavengers possibly excluded from most important regions
  - Absence of scavengers limits reduction of oxides formed during layup/shutdown
- Kinetic data on the effects of deposits required to assess hypothesis
- Hydrazine and carbohydrazide both tested

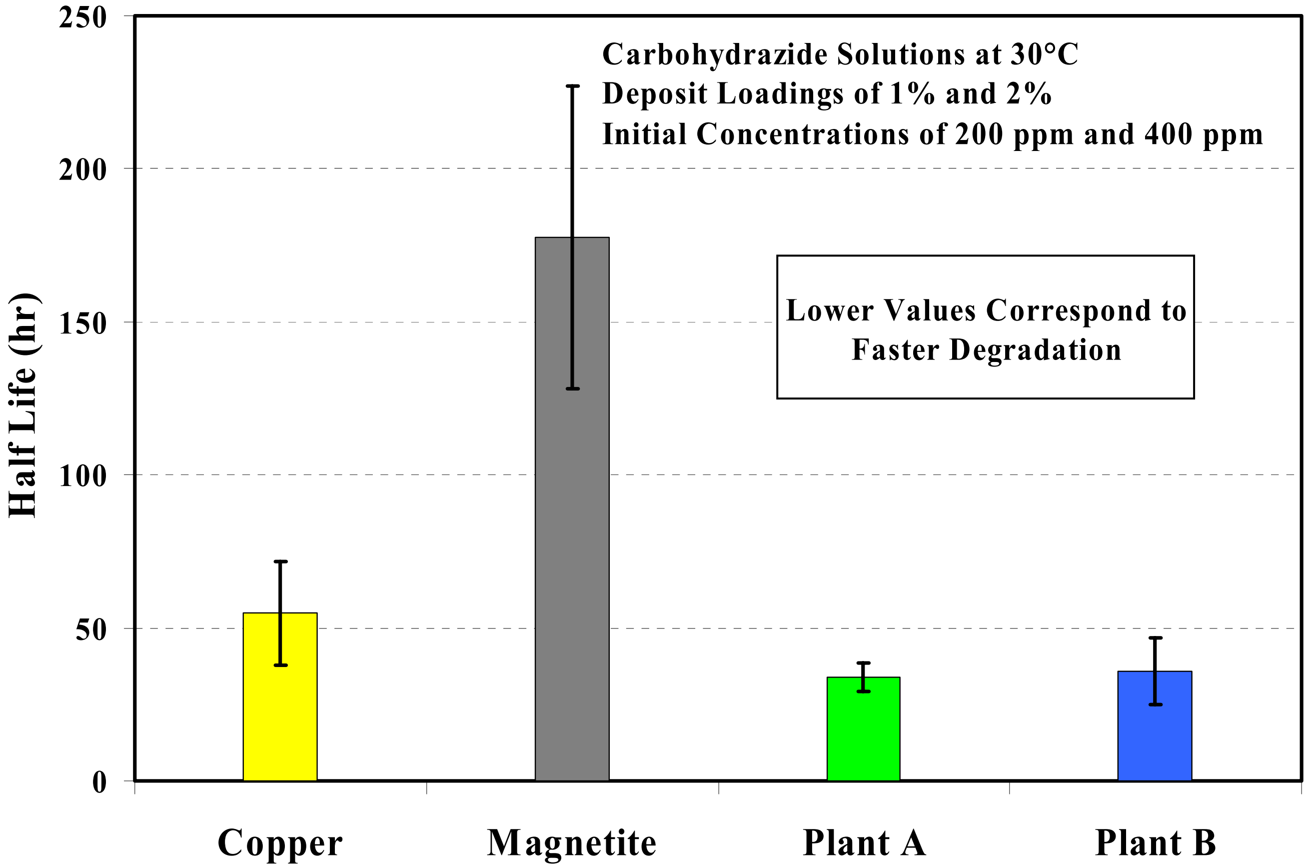
Oxygen Scavenger Decomposition

Hydrazine and SG Deposits



Oxygen Scavenger Decomposition

Carbohydrazide and SG Deposits



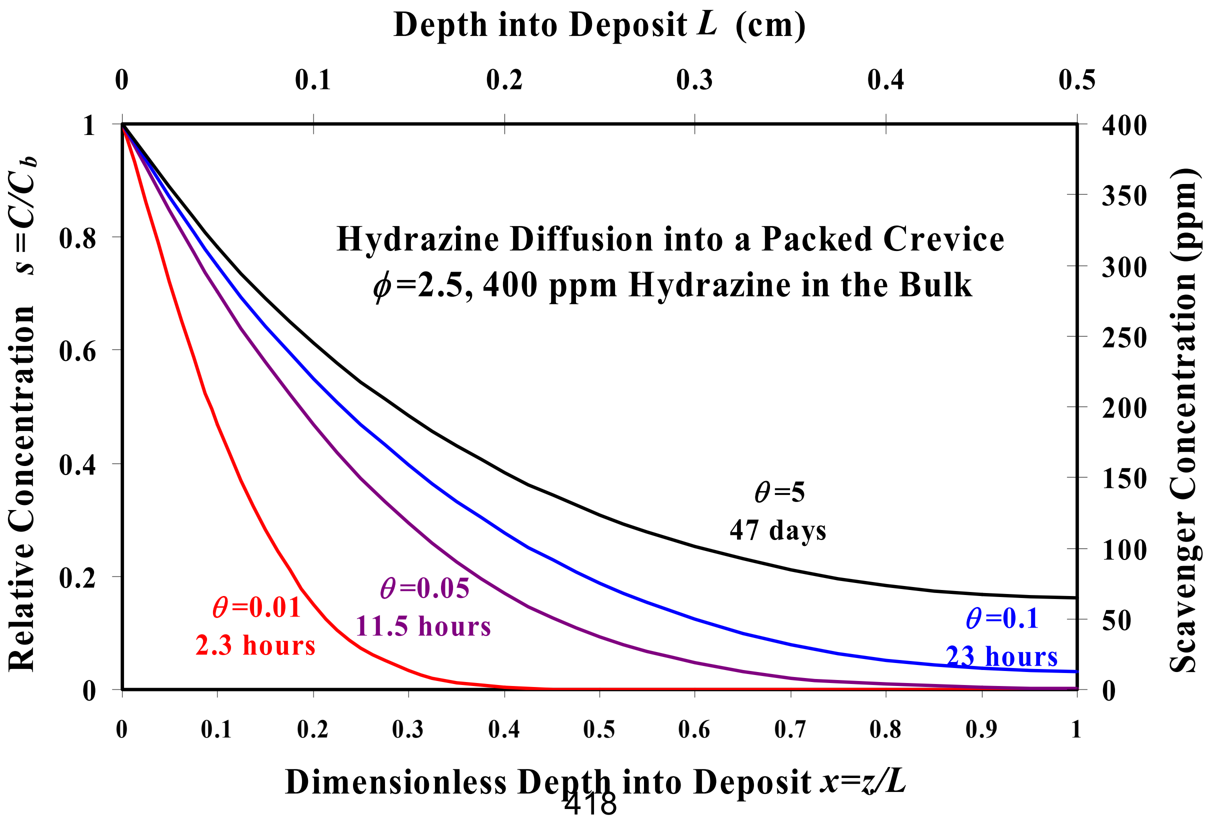
Oxygen Scavenger Decomposition

Diffusion/Reaction Modeling

$$\frac{C}{C_b}=1-\sum_{n=0}^{\infty}\frac{\frac{4}{(2n+1)\pi}}{\phi^2+\left(\frac{2n+1}{2}\pi\right)^2}\left[\phi^2+\left(\frac{2n+1}{2}\pi\right)^2 e^{-\left\{\phi^2+\left(\frac{2n+1}{2}\pi\right)^2\right\}\theta}\right]\sin\left(\frac{2n+1}{2}\pi x\right)$$

$$\phi=L\sqrt{\frac{k_d}{D_{eff}}}$$

$$\theta=\frac{t}{\Theta}=\frac{t}{\frac{L^2}{D_{eff}}}$$



Oxygen Scavenger Decomposition

Implications for Crevice Chemistry

- Crevice chemistry will involve more than just thermal concentration
  - Chemical decomposition of oxygen scavengers
  - Generation of decomposition byproducts (ammonia)
- Chemical reactions involving scavengers may be slower in crevices
  - Hematite (Fe_2O_3) may be formed
    - Kinetics may be favored at higher temperatures than those tested here
  - Copper oxides (CuO or Cu_2O) may not be reduced to copper metal

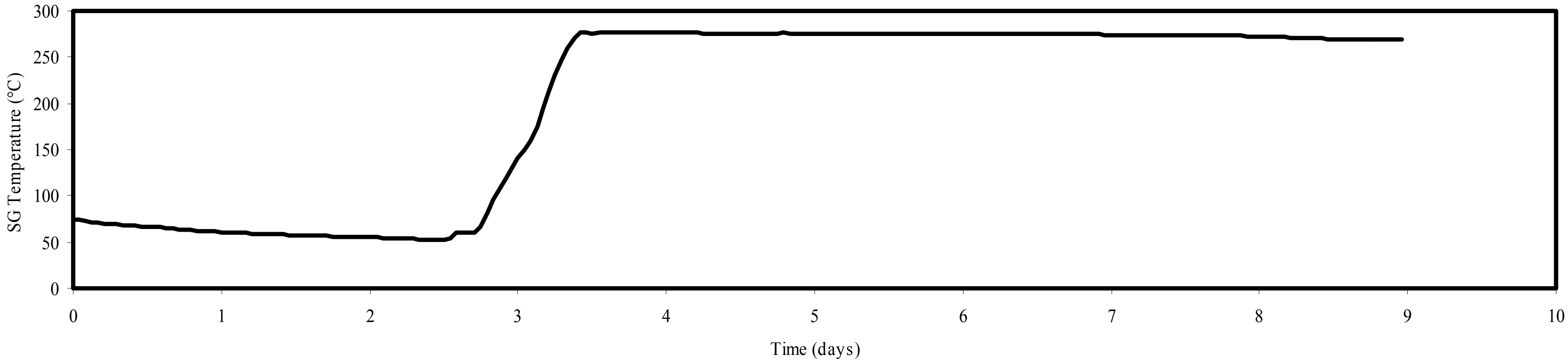
Startup Conditions

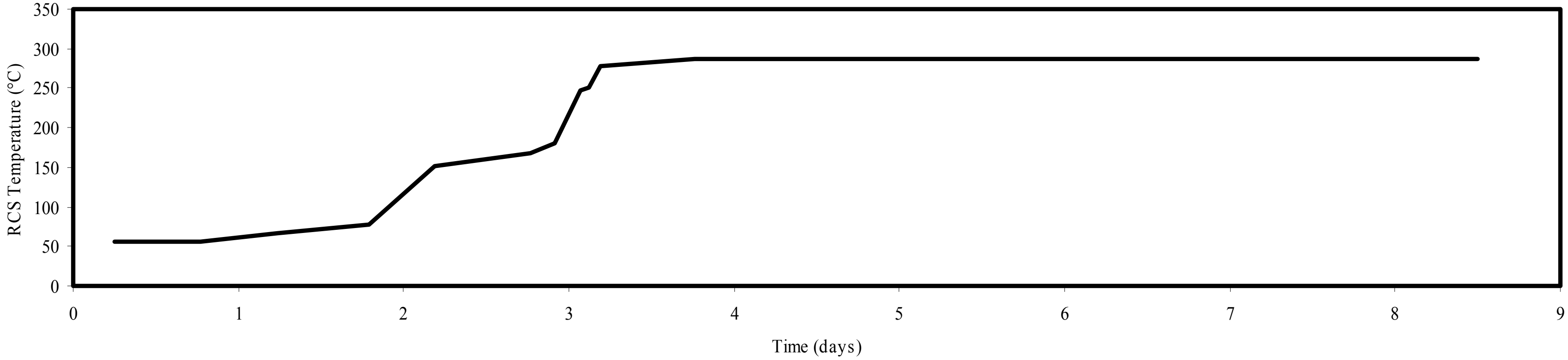
Differences between Plants

- Different layup strategies
  - Lead to different degrees of deposit (copper) oxidation
- Different startup sequences have different:
  - Temperatures
  - Chemistries
    - Oxygen concentrations
    - Oxygen scavenger concentrations
    - pH levels
- Different sequences can reduce different amounts of oxide

Startup Conditions

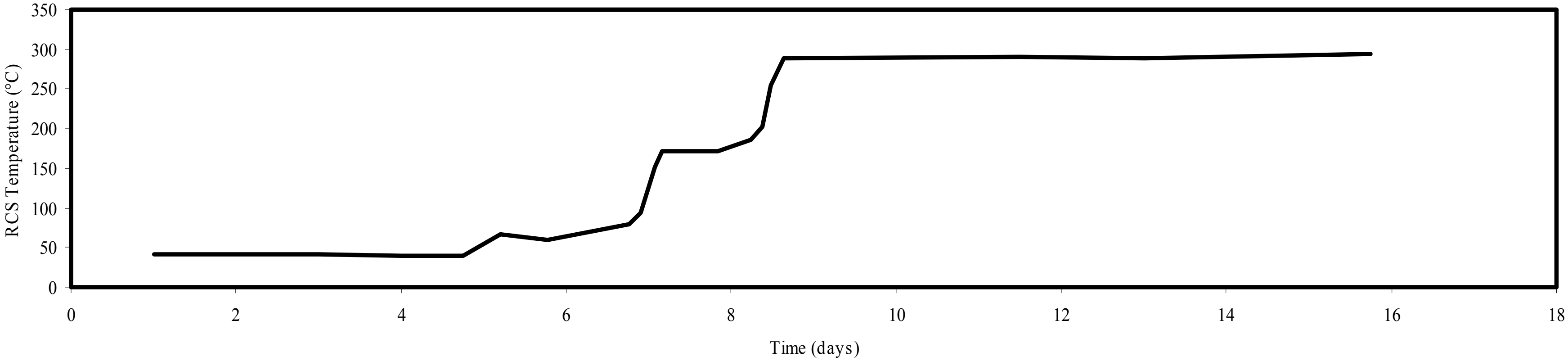
Sample Startup Sequences

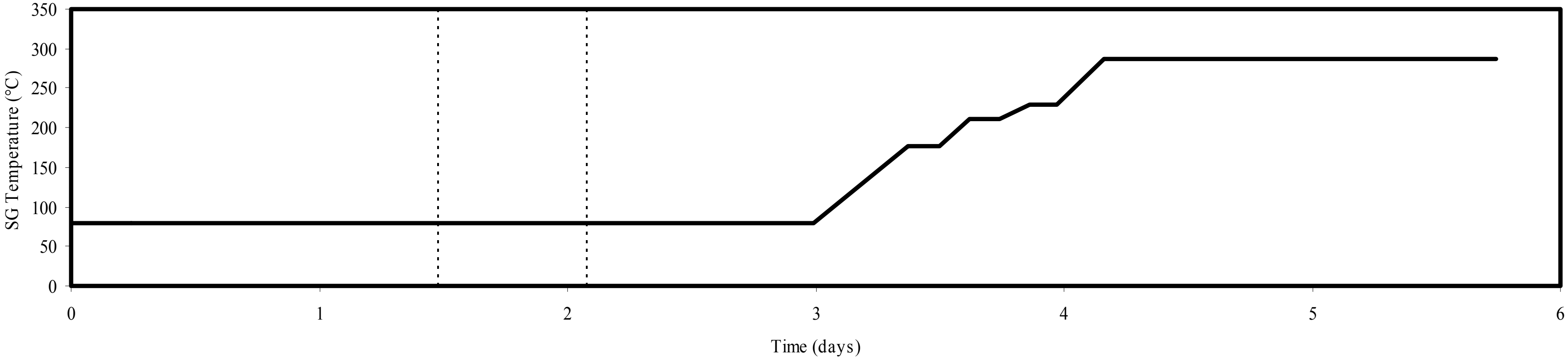




Startup Conditions

Sample Startup Sequences





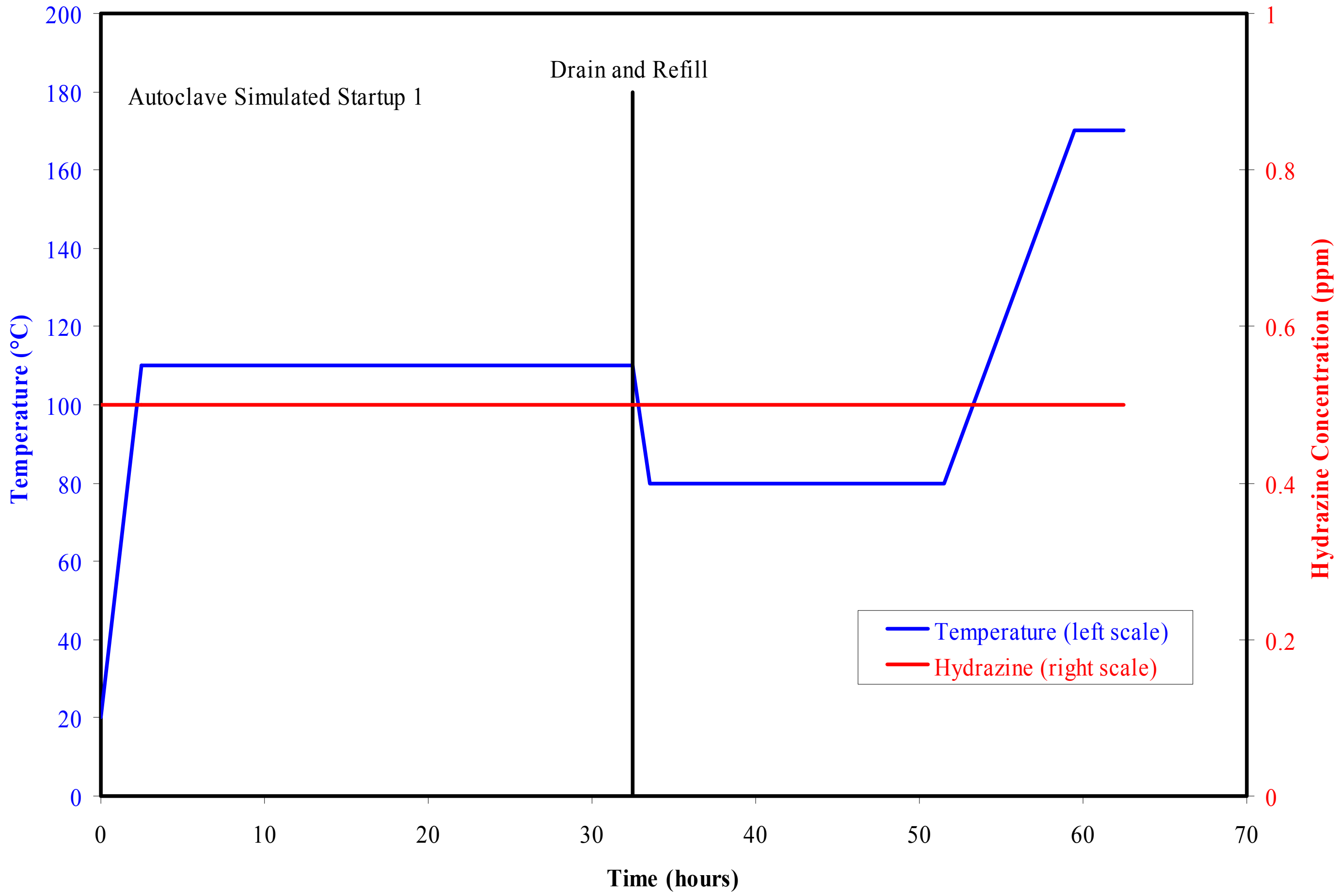
Startup Conditions

Sample Startup Sequences—Summary

- Essentially four temperatures:
    - Layup
    - Early startup (80-90°C)
    - Mid-startup (~160°C)
    - Operating
- Startup sequences differ in rate of change between these temperatures
- Startup sequences also differ in chemistry
    - Dissolved oxygen
    - Scavenger concentrations
    - pH
- Previous investigations show that mid-range temperatures (~150°C) are best for reducing deposit oxides

Deposit Oxide Reduction Experiments

Simulated Startup Sequences—Test 1



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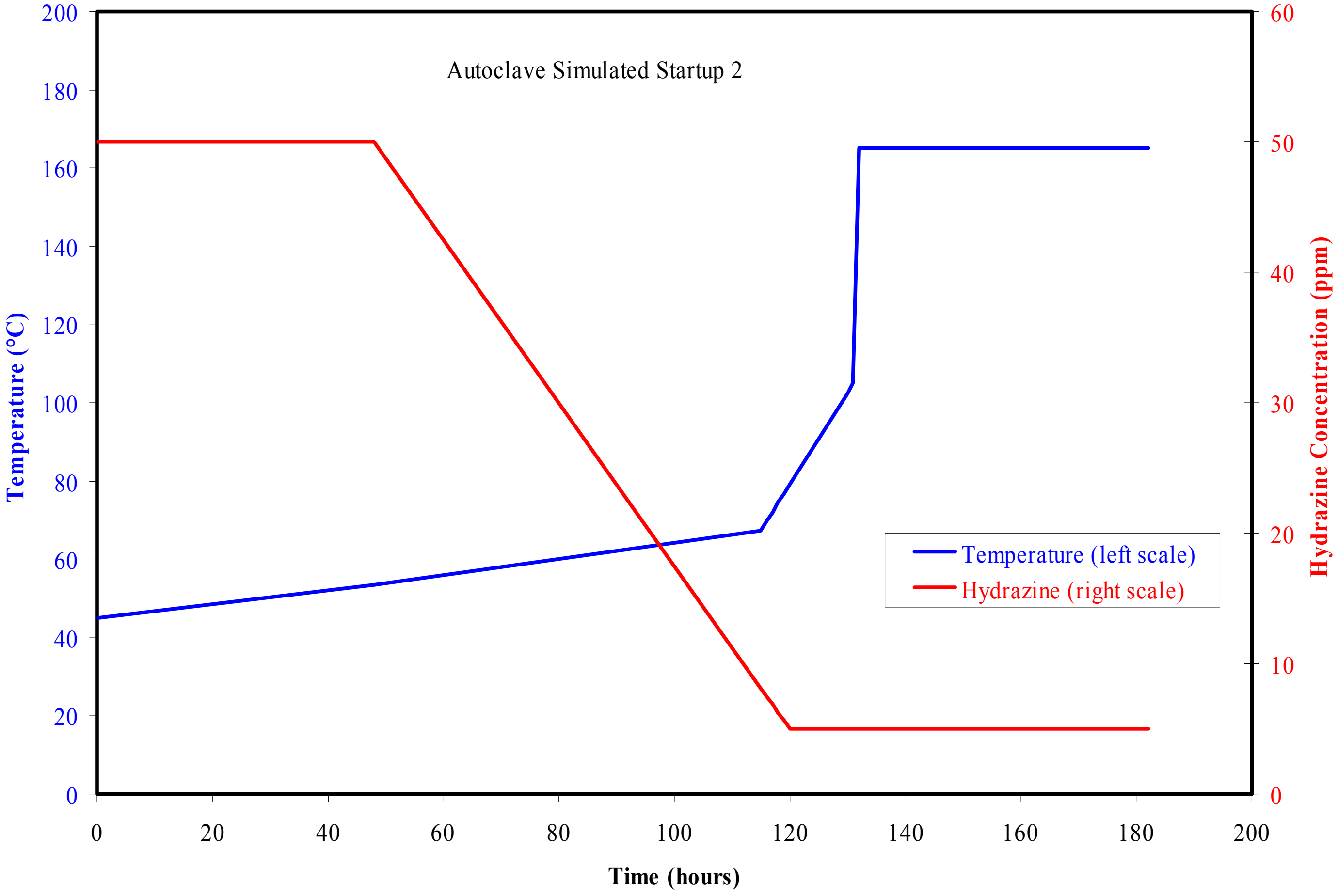
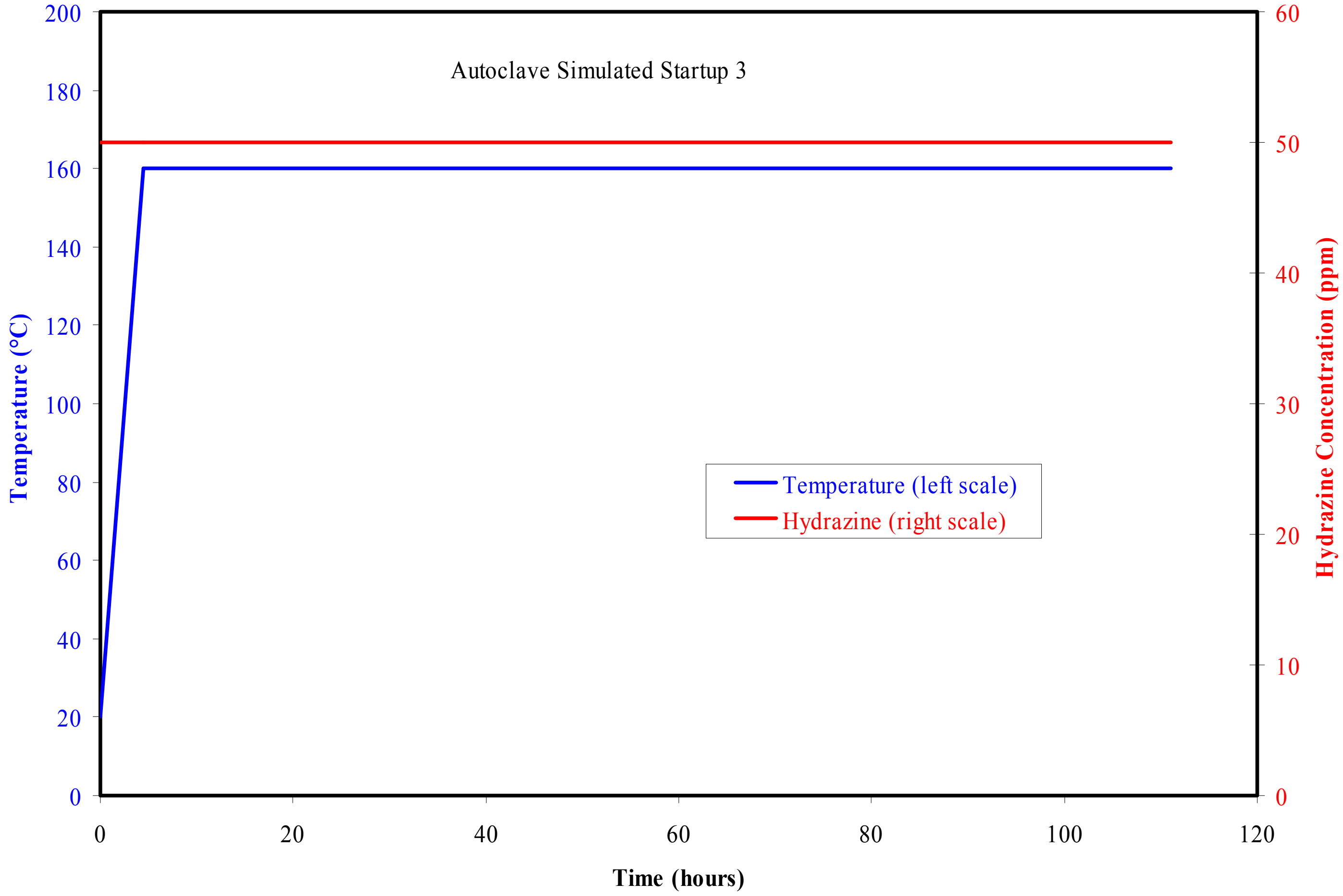
Deposit Oxide Reduction Experiments

Simulated Startup Sequences—Test 2



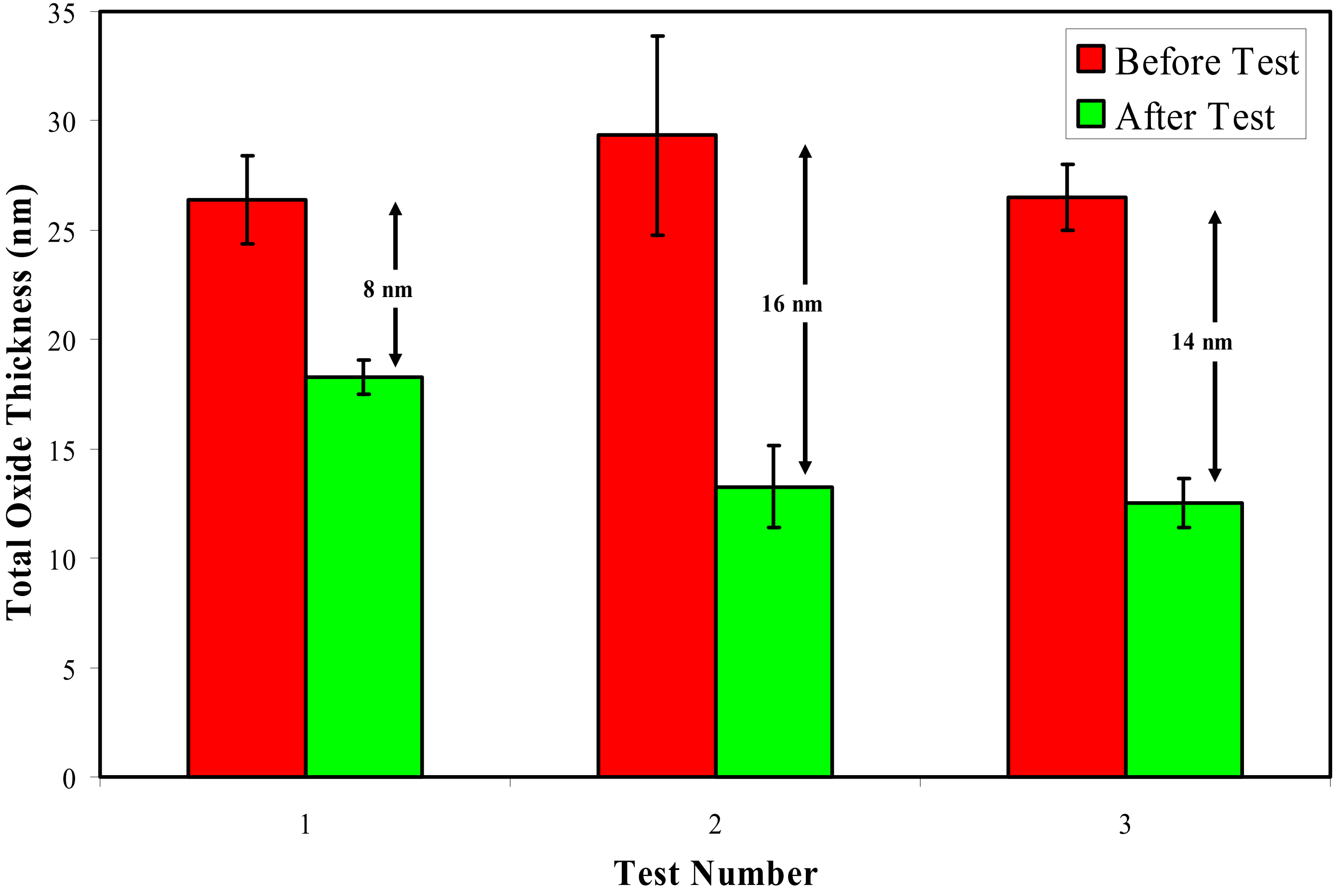
Deposit Oxide Reduction Experiments

Simulated Startup Sequences—Test 3



Deposit Oxide Reduction Experiments

Simulated Startup Tests—Results



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Evaluation of Specific Startup Sequences

Evaluation Methodology

- Evaluate degree of deposit oxidation during layup/shutdown
  - Atmospheric oxidation
  - Aqueous oxidation
- Compare startup sequence to experimental sequences
  - Do separate analyses for crevice and bulk conditions
- Evaluate likely oxide thickness reduced
- Compare reduced oxide to total inventory
- Because ECP is a surface phenomenon, any remaining oxide thickness may potentially accelerate IGA/SCC
  - Bulk concentration of oxide may not have much significance

Deposit Oxidization and Reduction

Additional Issues

- ↗ Transport of oxides to the SG during startup
  - Potentially more important than oxides formed in place
  - Reducible iron oxides (hematite) transported to SG during startup
    - Possible oxidation of deposited magnetite to hematite at startup temperatures
    - Slow kinetics of hematite reduction
- ↗ Combination effects of deposit compounds
  - Magnetite may reduce the influence of copper oxides
  - Numerous other species present in collar type deposits
- ↗ Model Verification Testing—Heated Crevice Testing
  - Aggressive and non-aggressive startups
  - Japanese procedures
  - Seabrook procedures

Conclusions

- Deposit oxides can raise the ECP and could accelerate IGA/SCC
- Deposits are mostly magnetite, but contain numerous other compounds
  - Tube scale has copper inclusions
  - Collars are highly heterogeneous and vary greatly
- Deposits can contribute to crevice chemistry through chemical reactions, not just phase changes
- Some startup sequences may not adequately reduce oxidized deposits

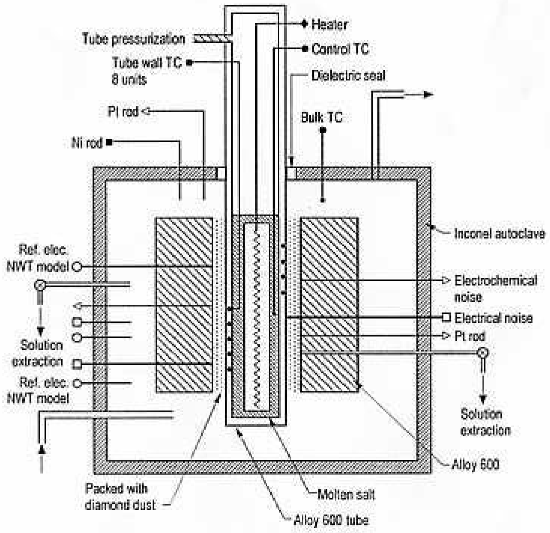
Evaluation of the Effect of Startup Oxidants on the ECP of a Crevice Filled with Deposits

Jesse Lumsden
Rockwell Science

Al Mcilree
EPRI

Heated Crevice Seminar
Argonne National Laboratory
October 7- 11, 2002

Effect of Startup Oxidants



Approach:

- **The heated crevice used without heat flux-autoclave heated externally**
- **Electrochemical Noise (planned), ECP of crevice and freespan recorded continuously**
- **Environments-air saturated (7 ppm O_2) DI water, pH 10 NaOH**
  - **100 ppm and 0.1 ppm hydrazine additions**
  - **Temperatures from 30°C to 200°C**
- **Crevice packing material**
  - **Diamond powder (magnetite powder, copper oxide/magnetite powder planned)**
- **Once-through water system (18 cc/min, 1700 cc autoclave volume)**

Effect of Startup Oxidants

- **Oxygen/Water Equilibrium reaction**

  $2H_2O = O_2 + 4H^+ + 4e^-$ **(in acid)**

  $4OH^- = O_2 + 2H_2O + 4e^-$ **(in alkali)**

  Reversible oxygen potential given by

  $E_{H2O/O2} = E^{\circ}_{\circ} - (2.3RT/F)pH + (2.3RT/4F)\log PO_2$

  Valid if no other reactions such as alloy dissolution, oxide formation, etc.

- **Hydrazine removes oxygen by the reaction**

  $N_2H_4 + O_2 = N_2 + 2H_2O$

  Hydrazine is a powerful reducing agent

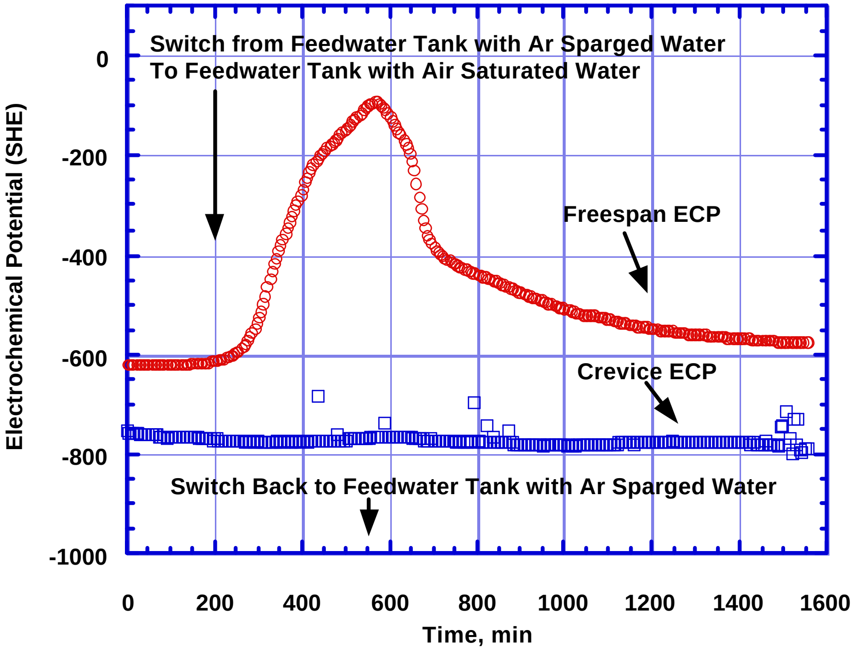
  $N_2H_4 + 4OH^- = N_2 + 4H_2O + 4e$

  Electrode Potential is given by

  $E = -1.216 + (2.3RT/F)pOH - (2.3RT/2F)\log aN_2H_4 + (2.3RT/2F)\log PN_2$

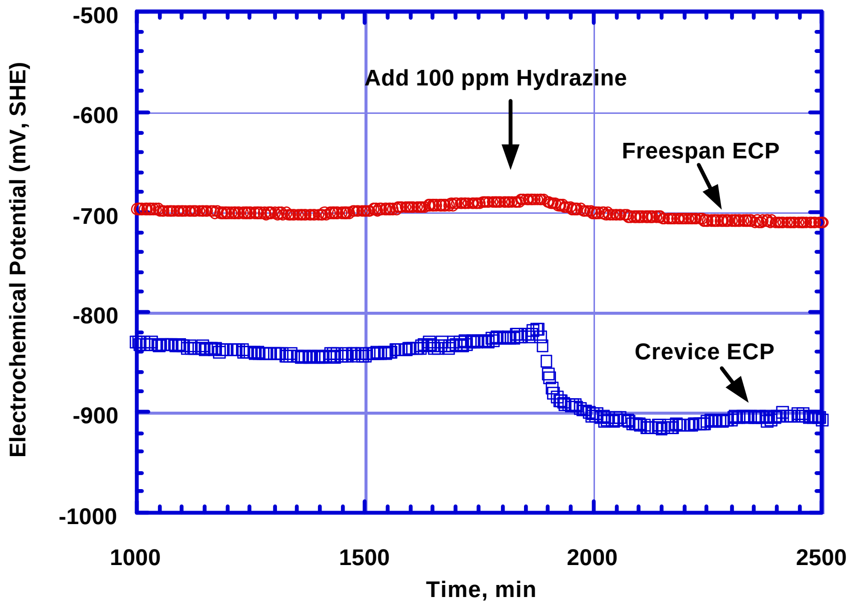
Does Dissolved Oxygen in the Feedwater Change the Crevice ECP Under Heat Transfer Conditions?

40 ppm NaOH
Bulk Temperature 275°C
Average Crevice Temperature 315°C
Crevice Packed with Magnetite
Flow Rate 15 cc/min



Does Hydrazine Change the Crevice ECP Under Heat Transfer Conditions?

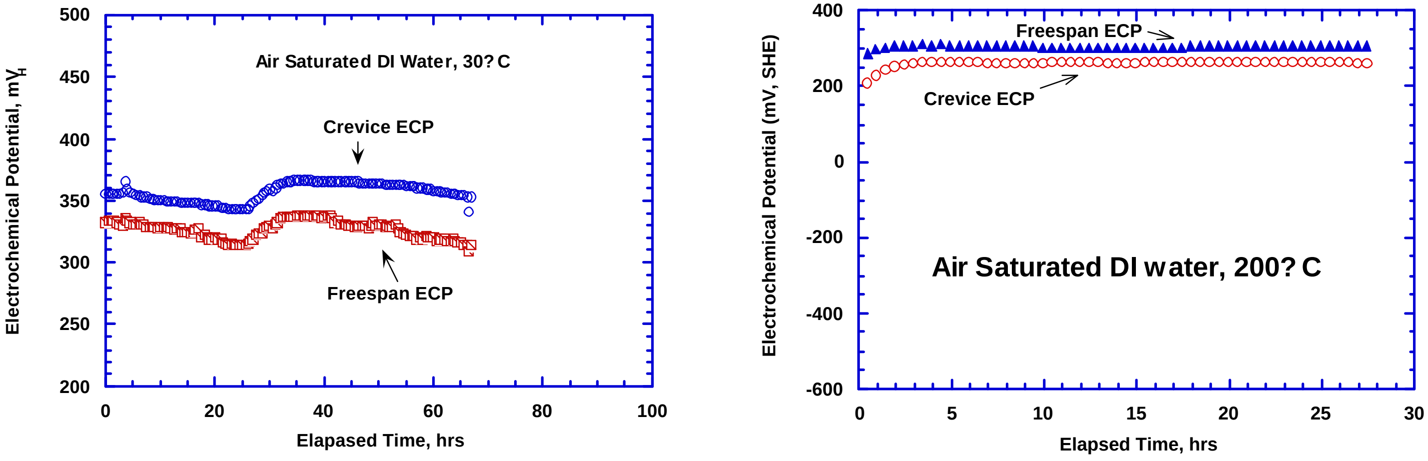
40 ppm NaOH
Bulk Temperature 275°C
Average Crevice Temperature 315°C
Crevice Packed with Magnetite
Flow Rate 15 cc/min
Ar Sparged Feedwater



$$E = -1216 + 120pOH - 60 \log aN_2H_4 + 60\log PN_2$$

Effect of Startup Oxidants

- O_2 Effluent same as O_2 feedwater, approximately 7.5 ppm
- Crevice packed with diamond powder
- Freespan ECP and crevice ECP approximately the same



Typical Data for Air Saturated DI Water

Effect of Startup Oxidants

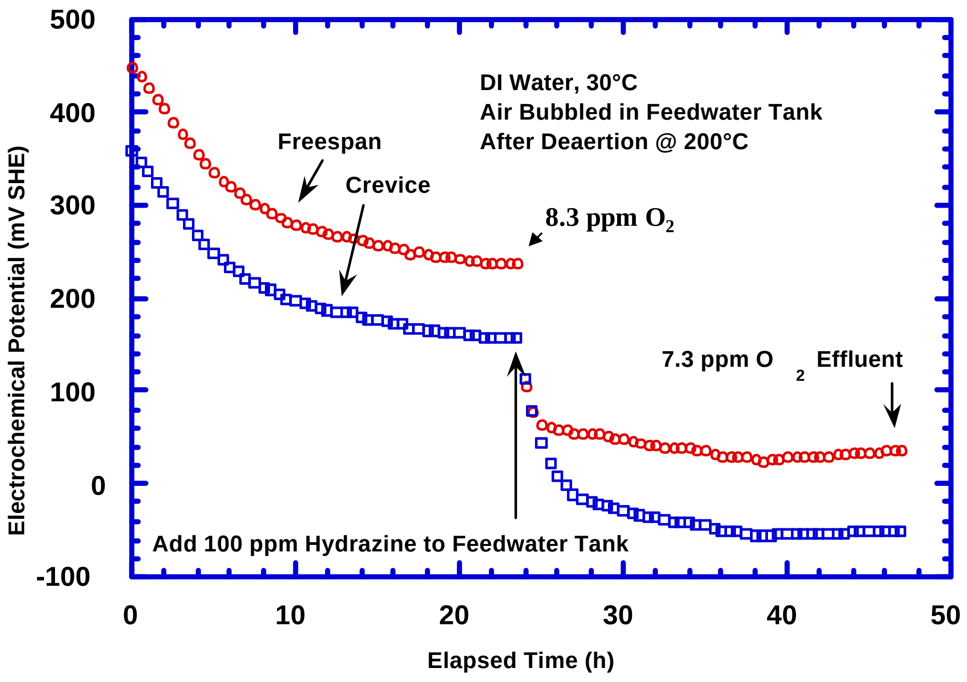
- The crevice ECP and freespan ECP in an air saturated condition are by 35 mV or less
- Reversible oxygen potential not observed - not unusual

Air Saturated DI Water

Temp	30°C	60°C	100°C	150°C	200°C
Freespan ECP	310 mV	232 mV	220 mV	295 mV	265 mV
Crevice ECP	330 mV	265 mV	235 mV	290 mV	250 mV
O_2 In	8 ppm	7.8 ppm	7.2 ppm	7.6 ppm	7.5 ppm
O_2 Out	8 ppm	7.7 ppm	7.2 ppm	7.5 ppm	7.4 ppm
$E_{H2O/O2}$	790 mV	750 mV	700 mV	630 mV	540 mV

Effect of Startup Oxidants

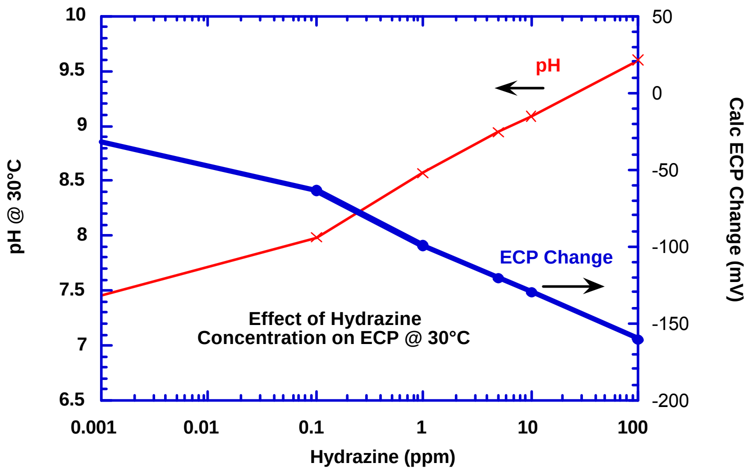
Effect of Hydrazine Addition to Air Saturated DI Water

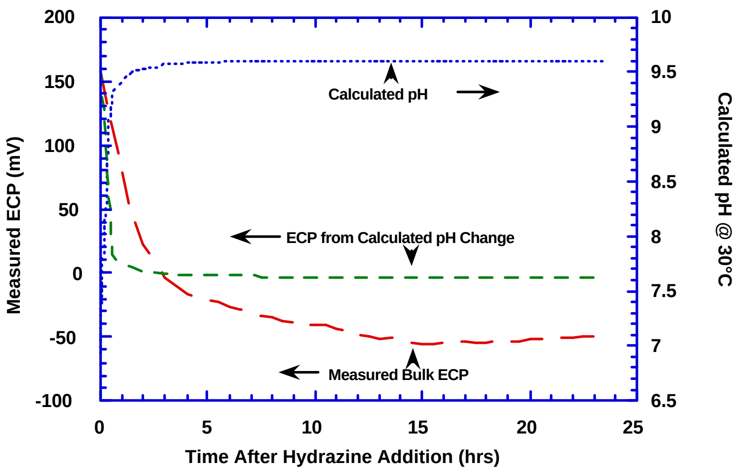


Effect of Startup Oxidants

Effect of Hydrazine Addition to Air Saturated DI Water

R. Eaker Calculations





$N_2H_4 + H_2O = N_2H_5^{+} + OH^{-}$ $K_{25°C} = 8.5 \times 10^{-7}$

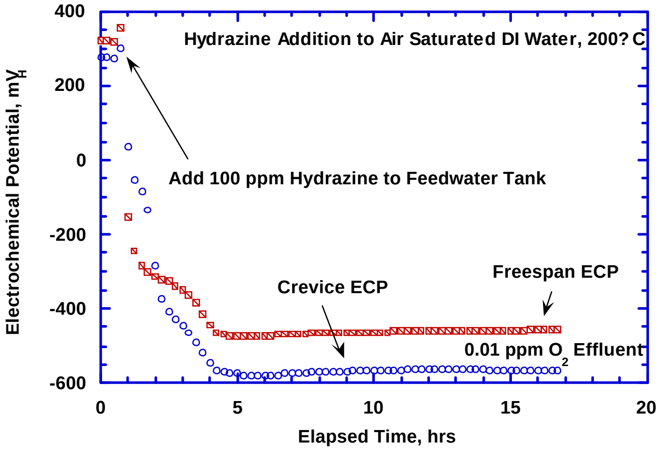
$N_2H_5^{2+} + H_2O = N_2H_6^{2+} + OH^{-}$ $K_{25°C} = 8.9 \times 10^{-16}$

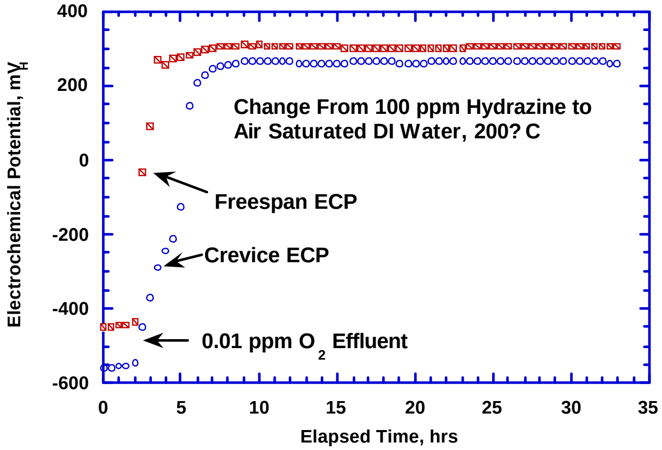
Bifunctional Base

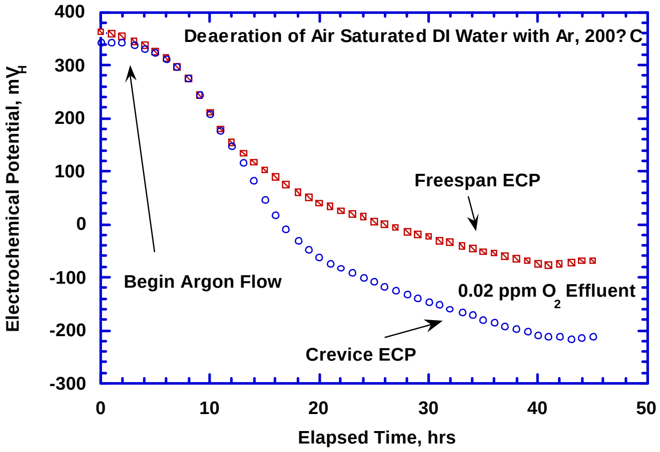
- Most of the change in ECP can be explained by change in pH
  - Assumes no hydrazine in autoclave initially
  - Assumed hydrazine well mixed
  - Assumes no hydrazine gradient in autoclave
- Calculated ECP reaches steady state in approximately 3 hours
- Comparison of calc ECP with measured ECP suggests non-ideal mixing

Effect of Startup Oxidants

Effect of Hydrazine Addition to Air Saturated DI Water

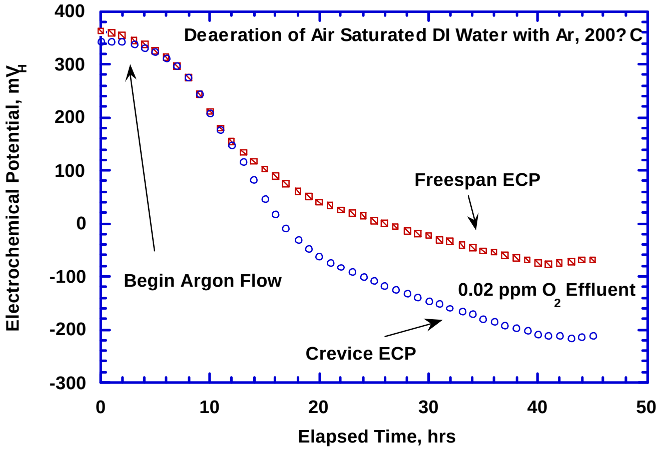


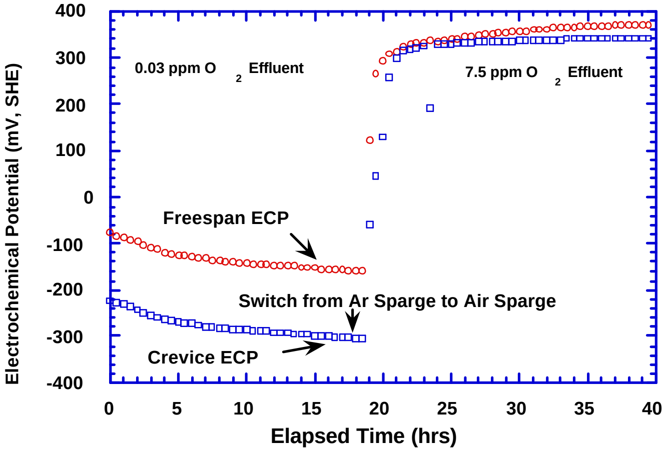




- At 200°C hydrazine lowers ECP by O_2 removal
- The ECP resulting from hydrazine addition is less than that resulting from deaeration
- ECP reaches equilibrium more rapidly with hydrazine that with argon
- ECP reversible
- Crevice ECP less than freesapn
  - The delta is greater in deaerated water

Effect of Startup Oxidants





Deaeration Effects Are Reversible

Effect of Startup Oxidants

- The crevice and freespan ECP in an air saturated condition are approximately separated by 30 mV or less
- The addition of 100 ppm hydrazine to air sat. water lowers the ECP (reduces O_2
- The ECP begins to decrease rapidly at approx. 100°C in 100 ppm N_2H_4
- With N_2H_4 the crevice ECP is approx. 100 mV lower than the freespan ECP

Air Saturated DI Water

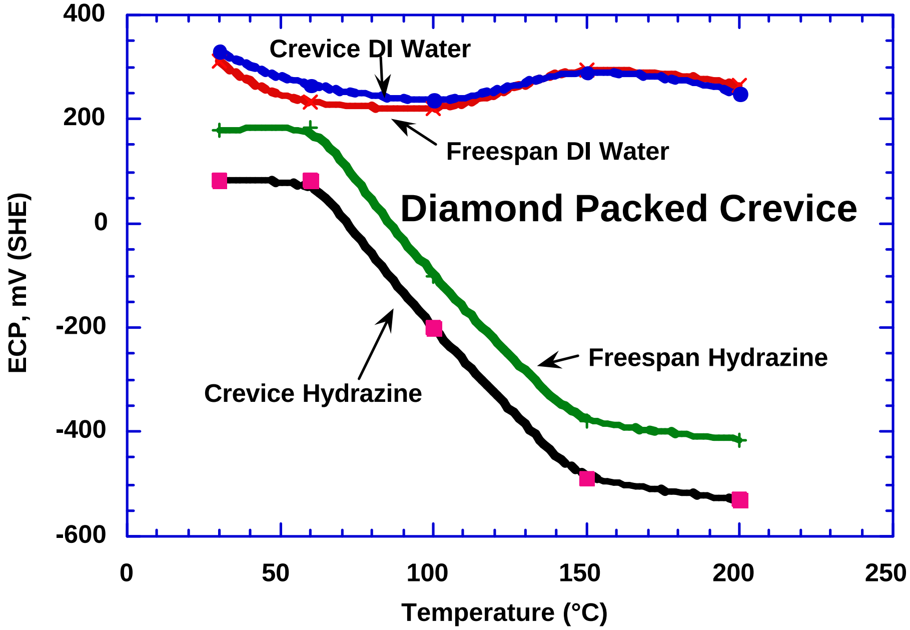
Temp	30°C	60°C	100°C	150°C	200°C
Freespan ECP	310 mV	232 mV	220 mV	295 mV	265 mV
Crevice ECP	330 mV	265 mV	235 mV	290 mV	250 mV
pH	6.9	6.5	6.1	5.8	5.6
$E_{H2O/O2}$	790 mV	750 mV	700 mV	630 mV	540 mV

Air Saturated DI Water/ 100 ppm Hydrazine

Temp	30°C	60°C	100°C	150°C	200°C
Freespan ECP	180 mV	185 mV	-100 mV	-380 mV	-415 mV
Crevice ECP	80 mV	80 mV	-200 mV	-490 mV	-530 mV
Hydrazine (out)	100 ppm	100 ppm	95 ppm	85 ppm	60 ppm
O_2 (out)	7.3 ppm	6.2 ppm	3.8 ppm	0.8 ppm	0.2 ppm

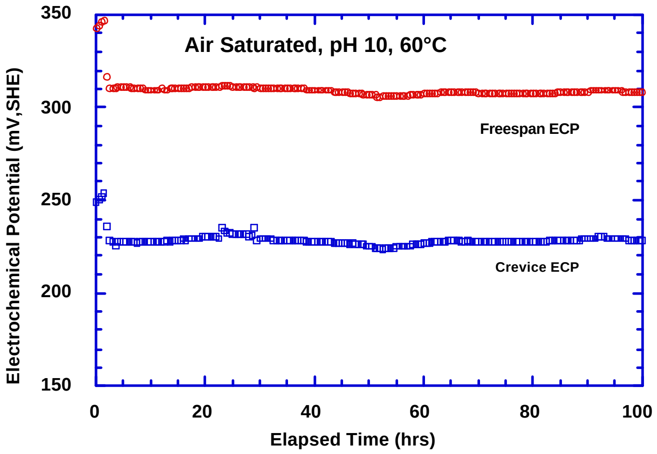
Effect of Startup Oxidants

Effect of Hydrazine Addition to Air Saturated DI Water

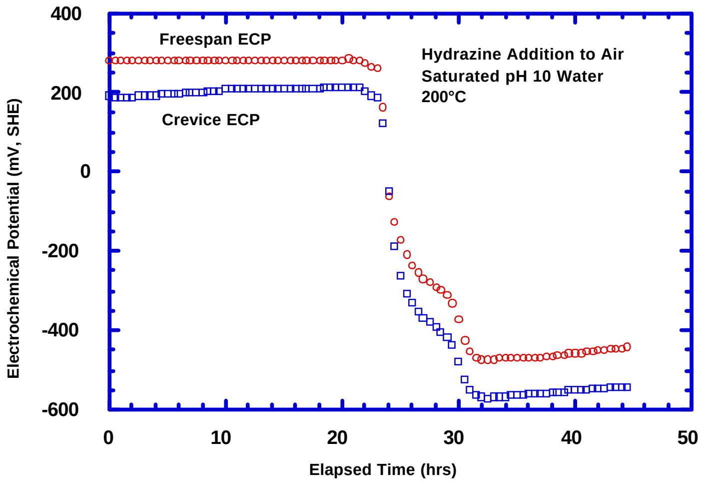


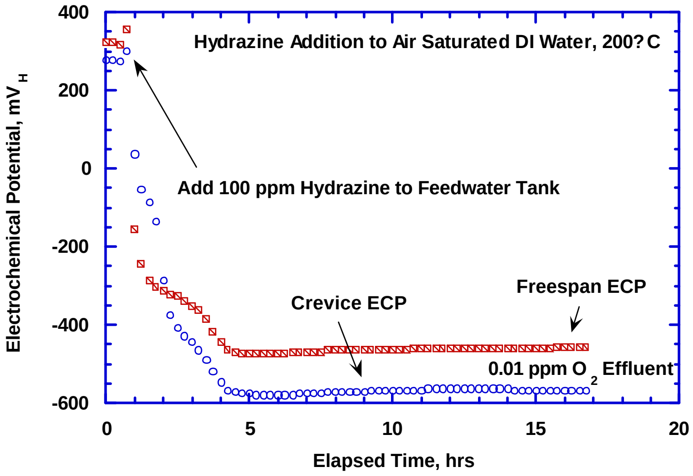
Startup Oxidants

Feedwater Adjusted to pH 10 with NaOH



- **Less drift in ECP at pH 10 than DI water**
- **Steady state ECP approximately same in DI water and pH 10 feedwater**





Effect of Startup Oxidants

pH 10 Feedwater

Air Saturated pH 10 NaOH

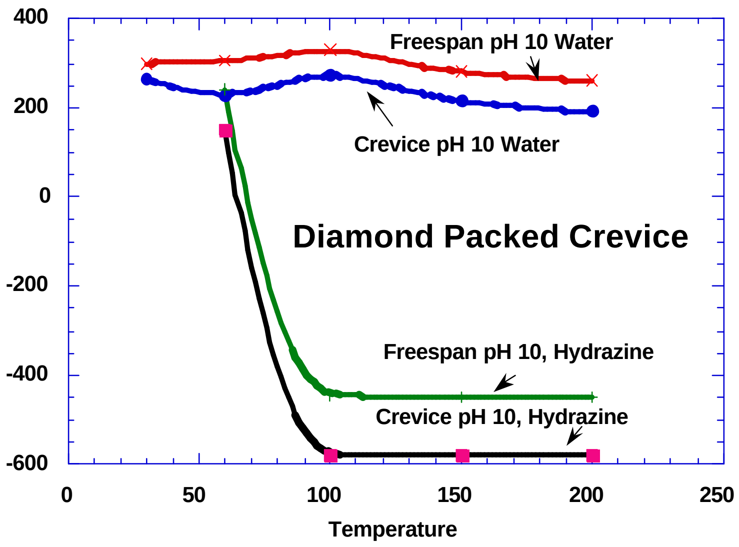
Temp	30°C	60°C	100°C	150°C	200°C
Freespan ECP	300 mV	305 mV	330 mV	280 mV	260 mV
Crevice ECP	265 mV	228 mV	275 mV	215 mV	190 mV
pH	10	9.2	8.6	7.9	7.6
$E_{H2O/O2}$	600 mV	570 mV	520 mV	450 mV	360 mV

Air Saturated pH 10 NaOH/ 100 ppm Hydrazine

Temp	30°C	60°C	100°C	150°C	200°C
Freespan ECP		-465 mV	-445 mV	-450 mV	-450 mV
Crevice ECP		-560 mV	-580 mV	-580 mV	-580 mV
Hydrazine (out)		90 ppm	90 ppm	85 ppm	60 ppm
O_2 (out)		6.2 ppm	1.6 ppm	0.02 ppm	0.03 ppm

Startup Oxidants

Feedwater Adjusted to pH 10 with NaOH



Summary

- Dissolved oxygen is “stripped” form the crevice during heat transfer
- Hydrazine concentrates in the crevice and lowers the ECP
- In DI water below 100 C decrease in ECP is a pH effect not O_2 reduction
- Hydrazine reduces O_2 more efficiently in pH 10 water than DI water

Mechanisms for Concentrating Impurities at Line Contact Tube Support Crevices in PWR SG's

Heated Crevice Seminar
Argonne
October 8-11, 2002

Peter Millett
Dennis Hussey
iSagacity

Outline of Presentation

- Introduction
- Line Contact Designs in Use
- Experimental and Field Observations regarding Line Contact Designs
- Approaches to Quantitative modeling
    - -3 step process
    - -review packed crevice model
    - -extrapolation to line contact crevices
- Summary

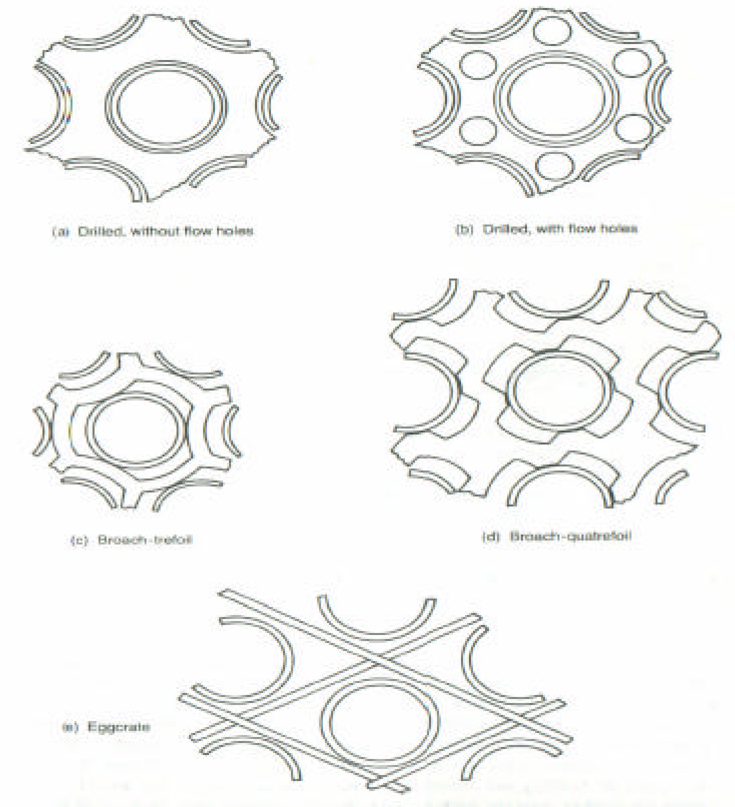
Introduction

- Corrosion of SG tubing at supports continues to be an industry problem
- New plants and replacement SG's use support plate design with a line contact at the tube
- Line contact designs are less susceptible to fouling and dryout….but they are not immune to the precursor to accumulation of aggressive chemicals
- Most of the industry R&D efforts over the past 20+ years regarding crevice concentration and corrosion mechanisms has been focused on fouled drilled hole support plates

Introduction

- An improved quantitative analysis of line contact crevices can lead to improved operational and maintenance practices for the current generation of SG’s
- How can we best extrapolate from drilled hole operating experience?
- Is our mechanistic understanding of these types of crevices sufficient ?

Line Contact Designs



(a) Drilled, without flow holes

(b) Drilled, with flow holes

(c) Broach-trefoil

(d) Broach-quatrefoil

(e) Eggcrate

Fleet Statistics for Support Structure Design Features

- Source: EPRI SG Degradation Database (September 2002)
- Includes design data for 237 plants world-wide
- 42% of the plants were originally designed with drilled hole support plates
  - 60% of those plants have replaced their SG's
    - 27% of replacements use grid/egg-crate design
    - 73% of replacements use broached design
- All replaced SG's were original drilled hole designs

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Review of Some Key Experimental Programs and Analytical Models

1. Curlee and Baum, Westinghouse, “Single-Tube Thermal and Hydraulic Tube Support Test,” EPRI NP 2046, September 1981
2. Bankoff, et.al., Northwestern University, “ Boiling Heat Transfer in a Narrow Eccentric Annulus,” EPRI NP 2610, September 1982
3. Merte, et.al, University of Michigan, “Boiling in Narrow Crevices in SG’s,” EPRI NP-2638, November 1982
4. Cassell and Vroom, CE, “T-H Tests of SG Tube Support Plate Crevices,” EPRI NP-2838, January 1983
5. Curlee and Baum, Westinghouse, “Tube Support Plate T-H Testing,” EPRI NP-3052, May 1983
6. Krupowicz and Rentler, CE, “Corrosion Performance of Alternative SG Materials and Designs,” EPRI NP-3044, July 1983

Objectives of EPRI Support Structure Design R&D Programs

- To better understand the T-H characteristics of alternative SG designs
- To characterize the onset and extent of dryout at the SG tube/support contact for alternative designs
- To provide a basis for the prediction of the onset of dryout
- To compare the susceptibility of different designs to fouling and accumulation of non-volatile chemicals

Experimental Findings (Dryout)

- Dryout as measured by increased wall superheat is a necessary condition for the concentration of chemicals
- Dryout occurs at or near the contact between the tube and support
- Dryout depends strongly on the primary/secondary temperature difference and shows no clear dependence on local quality, flow rate and pressure
- Drilled holes and Concave designs show dryout under prototypical SG conditions. Flat lands and Convex do not (non-fouled)

Experimental Findings (Fouling)

- Sludge deposits at or near the contact point first
- Fouling increases the superheat away from the contact point , enhances superheat at the contact point, and expands the dryout region
- Concave & Flat lands have a propensity to confine or entrap the outer precipitating oxide and sludge deposits
- All designs demonstrated dryout (to different degrees) after sludge was added to the experimental device

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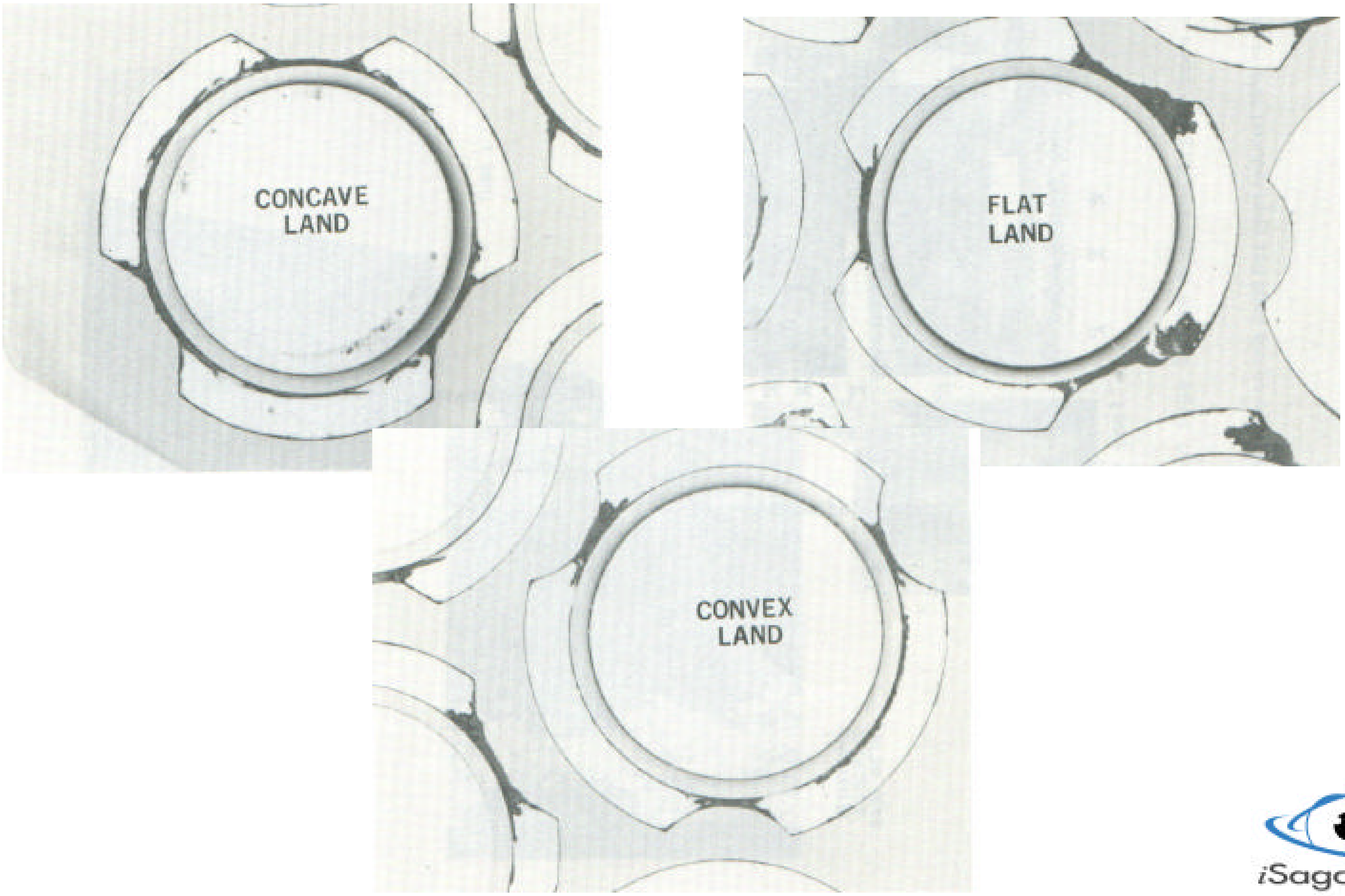
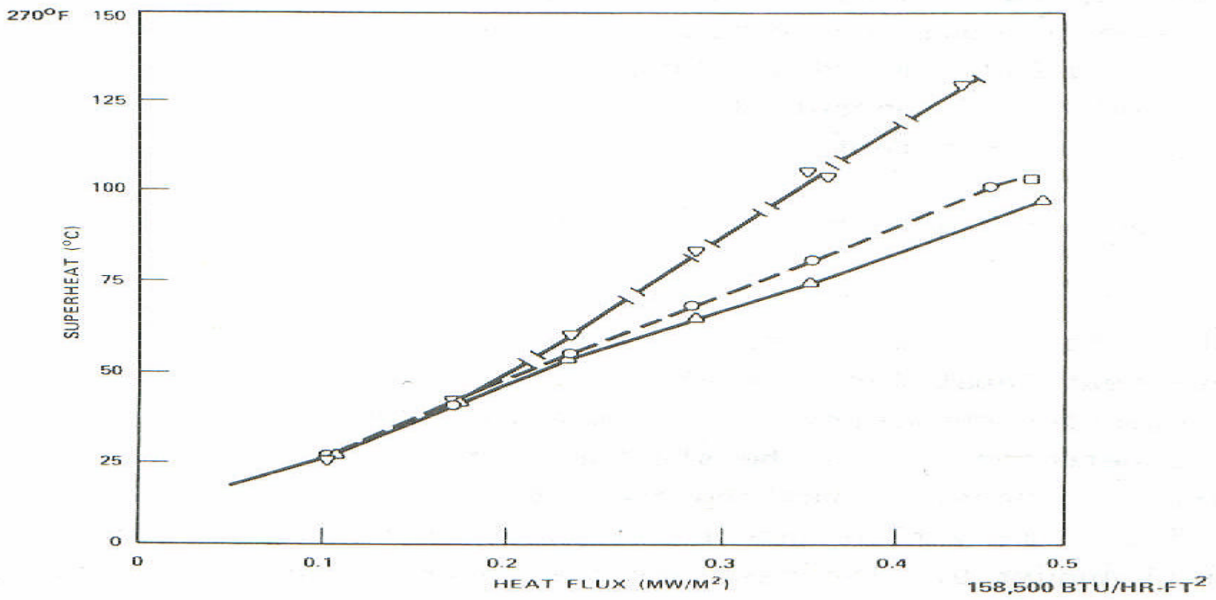
Corrosion in Trefoil Designs (NP3044)



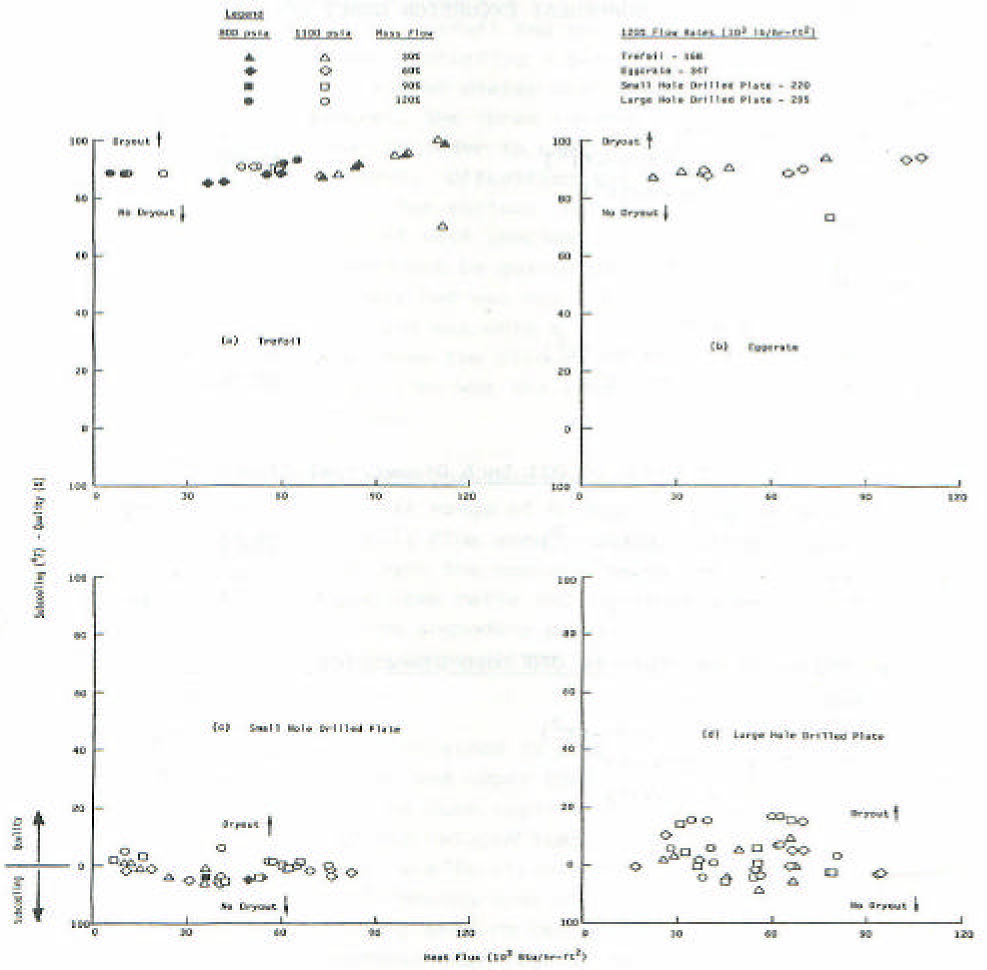
Effect of Heat Flux on Superheat (NP2046)



SYMBOL	DESIGN	MASS VELOCITY ($KG/S\text{-}M^2$)	QUALITY
▽	CYLINDRICAL HOLE	109	13.9%
○	CONCAVE QUAT	109	12.5%
△	NUCLEATE BOILING FLAT QUAT CONVEX QUAT	112 109	12.8% 16.2%

Dryout in Various Designs (NP2838)

Figure S-1. Tubewall Excursion Onset Conditions



Analytical Model Development & Observations

- SG crevice T-H models have been developed to describe boiling in the absence of fouling
- Early models focused on an eccentric drilled hole support. Approach was to solve heat/mass/mom. equations in the complex geometry
- Boiling in narrow gaps consists of three regimes:
  - isolated bubble regime
  - coalesced bubble regime
  - dryout regime
- Analytical models predict transition from one regime to the next and extent of dryout patch

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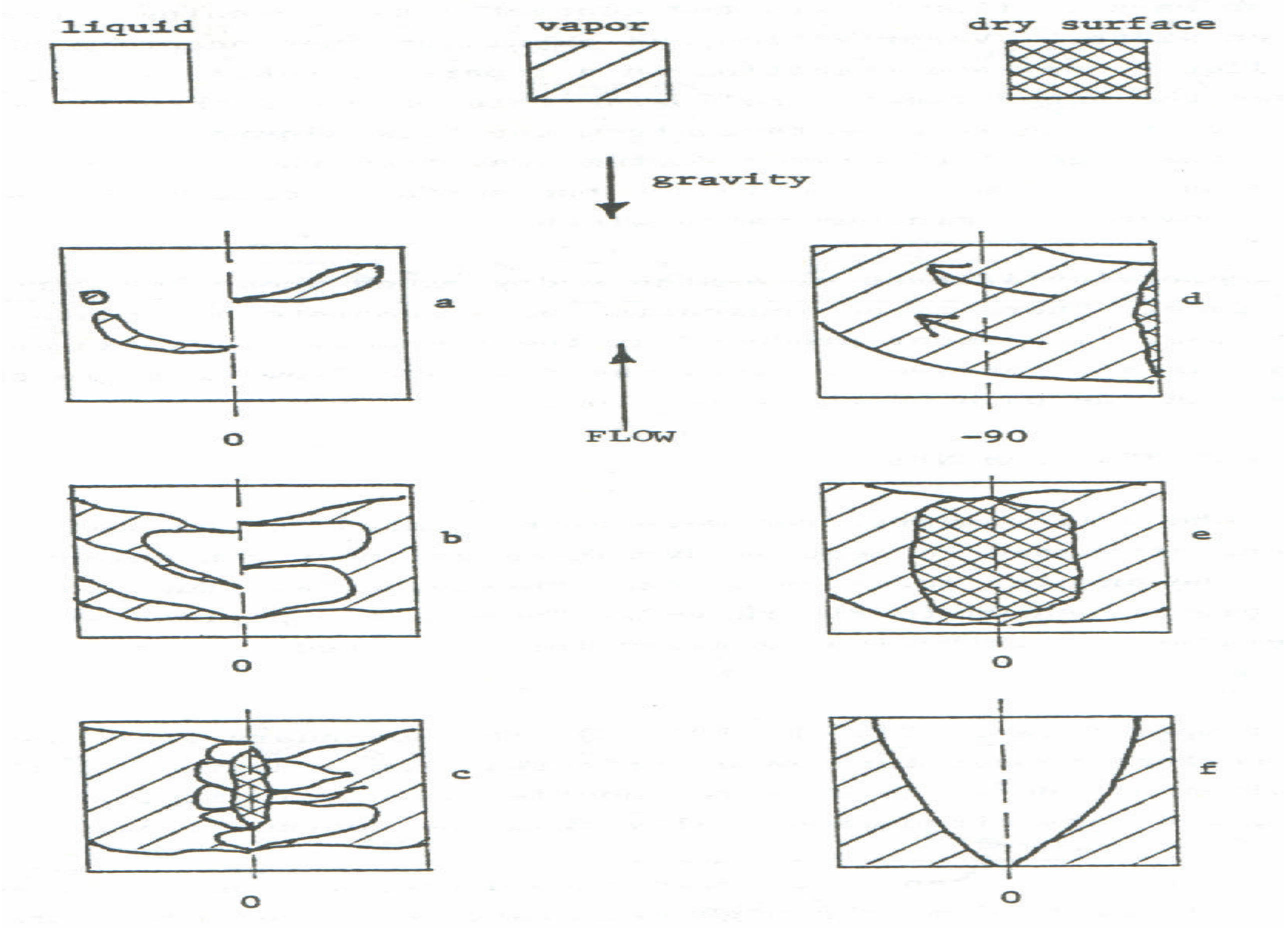
Visual Appearance of Crevice Boiling Phenomena (NP2610)



Limitations of Early Work to Present Concerns

- Emphasis is either on behavior of crevices in the absence of fouling/impurities or with excessive levels of fouling/impurities
- Modern SG’s operate with low levels of both soluble and insoluble impurities
- We may be most interested in the mild fouling condition and the long term behavior
  - transition to dryout
  - extent and location of concentration zone

Towards a quantitative basis for predicting current plant conditions

- Working assumption: Overall process can be adequately described by three mechanisms occurring in series

Step 1.- Dryout occurs at tube/line contact. Local T-H processes dictate location and extent

Step 2.- Local deposition of corrosion products from the feedwater at and near the dryout zone. Fouling increases size and location of the dryout zone

Step 3.- Non-volatile chemicals accumulate in the fouled crevice region through well-established T-H mechanism

Step 1: Predictive Modeling

- References 1,2,3 and others (notably, Ishabashi) can be used to guide further development if needed. Goal is to describe presence of and extent of dryout patch
- Much advanced CFD can be used to improve predictive capabilities
- Models can be benchmarked against T-H data from References 1-6.

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Step 2: Predictive Modeling

- Numerous Boiling Deposition models have been published in the literature (e.g. Beal-Westinghouse, Turner/Lister-AECL)
- For example:

$$dW/dt = P\frac{Q}{L}C - KW$$

W=weight of crud deposit at time t, g/cm2
C=crud concentration in reactor water, g/kg
P= probability of deposition, dimensionless
Q=heat flux on the fuel surface, kcal/cm2/day
L=latent heat of vaporization of water, kcal/kg
t=time, day
K=release constant, day^{-1}

- Deposition models require empirical constants
- Limitation will be lack of experimental data for geometries and chemistries of interest

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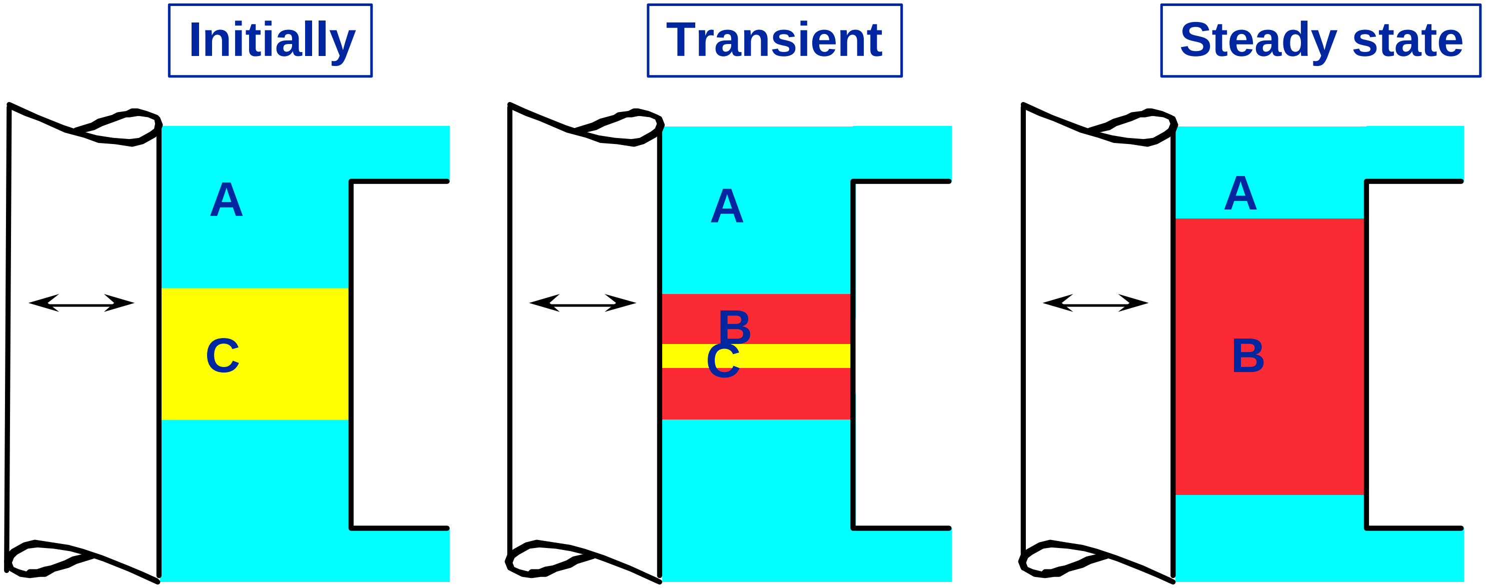
Step 3: Predictive Modeling



A : Bulk Water B : Impurities Concentrated C : Blanketed Region

If sufficient liquid cannot be drawn into the porous media to maintain nucleate boiling, a steam blanketed region will exist initially below the nucleate boiling region. As time evolves, impurities fill the crevice.

Packed Crevice Model

- One dimensional model : axial direction only
- Symmetry at the middle of the support plate assumed
- Single chemical specie
- Based on the conservation of mass momentum and energy
- The model predicts the factor of concentration of a species (concentration in the crevice / concentration in the bulk) as a function of the axial dimension

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Crevice Chemistry

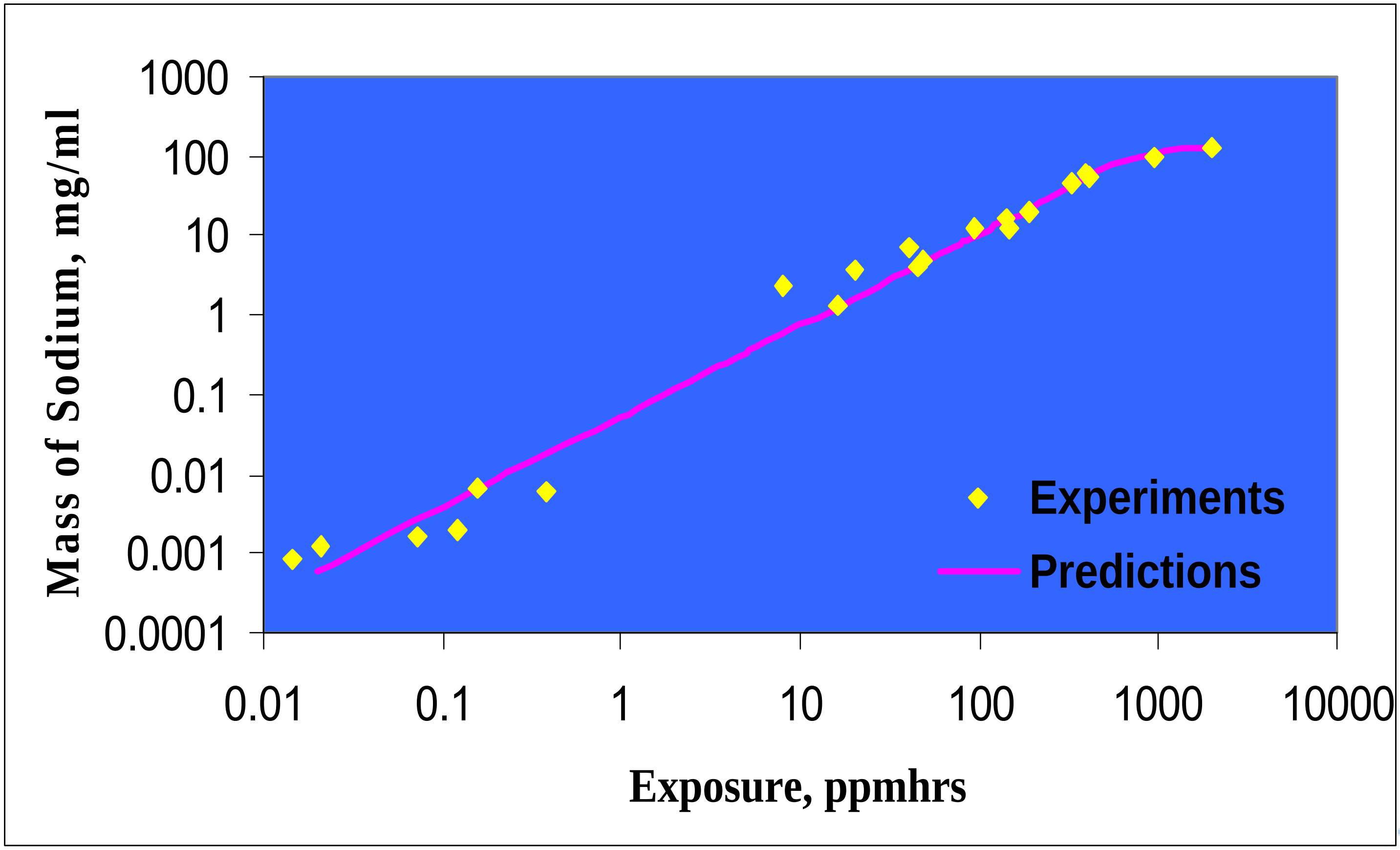
- Conservation of Species (e.g. Na)

$$eS[\dot{N}a] = -(v_l[Na])' + k_{vl}(v_l[Na])' - (DS[Na]')'$$

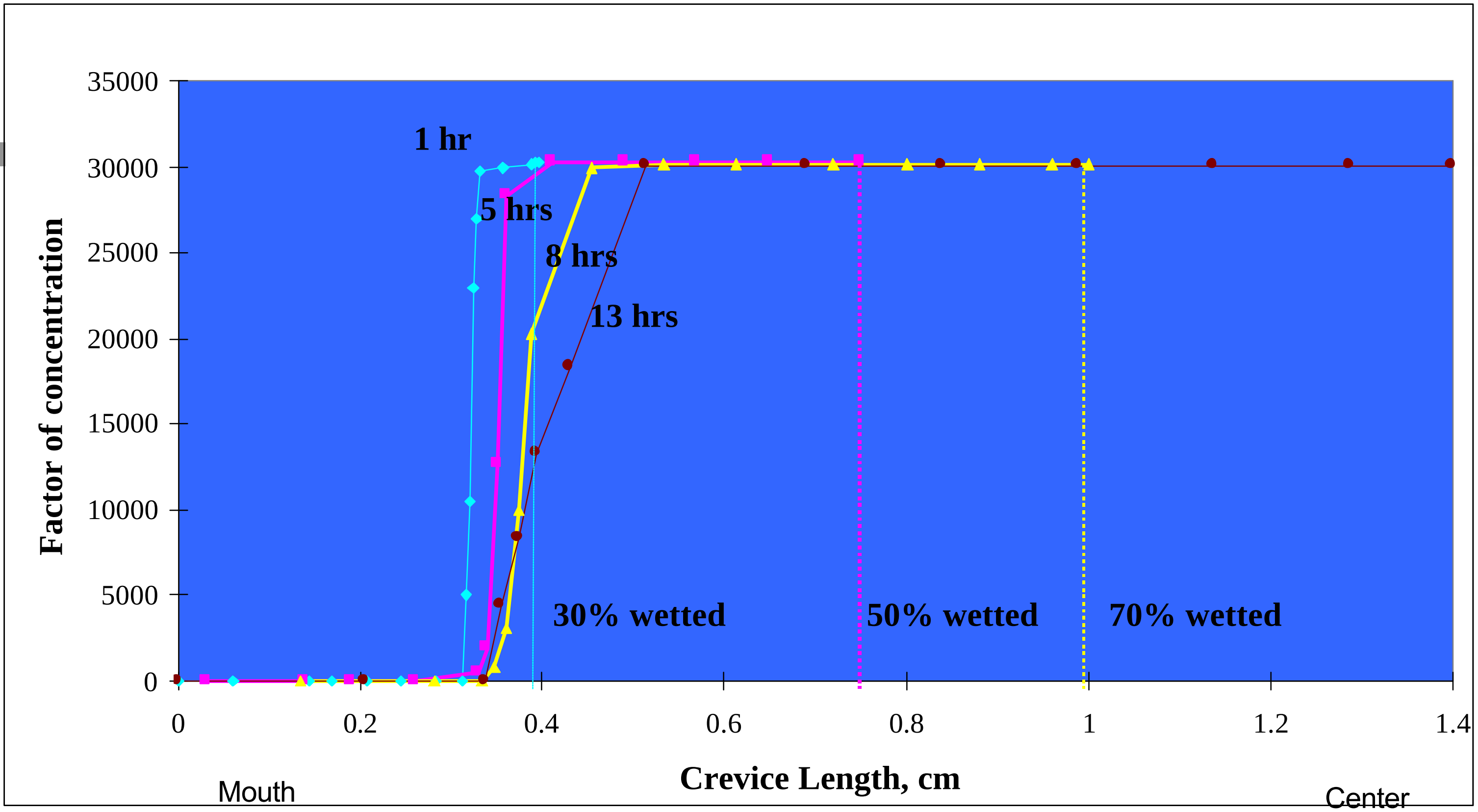
Rate of accumulation of Sodium = Convection - Volatilization - Diffusion

- Multi-component chemical equilibrium defines species interactions (e.g. MULTEQ-REDOX)

Boiling Crevice Model Benchmarking



Crevice Concentration Profile
Crevice exposed to 20ppm sodium



- After 1 hour, 30% wetted
- After 5 hours, 50% wetted
- After 8 hours, 70% wetted
- After 13 hours, FULLY wetted

The crevice slowly fills with a concentrated solution. The wetted length increases.

Summary

- Line contact designs are less susceptible to fouling and dryout….but they are not immune to the precursor to accumulation of aggressive chemicals
- An improved quantitative analysis of line contact crevices can lead to improved operational and maintenance practices for the current generation of SG’s
- Early laboratory testing and field observations would be useful in benchmarking new models
- Deposition modeling may be the most challenging

Hideout and Hideout Return in PWR Steam Generators: Predictions of Crevice Chemistry

S. G. Sawochka
NWT Corporation

Argonne National Laboratory
October 2002

Hideout During Normal Operation

- Species concentrate and may precipitate in flow restricted boiling regions
- Crevice concentration factors can exceed 10^8 at BPE limit
- Hideout on free surfaces also can be significant but concentration factors much lower
- Hideout and hideout return studies can provide valuable insights relative to local region chemistry

Hideout During Normal Operation

- Mass balance approach to hideout estimation not possible on a routine basis due to analytical sensitivity limitations
- However, hideout has been measured during normal operation
  - Inject chemical impurities at known rate into feedwater
  - Quantify blowdown removal
  - Recycle of impurities transported by steam eliminates need for steam data

Estimation of Hideout Rate Constant

$$\frac{d(MC_{SG})}{dt} = W_I C_I - W_{BD} C_{SG} - W_{HO} C_{SG}$$

Where:

C_{SG} = Contaminant concentration increase in the steam generator blowdown above level prior to injection, ppb

C_I = Contaminant concentration in the injection solution, ppb

W_I = Injection flowrate, kg/h

W_{BD} = Blowdown flowrate, kg/h

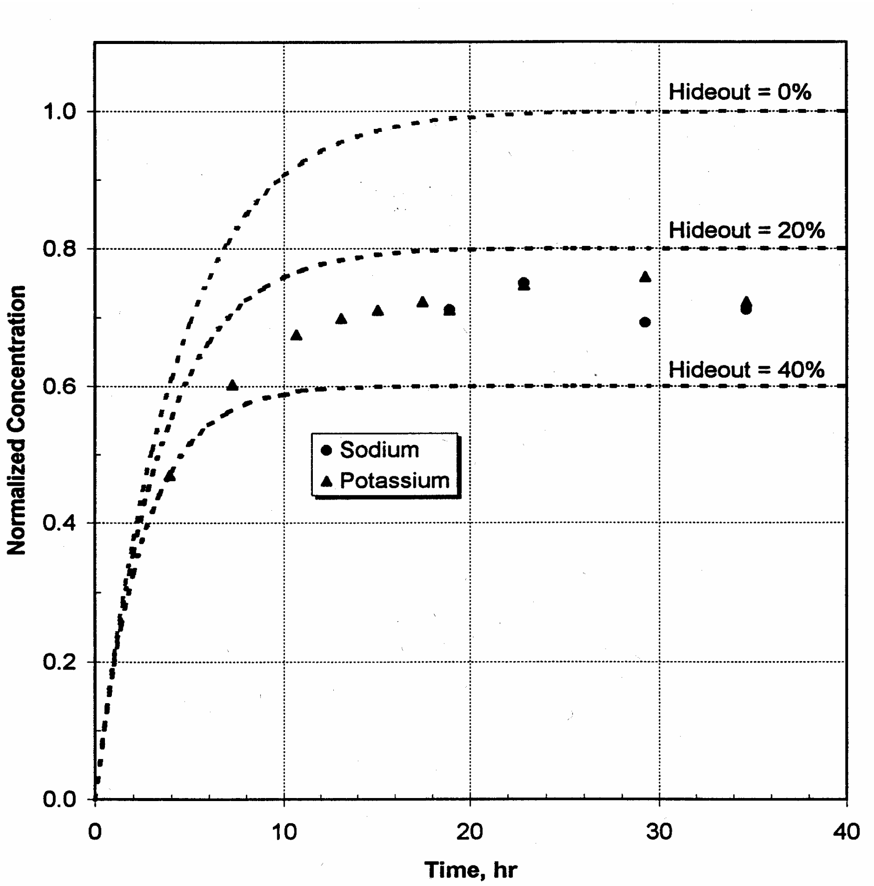
M = Mass of liquid in the steam generator, kg

t = Time, h

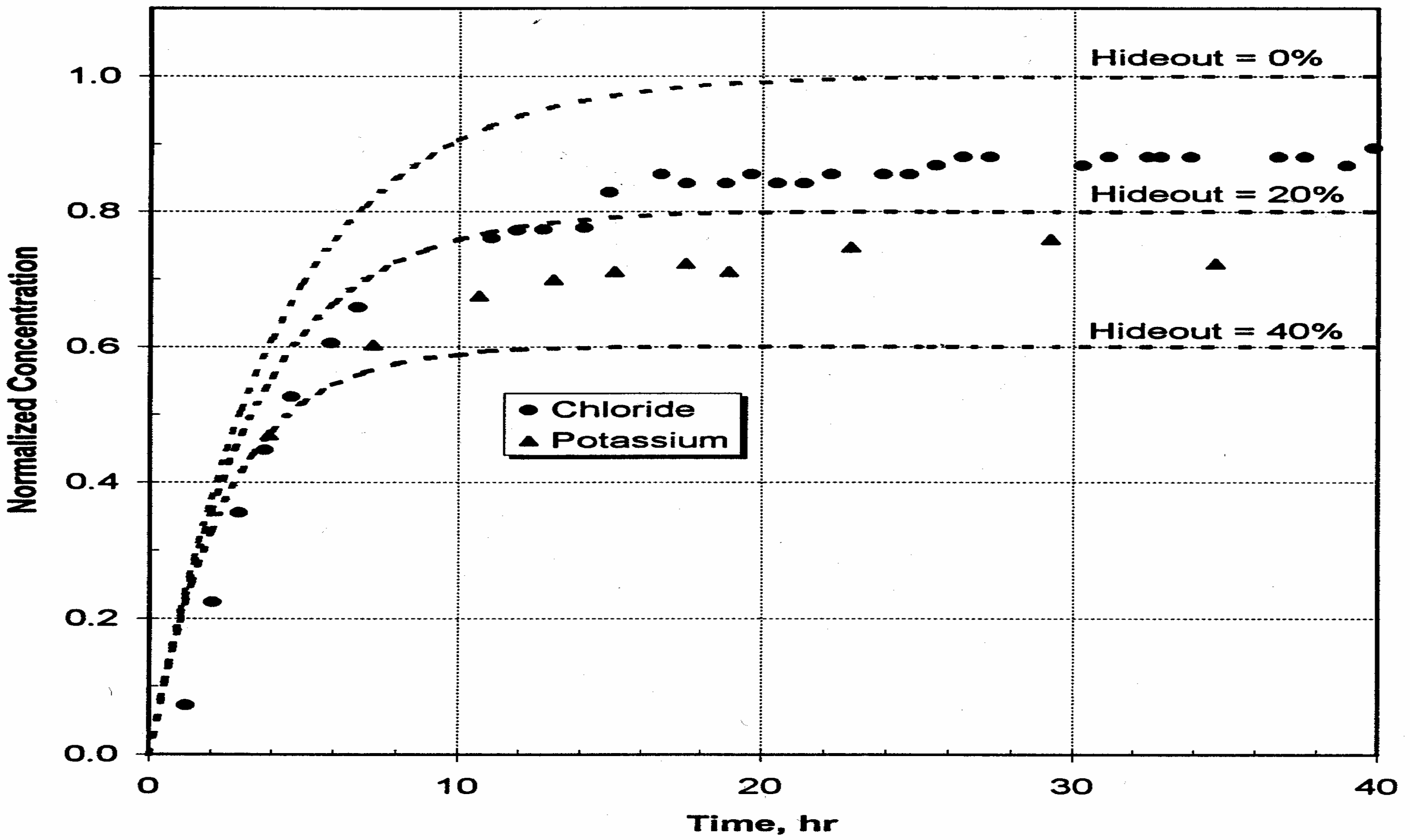
W_{HO} = Hideout rate constant, kg/h

- Hideout assumed to be governed by evaporation rate in crevice

Sodium and Potassium Hideout at 95% Power (W-51)



Potassium and Chloride Hideout at 95% Power (W-51)



Injection Test Results

- Conformance of data to model supported validity of model for sodium, potassium and chloride
- Hideout rate constants varied with species
- Technique to estimate crevice impurity inventory on real time basis appeared present
- Differences lead to crevice chemistry prediction uncertainties if reliance placed on contaminant ingress ratios or bulk water concentration ratios

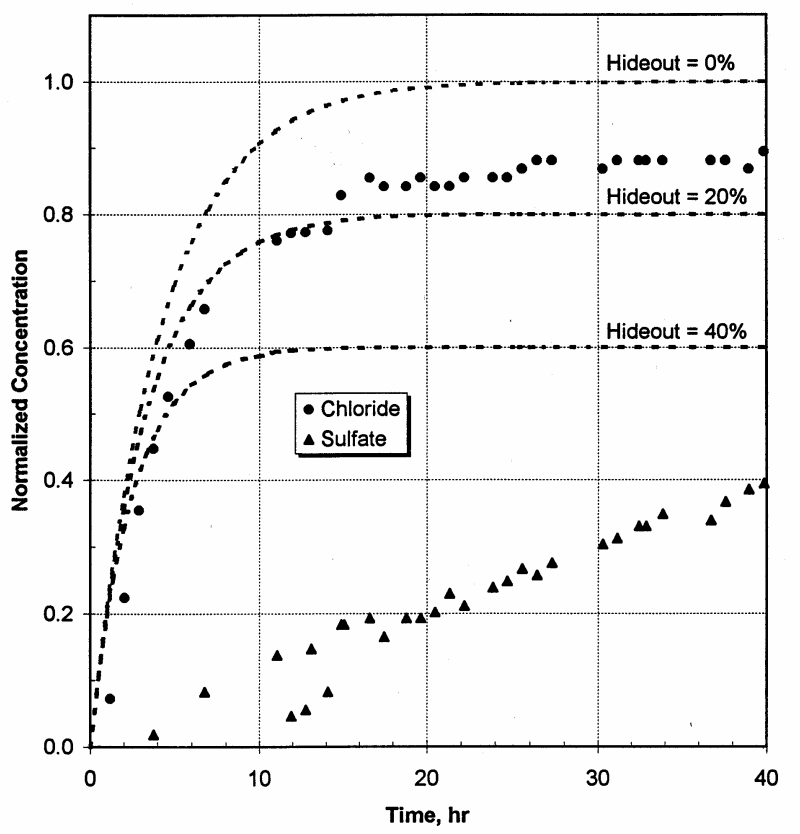
Conclusions: NaCl Ingress

- Assuming equal hideout fractions, a near neutral crevice pH is expected
- Basing crevice concentration ratios on bulk water concentrations yields an acidic crevice prediction
- Basing crevice concentration ratios on hideout rate data, a caustic crevice is predicted
- Mode of attack predictions vary:
  - Neutral pH – Minimal attack
  - Acid crevice – Denting/Pitting/Possible IGSCC
  - Caustic – IGA/IGSCC

Conclusions

- Recognition of difference in hideout fractions critical to crevice chemistry predictions
- Problem further complicated by non-conformance of sulfate hideout to model

Chloride and Sulfate Hideout at 95% Power (W-51)



Sulfate Behavior

- Initial model inadequately described process
- Adsorption process initially governs hideout

$$C_o = KC_b$$

Where

C_o = Surface concentration, kg/kg oxide

C_b = Concentration in the bulk, kg/kg water

K = adsorption coefficient (kg/kg oxide)/(kg/kg water)

- Evaporation mechanism governs once surface adsorption capacity satisfied

Results of Single Phase Adsorption Tests

- Sulfate adsorption quantified at low sulfate concentrations
- Desorption of sulfate by pure water occured over several days
- Results consistent with hypothesis developed from plant data
- No significant Cl, Na or Ca adsorption
- Phosphate adsorption significant (as expected)
- Magnesium “adsorption” also significant (not expected)

Summary of RSG Hideout Evaluations

- Hideout of sodium, chloride and potassium governed by a boiling process in flow restricted regions
- Sulfate hideout initially governed by surface adsorption; after adsorptive limit is reached, hideout by evaporative processes governs
- Calcium and magnesium hideout rate constants much higher than highly soluble species
- Hideout rate constants markedly impacted by steam generator design and cleanliness
- Decreased hideout at reduced power

Bases for Inventory Calculation

	Hideout Rate Constant (W_{HO}), lb/h		
	Sodium	**Potassium**	**Chloride**
Westinghouse			
Plant A (D4 SG)	18,000	21,000	11,000
Plant B (51A SG)	12,000	30,000	2,000
Plant C (51 SG)	3,500	6,000	2,900
Plant D (D5 SG)	0	700	300
Combustion Engineering			
Plant E (67 SG)	25,000	35,000	15,000

CREV-SIM

- Method of estimating impurity accumulation rates in crevices based on hideout rate constant

$$\text{Hideout Rate} = W_{HO}\ C_{BD}\text{, e. g.,}$$

$$= (1000)\ (1)\ (10^{-9}) = 10^{-6}\ \text{lbs/h Na}$$

- Results provide reasonable basis for real time crevice chemistry tracking using CREV-SIM code
- Correlations of CREV-SIM crevice inventory predictions and hideout return data attempted but not particularly successful

CREV-SIM Application Problems

- Hideout rate constant varies with plant design, power, operating history, etc.
- Hideout rate depends on crevice chemistry, e.g., chloride volatility will vary with pH
- Relation of hideout rate to blowdown concentration may not be linear; data available only at ~3 to 10 ppb
- Blowdown concentrations approaching LLD values at time of evaluation
- Incomplete return of hideout species expected

CREV-SIM Application Problems

- Resolution requires intermittent determination of hideout rate constants
  - Blowdown flowrate variation
  - Cycle mass balance – a simple approach
- Use of code has been minimal to author’s knowledge; emphasis placed on hideout return technique for EOC crevice chemistry prediction

Hideout Return in PWR Steam Generators

- Crevice and surface deposit impurities return to bulk liquid during shutdowns
  - Void collapse/rewetting
  - Diffusion to bulk

Hideout Return (HOR) = Inventory Increase + Blowdown Removal – Feedwater Input

- Approach based on assumption that species ratios reflect crevice ratios
- MULTEQ or Molar Ratio Index approaches used to assess chemistry

Hideout Return Data Applications

- Predictions of chemistry and corrosion tendencies in local regions
- Source term assessments
- Molar ratio control program assessments
- CREV-SIM updating

HOR Assessment

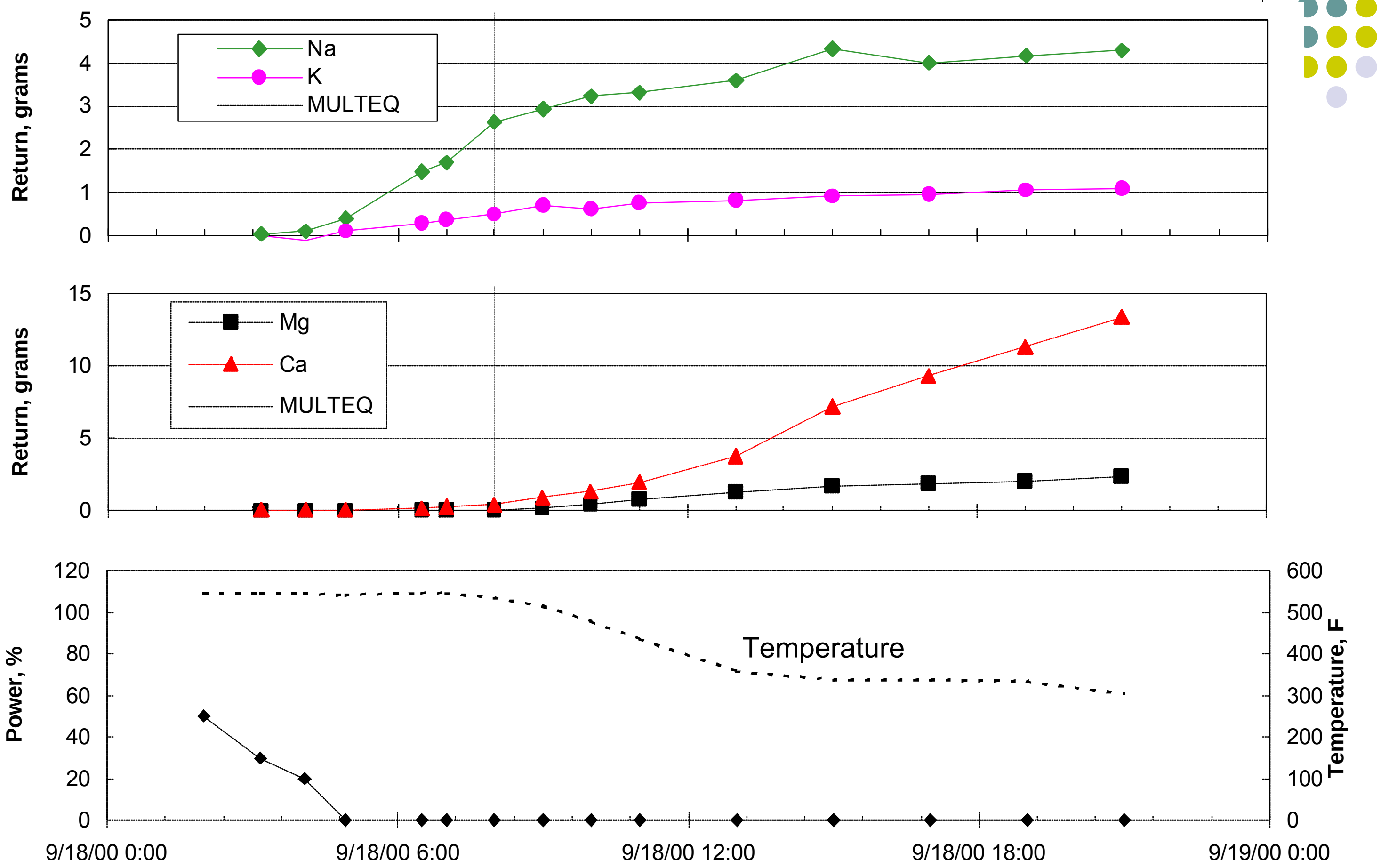
- Emphasis on hideout return immediately after shutdown for crevice chemistry predictions
  - Highly soluble species return rapidly
  - Precipitate return is delayed
- Data for total shutdown evolution used for source term assessments and confirmation of crevice chemistry inferences
- EPRI hideout return code available

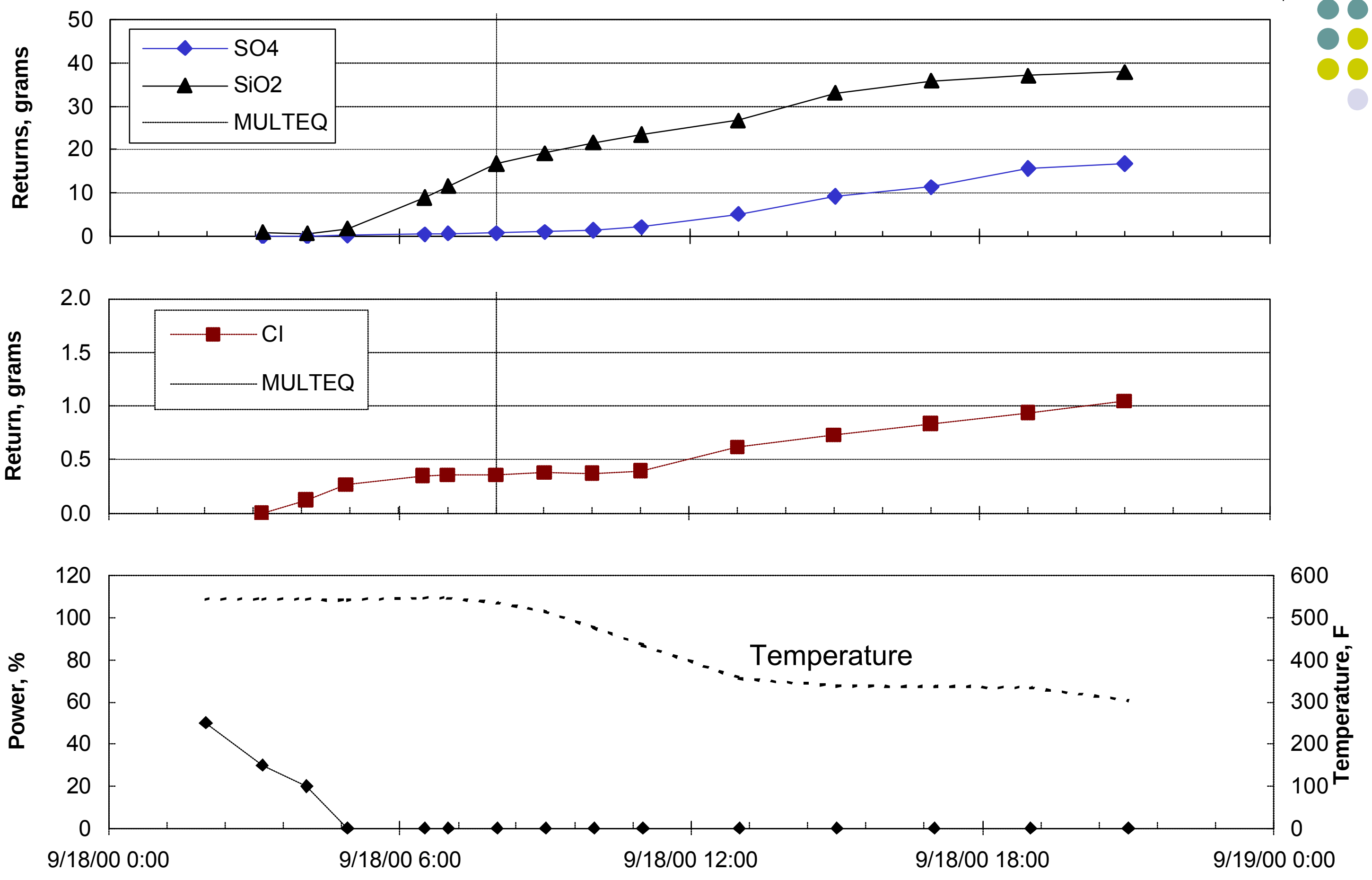
Inferences from Concentration and Return Data

- Species that return promptly on shutdown (before cooldown) probably present as solubles or highly soluble precipitates on tubing surfaces and in crevices
- Species that return preferentially during cooldown probably exist as precipitates during normal operation or are returning from very difficult to access regions
  - Many precipitates exhibit retrograde solubility
  - Simultaneous return of two species during cooldown infers their association as a compound
- Quantitative source breakdown not possible – reliance is on ratio similarity assumption

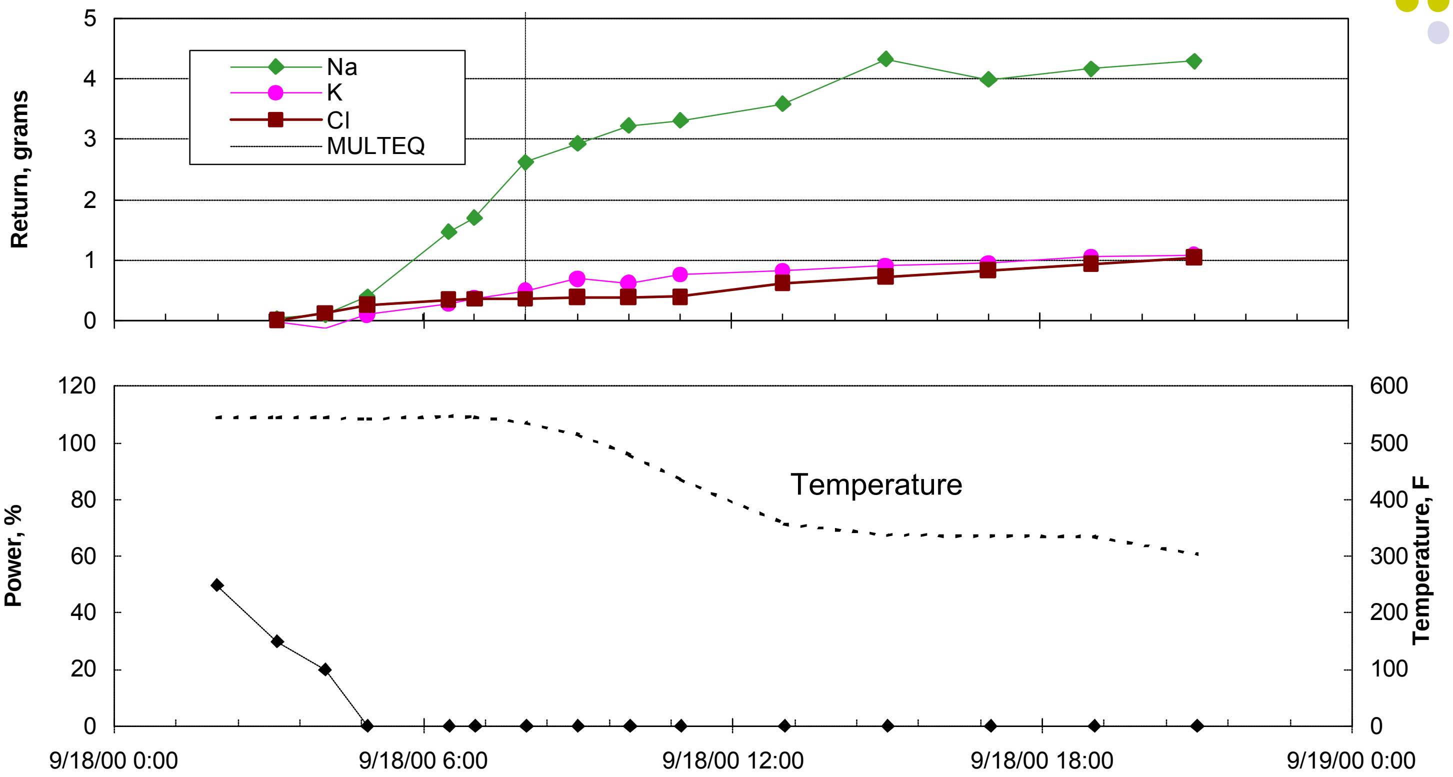
Predictions of Chemistry in Local Regions

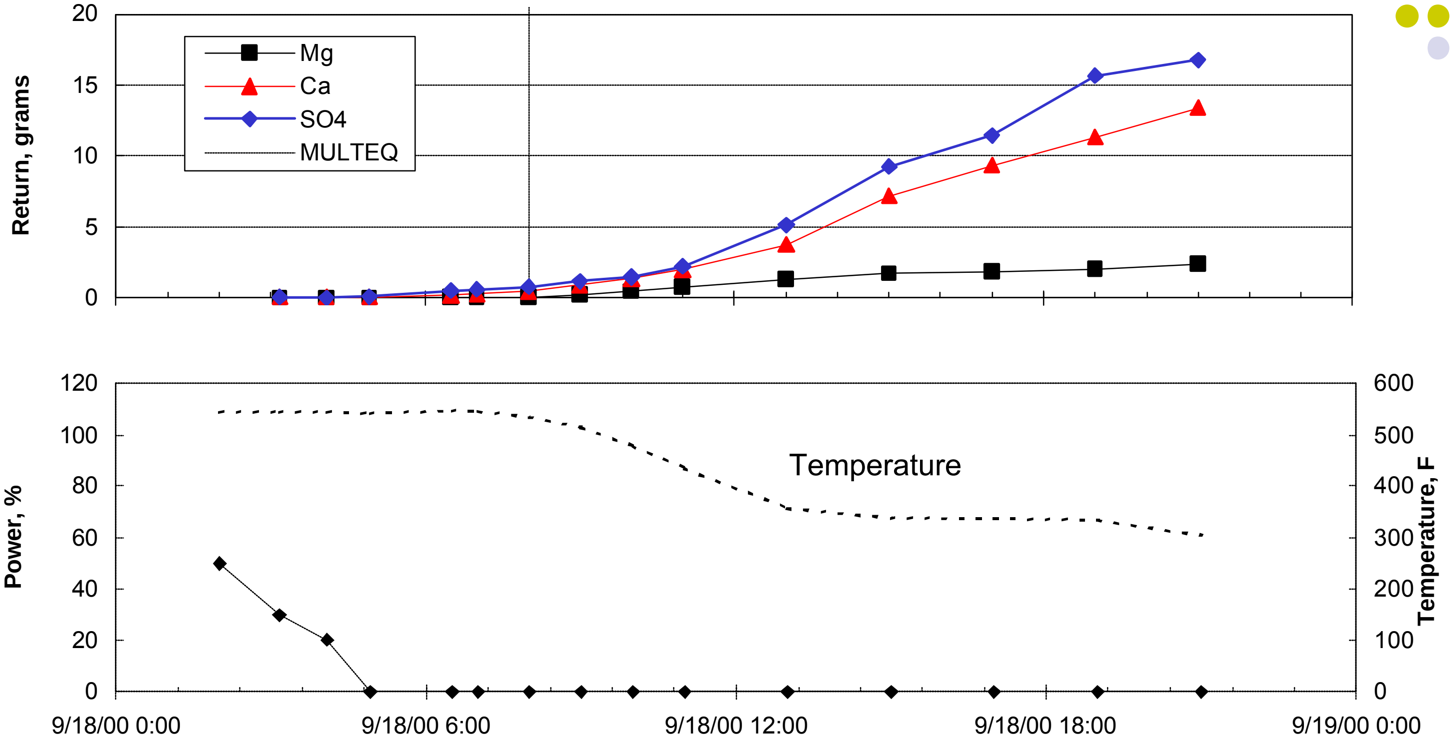
- Highly Soluble Species
  - Sodium
  - Chloride
  - Potassium
- Adsorbed Species
  - Silica
  - Sulfate
- Precipitated Species
  - Calcium
  - Magnesium
  - Aluminum
  - Sulfate
  - Silica

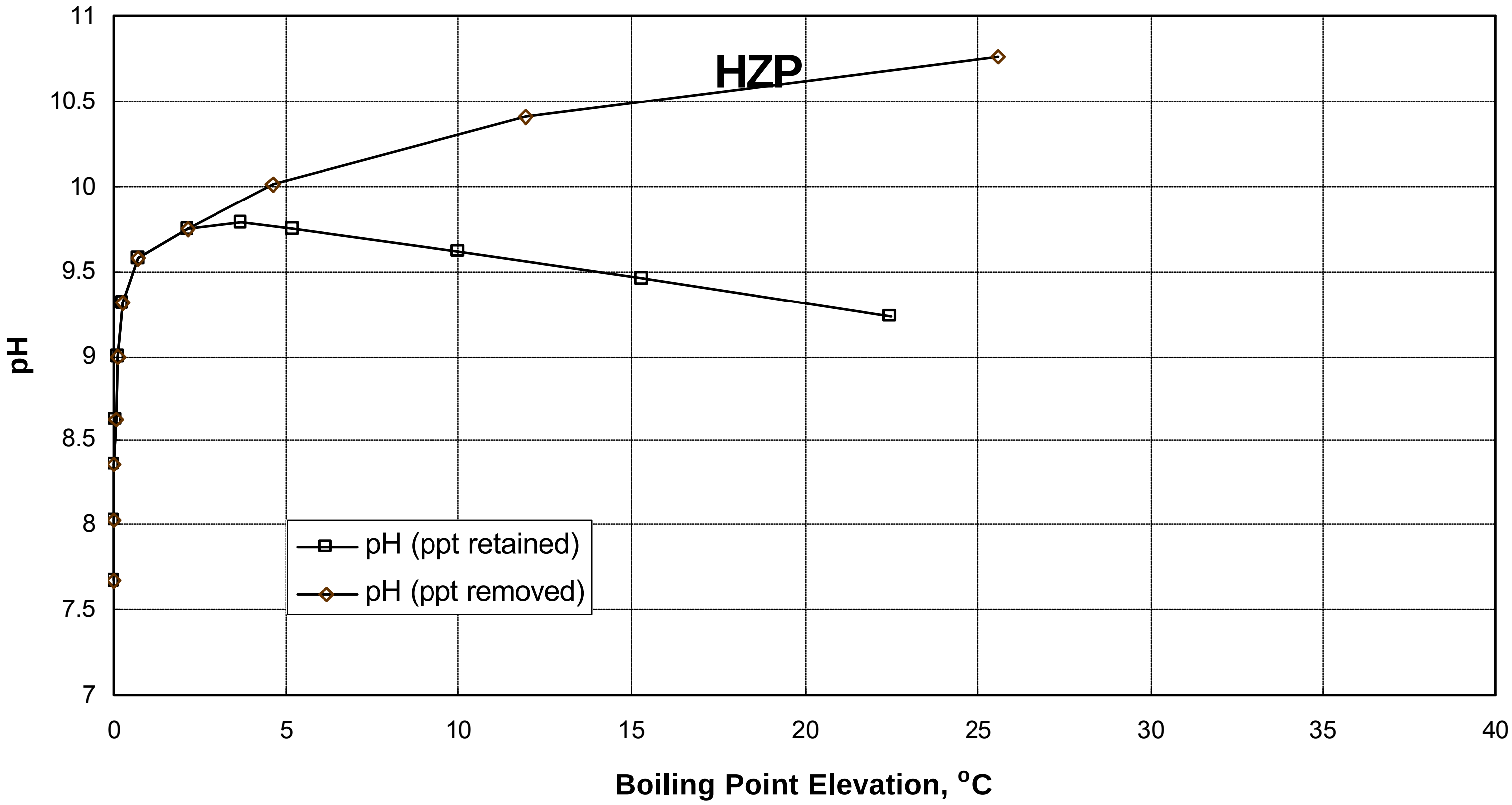

Return, grams
5
4
3
2
1
0
Na
K
MULTEQ
Return, grams
15
10
5
0
Mg
Ca
MULTEQ
Power, %
120
100
80
60
40
20
0
Temperature
Temperature, F
600
500
400
300
200
100
0
9/18/00 0:00
9/18/00 6:00
9/18/00 12:00
9/18/00 18:00
9/19/00 0:00



Returns, grams
50
40
30
20
10
0
SO4
SiO2
MULTEQ
Return, grams
2.0
1.5
1.0
0.5
0.0
Cl
MULTEQ
Power, %
120
100
80
60
40
20
0
Temperature
Temperature, F
600
500
400
300
200
100
0
9/18/00 0:00
9/18/00 6:00
9/18/00 12:00
9/18/00 18:00
9/19/00 0:00


5
4
3
2
1
0
Return, grams
Na
K
Cl
MULTEQ
120
100
80
60
40
20
0
Power, %
600
500
400
300
200
100
0
Temperature, F
Temperature
9/18/00 0:00
9/18/00 6:00
9/18/00 12:00
9/18/00 18:00
9/19/00 0:00


Return, grams
20
15
10
5
0
Mg
Ca
SO4
MULTEQ
Power, %
120
100
80
60
40
20
0
Temperature, F
600
500
400
300
200
100
0
Temperature
9/18/00 0:00
9/18/00 6:00
9/18/00 12:00
9/18/00 18:00
9/19/00 0:00


HZP
pH
11
10.5
10
9.5
9
8.5
8
7.5
7
0
5
10
15
20
25
30
35
40
Boiling Point Elevation, °C
pH (ppt retained)
pH (ppt removed)

Crevice Chemistry Predictions for Plant X

- MULTEQ Basis (precipitates retained)
- Caustic solution predicted, pH_T ˜ 9.2 (precipitates retained)
- Precipitates

  Na_2SO_4 $CaSiO_3$ SiO_2 $Ca_2Mg_5Si_8O_{22}(OH)_2$

  $Na_2Si_2O_5$ K_2SO_4 CaF_2
- Solution at BPE of 22°C
  - 3.1 MOLAL Na
  - 0.01 MOLAL Ca
  - 5.5 MOLAL K
  - 5.7 MOLAL Cl
  - 0.5 MOLAL SO_4
  - 5 (10^{-10}) MOLAL H^-
  - 0.2 MOLAL OH^-

Crevice Chemistry Predictions for Plant X

- Solution is not a concentrated acid or base
- Neutral salts are major ionics
- Laboratory corrosion data on which to base prediction of long term corrosion tendencies not available

HOR Variations

Plant	Cumulative Return						
	Na	Cl	K	Ca	Mg	SiO_2	SO_4
A	18	18	3	8	0.5	90	3.6
B	3	2	1.5	0.9	0.1	100	5
C	0.11	0.01	0.04	2.2	0.3	28	0.05
D	0.4	0.7	0.1	0.3	0.05	140	
E	0.15	0.12	0.04	0.20	0.03	35	0.35
F	0.2	0.1	0.3	0.6	0.1	600	18
G	2.5	0.35	0.5	0.4	0.07	16	0.8
H	0.6	0.8		2.5	1.0	21	2
I	0.3	0.8	0.25	28	0.6	30	0.9

Relation of HOR and Blowdown Chemistry

	MIHAMA-3	OHI-2[a]	MIHAMA-2[a]	Plant Y (U.S.)
Blowdown, ppb				
Na	<0.1	<0.1	3	0.4
Cl	0.64	0.23	2.2	0.3
SO_4	0.71	0.23	1.7	0.9
HOR, g/SG				
Na	0.35	0.59	3.71	2.5
K	0.07	0.21	1.16	0.5
Cl	0.79	0.34	1.82	0.35
SO_4	4.26	2.61	41.22	0.8
Mg	3.41	2.71	4.59	0.4
Ca	2.57	3.82	8.03	0.4

a) Takamatsu, et al, Airlie, 1995

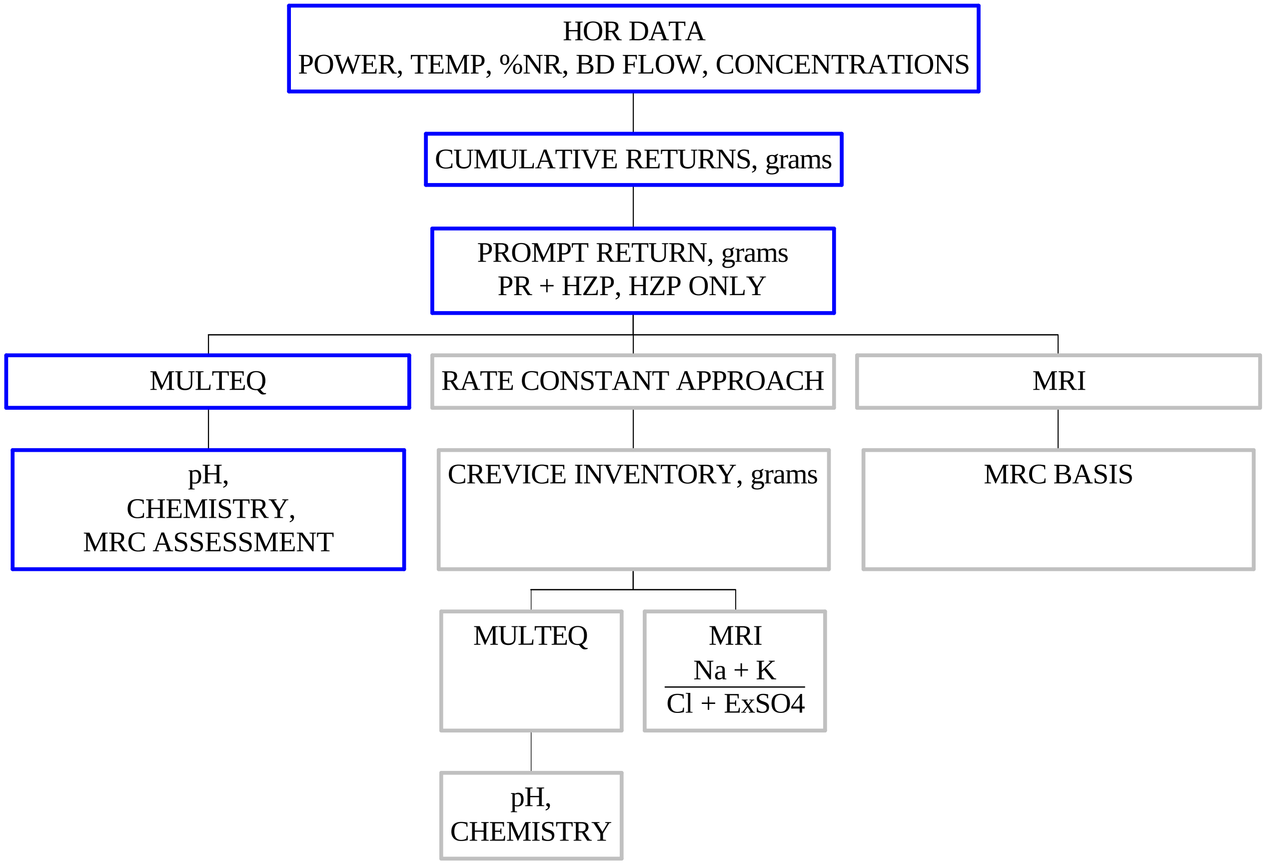
Hideout Return Data Overview

- Total returns for highly soluble species are in the range of 0.1 to 5 grams per SG (current generation clean units)
- Major variations between plants related to design and cleanliness
- Silica return generally exceeds return of other species, i.e., 20 to 500 grams (? adsorption)
- Hardness element and sulfate returns vary markedly with impurity sources
- Predicted crevice solutions normally are concentrated NaCl/KCl not concentrated acids or basis

Hideout Return Data Overview

- pH_T of 4 to 9.5 common but acidic and caustic cases do occur
- Limiting pH approached at low BPE
- Recent HOR data becoming difficult to assess due to low returns, effects of makeup water inputs, and presence of other species (Al)
- Soluble return compromises value of crevice artifact examination for solution matrix information, i.e., known highly soluble species infrequently observed on fracture faces

Hideout Return Evaluation Schematic



HOR DATA
POWER, TEMP, %NR, BD FLOW, CONCENTRATIONS

CUMULATIVE RETURNS, grams

PROMPT RETURN, grams
PR + HZP, HZP ONLY

MULTEQ

pH,
CHEMISTRY,
MRC ASSESSMENT

RATE CONSTANT APPROACH

CREVICE INVENTORY, grams

MULTEQ

pH,
CHEMISTRY

MRI

$\frac{Na + K}{Cl + ExSO4}$

MRI

MRC BASIS

Molar Ratio (Crevice Chemistry) Control

- Perform hideout return studies during each shutdown
- Perform MULTEQ/MRI calculations of crevice chemistry based on hideout return data
- Assess impact of changes in impurity ratios such as Na/Cl on crevice chemistry, i.e., MRC approach evaluation
- If appropriate, adjust ratio to improve crevice pH by:
  - Source reduction/elimination
  - Chloride injection
    - NH_4Cl
  - Other

Molar Ratio Index (MRI)
An Alternative Approach to Crevice Chemistry Prediction/Control

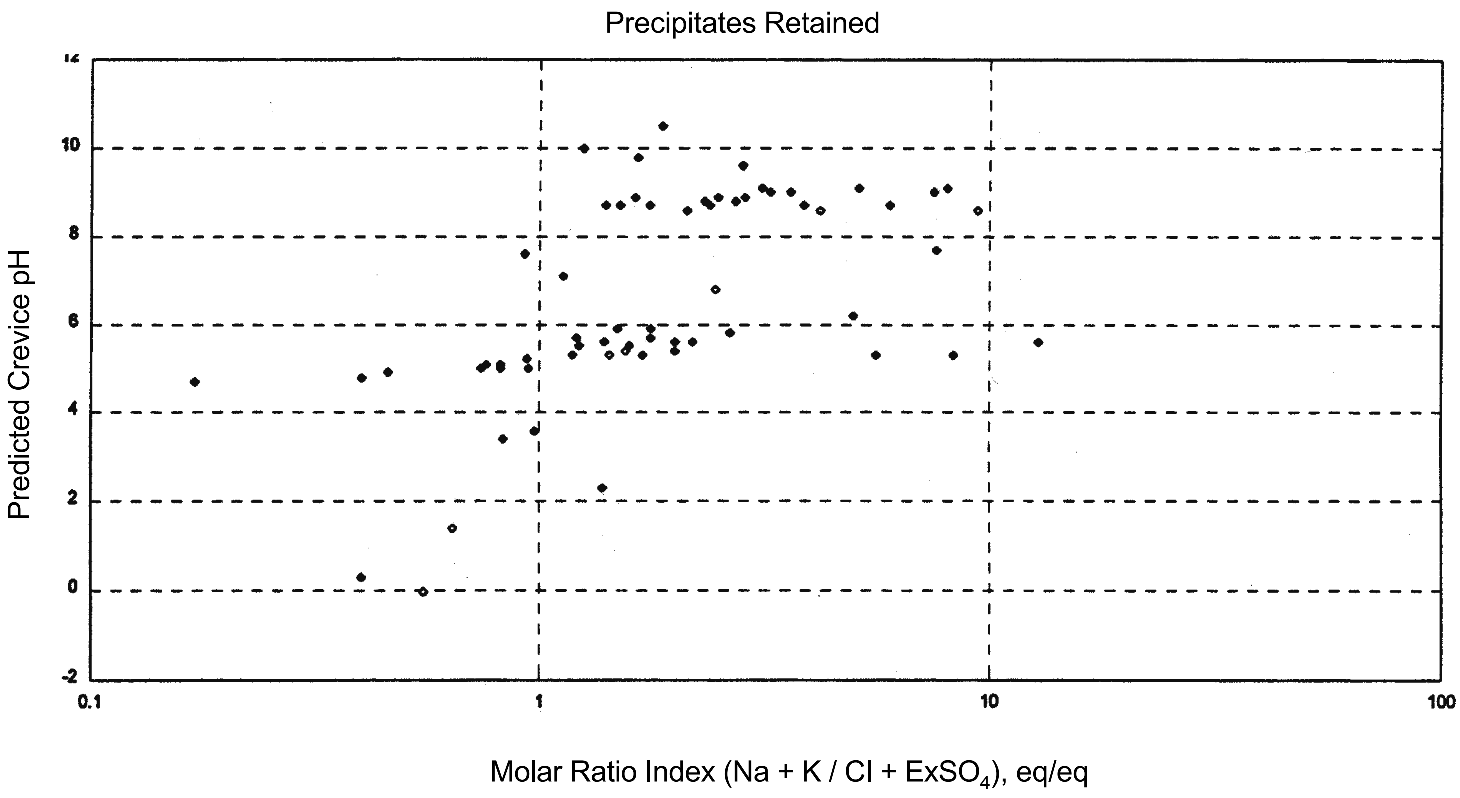
- Define the MRI

$$MRI = \frac{[Na]+[K]}{[Cl]+[ExSO_4]}$$

  - Where
    - All returns are in equivalents/liter
    - ExSO4 = [SO4] – [Ca] (+ values only)

- Not a quantification but an indicator of crevice pH range
  - MRI <1 indicates acidic to mildly caustic crevices
  - MRI >1 indicates near neutral to caustic crevices
  - For neutral crevice, adjust blowdown chemistry to yield HOR MRI =1

MRI Graph

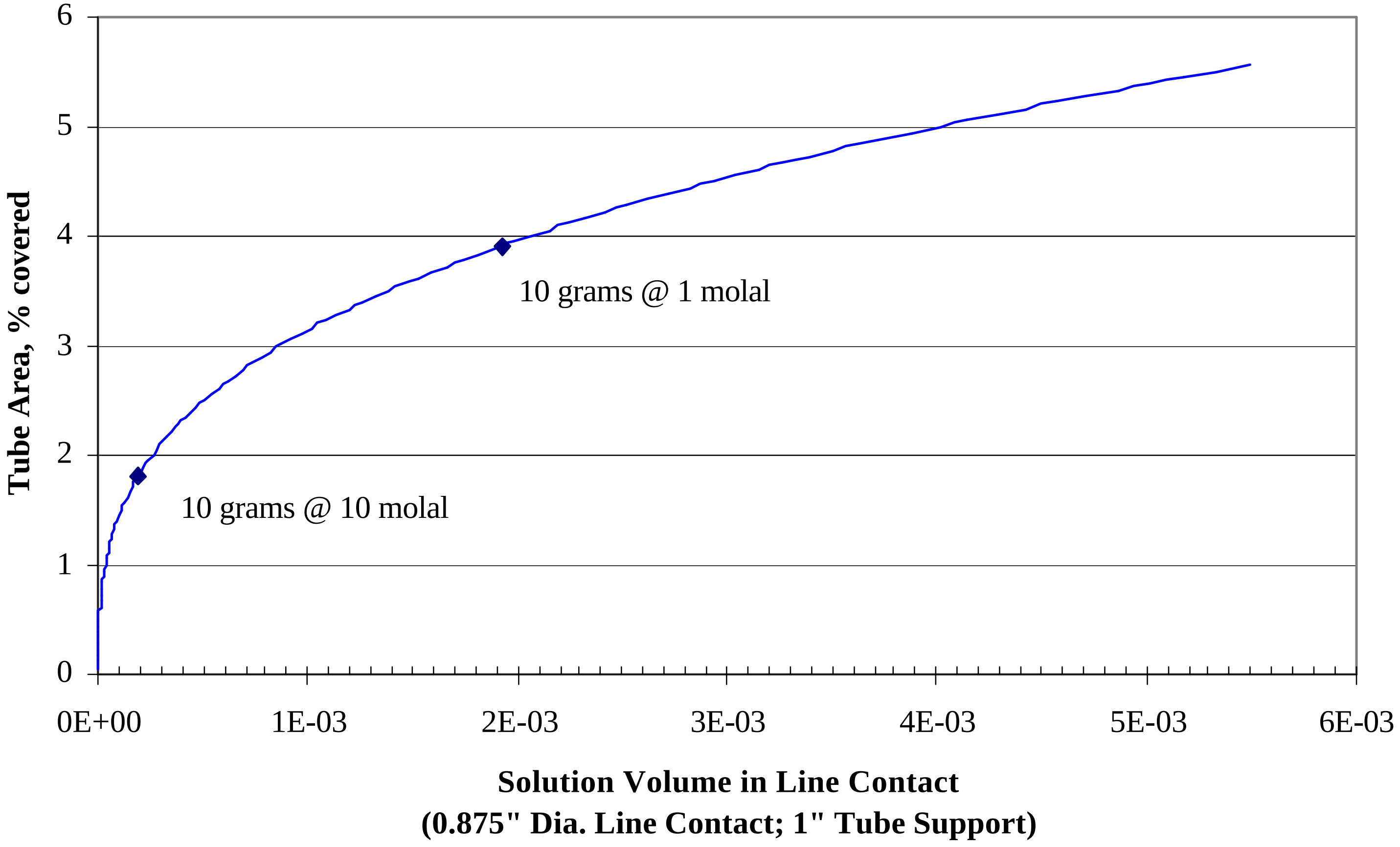

Precipitates Retained
12
10
8
6
4
2
0
-2
0.1
1
10
100
Predicted Crevice pH
Molar Ratio Index (Na + K / Cl + ExSO$_4$), eq/eq

HOR Mechanistic Considerations

- Return during power reduction probably from SG surfaces
  - More return from CE and fouled open structure W units
  - Return increases with fouling
  - Upper portions of bundle probably govern
- Subsequent Return Rate = $K_1 (C_{crevice} – C_{bulk})$
  - Linear: Solubilization Continuous
  - Exponential: All soluble initially (Rate Constant Approach)
  - Inconsistency of rate constants for monovalent species suggests mixed mode, i.e., accuracy of exponential predictive tool questionable

A Perspective

- Consider 10 grams of soluble species, e.g., NaCl
- Assume 140,000 line contact “crevices” in an RSG
  - 0.07 mg NaCl per crevice
  - For a 10 molal solution (BPE limit), this corresponds to ~2 (10^{-4}) ml of solution which covers several percent of the tube surface
- Even at low hideout rates, impurity accumulation in crevices can be significant from corrosion perspective


6
5
4
3
2
1
0
Tube Area, % covered
10 grams @ 1 molal
10 grams @ 10 molal
0E+00
1E-03
2E-03
3E-03
4E-03
5E-03
6E-03
Solution Volume in Line Contact
(0.875" Dia. Line Contact; 1" Tube Support)

A Perspective

- Fractional hideouts of Na and Cl low in clean units
  - 1100 MWe blowdown removal per cycle at 1 ppb concentration is approximately 700 grams
  - HOR approximately 0.1 to 10 grams
  - % Hideout =1%
- Hideout rate constant of <1000 lb $H_2$0/h based on HOR mass balance
- Tracer studies of new units yield =1000 W_{HO} values

Summary

- Hideout return data routinely being used for:
  - Assessment of crevice chemistry
  - Identification of impurity sources
- Routine evaluations recommended in Guidelines
  - Magnitude/relation of impurity sources can change
  - Correlations with steam generator corrosion observations/tendencies believed possible
  - Results provide basis for MRC program

Status of EPRI Software Tools for Evaluating Crevice Chemistry

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Software Development

- Over the last 20 years, EPRI has developed data and computer codes in support of the evaluation of crevice chemistry
- The different tools have been packaged together in a suite of software called ChemWorks
- These computer codes are windows based and many of the tools are in wide use

ChemWorks Tools for Crevice Chemistry

- MULTEQ
- CrevSim
- Hideout Return Spreadsheet
- Plant Chemistry Simulator
- SMART ChemWorks
- Integrated Exposure Calculator

MULTEQ Overview

- Interactive program to calculate composition, pH and electrochemical potential of an aqueous solution at elevated temperature
- Also designed to calculate the changing composition of the solution due to concentration processes.

MULTEQ Database

- Thermochemical library used by MULTEQ
- Text file called species.dat
- A committee reviews an approves all changes in a formal manner

MULTEQ Versions

- Currently distributed package contains MULTEQ Version 2.24 with species database #1396 (June 4, 1997)
- An update to the database (with complete documentation) is now available and labeled Version 3.0
- Version 3.0 of the program is underway and planned to be Excel based, but is not yet completed
- A Version 4.0 release of the database will be available in 2003

MULTEQ Database Versions

- Version 3 includes the following updates over the version (1396) distributed with MULTEQ 2.24
  - New Species
    - 5AP H5AP Piper Hpiper 15DAP H15DAP
    - 4AB H4AB Pyrrol Hpyrrol LiBO2
  - Updates to existing species
    - Cr+3 ETA NaOH
    - MgOHFe+3 Cu+2
    - ZnOH Zn(OH)2 Zn(OH)3
    - Zn(OH)4 AlOH PbOH
    - Pb(OH)2 Pb(OH)3 MgSiO3
    - Mg5(CO3)4(OH)2.4H2O CaSiO3 Fe(BO2)2
    - ZnO CaMg(SiO3)2 Ca2MgSi2O7
    - SiO2 PbO PbSO4
- This version only works with MULTEQ-REDOX 2.1 or later

CrevSim

- An Excel based code
  - Track SG bulk concentrations
  - Estimate amount of impurities hiding out (based on an assumed hideout rate for each species)
  - MULTEQ embedded to determine the crevice conditions (pH) based on amount of each species hiding out and a prescribed boiling point elevation
  - Feedback loop to back-calculate hideout rates based on data retreived during hideout return
- Last updated in 1996
- Not currently in wide use

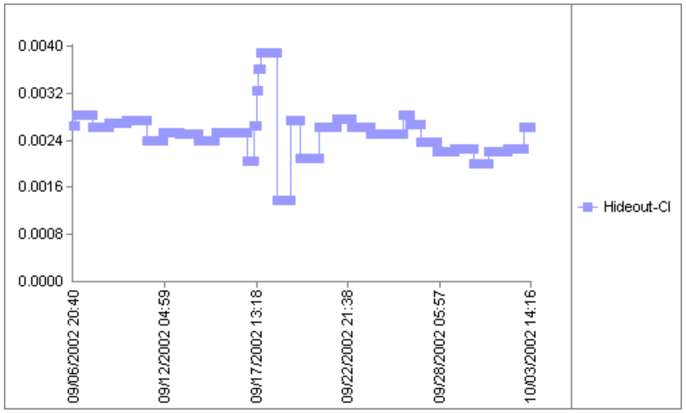
Hideout Return Spreadsheet

- Excel based program to evaluate data collected during shutdown
- Integrates amount of each species returned from crevice
- Uses a model to extract the portion of return believed to have come from crevices
- Also makes adjustments for that amount of species introduced through auxiliary feed sources
- Incorporates Molar Ratio assessment of crevice chemistry
- Output from the Hideout Return Spreadsheet is often used as input to MULTEQ for further evaluation of the potential crevice environment
- Current Version (3) released in 2001

Plant Chemistry Simulator

- This tool is a complete model of the steam cycle
- Two features built in that can help assess crevice chemistry
  - ‘Internal SG Calculations’
    - Allow user to specify up to 10 locations in the SG, identified by a steam quality
    - The calculated bulk steam generator solution is then concentrated to achieve the desired quality, and the resulting concentrations and pH are output
  - ‘Hideout Rate’
    - Based on a user defined hideout factor (similar to CrevSim)
    - The code can output the hideout rate (mass per time) of each species

SMART ChemWorks



- Monitoring and diagnostic system linked directly to real-time plant data
- Plant chemistry simulator is embedded and runs automatically
- Hideout factor can be entered for each species
- Can output the hideout rate of each species as a 'virtual sensor'

Integrated Exposure Calculator

- Excel based program that calculates the ‘integrated exposure’ for a steam generator based on plant data.
- Integrated Exposure is a concept put forth in the current EPRI guidelines
- Based on the premise that the amount of impurities hiding out is proportional to the bulk concentration and time
- Allows for comparisons between acute imputiry ingress and chronic impurity ingress
- Actual Integrated Exposure is compared to reference conditions
- Version 1 was released in 2001

Future Plans

- MULTEQ Database Version 4 (2003)
  - Nickel oxide
  - nickel ferrite
  - DEAE
  - DMEA
  - Formate
  - zinc
  - H_2SO_4
  - DEA
  - DMAIP
- Excel based MULTEQ (2003+)
- Add Integrated Exposure calculation to SMART ChemWorks (2002)
- Upgrade CrevSim ?

Heated Crevice Seminar

Modeling and Analysis Supporting Argonne Model Boiler Facility Development

by Ken Kasza

**Contributors: John Oras, Jeff Franklin, Jangyul Park, Yigang Cai,
Dave Kupperman, Bill Shack**

Argonne National Laboratory

October 8-11, 2002

NRC cognizant staff: Jim Davis (Program Manager) Joe Muscara (Senior Technical Advisor)

Presentation Outline

- Introduction
- Model Boiler Concept Overview
- Modeling/Analysis
  - Prototype/Boiler Crevice Region Heat Transfer and Hideout
  - Long Range Computational Needs

Introduction

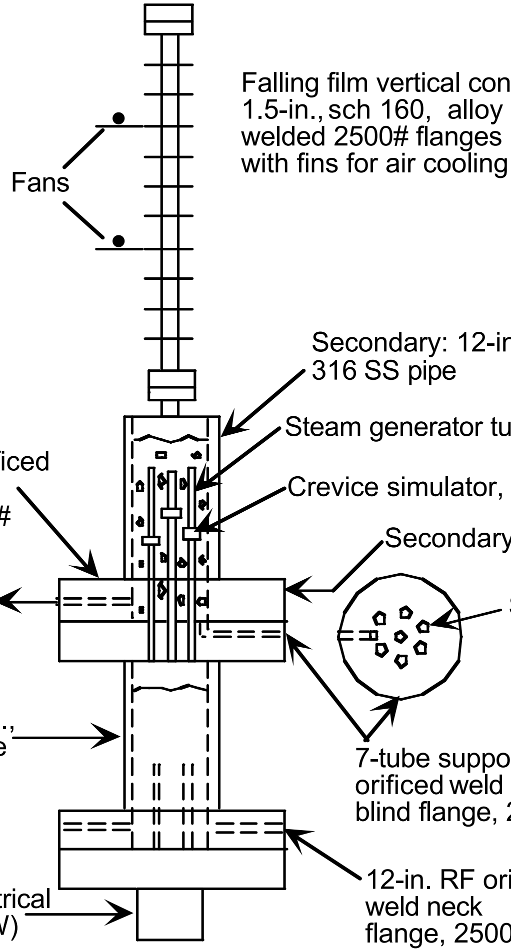
- Steam generator tube ODSCC is not a well understood degradation mechanism
- Research is needed to improve predictions of potential for SCC during extended field service with Alloy 600 and 690TT
- Argonne Model Boiler Facility will study SG thermal-hydraulics and hideout chemistry for the support-plate / tube crevice region
- Studies will compliment Argonne autoclave studies of crack evolution and growth

Boiler Concept; Overview

Seven-tube boiler configuration used (longer range studies may involve a single tube boiler)

- simplified design (absence of pumped primary and secondary loops)
- primary reflux boiler chamber heated by 40Kw electrical heater used to create heat transfer across seven 12-in. long SG tubes (each with a crevice simulator)
- steam condensation occurs inside the SG tubes / boiling on the OD
- secondary-side contains a steam condenser which rejects heat to the ambient (maintains constant boiling conditions on the tube OD)

Argonne Model Boiler



Falling film vertical condenser
1.5-in., sch 160, alloy 800 pipe,
welded 2500# flanges
with fins for air cooling

Fans

Secondary: 12-in., sch 160,
316 SS pipe

Steam generator tube

12-in. RF orificed
weld neck
flange, 2500#

Crevice simulator, 3 types

Secondary water feed

Secondary
water bleed

Swagelock tube holder

Reflux primary: 12-in.,
sch 160, 316 SS pipe
Saturated steam
338°C (640°F)
14.2 MPa (2059 psi)

7-tube support RF
orificed weld neck
blind flange, 2500#

12-in. RF orificed
weld neck
flange, 2500#

Flanged electrical
heater (40 kW)

Argonne Model Boiler
(Primary / Secondary Chambers)

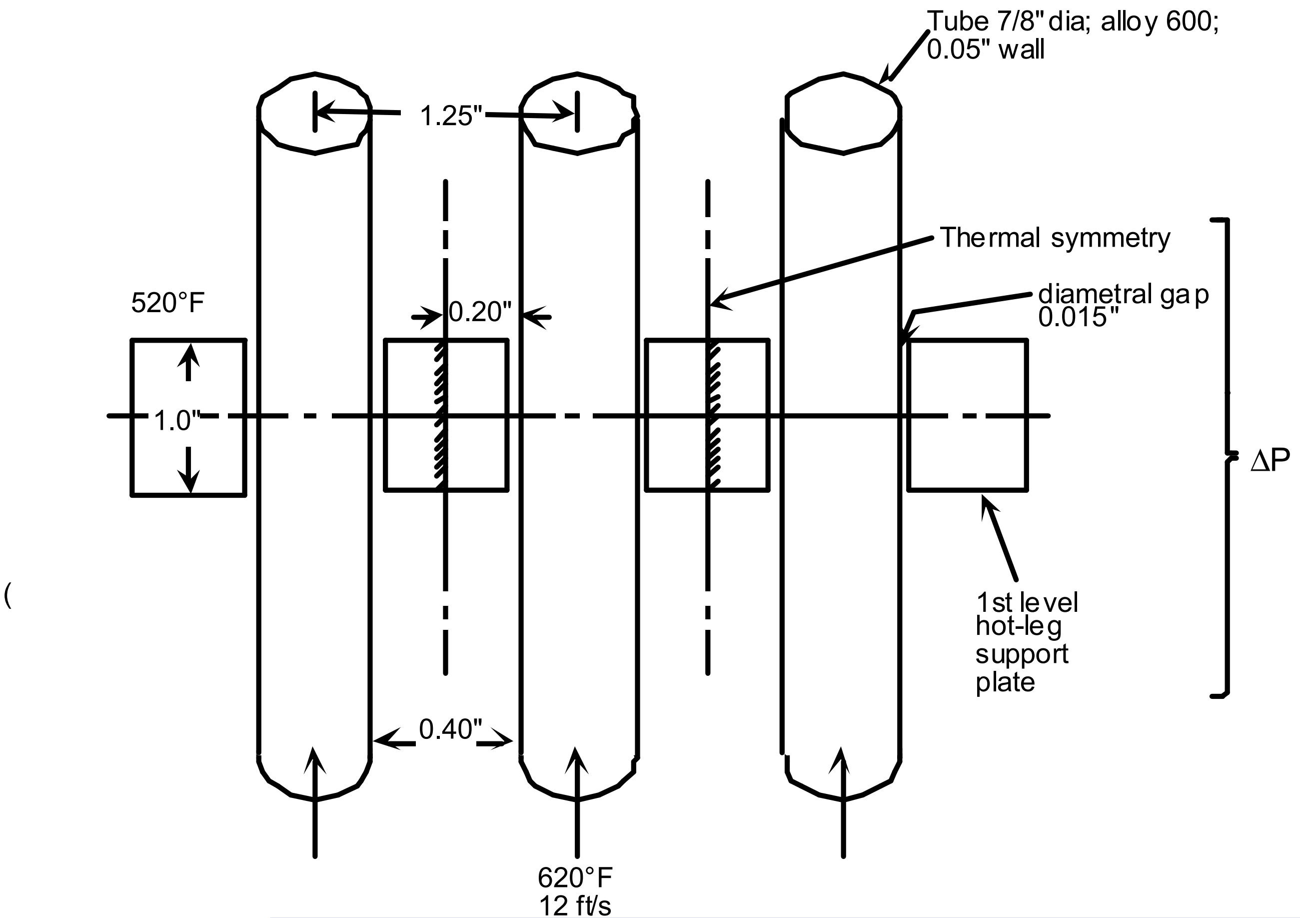
Boiler Concept

- Primary side saturation temp/press controlled by controller set point on 40 Kw heater operating on bulk water temperature thermocouple
- Secondary bulk water thermocouple input to programmable speed controllers on fan(s) blowing air over the finned steam condenser pipe is used to maintain desired temp/press by controlling heat rejection to ambient from the condenser
- achieves prototypical crevice temperatures/heat fluxes and superheats using prototypical primary and secondary pressure/temperature
- SG tubes and crevice simulators are made of prototypical materials
- secondary water chemistry, thermal conditions, and crevice design can be varied to simulate other conditions of research interest or to accelerate cracking
- designed for unattended operation; run continuously for weeks
- facility meets ASME Code, Section VIII, Div 1 for a maximum allowable working pressure of 3000 psi and temperature of 680°F.

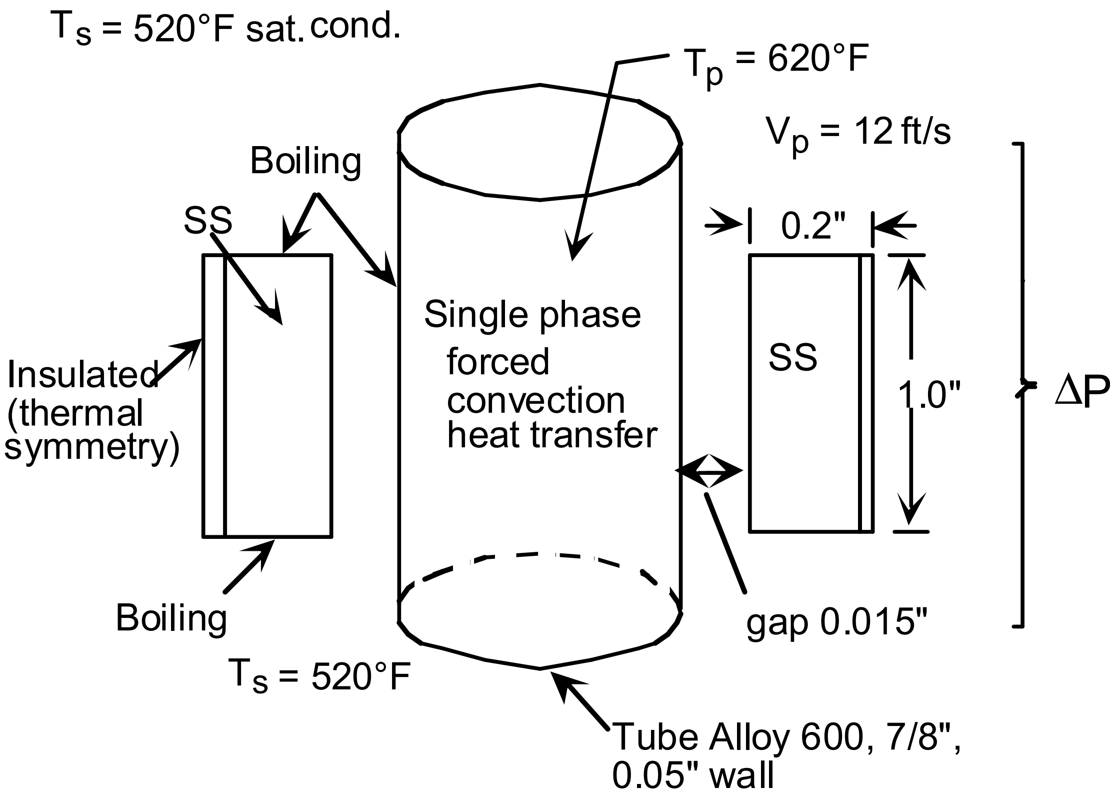
Crevice Modeling

- Thermal-hydraulics of prototype and boiler crevice regions are three dimensional
- NRC and Argonne are initiating an effort to model crevice region as a 3-D CFD problem (with fluid / thermal behavior coupled to crevice structure heat transfer)
- Initial analysis uses 1-D cylindrical model
- Analyzed heat transfer across the crevice as a function of the primary and secondary thermal-hydraulic conditions and for drilled hole crevice geometry
- T&H conditions used are those in the hot-leg at the first tube support plate (conditions for hideout are believed to be greatest at this location)
- Results for prototype and boiler crevices are compared
- Analysis guides boiler design to ensure prototypicality and aids in operation of the facility

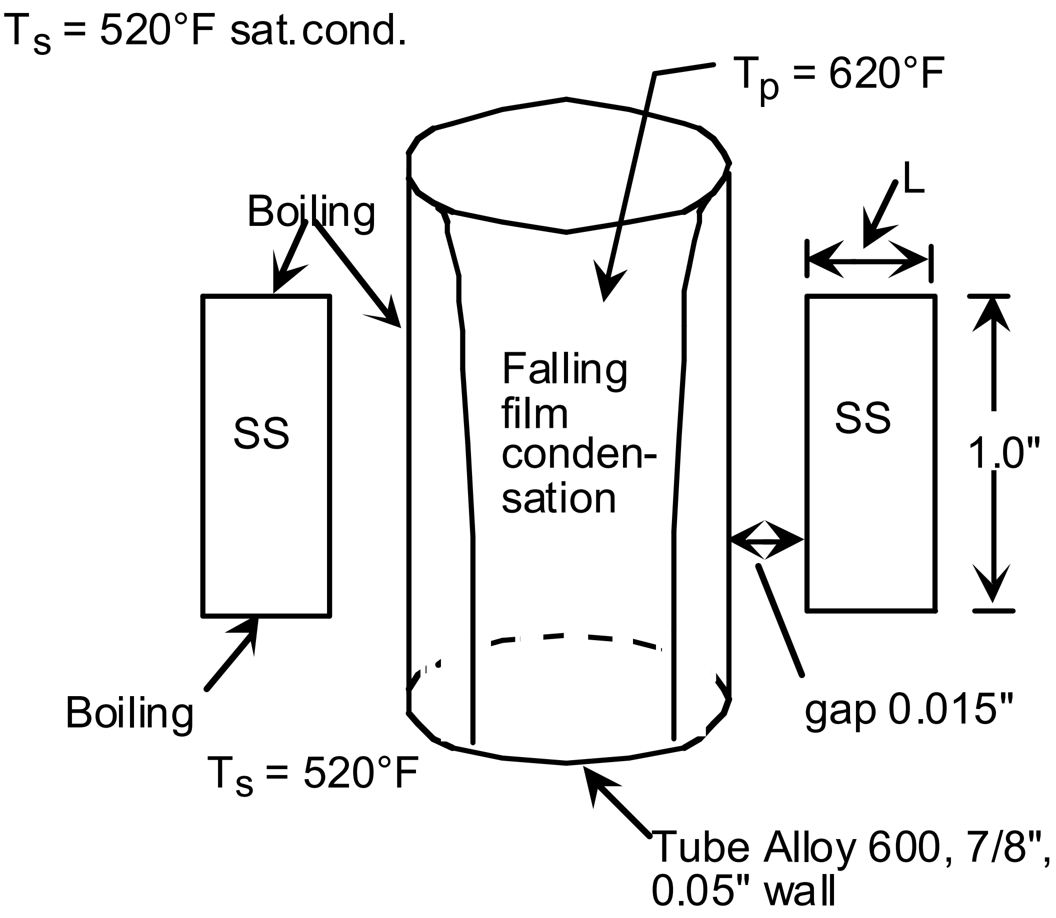
Modeling
Prototype Drilled Hole Support-Plate/ Tube Crevice Region



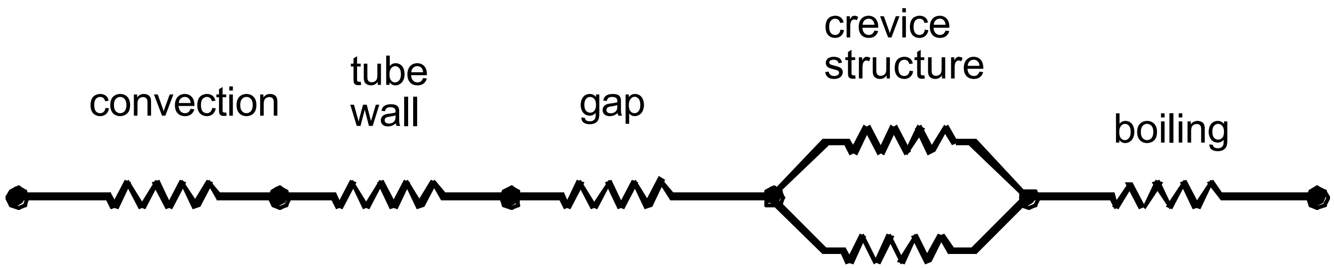
Modeling
Simplified Prototype Crevice Region



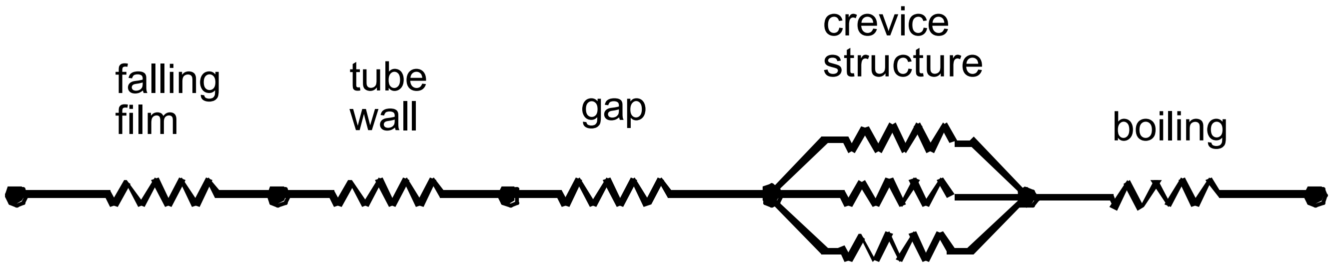
Modeling
Model Boiler Crevice Region



Modeling
Crevice Region 1-D Heat Transfer Electrical Circuit Analogy For The Simplified Prototype and Model Boiler Crevices



a. Simplified Prototype



b. ANL Model Boiler

Modeling
Crevice Region

- Phenomena modeled and analyzed in comparing prototype tube/crevice behavior with that of the boiler were as follows:
  - forced convection heat transfer inside tube (prototype)
  - falling film condensation heat transfer inside tube (boiler)
  - heat conduction through the SG tube and crevice wall (prototype and boiler)
  - heat transfer through crevice gap fluid
  - boiling on the secondary (prototype and boiler)

Modeling
Crevice Region Equations

- The heat flux across the crevice/tube is given by; $q = h_a (T_p - T_s)$
- where T_p and T_s are the primary and secondary temperatures
- h_a is the overall heat transfer coefficient and represents the thermal resistance series for the problem; composed of five contributions

$$h_a = \frac{1}{\frac{d_{c\,out}}{d_{in}}\frac{1}{h_v} + \frac{d_{c\,out}\ln\frac{d_{out}}{d_{in}}}{2k_w} + \frac{d_{c\,out}\ln\frac{d_{c\,in}}{d_{out}}}{2k_c} + R + \frac{1}{h_b}}$$

$$R_P = \frac{R_1}{2}$$

$$R_B = \frac{R_1 R_2}{2R_2 + R_1}$$

Modeling; Crevice Region Equations

1. model boiler falling-film condensation heat-transfer coefficient, hv, is given by the Roshenow correlation

$$h_v = 0.943\left[\frac{\rho_l(\rho_l - \rho_v) g h'_{fg} k_l^3}{\mu_l L (T_{sv} - T_{sw})}\right]^{1/4}$$

or, for the prototype, the heat transfer coefficient h for forced convection single phase flow inside a SG tube is given by

Colburn equation from p. 260, Eq. 7-49 in Gebhart:

$$\left(\frac{h}{\rho V C_P}\right)_m \left(\frac{C_P \mu}{k}\right)_f^{2/3} = 0.023\left(\frac{DV}{\nu_f}\right)^{-0.2}$$

Modeling; Crevice Region Equations

2. heat-transfer coefficient for the tube wall is given by

$2\ k_w\ /\ d_{cout}$

3.heat transfer coefficient for the crevice gap fluid, assuming all boiling is suppressed by the chemical hideout, is given by

$2\ k_c\ /\ d_{cout}$

4. heat transfer coefficient for the crevice wall is given by Rp and Rb

5. nucleate-pool-boiling model of Rohsenow is used to represent the heat transfer coefficient on the crevice/tube outer surfaces:

$$\frac{c_{p\mathrm{l}}\left(T_{bw}-T_{sb}\right)}{h_{fg}P_{r\mathrm{l}}^{1.7}} = C_{sf}\left[\frac{q}{m_{\mathrm{l}}h_{fg}}\sqrt{\frac{s}{g\left(r_{\mathrm{l}}-r_{v}\right)}}\right]^{0.33}$$

Modeling; Chemical Hideout

- bulk-water, low-concentration, low-volatility, impurities can concentrate locally
- typical locations are the crevices between tube and support plates, crevices within tubesheets, sludge piles that surround SG tubes, and porous scale deposited on tubes
- crevice temperature elevation above the bulk secondary saturation temperature occurs and is called the local superheat which is based on tube outer wall temperature
- boiling draws bulk water into the crevice and expels steam or a mixture of steam and water; some of the low-volatility impurities drawn in with bulk water remain behind to concentrate
- concentration can increase to the solubility limit and solid will precipitate which can block or alter access and escape paths for fluid or vapor
- concentration can also increase to the extent that the boiling point of the crevicel fluid is significantly increased over the boiling point of the bulk water. Crevice boiling will stop when the concentration increases to the point that the boiling point elevation equals the local superheat; “thermodynamic limit”

Modeling; Chemical Hideout

- concentration buildup can stop before the thermodynamic limit which is called "kinetically limited"

- which occurs depends on many factors: including the geometric configuration of the crevice, pathways that connect it to the bulk water, the local temperature and heat flux, constituent boiling point, and other characteristics of the fluid

- based on the thermodynamic limit the boiling point of a solution that contains impurities is related to the mole fraction of the impurities by

$$\text{Ln } X_A = \frac{\Delta H_{vap}}{R}\left(\frac{1}{T} - \frac{1}{T_o}\right)$$

Where X_A = mole fraction of water,
DH_{vap} = molar heat of vaporization of H_2O,
R = universal gas constant, 1.98717 cal/mole-K,
T_o = boiling point of pure H_2O (K), and
T = boiling point of solution (K),

Set (To-T) = crevice superheat

Modeling Results
Prototype / Boiler

- Argonne 1-D code calculates the temperatures of the various zones, the heat flux across the tube/crevice from the primary to the secondary, and crevice hideout for low levels of impurity in the secondary water

- Prediction results

- prototypical crevice thermal conditions are achieved in the boiler
- crevice conditions can be varied by adjusting the crevice geometry or the primary and secondary temperatures
- significant crevice superheats occur with potentially high levels of chemical hideout (crevice concentration factors 50,000 - 80,000 for NaOH)

Modeling Results
Prototype/Boiler
Tp = 620F; Ts = 520F or 510F

Crevice Parameters		Model Boiler Crevice			Prototype Crevice
Tp = 620 F Ts = 520 F	Crevice Wall Thickness (in.)	0.2	0.5	1.0	0.2
	Superheat (F)	76.2	77.2	77.8	87.3
	Flux (Btu/hr ft2)	11,842	7,805	4,975	11,820
Tp = 620 F Ts = 504 F	Crevice Wall Thickness (in.)	0.2			
	Superheat (F)	87.4			
	Flux (Btu/hr ft2)	13,647			

Modeling
Long Range Needs

- Current analysis of crevice region thermal behavior and hideout is 1-D
- Thermal fields and heat flux in local crevice/tube geometry strongly influence hideout
    - rate of accumulation
    - ultimate concentration limit
- Complex problem involving structure/fluid interactions, change of phase, and chemical species migration dependent on detailed thermal distributions in structure and the fluid all being multi-dimensional
- Different crevice designs will have an important influence on behavior of the water/steam in a particular design (as important as the primary and secondary bulk water thermal-hydraulic conditions)
- In order to ultimately be able to relate laboratory boiler and autoclave results to the field experience and the different design support plate/tube geometry’s, multi-dimensional interacting CFD and crevice structural thermal behavior computer simulations are needed.

Modeling
Long Range Needs

Benchmark Computational Problem

- Drilled hole support-plate / tube crevice geometry is good benchmark computational problem
  - supports model boiler experiments/studies
  - represents a field design and is a common geometry used in past crevice studies
  - shifting the tube off-center can be used to explore conditions approaching line contact

Numerical Modeling of Steam Generator Crevice Thermal-Hydraulics

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Abstract

Thermal-hydraulics and the deposition of corrosive compounds in the crevices formed by steam generator tubes and their support plates have long been recognized as complex and poorly understood phenomena. Bubble nucleation, growth and departure in confined spaces are significantly different from those which occur along an unrestricted surface. Thus, experimental data and numerical models of boiling and mass deposition processes can not be reliably applied to the steam generator crevice problem.

With advances in computing speed and refinements in analytical modeling of boiling phenomena, it is now possible to numerically simulate the fluid flow and heat transfer near a bubble growing on a surface. This paper discusses modeling possibilities and recommends an approach intended to estimate temperature, void, and flow distributions in a steam generator crevice. Two relatively simple models are described that will help characterize surface superheat in the crevice, along with a more complex model using direct numerical simulation of the flow field. The long term objectives of the numerical studies are to provide useful information for the accompanying experimental work, and to eventually predict the locations and thermal-hydraulic conditions favorable to hideout.

Introduction

The crevices formed between steam generator tubes and support plates have resulted in several unique problems that must be solved by designers and operators of pressurized water reactor (PWR) steam generators (SG). The crevices are likely responsible for crud build up and local dryout that may cause SG tube failure. Flow and heat transfer in and near the crevice is complex due to the restricted flow area and the effect it has on local vapor generation. Efforts to simulate the phenomena leading to chemical deposition in the crevice have been hampered due to a lack of basic experimental information along with the difficulties in modeling boiling and two-phase flow.

Numerical simulation of SG crevice thermal-hydraulics may be highly valuable. Estimates of local void, flows and wall superheats are useful in designing experiments to investigate crevice behavior, and analytical methods to predict long-term SG performance are of considerable practical importance.

This paper describes potential numerical approaches for modeling the SG crevice problem, and the pros and cons of each. Three options are discussed, ranging from one which is simple (but inaccurate), to a comprehensive mechanistic model that will require significant effort.

Multidimensional Conduction: The simplest approach would be to perform a 2D or 3D conduction solution to obtain the temperature distribution in the SG tube wall, the crevice gap itself and the support. Assuming no flow through the gap greatly simplifies the calculation. Two cases would be considered; one with the gap liquid filled and another with the gap filled with vapor. The main difference in the two temperature profiles would be due to the thermal conductivities of the gap fluid. Results would provide temperature distributions along both walls of the crevice and thus provide a crude estimate of wall superheats. Heat transfer coefficient boundary conditions would be applied on the inner surface of the SG tube wall and on the edges of the support plate. These could be determined using conventional correlations for flow boiling.

By ignoring flow through the crevice and assuming a high heat transfer coefficient on the SG outer wall above and below the support plate, the conduction solution will be symmetric about the support plate midheight. The maximum wall superheat would occur at that elevation. Figure 1 shows a schematic of this approach and the expected wall superheat distribution.

There are several computer codes that could be used to perform the calculations. Structural analysis packages such as ANSYS or ABAQUS are available and have been used by the NRC staff in the past. For the simple 2D schematic shown in Figure 1, it is a relatively simple task to devise a finite difference nodalization and solve for the temperature distribution. Thus, the “pro” of this approach is its simplicity and low cost.

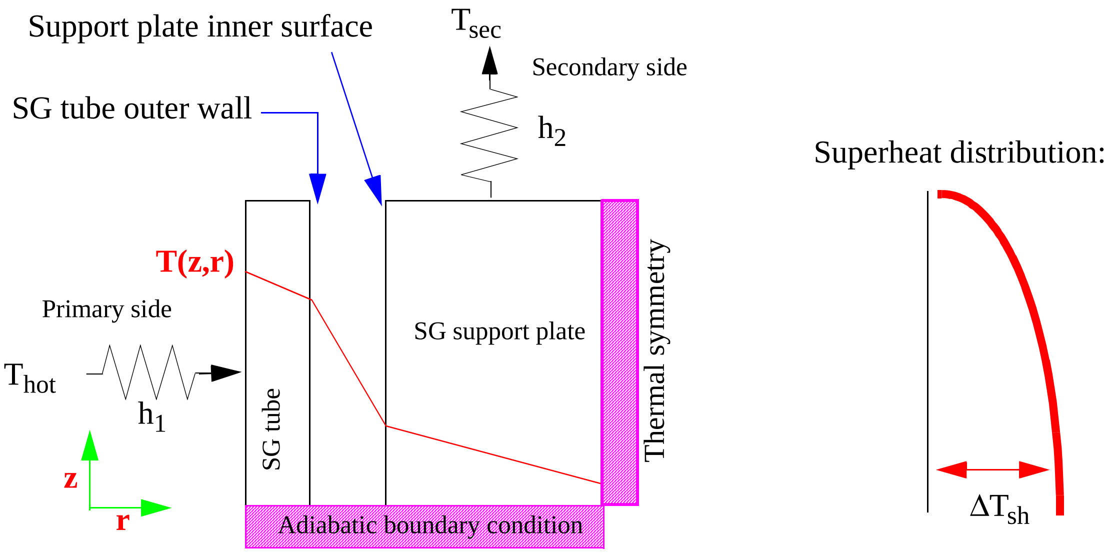

Figure 1. Schematic of Conduction Solution.

The obvious problem with this approach is that it ignores flow and phase change within the crevice. No nucleation would be predicted with this model, regardless of the wall superheat. The temperature distribution predicted would not be correct for the situations when phase change took place. Thus, the “con” of this approach is inaccuracy as bubble nucleation occurs.

Computational Fluid Dynamics: Computational fluid dynamics (CFD) has been used to investigate a wide range of complex thermal-hydraulic problems. It can provide detailed temperature, velocity, and concentration profiles in a complex geometry although the state-of-the-art is limited to single phase fluids. In this proposed CFD approach, velocity and temperature distributions without phase change would be calculated in the crevice. Temperature distributions along the crevice boundaries would be obtained. These temperature distributions would show less wall superheat than in the simple multidimensional conduction calculation because of the cooling effect of flow through the crevice. In this calculation, the crevice would be “open”. That is, flow would enter from the bottom and exit out the top, dis-allowing the adiabatic boundary (symmetry) condition in the conduction approach. This would increase the size of the numerical grid. Figure 2 shows a schematic of this approach. Unlike the conduction solution, wall superheat would increase from the bottom of the crevice, as the fluid is heated.

This calculation could be done with a commercial CFD package such as FLUENT, CFX or StarCD, or with the NRC developed code, NPHASE. The NPHASE code utilizes an Euler-Euler methodology and allows mass and energy transfer between phases. Technically NPHASE could provide details on phase change in the crevice. However, implementation of nucleation and bubble growth models has not been part of NPHASE development. The NRC staff has experience in using FLUENT, but no internal experience with NPHASE.

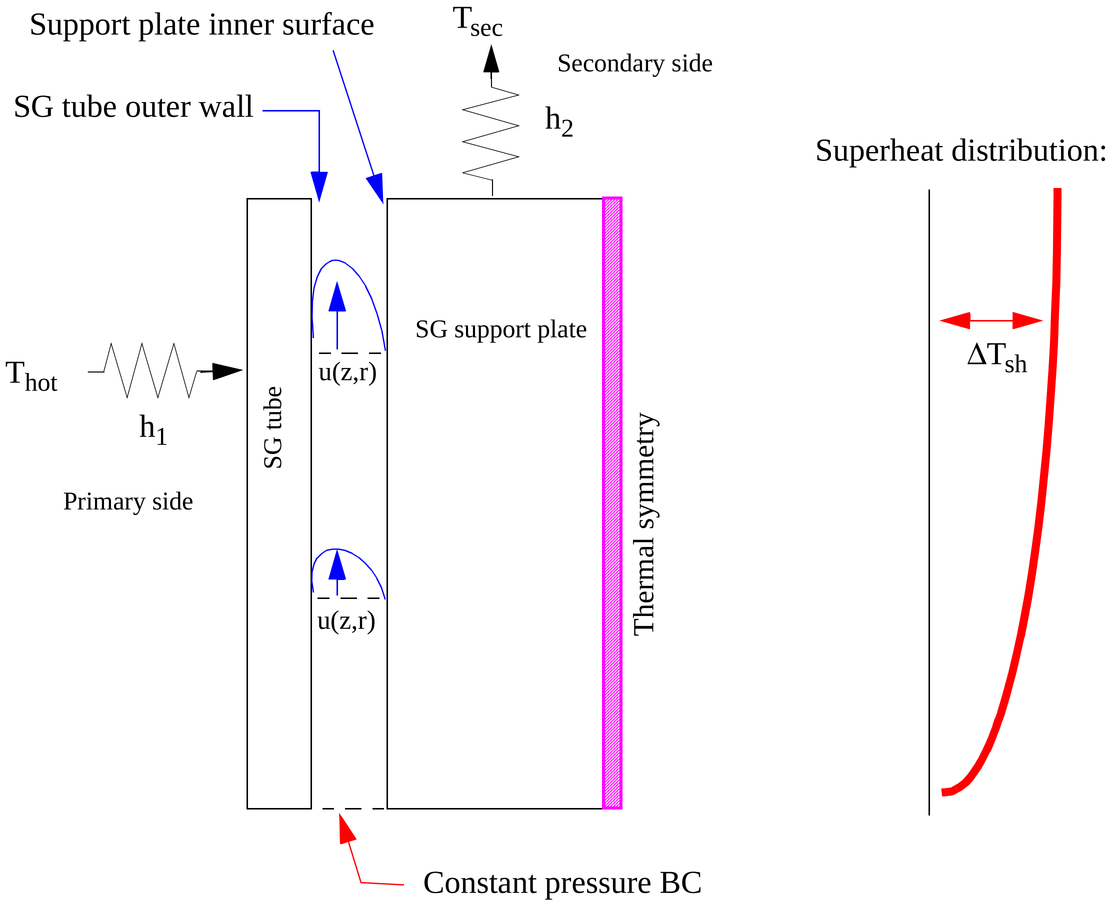

Figure 2. Schematic of CFD application to the SG heated crevice problem.

The “pro” of the CFD approach is the more detailed calculation of velocity and concentration profiles in the crevice than what might be obtained in the multidimensional conduction model approach. Commercial, or relatively mature computer code packages could be applied, which include features that would allow a wide range of crevice geometries to be examined. This is important to the SG crevice problem, as there are several types of supports that are in use.

As with the conduction approach, the “con” of the CFD approach is that the solution again ignores phase change within the crevice. Thus, application of a CFD approach to the SG heated crevice problem is not expected to yield significant insight unless there is development and implementation of models for bubble nucleation and growth.

Mechanistic Modeling: An approach that is capable of producing a reasonably accurate representation of phenomena within the crevice is mechanistic modeling of bubble growth and film formation. Because of advances in computing speed. It is now possible to solve the mass, momentum and energy equations for liquid and vapor phases simultaneously while a two-phase interface is developing. Such a solution provides not only the temperature, velocity and concentration profiles in the fluids, but also the shape of the interface. This approach is attractive, as previous experimental work has shown that localized dryout and rewetting of the crevice surfaces is important to the problem. Visualizations by Yao and Chang (1983) for example, found four different types of boiling patterns in an annular crevice. Relatively large regions of the gap were found to be occupied by the expanding bubble. Figure 3 shows some of the patterns observed by Yao and Chang. (One of the geometries considered was for a 25.4 mm high, 0.32 mm gap which is close to dimensions of interest in the SG crevice problem.) Likewise, the experiments by Tieszen et al. (1987) identified three confinement dependent flow regimes in the crevice. Each of these studies indicate that successful numerical modeling of crevice thermal-hydraulic conditions must account for two-phase interfaces.

Mechanistic modeling of bubbles and evaporating films track an interface while solving the mass, momentum, and energy equations of the liquid and vapor fields simultaneously. The approach generally divides the computational domain into micro and macro regions in which various physical processes dominate and some simplifications can be made. Dhir (2000) provides an overview of the mechanistic modeling of single and multiple bubble growth and also for film boiling. Son and Dhir (1997) provide details of modeling saturated film boiling, with Son (1996) describing the application to several multiphase problems.

In the SG crevice problem, both single bubble growth and film boiling (dryout) is expected. Because the support plate is cooler than the SG tube itself, and sufficient superheat to nucleate and/or allow local evaporation at the tube wall is expected, bubble growth initiated at the SG tube wall should dominate the gap behavior. The support plate will be cooler and may allow a liquid film to remain attached to it. Vapor formation at the SG tube will drive the flows which may be “fed” by liquid entering either the bottom or top of the crevice depending on superheat on the SG support plate surface. Because of the rapid volumetric expansion of the vapor and periodic bubble departure from the crevice, the process may be cyclic with vapor generation “flushing” the gap which later fills with liquid as the vapor departs from the crevice. Bubble growth and departure will be strongly influenced by the crevice dimensions. A bubble may initially nucleate, but because of the expected high superheats a stable vapor film may remain in the crevice and the mechanism of vapor production will be evaporation from the interface. Thus, models for interface behavior during film boiling may be applicable. Axial conduction along the SG tube may be important, and should be included in the calculations. Figure 4 shows a schematic of crevice boiling.

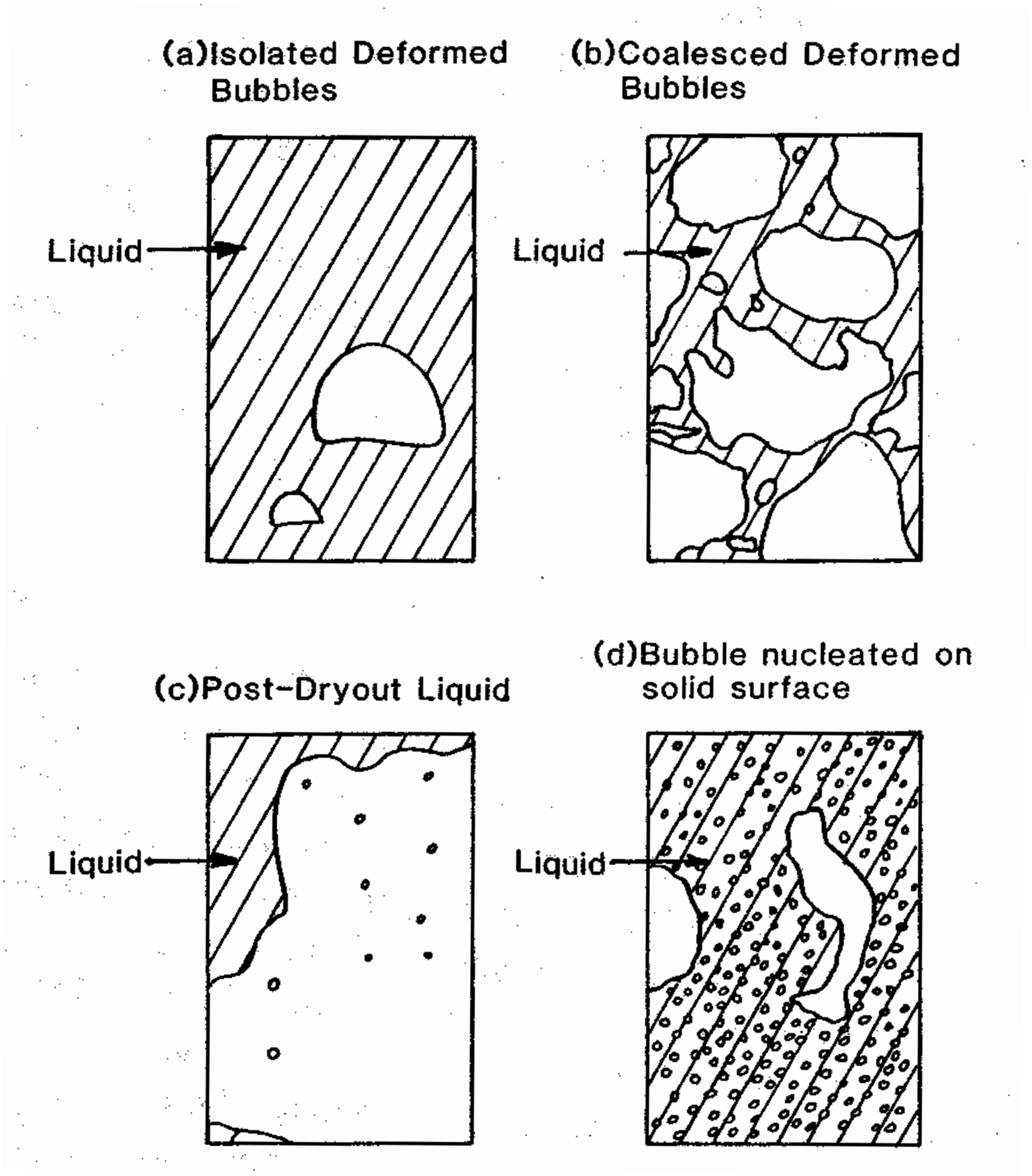

Figure 3. Boiling phenomena in a confined space. From: Yao and Chang (1983).

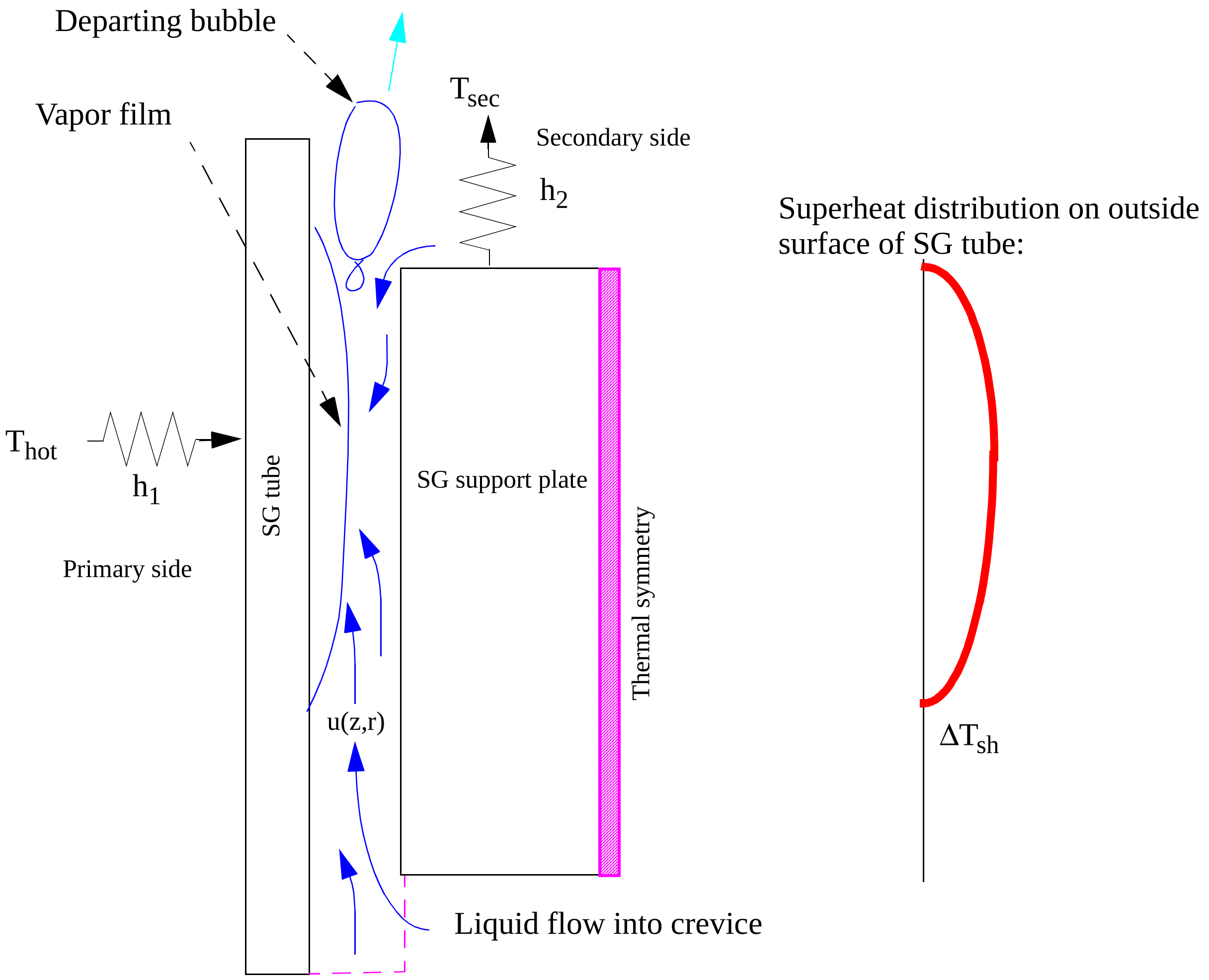

Figure 4. Bubble growth in a SG crevice.

The “pro” of this approach is its technical validity. A mechanistic modeling of crevice phenomena would provide the most accurate representation of phenomena of importance and may result in a tool suitable for predicting conditions and geometries less prone to chemical hideout. This may be the only approach that might provide the correct physics, be extendable to similar geometries, and be capable in the long run of predicting if and where species deposition will occur.

The “con” is expense, and relatively long time frame required. Numerical calculations of this type are possible, but they are difficult. The mechanistic approach has been successful for relatively simple geometries; single bubbles, multiple bubbles growing in a uniform array, film boiling, and phase change with sublimation. However, no work has been performed with multiple solid boundaries as is the case in the SG crevice. A multi-year effort is anticipated.

Conclusions

Numerical simulation of SG crevice thermal-hydraulics is feasible, although developing an accurate model capable of predicting chemical hideout will require significant effort. Simple models (multidimensional conduction and CFD) can estimate surface temperatures with relatively little effort, but their validity is limited to single phase fluid conditions. Given the long-term effects of SG crevice phenomena on tube integrity, steam generator operation and performance, it is recommended that a multi-pronged approach be undertaken. A simple conduction model will provide crude estimates of temperatures in the crevice and surrounding structures. This may help in the design of experiments. The long term effort should include development of a mechanistic model for crevice phenomena. Development of a mechanistic model, in conjunction with a well planned experimental program should provide an important tool for dealing with the SG crevice problem.

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Heated Crevice Seminar

Application of Chemical Equilibrium Model to the Evaluation of Magnetite-Packed Crevice Chemistry

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In Hyoung Rhee
Soonchunhyang University

October 7-11, 2002
Argonne Guest House, ANL

Contents

- Introduction
- SG Crevice Simulation Experiments
- Rationale & Approach
- Thermodynamic Aspects: Pourbaix Diagram
- Chemical Equilibrium Model
  - Approach
  - Species & Reactions
- Results & Discussion
- Summary & Conclusions
- Future Work

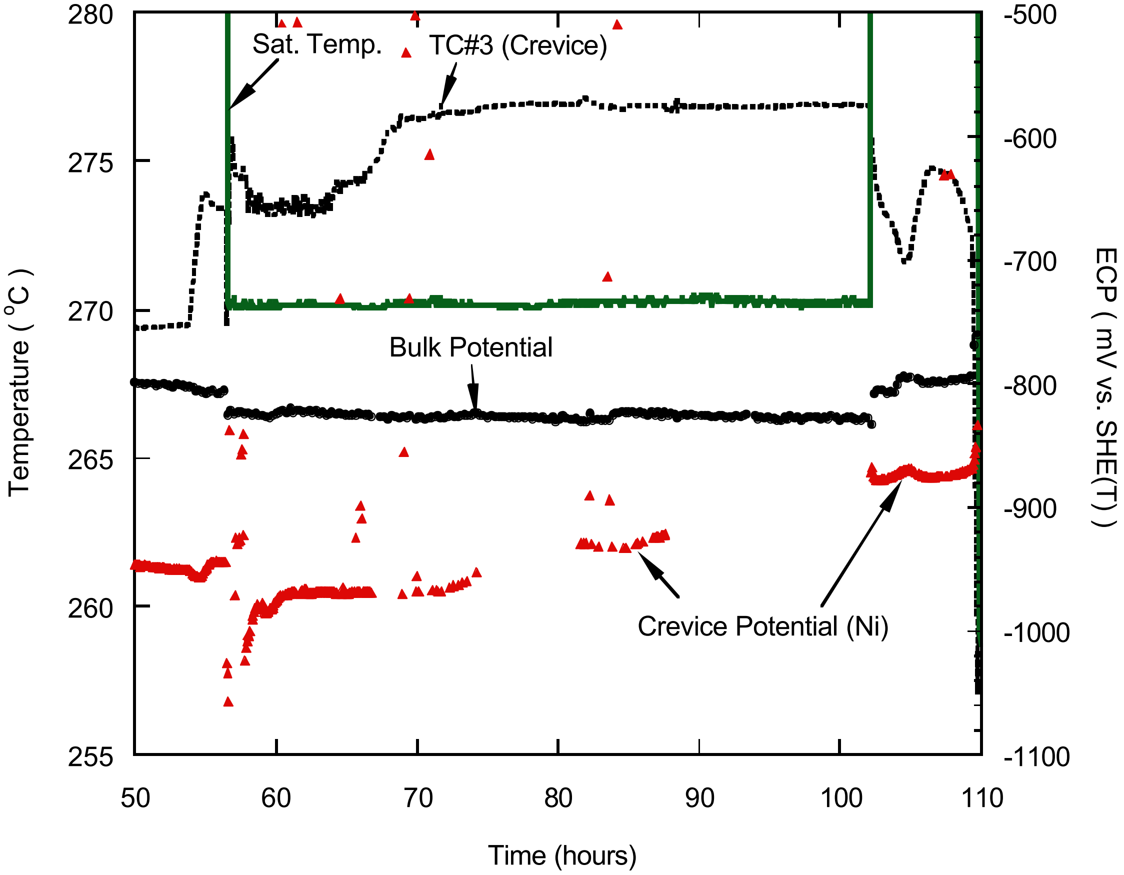
Introduction

- It is needed to develop a combined model taking into account the thermal-hydraulic and chemical phenomena.
- As a first step towards developing the combined model, a chemical equilibrium model that predicts the chemical speciation in a magnetite-packed crevice under an equilibrium state was developed.

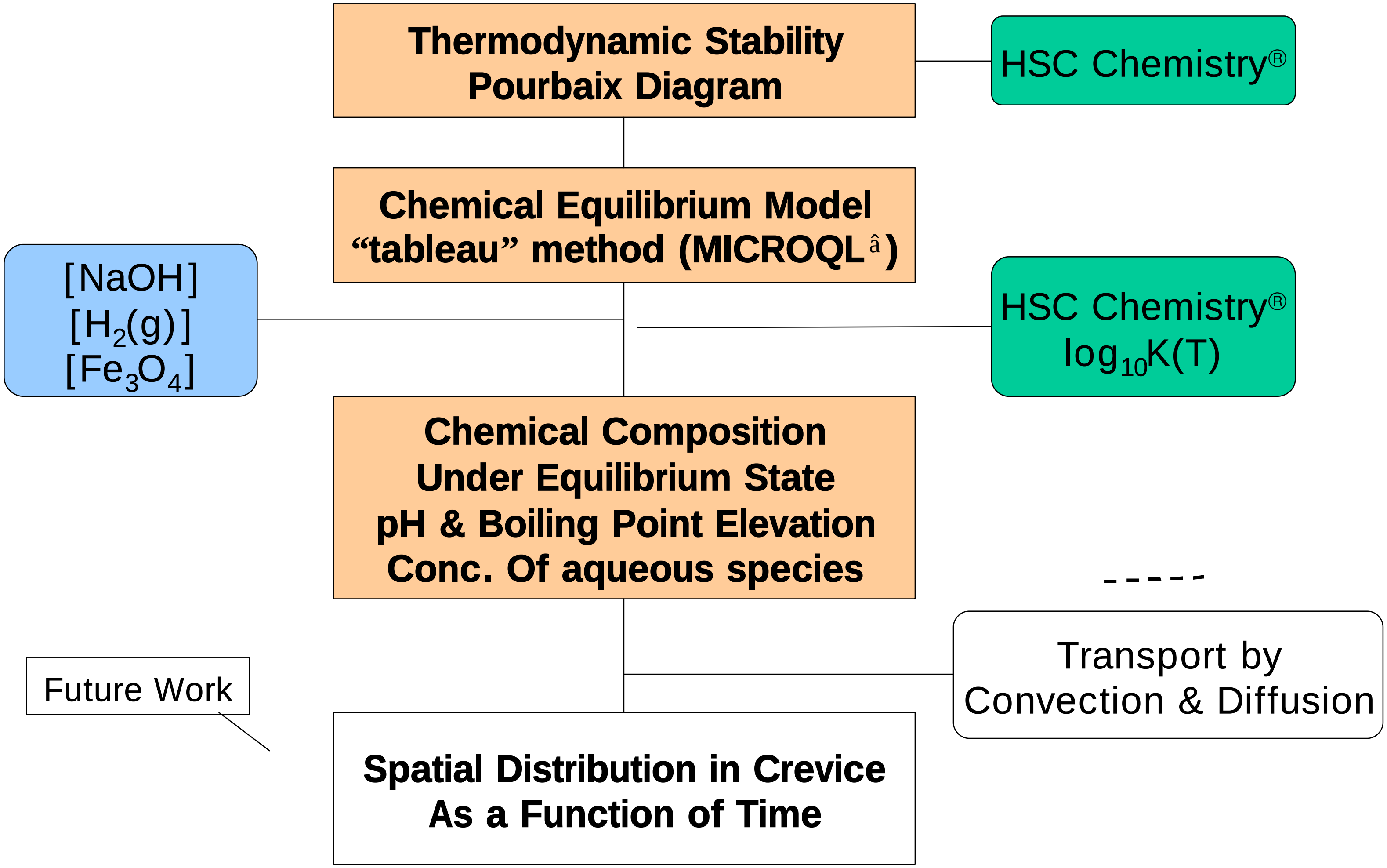
SG Crevice Simulation Experiment

Results: Temperature & ECP

Magnetite - Packed Crevice Condition, DT=20 °C



Rationale & Approach



Thermodynamic Stability
Pourbaix Diagram

HSC Chemistry®

Chemical Equilibrium Model
“tableau” method (MICROQLâ)

[NaOH]
[$H_2(g)$]
[Fe_3O_4]

HSC Chemistry®
$\log_{10}K(T)$

Chemical Composition
Under Equilibrium State
pH & Boiling Point Elevation
Conc. Of aqueous species

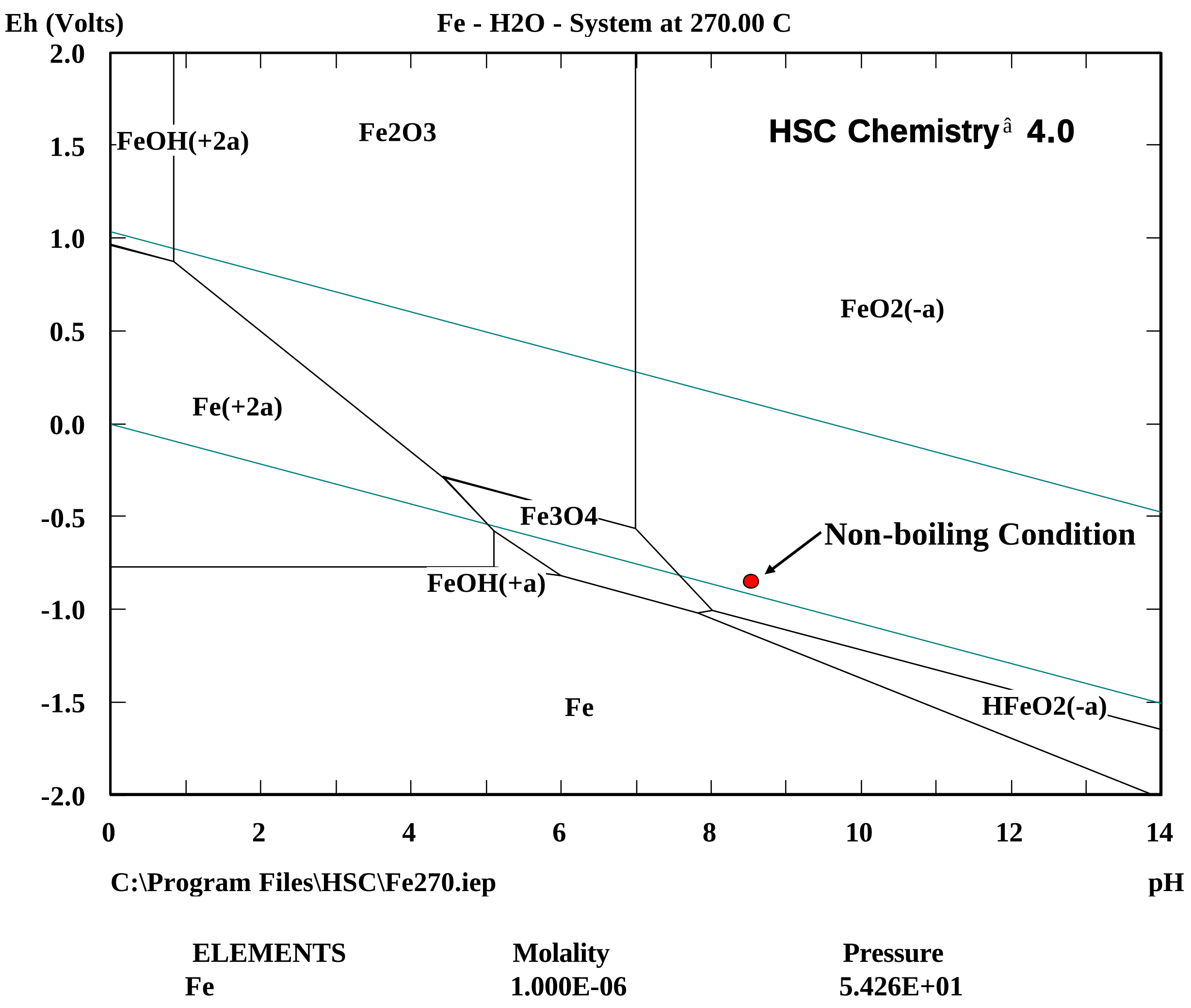
- - - - -

Transport by
Convection & Diffusion

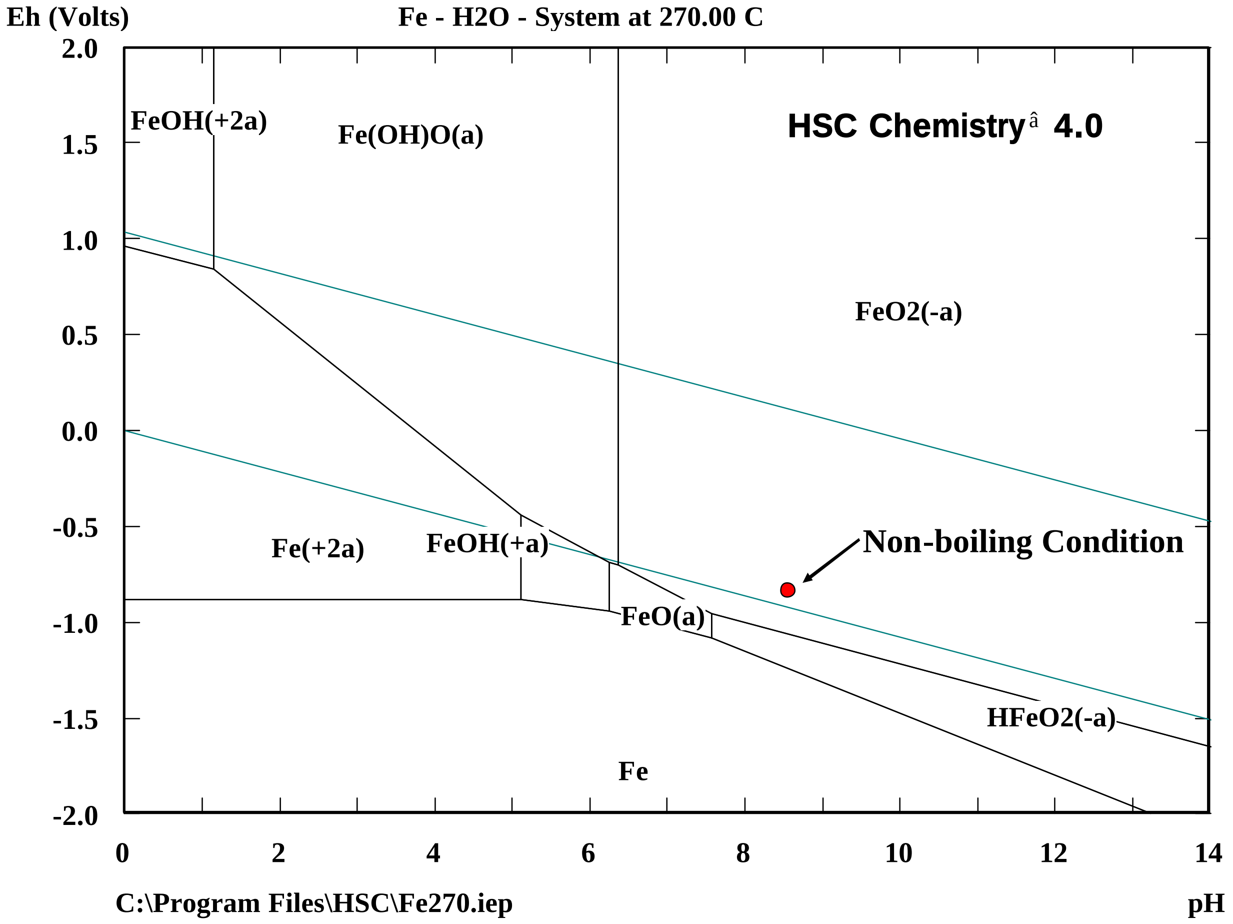
Future Work

Spatial Distribution in Crevice
As a Function of Time

Pourbaix Diagram: Fe - H_2O System



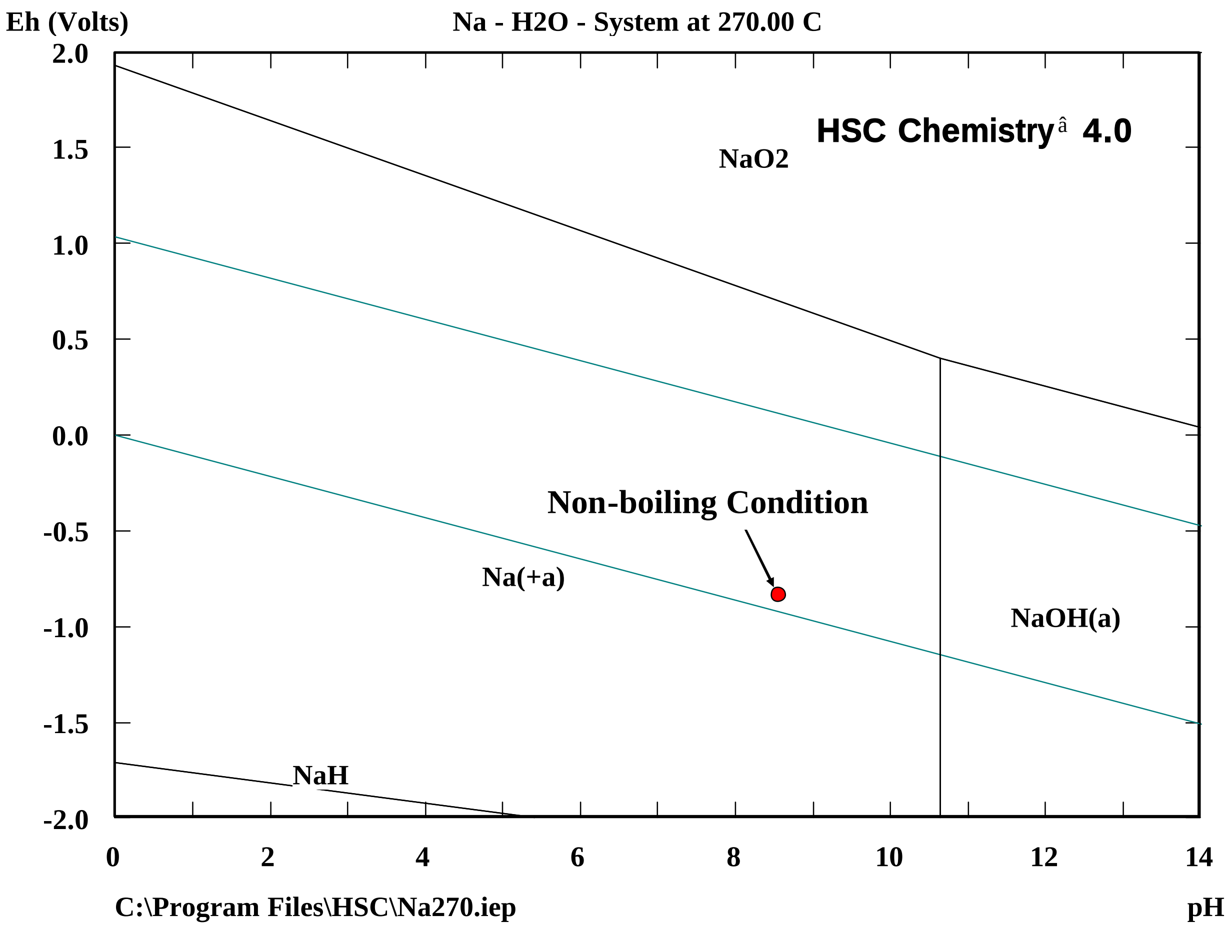
Pourbaix Diagram: Fe - H_2O System



Non-boiling Condition

ELEMENTS	Molality	Pressure
Fe	1.000E-08	5.426E+01

Pourbaix Diagram: Na-H_2O System



ELEMENTS	Molality	Pressure
Na	1.000E-06	5.426E+01

Chemical Equilibrium Model

- The equilibrium state of a closed chemical system is defined by its minimum free energy within the constraints of mass conservation.
- Two sets of equations, mole balances and the mass action laws, define a well-posed mathematical problem that can be shown to have one solution: the concentrations of the species at equilibrium.
- The “tableau” methodology is a convenient way to express the stoichiometric relations between species and components.
- MICROQL® is a chemical equilibrium program written by John Westall(1979) and essentially is a stripped down version of the program MINEQL® (Westall et al., 1976).
- Equilibrium constants of each reaction were calculated as a function of temperature by using HSC Chemistry®.

Chemical Equilibrium Model

Species & Equations

$$H^+ + OH^- = H_2O$$

$$H_2(aq) = H_2(g)$$

$$Na^+ + OH^- = NaOH(aq)$$

$$Fe^{2+} + H_2O = Fe(OH)^+ + H^+$$

$$Fe^{2+} + H_2O = FeO(aq) + 2H^+$$

$$Fe^{2+} + 2H_2O = HFeO_2{}^- + 3H^+$$

$$2Fe^{3+} + H_2(g) = 2Fe^{2+} + 2H^+$$

$$Fe^{3+} + H_2O = Fe(OH)^{2+} + H^+$$

$$Fe^{3+} + H_2O = FeO^+ + 2H^+$$

$$2Fe^{3+} + 2H_2O = Fe_2(OH)_2{}^{4+} + 2H^+$$

$$Fe^{3+} + 2H_2O = Fe(OH)O(aq) + 3H^+$$

$$Fe^{3+} + 2H_2O = FeO^{2-} + 4H^+$$

$$Fe_3O_4(s) + 6H^+ + H_2(g) = 3Fe^{2+} + 4H_2O$$

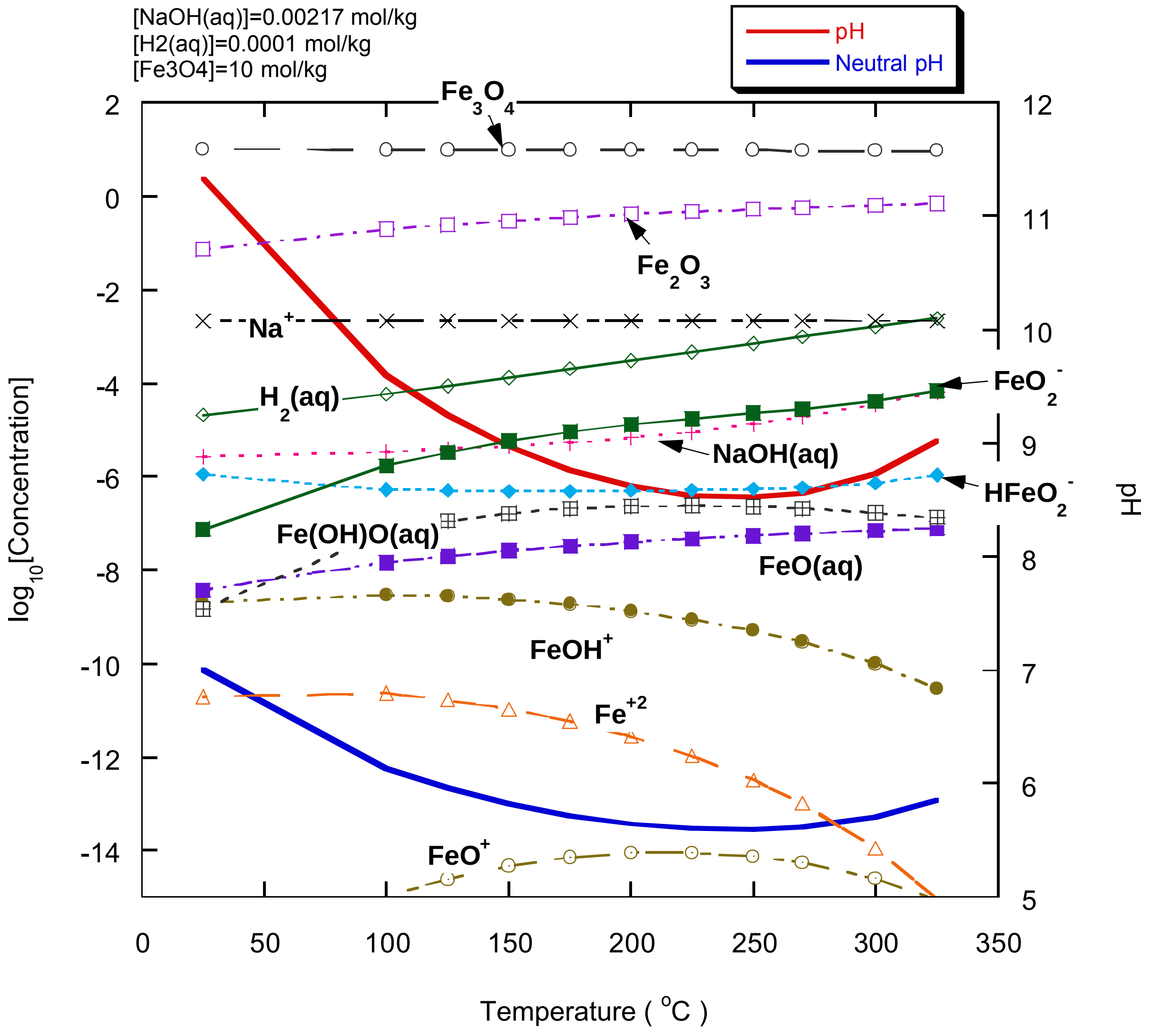
$$Fe_2O_3(s) + 4H^+ + H_2(g) = 2Fe^{2+} + 3H_2O$$

- 18 Species
  - H^+, OH^-
  - $H_2(aq)$, $H_2(g)$
  - Na^+, $NaOH(aq)$
  - Fe^{2+}, $FeOH^+$, $FeO(aq)$, $HFeO_2^-$
  - Fe^{3+}, $FeOH^{2+}$, FeO^+, $Fe_2(OH)_2{}^{4+}$, $Fe(OH)O(aq)$, FeO_2^-
  - $Fe_3O_4(s)$
  - $Fe_2O_3(s)$
- 14 Reactions

Calculation Results

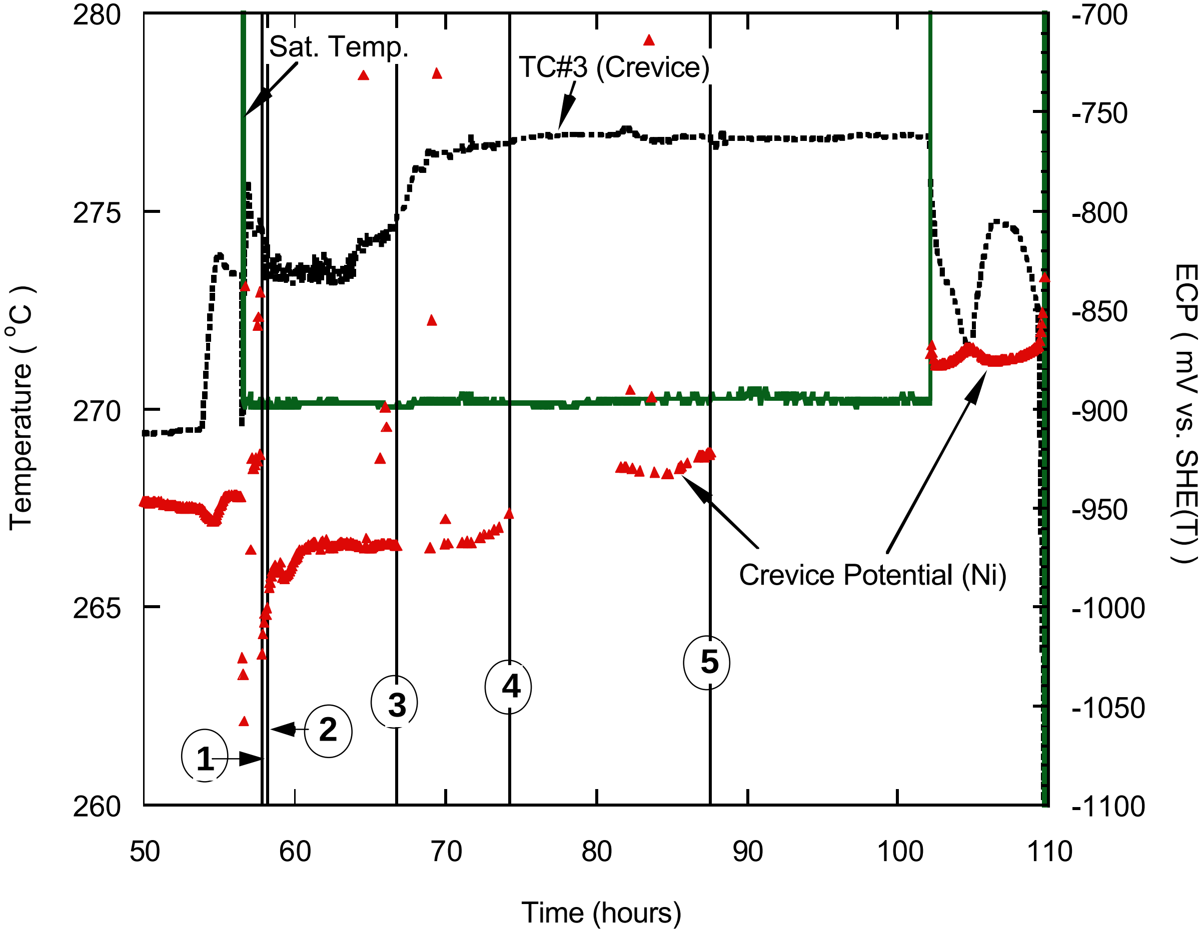
- Chemical Speciation Under Non-Boiling Condition: no chemical concentration
- Crevice Chemistry Evaluation from Experimental Results
  - Estimation [NaOH] from the temperature data
  - [H_2(aq)] Calculation from the ECP data
  - pH, Concentrations of aqueous species

Results: Non-Boiling Condition



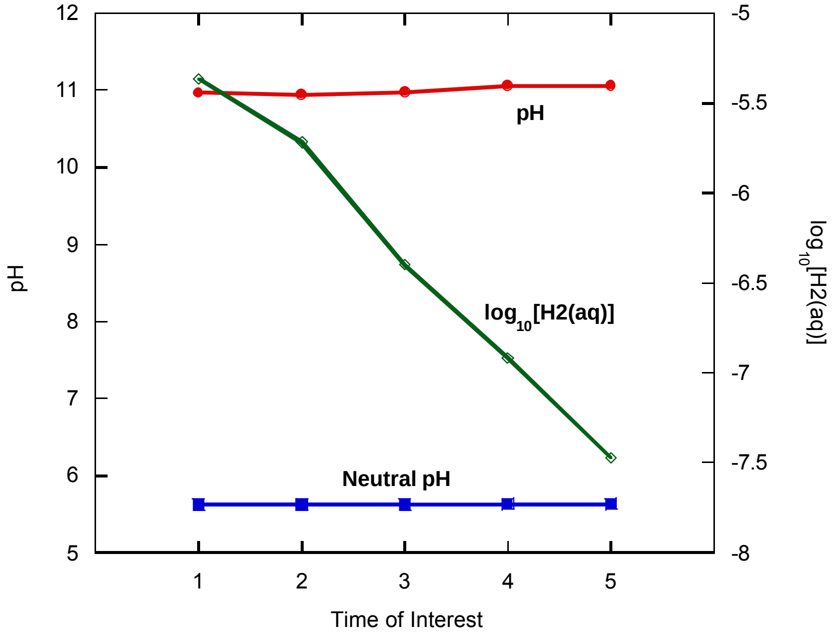
Results

Specific Time to Analyze Crevice Chemistry

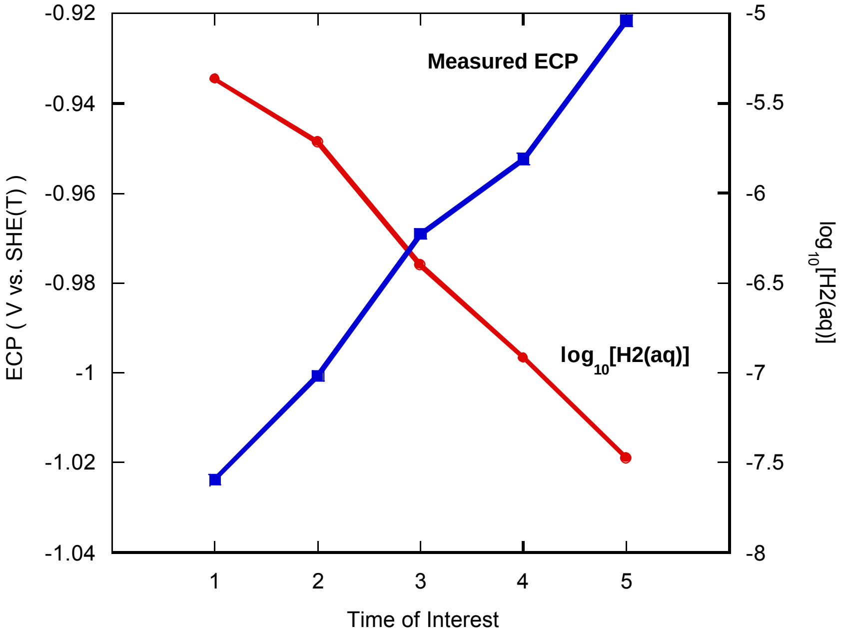


Results

pH & [H_2(aq)] Variation



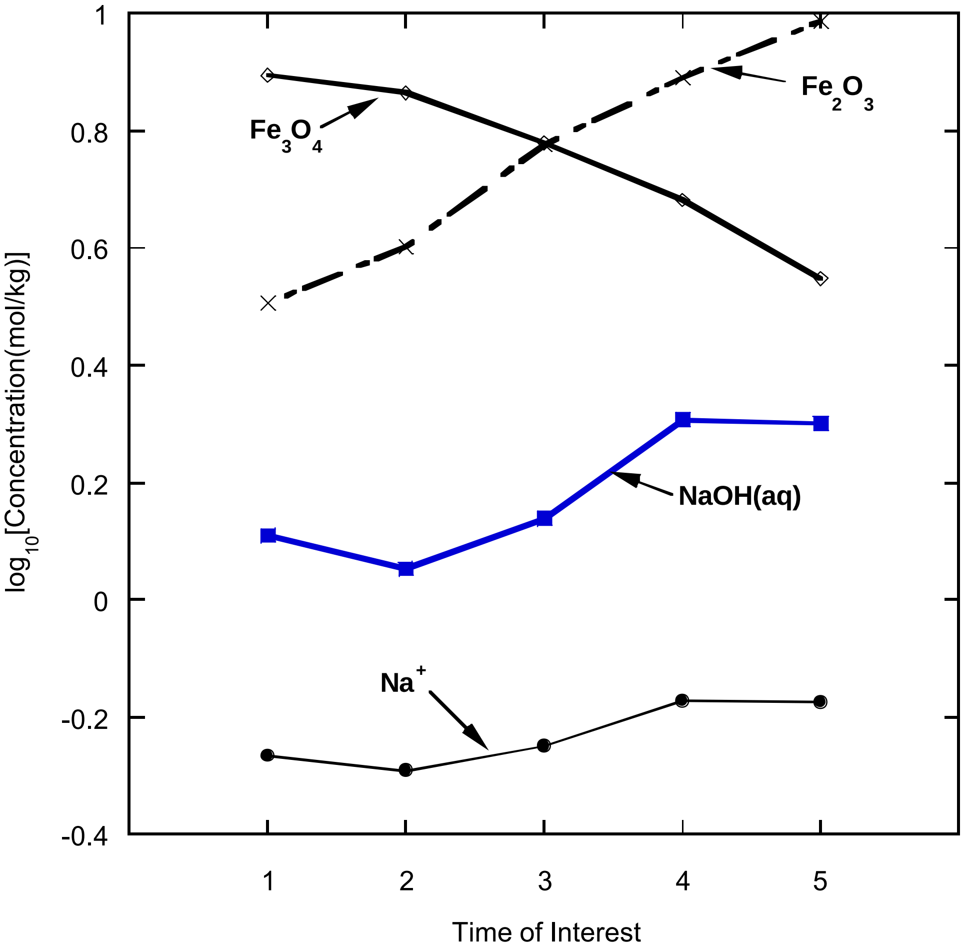
	1	2	3	4	5
[NaOH] mol/kg	1.83	1.64	1.94	2.70	2.67
[Fe3O4] mol/kg	10	10	10	10	10.



	1	2	3	4	5
[NaOH] mol/kg	1.83	1.64	1.94	2.70	2.67
[Fe3O4] mol/kg	10	10	10	10	10.

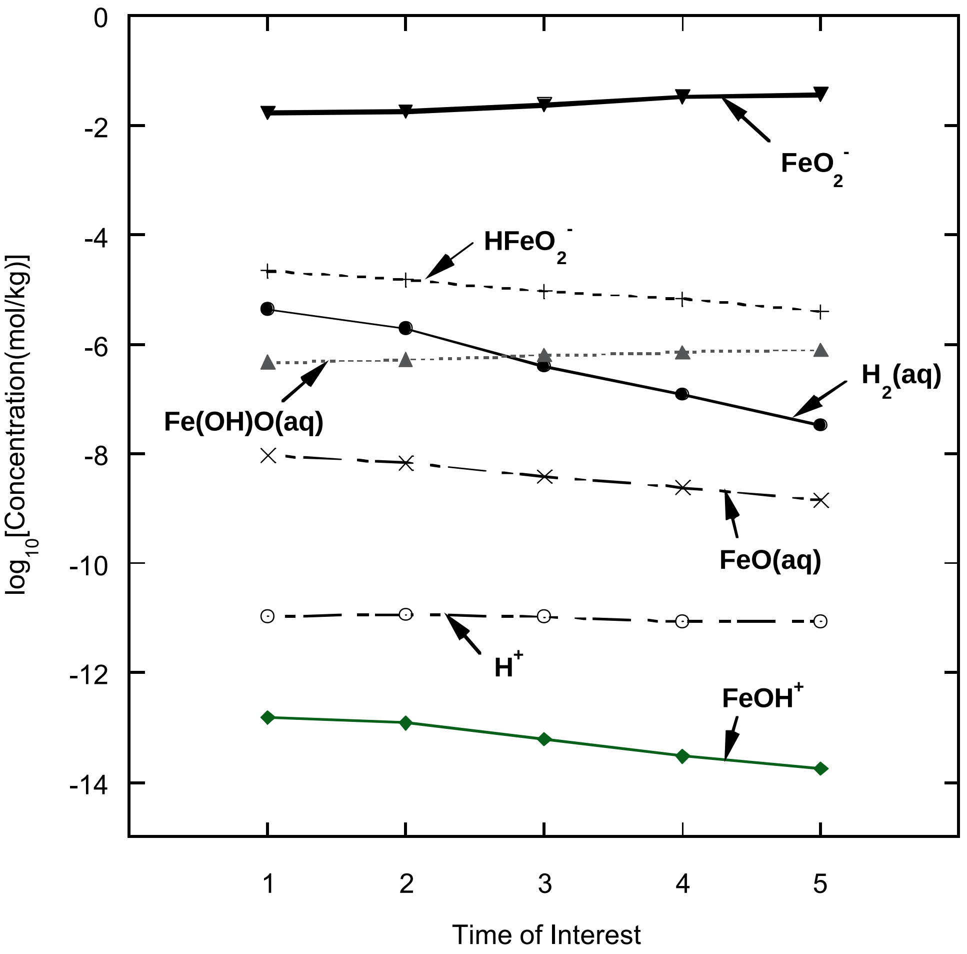
Results

Chemical Speciation



Results

Chemical Speciation



Summary & Conclusions

- Fe-H_2O stability diagrams at high temperature by using HSC Chemistry® 4.0 were constructed.
- To compute the chemical speciation under an equilibrium state in a magnetite-packed crevice environment, the “tableau” method was adopted.
- Based on the experimental results, pH, [H_2(aq)], and concentration of various species were calculated. The increase in ECP during the packed crevice test is rationalized by the decrease of dissolved hydrogen concentration by boiling process.
- Caustic crevice chemistry was developed by concentration of NaOH and it led to the dissolution of Fe_3O_4. Dominant aqueous species of iron was FeO_2^-.
- At the condition of low dissolved hydrogen, caused by crevice boiling, magnetite was transformed to hematite(Fe_2O_3) in equilibrium state.

Future Work

- Systematic consideration of the effect of volatile species, such as $H_2(aq)$ or $HCl(aq)$
- Predicting chemical distribution in a given crevice as a function of time by introducing convection and diffusion effects

The Conditions Known to Produce Crevice Corrosion by the *IR* Mechanism and Those Yet to be Investigated

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ABSTRACT

Some principles of current distribution in cracks for polarization in the Tafel region that were developed in the middle of the last century by Carl Wagner are a basis for understanding crevice corrosion. Many characteristic features of crevice corrosion were also discovered at roughly the same time. The so-called *IR* mechanism of crevice corrosion that was proposed in 1985 for metals with their outer surface in the passive state is based on these principles and known characteristics. Subsequent experimentation and modeling have so far been successful in testing its applicability for describing the two broad classifications of crevice corrosion: crevice corrosion that occurs immediately and the delayed form that occurs after an induction period. Its operation in intergranular corrosion and other forms of corrosion are discussed.

INTRODUCTION

An explanation of the role of *IR* voltage and the $IR > \Delta\phi^*$ criterion of the so-called *IR* mechanism of localized corrosion, where I is the ionic current within, R is the resistance of, and $\Delta\phi^*$ is defined below in terms of the polarization curve, starts with the principles of current distribution within recesses. These principles are well known but do not appear in most corrosion books. This paper traces the development of the $IR > \Delta\phi^*$ criterion, and examines a few of its less obvious consequences. An example of the latter is that crevice corrosion is more likely to occur when the anodic and cathodic reactions are well separated. The corresponding large corrosion circuits give large R values and hence large *IR* voltages. Similarly, if the oxidant availability increases at the outer surface, e.g., due to stirring, I increases. When $IR > \Delta\phi^*$, crevice corrosion commences.

CURRENT DISTRIBUTION IN RECESSES

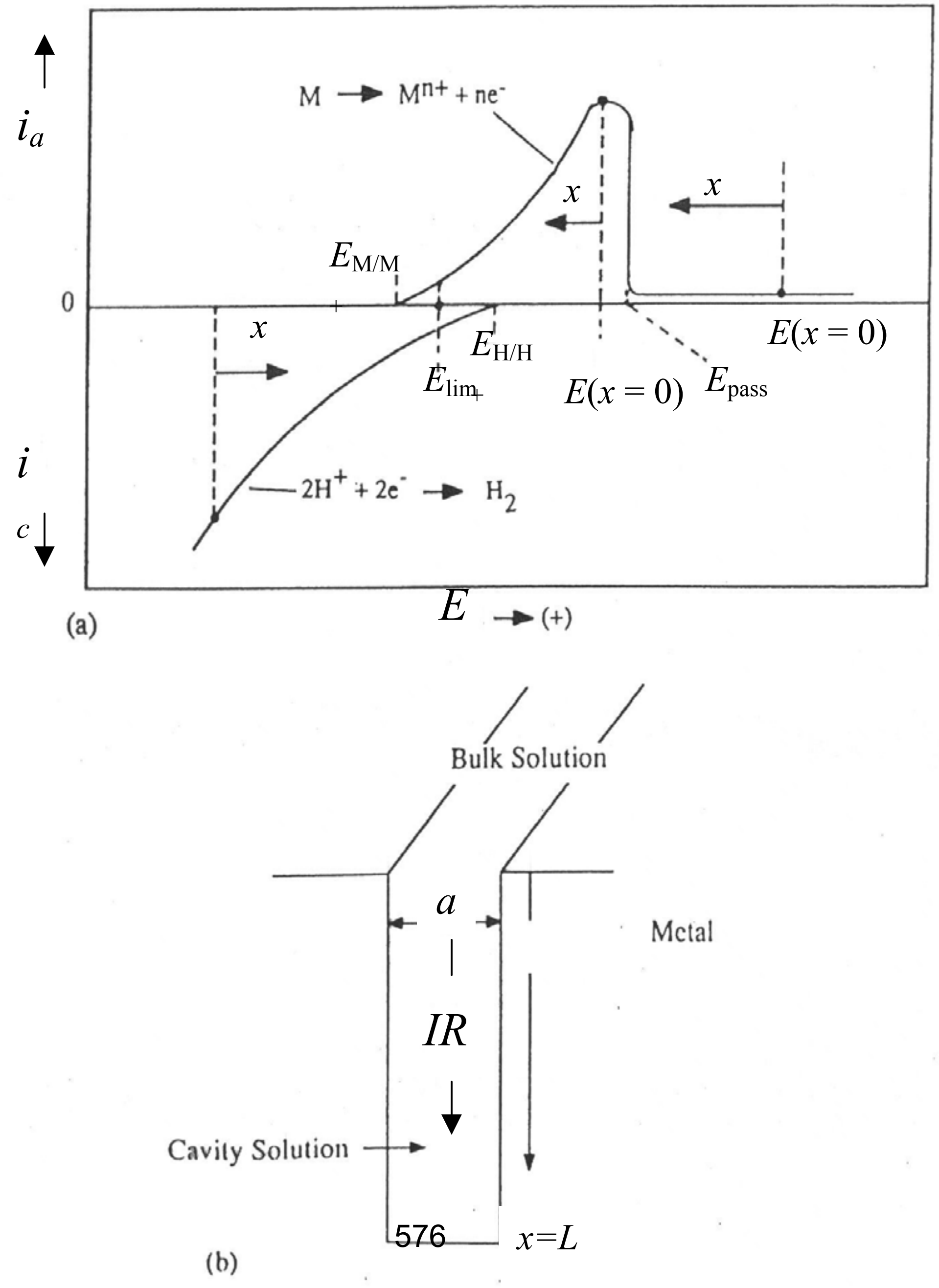
Tafel Region

In 1961 Carl Wagner (1) calculated the current distribution for electrodeposition on the walls of recesses in the surfaces of cathodes. The E_x profile ranged from its value at the outer surface, $E_{x=0}$, to more and more positive values as distance, x, increased into the recess (1, 2). Thus, a part of the cathodic polarization curve existed on the cavity's walls during the plating process. Garmon and Leidheiser (3) experimentally measured the decreasing deposit thickness with increasing x under conditions of low concentration polarization and found good agreement with that predicted by the Wagner (Laplace equation) model (1). Modeling by Ateya and Pickering (4) of the HER on a crack wall, taking into account the composition gradients using the general flux equations, showed similar trends in E_x and i_x that are schematically illustrated in the cathodic curve in Fig. 1.

Wagner (5) similarly modeled metal dissolution in recesses. The rate, i_x, again decreases but E_x becomes more negative, rather than positive, with increasing distance x into the cavity for $E_{x=0}$ in the Tafel region as shown in Fig. 1 and by (1, 4)

$$E_x = E_{x=0} - IR_x \qquad (1)$$

where I is defined as positive when flowing in the $-x$ direction as during anodic



polarization, and $IR_x = \phi_x$ with $\phi_x = 0$ at $x = 0$. Thus, with a surplus of oxidant at the outer surface or using a power supply, the shape evolution of the corrosive attack on the crevice wall largely reflects this decreasing i_x with increasing distance, x, into the crevice. With $E_{x=0}$ in the active region, the highest rate of metal dissolution occurs at the x = 0 (opening) location on the wall and on the unprotected outer surface, and the E_x profile inside the crevice is given by Eq. 1. In practice, if the outer surface is painted or otherwise protected, only the crevice wall shows corrosive attack upon contact with the electrolyte. In such cases all of the crevice wall undergoes active metal dissolution, in contrast to polarization into the passive region (see below) where the *IR* mechanism explains how a part of the crevice wall nearer the opening at $x = 0$ can be in the passive state while the rest of the wall is in the active state. In both cases, the i_x distribution on the crevice wall can include an increasing HER rate with increasing x between E_{rev} of the HER and the E_{lim} value defined elsewhere (6, 7). In practice, the occurrence of the HER beyond x_{rev} can be recognized by its signature: (H_2) gas evolution from the local cell.

Passive Region

Anodic polarization of the outer surface of the electrode into the passive region gives a more complicated result with respect to the E_x and i_x distributions. The shift of E_x in the negative direction again occurs in accord with a net ionic current, *I*, flowing out of the crevice during anodic polarization, Eq. 1. However, initially upon polarizing from the open circuit potential, E_{oc}, in the active region into the passive region, the active current decreases to the low passive value on the outer surface and either on the entire crevice wall or only on a part of the wall closer to its opening. In the latter case the rest of the wall remains active with E_x in the active region of the polarization curve. Herbsleb and Engell (8) interpreted their measured E_x profiles inside pits as being in the active region, noting that their result was as U. F. Franck had proposed. Many investigators of that period also measured *IR* voltages of up to 10^3 mV between the inside and outside of pits and crevices (9-12). This polarization situation is also illustrated in Fig. 1 with $E_{x=0}$ in the passive region, and is presented in more detail elsewhere (13).

Fig. 1. Schematic representation of the cathodic and anodic polarization curves and their distributions on the cavity's walls (13).

Similar (Laplace) modeling for anodic polarization into the passive region by Xu and Pickering (14, 15) revealed the factors which decide between the two possibilities: passivity of all the electrode's surfaces including the walls of the cavity vs. immediate, sustained high rates of metal dissolution on the deeper part of the cavity's walls. These factors are: (i) the opening, *a*, and depth, *L*, dimensions of the cavity, (ii) applied, E_{app} (= $E_{x=0}$), potential in the passive region, (iii) the resistivity of the electrolyte, and (iv) the bulk solution's anodic polarization curve. For given factors (ii) to (iv), the onset of immediate crevice corrosion vs. no corrosion (passive wall) was shown to depend only on the aspect ratio, AR, of the crevice (14-16). The model predicts that if AR is larger than the critical aspect ratio, $\mathrm{AR_c}$, crevice corrosion will occur immediately when the sample's outer surface is polarized from its E_{oc} value in the active region to a value, $E_{x=0}$, in the passive region. These modeling results are discussed more completely in later reviews (13, 17, 18). The predicted $\mathrm{AR_c}$ value was tested and found to be in good agreement with the experimentally determined value using two different metal/electrolyte systems, iron in acetate buffer (15) and nickel in acidic sulfate solution (16). In order to compare the model and experimental results at times beyond the immediate start of crevice corrosion,

x

experimental techniques were used which minimized changes in the composition of the crevice electrolyte so that factors (iii) and (iv) did not change appreciably during continuation of the crevice corrosion process. A similar, updated modeling of the E_x and i_x distributions and the AR_c value will soon be available (19).

Eq. 1 was adopted by Pickering and Frankenthal (9) to explain their measured E_x profiles in pits and crevices in iron during localized corrosion, and by Ateya and Pickering (4) for describing cathodic polarization inside cracks. Others of that period, although not referring to Eq. 1, attributed their measured less noble E_x values in pits and crevices during localized corrosion in titanium (12) and iron (8, 10) to *IR* voltage and salt films, respectively. Membranes covering (20, 21) and gas bubbles at the opening (22) or at the bottom (9) of pits were also suggested to account for the more negative E_x values.

In the sixties and seventies there were several reports of gas bubbles rising out of pits and crevices during localized corrosion (9, 23-28). The escaping gas was collected and analyzed during pitting in iron, titanium and aluminum and found to be hydrogen by Pickering and Frankenthal (9), Beck (27), and Bargeron and Benson (28), respectively. Other gases have also been detected emanating from pits (25, 28-30), such as CH_4, H_2S, N_2 and NO in the case of aluminum, which has been interpreted in terms of a reaction between the anion and the aluminum surface (28).

Pickering and Frankenthal (9) discovered that pit interiors were actually occupied by the gas and that the small hydrogen bubbles seen rising out of pits were fragments of this reservoir of gas. In more recent studies at Penn State, where the wall of the crevice and the tip of the Luggin capillary of the potential microprobe could be observed in-situ during the experiment, the gas bubbles which adhered to the walls of the crevice were found and to form and grow on the deeper part of the wall where the E_x value was in the region of the HER (31, 32). This observation, coupled with the earlier analysis of the collected gas bubbles as H_2 (9), provided a strong indication that the source of the gas was the HER and not escaping hydrogen that had previously entered the metal. This observation was also a strong independent confirmation of the potential microprobe measurement of the magnitude of the E_x profile. Gas was also demonstrated to fill crevices in iron during cathodic polarization (4, 33). These in-place gas reservoirs represent a significant resistance to current flow, i.e., *R* is large, since the electrolyte path is reduced in cross section to the very thin layer of electrolyte between the gas reservoir and the wall of the cavity (9). Thus, in the case of open pits in iron with the sample polarized well into the passive region, the metal dissolution current density on the pit wall, even though reduced by the bubble to below that given by the bulk solution polarization curve (9, 16, 34), can produce a very large *IR* voltage (> 1 volt was measured), whereas the calculated *IR* voltage along the *x* direction of the open pit in the absence of the gas is very much smaller (9). Formation of the H_2 bubble required that the E_x value was at least momentarily less noble than the reversible potential of the HER, e.g., as a result of an initial current spike at the moment of passive film breakdown (9).

Solid corrosion products (35), e.g., salt films, that have been suggested to form in the crevice or pit (8, 10) or as covering films (20, 21), can also produce larger *IR* voltages than would be possible in their absence for the dimensions of the cavity, in this respect having the same role as the gas reservoirs. In open pits or open crevices, gas reservoirs or other constrictions, would seemingly be required for arriving at sufficiently large *IR* voltages. However, constrictions are not always required. Under weak oxidizing conditions the *IR* need not be large to place the bottom of the local cell in the active region (9). Also, crevices typically have very small opening dimensions, e.g., the small space between a metal washer and bolt assembly or at the interface of an organic coating whose bonding has been compromised, where the *IR* is large because *R* is large (35).

Extending the theory of mixed potentials established by Wagner and Traud (36) to local cells, one concludes that the occurrence of the HER, as well as other cathodic reactions, at the anodic sites within the crevice, leads to a reduction of the ionic current, *I*, that can flow out of the cavity. Hence, the magnitude of the *IR* voltage is also reduced, in the limit to zero in which case localized corrosion by the *IR* mechanism is not possible (6, 37). A reduction in *R* gives the same result. Thus, separation of the anodic and at least some of the cathodic reactions is necessary for the occurrence of crevice corrosion by the *IR* mechanism, as shown below in experiments where stable crevice corrosion was suddenly terminated by adding oxidant to the crevice electrolyte (37).

That the walls of pits and crevices were in the active state in those early papers on localized corrosion was indicated by various results, including the measured E_x values at the bottom of pits and crevices (8-10, 12). Herbsleb and Engell (8, 38) found that the pit walls in iron contained sulfate films just as form in the active region of its polarization curve. Others have shown facets on the walls of pits and crevices that are characteristic of the Tafel region of the anodic polarization curves of metals, e.g., in pits in nickel (39) and iron (40), and more recently in crevices in nickel (41).

At about the same time in the anodic protection industry, similar reasoning was advanced by Edeleanu and Gibson (42) and others (43, 44). These investigators analyzed the potential distribution and distance at which the passive-to-active transition occurred along a wire which was in a tube and polarized into the passive region at its one end (42). They found that passivity broke down and the protection system failed at the other end of the wire. They concluded that a possible cause was a shift of the local electrode potential into the active peak region of the polarization curve.

FORMALIZING THE *IR* VOLTAGE CONCEPT

$IR > \Delta\phi^*$ for the Immediate Onset of Crevice Corrosion

Using the understanding illustrated in Fig. 2 which was first presented at the NACE annual meeting in 1985 and published the next year (7), a formalism was proposed for susceptibility to localized corrosion (45, 46),

$$IR > \Delta\phi^* \qquad (2)$$

$\Delta\phi^*$ is the difference between $E_{x=0}$ and E_{pass} ($E_{\text{A/P}}$ in (a) of Fig. 2), and has the magnitude given by the polarization curve existing in the cavity at the start of crevice corrosion, which is the bulk solution curve in the case of immediate crevice corrosion. The Xu-Pickering model (14, 15) correctly predicted that when the crevice's aspect ratio, *AR*, was greater than the critical aspect ratio, AR_c, Eq. 2 was met immediately (15, 16). The model also revealed that when $AR > AR_c$ the initial location of the corrosive attack and of the passive/active boundary, x_{pass}, on the crevice wall was at smaller x values for smaller a values, in agreement with field observations (7, 47).

$IR > \Delta\phi^*$ for Ending the Induction Period

In the case of delayed crevice corrosion, Pickering (7, 45, 46) suggested that the induction period would end and crevice corrosion would start when $IR > \Delta\phi^*$ (i.e., $IR < \Delta\phi^*$ switched to $IR > \Delta\phi^*$), e.g., when an active peak grew larger as from acidification of the crevice electrolyte or increase in temperature thereby decreasing $\Delta\phi^*$ (sketch e in Fig. 2); the passive current increases (sketch d), increasing I; or constrictions form, increasing R. Then, crevice corrosion would begin at the bottom of the crevice where $IR > \Delta\phi^*$.

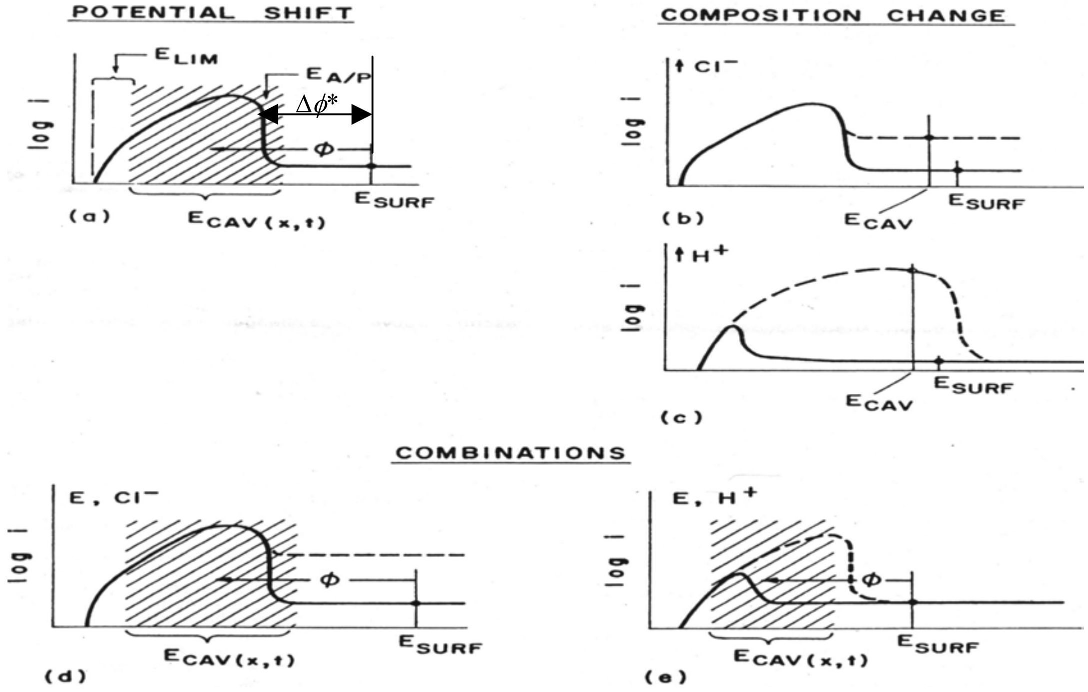


Fig. 2. Schematic representation of the IR voltage form of crevice corrosion for the two classifications: immediate onset of crevice corrosion (a), and the delayed form which requires certain changes in the polarization curve, e.g., due to a change in temperature or composition of the crevice electrolyte (d and e). Also shown is the critical solution composition mechanism where no consideration is given to the E_x distribution on the crevice wall (b and c) (7). An example of $\Delta\phi^*$ is shown in (a).

There are numerous studies in the literature where this criterion could have operated, i.e., the induction period ended and crevice corrosion started at the bottom of the crevice when the inequality in Eq. 2 was met. Some authors recognized this possibility to some extent. A recent example is the study of stainless steel in dilute NaCl solution by Brossia and Kelly (48). Although, as in most other past studies of localized corrosion it was not possible to measure E_x during the induction period, let alone the pH or chloride ion gradients, these authors reported that the corroded crevice wall was in the active state. These kinds of data (e.g., E_x as in Fig. 7 below) are needed to document whether the IR mechanism is or is not operating. Thus, many past localized corrosion studies need to be re-examined, even though the authors may have concluded, without the benefit of such documentation, that the *IR* mechanism was not operating in their study.

PROOF-OF-CONCEPT EXPERIMENTS

Immediate Crevice Corrosion

A mechanism controversy developed some 15 years ago when Valdes (31, 49, 50) and then others (14-16, 51, 52) at Penn State presented data for crevice corrosion using a novel experimental design (31, 34, 49) and orientation (16). Prior to this time the *IR* voltage was either considered negligibly small or a quantity that developed after stabilization of the local cell process by the then generally accepted, solution-composition-change mechanism. The strategy of the Penn State experiments was to either hold the pH constant in the crevice electrolyte (31, 49, 50) or to maintain good mixing of the crevice and bulk electrolytes (16), and then measure the E_x distribution inside the crevice as crevice corrosion started and stabilized. A fine Luggin capillary mounted on a 3-dimensional, translational stage and connected to a reference electrode was used to measure the E_x distribution. In this way if crevice corrosion occurred, it would show that the *IR* voltage was the key variable for the stabilization of crevice corrosion. In addition, if crevice corrosion occurred immediately, this in itself would preclude the operation of the solution-change mechanism. The occurrence of crevice corrosion was indicated by a measured current in the mA range and by visual observation through a transparent medium constituting another wall of the crevice. Crevice corrosion was found to occur immediately and only on that part of the crevice wall that was in the active peak region of the polarization curve (15, 16, 31, 32, 34, 37, 41, 49-54). These results were a powerful statement for the operation of the *IR* mechanism in crevice corrosion. When coupled with the above mentioned computational model results, they went a long ways towards resolving the controversy between the *IR* mechanism and the change-in-solution-composition mechanism for crevice corrosion, in favor of the former.

Typical results of these investigations for spontaneously active systems with crevices whose aspect ratio was larger than the critical value are shown in Fig. 3 to 5 for a stainless steel (34). Similar results were obtained for iron (15, 16, 31, 41, 45, 46, 49-52), steel (53), and nickel (16, 41, 54). The results were clear in showing that crevice corrosion was initiated and stabilized by the above-mentioned *IR* mechanism. Firstly, the measured current was immediately in the mA range. Secondly, the corrosive attack on the crevice wall matched the E_x region of the bulk solution polarization curve. This was determined by the in-situ microprobe measurements of E_x during crevice corrosion, Fig. 3. Thirdly, the in-situ measured E_{pass} value, at the visually observable (through a transparent wall of the crevice) x_{pass} location on the crevice wall, was the same as the E_{pass} value of the 2M H_2SO_4 + 2M HCl + 1M NaCl bulk solution, i.e., was within the potential region of the passive-to-active transition of the bulk solution polarization curve. The equality of these two E_{pass} values for the duration of the crevice corrosion process indicted that there was no significant change in the polarization curve of the crevice solution from the bulk solution curve. This conclusion was supported by the in-situ measured pH value of the crevice solution and of the bulk solution (both were less than pH 0 for this system). The common features in the results for iron, steel, nickel and stainless steel mentioned above and illustrated in Figures 3 to 5 are that all of the tested metal/electrolyte systems were spontaneously active systems and all of the crevices initially had aspect ratios, AR, that were larger than their respective critical aspect ratios, AR_c. These are, in fact, the requirements for the immediate onset of crevice corrosion by the *IR* mechanism (14-18).

Termination/Reinitiation of Crevice Corrosion.

In principle, a decrease in *I* or *R* and/or an increase in $\Delta\phi^*$ could invert Eq. 2, causing immediate termination of crevice corrosion. In recent experiments oxygen saturated bulk solution was added to the crevice electrolyte, effectively moving the cathodic reaction close to the anodic sites on the crevice wall. This caused $E_{x=L}$ and *I* to abruptly and simultaneously rise to near the outer surface, $E_{x=0}$ value and decrease to the passive value, respectively, terminating the crevice corrosion process, Fig. 6. Sudden reinitiation of crevice corrosion on the passive wall by change of the composition of the crevice solution, e.g., increasing the chloride ion concentration (increasing i_{pass}), was also experimentally demonstrated (37).

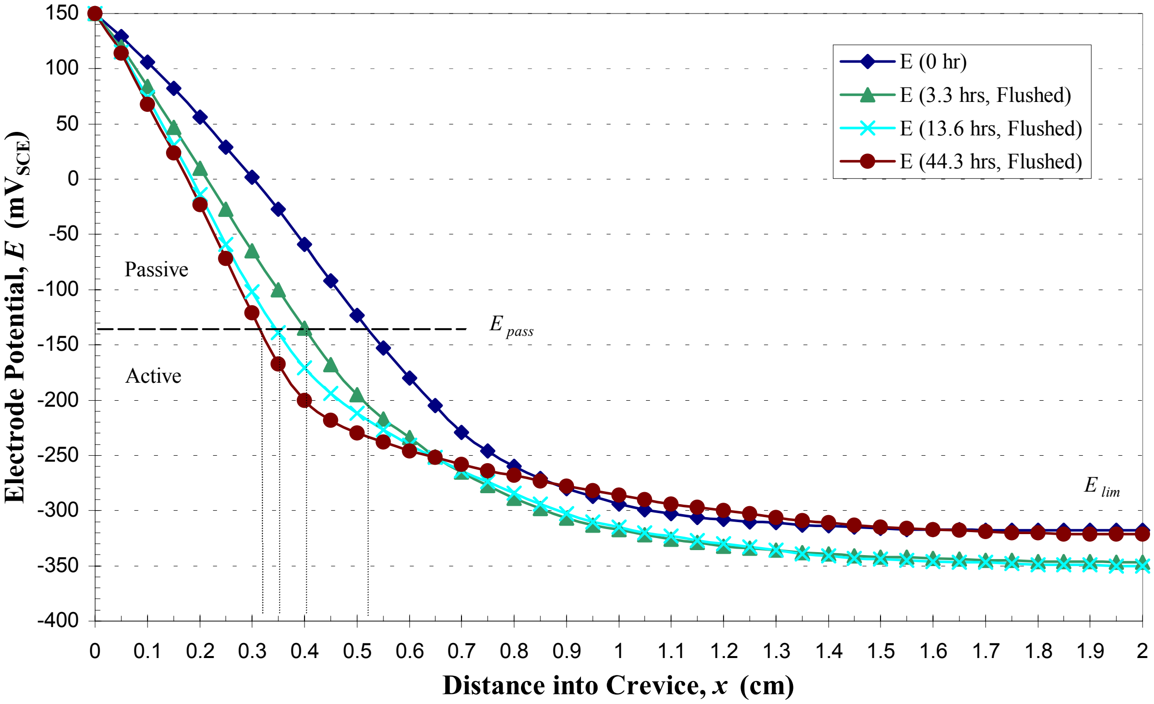


Fig. 3. In-situ microprobe measurements of E_x during crevice corrosion of T-2205 duplex stainless steel in strongly acidic chloride solution showing that E_x has shifted over 300 mV in the negative direction into the active peak region of its polarization curve, thereby stabilizing the crevice corrosion process (34).

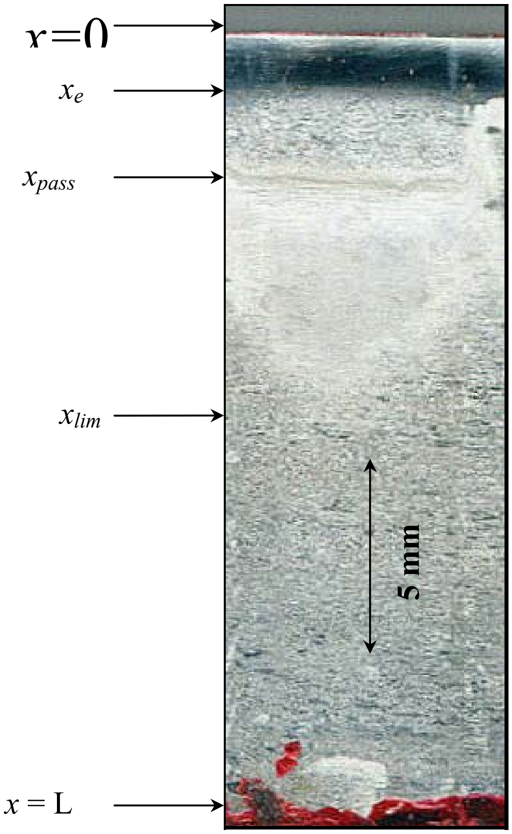


Fig. 4. The crevice wall of the sample in Fig.3 showing the corrosive attack below the x_{pass} boundary. This photograph was recorded in-situ at 14 hours (x_{pass} = 0.34 cm) (34).

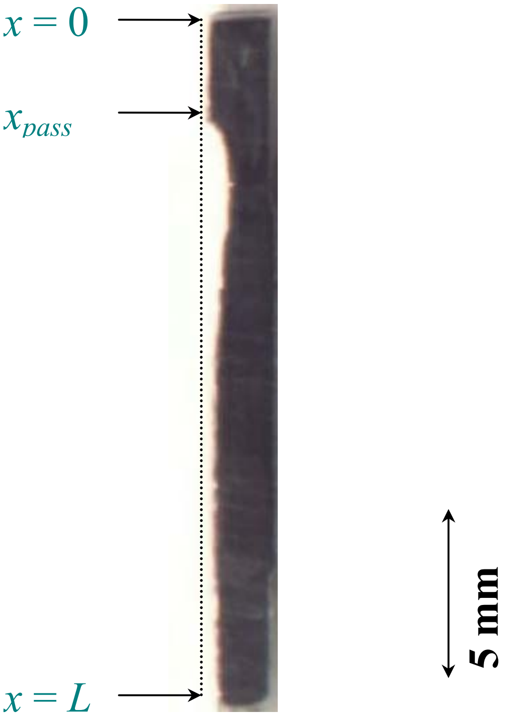


Fig. 5. Cross-sectional photograph after completion of the experiment in Fig. 3 showing the corrosive attack below the x_{pass} location on the crevice wall (34)

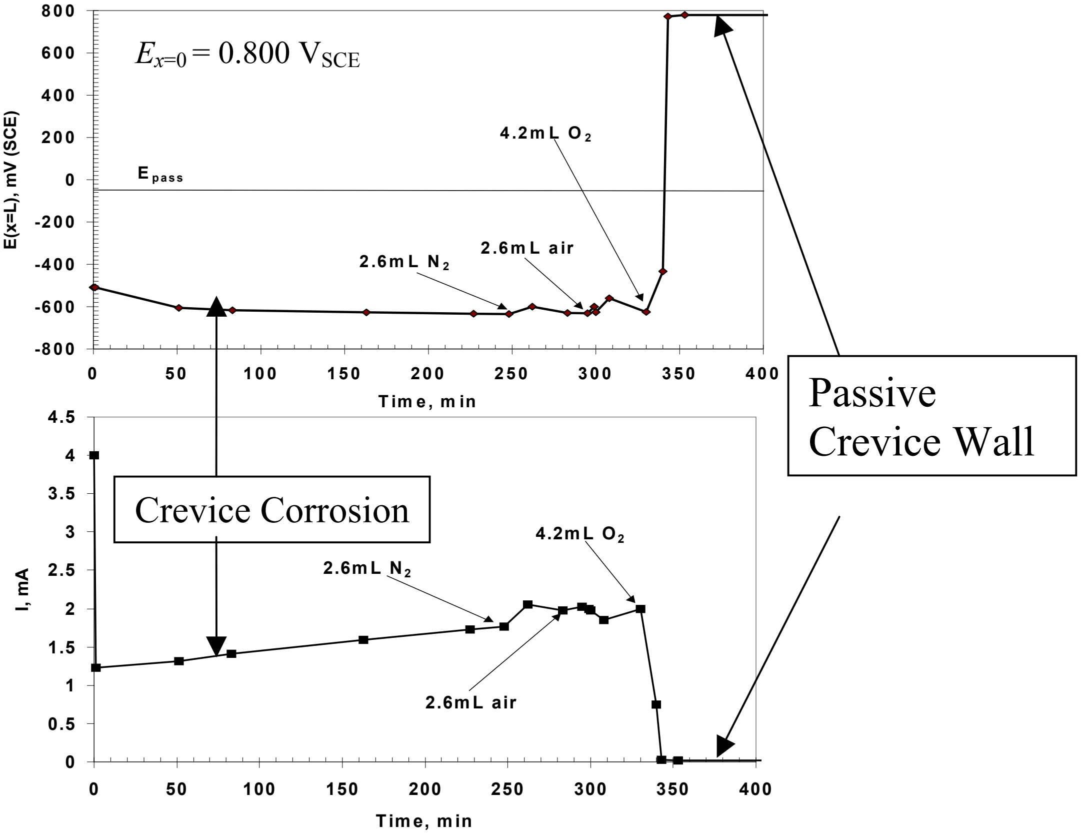


Fig. 6. Upon adding O_2 to the crevice electrolyte at 328 min., termination of crevice corrosion occurred, as indicated by the steep (a) ascent of $E_{x=L}$ = -600 mV_{SCE} from the active region to near the outer surface $E_{x=0}$ = 800 mV_{SCE} value in the passive region and (b) decrease of the mA ionic current, *I*, to that for the passive current. Fe/0.5 M Na_2SO_4 - 0.1 mM NaCl. See source for other details (37).

Delayed Crevice Corrosion

If initially the condition in Eq.2 (or AR > AR_c) is not met resulting in passivation of the entire crevice wall, there are the above-mentioned changes in the system that could occur during an induction period that would allow this condition eventually to be met (7, 14-16, 45, 46). The moment $IR < \Delta\phi^*$ switches to $IR > \Delta\phi^*$ (or AR < AR_c switches to AR > AR_c) the induction period would end and crevice corrosion would commence. These changes include one or more of the following (14-16): (i) the corrosion, E_{corr}, or applied potential, E_{app}, becomes less noble ($\Delta\phi^*$ decreases), (ii) the composition of the stagnant crevice electrolyte changes in such a way that it tends to increase the size of the active peak ($\Delta\phi^*$ decreases), passive current increases (*I* increases) and/or solution resistivity increases (*R* increases), and/or (iii) there is a decrease in the effective cross sectional area of the electrolyte volume in the crevice due to gaseous or solid corrosion product formation (*R* increases). All of these variables and respective given directions of change tend to promote the inequality in Eq. 2 and to decrease the value of AR_c.

The first experimental data that were consistent with this *IR* explanation of the end of the induction period and start of crevice corrosion that is illustrated in Fig. 2, were obtained over a decade ago and are shown in Fig. 7 (52). A fine Luggin capillary microprobe was used to measure the electrode potential half way into the crevice as a function of time during the induction period. Fig. 7 shows that the electrode potential inside the crevice abruptly shifted in the less noble direction by over one volt just as the induction period was ending and crevice corrosion was starting at approximately 13.5 hours for this iron sample in buffered alkaline (pH 10) solution. The start of crevice corrosion was shown by the simultaneous increase in the measured current at 13.5 hours in Fig. 7. These data indicate that the *IR* voltage framework of crevice corrosion illustrated in Fig. 2 was the explanation of the end of the induction period and start of crevice corrosion. Close examination of Fig. 7 shows *I* increasing and *E* decreasing slightly with time from the start of the induction period, in accord with Eq. 1. This slight increase in *I* over most of the induction period represents a gradual increase in i_{pass}, as illustrated in sketch (d) of Fig. 2. It is also conceivable that in this experiment the active peak was increasing in size during the induction period as the buffer became less effective inside the crevice, sketch (e), thereby decreasing $\Delta\phi^*$. The latter could have been resolved at the time by in-situ pH measurements of the crevice electrolyte during the induction period. Thus, the increase in *I* and any decrease in $\Delta\phi^*$ seemingly led to the end of the induction period and start of crevice corrosion at 14 hours when $IR < \Delta\phi^*$ switched to $IR > \Delta\phi^*$. This framework of crevice corrosion has also been used by Shaw, et. al. (55), and considered by Lillard, et. al. (56, 57), for describing the end of the induction period and onset of localized corrosion in alloy 625, a corrosion resistant commercial nickel base alloy. DeJong and Kelly (58) have presented evidence of its operation in nickel.

Recent experiments of the type in Fig. 7 for a spontaneously passive system included the in-situ measurement of the pH (59). This unbuffered system was found to change to a spontaneously active system through formation and growth of an active peak as the pH decreased from its initial pH 9 value. At the end of the 7 minute induction period and start of crevice corrosion, the measured pH inside the crevice was pH 4. At this time the electrode potential at the bottom of the crevice, $E_{x=L}$, decreased and *I* increased steeply in the simultaneous manner already shown in Fig. 7 (59).

OTHER CORROSION FORMS SUBJECT TO THE *IR* > $\Delta\phi^*$ CRITERION

Pit Initiation

Early discussions of *IR*-induced pit initiation focused on how the system could provide the necessarily large *IR* voltage when the pit was early in its growth or, indeed, at its very inception. The results described in the early Pickering-Frankenthal papers (9, 40, 60) led these authors to suggest a mechanism of pit nucleation which was based on the *IR* voltage and bubble formation within the pit electrolyte: When local breakdown of the passive film occurs, the initial current spike due to metal dissolution, though quickly subsiding as polarization occurs, could momentarily produce a large *IR* voltage (9). Its momentary presence within the small cavity in the passive film and into the incipient pit, could produce an $E_{x=L}$ value at the pit bottom that would promote H_2 gas formation and

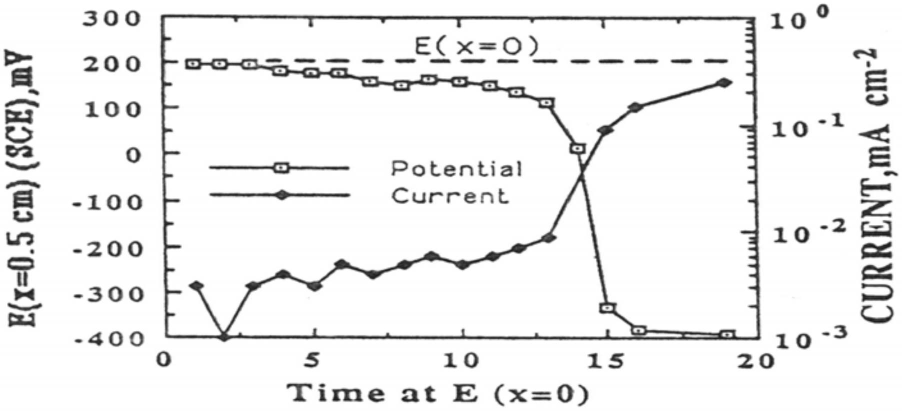


Fig. 7. E_x and I data showing the onset of crevice corrosion after a 14 hour induction period. The large *IR* voltage shown by the several hundred mV shift of E_x at the end of the induction period and simultaneous start of crevice corrosion indicates operation of the *IR* voltage form of crevice corrosion (52).

its inclusion within the pit, thereby stabilizing the large *IR* voltage and the pitting process itself. Later, it was proposed that a repetitive process of pit initiation and repassivation at the same incipient (metastable) pit sites could eventually produce a cavity shape with a large enough aspect ratio so as to exceed the system's critical aspect ratio, $\mathrm{AR_c}$ (15). These first and second generation proposals are based on the *IR* mechanism, the latter of which incorporates metastable pits which eventually become stable pits.

Lace-Like Pattern During Pit Growth

Pit growth often continues until the pit consumes all of the metal in its growth direction. Sometimes the growth also occurs backwards towards the surface on which the pit originated. Upon penetrating the original surface the metal around the new hole passivates, and the process repeats eventually forming a lace-like pattern of holes around the original pit opening (9). Streicher (61) and others (40, 62) had already shown a similar pattern of small pit-like holes around the original, usually larger pit opening. Frankenthal and Pickering (40) observed that the original pit opening at the center of the pattern usually formed at an inclusion in their austenitic stainless steel samples, and that . the outer circle of the concentrically growing holes represented the extent of growth of a single large pit underneath the lace-like cover. They proposed that the steep E_x profiles found for their open (uncovered) pits in iron (9) also existed in these covered pits, while also invoking the enhancement of chloride ion accumulation for these covered pits (40). In a series of SEM stereo-micrographs they found that the outer surface between the holes of the lace-like cover remained smooth (from the original metallographic polish of the surface), whereas the underneath surface of the lace-like cover was rough. Similar observations were made by Streicher (61) and Rosenfeld and Danilow (62). Hence, it was concluded that the pattern formed by dissolution and breakthrough of the surface was caused by active metal dissolution from inside the growing large pit that supported the lace-like cover (40). Later, researchers at Penn State elaborated on this *IR* mechanism for the lace-like pattern based on its appearance in iron (15, 31) and nickel (16) samples and their above mentioned proof-of-concept experiments for the *IR* mechanism.

Grain Boundary Corrosion and Cracking (IGSCC)

Bennett and Pickering (63) noticed in their studies of grain boundary corrosion of sensitized austenitic stainless steel that the resulting grain boundary grooves were wider and uneven in width, sometimes by as much as one or two orders of magnitude, than the predicted chromium depleted-zone width. This result was also apparent in micrographs in papers by Briant (64) and Streicher (65). The predicted value of the grain boundary chromium depleted-zone width was based on the chromium depletion theory of grain boundary corrosion discovered by Strauss, et. al., (66) and Bain, et.al., (67) for austenitic stainless steel and by Baumel (68) and others (69, 70) for ferritic stainless steel. Thus, bulk austenitic stainless steel with its normal (>18 %) chromium content was seemingly under going high rates of anodic dissolution, a result not explained by the chromium depletion theory. Bennett and Pickering (63) concluded that a secondary corrosion process occurred that attacked the bulk 18 % Cr austenitic stainless steel while the chromium depleted alloy along the grain boundary was being anodically dissolved via the chromium depletion mechanism.

More recently, Zamanzadeh et. al., (71) concluded the same based on an investigation of a stainless steel tube which failed in acid service from intergranular corrosion and stress corrosion crack (IGSCC) propagation. In a laboratory investigation of this phenomenon in a sensitized ferritic stainless steel, Kelly, et. al., (72) showed that the second intergranular corrosion mechanism was crevice-like in nature. They concluded, based on evidence of a large IR voltage inside the groove and the absence of acidification or chloride ion build up within the corrosive solution inside the grain boundary groove, that the above described $IR > \Delta\phi^*$ criterion eventually became operative and caused the significantly increased grain boundary corrosion of the bulk 18 % Cr ferritic stainless steel. Thus, the $IR > \Delta\phi^*$ criterion and IR mechanism of localized corrosion became established as a secondary mechanism of intergranular corrosion at the moment the aspect ratio of the grain boundary groove (which increases with time during operation of the chromium depletion mechanism) just exceeded the critical aspect ratio, AR_c, of the system (which typically decreases with time as stagnation (e.g., acidification) of the grain boundary groove occurs) (13). This moment is when the $IR < \Delta\phi^*$ condition switches to the $IR > \Delta\phi^*$ criterion of Eq. 2 at the base ($x = L$) of the grain boundary groove or tip of an insipient crack initiation event.

The required high tensile stresses for crack initiation could exist at the base of the groove which functions as a stress raiser. This state-of-stress/electrochemistry condition at the base of the grain boundary groove at the moment the $IR > \Delta\phi^*$ is met, can be visualized as the trigger for the initiation of a stress corrosion crack (IGSCC) propagation (73).

Porous Sintered Electrodes

Powder metallurgical structures of metal/electrolyte systems exhibiting active/passive behavior can be susceptible to the $IR > \Delta\phi^*$ form of localized corrosion. An example is sintered iron in aqueous ammoniacal solution (74, 75). The anodic polarization behavior of sintered iron powder was similar to that of bulk iron in ammoniacal solution, showing active, passive and oxygen evolution regions. A very high current density observed with the outer surface polarized into the passive region for some sintered specimens and sintering conditions, was attributable to active dissolution of the metal pore walls within the pore structure, analogous and equivalent to conditions during crevice corrosion by the $IR > \Delta\phi^*$ mechanism. This phenomenon can also be the explanation of the more negative measured corrosion potential of a powder metallurgy sample than its wrought bulk equivalent composition (76).

CONCLUSIONS

1. Carl Wagner, a half century ago, provided the theoretical foundation for *IR*-induced current and potential distributions in cavities during polarization into the Tafel region. This theory can be directly used to explain crevice corrosion and the shape evolution of the corrosive penetration on the crevice wall of coated metals when the outer surface potential, $E_{x=0}$, is in the active region. An extension of these concepts, supported by mathematical modeling, provide a similar underpinning for the *IR* mechanism of localized corrosion in the case of polarization in the passive region.

2. The *IR* mechanism for polarization into the passive region, defined by the $IR > \Delta\phi^*$ condition, has been established in cases of immediate crevice corrosion. When crevice corrosion occurs immediately it means that the crevice's aspect ratio is initially larger than the critical aspect ratio that applies for the particular metal/electrolyte system, temperature and existing or applied electrode potential at the outer surface, i.e., $AR > AR_c$ initially holds for the bulk, ambient electrolyte and applied $E_{x=0}$ value in the passive region. The value of AR_c can be obtained from the Xu-Pickering model (14, 15) or from experiment.

3. Adding oxidant to the crevice solution, can cause sudden termination of crevice corrosion by inverting the inequality $IR > \Delta\phi^*$ via a decrease in I (or inverting $AR > AR_c$ via an increase in AR_c). These results show the need for separation of the anodic and cathodic reactions, provide an improved understanding of the role of oxygen depletion in the crevice's electrolyte and provide a further proof of the operation of the *IR* mechanism.

4. The in-situ observations of H_2 gas formation confirms the magnitude of the measured E_x profiles and that its source is the HER rather than the escape of hydrogen from the metal.

5. Based on a few results to date, the *IR* mechanism controls the length of the induction period, i.e., both the electrode potential at the bottom of the crevice, $E_{x=L}$, and the ionic current, *I*, flowing out of the crevice simultaneously assumed values characteristic of *IR*-induced crevice corrosion at the end of the induction period. This was furthered supported by the in-situ measured pH at the end of the induction period, which had decreased to pH 4, characteristic of an active peak in the polarization curve in this otherwise spontaneously passive system.

6. The *IR* mechanism has been proposed to account for pit initiation, transition from metastable to stable pitting, pit growth, formation of the lace-like structure, corrosion in the pores of sintered metals, and secondary grain boundary corrosion of sensitized stainless steel based on some corroborating experimental evidence.

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Agenda for Summarizing Seminar on Heat Transfer Crevices
Summary session: “Take home” from meeting

1. **Primary scope: Predicting properties of line contact heated crevices with respect to occurrence of corrosion of Alloys 600TT and 690TT.**

2. **Incentives**

    a. **Seabrook shows that line contact geometries with Alloy 600TT can sustain SCC. This occurrence should be considered to be the “first-of-many failure.”**
        - **Seabrook SCC driven by exceptional high residual stress in some tubes**
        - **However, concave quatrefoil support developed aggressive chemistry**
        - **Industry does not have technique of identifying equivalent high residual stress elsewhere**
        - **TT location known to have high stresses at expansion transition at supports in other SGs.**

    b. **Lengthen time between inspections based on quantitative criteria.**
    c. **Demonstrated corrosion of Alloys 600TT and 690TT in pH ranges relevant to SGs.**
    d. **Not wait for the “inevitable” failures.**
    e. **Prevent future failures**
    f. **Permit conducting credible operational assessments.**

3. **Demonstrated vulnerabilities of Alloys 600TT and 690TT in relevant environments**

    a. **PbSCC (testing in progress with EPRI/Rockwell**
    b. **S^{y-}SCC**
    c. **Si-Al type SCC (testing done by EPRI and EdF/Framatome**
    d. **AcSCC**
    e. **“Complex environments”**
    f. **AkSCC**

4. **Predicting performance of line contact crevice deposits should include:**

    a. **Rate of crevice deposit accumulation**
    b. **Superheat/concentration factor evolution**
    c. **Low solubility precipitate accumulation**
    d. **Species accumulation**
    e. **Contribution of streaming potential**
    f. **Applicability of information from drilled hole studies.**

   - **g. Effect of diffusion of primary-originated hydrogen into secondary crevices**
   - **h. Environment definition, models**

5. Critical experiments in model boilers that should be undertaken

   - **a. Rate of development of deposits, solution chemistry.**
   - **b. Properties of deposits: superheat condition, concentration of species, geometry of deposits, pH, potential, deposits.**
   - **c. Chemical interactions: Reduction of sulfur**
   - **d. Effects of flow velocities; streaming potential.**
   - **e. Develop methods of detecting fouling in line contact crevices.**
   - **f. Bench marking models.**

6. Critical experiments in heat transfer lab experiments

   - **a. Facilities available and attributes throughout the world.**
   - **b. Present plans for respective facilities.**
   - **c. How integrate work?**

7. Other experiments

   - **a. Examine tubes**
   - **b. NDE detection of critical crevices.**

8. Compilation of data sources

   - **a. Cycle averaged chemistry**
   - **b. Prompt hide out return**
   - **c. Tube examinations: deposits, crack face, corrosion morphology.**
   - **d. Chemical cleaning**

Panel Discussion Outline

Allen Baum
Bettis Atomic Power Laboratory

- Issues Summary
- Ongoing and Future Work
  - Canada – Peter King
  - France – François Vaillant
  - Sweden – Per-Olaf Andersson
  - U.S. – Keith Fruzzetti
- Corrosion Prediction – Roger Staehle
- Recommended initiatives – Roger Staehle

Issues Summary

- Offensive
  - Tubing materials
  - TSP design
  - Tubesheet joint design
  - Improved chemistry control
  - Fewer lead-bearing components
- Defensive
  - Seabrook evaluation
  - Design concerns
  - Accelerated 600 & 690TT corrosion

TSP Design Issues

- Benefits
  - Lower temps and superhts
    - Lower concentration factor
    - Shorter transport span
    - Less HO & HOR
  - Slower fill for flat configs.

- Liabilities
  - > 2X entrance region
  - Smaller reservoir
  - θ transport
    - Longer cracks
    - Less TSP restraint
  - Flat config. crevices could have more lead

Ongoing/Future SG Research in Canada

Presented by Peter King

B&W Canada

- Long-term expectations for Alloy 690 TT
    - general oxidation testing in AVT
    - detailed passive film evaluations
        - Auger, XPS, SIMS, FESEM, ATEM??
        - other properties
    - evaluate cracking pre-cursors
        - stressed/unstressed
    - compare to 600 MA
        - may include 600 SR, 600 TT, 800
    - formulate expectations for crevice chemistries
        - nature of possible chemistry
        - likelihood of occurrence of various outcomes
    - oxidation testing in crevice environments
        - specific solute influences
        - complex environment
- SCC testing of pre-filmed alloys?

- time to critical crevice deposits
- how to interpret & use extensive field data & relate it to 690 TT expectations

Future SG Work in Sweden

Presented by P. Andersson

R2-repl-89:690 TT
R3-repl-95:690 TT
R4-origin-84:600 MA

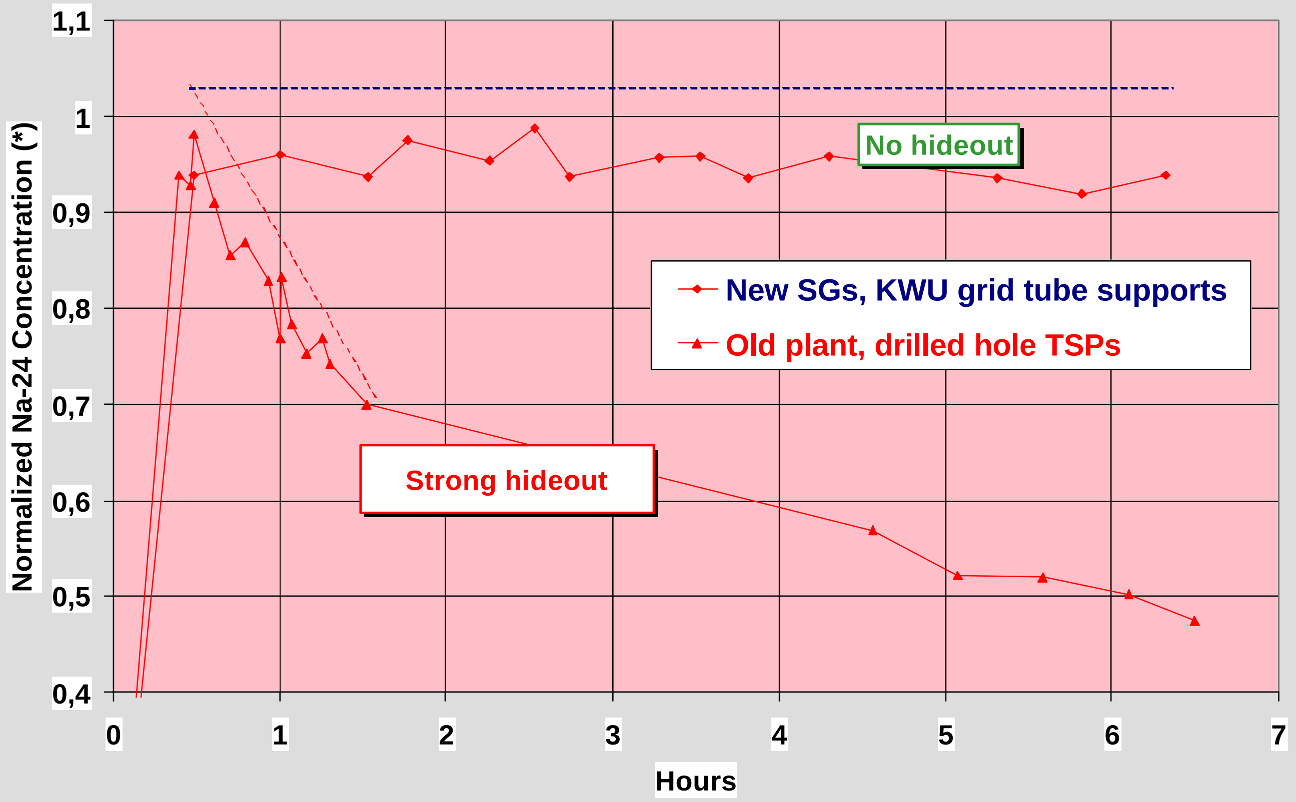
1. Transport into/in packed crevices
   - kinetics for HO and HOR
2. Examination of the used crevice
   - deposits physical properties
     chemical properties
3. Repeat earlier HO-tests with Na-24

   Compare with earlier data
   - Does concentrating occur?
   - changes?
4. CGR for 690 TT
   - primary coolant, started
   - secondary??

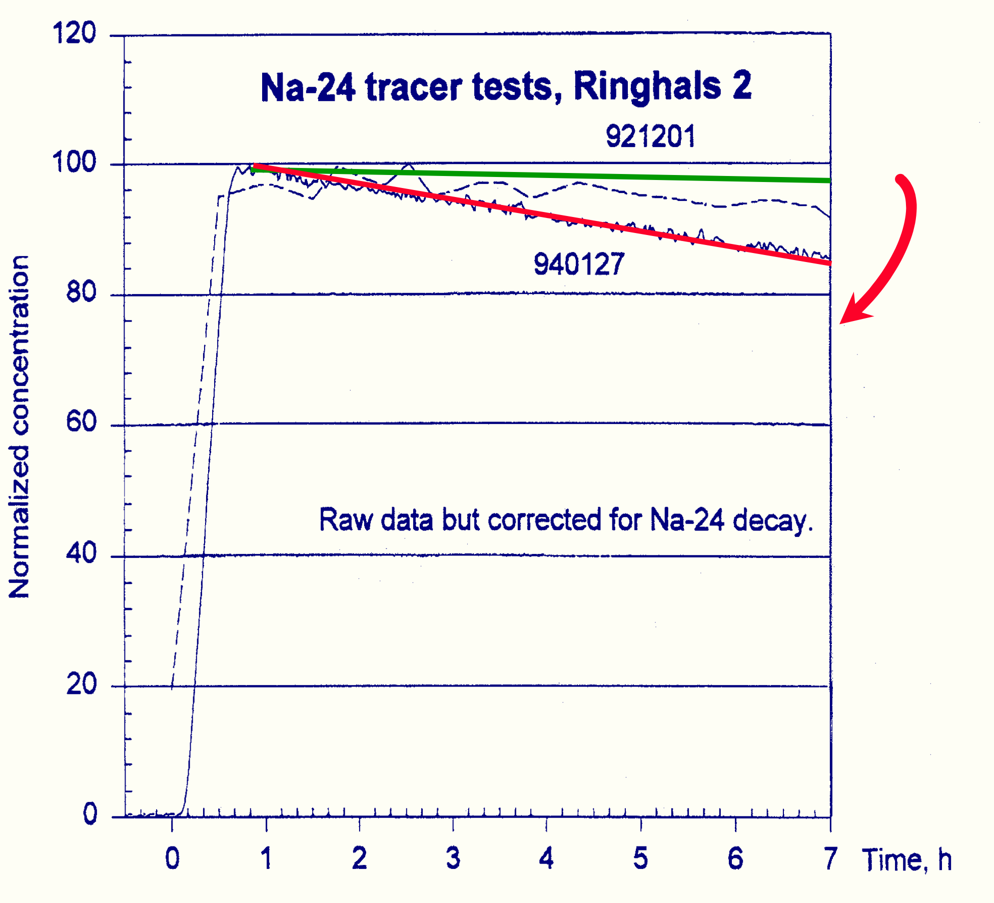
Hydrazine Ratio and Na-24 Hideout Studies

Suat Odar
Framatome-ANP GmbH

Does Corrosion Risk increase with Increasing Hide-Out?

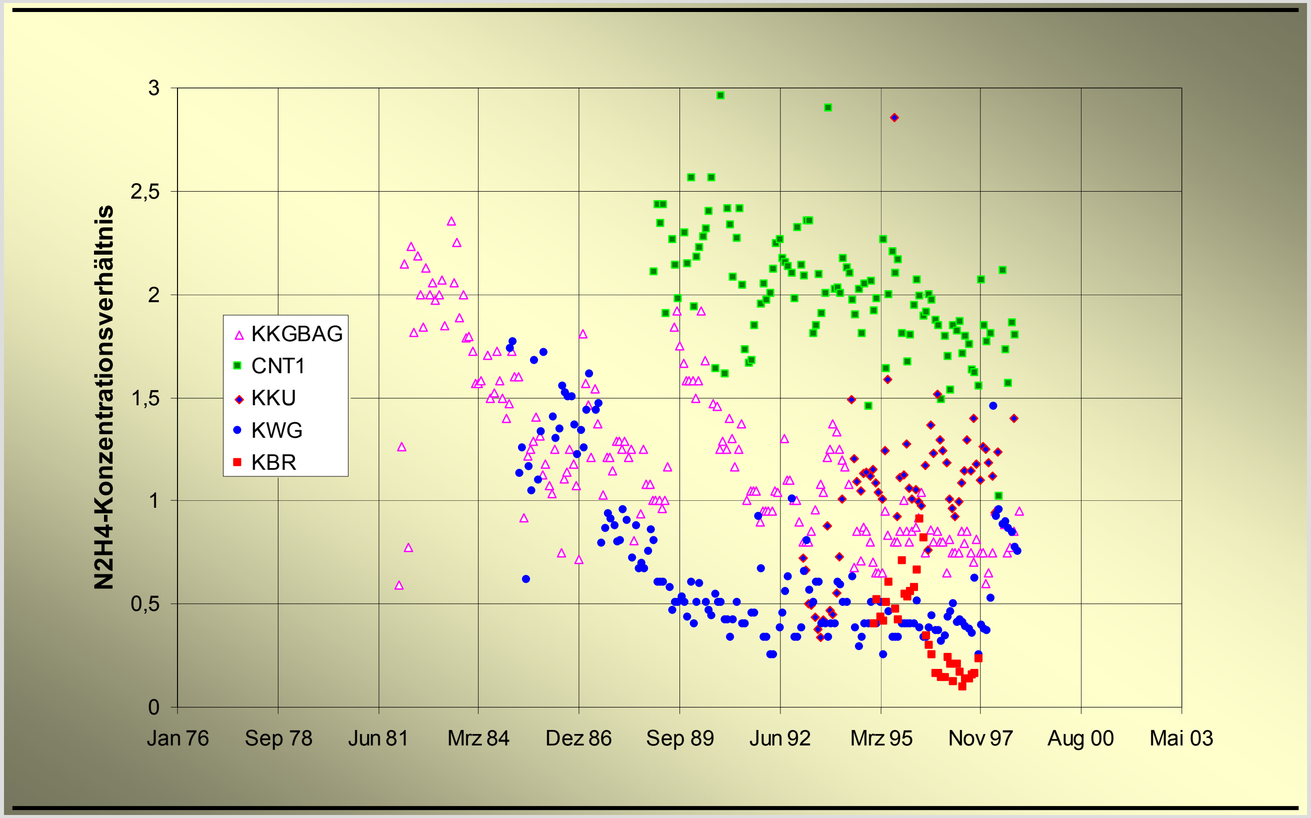


Hide-Out Increase with Operating Time



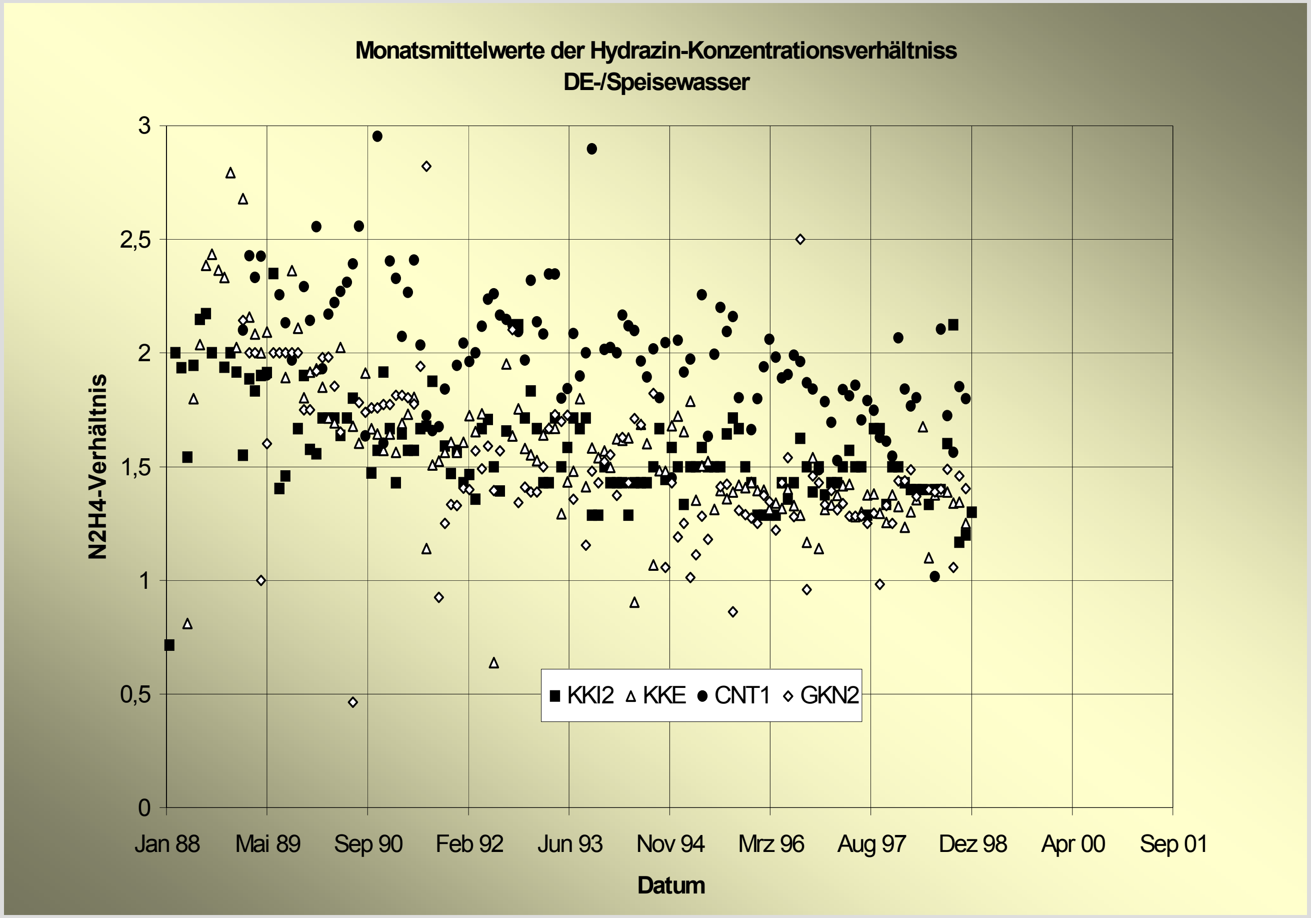
N_2H_4 Concentration Ratio SG / FW

FW Fe Concentration ~ 1-2 ppb

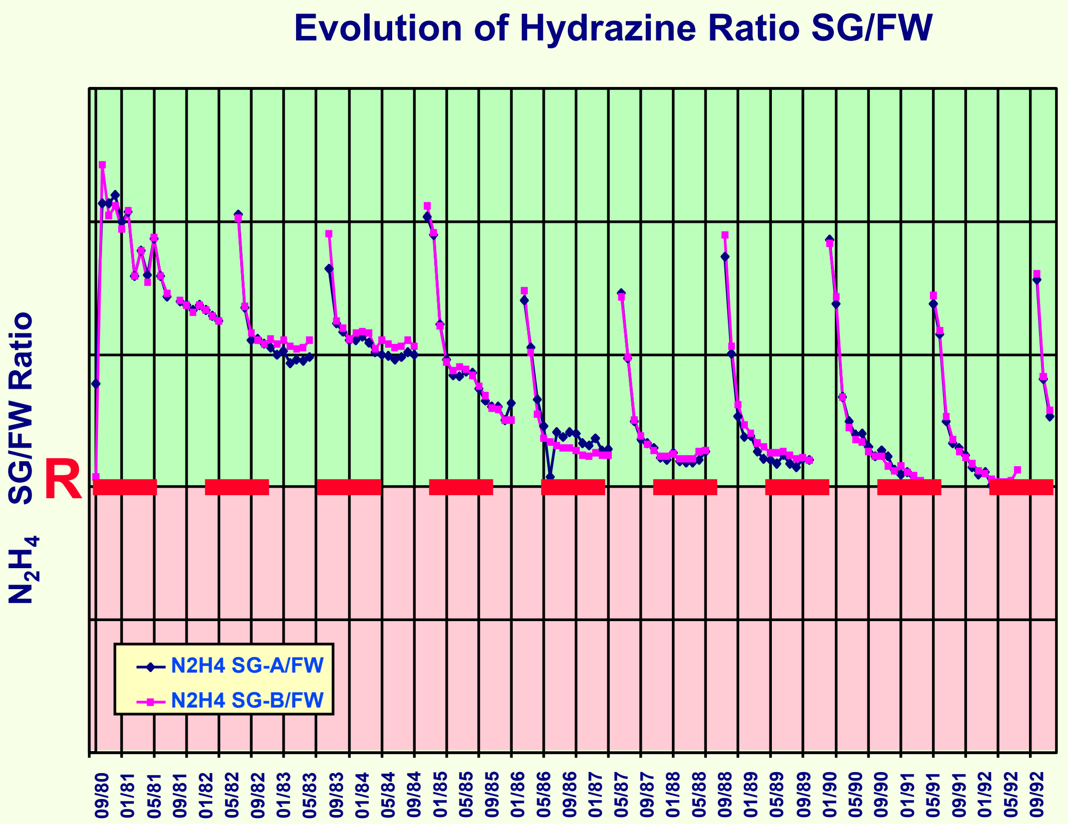


N_2H_4 Concentration Ratio SG / FW

FW Fe Concentration < 1ppb

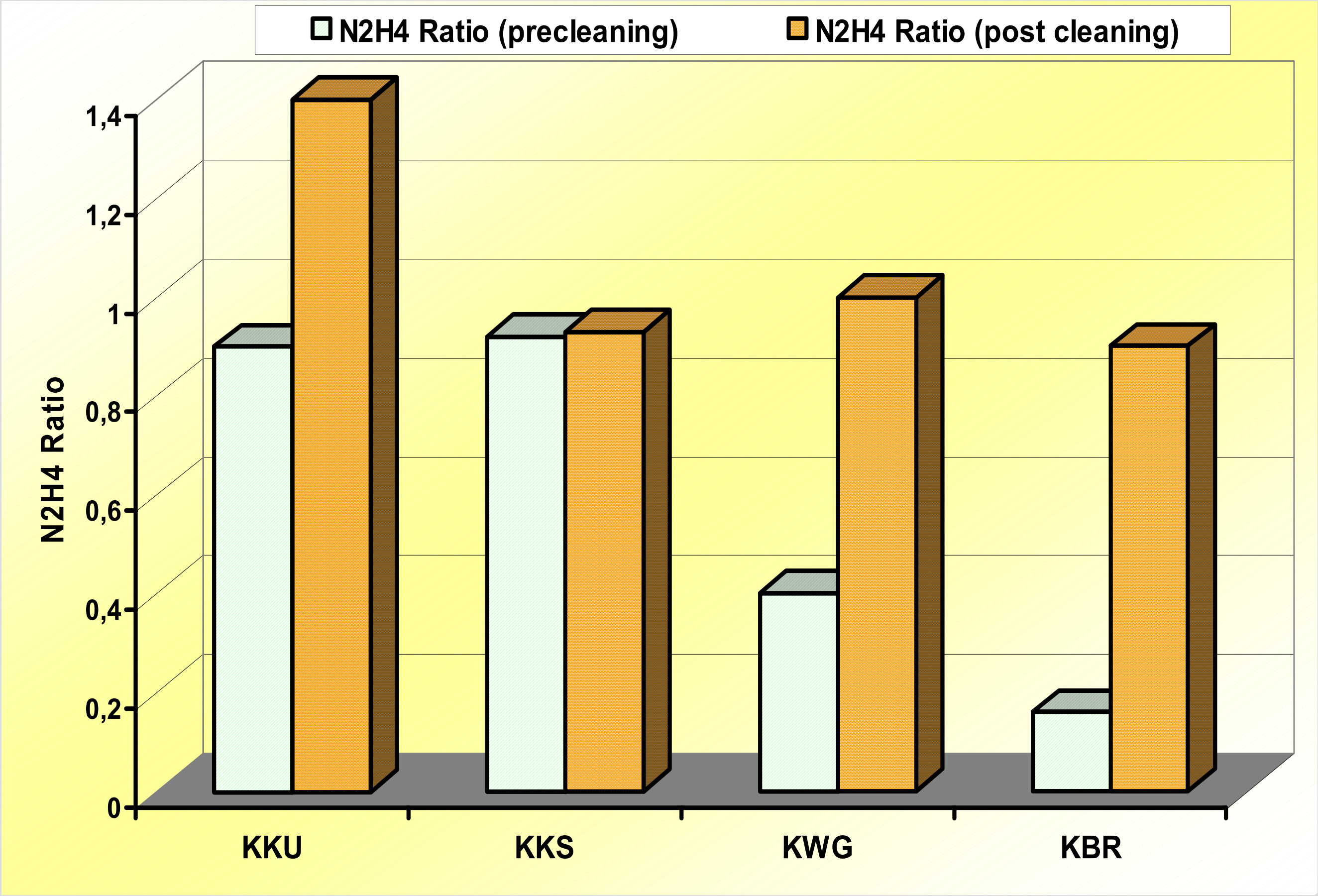


Hydrazine Ratio Time Evolution


Evolution of Hydrazine Ratio SG/FW

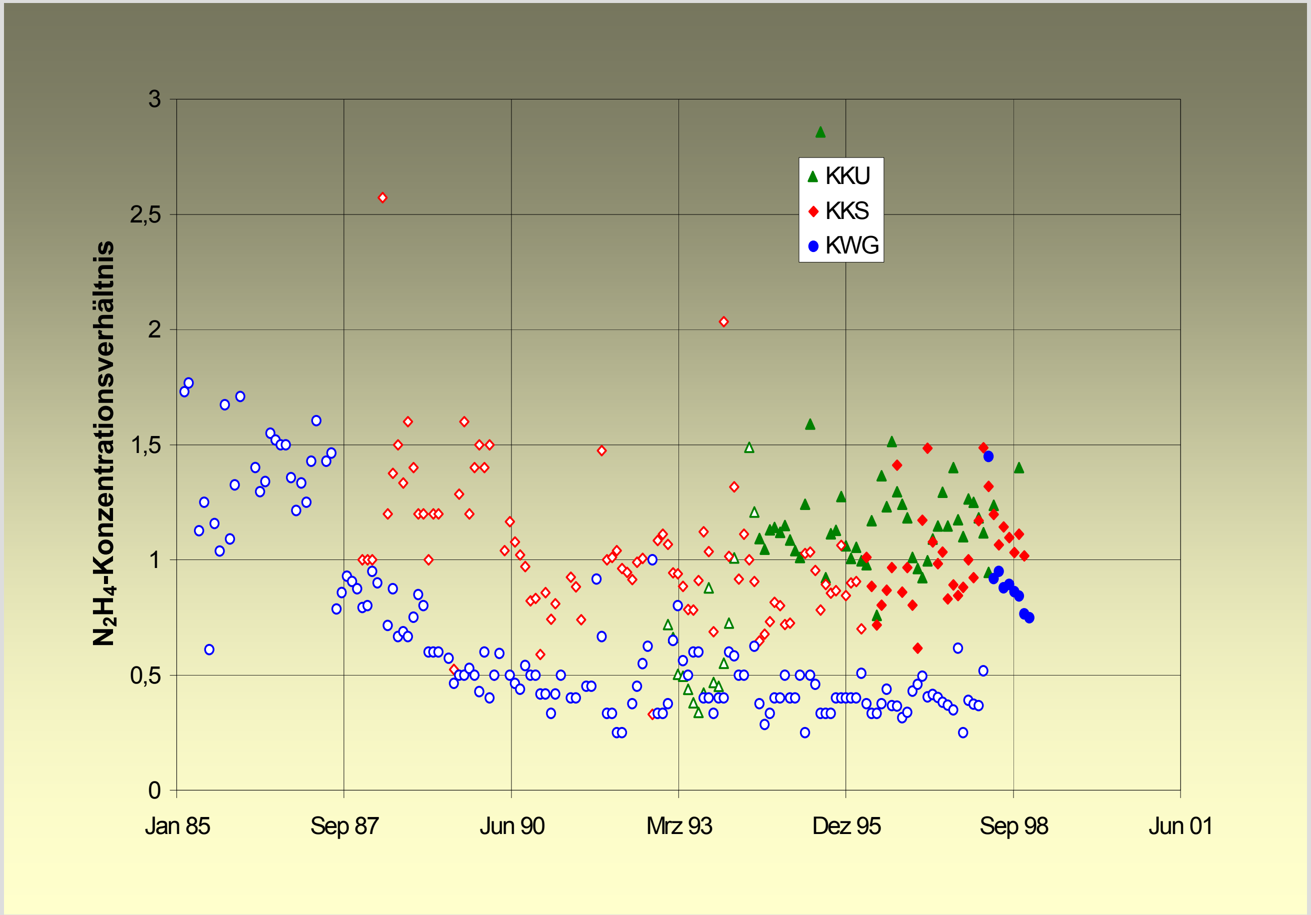
Application Results

Thermal Composition of Hydrazine



N_2H_4 Concentration Ratio SG / FW

SG Chemical cleaned PWRs



Ongoing/Future SG Research in France

Presented by F. Vaillant

HELP TO PLANT OPERATION

- [Hydrazine] requirements
  - compatible with risk of SCC by reduced sulfates

    corrosion tests in loop
  - compatible with risk of SCC in (hydrogenated)
  - to avoid FAC
- SCC with shutdowns/start-ups
  - initially tests on Ajax loop
  - simulation in NaOH (static autoclave)

LIFE PREDICTION + FREQUENCY OF NDE

- Based on corrosion model in laboratory:
  - sodium hydroxide
  - neutral to slightly alkaline sulfates
  - complex environments
    (SiO_2, Al_2O_3, organics, phosphates) in AVT

Proposed 2003 EPRI Programs addressing SG Fouling and Crevice Issues

Project Manager: Keith Fruzzetti

Heated Crevice Seminar
October 7-11, 2002
Argonne, IL

TAG 1

Heated Crevice Program

Rockwell (Jesse Lumsden)

- Current 2002 Program
  - Evaluating sulfate hideout and formation of reduced Sulfur species by hydrazine
    - Reduced S causes SCC in Alloy 600 and Alloy 690
- Proposed 2003 Program
  - Complex Chemistry
    - Precipitate formation (Raman)
    - Crevice extraction to determine soluble species
    - Hideout return evolution

Evaluation of Line Contact Crevices

iSagacity (Peter Millet)

- Evaluate the susceptibility to tube corrosion at line contact support locations
  - Performed detailed review of experimental and modeling programs (including EPRI projects S118, S119, S121, S180, S192, S133, S134)
  - Develop a qualitative fouling (deposition) model for line contact crevices
  - Rank the susceptibility of various designs to fouling based on experimental and modeling database
  - Determine if a fouling threshold can be obtained from the existing database

Multivariable Influence on SG Fouling and FAC

B&W Canada (Peter King)

Project Objective:

- Improve the fundamental knowledge of processes responsible for corrosion, corrosion release and transport, and deposition in the steam generator
  - Improve tools for multivariable analysis to enable preventative strategies against FAC and SG fouling
  - Improve current models for predicting the effect of the chemistry environment on FAC

TAG 4

Multivariable Influence on SG Fouling and FAC

Task 1: Collection and Evaluation of Plant Data and Experiences

- Dissolved and particulate Fe conc's
- pH, Hydrazine, Oxygen, ECP
- Fouling Data

Task 2: Literature Review on fouling and FAC

Task 3: Research into the fundamental role of soluble iron

- FAC & Electrochemistry under soluble iron transport conditions (MTI)
- The role of soluble iron in SG fouling (AECL)

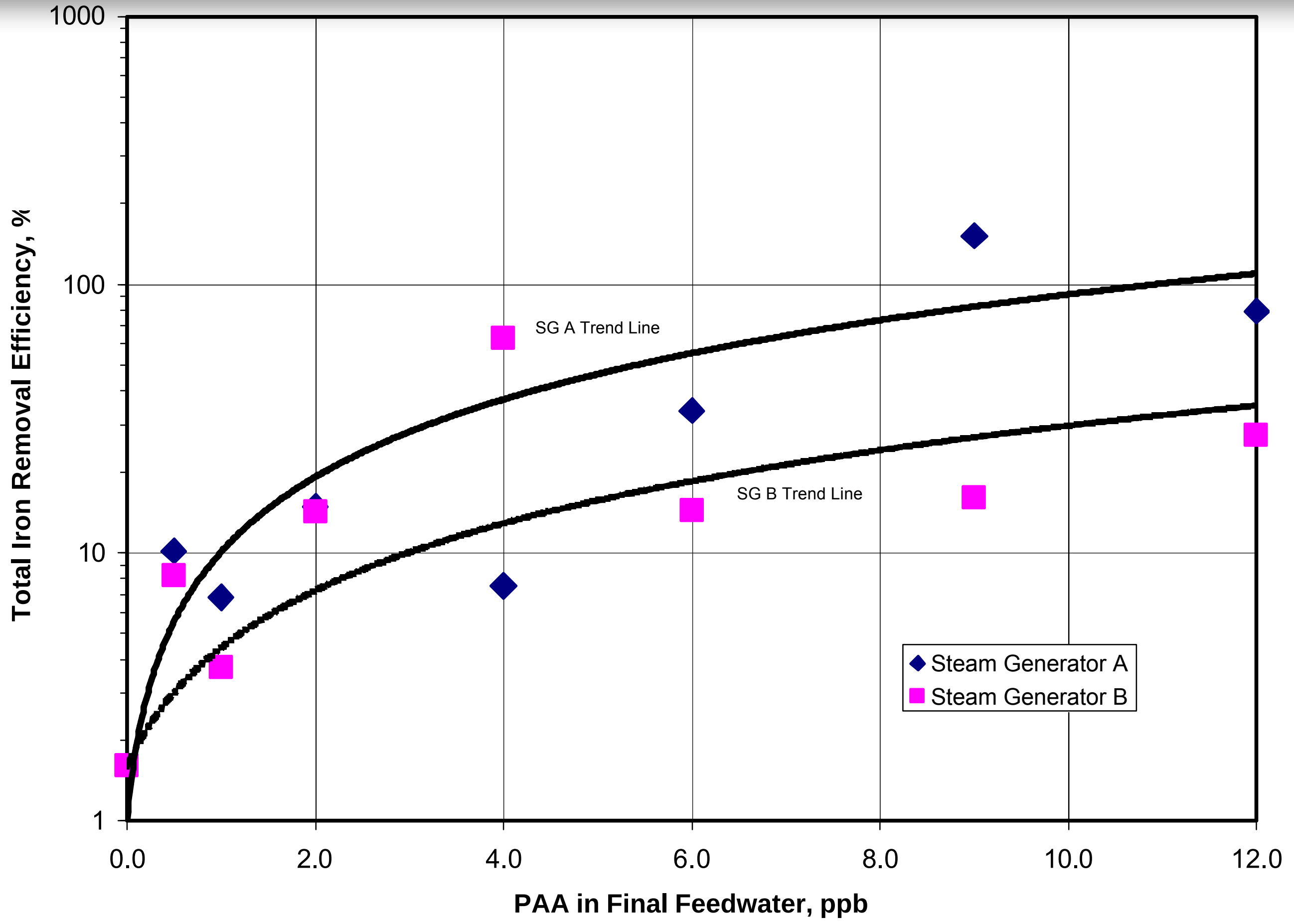
Task 4: Model development for prediction of ECP in the steam cycle

- Facilitate prediction of the operating margin for stability of the protective oxide

Dispersant Program to Mitigate SG Fouling

- Short-Term Trial Completed (ANO-2)
  - Qualification Report completed 3/29/01 (1001422)
  - Trial Report Completed 9/24/01 (1003144)

Short-Term Trial Results



TAG 7

Dispersant Program to Mitigate SG Fouling

Replacement 690 Steam Generators (W and BWC)

- Long-Term Trial Effort in Progress
  - Engineering Assessment for Replacement 690 Recirculating SGs (DEI)
    - Thermal/Hydraulic and thermal margin assessments
    - Separator performance assessments
  - Vendor Reviews in Progress
  - Potential Trial Site Expanded
    - Westinghouse and BWC
    - ANO-2 ready to inject with vendor concurrence

Dispersant Program to Mitigate SG Fouling

Complete Long-term Qualification Work

Vendor Review: Phase 1 (2002 Effort)

Concurrence by Vendors for a Long-term Trial in a Replacement 690 Recirculating SG

Perform Long-Term Trial (ANO-2)
and assess results

Vendor Review: Phase 2 (2003 Effort)

Concurrence by Vendors for Long-term use in fleet of domestic W/CE & BWC Recirculating SGs

TAG 9

2003 SG Secondary Side Management Conference

- 3 Day Meeting: February 10-12, 2003
  - Savannah, GA

- Four Main Topical Areas
  - Deposit Generation and Transport
  - Deposit Control and Mitigation
  - Deposit Consolidation and Removal
  - Short and Long Term Strategic Planning

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Notes from Panel Discussion Session (Friday October 11)
by D. R. Diercks

Roger Staehle began by stating that the principal objective of the panel discussion was to "bring things back into focus." He then handed out a proposed agenda for the discussions.

Alllen Baum then opened the first portion of the discussion with a short presentation.

Gorman began the discussion by inquiring about the nature of the cracking seen in the Alloy 600 TT tubes at Seabrook. McIlree replied that the cracks were short and separated by ligaments. He said that even if they were 99+% throughwall, they would not threaten the pressure integrity of the SGs.

McIlree then noted that if Alloy 600 or 690 TT tubes were properly processed at the mill, in principle there should be no residual stresses present to drive cracking. At Seabrook, however, they found that the tubes were re-straightened after the TT heat treatment, thereby introducing residual stresses. It seems likely that other TT tubing is out in the field with similar residual stresses. He wondered if we could develop NDE techniques to detect residual stresses in tubes in the field or to determine if the TSP lands were becoming active crevices.

Jim Davis (NRC) then commented that the Seabrook tubes appeared to have a MA metallurgical microstructure rather than a TT microstructure. McIlree observed that there is a great variation in TT microstructures, and some in fact resemble the MA microstructure. He stated that one cannot judge SCC resistance from the microstructure. The response of the microstructure to the heat treatment appeared to depend upon the C level. Gorman added that EDF experiments indicate that ≤ 0.033 wt. % C was needed to obtain the expected microstructural response to the TT heat treatment.

Davis noted that cracking had also been seen in Alloy 600 TT at a Korean plant, and Baum and Diercks (ANL) said that this was the Kori 2 plant. McIlree added that again the microstructure did not have the appearance normally associated with the TT heat treatment. McIlree said that we must assume that there are other "poor" TT microstructures in the field, and we must control residual stresses and environment in these plants to avoid cracking. He felt that most, but probably not all, of the plants with Alloy 600 TT tubes have low residual stresses.

Staehle observed that the highest stresses in SG tubes are typically at the top of the tube sheet. He suggested that perhaps our focus on chemistry at the line contact region of the tube sheets might therefore be somewhat misplaced. If we could somehow reduce the residual stresses from tube manufacture and SG fabrication, we might not have to worry so much about the operating environment. However, this does not seem likely. He agreed with McIlree that perhaps the use of NDE techniques to detect residual stresses in tubes in the field should be looked into further.

Duncan suggested that we should determine if there is a small population of high stress tubes in service that need to be followed more closely. Baum said that his earlier model boiler work focused on tube sheet joints, where the residual stresses were highest. Nevertheless, that one incident of ODSCC in Alloy 600 TT tubing was in a TSP crevice rather than a TS crevice.

Staehle then suggested that another important consideration is to figure out how to lengthen the time between inspections. He also noted that, in laboratory tests, both Alloy 600 TT and 690 TT can be cracked in environments not greatly different from those in service. He wondered why they are not cracking in service in significant numbers. Finally, he stated that we must be proactive in anticipating failures in Alloy 690 TT. We need to do the research now so that we are in a position to prevent failures in the field. As a part of this, we need to do research to enable us to conduct credible operational assessments.

Duncan stated that in addition to lengthening the time between inspections, we must make decisions about appropriate inspection intervals in the case where we have an existing crack. We therefore need crack growth rate data under the relevant conditions.

Muscara said that regulators must take the position that undetected cracks exist in the field, and these cracks must be properly dealt with. He also noted that should not totally shift our emphasis away from the TSP region, since conditions for mild denting exist there and even this mild denting can lead to cracking.

Gorman agreed that crack growth rate data are essential for doing a proper operational assessment. He also noted that the subject of mild denting at the top of the tube sheet was considered at a secondary side workshop in 1995. He expects to see more such denting in the future, leading to tube cracking.

Muscara noted that in terms of crack evolution and operational assessments, we must consider when to use ligament correlations for existing cracks and when to use a planar crack correlation.

Baum then offered one last comment on the Seabrook cracking, noting that while the greatest concern is on the mechanical aspects (i.e., residual stresses), there is also a chemical aspect to the problem. He noted that Seabrook had low silica (5-10 ppb) in the bulk water chemistry compared to other plants, and he wondered if this was significant.

Peter King then briefly reviewed ongoing SG research in Canada (Denise is typing up his handwritten overheads).

King noted that the precursors for cracking do not appear to form in Alloy 690 like they do in Alloy 600, at least not in reasonable times. He felt that the major questions to be answered were the time to critical crevice deposits and how to interpret and use the extensive available field data and relate it to our expectations for Alloy 690 TT.

Chambers then made several points. He first noted that residual stresses from manufacture are unavoidable. In addition, one would expect operating stresses in tubes from temperature cycling. He also suggested that *in situ* monitoring of autoclave and heated crevice test (e.g., Raman spectroscopy) could be very enlightening. Finally, he wondered how crevice chemistry might change under zero-power hot conditions.

King responded by first noting the work of Lumsden and others on monitoring crevice chemistry. With respect to the effect of zero-power hot conditions on crevice chemistry, he noted that people are working on this problem. He added that it is very difficult to get crack growth rate data under field conditions. He also agreed that we must assume that tubes, in general, have residual stresses from manufacture, and we must also assume that operations will produce aggressive environments somewhere in the SG. Therefore we must have the most crack resistant tube material possible, and this is why the industry is going with Alloy 690 TT at present. He stated that BWC is still interested in model boiler testing and crevice monitoring, but these tests are very expensive. He expressed the hope that future work at ANL can address these areas.

Per-Olaf Andersson then briefly reviewed ongoing SG research in Sweden. He noted that Sweden has only three PWRs, namely Ringhals 2, 3, and 4. Units 2 and 3 have replacement SGs, and there have been no problems with these. Unit 4 still has the original Westinghouse Model D-3 SG with Alloy 600 MA tubes from 1984, and this unit has experienced very little tube cracking.

Odar supplemented Andersson's presentation by showing results obtained from Na-24 hideout studies conducted in the Ringhals 3 plant simulator before SG replacement. Significant Na hideout was observed. The new KWU SG with grid tube supports showed virtually no hideout. Tests conducted three years later showed some hideout, indicating sludge buildup. The hydrazine concentration ratio in the SG feedwater for plants with higher Fe (1-2 ppb) decreased with time. For lower Fe (<1 ppb), the decrease was less rapid, thus suggesting increased sludge loading.

François Vaillant then summarized ongoing SG research in France. He reviewed work on life prediction and frequency of NDE inspections as well as on hydrazine requirements and SCC under plant shutdown and startup conditions.

Keith Fruzzetti reviewed EPRI-sponsored work on SGs.

Staehle then continued the discussion by noting that in order to predict cracking in a specific environment, we must have sufficient relevant data. However, almost no relevant data exist on cracking associated with reduced S species. With respect to silica effects, he cited a 1985 paper by Berman, who found a specific region in the silica-alumina system where cracking occurs in Alloy 690 MA. He felt that acid SCC had been pretty well characterized, as had alkaline SCC, though both remain issues. Cracking in complex environments has not been well defined, but relevant work is being conducted in France. Overall, he felt that there was much room for serious work to determine the dependencies for several of these submodes. He added that we cannot predict the behavior if we do not know the dependencies.

Gorman stated that, with respect to sulfate chemistry and complex environments, he has difficulty in understanding the process for attack since the species involved are not liquid at the superheats present in drilled hole crevices. He felt that further testing and/or modeling was needed.

Lindsay made an impromptu presentation on the subject of predicting the performance of line-contact crevice deposits, noting that, on the molecular scale, the tube surfaces and the TSP lands look flat. We must consider things on this scale. When things are considered on this scale, it is clear that chemical reactions in solution within the various types of crevices are not different from each other or from reactions that can take place in bulk water. The differences among crevice types are most likely due to their differing susceptibility to fouling. Lindsay added that he was not aware of any significant engineering science relating to crevice fouling under boiling heat transfer conditions. Good engineering science research is needed in this area. Staehle concluded that the important question is what remains to be done in this area and what resources are available to do it.

On the subject of critical experiments in model boilers, Staehle noted that there are only one or two model boilers available at present. How do we best use them and what alternative experimental techniques do we have? Duncan agreed that model boiler tests are needed, since codes and modeling cannot answer all of the questions that must be addressed. He said that model boiler experiments should emphasize multiple variable validation experiments. He felt that a different model boiler design from that being developed at ANL was needed to understand the fouling process at the crevices. Muscara noted that the ANL model boiler was not designed for such studies, but rather to study the evolution of crevice chemistry and how it leads to crack initiation.

Baum added that MULTEQ is a useful tool. But model boiler experiments were nonetheless needed to determine crevice chemistries with confidence. Duncan contended that model boiler results cannot reliably predict absolute cracking rates—they can only provide relative rates.

Staehle then stated that he felt that items 6-8 on the panel discussion agenda had already been thoroughly considered in the previous sessions, and, in view of the short time, they would not be further discussed here.

Muscara observed that, with respect to the data base, a tremendous amount of work was still needed. He suggested that perhaps an international group should be constituted to coordinate this work, and he suggested that perhaps the NRC and EPRI could pull this together.

Staehle suggested that discussions be ended on that note, and he thanked all of the participants.

Questions/Answers and Comments

October 8 (Tuesday) Topic: Corrosion in Crevice Geometries

An Overview of Recent French Studies of Possible Secondary Side Crevice Environments Causing IGA/IGSCC of Mill Annealed Alloy 600 SG Tubes by P. M. Scott and F. Vaillant [Keynote Talk]

Question to Francois Vaillant/Peter Scott by Jeff Gorman

1 Re the plant with TGSCC in the TTS area, did it also experience significant SCC in TPSs? If not, why not? (Why did lead only affect TTS area, if this is the case?)

2. In France, were some TT 600 tubes restraightened after TT? If so, were they re-TT'd?

3. What are the pH and potential dependence of CGR & crack initiation in complex environments?

4. Has anyone done tests in doped superheated steam at 320°C (with various levels of hydrogen)? ANS – last slides – tests in process – C-rings – 600 MA will crack.

5. Could the gap size – BPE effect allow more complex solutions to stay liquids (?), e.g., wall based solutions?

Response to Jeff Gorman by Francois Vaillant

1. TGSCC was found in one plant, with lead near the crack. I am not sure that investigations (of cracks and deposits) were performed in other parts of the tubes … and on other tubes.

2. I am not aware of restraightening of heat-treated tubes in Alloy 600.

3. Most of the results (at least in EDF) in complex environments were within the range 5 to 6.5. the influence of pH was not investigated, but the ratios of the different species or the addition of same species (carbonates) which could modify the pH are the matter of the ongoing program in EDF. The influence of the potential is still to be clarified.

4. The influence of hydrogen in superheated polluted steam could be investigated in future programs, and not yet scheduled.

5. I don't know at now, but yes in the principle.

Question to Peter Scott by Peter King

1. You talk about both brittle, non-protective chromium hydroxide gel. Could you please comment further on the use of these two terms: are they referring to the same thing but at different physical points (i.e., dry at ambient temp. vs. at operating temp in aqueous system) or are they different?

2. In your presentation the occurrence of IGA/IGSCC in complex environments is related to the breakdown of the passive film by formation of alumino-silicates, etc. In these conditions, you have said that 600 TT is more resistant and that 690 TT is immune.

    a. Why would the passive film on 600 TT be better than that on 600 MA?

    b. Is 690 TT truly immune or is testing too short? Have passive films on 690 TT been shown to resist becoming non-protective?

3. Arguments for dryout apply to deposit blocked TSP locations. How do they apply to deposits on free tube surfaces?

Response to Peter King by Peter Scott

1. The two terms are used interchangeably to describe the same thing. The implication of the word “gel” is that molecules of water are incorporated into the molecular structure. No effect of temperature between the two terminologies is implied.
2. Our interpretation of the comparative behavior of alloy 600 MA and TT is primarily an effect of grain boundary structure on propagation rates. Obviously no intrinsic difference in passive film behavior between the two having the same composition is expected. However, alloy 690 with its higher chromium content appears to resist formation of the non-protective chromium hydroxide “gel”. Whether long term exposure could change that situation is an open question, although I doubt it in these environments. The presence of minor amounts of lead (Pb) could be expected to degrade completely the protective qualities of the passive film so there may be the possibility of synergism between Pb and the alumina-silicates.
3. We have not observed such dense deposits on the free span; they are only seen in the crevices and then primarily at the entrance and exit to the crevice.

Question to Francois Vaillant by Peter King

1. You reported circumferential cracking <u>under</u> the top surface of the TS. Normally, this would be taken to mean the expansion-transition region. Could you please comment further on your use of the term "under the top surface of TS?"

2. Please comment further on the observation that cracking seems to be more predominant in low yield stress material (your graph of degradation vs YS) and the relation of this to threshold stress (EDF caustic model). I would interpret this to mean that some amount of plastic strain is necessary for cracking to proceed.

Response to Peter King by Francois Vaillant

1. The observed circumferential cracks were located in the crevice at the roll-transition, the low contact between tubes and the tube sheet being under the surface of the tube sheet.

2. The relationship between the high susceptibility of tubes with low YS (field experience) and the low value of the threshold stress in laboratory, could result from the fact that most of the tubes at the TSP level may have similar stress levels (residual stresses and operating stresses). At a given stress level, the difference between the stress and the threshold stress is the highest on the tubes with low YS, inducing severe degradation. Some plastic deformation is likely, even if the threshold stress is slightly lower than YS (σ_s = 0.55 YS + 82 for the average line).

Approach to Predicting Corrosion of SG Tubes Based on Quantifying Submodes of SCC in a Statistical Frame Work by Roger W. Staehle [Keynote Talk]

Question to Roger Staehle by Peter King

I continue to have difficulty with the idea that there is a fundamental basis for the value of β. β is an empirical fit parameter for the failure process, not the direct consequence of fundamental processes. In this context, I think that a search for a functional relationship for β is problematic.

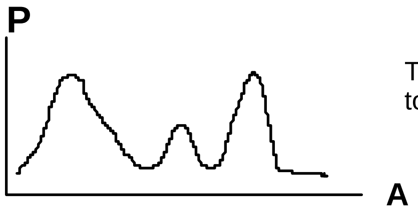
I do not argue that a Weibull distribution is an appropriate representation of a real world failure distribution. However, I believe that the value of β is the consequence of stochastic variability of the input factors, rather than being a consequence of the absolute value of the input factors. In other words, β is a function of the uncertainty in the input data, not the inputs themselves. This would be true for both laboratory experiment and field data.

I would suggest that a better approach to obtaining a final β would be to apply Monte Carlo techniques to a deterministic model of cracking. Stochastic variability (probably not a Weibull distribution) in the various input parameters will yield a distributed outcome. I suspect that said outcome would be well fitted by a Weibull distribution.

For instance:

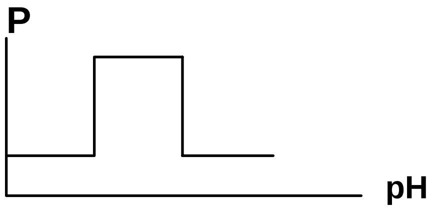
$$x = \left[H^{+}\right]^{n}[\gamma]^{p}\sigma^{m}e^{\left(\frac{E-E_{0}}{b}\right)}e^{\left(\frac{Q}{RT}\right)}t^{q}\ .$$

is deterministic. However, if each of the parameters are represented by probability functions (i.e., allow for parameter uncertainty), then the outcome x is a distributed function,

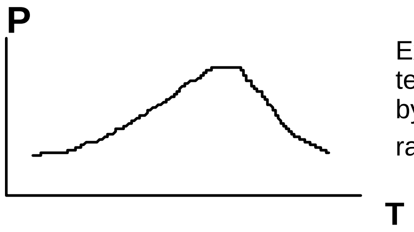


Alloy effect
based on variable
behavior of large
number of heats
in a SG

Tendency for material
to show different cracking rate



pH



T

Expected surface
temperature limited
by T_{prime} but could
range down to T_{sec}

Response to Peter King by Roger Staehle

The shape parameter is fundamental to the physical processes. Surface controlled processes give characteristically $\beta \approx 1.0$. Propagation controlled processes give $1.6 < \beta < 10$ depending on the system. There has never been an effort to explain β except for this first order difference. Rather than β representing an arbitrary stochastic representation, it is rather the result of the mechanistic process. Aside from mechanistic interpretation β is affected by the aggregation or data as explained in my TMS paper.

Question to Roger Staehle by Jiaxin Chen

It is very good to start to study the corrosion problem through a fundamental approach such as the one started by Prof. Staehle.

My questions basically concern:

1. Probability theory as used by Prof. Staehle is feasible if those “submodes” probability functions can be considered as independent from each other. The independency should mean that each involved probability function could stand alone without being necessarily connected to some parameters that are used simultaneously for other “submodes.” This is the start-up point when one could write the “total probability” function.

2. Probability theory is generally more useful when the 'event" involves physical processes. When chemical processes are involved, it has problem. The problem is caused by the fact that, in such a case, it is not the quantity" it changes, but probably the "nature" it changes. In other words, the total probability function may not be a continuous function (mathematically) of the "submodes" probability functions which are likely non-continuous function, too.

Therefore, interpretation of the "total probability" function may be difficult. But, the above-mentioned problems should not hinder further refinement of the thinking which may lead us to a better understanding of the mechanisms.

I look forward to reading more about Prof. Staehle progress in this exciting field as he is exploring now.

Response by Roger Staehle

I appreciate your comments.

October 8 (Tuesday) Topic: Experimental Methods

Heated Crevice - Design, Experimental Methods, and Data Interpretation by Jesse B. Lumsden and Keith Fruzzetti [Keynote Talk]

Question to Jesse Lumsden by Francois Vaillant

Are SCC experiments scheduled (as model boilers?) to verify the hypothesis that oxidizing period during layup and start-ups could be relevant to explain IGAICC in plants?

Response to Jesse Lumsden by Francois Vaillant

Yes, electrochemical noise will be monitored while the tube is pressurized. The noise will detect the initiation and propagation of SCC.

Experimental Simulation of Crevice Chemistry Evolution by C. B. Bahn, S. H. Oh, and I.S. Hwang

Question to Chi Bum Bahn by Peter King

Your graphs of axial temperature profiles show temperatures on the secondary side well below saturation temperature. Can you comment on these measurements and on the inlet temperature to the crevice vessel?

Response by Chi Bum Bahn

> The secondary water was charged by a diaphragm pump and ejected through a back pressure regulator. Flow rate of the secondary system was maintained at 4 L/hr. The secondary pressure was adjusted automatically by a PID-controlled back pressure regulator at 5.50 ± 0.04 MPa with a saturation temperature of 270°C. The inlet temperature of the crevice vessel was not controlled. Therefore, it was affected by the primary water temperature. To maintain the constant secondary temperature, a preheater can be installed before the inlet line.

Question to Chi Bum Bahn by Zhongquan Zhou

> Compared with internal reference electrode, what's the advantage to choose external reference electrode for monitoring ECP?

Response to Zhougquan Zhou by Chi Bum Bahn

> As I know, internal-type Ag/AgCl (water) electrodes have worked very well at high temperature/high pressure aqueous environments. But the AgCl solubility at about 300°C is around 10^{-3} mol/kg and that at room temperature is around 10^{-5} mol/kg. The concentration gradient in the case of internal-type electrode is higher than that of the external-type electrode. For both internal and external-type Ag/AgCl (water), high purity water was used as the filling solution in which Cl^- ion activity can be established and maintained at the solubility of AgCl even with the sustained leakage for a long period. But, although I did not compare two electrodes in the same environment, the life of internal-type Ag/AgCl (water) will be shorter than that of external-type Ag/AgCl (water) because of higher diffusion rate.

Question to Chi Bum Bahn by Jiaxin Chen

> I wonder the type and distance of the thermocouples to the tube (primary).

Response to Jiaxin Chen by Chi Bum Bahn

> They are k-type and distance is 0.5 mm
>
> .

Experience of Heated Crevice Experiments at Studsvik by H-P Hermansson, A. Molander and P-O. Andersson

Question to Jesse Lumsden, Chi Bum Bahn, Anders Molander, and Hans-Peter Hermansson by Jeff Gorman

I. What do we really want to be able to measure in heated crevice tests to help predict corrosion? Are they:

   1. pH?
   2. potential relative to Ni/NiO stability point?
   3. when become liquid filled?
   4. All of the above as a function of bulk water chemistry?

I. What are the plans for test design improvements directed at obtaining answers to the above questions?

Response to Jeff Gorman by Chi Bum Bahn

I. As you know, the real crevice environments are very complicated. Therefore, various factors should be considered simultaneously. But I'd like to emphasize the surface film formed on the heated crevice tubes. The oxide and deposit characteristics and the interaction between oxide and surface deposit as a function of time and water chemistry can be studied.

II. I do not have any specific plan to the heated crevice testing. Briefly speaking, microstructural analysis for corroded tubes in a model boiler by using SEM, AES, TEM, etc. will be helpful to get answers to heated crevice environments.

General comment by Jiaxin Chen

> We have discussed a lot about the impact of crevice chemistry on the precipitation inside crevice. We should also remember that corrosion process inside crevice region actually produces corrosion products inside the crevice. This produced corrosion products fill up the space inside the crevice and will continue to fill the dense crevice so that the density of crevice packing will increase with time. It increases the stress on the oxide layer constantly.

High Temperature Ph Probes for Crevice/ Crack Tip Solution Chemistry Applications- A Preliminary Study by R. Srinivasan and Y. Takeda and T. Shoji

[Not attending paper included in proceedings]

October 9 (Wednesday)   Topic: Results from Experimental Studies

Limits to Crevice Concentration Processes by Allen Baum [Keynote Talk]

Question to Allen Baum by Peter King

1. Please comment further on your distinction that sulfates adsorb but phosphates precipitate.

2. Can you comment on the degree of surface coverage of sulfate that might have occurred in your tests.

Response to Peter King by Allen Baum

1. We tested ammonium sulfate and sodium phosphate. This was infrared in the statement, but was not explicit. Had we tested ammonium phosphate and sodium sulfate, we would likely have reported different results.

3. No. Because of the large radial gradients in the concentrations, it would be difficult to assign the appropriate surface area.

Question to Allen Baum by Jeff Sarver

By what mechanism do you feel that sodium increases the transport of Pb into the crevice?

Response to Jeff Sarver by Allen Baum

Because of its low solubility, lead would either precipitate at the tube surface while the crevice is filling with corrosion products (after which it would be in a superheated steam environment or it would precipitate at the edge of the novice. Sodium increases the transport of lead to the crevice interior in three ways.

1. Soluble lead in the bulk water may concentrate together with sodium in the crevice, with the lead remaining soluble in the concentrated caustic solution where it would then migrate to the crevice interior.

2. Caustic may dissolve lead that has precipitated near the crevice periphery and carry it to the interior of the crevice.

3. Likewise, caustic may dissolve lead that had originally precipitated at the tube surface and carry it further into the interior.

Question to Allen Baum by Jiaxin Chen

> Comment on slide Nr. 31 where interpretation of “activation energy.” I think one should not attribute the activation energy to any particular corrosion process. This is actually an “apparent activation energy” which shows the temperature dependence of the measured parameter as the data are obtained.

Response by Allen Baum

> I agree. I did not mean to suggest that any corrosion process would produce such a high activation energy, but rather some mechanism unrelated to a conventional corrosion process must be responsible for the very strong observed temperature variation. The Crevice chemistry Test results suggest that the progressive volatilization of anions with increasing temperature and superheat causes the environment to be more aggressive at the hottest crevice locations.

My Conclusions after 25 Years of Model Boiler Testing by Jacques Daret (CEA)
[presented by A. Baum]

Inferences Regarding PWR SG Crevices from Plant Operating Experience by Jeffrey A. Gorman
[Keynote Talk]

Inferences Regarding PWR SG Crevices from Model Boiler Results by Jeffrey A. Gorman
[Keynote Talk]

Question to Jeffrey Gorman by Steve Chamber

> In Jeff's first presentation (plant operating experience), Jeff mentioned some Case 5 (Japanese) plants started up on PO4. Question: Did use of PO4 lead to any benefit or detriment in re IGA/SCC at TS or TSPs, either while on PO4 or after switch to AVT?

Response to Steve Chamber by Jeffrey Gorman

> There were no reports of IGA/SCC being experienced at Japanese units while on PO4, although wastage did occur at Mihama 1. With regard to post PO4 experience, the units that had prior operation on PO4 (Mihama 1 and 2 and Takahama 1) seem to have experienced IGA/SCC at a somewhat less severe rate than most of those that started up on AVT immediately after those units (Takahama 2, Genkai 1 and Ohi 1). However, the situation is made less clear by the fact that other non PO4 units (e.g., Ohi 2, Mihama 3, Ikata 1 and 2, Genkai 2) also experienced IGA/SCC at low rates or avoided it altogether. The Japanese concluded that the prior phosphate experience

was not a major factor (see the paper by Kishida, et al., "The Causes and Remedial Measures of Steam Generator Tube Intergranular Attack in Japanese PWR," Proceedings of the Third International Symposium on Environmental Degradation of Materials in Nuclear Power Systems - Water Reactors, p465-471, TMS, 1988).

Laboratory Experiments on Steam Generator Crevice Chemistry by P. V. Balakrishnan and G. L. Strati

Question to Gina Strati by Francois Valliant

What is the % de sulfate which could be adsorbed by magnetite, and an alloy 600 or S steel?

Response to Francois Vaillant by Gina Strati

In the one test we reported on, 30% of the sulfate that passed through the magnetite-packed bed adsorbed on the bed. At saturation, the surface concentration amounted to 12 $\mu g/m^2$ (based on a surface area of 1.2 $\mu g/m^2$ and the assumption that the surface of all the particles was available).

From our experiments, we cannot say how much adsorption there will be on Alloy 600 a stainless steel. (There will be no adsorption beyond the point of saturation of the magnetite surface.)

The Hideout and Return in a Sludged Ringhals TSP Crevice by P-O. Andersson, A. Molander, J. Chen, and P. Gillen

Question to P-O. Andersson by Feron Damien

These results have to be compared to the results obtained by Brumel & Campan on Clairnette loop. They also studied the hideout of ^{24}Na on 2 plant crevices. With one of these two crevices, they found the same results as those presented; sodium was accumulating in the crevice under boiling . But with the other crevice, no accumulation was found. These results have been published as in EPRI report (and presented in some conferences).

Response by P-O. Andersson

The presented data is not from a systematic study. It is a study of a given condition, crevices from the retired R3 SGs, in order to verify if sodium will accumulate or not.

Comments for general discussion by Jiaxin Chen

About Pb in crevice:

Pb presence at the metal/oxide interface, if so, could it be the similar phenomenon as Pt marked in corrosion study in general, when the inward/outward diffusion processes are to verify? In other words, Pb presence from the beginning and with corrosion outward diffusion of metal atoms makes the Pb stay at the metal/oxide interface.

As Pb has higher concentration at the metal/oxide interface, there is indeed no reason why they could not diffuse, via grain boundaries, to the crack tips as observed.

Experimental Study of Concentrated Solutions Containing Sodium and Chloride Pollutants in SG Flow Restricted Areas by D. You, S. Lefevre, D. Feron and F. Vaillant

Question to Damien Feron by Jeff Gorman

Please explain in more detail what you mean by saying that hideout return is not the opposite of hideout. Do you mean that the timing of the return is different?

Response by Damien Feron

It means that, if you have some precipitates which have been formed during the hideout

- the timing of return will be different if these precipitates are soluble
- the quantities and nature of chemicals which will return, will be different if these precipitates are insoluble under hideout return conditions

These differences between hideout and hideout return data have been illustrated by the trisodium phosphate study presented at the last Studsvik seminar on crevice chemistry in 1998.

Some Effects of Steam Generator Deposits on Crevice Chemistry by Chuck Marks

Evaluation of the Effect of Startup Oxidants on a Crevice Filled with Deposits by Jesse B. Lumsden and Al McIlree

October 10 (Thursday) Topic: Modeling

Mechanisms for Concentrating Impurities at Line Contact Tube Support Crevices in PWR SG's by Peter Millett and Dennis Hussey [Keynote Talk]

Predicting Crevice Chemistry in PWRs based on Hideout Return Chemistry by Steve Sawochka [Keynote Talk]

Question to Steve Sawochka by Jim Davis

Is it possible that species observed in the vicinity of the crack tip could come from the alloy rather than the solution? Roger Staehle and I did work on SCC on high purity alloys and did not observe species in the vicinity of the crack tip. With commercial alloys with the same nominal composition species were observed in the vicinity of the crack tip.

Response by to Steve Sawochka

Certainly, some elements that are present in the base material could concentrate along the crack face during the corrosion process. However, this effect should not be of importance relative to species believed to control solution chemistry in the crevice, e.g., sodium, chloride, potassium, sulfate, etc.

Question to Steve Sawochka by Tina Gaudreau

Have observations of hideout return from plants that have added chloride indicated that those efforts have been successful in modifying the crevice chemistry?

Response by Steve Sawochka

Detailed studies performed at several plants have demonstrated that crevice chemistry can be controlled by chloride injection, i.e., molar ratio control.

Status of EPRI Software Tools for Evaluating Crevice Chemistry by Tina Gaudreau

Question to Tina Gaudreau by Peter King

Could you please expand on the similarities and differences of MULTEQ and CREVSIM. I understand that CREVSIM is built on MULTEQ but it is not clear which tool would apply to what circumstances. For example, if I run a laboratory test with flowing water in which hideout is occurring (and hideout rates may be different) and I want to estimate crevice chemistry, would MULTEQ or CREVSIM be the better tool, and what factors determine the choice?
I think that this issue is relevant to the consideration of integrating chemical and CFD models, for instance.

Response by Tina Gaudreau

In this example MULTEQ is a better choice. While CREVSIM will model the hideout, the user must enter an approximate ‘hideout fraction’ so the result is an estimate.
In MULTEQ, the amount of impurity left behind with each step in the concentration model is determined based on the physical properties of each species. So nonvolatile species will accumulate to a higher concentration factor than volatile species as the solution is boiled.

Question to Tina Gaudreau by Zhongquan Zhou

1. What database does MULTEQ use? The thermodynamic data in the database is dependent on the low temperature data. For the high temperature calculation, the data are extrapolated from the low temperature. Are the results reliable? How would one check it and improve it?

2. Compared with other commercial available software, what's the advantage of MULTEQ?

Response by Tina Gaudreau

1. The MULTEQ code used a database of thermodynamic information for each species. The database is controlled by a committee of experts who approve each change or addition to the database. In as many areas as possible, the database entries are based on high temperature testing. Continual updates allow for inclusion of new test results as they are available.

2. The database described above is the advantage of MULTEQ.

Modeling and Analyses Supporting Argonne Model Boiler Design by Kenneth E. Kasza and et. al.

Multidimensional CFD and Thermal Modeling of the SG Tube and Support Plate Crevice Region by Stephen Bajorek and Donald Helton

Application of Chemical Equilibrium Model to the Evaluation of Magnetite-Packed Crevice Chemistry by C. B. Bahn, I. H. Rhee, and I. S. Hwang

Comments to Chi Bum Bahn by Jiaxin Chen

General comment on the use of thermodynamics in crevice chemistry:
Crevice environment is an open system where not only mass transport in and out occurs but also heat transfer in and out proceeds constantly. In Bahn's treatment, you have even included some solid phases whose interaction with liquid environment is also a slow process (kinetically controlled). In such a system (crevice area) none of the thermodynamics pre-requests are satisfied, there is a great risk that any calculation and its implication may mislead us.

Response to Jiaxin Chen by Chi Bum Bahn

As you commented, the crevice environment can be far from thermodynamic equilibrium. To consider kinetically controlled process, the reaction rate constant for each reaction should be introduced. This is very difficult work.
I think, at high temperature, the thermodynamic equilibrium assumption is a first approach we can do.

Question to Chi Bum Bahn by Zhongquan Zhou

Have you performed any experimental tests to verify the calculation used in your model? Without experimental confirmation of the thermodynamic equilibrium phases, it is not very ensuring by just inputting data and getting outputs from software calculations.

Response to Zhongquan Zhou by Chi Bum Bahn

I did not conduct any experimental test to verify the calculation. At first, I tried to use MULTEQ®. But MULTEQ could not manage some soluble iron species such as FeO_2^-. This is the reason why I did not use MULTEQ®. As you commented, the verification of model is very important especially for the thermodynamic database. HSC Chemistry® uses the revised HKF model to calculate the Gibbs energy of soluble species. The revised HKF model originated from geochemical field is published at available journals.

The Conditions Known to Produce Crevice Corrosion by the IR Mechanism and Those Yet to Be Investigated by Howard W. Pickering

[Not attending paper included in proceedings]

October 11 (Friday) Panel Discussion

Post-Seminar Comments and Thoughts from Jeffrey Gorman

Thanks for letting me participate in the heated crevice meeting. It was interesting and thought provoking. I want to briefly describe with my main thoughts based on the meeting regarding prediction of IGA/SCC at heated crevices:

The steps involved in the likely occurrence of IGA/SCC in new SGs with 600TT or 690TT tubes seem to be pretty well understood, as discussed at the meeting, and include:

(1) Gradual fouling of the initial as-built crevices at TSPs and TTS areas, with the superheat at these areas increasing steadily as deposits build up and densify.

(2) As the superheat at crevices increases, the concentration of dissolved species in them increases, and the aggressiveness of the under deposit environment increases. In addition, as the thickness and density of deposits increases, the environment at the tube surface may become superheated steam, at least for early parts of the fuel cycle.

(3) Because the tubes mostly have low stresses and since the superheats in the newer design SGs are relatively low (with resulting low concentration impurities), corrosion is likely to often involve a long slow IGA phase.

(4) When the IGA gets deep enough such that either the stress intensity reaches a threshold value, or the crack tip chemistry conditions reach some critical state, IGSCC is likely to start, with significantly increased growth rates after the IGSCC starts.

(5) Possible aggravation of IGA/SCC, with resulting bursts of corrosion, may be caused by episodic exposure to startup oxidants. Another similar possibility was hinted at by Chambers related to attack by chemicals released at shutdown, but I don't know enough about this possibility to discuss it here.

My comments regarding the knowns and unknowns involved in the above steps, and ways to best address the unknowns, are as follows:

(1) I think that, for the immediate future, the best way to deal with the deposit buildup step it to do what Fruzzetti's presentation indicated that Millett is contracted to do for EPRI, i.e., develop an empirical model based on available plant and test data and experience. In this regard, the 30 year history at Siemens SGs should not be ignored, since they have geometries and materials similar to those of our new SGs and also have had, at least for plants that started up in 1982 and later, low iron ingress rates similar to those now seen in the USA. In the longer term, it would be desirable to quantify models that show how plant chemistry parameters affect deposition rates (parameters such as iron ingress rates, feed water pH, pH control agent used, presence or absence of boric acid). Some of this information may already be available, such as from AECL testing and from Japanese investigations regarding

effects of hydrazine on deposit densification. Some additional testing may be needed, but I would first see what the current EPRI/Millett project develops.

(2) A lot of work has been done on identification of the various types of environments that might develop in heated crevices and attack 600TT and 690TT, as discussed in Roger's NRC report. It seems to me that the main tasks that still need to be worked on include:

a) For all of the chemistry environments, a systemic gathering and quantification of the rates of IGA and then IGSCC for both of the alloys as a function of superheat (i.e., concentration), stress, temperature and potential. This needs to consider the range of compositions and thermal histories of the alloys, which apparently is quite a large range for 600TT. I believe that Roger's work is addressing this aspect, and that he will be identifying the areas that need additional testing.

b) For some (possibly all) of the potentially important environments it is not known whether IGA/SCC can occur in superheated steam at 325C or not. The answer is important since, if the attack can occur in superheated 325C steam, it takes very little impurity to result in an aggressive environment under the deposit. If this is the case, then the main defense has to be by control of the mix of the impurities, and not on the amount of impurities. In other words, ALARA chemistry is not good enough, and plant chemistry control also should include molar ratio and/or other impurity composition controls. Model boiler tests might be a useful way to address this question, but I think that autoclave tests using 325C doped superheated steam (with controlled and varied levels of hydrogen) should precede them.

c) Related to the above item is the need to determine if some of the identified aggressive environments actually develop at tube surfaces in heated crevices. This is especially true for the sulfate, complex, and alumino-silicate environments. Model boiler tests seem to be a useful way to address this question.

d) The aggravating effect of startup oxidants, including hematite washed in from the secondary system (particularly during early power operation following startup), is not well characterized. Tests in caustics have been shown to be very sensitive to the oxidizing nature of the sludge, with both copper oxide and hematite (unpublished MHI test) leading to very large increases in crack initiation and growth rates. The effects of oxidizing corrosion products on many of the other aggressive environments are not as well characterized and warrant detailed study. This is another area where model boiler tests may help, although most of the tests probably should be autoclave tests.

e) As was discussed at the meeting, lead is very aggressive but seems to mostly be tied up by other species. Understanding this in depth, so that utilities can avoid conditions that release the lead that is present in their crevices, is important.

(3) Verification of any predictive model is important to make sure that it provides reasonable and reliable results. The industry events and the model boiler results I summarized at the meeting may provide a start at identifying cases that can be used to verify and adjust predictive models. However, these cases would first need to be fleshed out with detailed supporting information such as chemistry histories, pulled tube examination results, etc. In addition, and probably more importantly, these cases should be reviewed by an expert panel to make sure that both the data and conclusions are reasonable and correct. I will provide Keith with a suggested list of cases that could be pursued for this purpose.

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10. SUPPLEMENTARY NOTES

J. Davis, NRC Project Manager

11. ABSTRACT (200 words or less)

An international Heated Crevice Seminar, sponsored by the Division of Engineering Technology, Office of Nuclear Regulatory Research, U.S. Nuclear Regulatory Commission, Argonne National Laboratory, and the Electric Power Research Institute, was held at Argonne National Laboratory on October 7-11, 2002. The objective of the seminar was to provide a working forum for the exchange of information by contributing experts on current issues related to corrosion in heated crevices, particularly as it relates to the integrity of PWR steam generator tubes. Forty-five persons from six countries attended the seminar, including representatives from government agencies, private industry and consultants, government research laboratories, nuclear vendors, and electrical utilities.

The seminar opened with keynote talks on secondary-side crevice environments associated with IGA and IGSCC of mill-annealed Alloy 600 steam generator tubes and the submodes of corrosion in heat transfer crevices. This was followed by technical sessions on (1) Corrosion in Crevice Geometries, (2) Experimental Methods, (3) Results from Experimental Studies, and (4) Modeling. The seminar concluded with a panel discussion on the present understanding of corrosive processes in heated crevices and future research needs.

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