B-T-3470

LIMITS TO CREVICE CONCENTRATION PROCESSES

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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	$= 0$	$\neq 0$	> 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

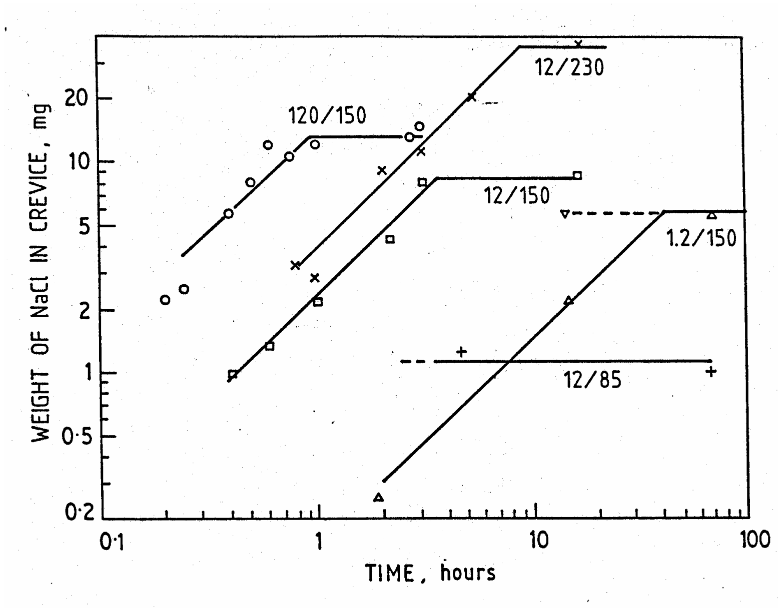
- Early thermal-hydraulic testing
- Concentration testing
  - CERL (cartridge heat)
  - Rockwell (cartridge heat)
- Crevice ECP test - Westinghouse (temperature controlled)
- Corrosion tests
  - Westinghouse sodium carbonate tests
  - CEA sodium hydroxide tests
  - CEA, CE, Ciemat, and Westinghouse acid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

Early Thermal-Hydraulic Testing Laid Foundation for Later Work

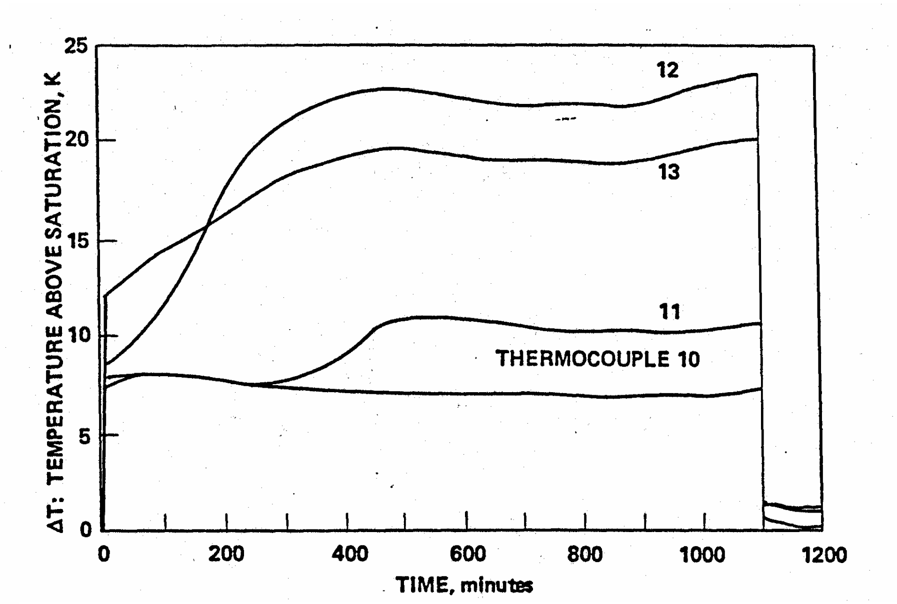
Researchers	Experimental	Contributions
Ishibashi & Nishikawa, Kyushu U., 1968	Cylindrical crevice, large diameter tube, atmospheric pressure	Crevice boiling regimes, nucleate boiling effectiveness increases with decreasing gap
Jensen, Cooper, & Bergles, Iowa State, 1976	Cylindrical and chamfered, horizontal	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)

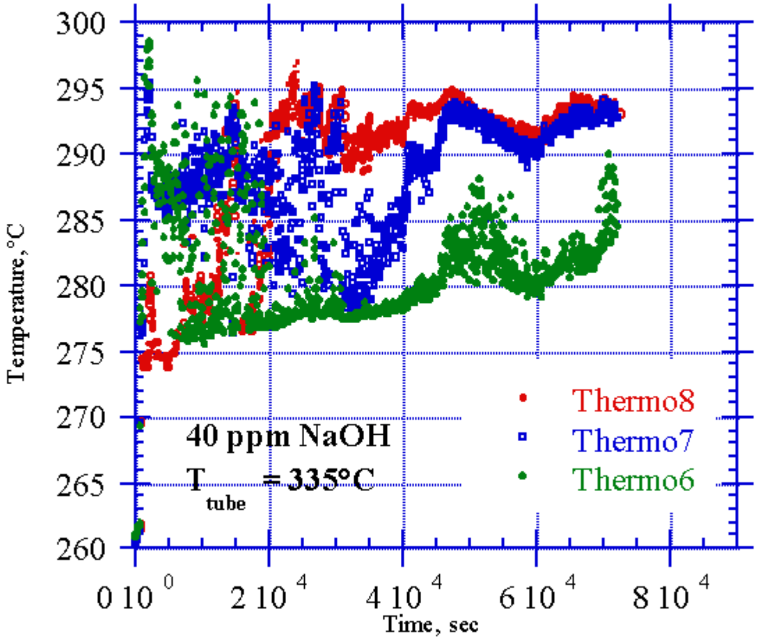


Superheat Response for 12 ppm NaCl and 120 kw/m² (45ºK)



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



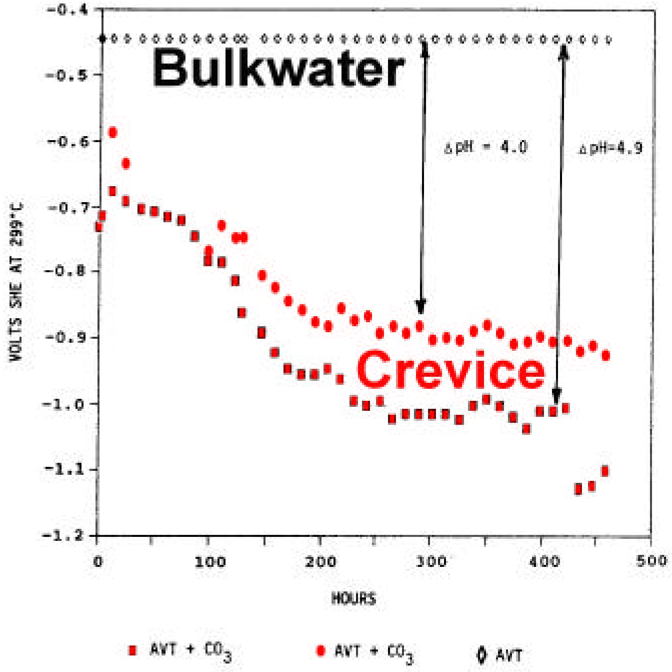
TC 8 at z/L = 0.71
TC 7 at z/L = 0.86
TC 6 at z/L = 1.0 (bottom)

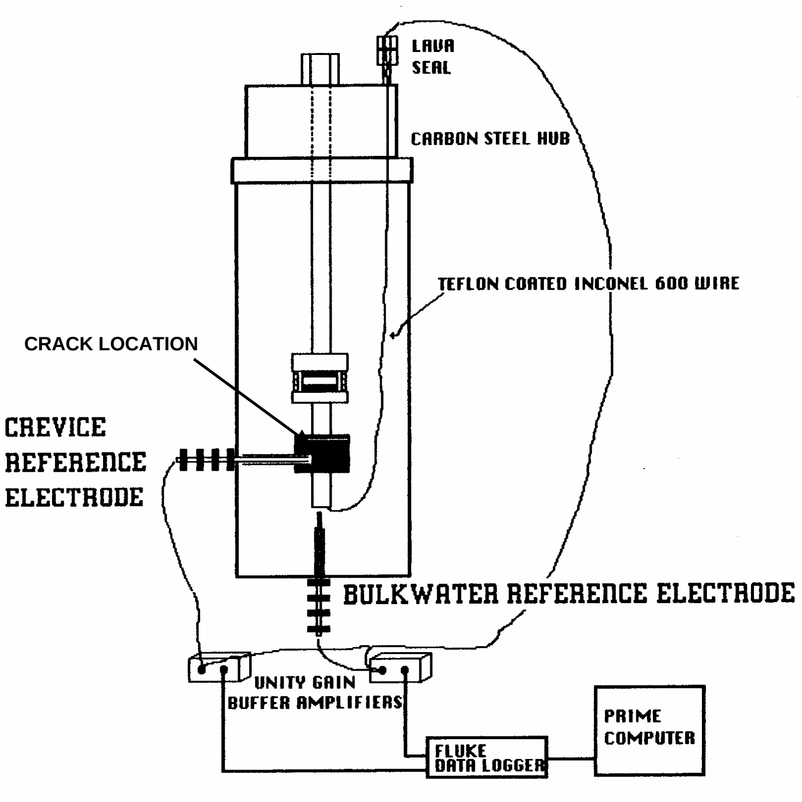
J. B. Lumsden, et al, "Hideout in Prototypic Tube/Tube Support Plate Heated Crevices," Eighth Int. Sym. on Env. Deg., 1997. Copyright 1997 by the American Nuclear Society, La Grange Park, Illinois. Reprinted with permission from ANS and Jesse Lumsden

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

0.3 ppm Sodium Carbonate

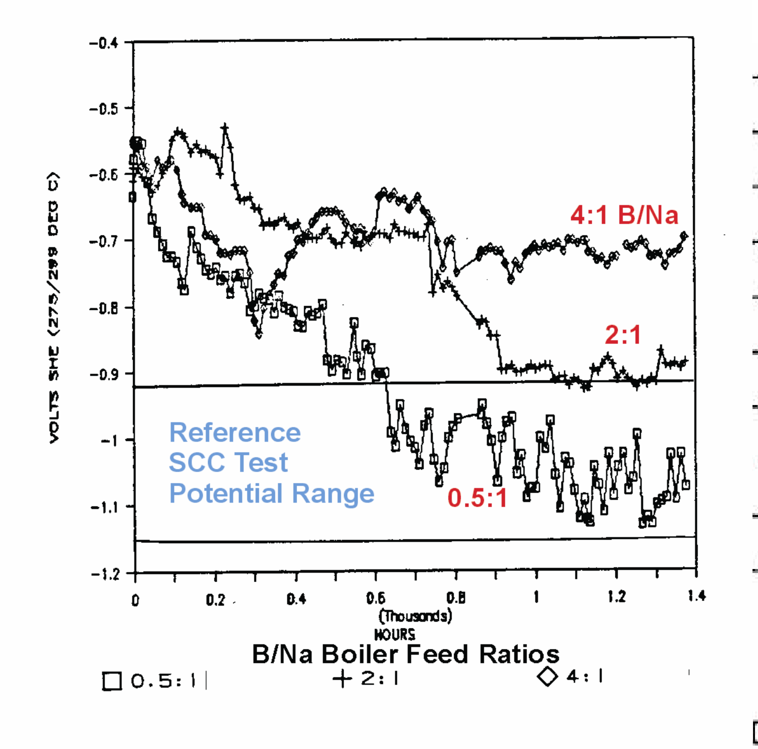
(~ 500 ppb Na^+ in boiler)

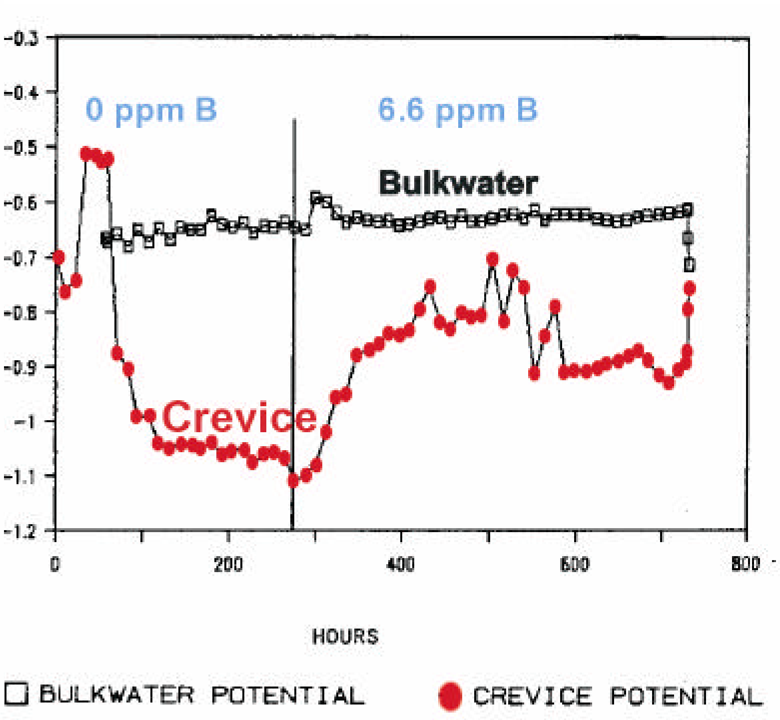




R. E. Hermer, et al, "The Effect of Morpholine/Boric Acid/ Hydrazine Chemistry on Alloy 600 Steam Generator Crevice Corrosion," CORROSION89, 1989. [Reprinted with Permission from NACE, 2002]

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
W STMB #1	90	0.5	~14.	9	0.05
W 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

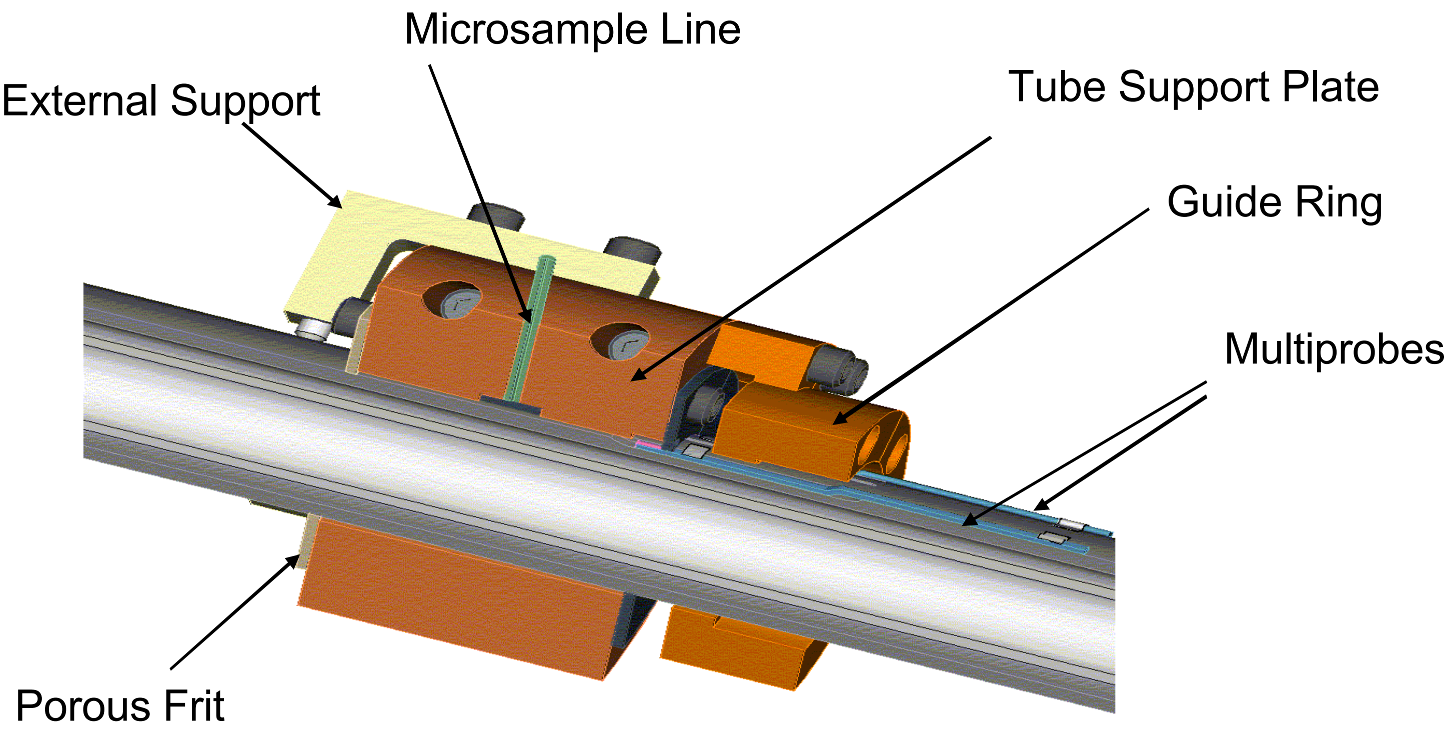
Summary

- 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

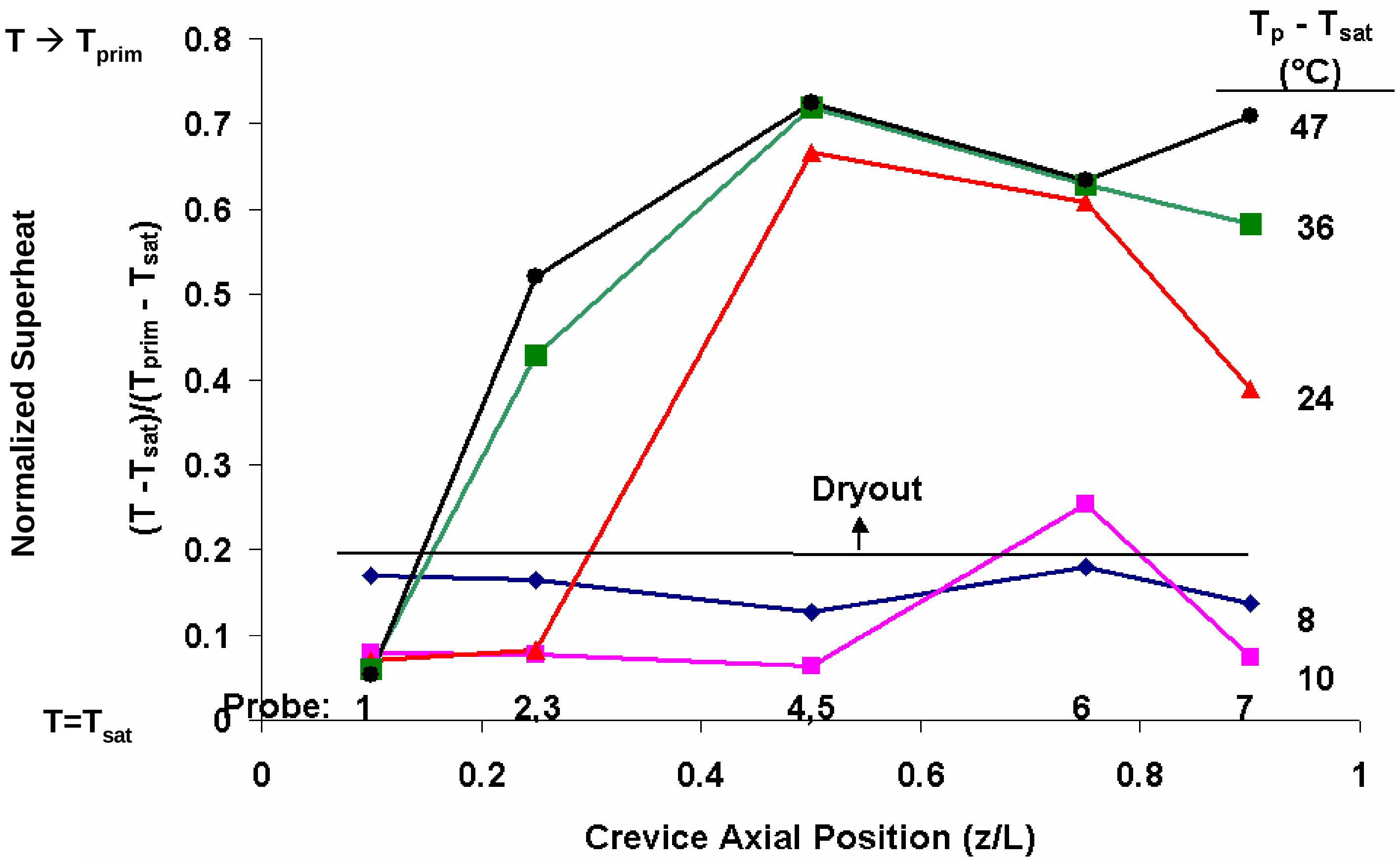
Crevice Chemistry Testing and Applications

- 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^oC ΔT



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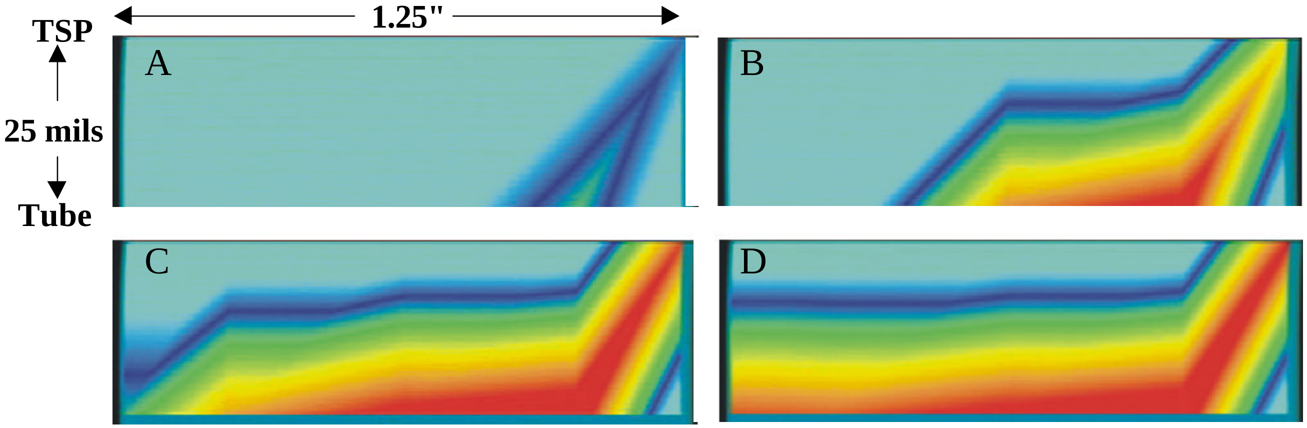
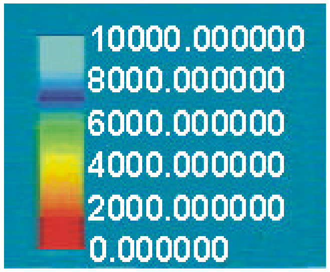
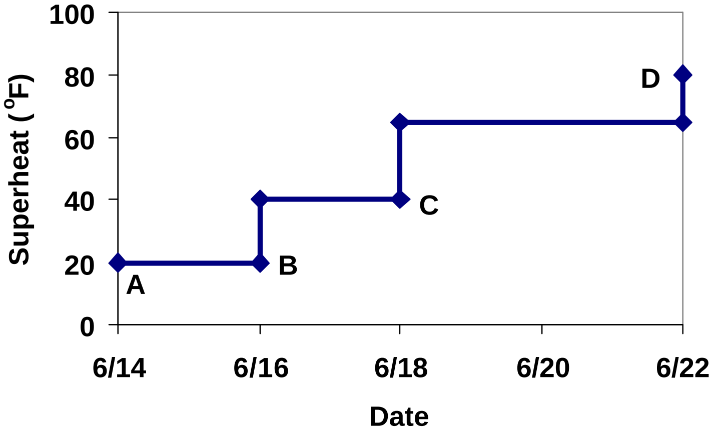
Impedance Response of 300 ppb Cl$^-$ as Seawater Showed Local Concentration at Tube Surface

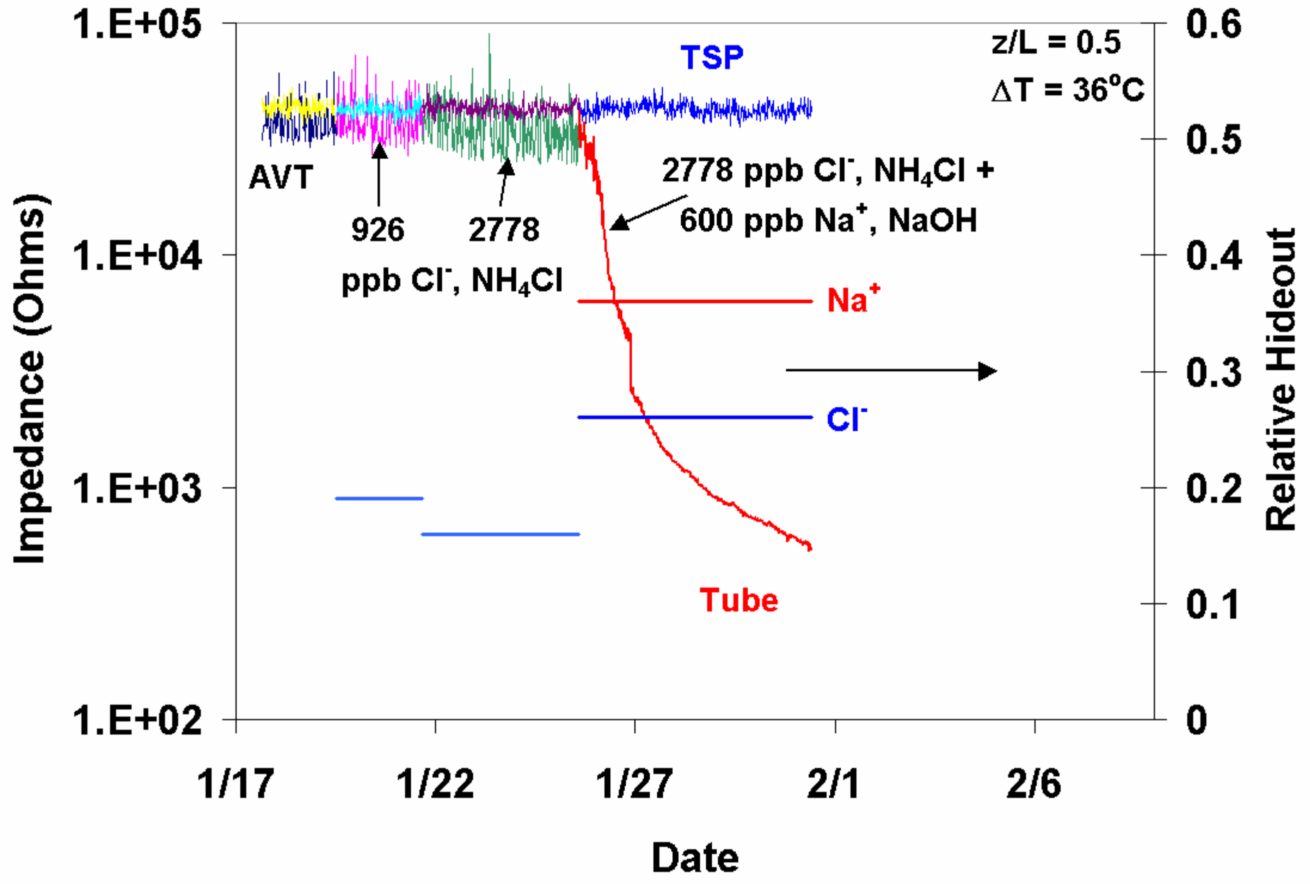


Color Key

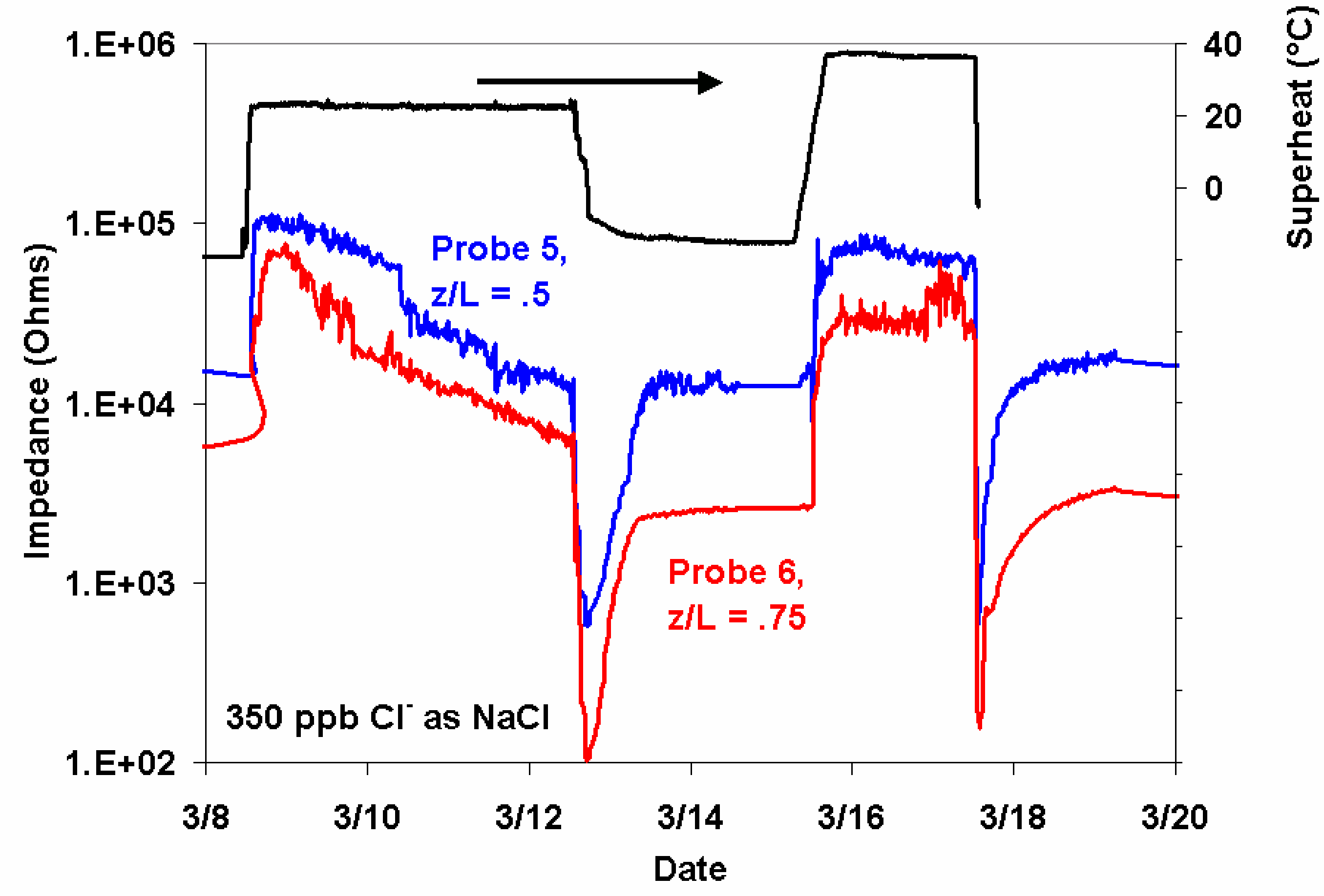




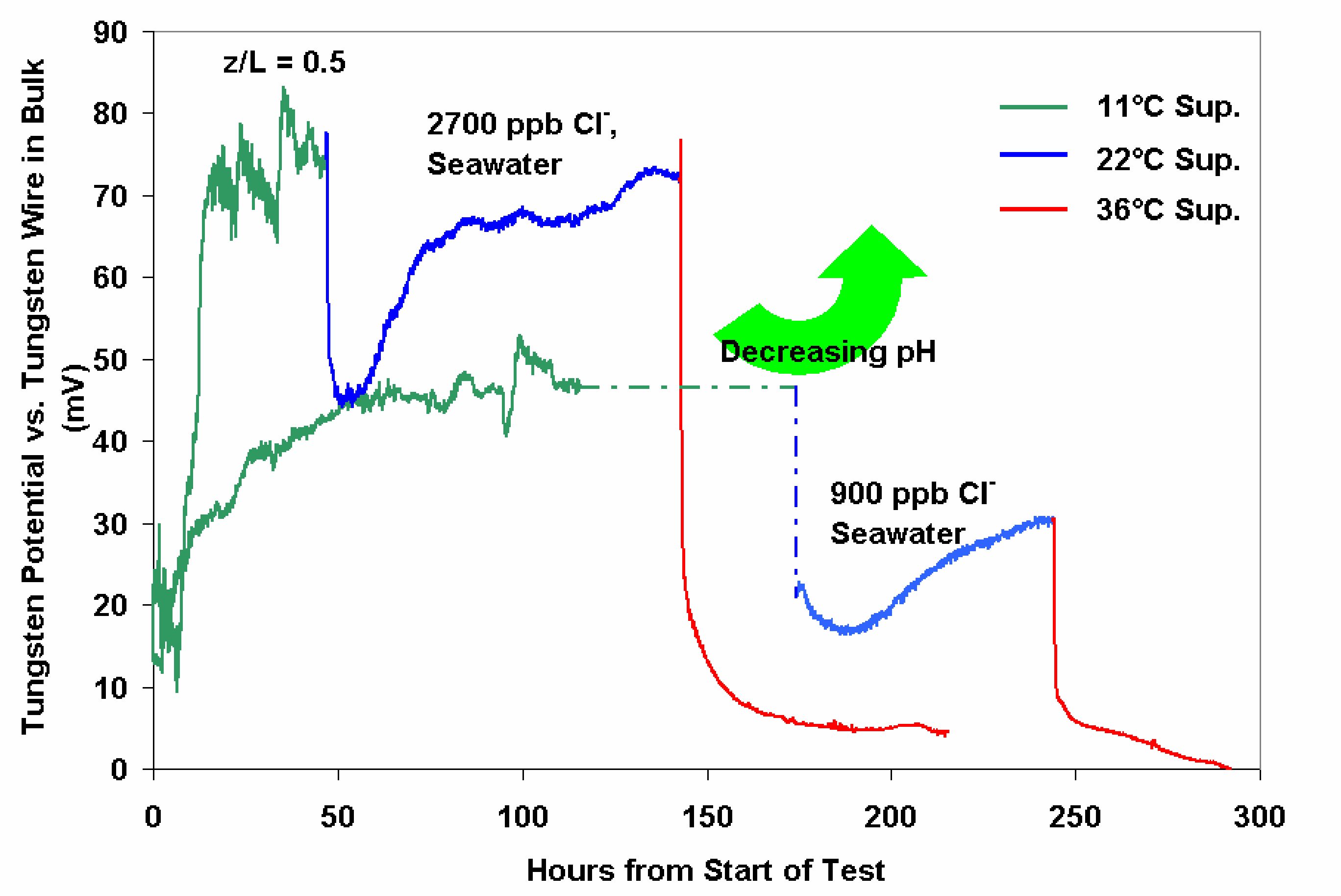
Chloride Concentration Limited Both by Volatility and Adsorptivity



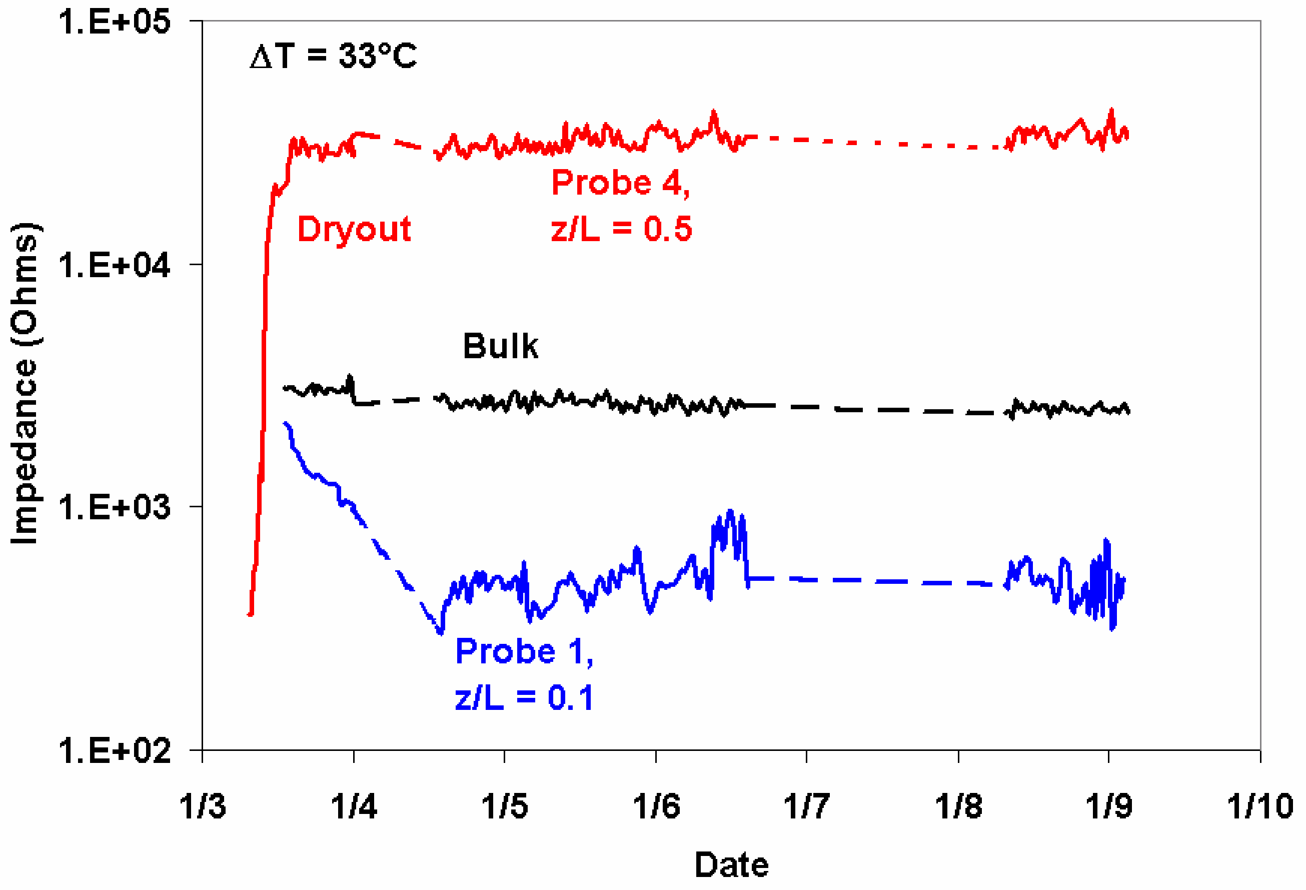
NaCl Precipitated at Highest Superheats



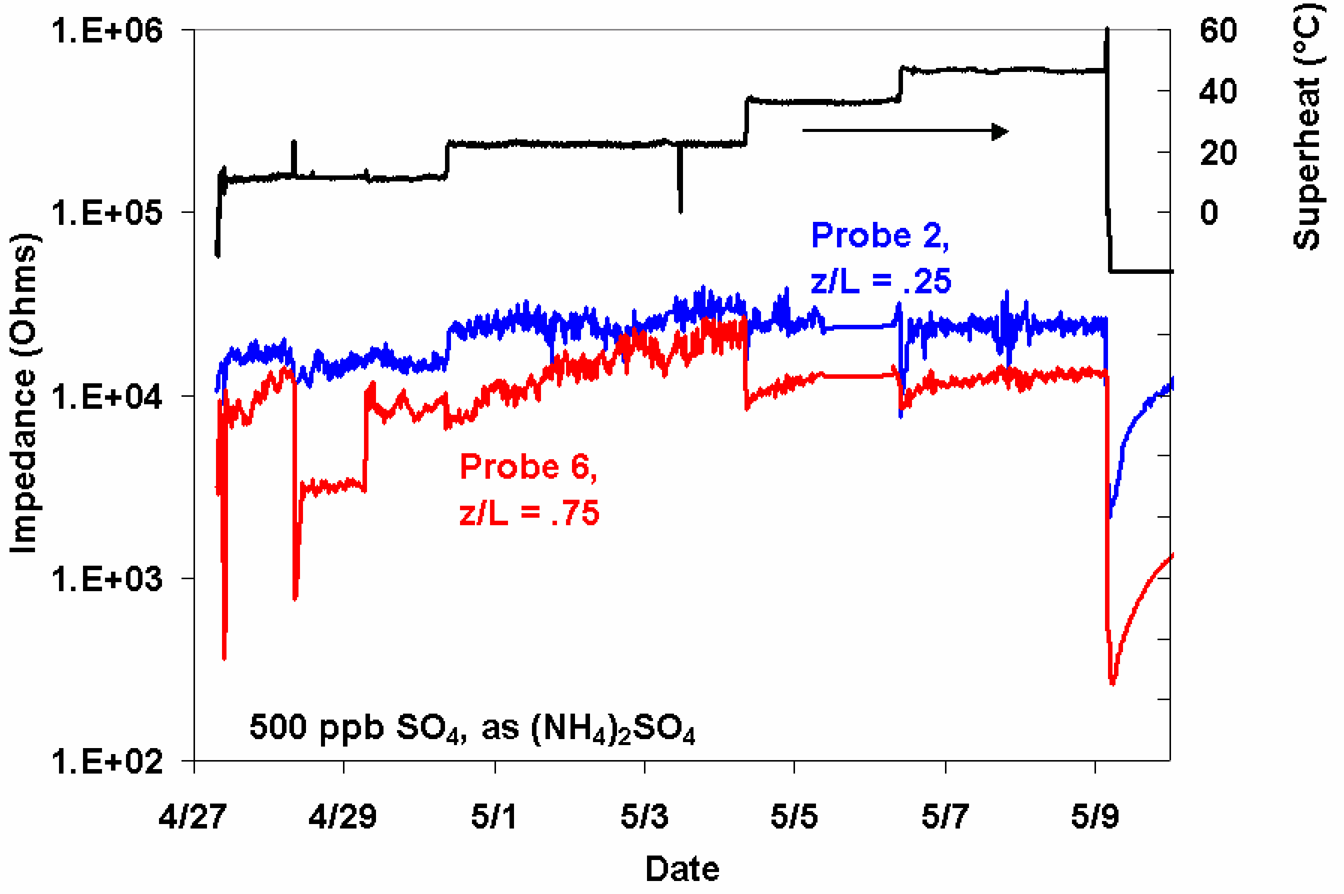
Seawater Concentrate Lost Acidity with Increasing Superheat



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



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



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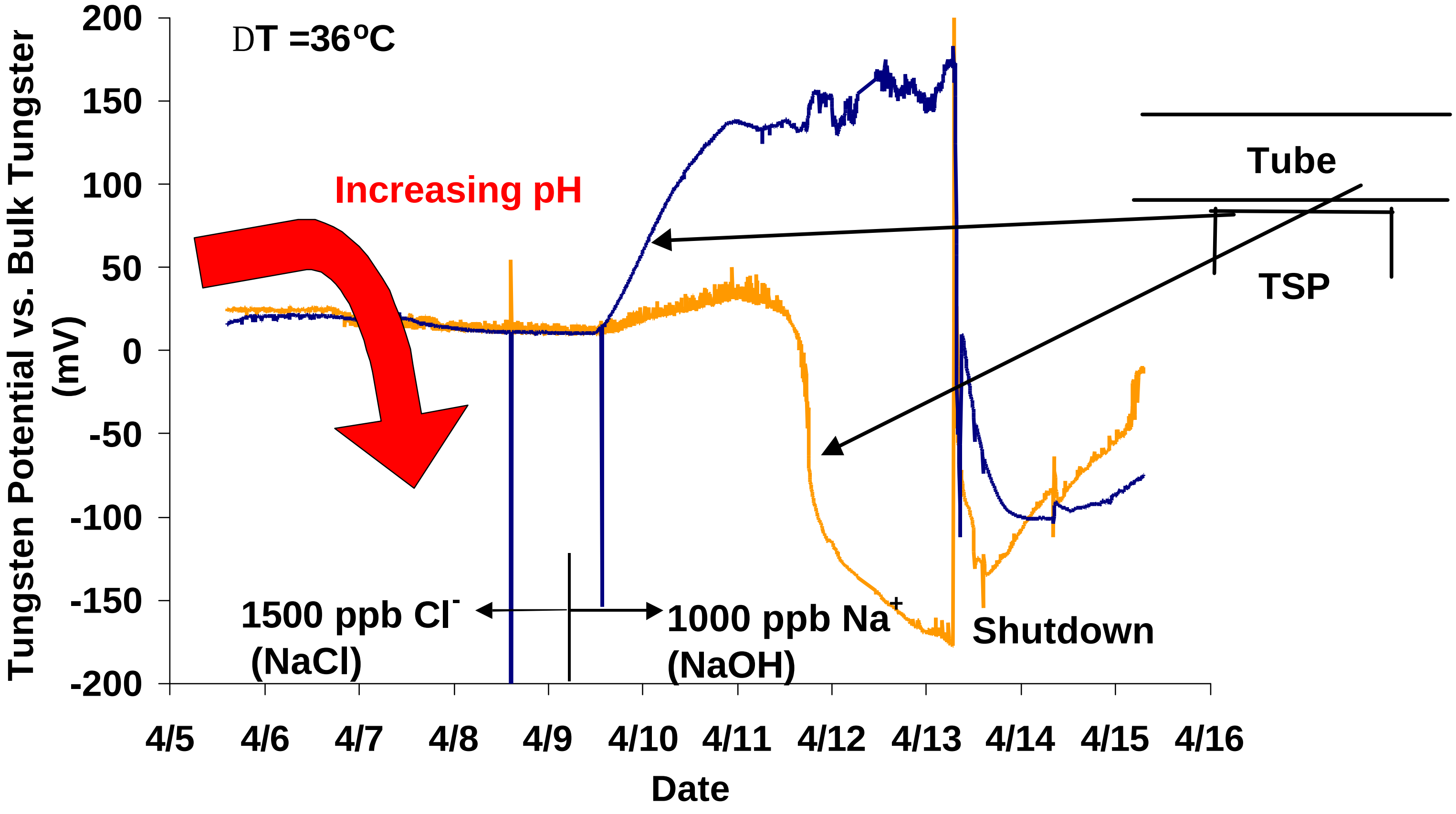
Large Radial pH Gradients in Caustic Test may have Resulted from Chloride Desorption



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

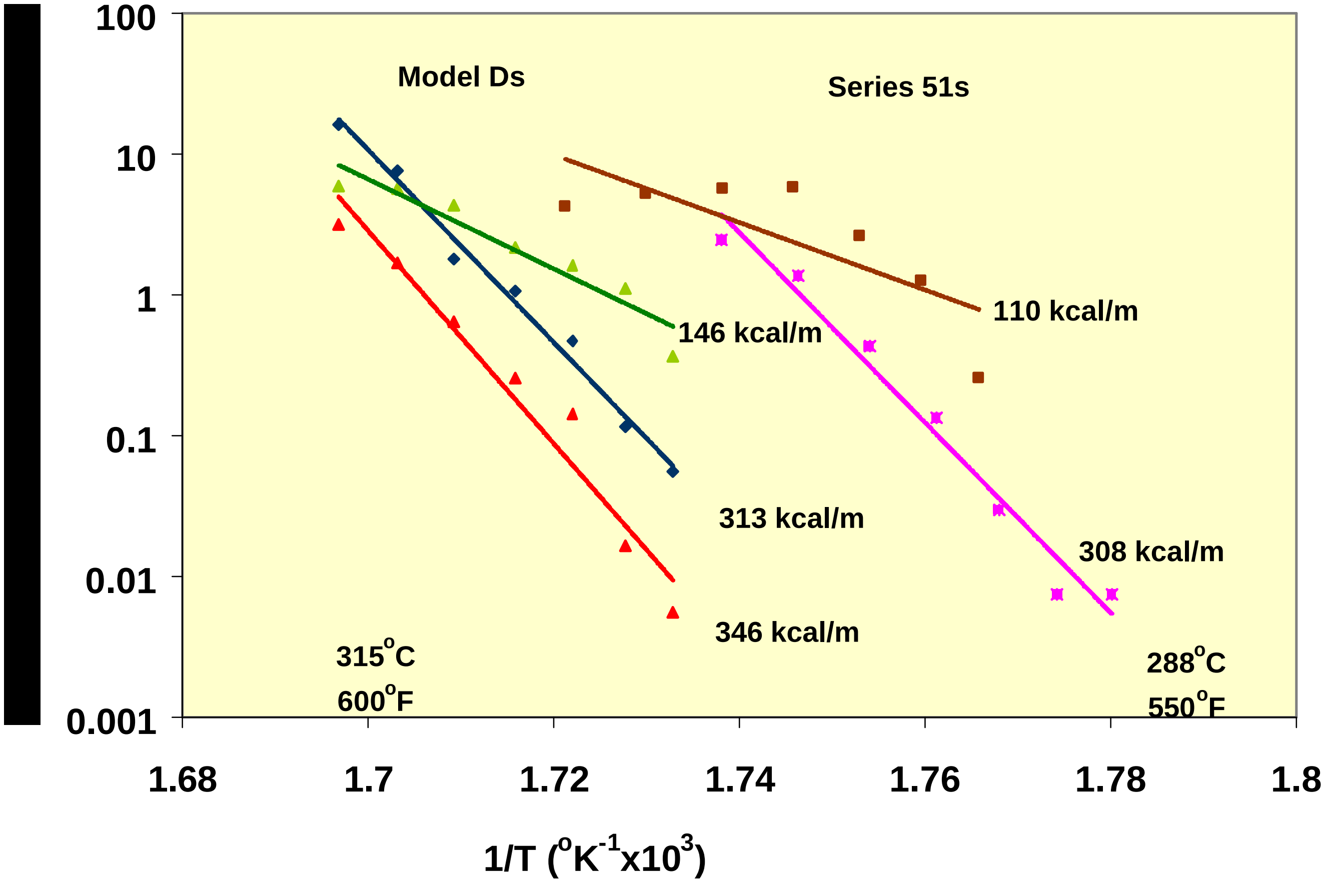
- Phosphate precipitated
  - As would less soluble species

- 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



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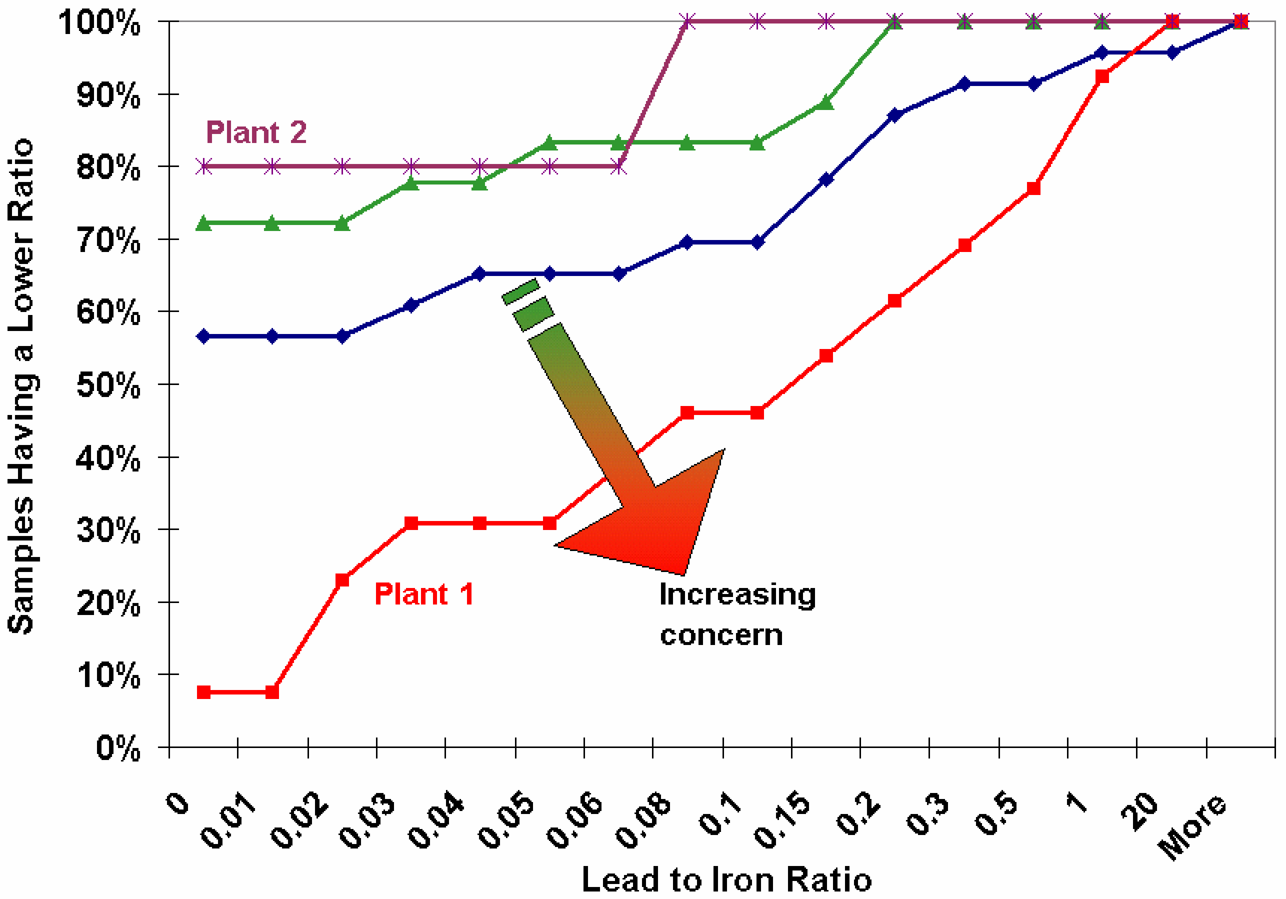
CEA Model Boiler Test Found that Lead Produced Little SCC, Consistent with Low Solubility

	AJAX Test 14-10 (LETC/292/92, 12/92)	CEA and W NaOH Model Boiler Tests
Concentration (ppb)	(Pb)	(Na+)
Makeup Tank	1000	600
Blowdown	59	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



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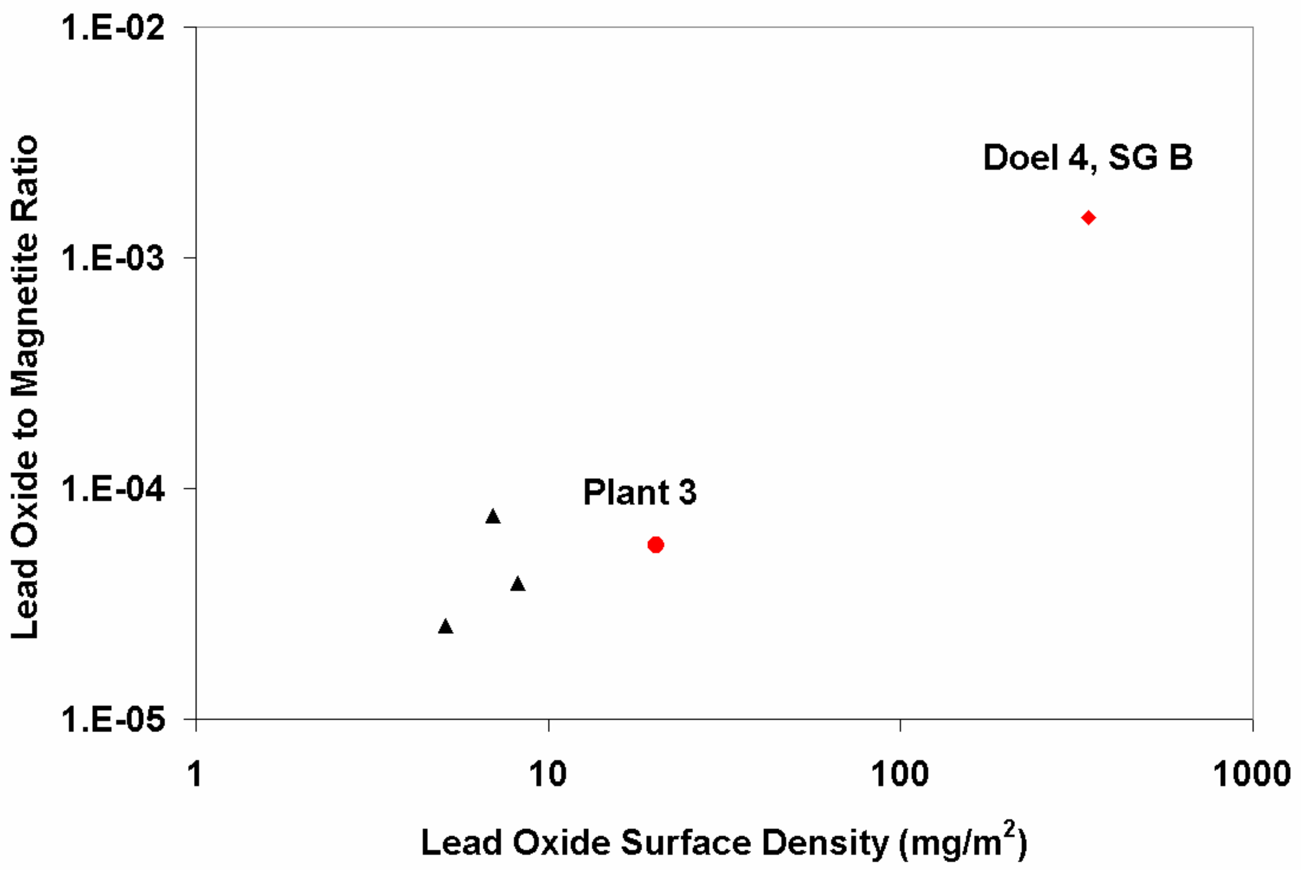
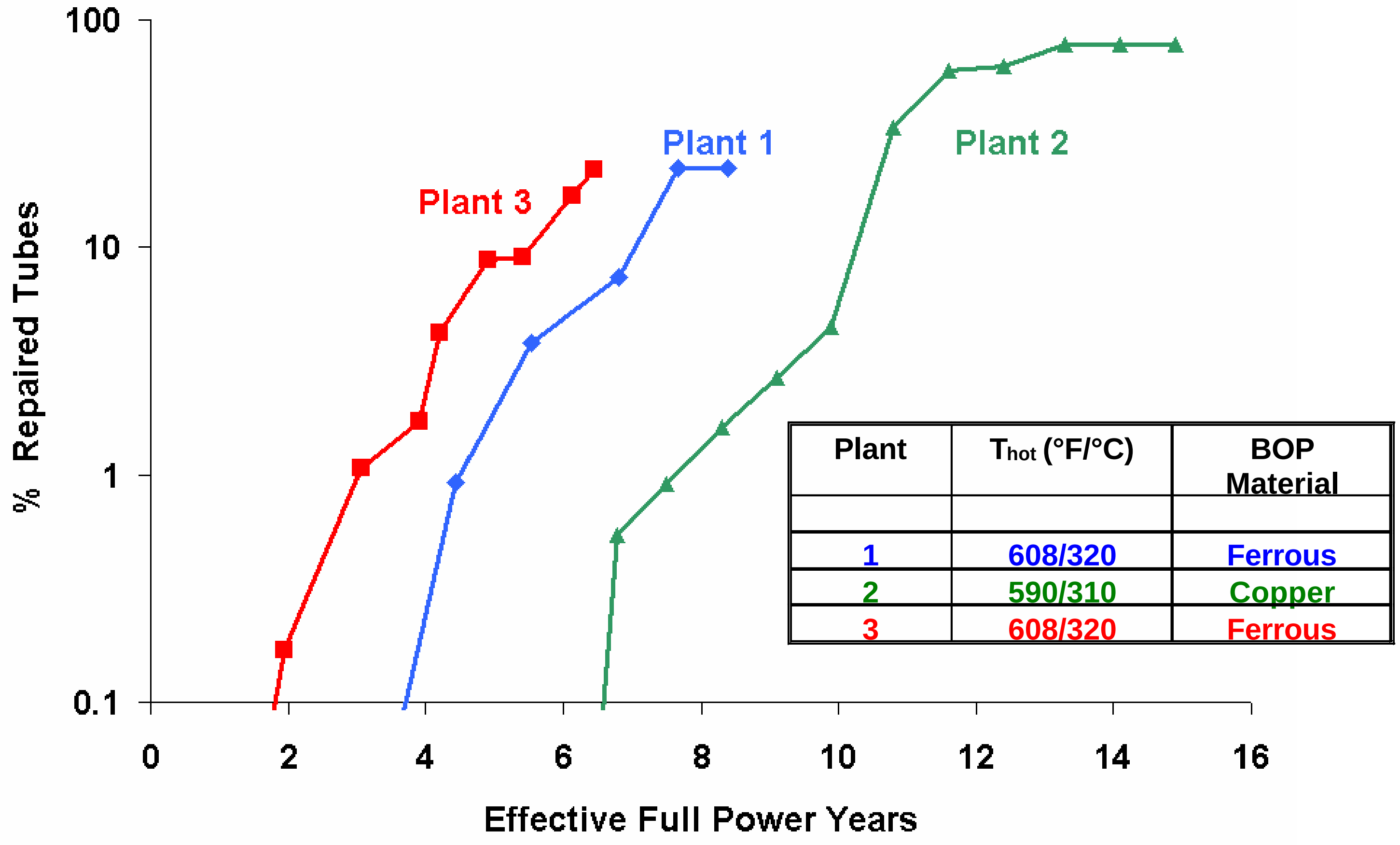
Two Measures for Comparing Lead Removed by Chemical Cleaning

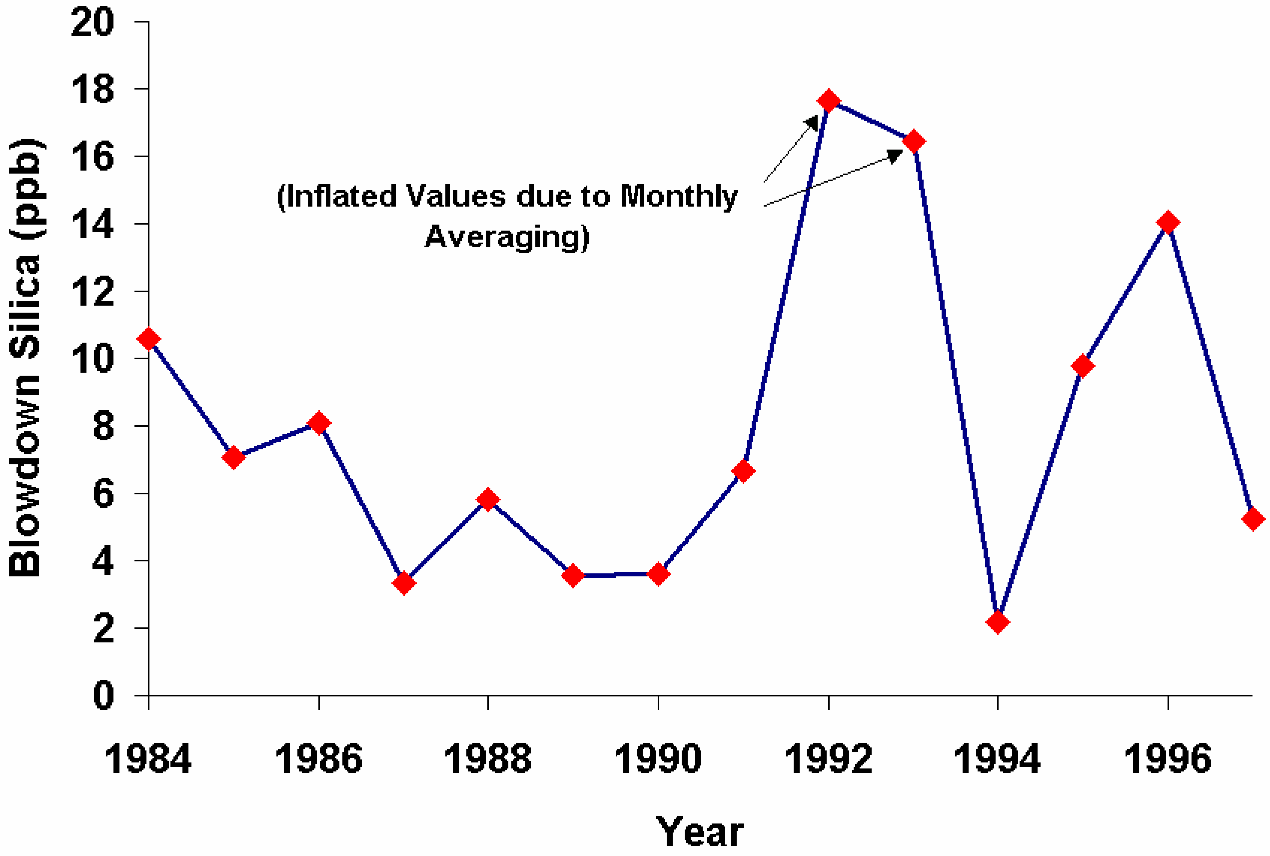


All Three Plants Experienced Extensive SCC in Crevice Interior

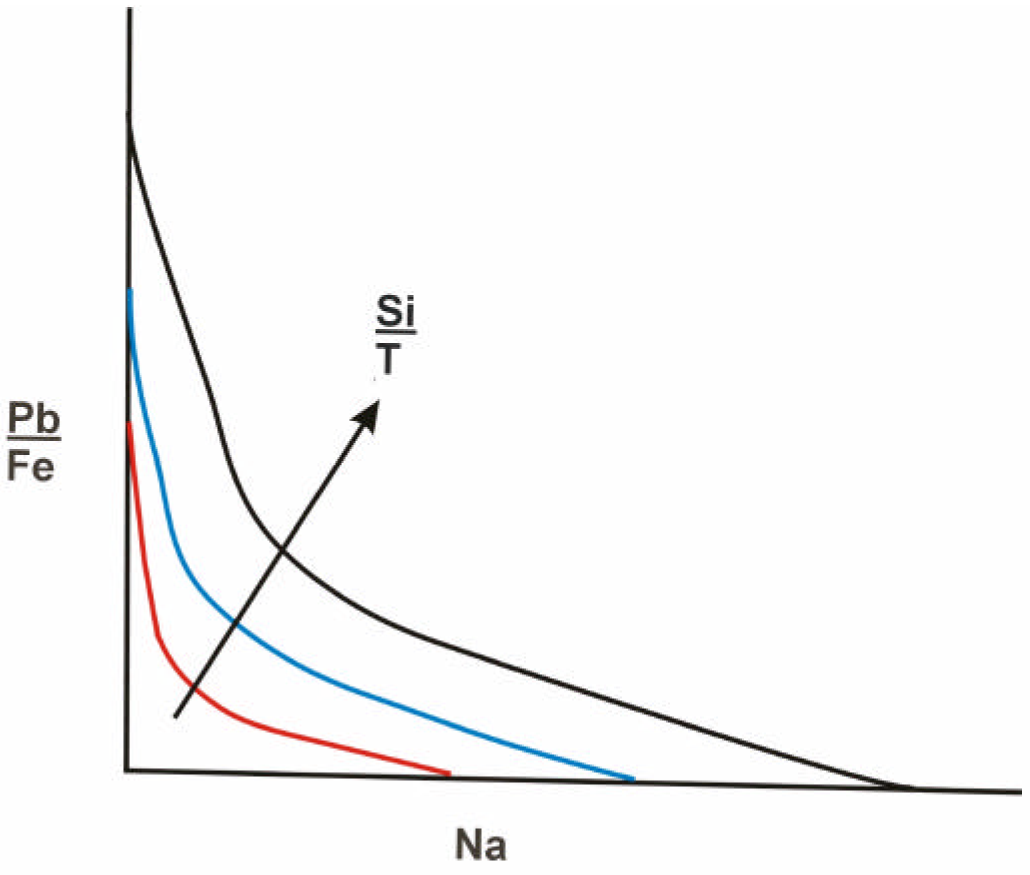


Plant	T_{hot} (°F/°C)	BOP Material
1	608/320	Ferrous
2	590/310	Copper
3	608/320	Ferrous

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



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 ($pH_{25°C}$ > 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)

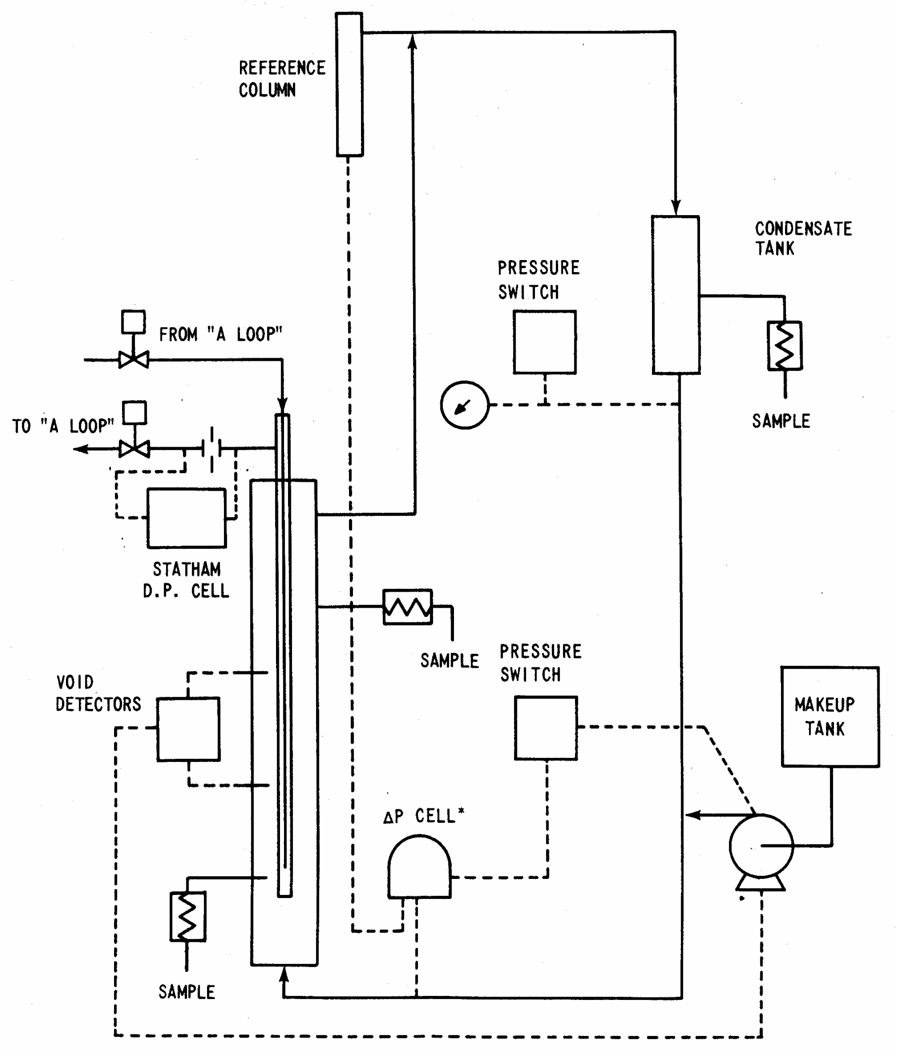


Figure 3-1. Schematic Diagram of Forest Hills Model Boiler System

Tube Sheet Simulant (from WCAP-10273)

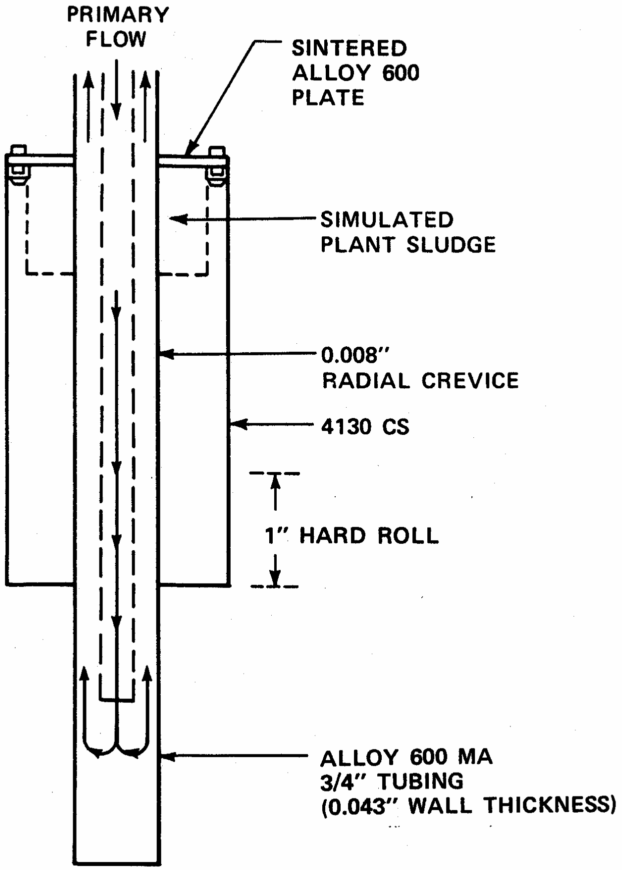


Figure 3-2. Schematic Diagram of Tubesheet Simulant

CEA's AJAX MB (from Daret, 1997)

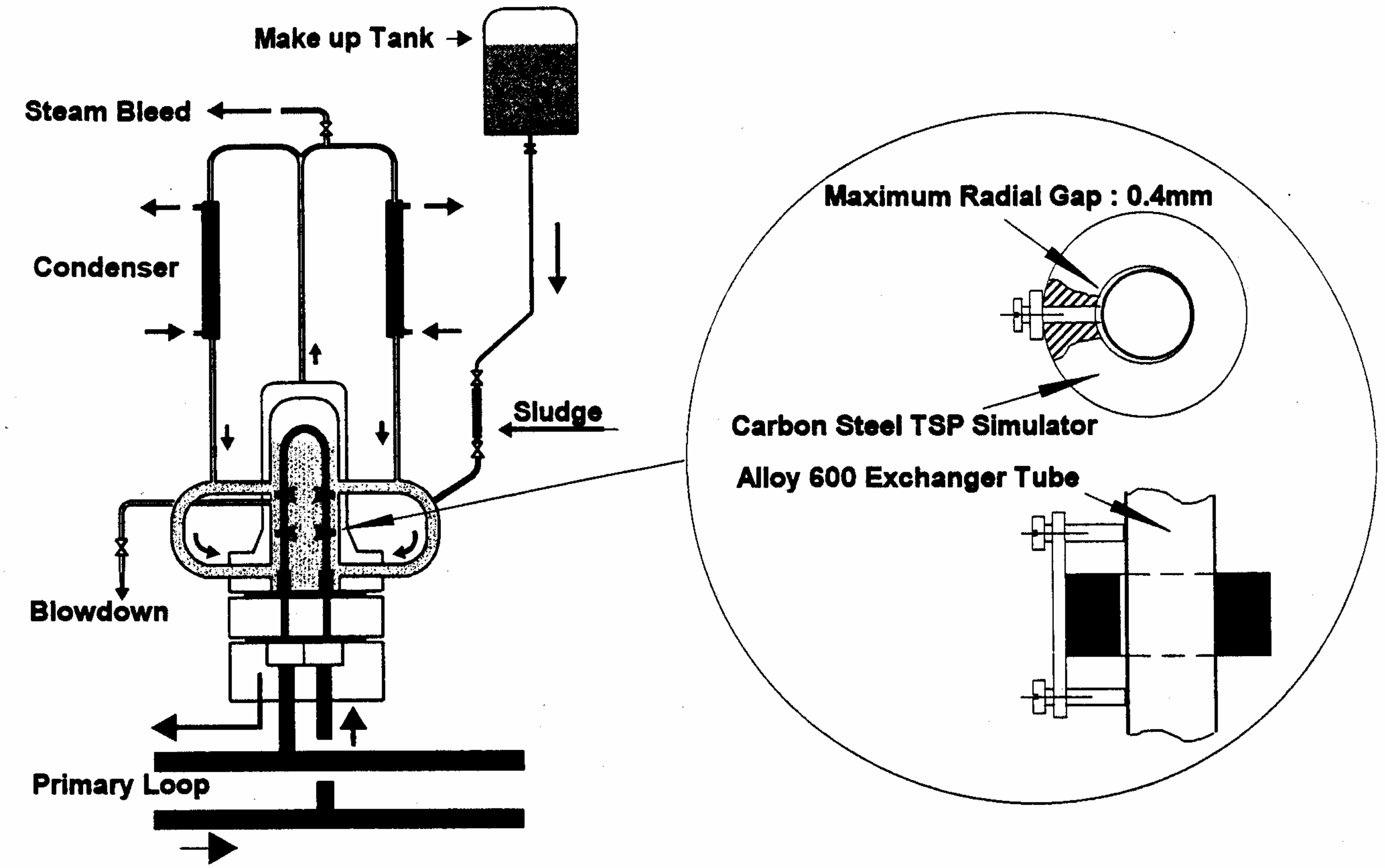


Figure 1. Schematic flow sheet of an AJAX model boiler, with a close view of a simulated tube-tube support plate intersection

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 mm/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 mm/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 μm/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 mm/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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3	W. M. Connor, et al., Neutralization of Tubesheet Crevice Corrosion, EPRI NP-3040, May 1983
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Laboratory Experiments on Steam Generator Crevice Chemistry

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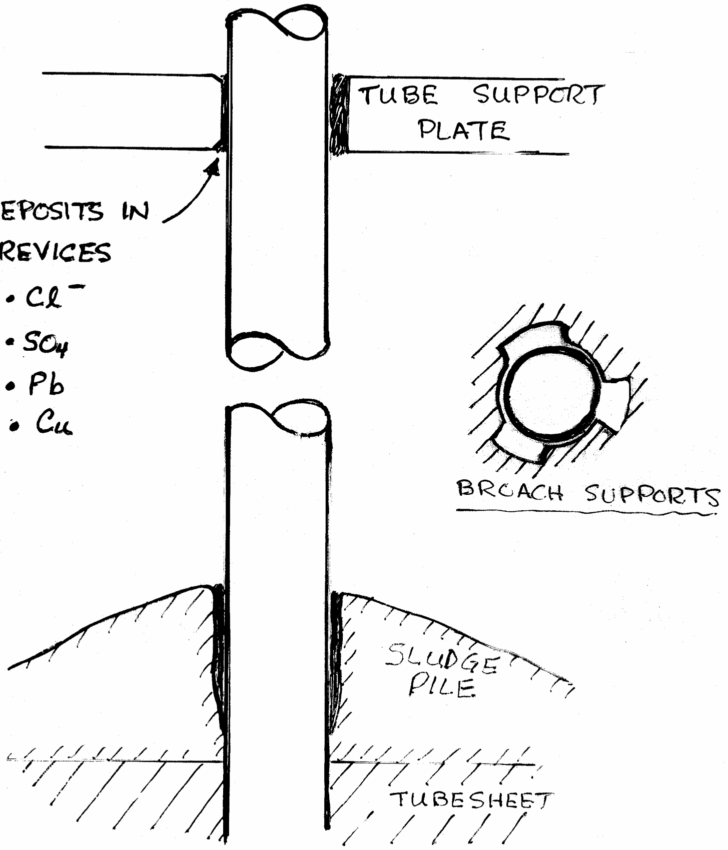
Canada

AECL Atomic Energy of Canada Limited

- **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.

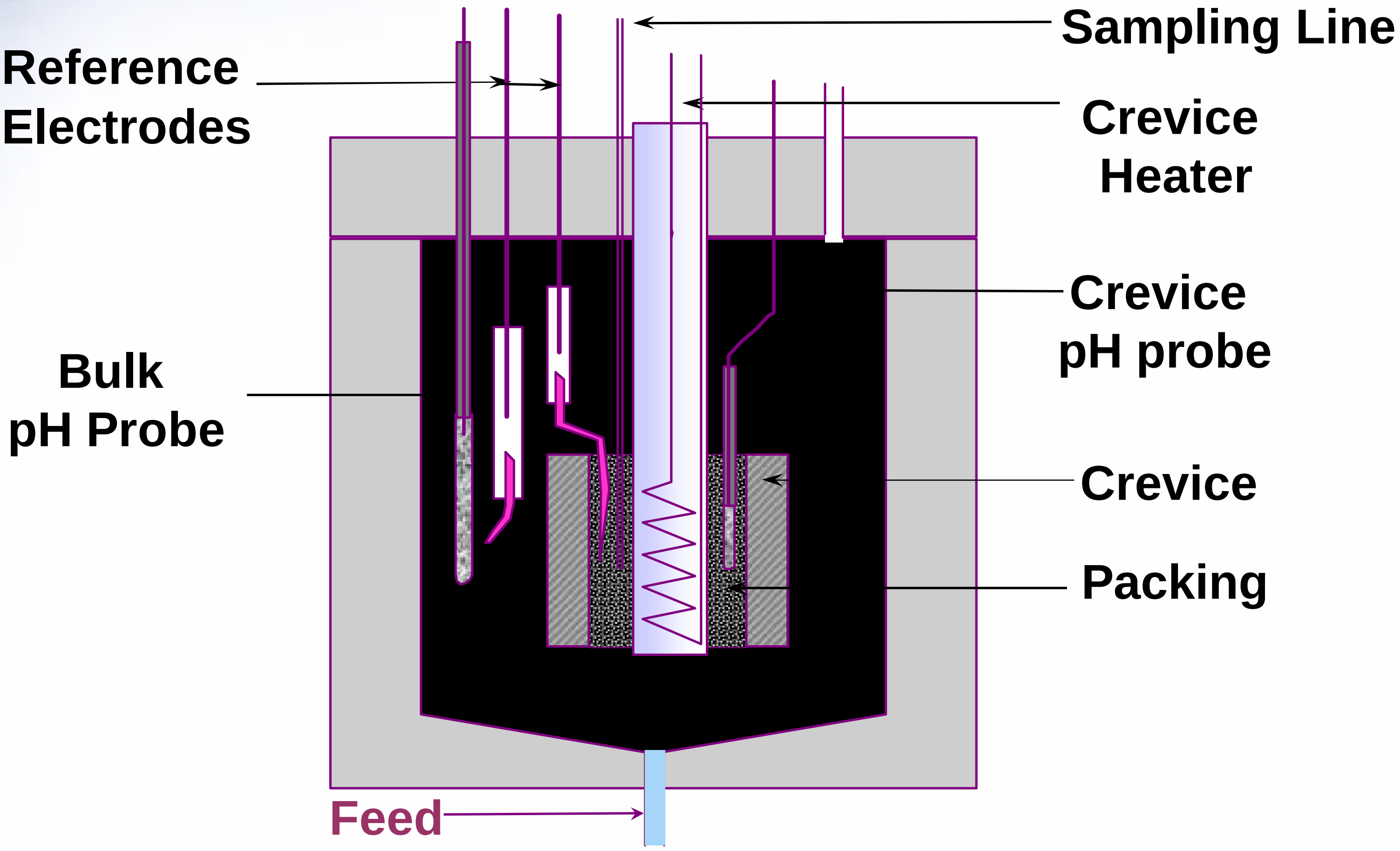
Experiments

- **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



Reference Electrodes

Bulk pH Probe

Sampling Line

Crevice Heater

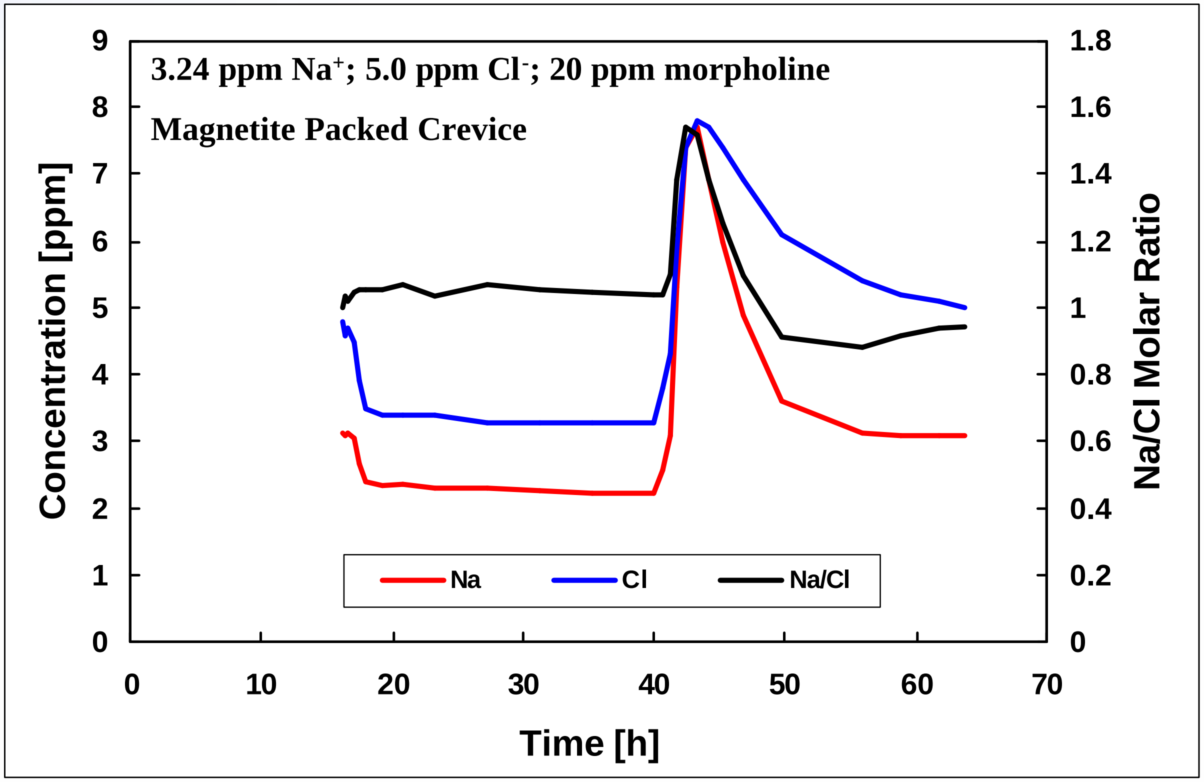
Crevice pH probe

Crevice

Packing

Feed

Typical Hideout/Hideout Return Profile



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

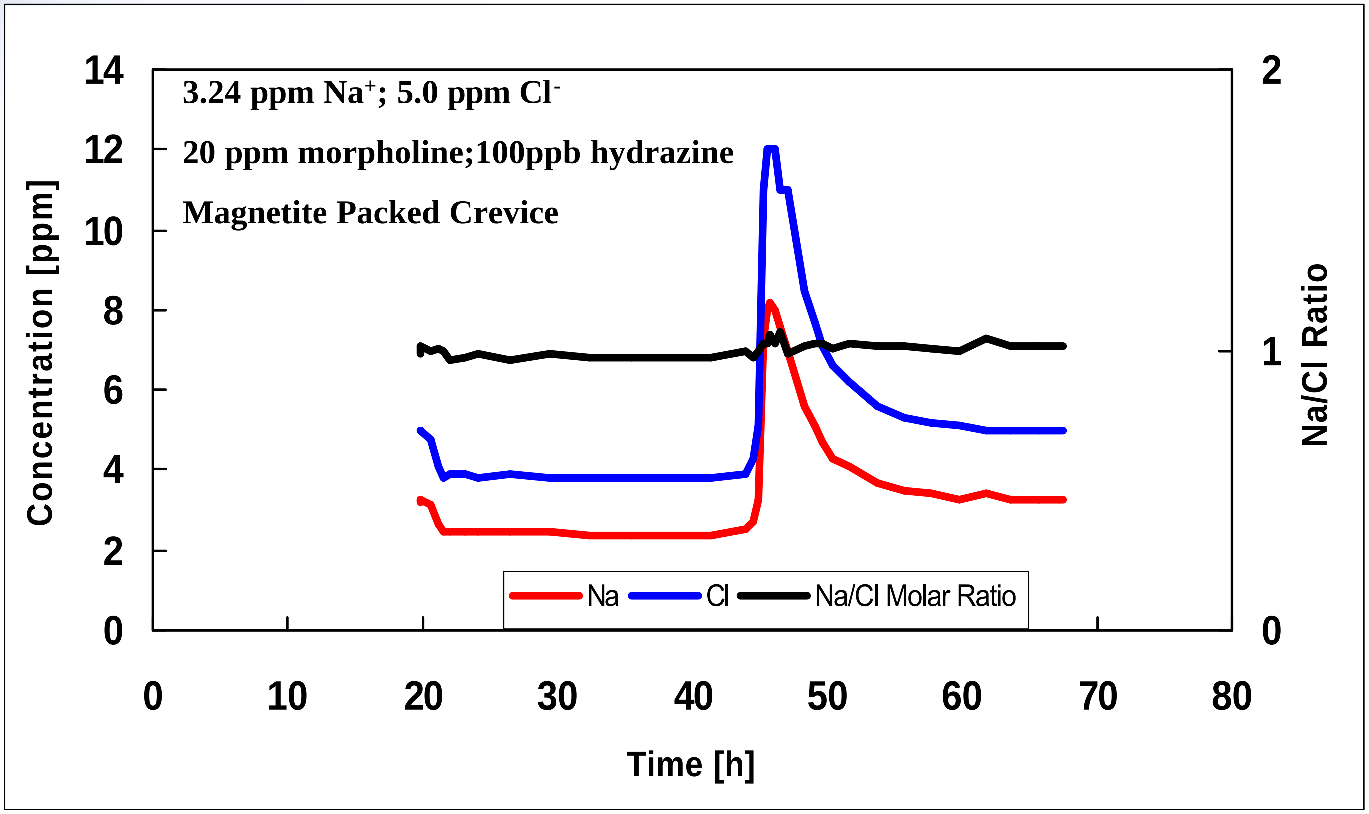
Hideout/Hideout Return

- 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

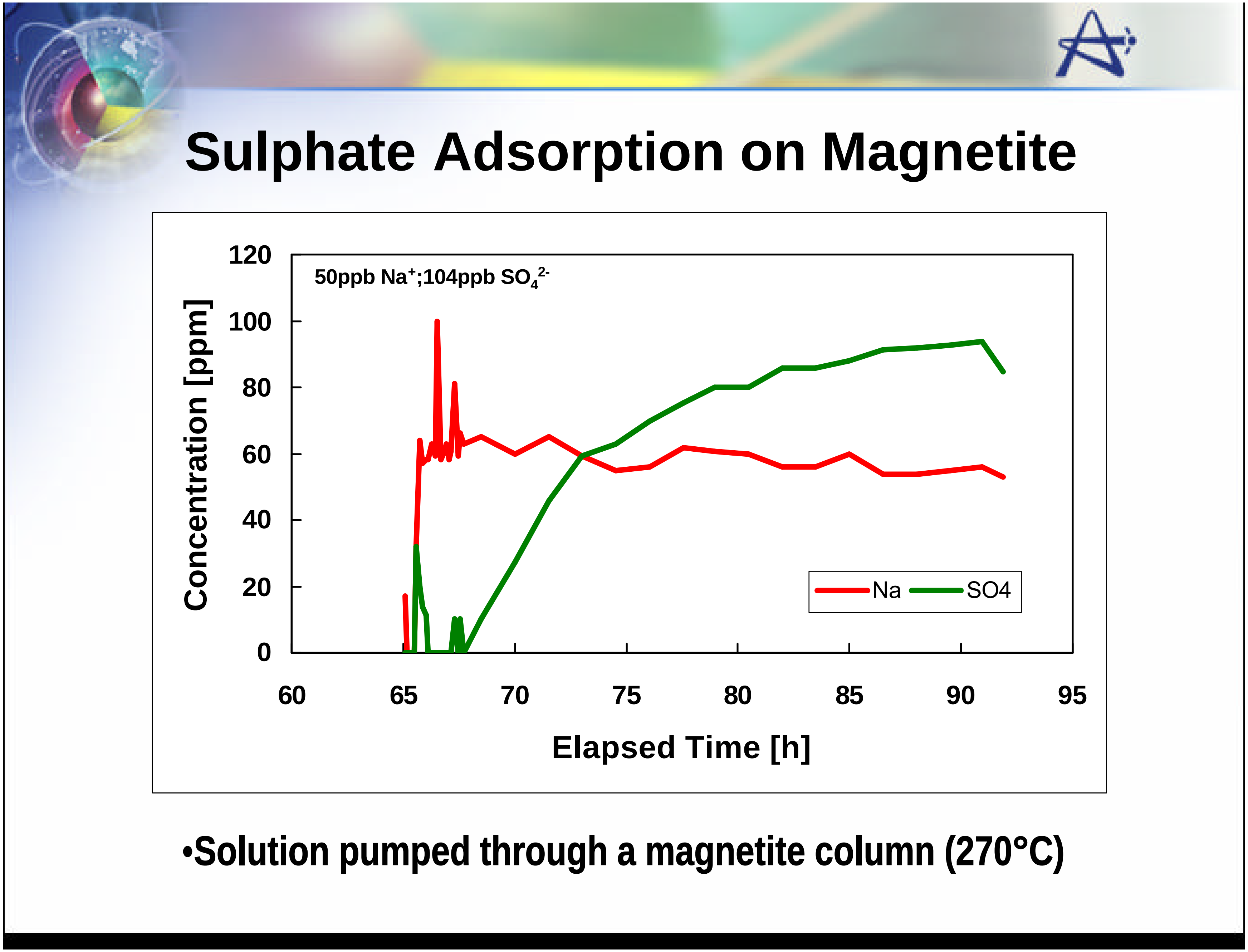
- NaCl with addition of morpholine and hydrazine
- Low concentrations, high heat flux, smaller crevice

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

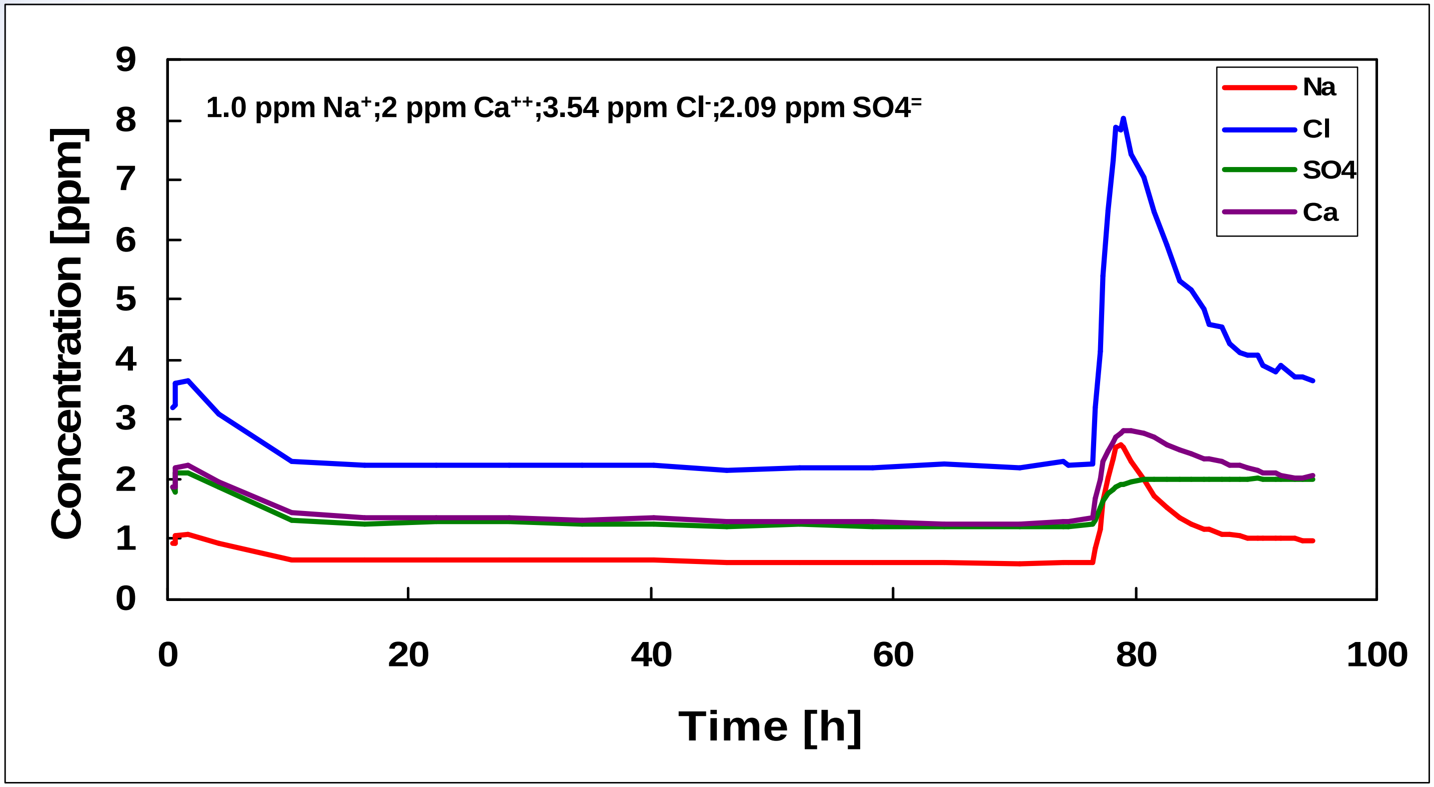
- **Redox conditions**
- **Volatilization ⬇Cl^-**
- **Adsorption behavior⬇SO_4^{2-}**



Sulphate Adsorption on Magnetite

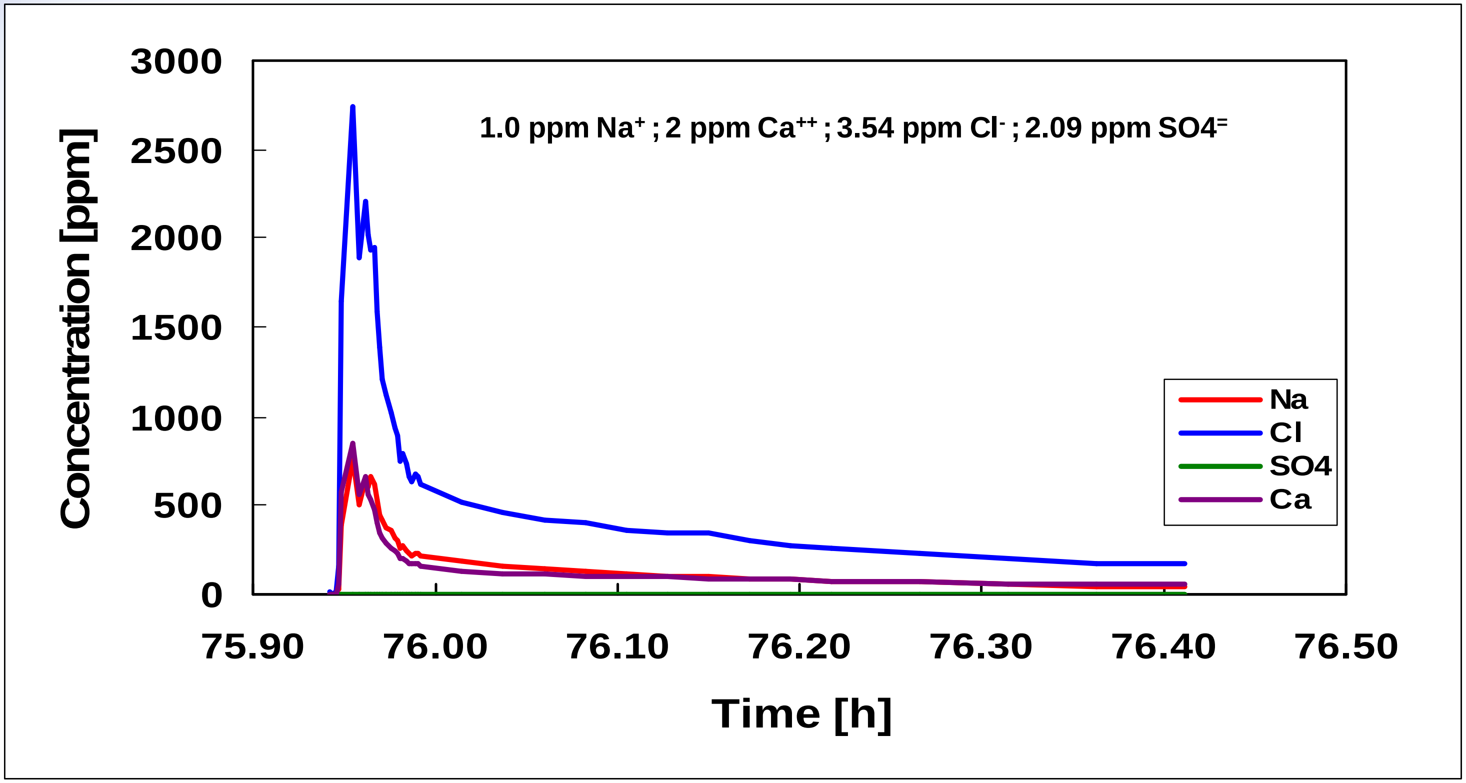
- Solution pumped through a magnetite column (270°C)

Hideout/Return of Complex Solutes



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

Crevice Sampling



1.0 ppm Na^+ ; 2 ppm Ca^{++} ; 3.54 ppm Cl^- ; 2.09 ppm SO4$^=$

- 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

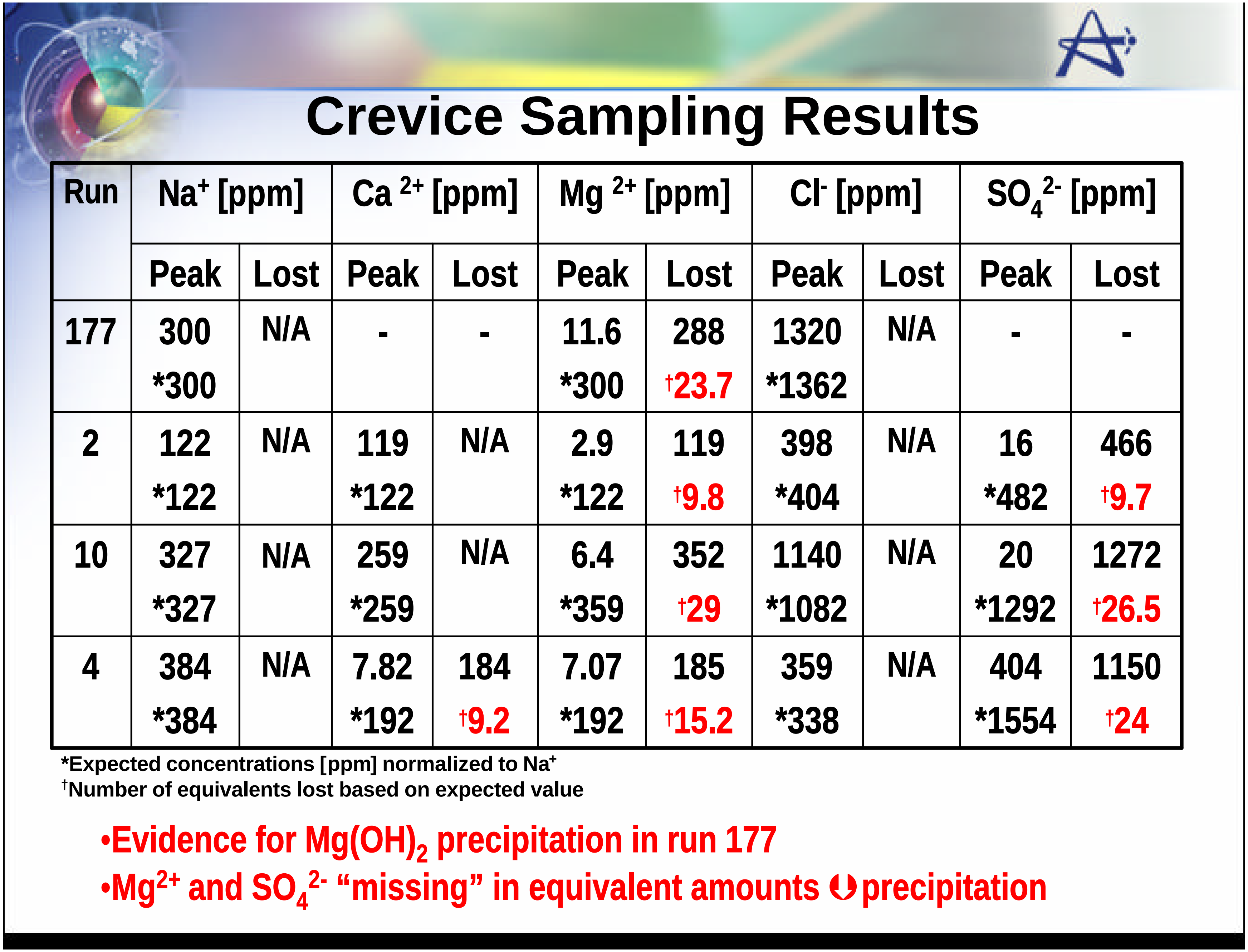
Crevice Sampling Results

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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Background

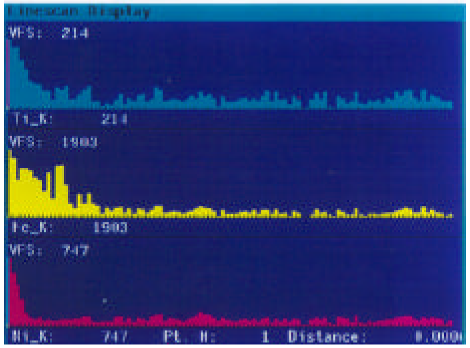
Data from two tests performed with TiO_2 addition:

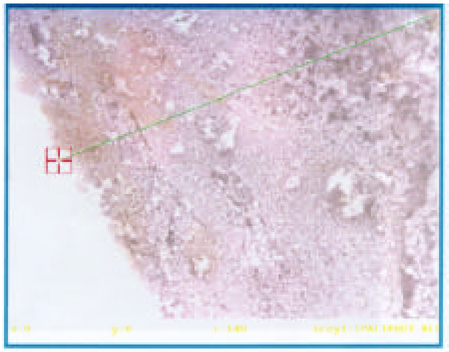
1) In lab test on retired tube/tubesheet intersections from EDF
2) In field test on Ringhals unit 3 (now retired SG's) gave similar information: Little penetration of Ti^{4+} into the packed crevices.

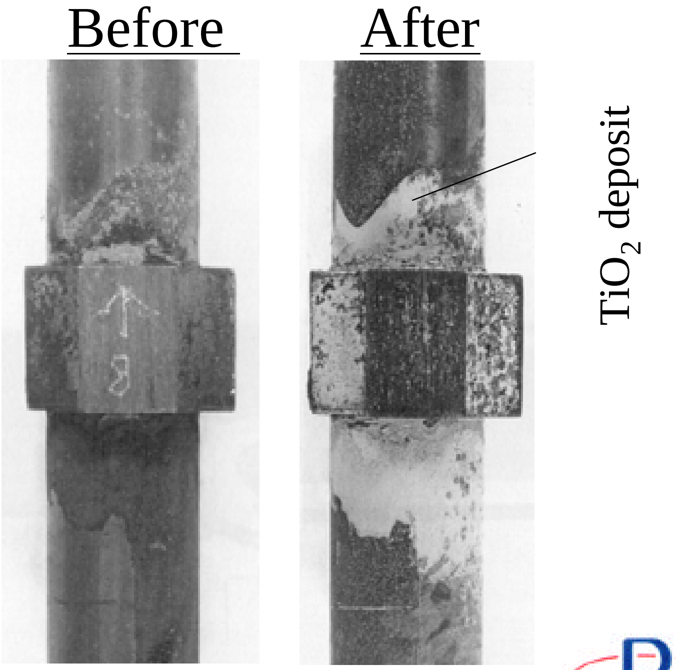
Question:

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

Ti penetration tests on a sludged TSP crevice





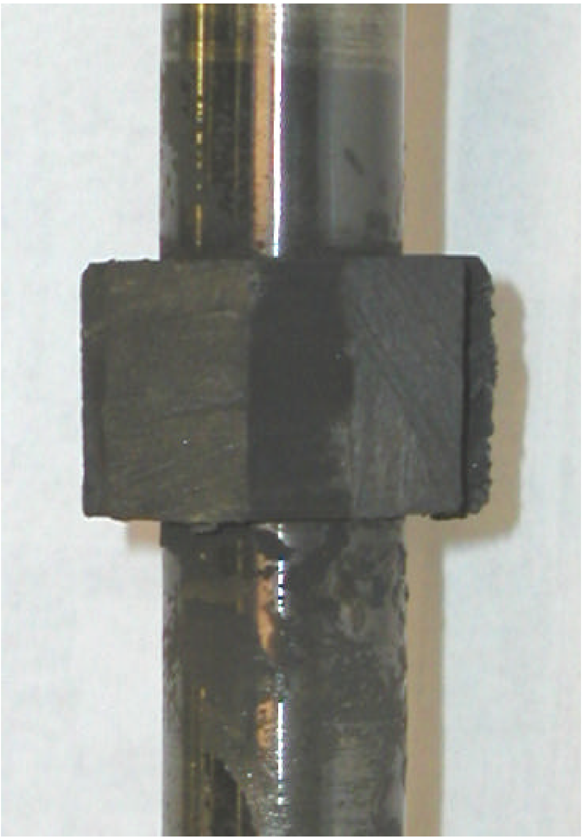


TiO_2 deposit

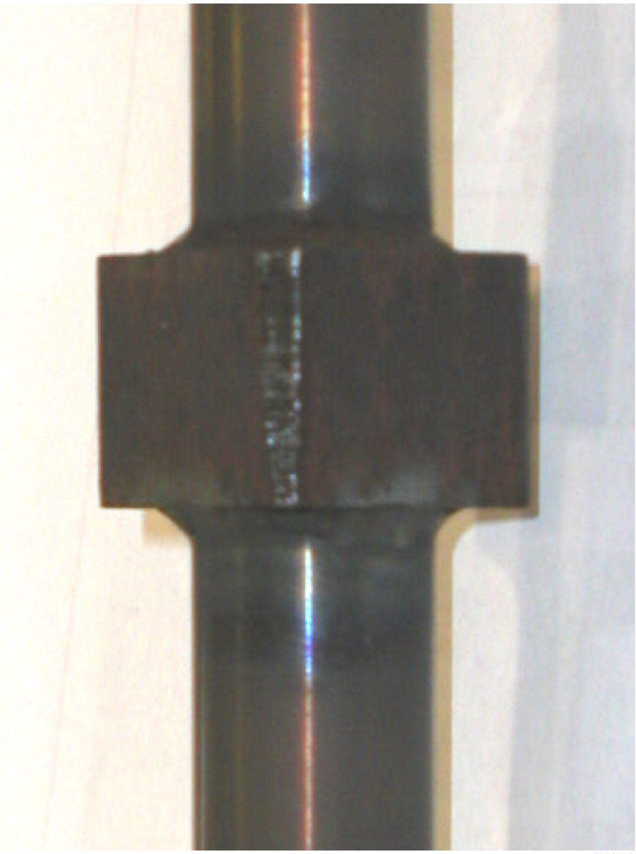
This presentation

- 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.

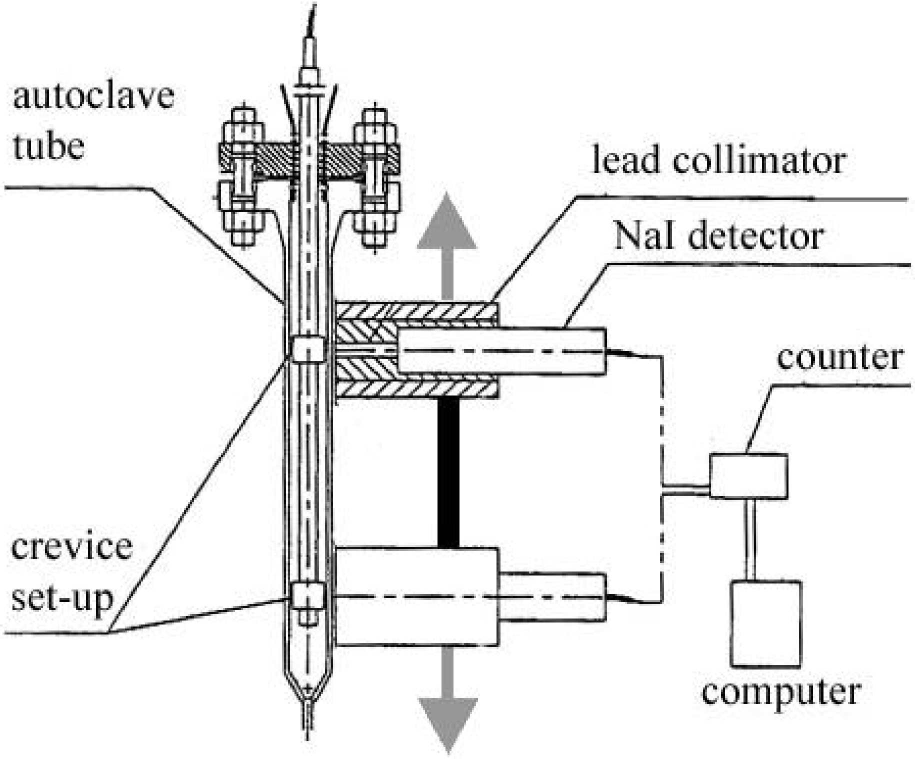
Ringhals 3



Dummy

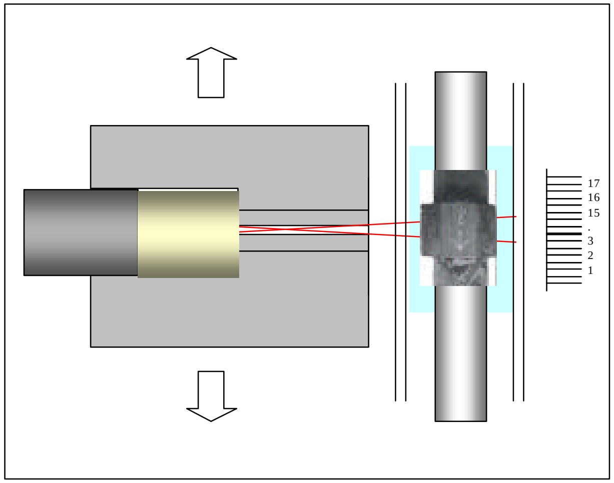


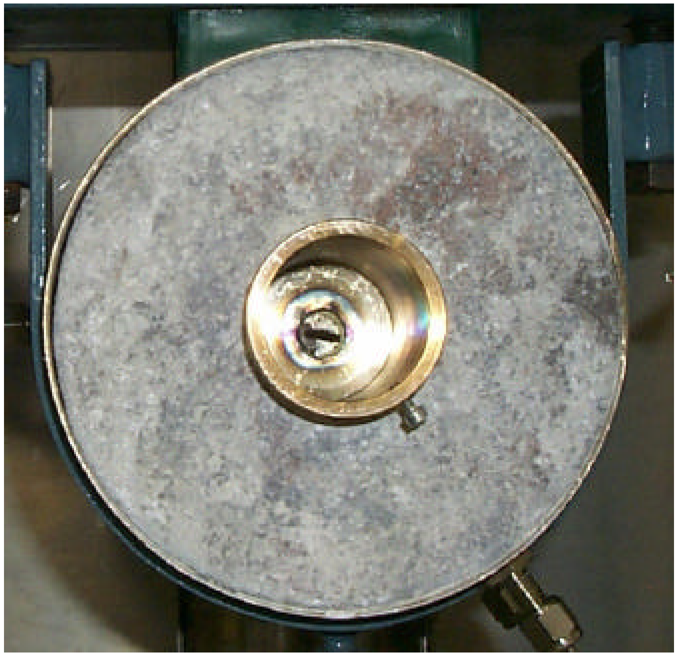
Autoclave setup



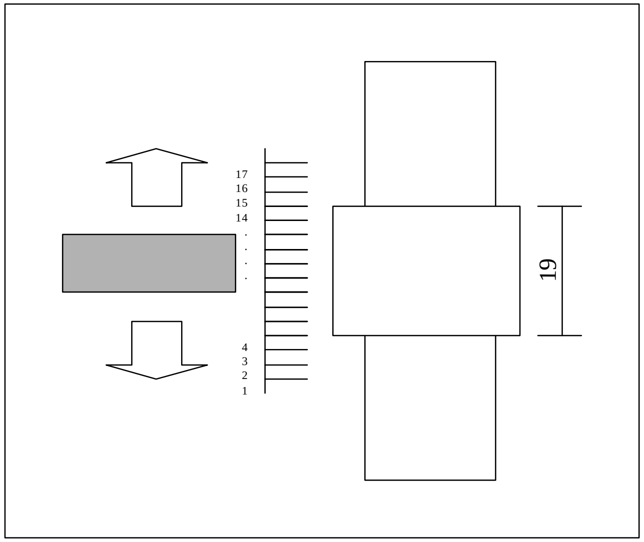
Slit

Dimension: 2 x 10 mm



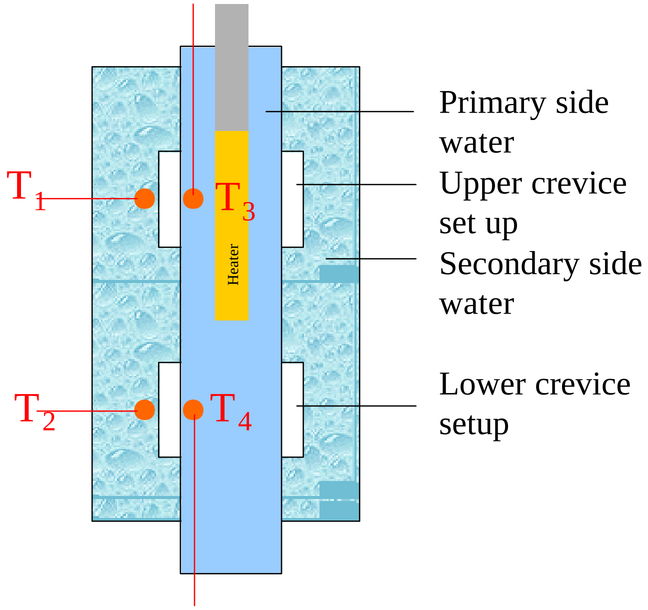


γ-scanner



Control systems

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



Studsvik® Nuclear

Ringhals

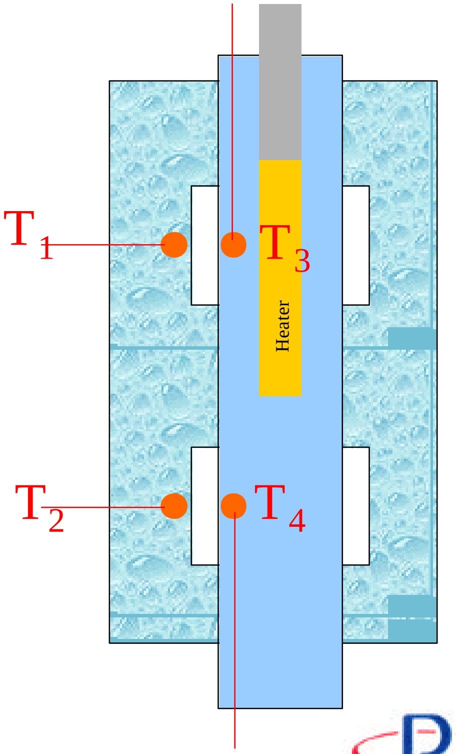
Examination on

Sludged Ringhals TSP

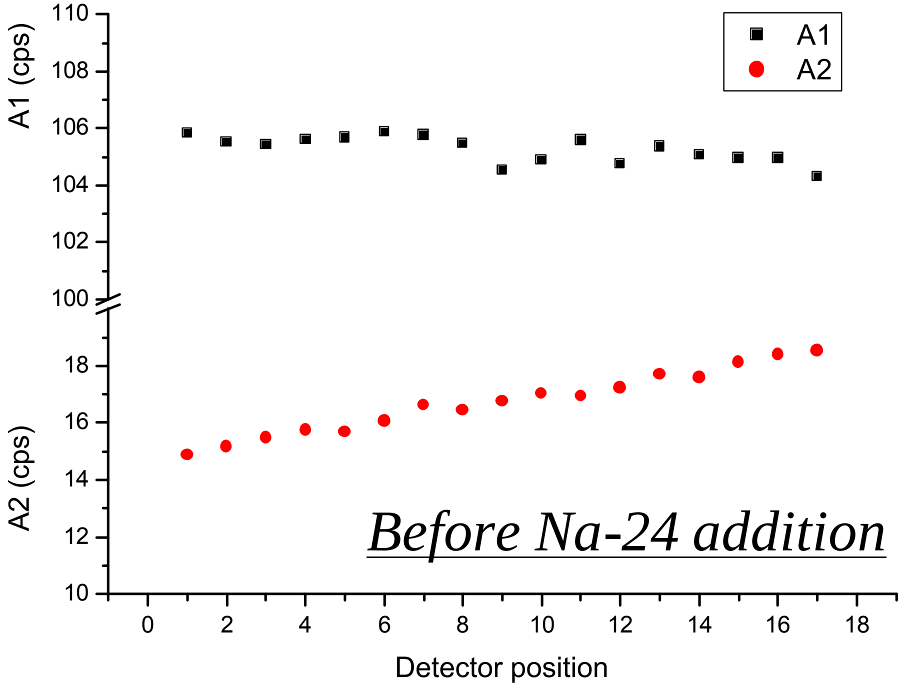
Test conditions

- [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



Activity of as-received Ringhals TSP sample

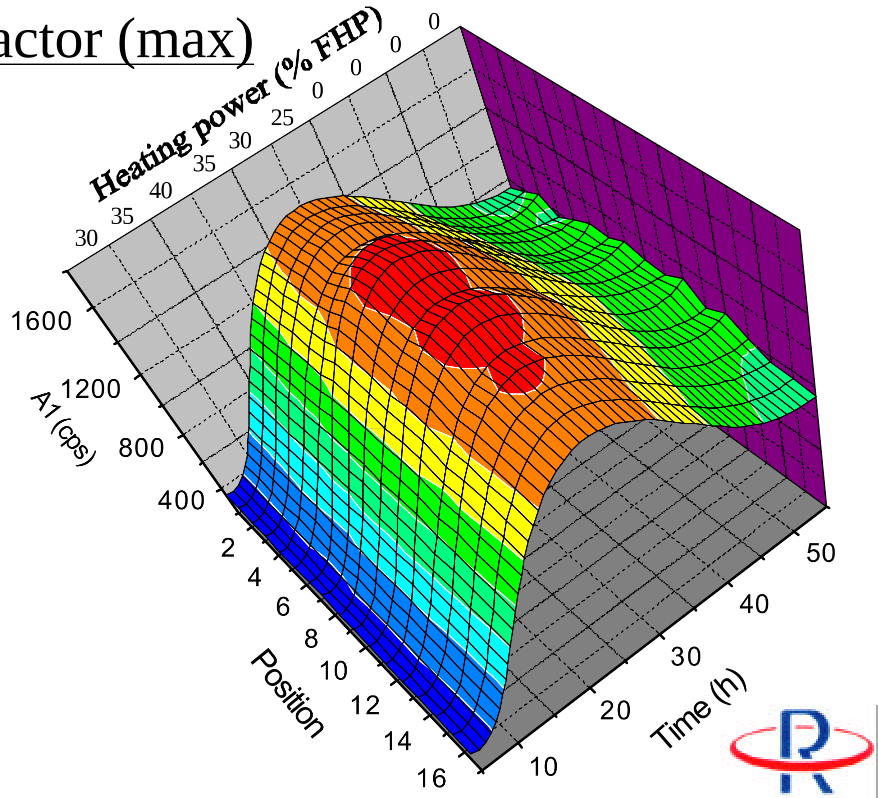


Before Na-24 addition

Studsvik® Nuclear

Ringhals

Hideout and return at the crevice



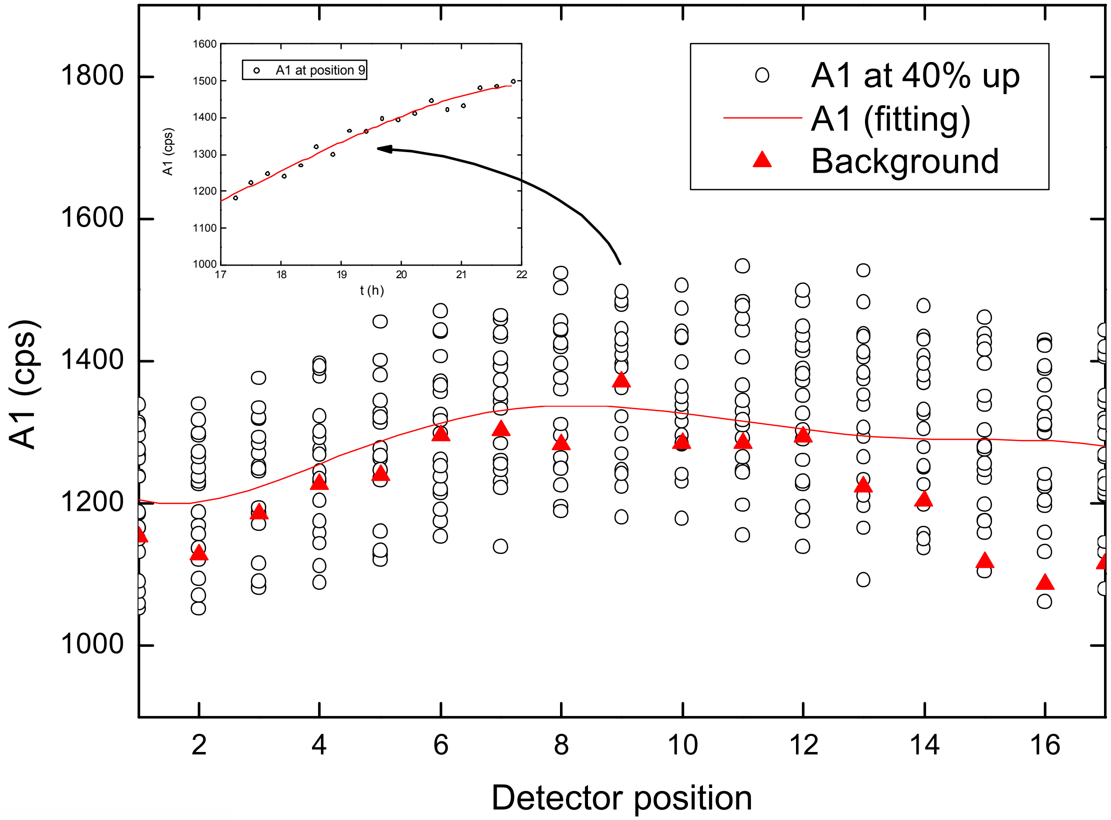
Estimated concentration factor (max)

~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



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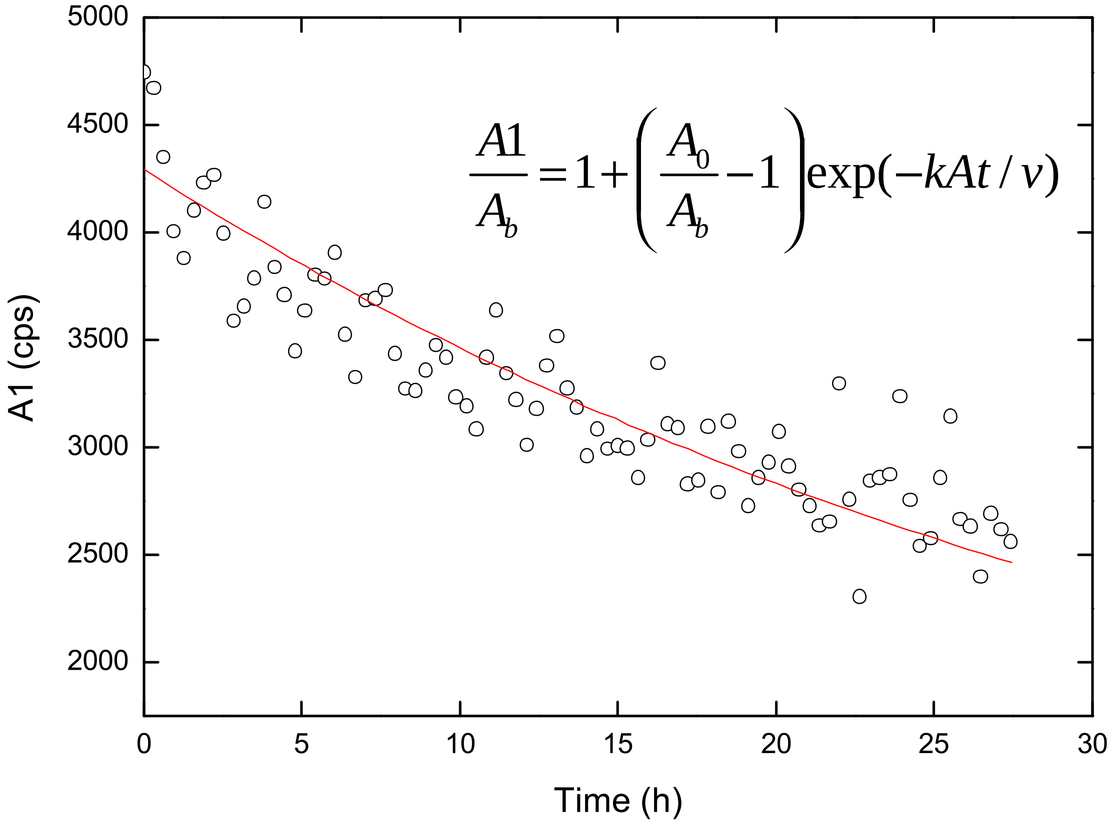
Ringhals

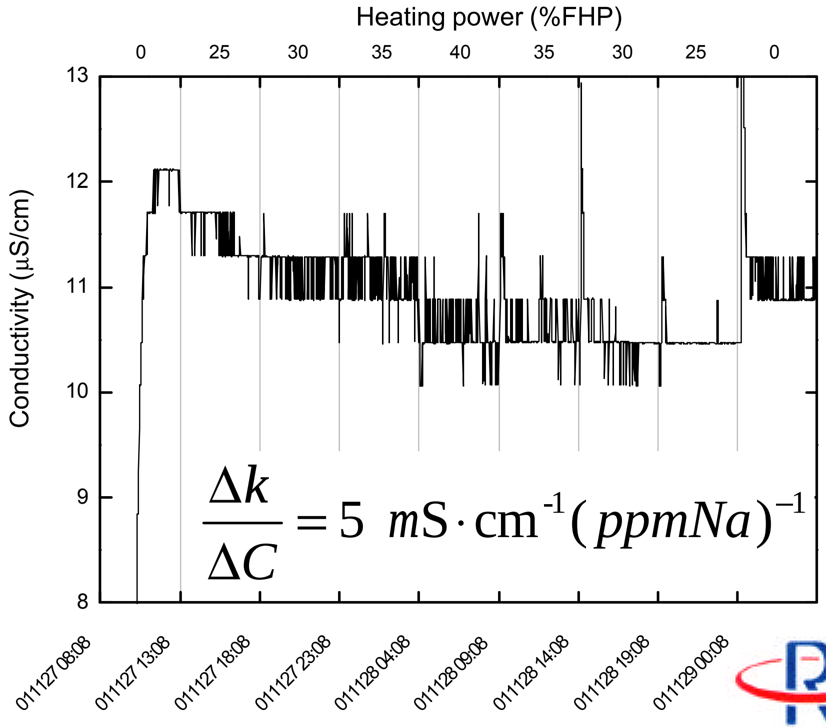
The return



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

Water conductivity change during hideout and return

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



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

Studsvik® Nuclear

Ringhals

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.

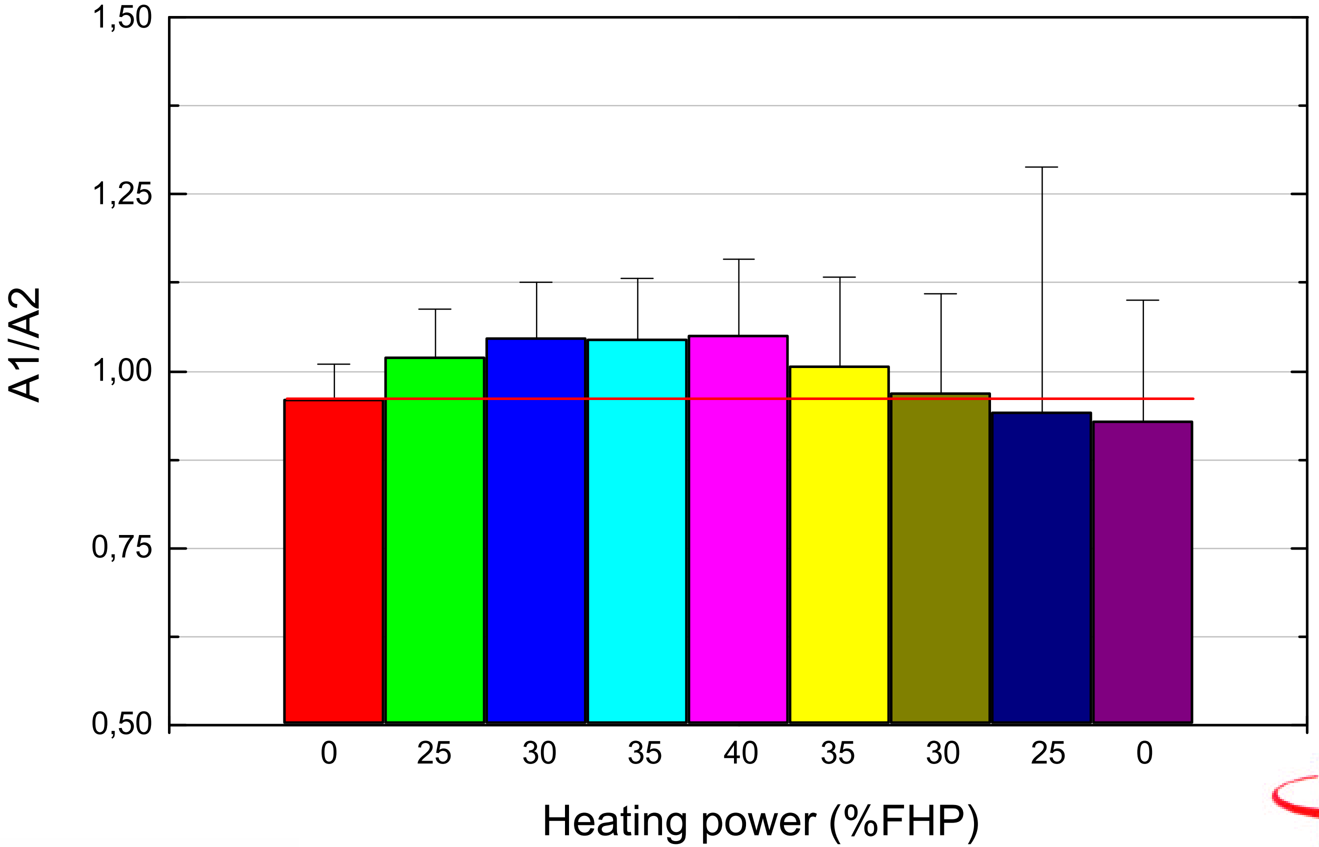
Conclusions (cont.)

- 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.

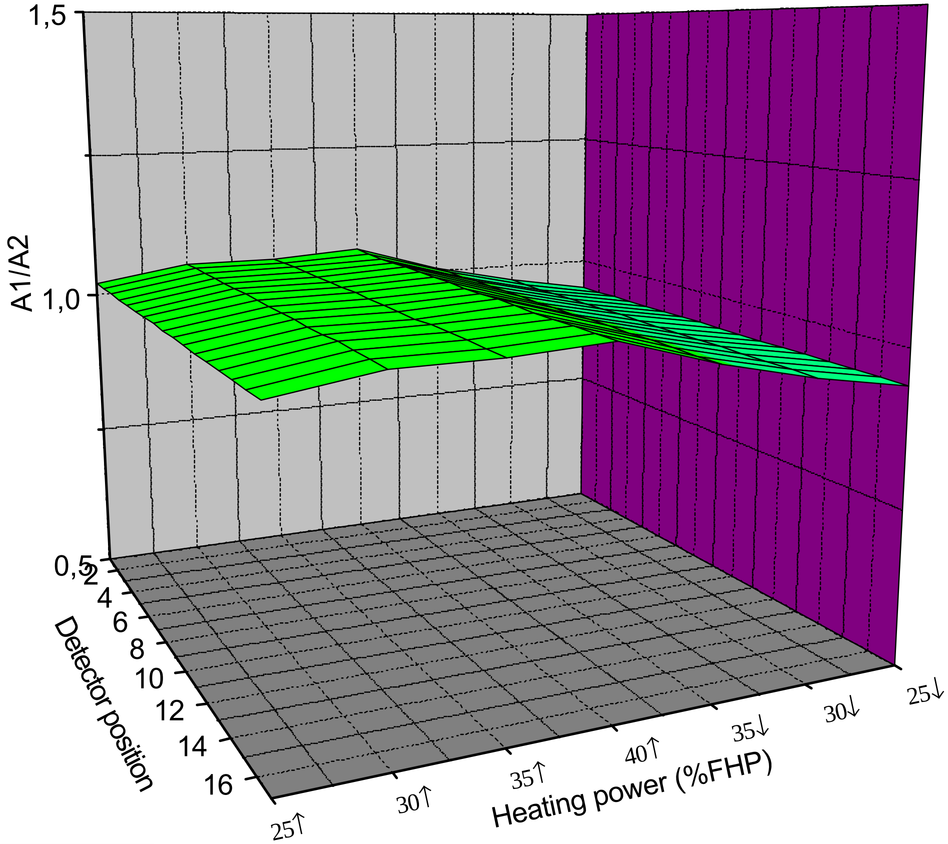
Examination on

A dummy TSP

Dummy crevice test



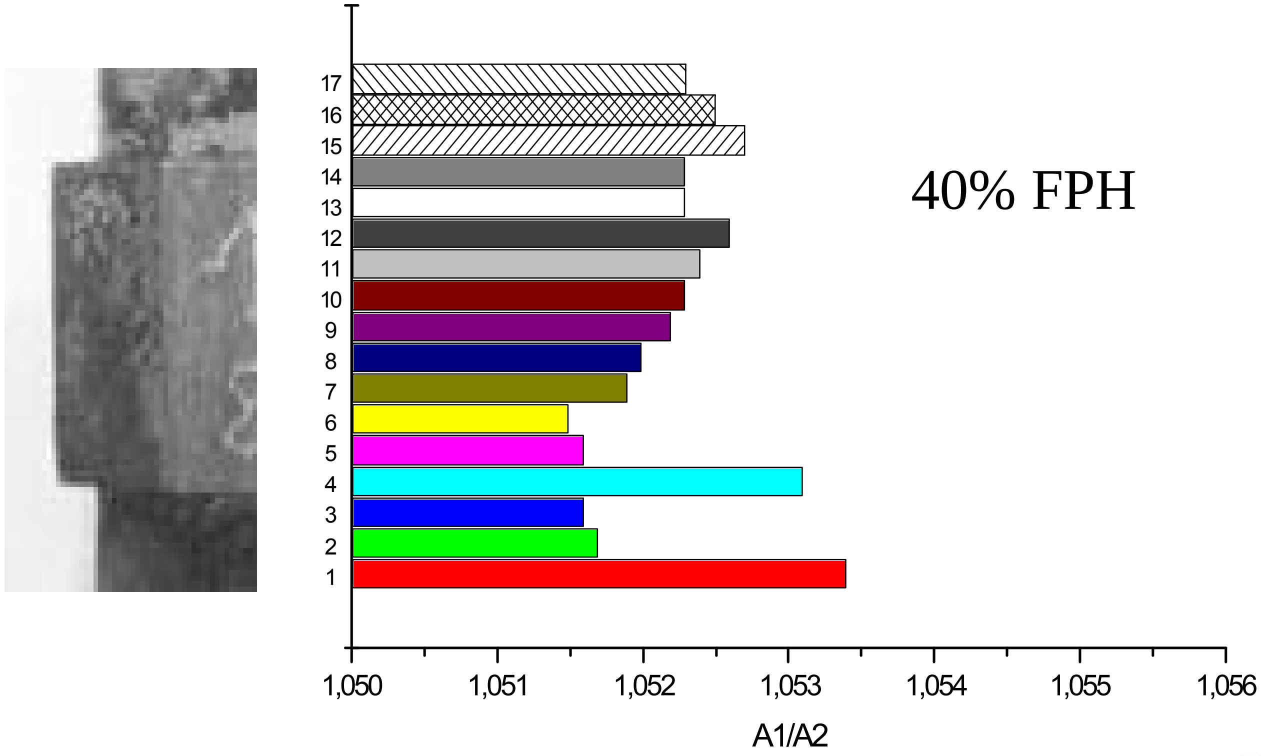
Axial profile of the activity ratio



Studsvik® Nuclear

Ringhals

Axial profile of the activity ratio



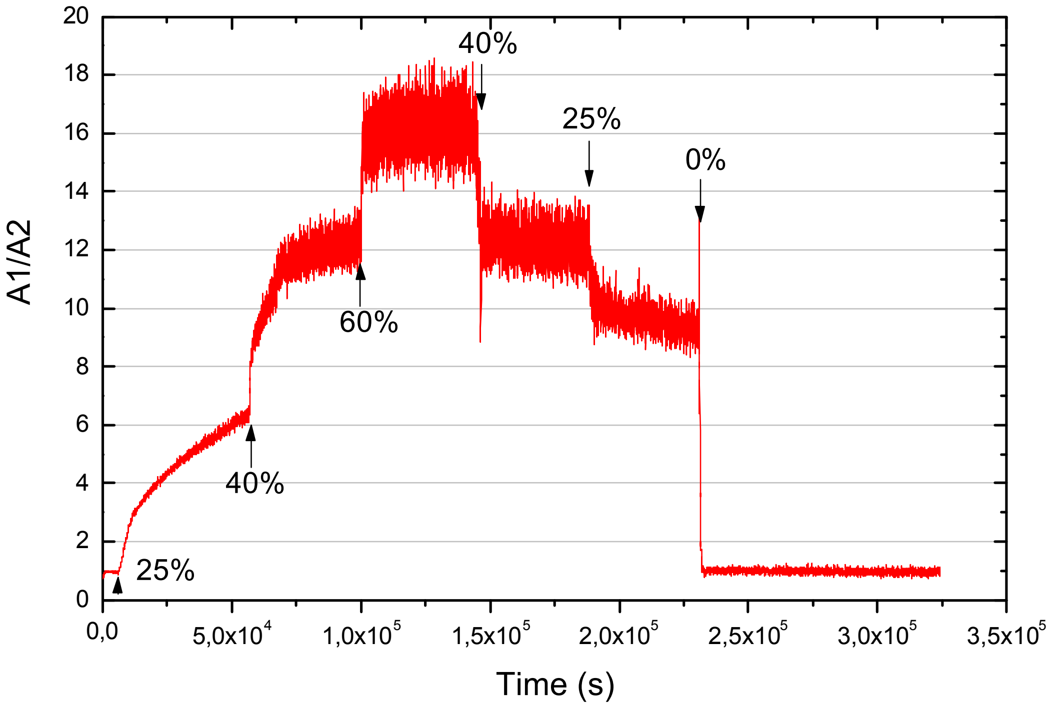
Conclusions for the dummy crevice

- 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

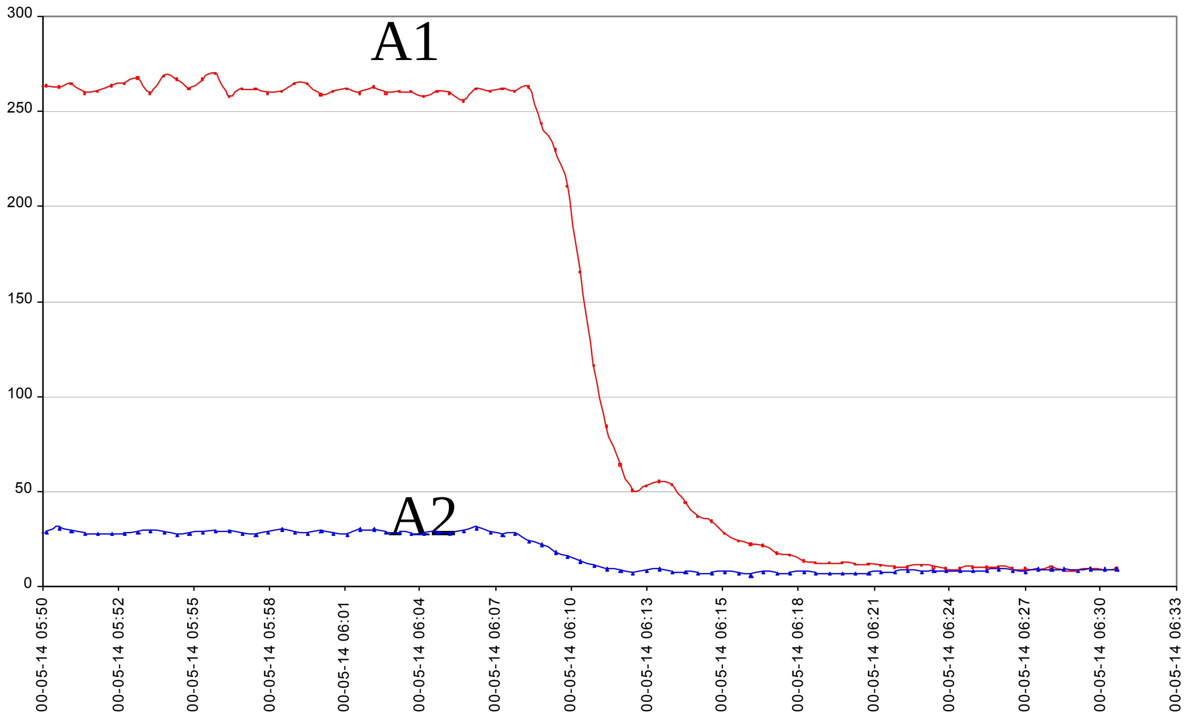
Hideout and return of a metal-net filled TSP crevice



Studsvik® Nuclear

Ringhals

Rapid return at zero power



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

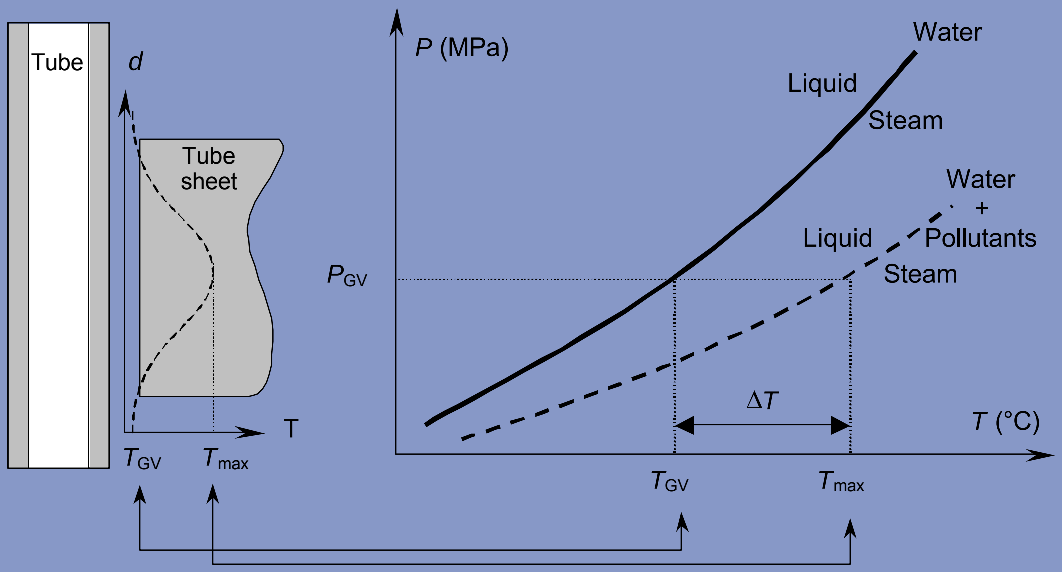
Content

- 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, ...)

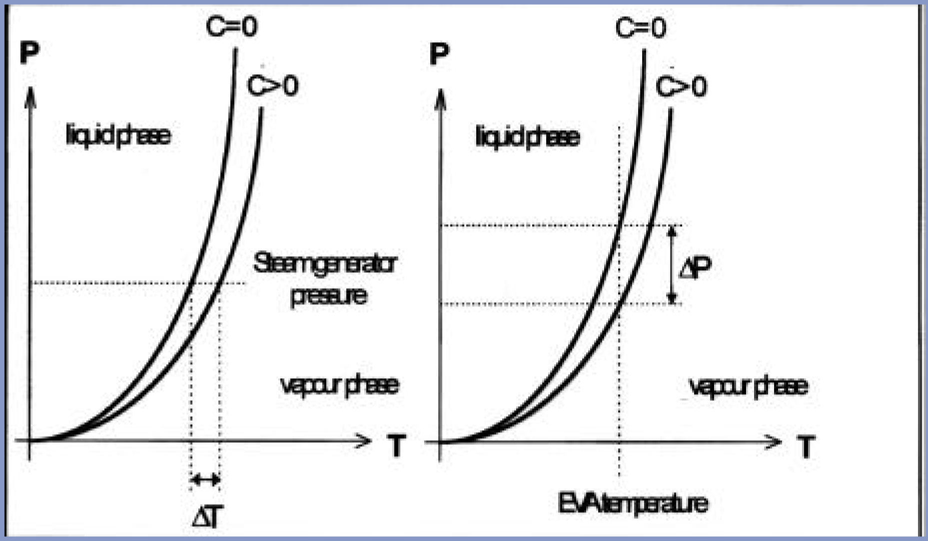
Liquid/vapor equilibrium in crevices



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

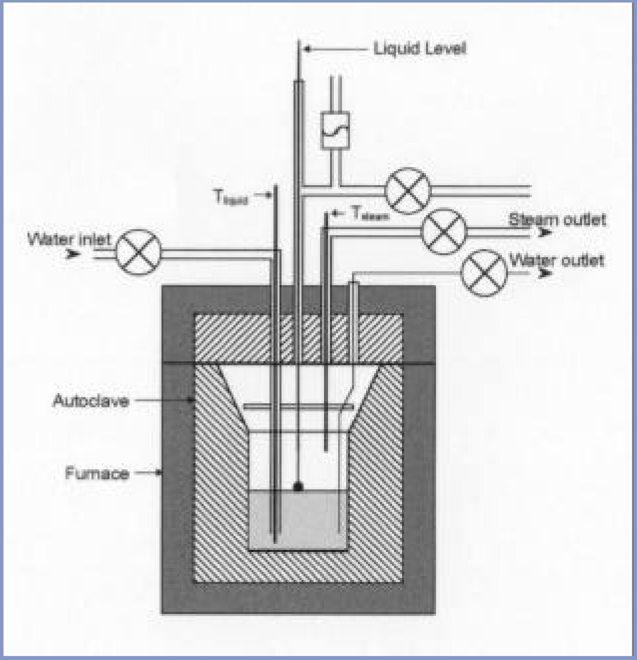
Methodology

- 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

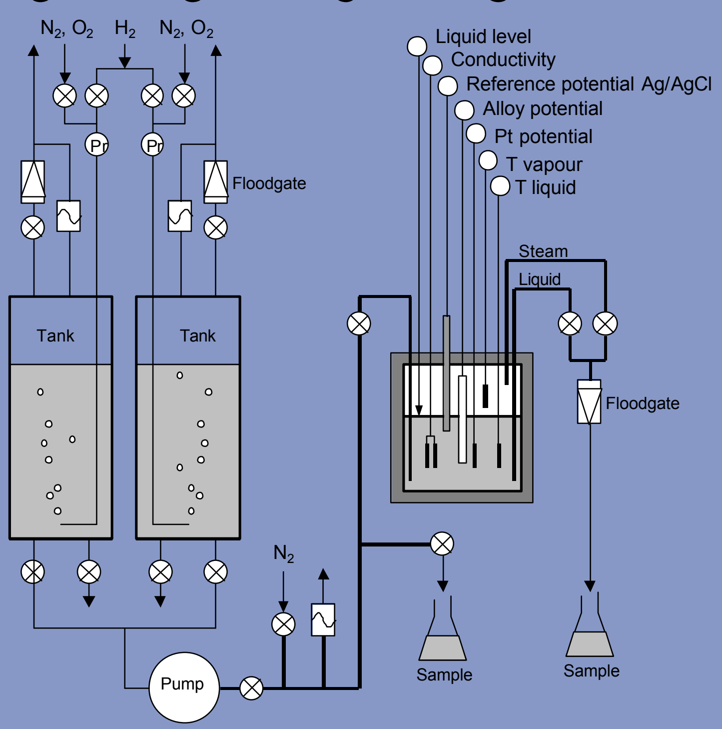


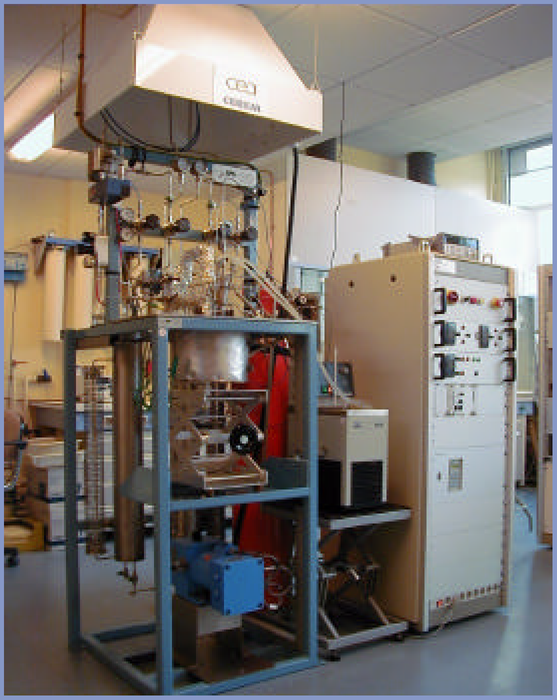
EVA facility

- 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

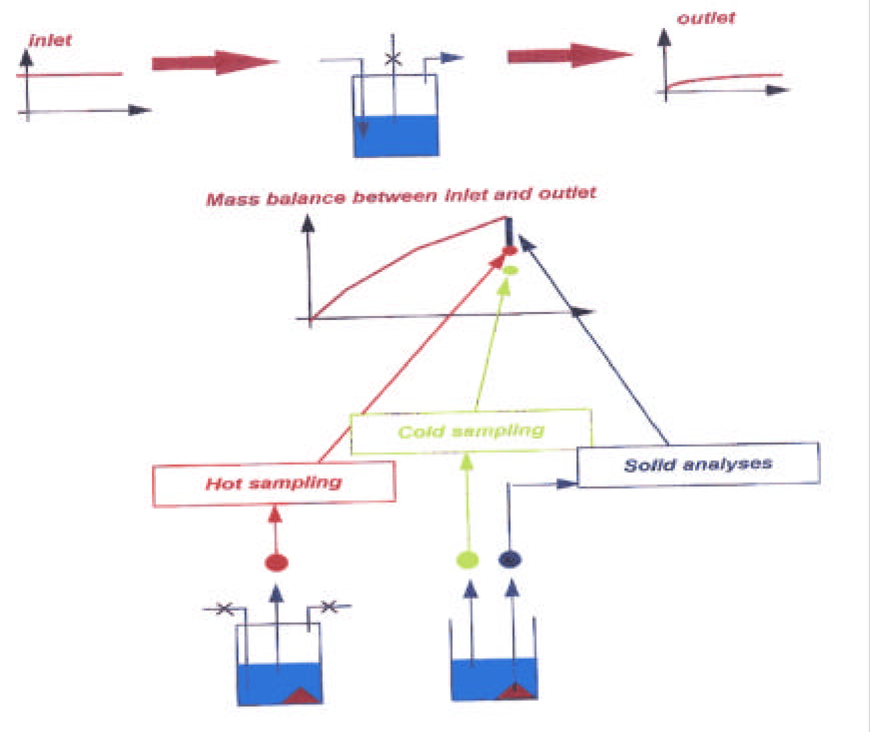


EVA facility (cont'n)





Test methodology



1- Inlet and outlet analyses

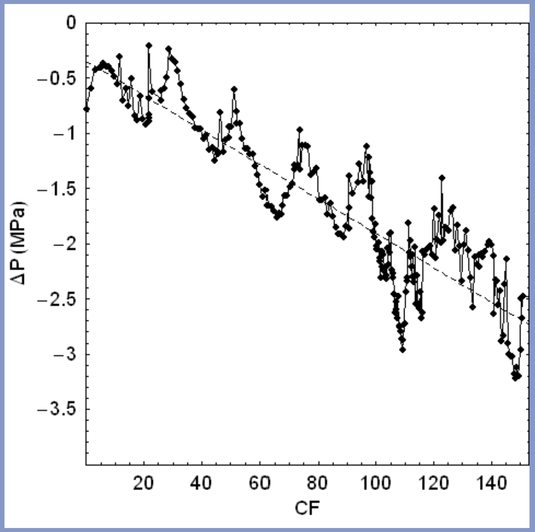
2- Mass balance calculations

3- Sampling at the end of

1. Hot liquid phase (or a hideout return phase)
2. Cold liquid phase
3. Solid phases

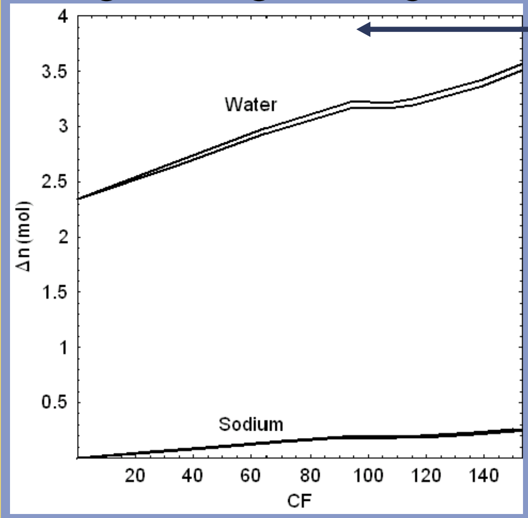
NaOH results (1)

- 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)

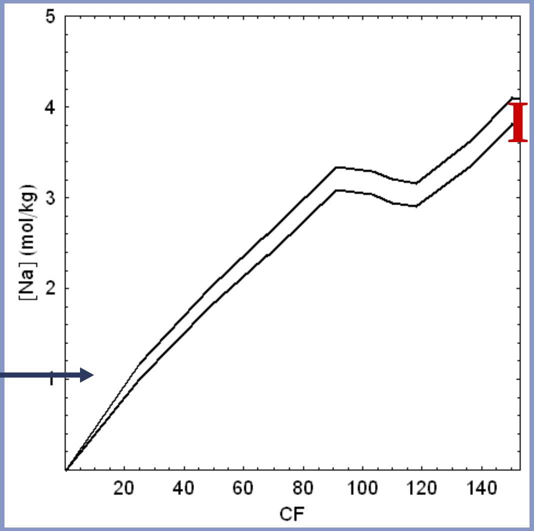


Decrease of the internal pressure during the caustic EVA hideout test

NaOH results (2)



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

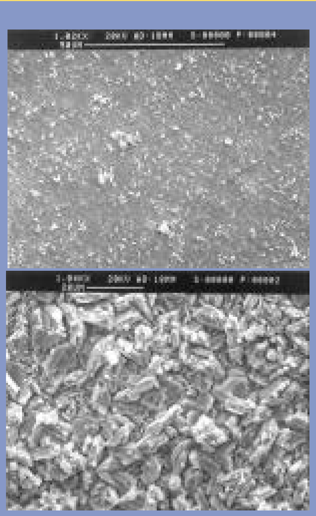


Evolution of the caustic concentration inside the EVA device during the caustic hideout test: good agreement with the sampling of the liquid phase at the end of the hideout period

NaOH results (3): after test examinations

Vapour phase

Liquid phase



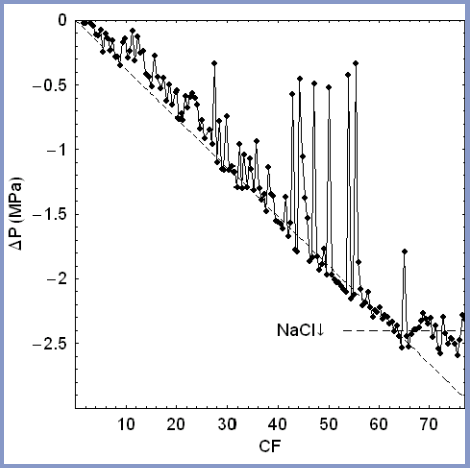
Hydrated iron and nickel silicate
$(Ni,Fe)_3Si_2O_5(OH)_4$

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

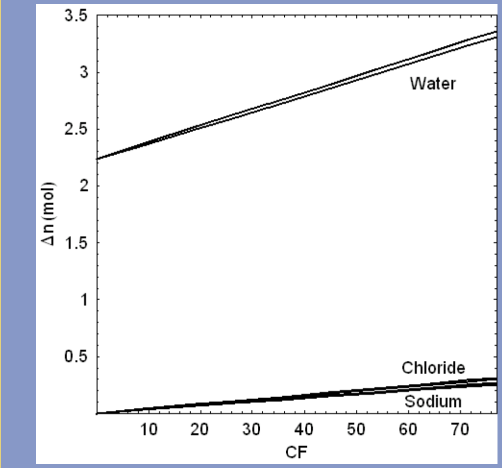
« NaCl » results (1)

- 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).

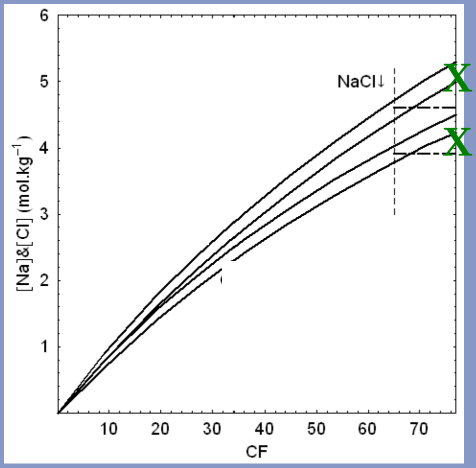


Evolution of the internal pressure during the NaCl pollution test

NaCl results (2)

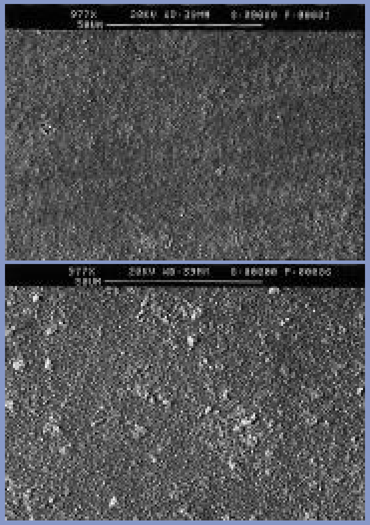


Increase of water and sodium masses during the “NaCl” hideout test (density of the liquid phase: +85%)



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



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.

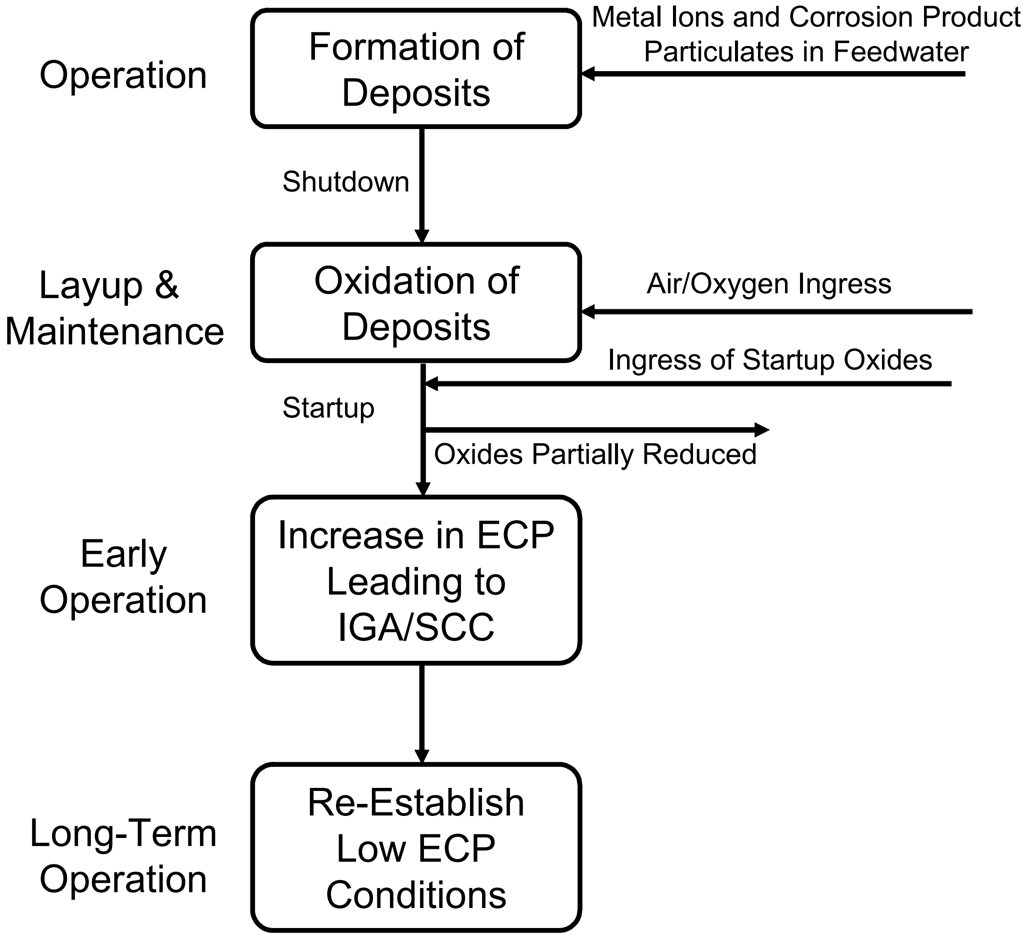
Dominion Engineering, Inc.
11730 Plaza America Drive
Reston, Virginia 20190

Overview of Presentation

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

Project Background

Startup Oxide Theory



Operation

Formation of Deposits

Metal Ions and Corrosion Product Particulates in Feedwater

Shutdown

Layup & Maintenance

Oxidation of Deposits

Air/Oxygen Ingress

Ingress of Startup Oxides

Startup

Oxides Partially Reduced

Early Operation

Increase in ECP Leading to IGA/SCC

Long-Term Operation

Re-Establish Low ECP Conditions

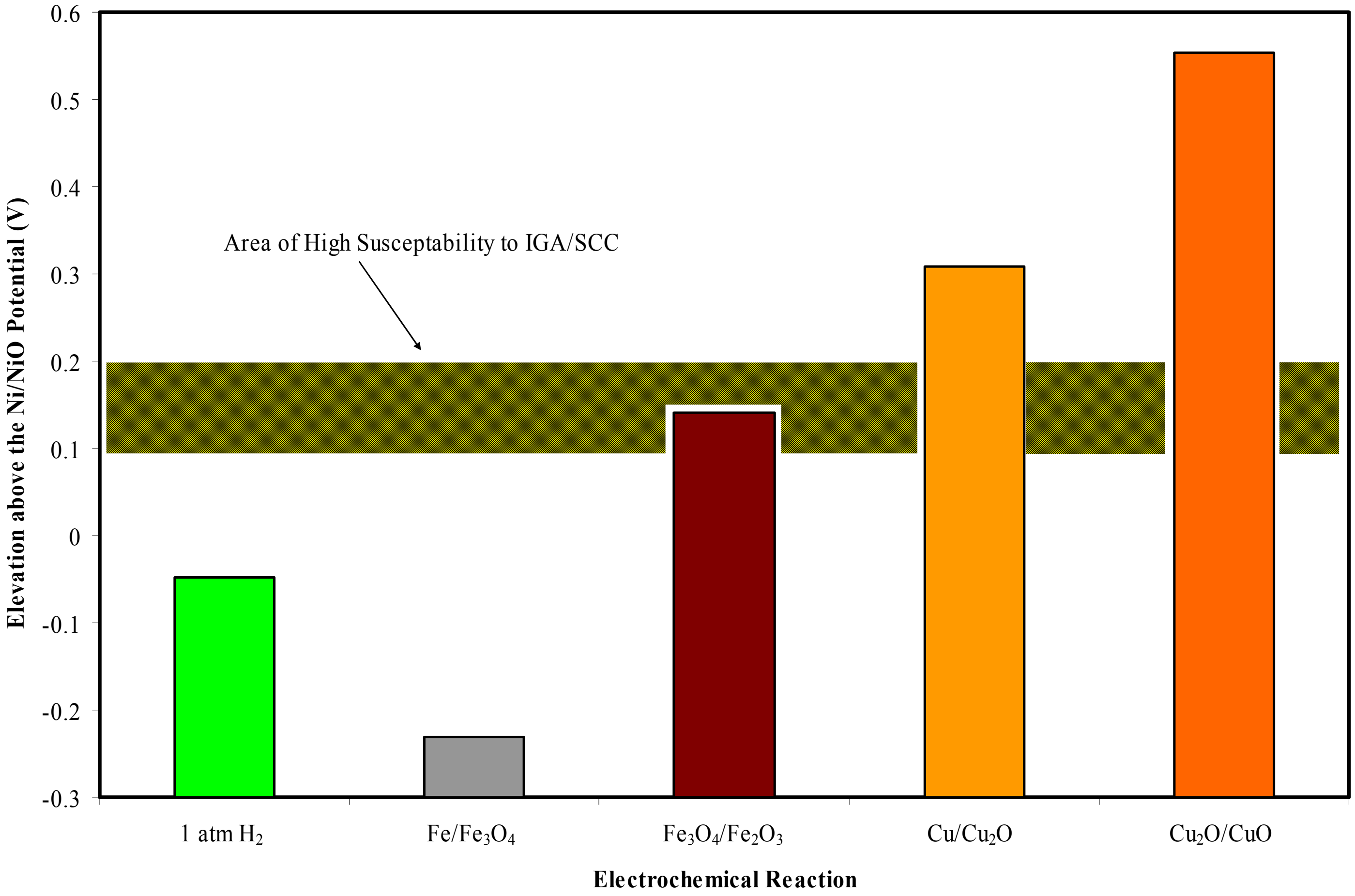
Project Background

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

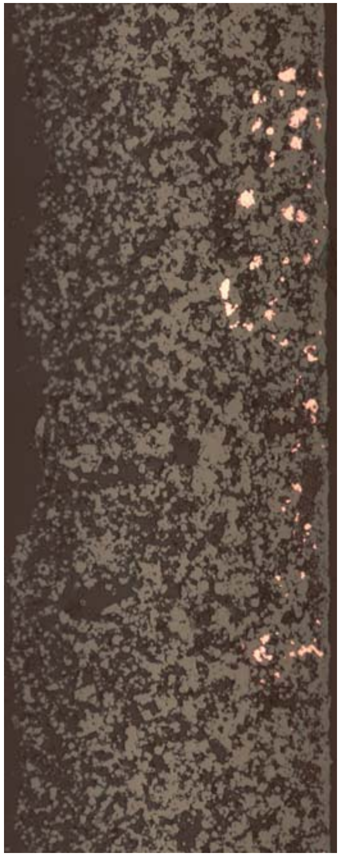
Deposit Characterization

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

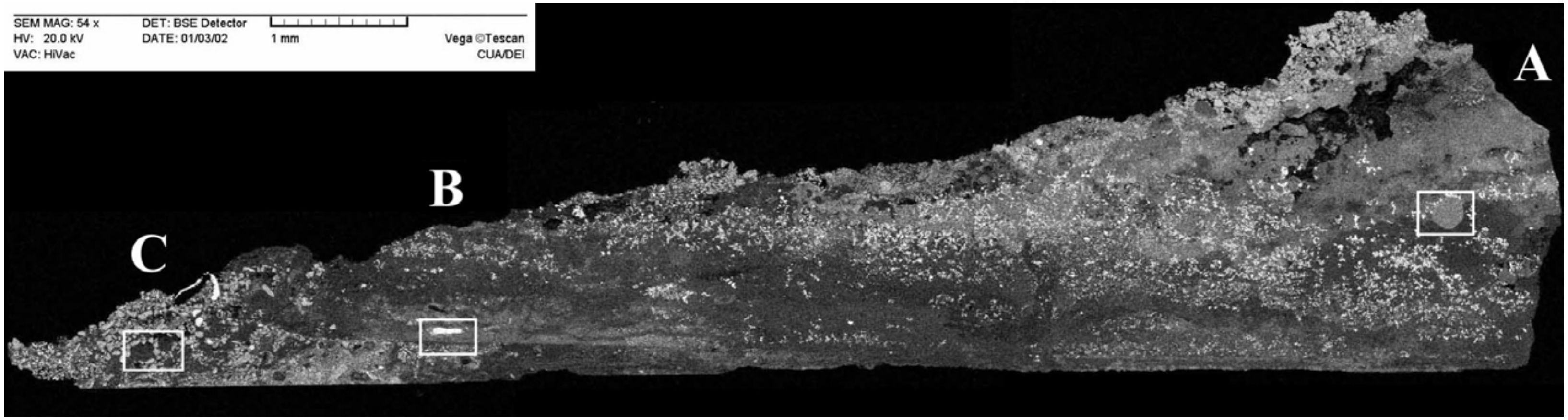
Collar (Deposits Adjacent to Crevices) Compositions

- 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

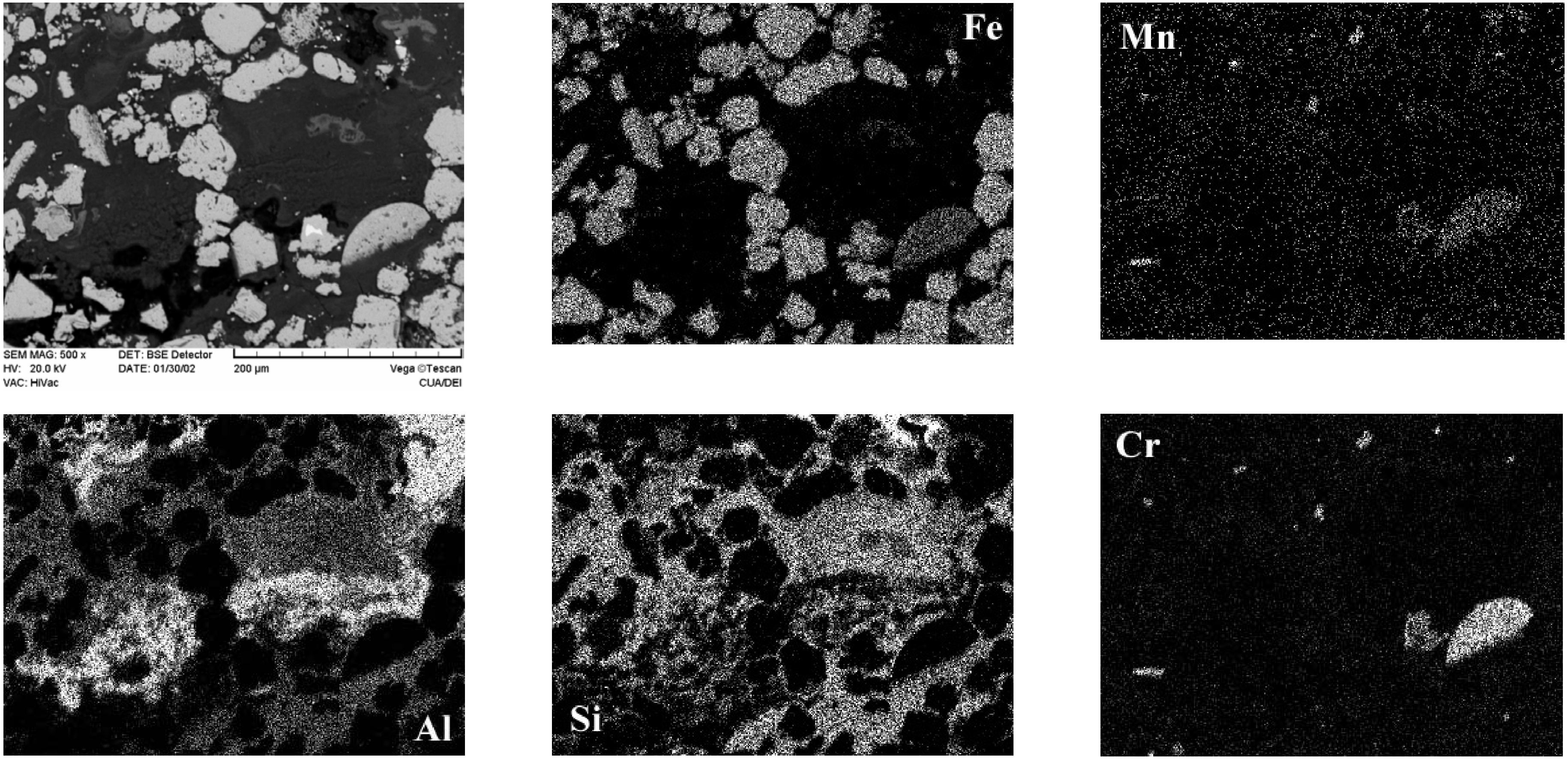
Deposit Characterization

"Typical" Collar



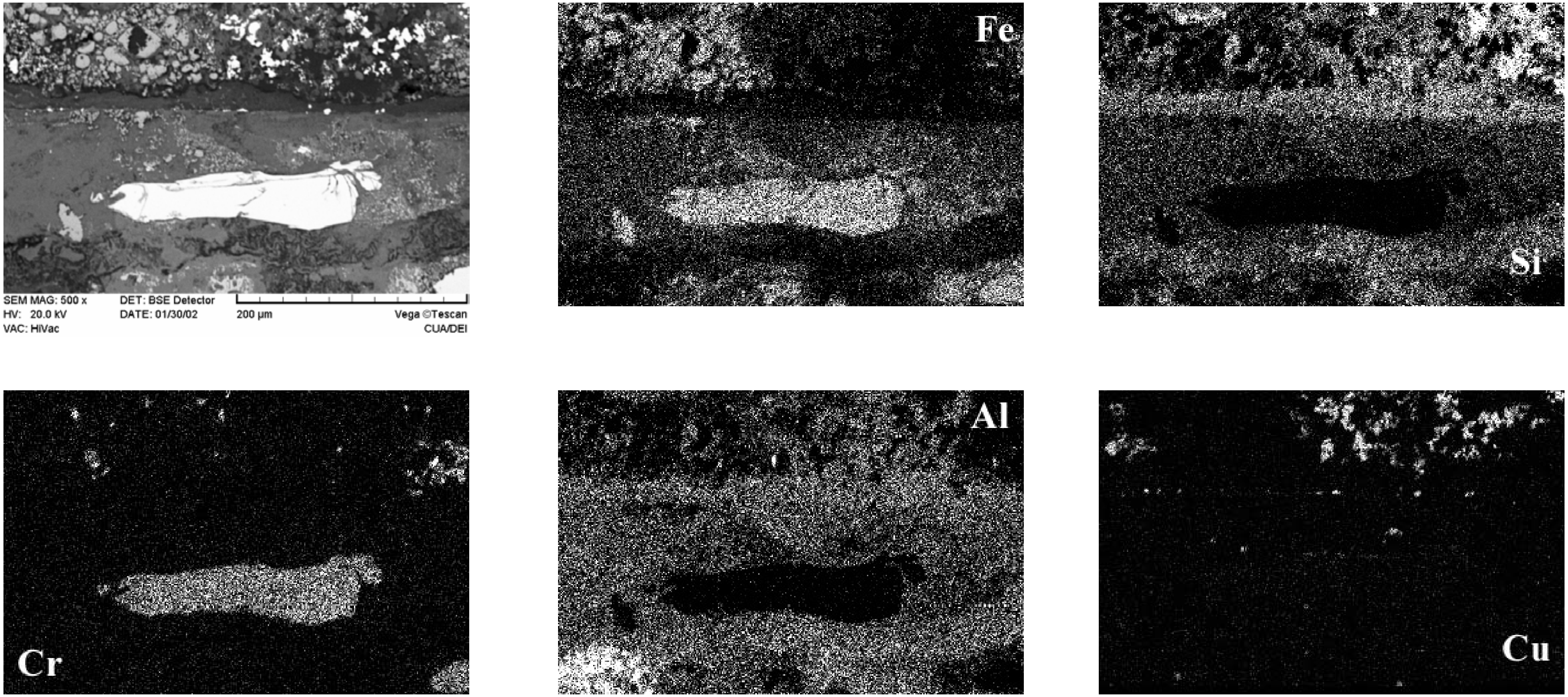
Deposit Characterization

Heterogeneous Morphology—Area A



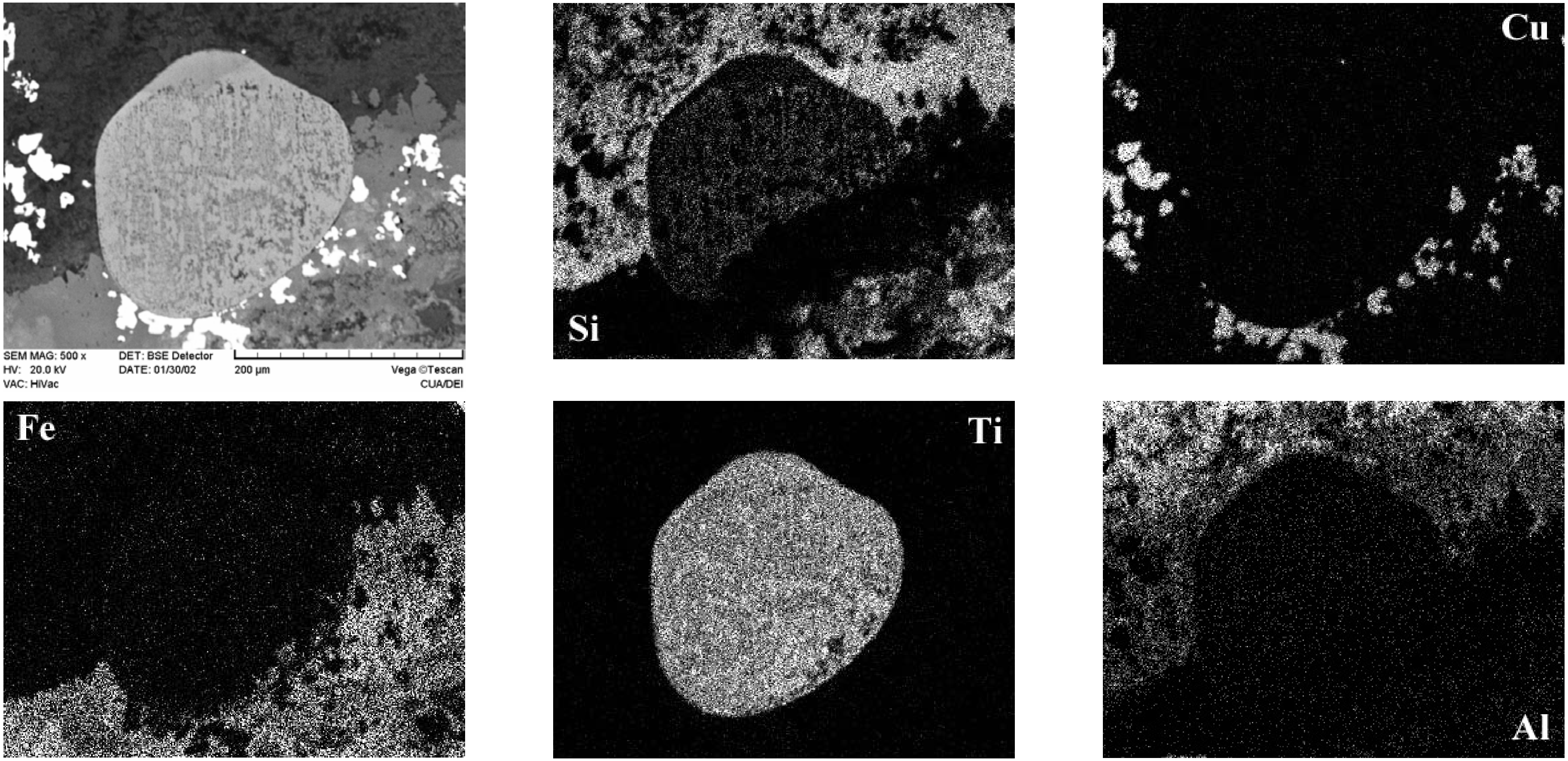
Deposit Characterization

Heterogeneous Morphology—Area B



Deposit Characterization

Heterogeneous Morphology—Area C



Deposit Characterization

Implications for Crevice Chemistry

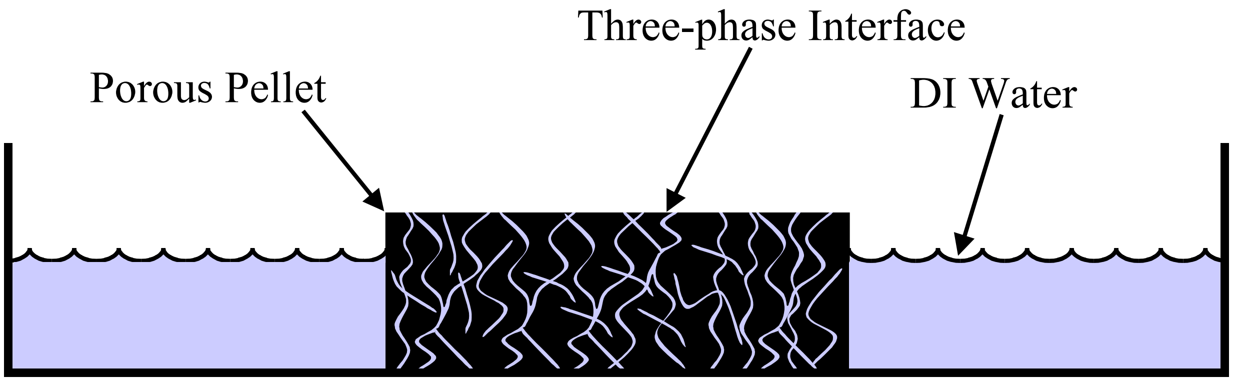
- Variations in crevice chemistry
  - Plant to plant variability
  - Crevice to crevice variability
  - Magnetite packing is not necessarily realistic
- May need to consider plant history
  - Collars may contain residual chemicals from early operation
- Deposit variability may be mitigated by consolidation 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

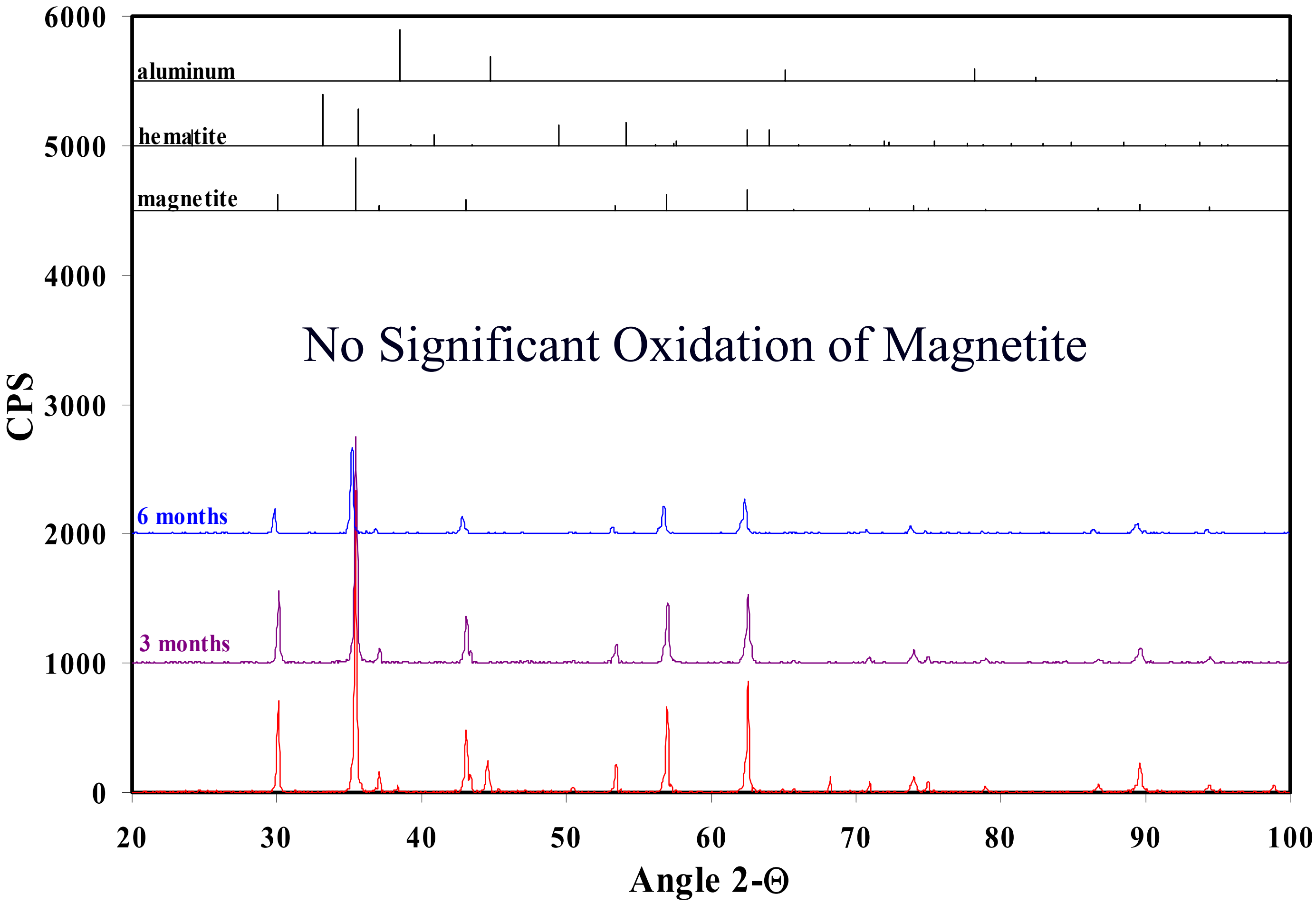


Room Temperature
Untreated DI water
6 month exposure
Pellets of SG Powder, Crushed SG Flakes or Synthetic Magnetite

Oxidation determined by XRD of Pellet

Deposit Oxidation Rates During Layup/Shutdown

Magnetite—Pellet Experiment Results



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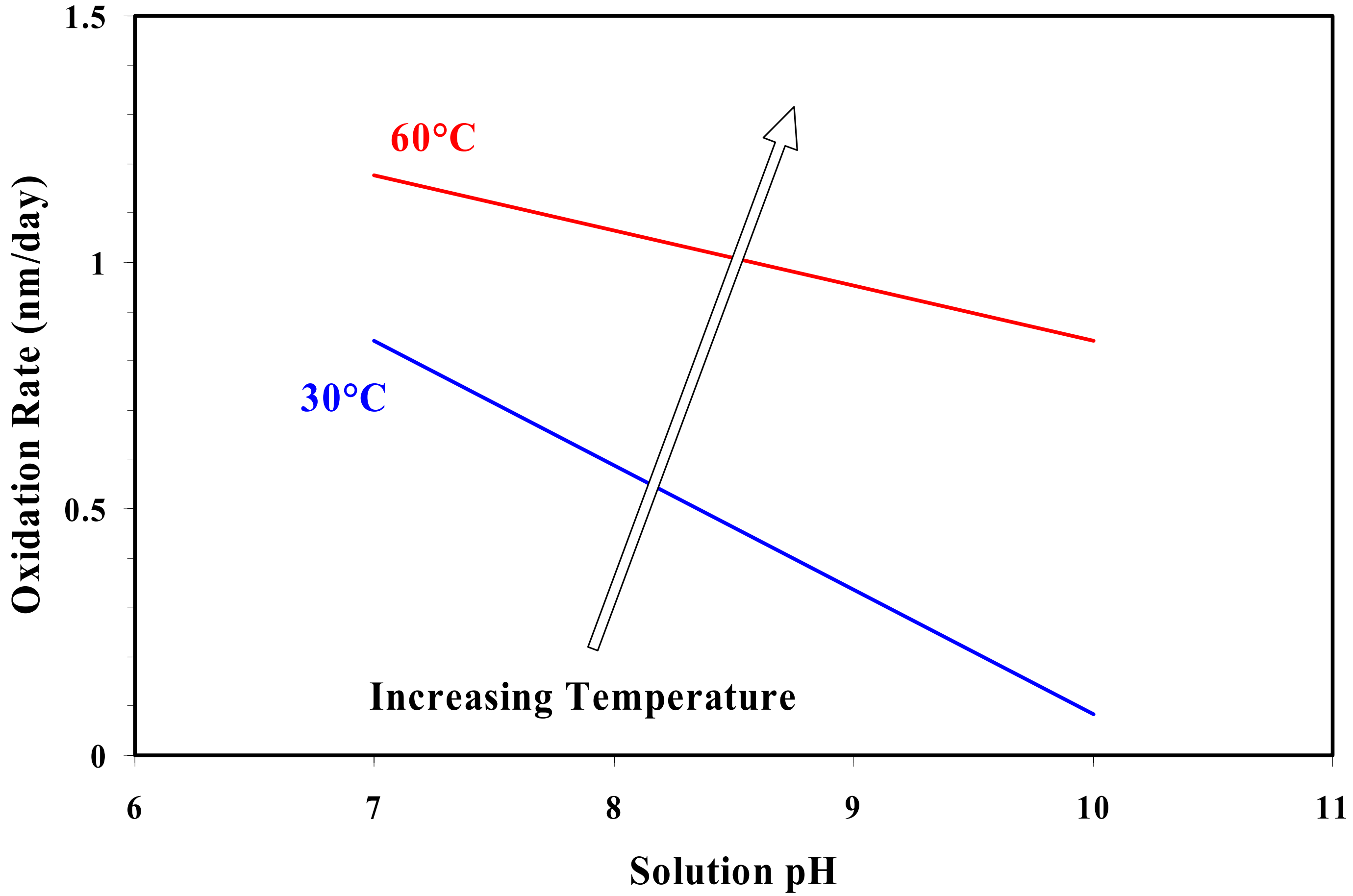
Deposit Oxidation Rates During Layup/Shutdown

Copper—Aqueous Oxidation



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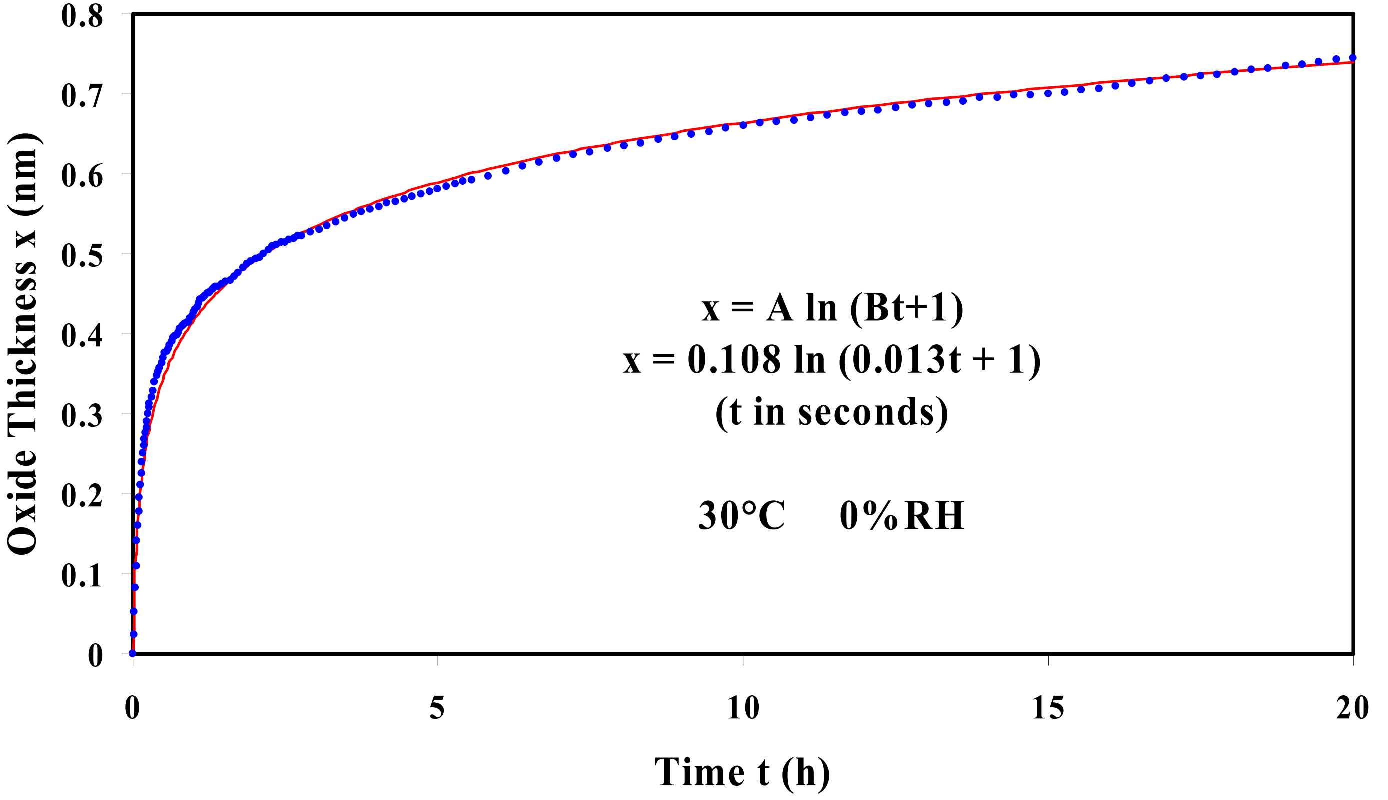
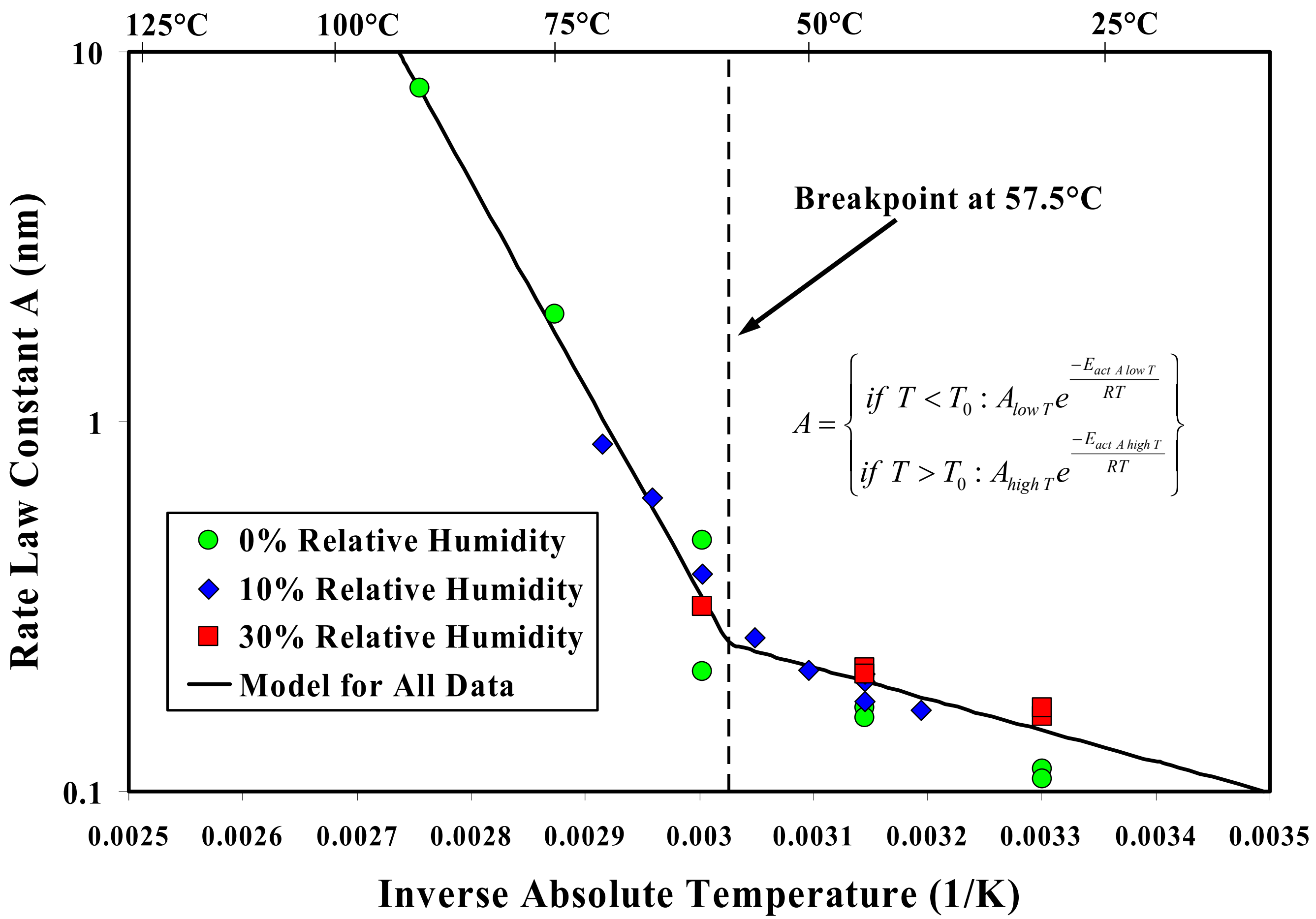
Deposit Oxidation Rates During Layup/Shutdown

Copper—Atmospheric Oxidation



Deposit Oxidation Rates During Layup/Shutdown

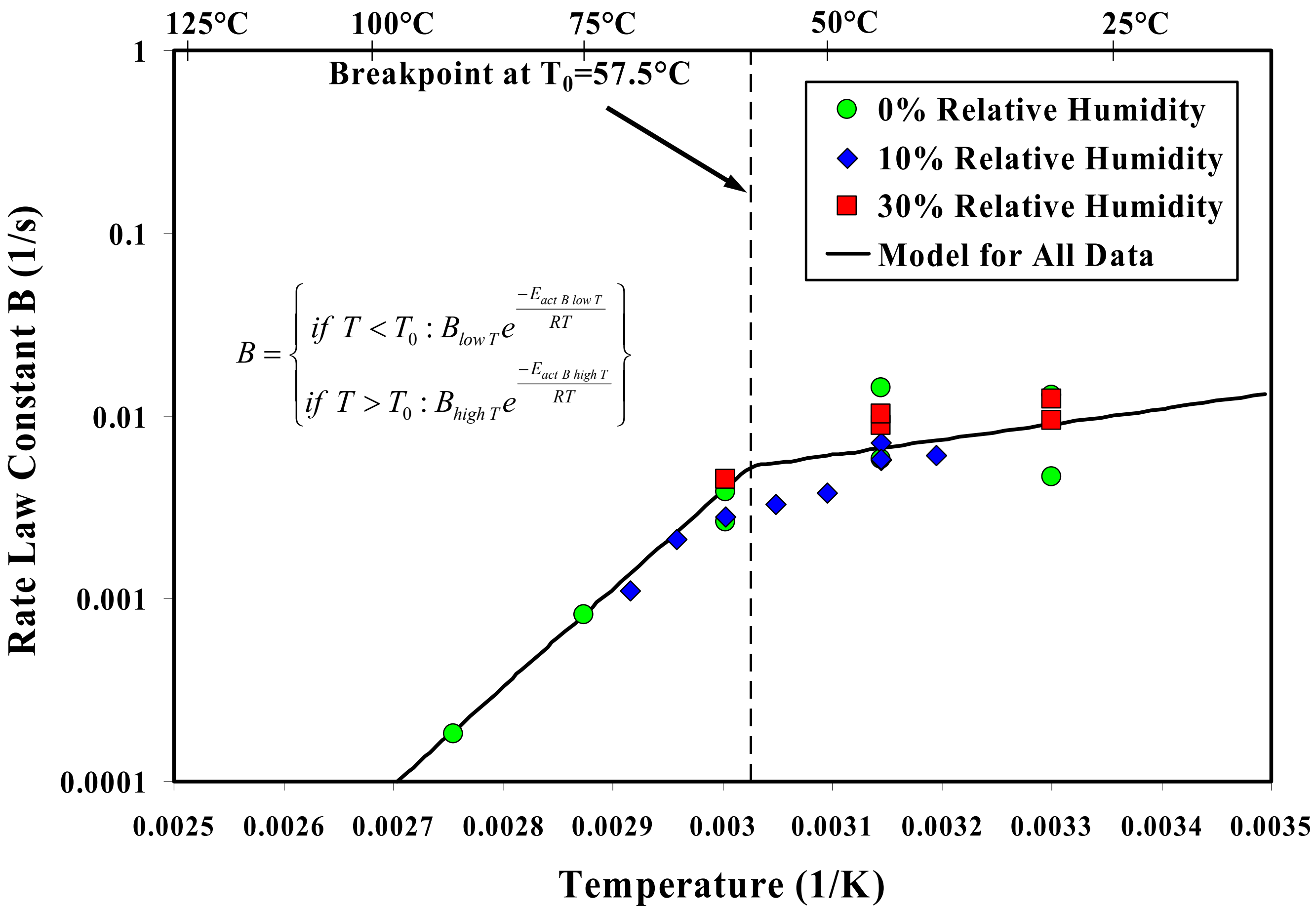
Copper—Atmospheric Oxidation Parameters



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

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

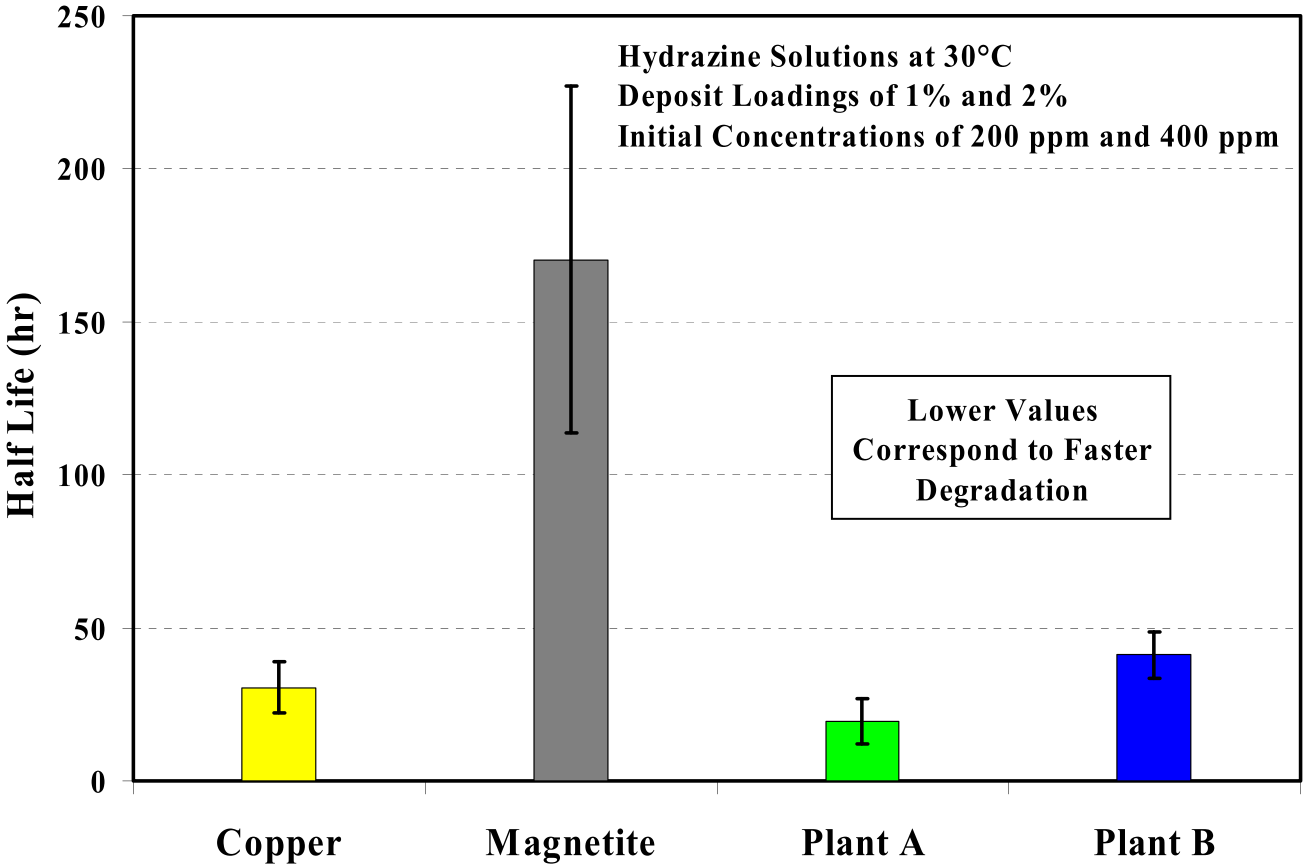
- No significant oxidation of magnetite
- Copper is easily oxidized
- Copper oxidation rates characterized
  - Atmospheric oxidation
  - Aqueous oxidation
- Can determine the extent of oxidation (oxide thickness) from outage schedule
  - Necessary component to assessing degree of oxidation at operating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

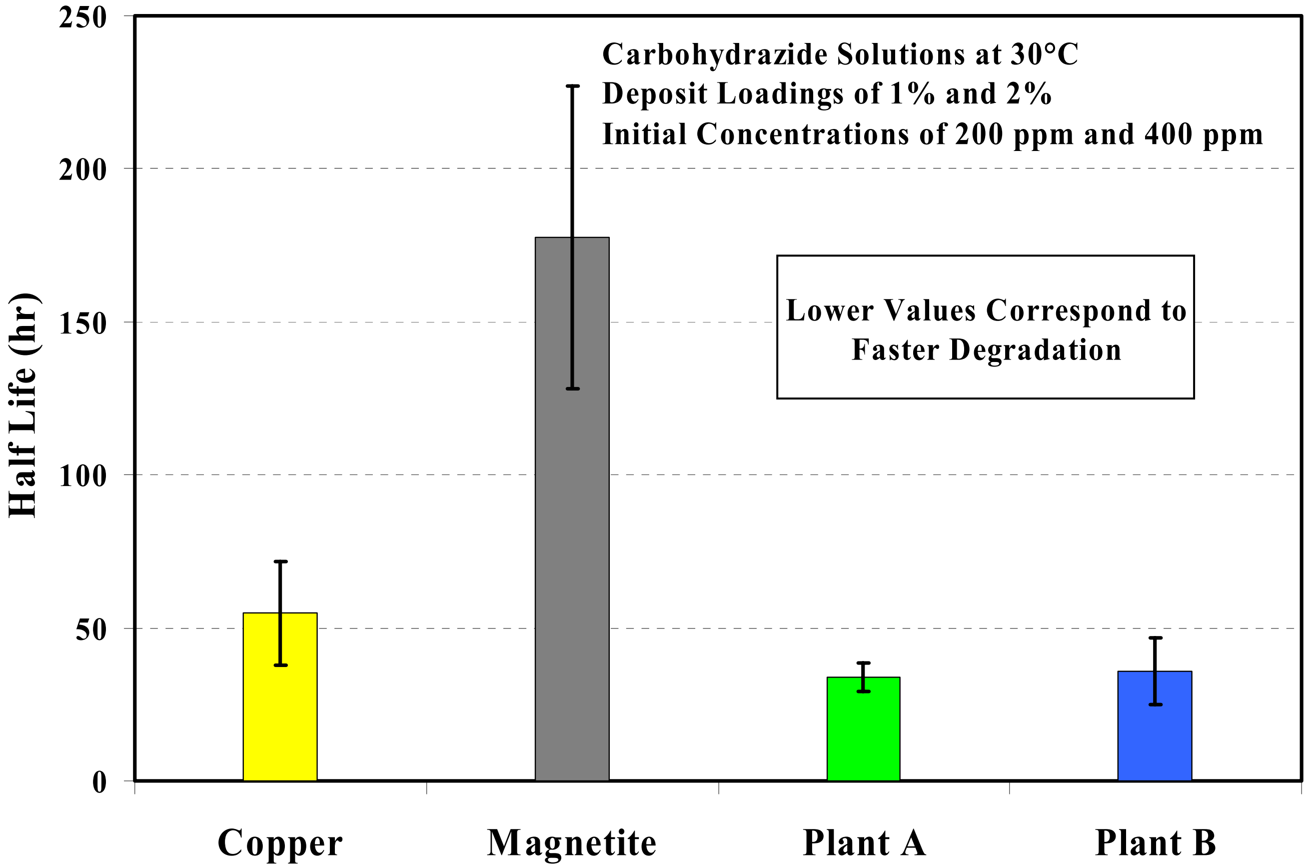
Oxygen Scavenger Decomposition

Hydrazine and SG Deposits



Oxygen Scavenger Decomposition

Carbohydrazide and SG Deposits

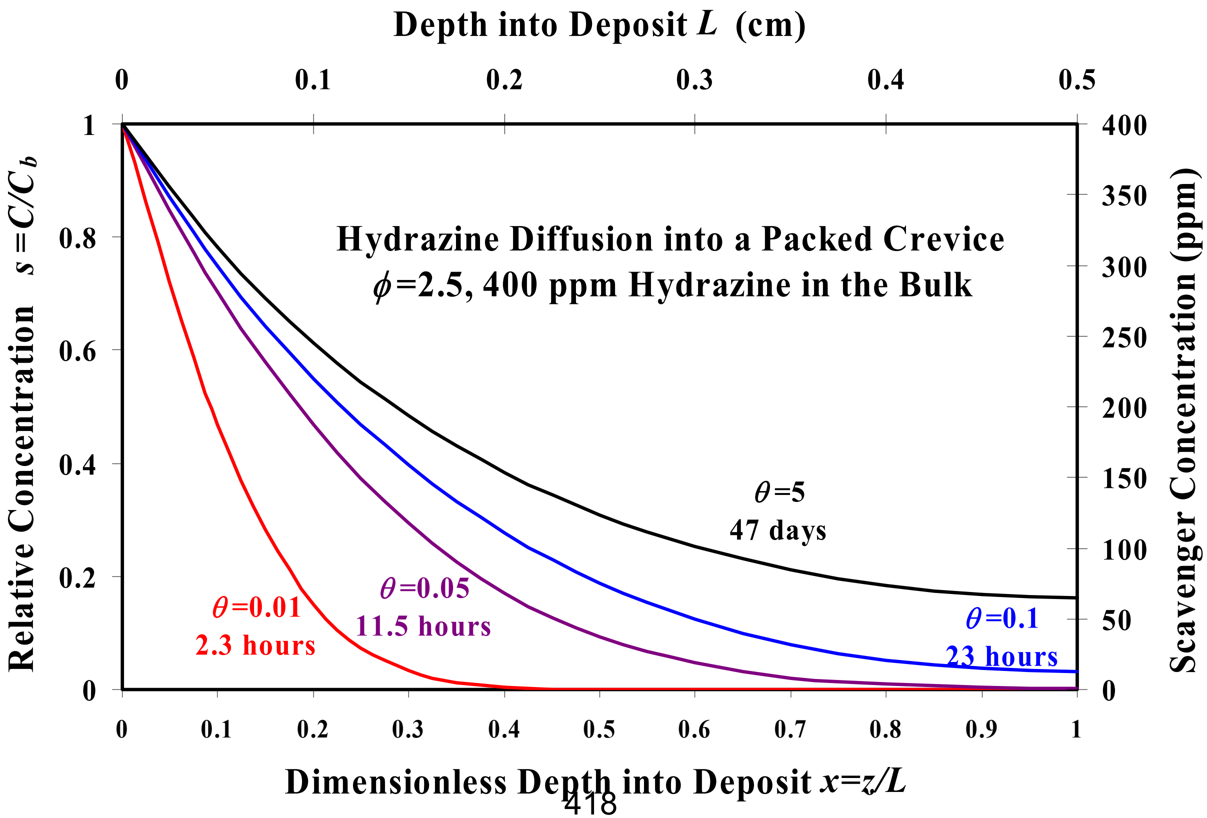


Oxygen Scavenger Decomposition
Diffusion/Reaction Modeling

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

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

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



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

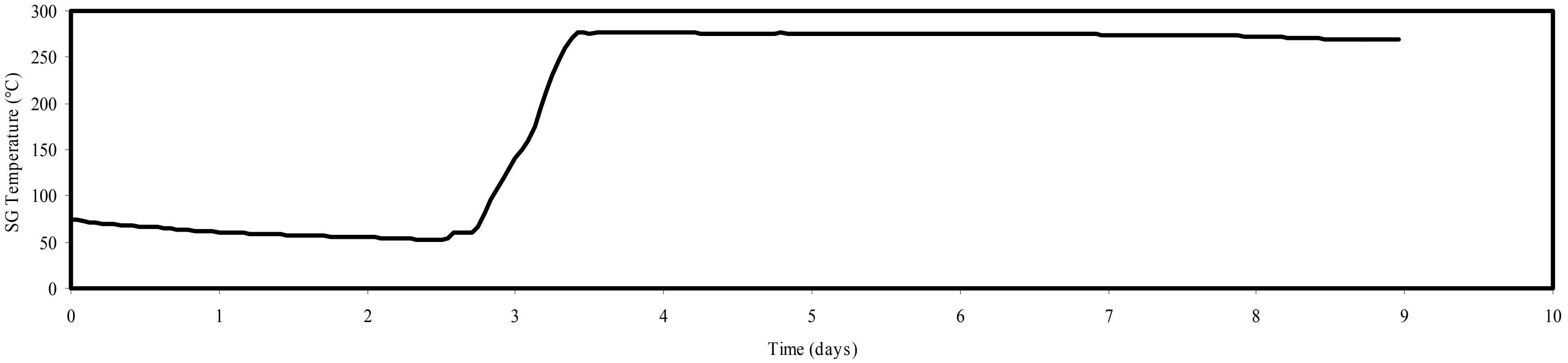
Startup Conditions

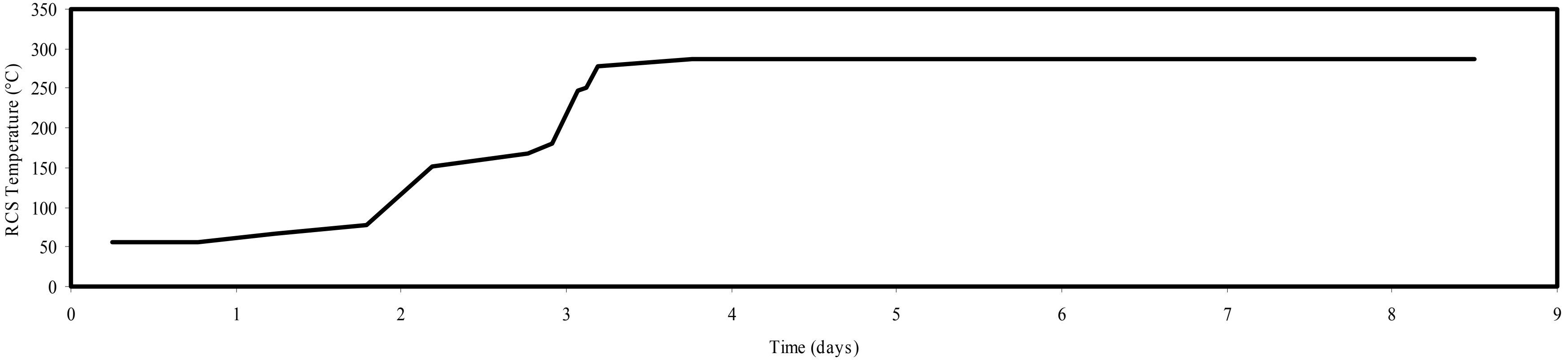
Differences between Plants

- 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

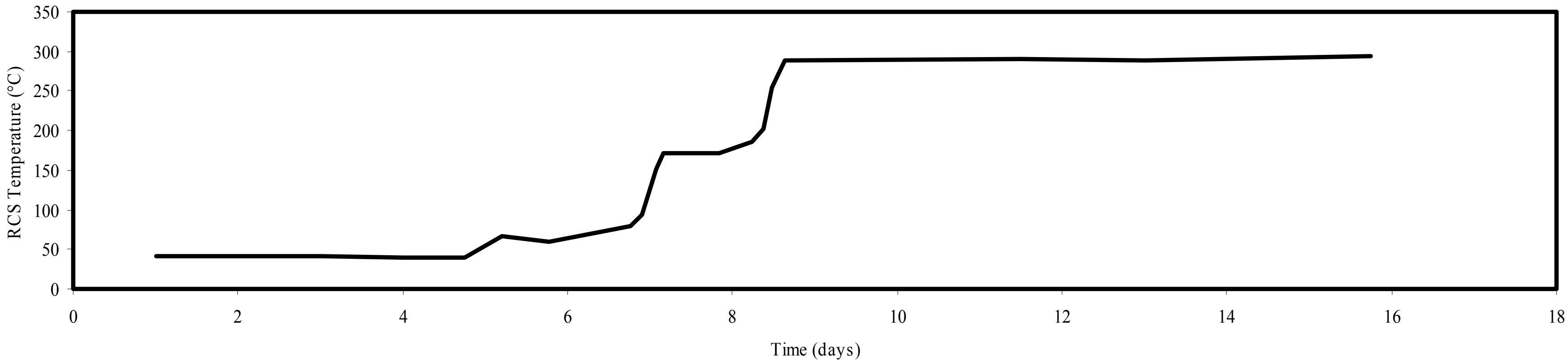
Sample Startup Sequences

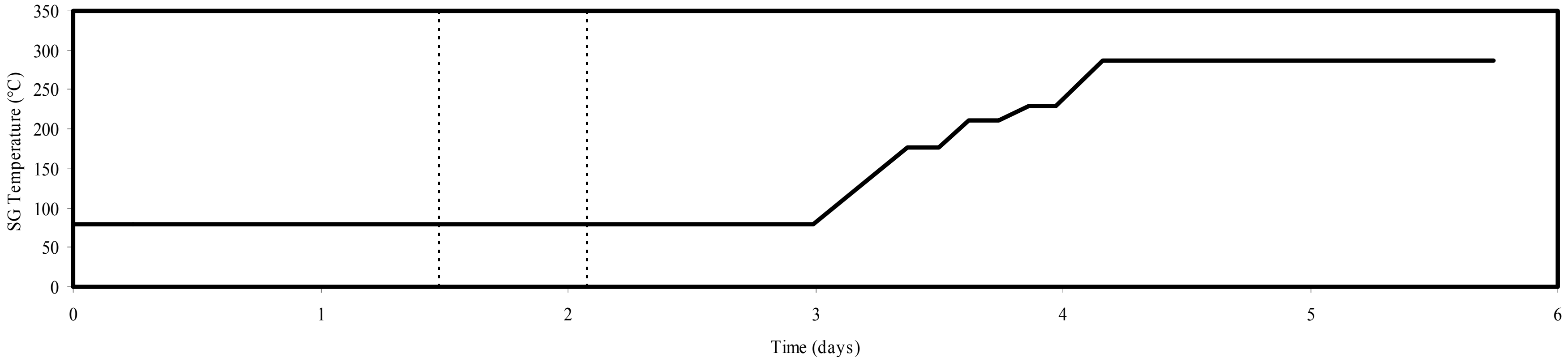




Startup Conditions

Sample Startup Sequences





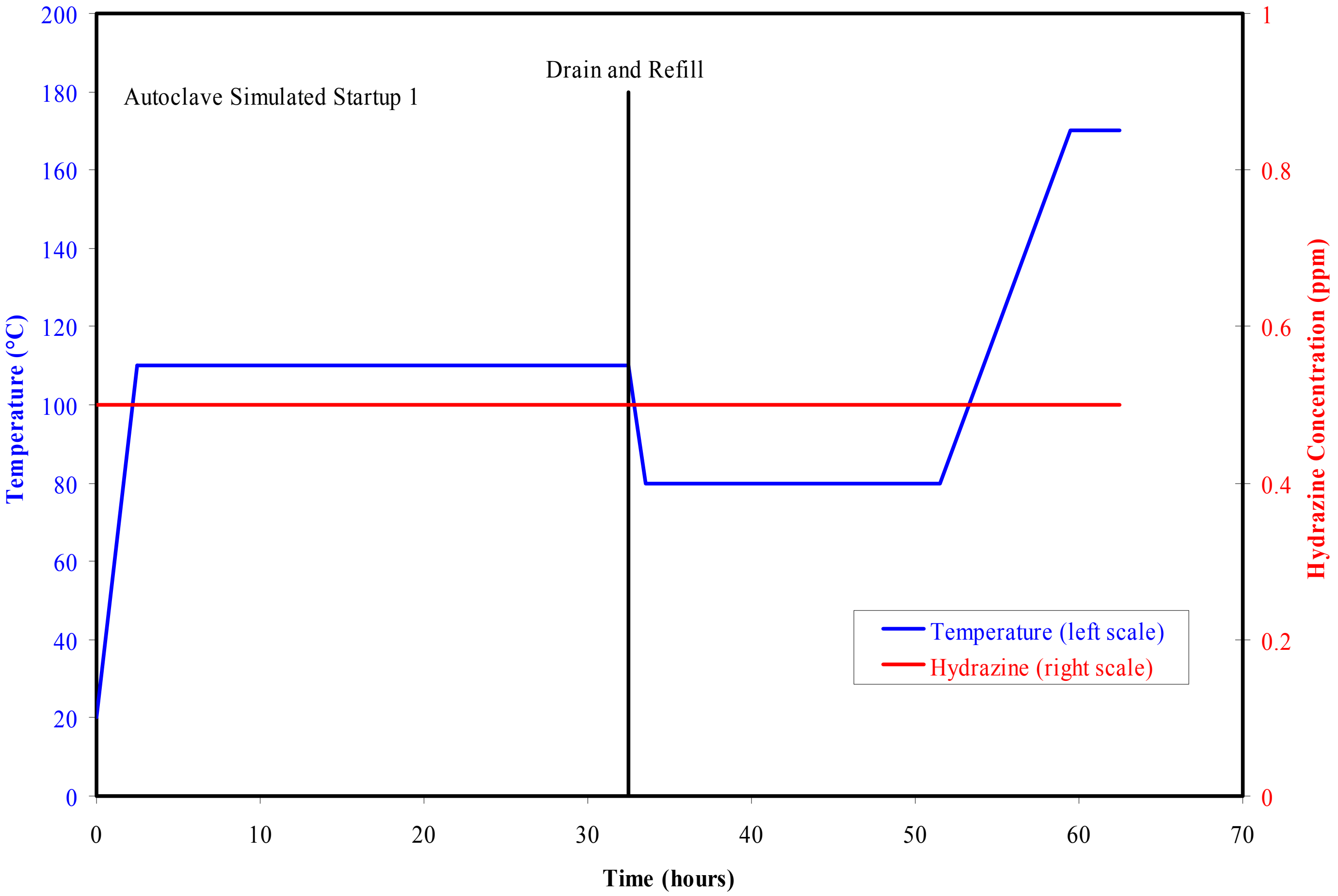
Startup Conditions

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

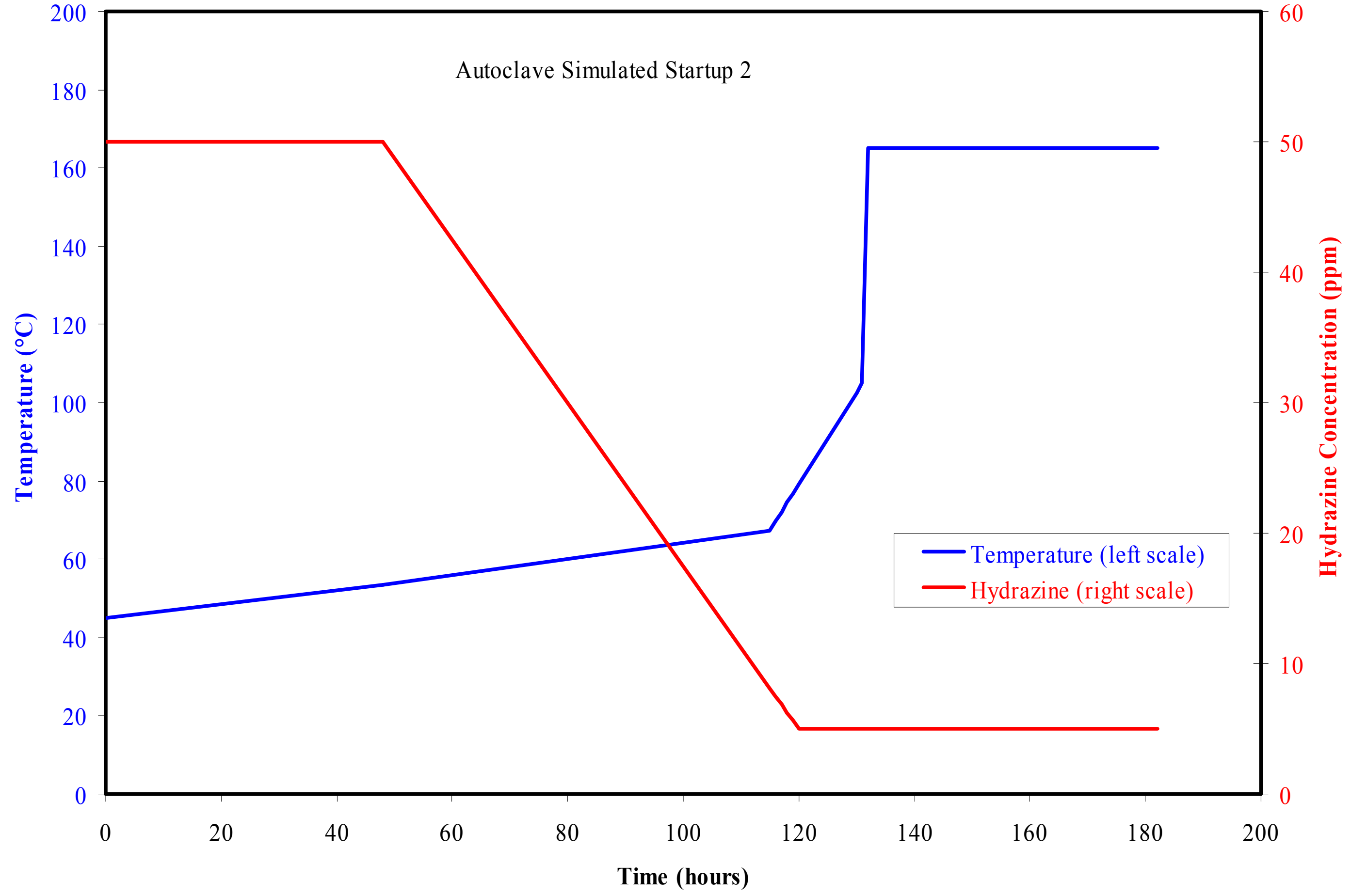
Deposit Oxide Reduction Experiments

Simulated Startup Sequences—Test 1



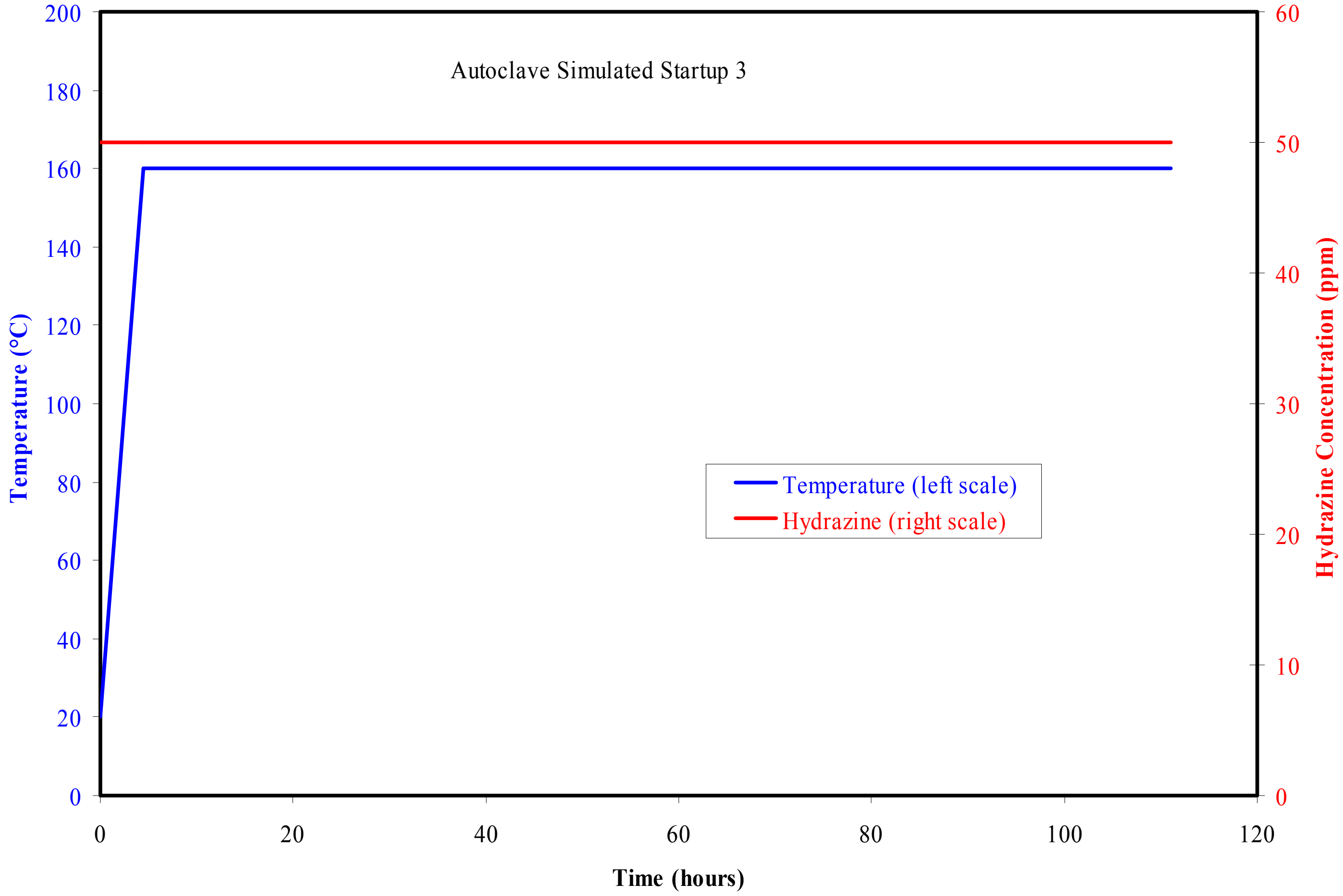
Deposit Oxide Reduction Experiments

Simulated Startup Sequences—Test 2



Deposit Oxide Reduction Experiments

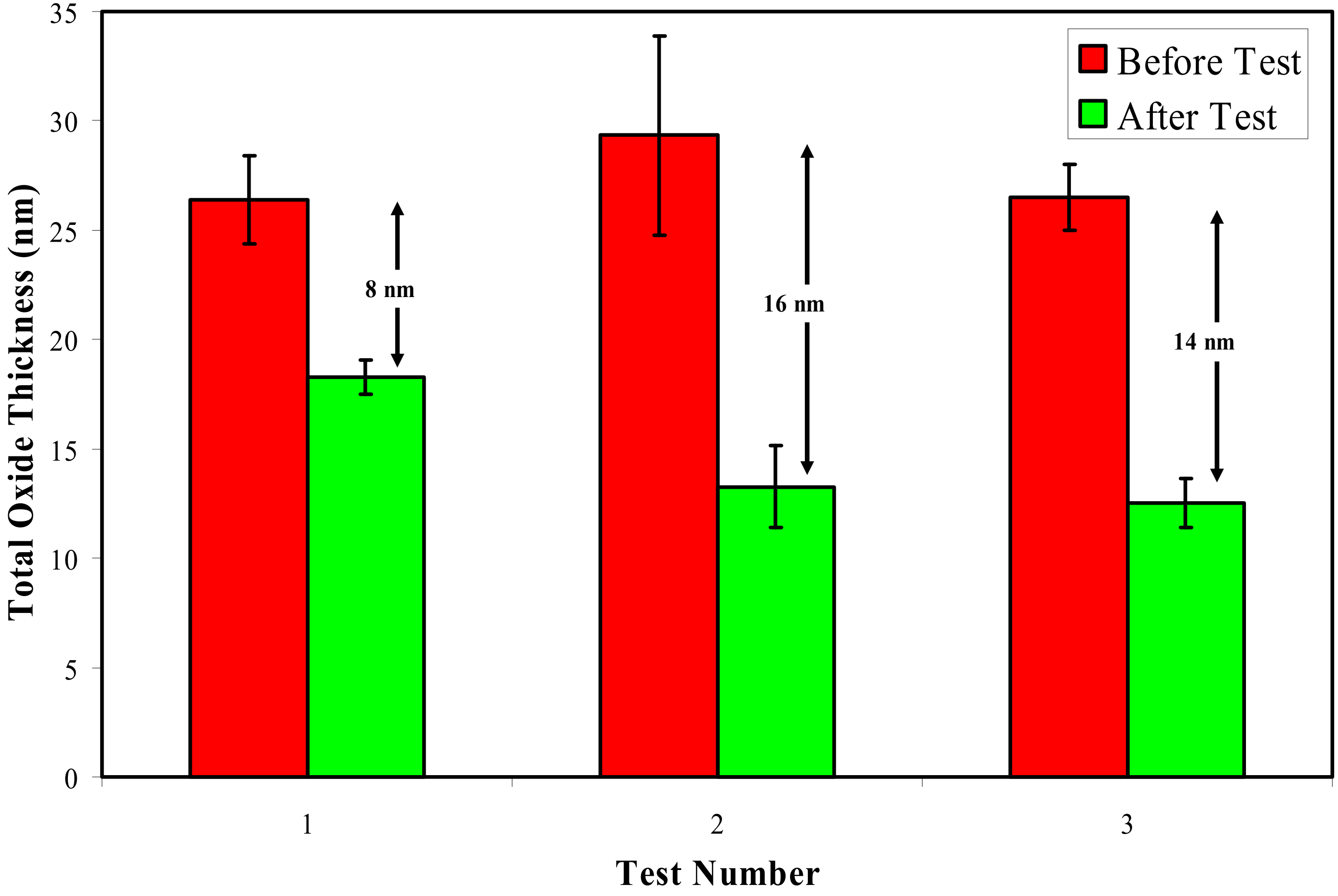
Simulated Startup Sequences—Test 3



426

Deposit Oxide Reduction Experiments

Simulated Startup Tests—Results



427

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

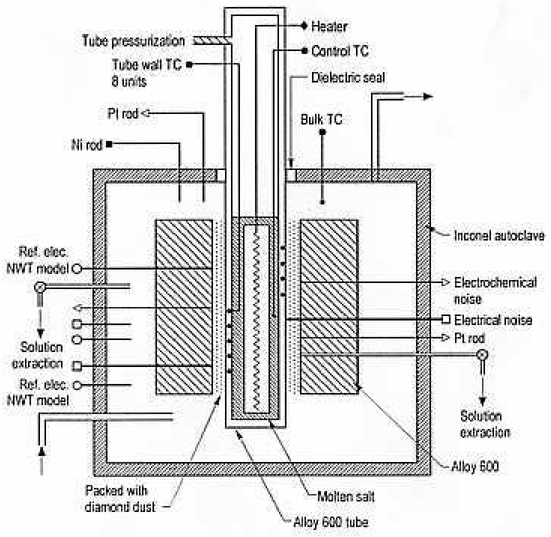
Evaluation of the Effect of Startup Oxidants on the ECP of a Crevice Filled with Deposits

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

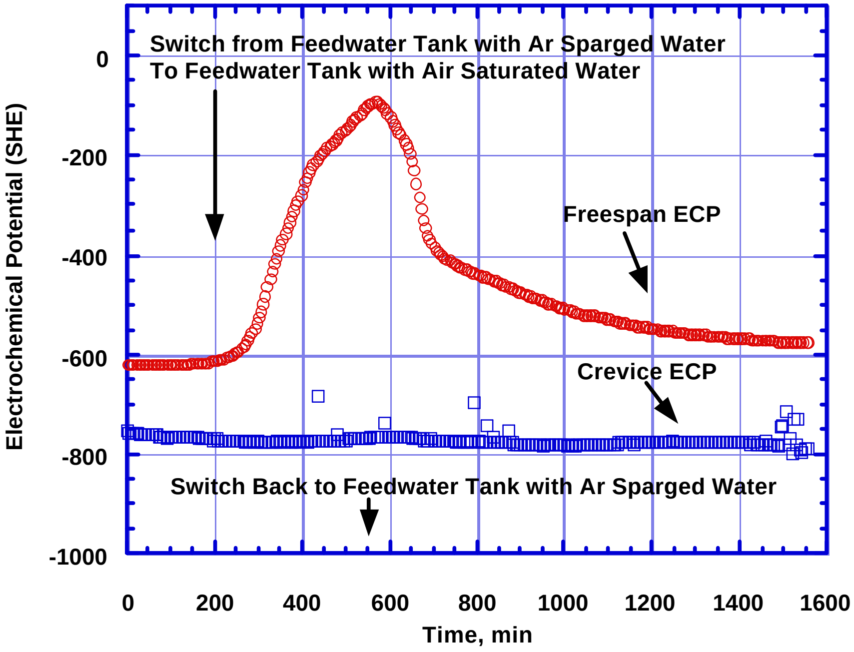
  $N_2H_4 + 4OH^- = N_2 + 4H_2O + 4e$

  Electrode Potential is given by

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

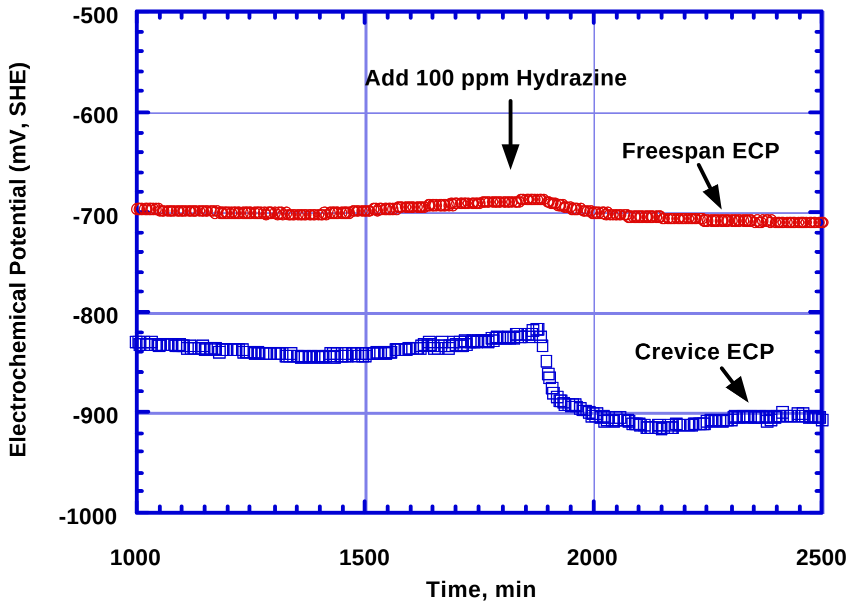
Does Dissolved Oxygen in the Feedwater Change the Crevice ECP Under Heat Transfer Conditions?

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?

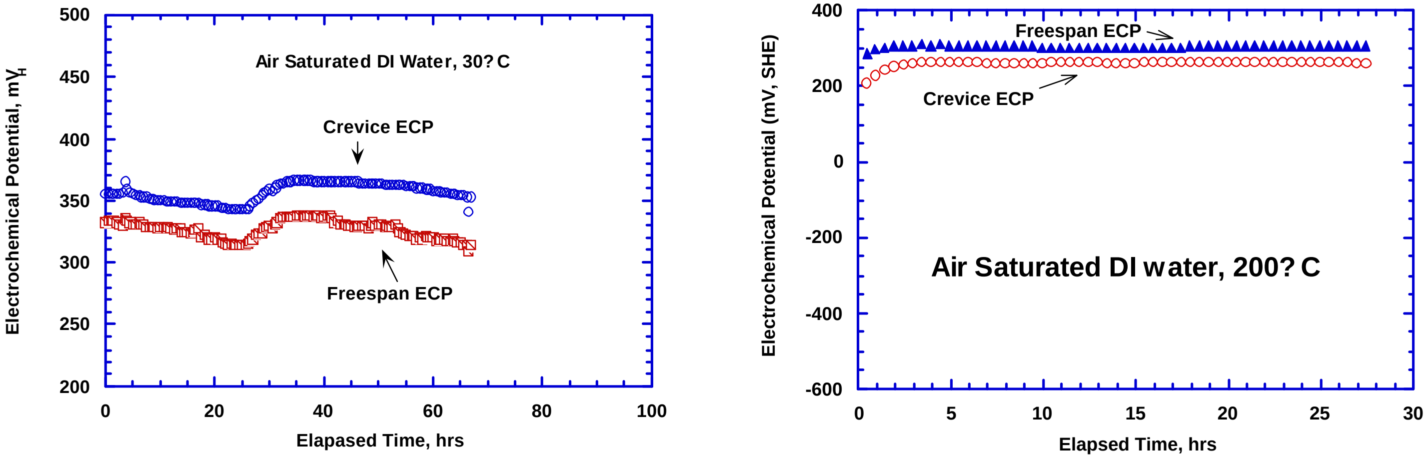
40 ppm NaOH
Bulk Temperature 275°C
Average Crevice Temperature 315°C
Crevice Packed with Magnetite
Flow Rate 15 cc/min
Ar Sparged Feedwater



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

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

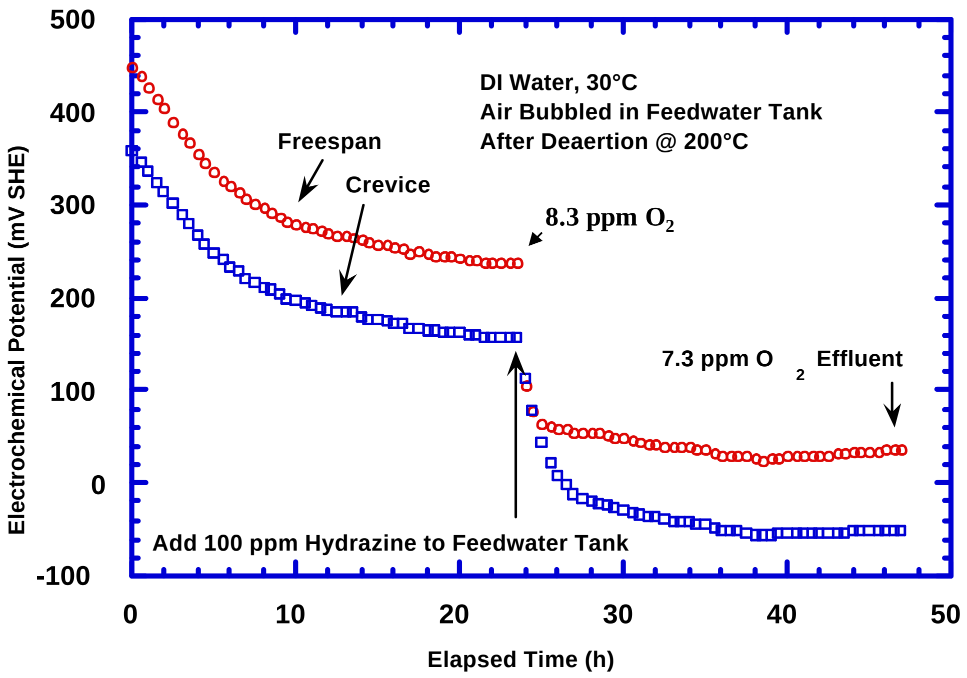
- The crevice ECP and freespan ECP in an air saturated condition are by 35 mV or less
- Reversible oxygen potential not observed - not unusual

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

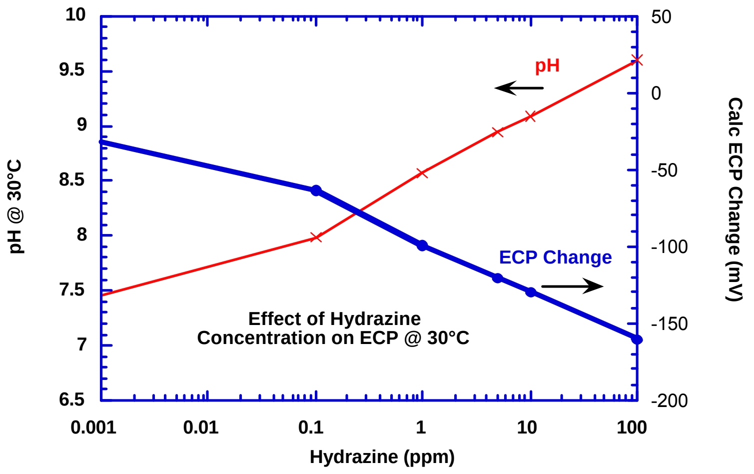
Effect of Hydrazine Addition to Air Saturated DI Water

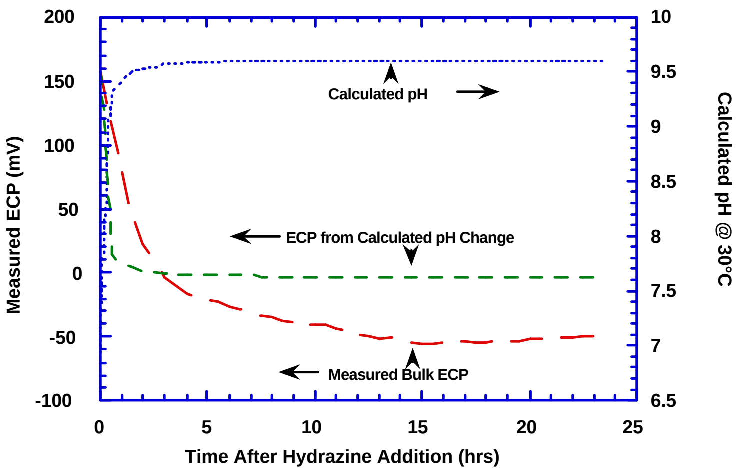


Effect of Startup Oxidants

Effect of Hydrazine Addition to Air Saturated DI Water

R. Eaker Calculations





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

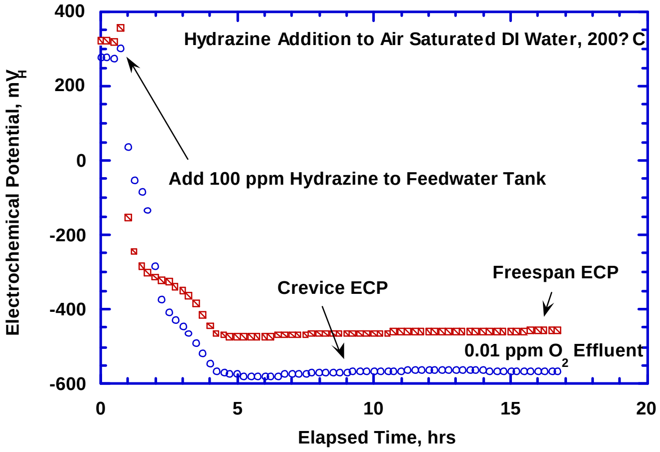
$N_2H_5^{2+} + H_2O = N_2H_6^{2+} + OH^{-}$ $K_{25°C} = 8.9 \times 10^{-16}$

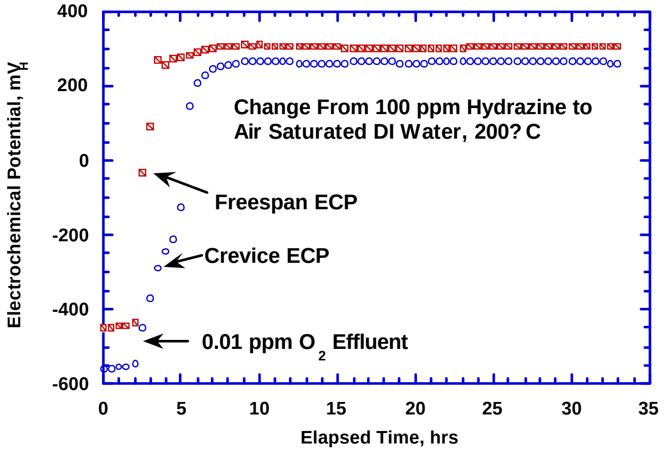
Bifunctional Base

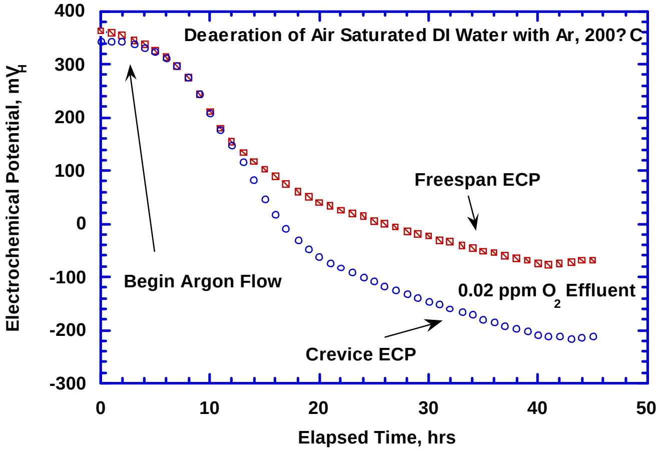
- **Most of the change in ECP can be explained by change in pH**
  - **Assumes no hydrazine in autoclave initially**
  - **Assumed hydrazine well mixed**
  - **Assumes no hydrazine gradient in autoclave**
- **Calculated ECP reaches steady state in approximately 3 hours**
- **Comparison of calc ECP with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

Effect of Startup Oxidants

Effect of Hydrazine Addition to Air Saturated DI Water

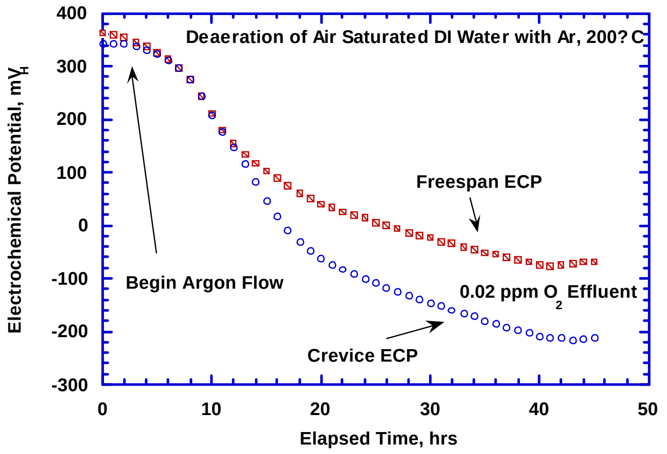


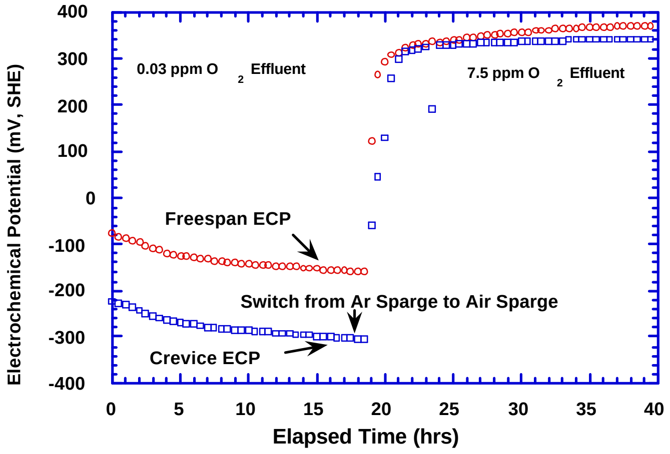




- At 200°C hydrazine lowers ECP by O_2 removal
- The ECP resulting from hydrazine addition is less than that resulting from deaeration
- ECP reaches equilibrium more rapidly with hydrazine that with argon
- ECP reversible
- Crevice ECP less than freesapn
  - The delta is greater in deaerated water

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

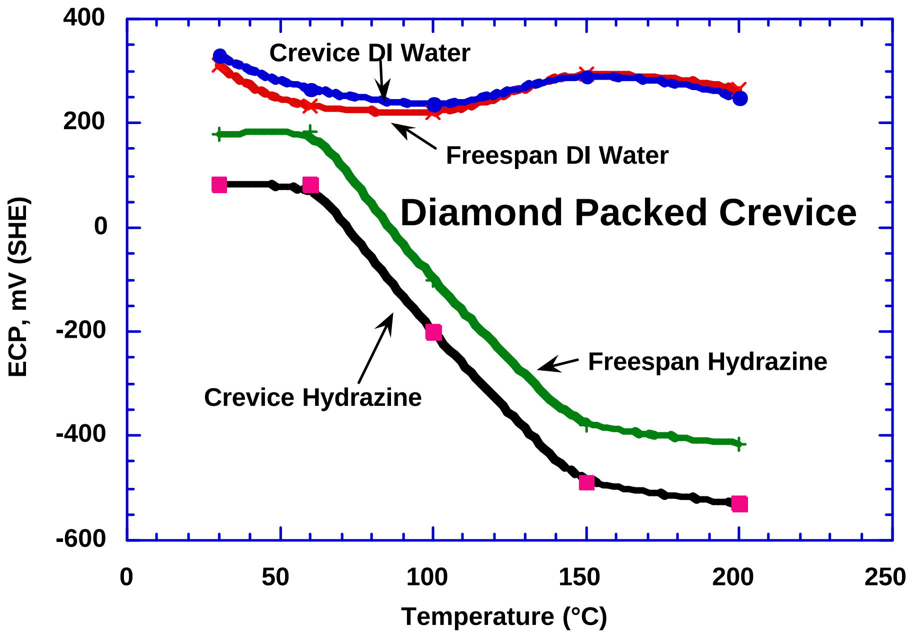
Temp	30°C	60°C	100°C	150°C	200°C
Freespan ECP	310 mV	232 mV	220 mV	295 mV	265 mV
Crevice ECP	330 mV	265 mV	235 mV	290 mV	250 mV
pH	6.9	6.5	6.1	5.8	5.6
$E_{H2O/O2}$	790 mV	750 mV	700 mV	630 mV	540 mV

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

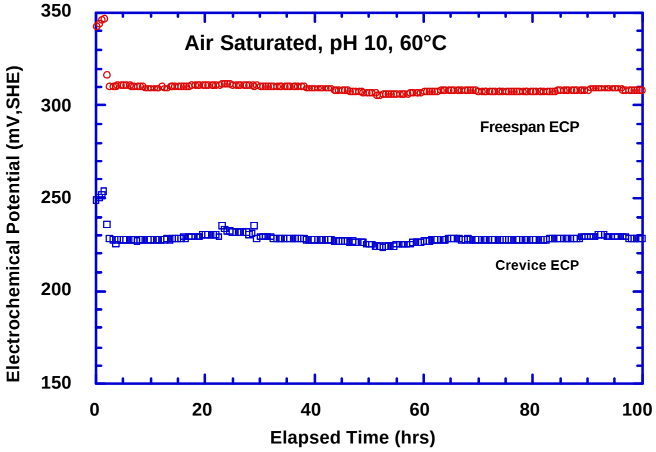
Effect of Startup Oxidants

Effect of Hydrazine Addition to Air Saturated DI Water

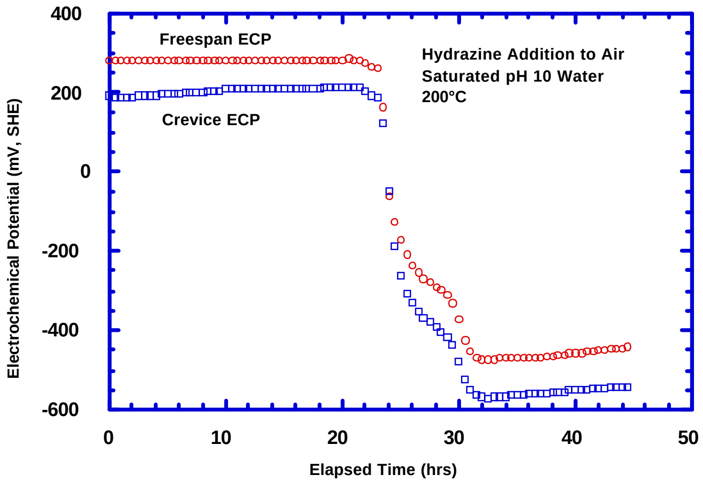


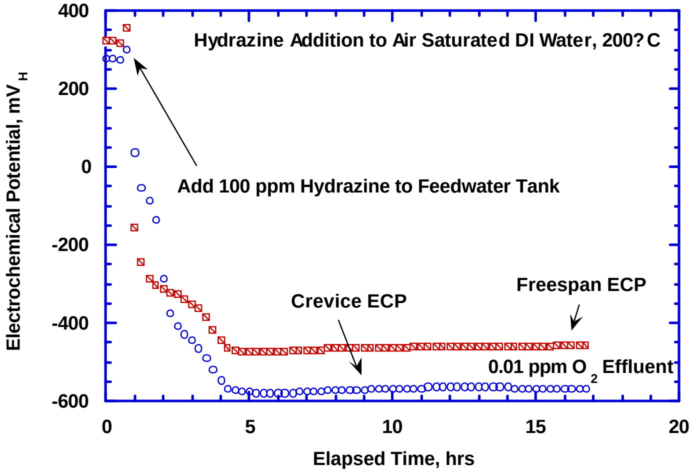
Startup Oxidants

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

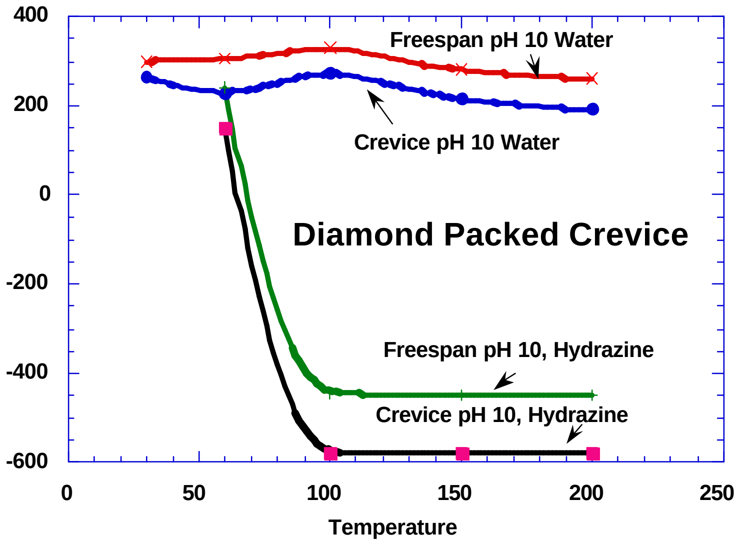
Temp	30°C	60°C	100°C	150°C	200°C
Freespan ECP	300 mV	305 mV	330 mV	280 mV	260 mV
Crevice ECP	265 mV	228 mV	275 mV	215 mV	190 mV
pH	10	9.2	8.6	7.9	7.6
$E_{H2O/O2}$	600 mV	570 mV	520 mV	450 mV	360 mV

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