UNITED STATES
NUCLEAR REGULATORY COMMISSION
WASHINGTON, D.C. 20555-0001

April 14, 1998

MEMORANDUM TO: N. King Stablein, Acting Chief
ENGB/DWM/NMSS

Michael J. Bell, Acting Chief
PAHL/DWM/NMSS

THRU: Richard A. Weller, Section Leader RAW
Engineering and Material Section
ENGB/DWM/NMSS

FROM: Kimberly A. Gruss, Materials Engineer
Kien Chang, CLST KTI Team Leader
Tae Ahn, Materials Engineer
Engineering and Material Section
ENGB/DWM/NMSS

Gustavo Cragnolino, Principal Scientist Kay for GAC
CNWRA

SUBJECT: ATTENDANCE AT THE FOURTH WASTE PACKAGE DEGRADATION EXPERT ELICITATION WORKSHOP HELD IN VIENNA, VA, FEBRUARY 2, 1998

The U.S. Department of Energy (DOE) held its fourth expert elicitation workshop on waste package degradation for the proposed high-level waste repository at Yucca Mountain, Nevada, on February 2, 1998. Recently, DOE changed its reference waste package design by selecting alloy C22 as the inner barrier corrosion-resistant material, replacing alloy 625. The goals of this waste package degradation expert elicitation (WPDEE) workshop were: to provide the expert panelists with the opportunity to discuss both general and localized corrosion rates of alloy C22 as a function of various environmental parameters; to review the new corrosion testing data and corrosion rate models that have been developed since the last workshop (which was held on June 10-11, 1997); and to outline the steps required to finalize the experts' assessments and uncertainties in the available data and information on the corrosion of alloy C22. A formal expert judgment process is being followed to obtain the needed inputs to accomplish these objectives. Five members of the previous six-member expert panel were present for this workshop. The attendance list is included as Attachment 1.

The workshop began with an introduction by K. Coppersmith (Geomatrix), who discussed the objectives of the workshop and reviewed the list of questions that the experts will be asked to answer in their formal elicitation interviews. Attachment 2 contains this introductory material, while Attachment 3 contains the meeting agenda. A summary of the previous expert panel

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PDR WASTE
WM-11 PDR

conservative approach in light of the fact that there is limited data on the corrosion resistance of alloy C22. Attachment 4 contains the set of transparencies that were used during the workshop. Copies of the transparencies can be obtained from either K. Gruss or G. Cragnolino.

The results of the elicitation interviews will be summarized in a Revision 1 to the previously published WPDEE Project report (dated August 15, 1997). This report should be available in April 1998. However, with this schedule, it may be difficult for DOE to incorporate the results of this elicitation into the Viability Assessment (VA) because DOE is also planning to initiate internal reviews of pertinent waste package degradation VA documents in April 1998.

It should also be noted that DOE is currently working on a thin-walled, double barrier (alloy C22-titanium) waste package design. It is possible that the materials degradation issues associated with this configuration will be addressed in other expert elicitations. This design will not be considered in any detail in the VA.

Attachments: As stated

DISTRIBUTION: (*w/att) Central File* ENGB r/f* PUBLIC
MFederline KMcConnell MLee BJDavis RCodell
BLeslie NSridhar

DOCUMENT NAME: S:\DWM\ENGB\KAG\WPTRP4.RPT (*see prev. concurrence)

OFC	ENGB*		ENGB*		ENGB*		CNWRA*		ENGB	
NAME	KGruss/eb/prf rd		KChang		TAhn		GCragnolino (KAG for)		RWeller Raw	
DATE	4/9/98		4/9/98		4/13/98		4/9 /98		4/14/98	

OFFICIAL RECORD COPY

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OFC	ENGB		ENGB		ENGB		CNWRA		ENGB	
NAME	KGruss/eb/prf rd		KChang		TAhn		GCragnolino		RWeller	
DATE	4/9/98		4/9/98		4/8/98		4/9/98		4/ /98	

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Attachment 1

WASTE PACKAGE DEGRADATION EXPERT ELICITATION PROJECT
WORKSHOP ON CRM CORROSION RATES – FEBRUARY 2, 1998

ATTENDANCE SHEET

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Richard PARIZEK	NWTRB	751 McKee Street State College PA 16803	Richard R Parizek
HUGH BENTON	M&O - WASTE PKG OPS LAS VEGAS NV	702-295-4389	Hugh Benton

Attachment 2

PURPOSE OF WORKSHOP AND QUESTIONS TO BE ASKED

WORKSHOP ON CRM CORROSION RATES

WASTE PACKAGE DEGRADATION EXPERT ELICITATION PROJECT (WPDEE)

Kevin J. Coppersmith

Geomatrix Consultants

February 2, 1998

WORKSHOP ON CRM CORROSION RATES
WASTE PACKAGE DEGRADATION EXPERT ELICITATION PROJECT

PURPOSE OF WORKSHOP:

- To provide the expert panel an opportunity to discuss the corrosion rates of the corrosion resistant material (CRM) of the waste package, which is now alloy C-22
- To review new corrosion testing data and new modeling of corrosion rates that have been developed since the last workshop
- To discuss the general and localized corrosion rates for C-22 as a function of various environmental conditions
- To outline the steps required to finalize the assessments and associated uncertainties

QUESTIONS REGARDING THE CORROSION RATE OF CORROSION-RESISTANT INNER BARRIER

1) What is the general corrosion (or passive dissolution) rate of the inner barrier in humid-air conditions (i.e., without drips) at 25, 50 and 100°C?

2) What is the general corrosion rate of the inner barrier under drips at 25, 50 and 100°C?

2-a) 1X to 10X of the J-13 chloride concentration
2-b) 10X to 1000X of the J-13 chloride concentration
2-c) 1000X and higher of the J-13 chloride concentration

} can change this to anything

3) What are important parameters to be considered in determining the initiation threshold of crevice corrosion of the inner barrier, and what are the threshold values of the parameters?

4) What is the most appropriate way to express the behavior of localized corrosion of the inner barrier in the crevice and under-deposits conditions as described above?

4-a) Exponential pit growth law is expressed as follows pit depth = $B * t^n$

4-b) Logarithmic pit growth law is expressed as follows pit depth = $k * \exp(Q/T) * \log t - x_0$

GROUND RULES FOR WORKSHOPS

1. The workshops are an opportunity for the Expert Panel to:

   - Exchange data
   - Present interpretations
   - Challenge and defend technical hypotheses
   - Be trained in elicitation procedures
   - Gain information on the project
   - Interact and ask questions

   Therefore, the focus of each workshop is the *Expert Panel*

2. The MDT runs the workshops and is responsible for keeping to the schedule, logistics, etc.
3. The conduct of the technical discussions at the workshops will be at the highest professional level. Personal attacks or confrontations will not be permitted (especially those directed at the MDT)
4. Discussions will be among the Expert Panel and the Presenters
5. Observers are provided with a period each day for brief statements or questions (3 minutes each)
6. If an Observer has a burning question, please write it down and give to a member of the MDT; they will attempt to have it answered during the course of the discussions
7. The data bases supplied to the Expert Panel will not be supplied to the Presenters or Observers; a list of all materials supplied will be available
8. A workshop summary will be supplied to all workshop participants who have signed in

SCHEDULE FOR WPDEE
CRM CORROSION RATE ASSESSMENTS

February 20	Preliminary assessments
February 27	Draft elicitation summaries
March 13	Final elicitation summaries

- no interview sessions planned

Summaries go out to EE

Rev. 1 will contain update from 1st Summary document

Peter - wants env. part to get worked out in panel type.
Kevin - will make crack at it.

Attachment 3

GEOMATRIX

FINAL AGENDA

WORKSHOP ON CRM CORROSION RATES
WASTE PACKAGE DEGRADATION
EXPERT ELICITATION (WPDEE) PROJECT

February 2, 1998
TRW Environmental Safety Systems, Inc.
The MetroPlace Building, Vienna, Virginia

PURPOSES OF WORKSHOP:

- To provide the expert panel an opportunity to discuss the corrosion rates of the corrosion resistant material (CRM) of the waste package
- To review new corrosion testing data and new modeling of corrosion rates that have been developed since WPDEE Workshop 3 in June, 1997
- To outline the activities required to finalize the assessments of general and localized corrosion rates and associated uncertainties

MONDAY, FEBRUARY 2, 1998

7:30 - 8:00	Purpose of workshop and questions to be addressed (K. Coppersmith, Geomatrix)
8:00 - 8:45	Summary of CRM general and localized corrosion rates made by WPDEE panel (R. Youngs, Geomatrix)
8:45 - 9:30	Sensitivity studies and use of results in TSPA (J. Lee, M&O/DESI)
9:30 - 9:45	**Break**
9:45 - 10:15	Rationale for selection of C-22 as base case alloy (D. Stahl, M&O/FCF)
10:15 - 11:00	Recent CRM testing results (D. McCright, M&O/LLNL)
11:00 - 11:45	Recent modeling of CRM corrosion rates (J. Farmer/M&O/LLNL)
12:00 - 1:00	**Lunch**
1:00 - 1:30	Long term corrosion of nickel alloys (B. Ross, R. Moeller, NRI)
1:30 - 2:00	Assessment of localized corrosion of alloys 825, 625, and C-22 for HLW containers (G. Cragnolino, CNWRA)
2:00 - 3:00	Discussion of CRM corrosion rates and uncertainties (panel)
3:00 - 3:15	Where we go from here (K. Coppersmith)
3:15 - 3:30	Comments from observers

Attachment 4

SUMMARY OF PANEL ASSESSMENTS TO DATE FOR CRM CORROSION RATES

Workshop on CRM Corrosion Rates

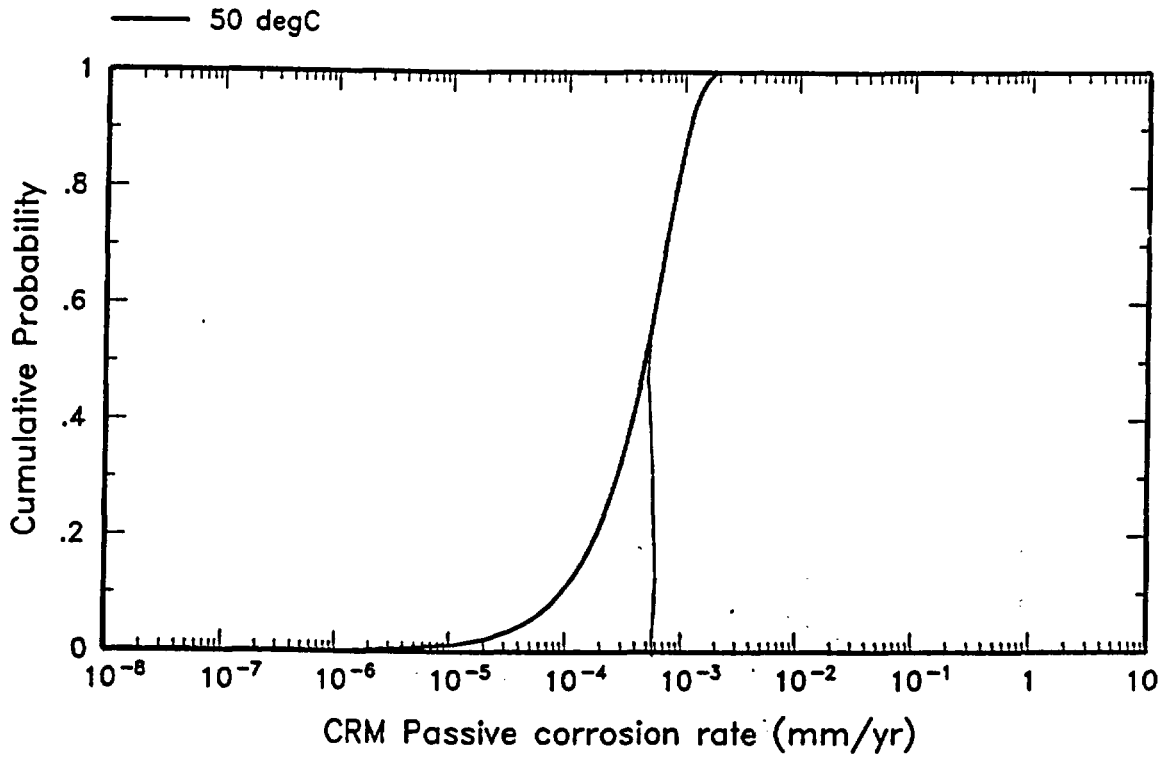
Waste Package Degradation
Expert Elicitation Project

Robert R. Youngs
Geomatrix Consultants

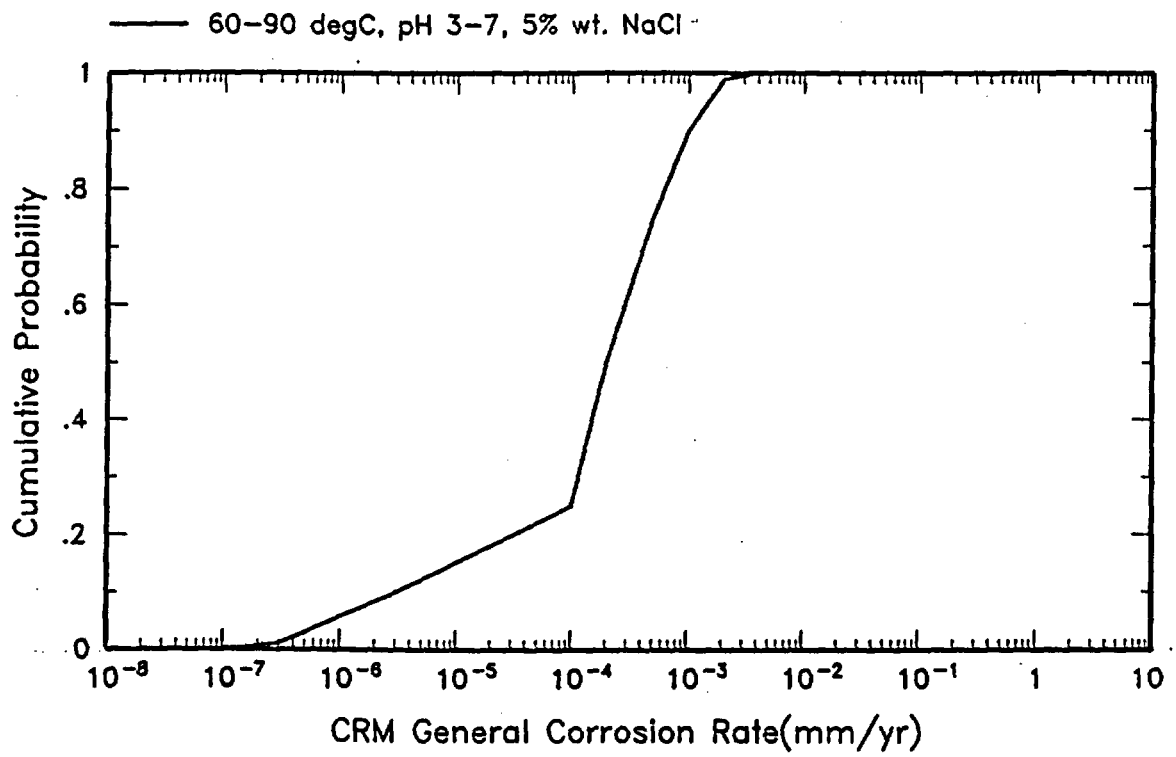
February 2, 1998

Assessments for CRM General Corrosion

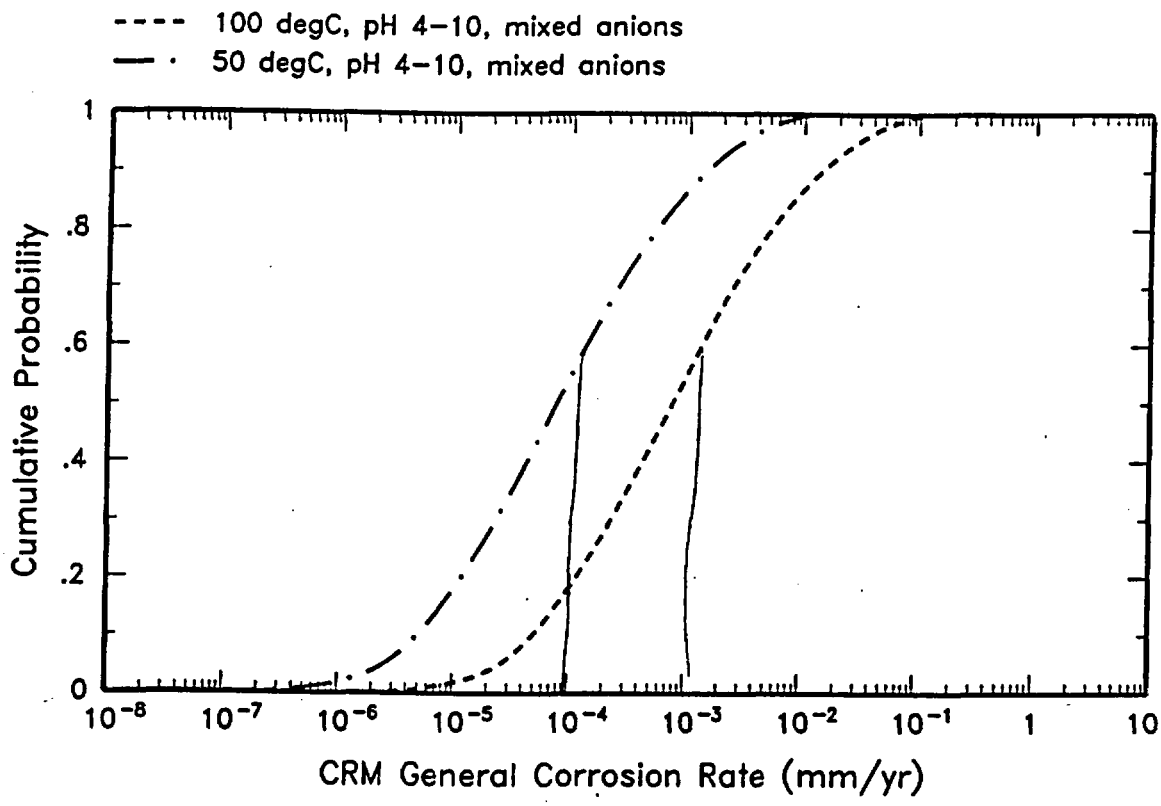
Expert	Environmental Conditions
David Shoesmith	50° C
Joe Farmer	60°-90° C, pH 3 to 7, 5% NaCl
Peter Andresen	50° C, pH 10, mixed anions 100° C, pH 10, mixed anions
John Scully	20° C, neutral pH, initial and long term rates 100° C, aggressive pH, initial and long term rates
Dan McCright	50° C, J-13 water 80° C, J-13 water 100° C, J-13 water
Aggregate Distributions	50° C, DS, PA, & DM 100° C, JF, PA, JS (late), DM } experts



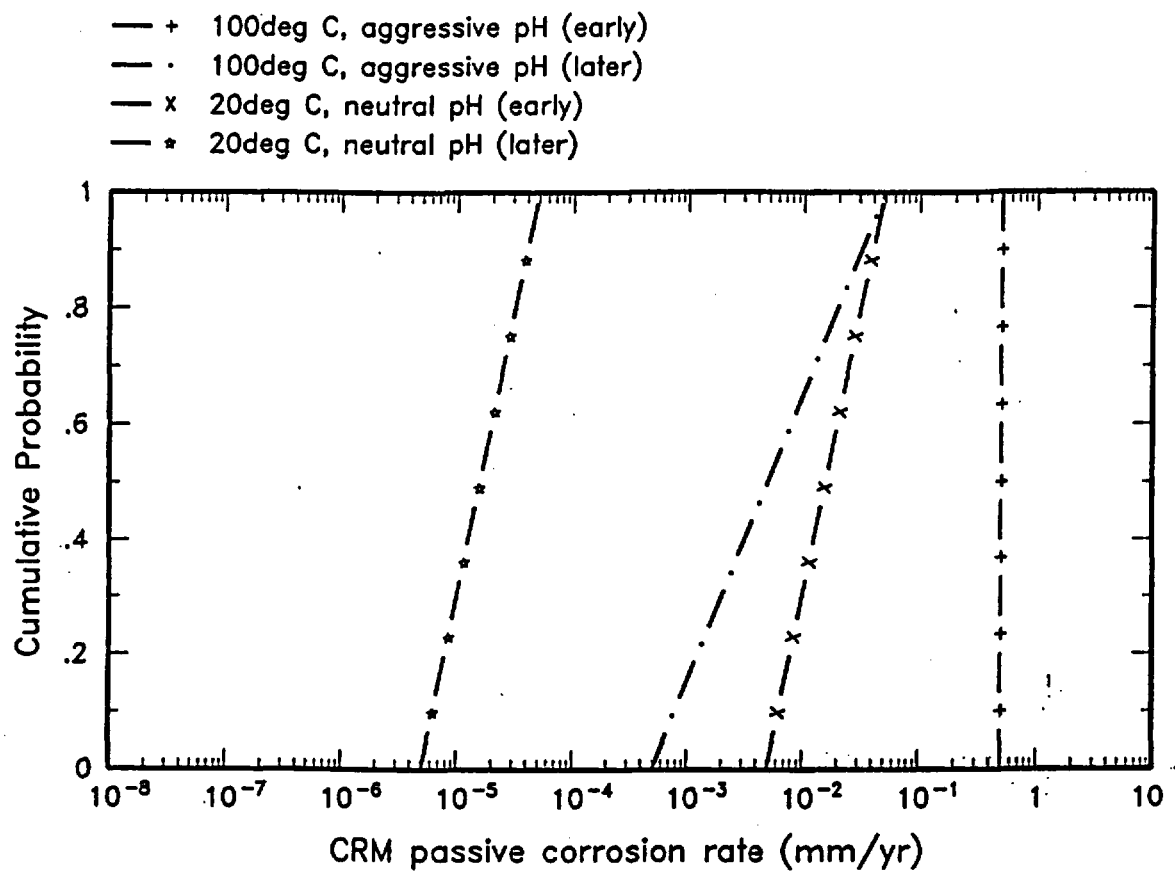
Distribution for David Shoesmith



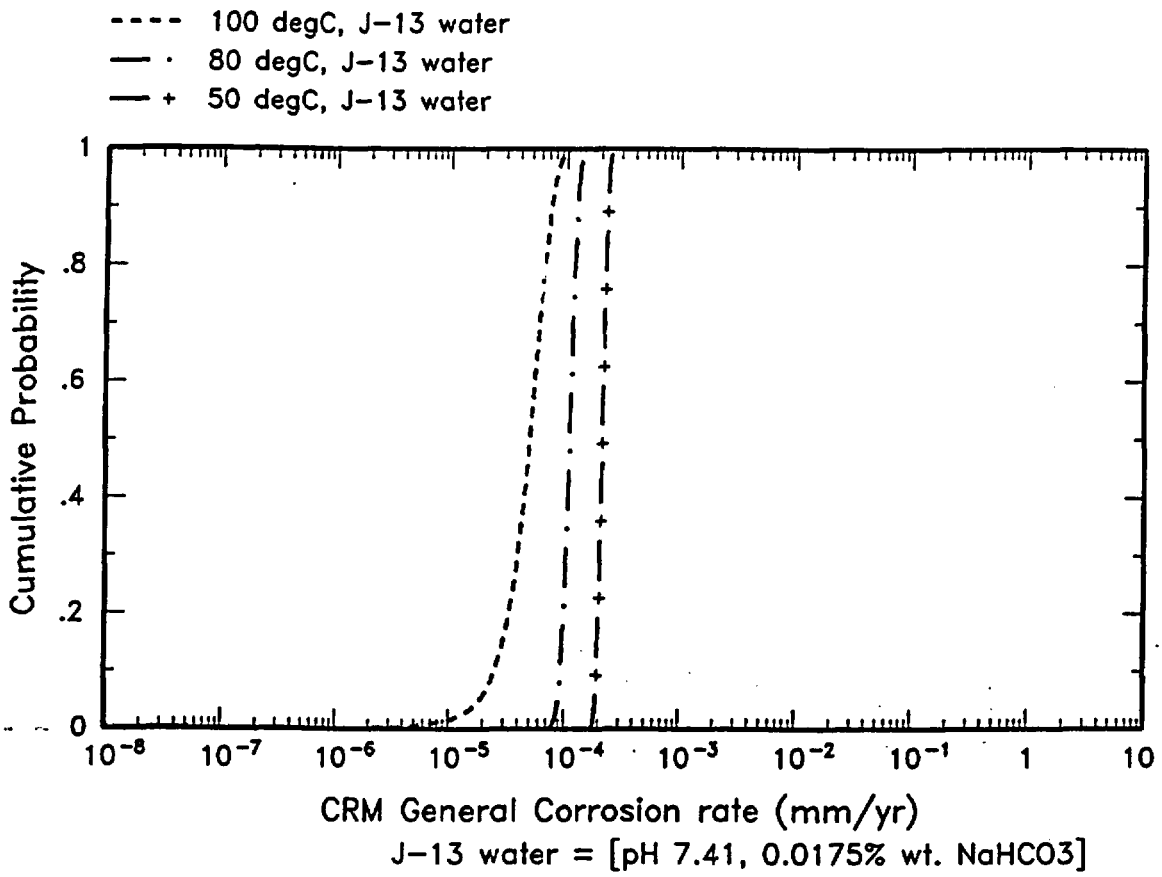
Distribution for Joe Farmer



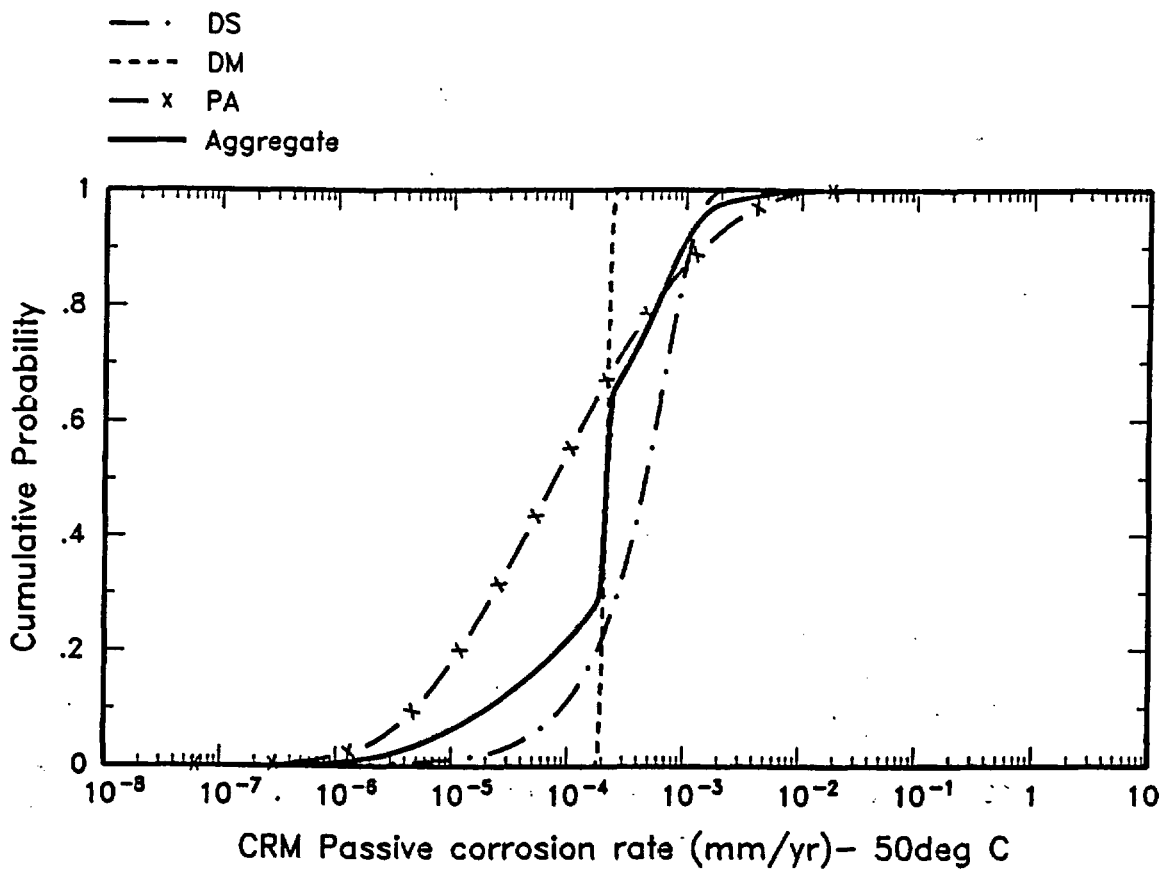
Distribution for Peter Andresen



Distribution for John S ully



Distribution for Dan McCright


DS
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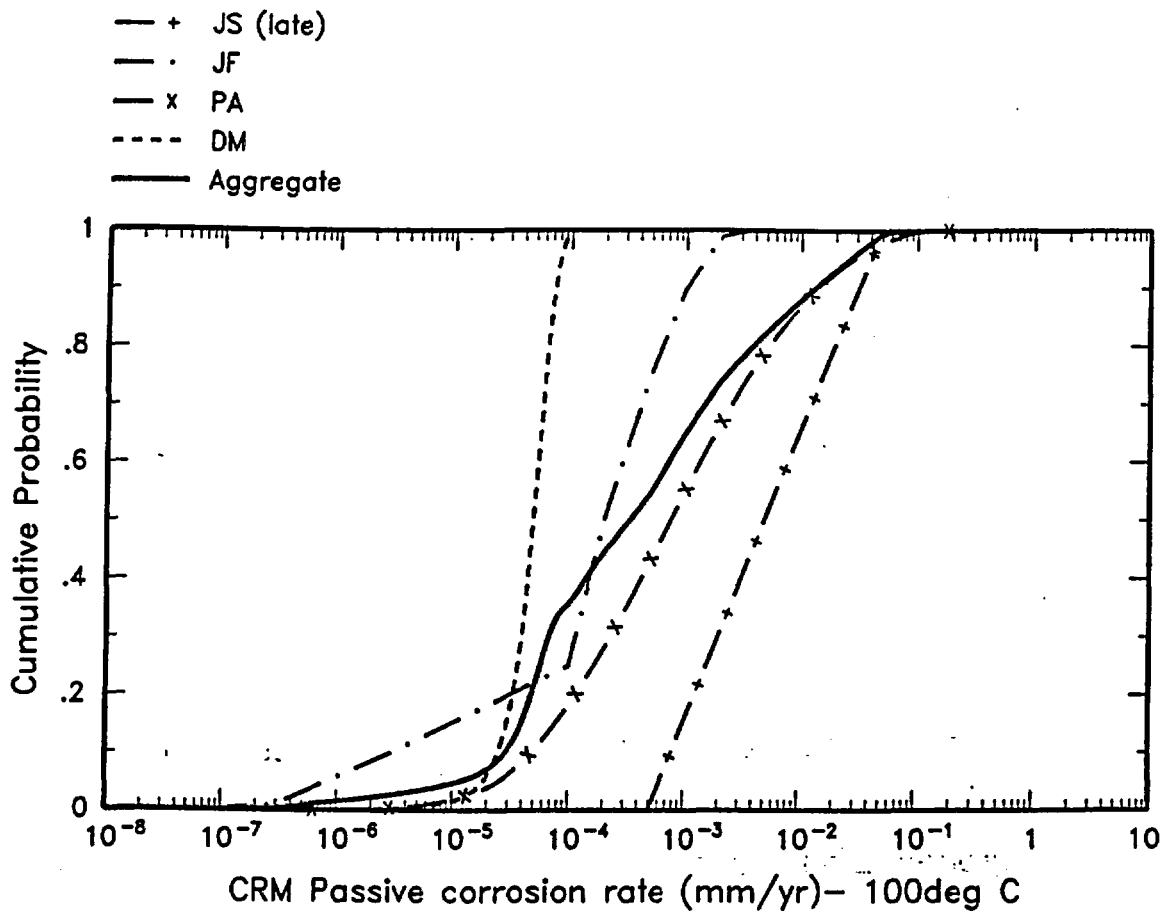
CRM Passive corrosion rate (mm/yr)– 50deg C


JS (late)
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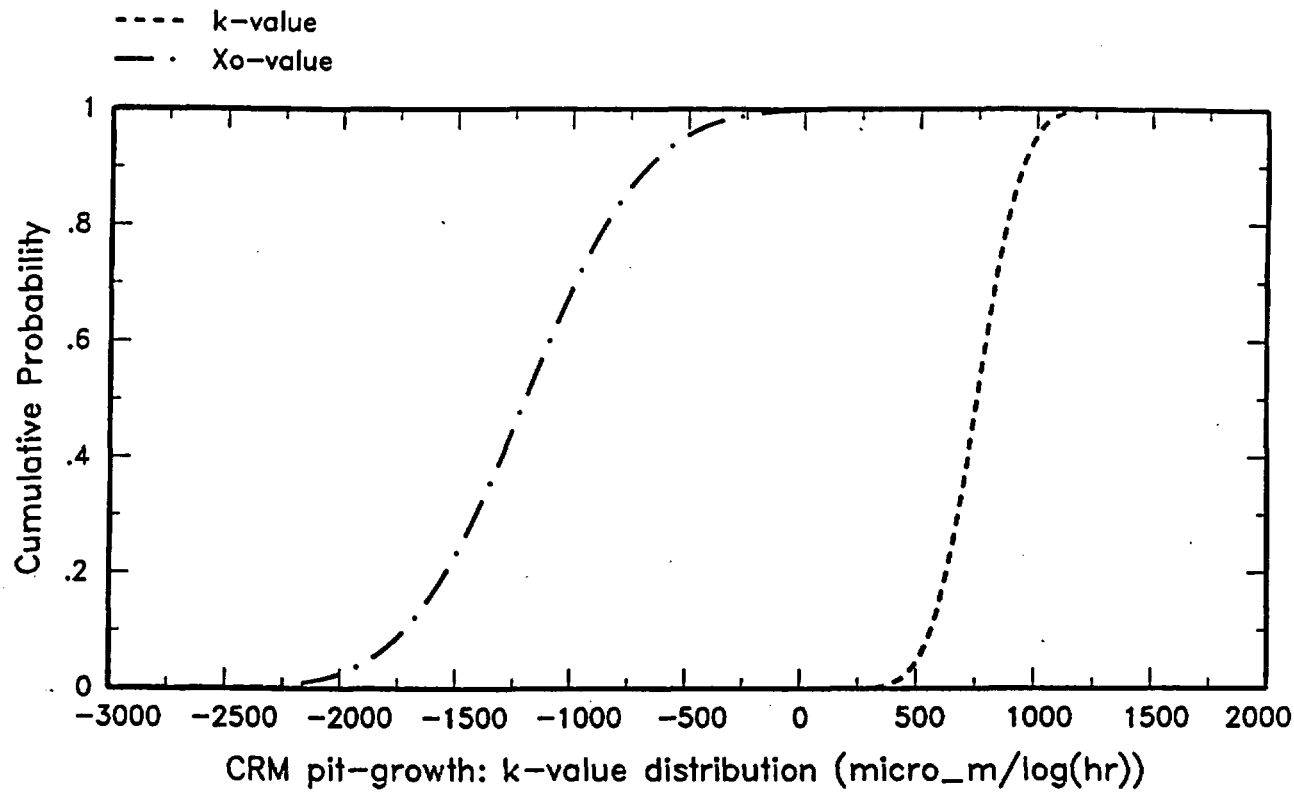
1
10
CRM Passive corrosion rate (mm/yr)– 100deg C

Assessments for CRM Localized Corrosion

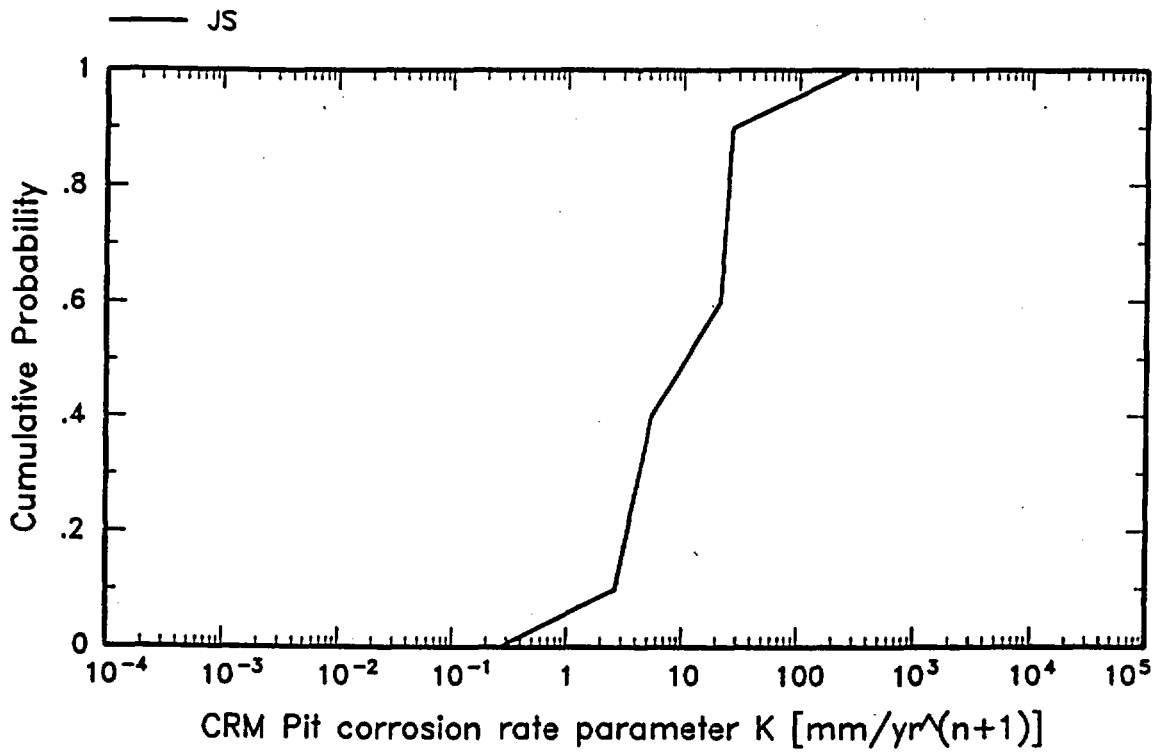
Expert	Model and Environmental Conditions
David Shoesmith	$d = k \times \log(t) - x_0$ d=depth
	k, x_0 assessed for 100° C
	$k \propto \exp(Q/T)$ with $Q = 55 \pm 17$ kJ/mole, T in ° K
John Scully	$d = Bt^n$, B assessed for high pH, 60° - 100° C
	n assessed for general conditions

Joe Farmer and Dan McCright also provided assessments for n

Aggregate Distribution for n JF, JS, & DM

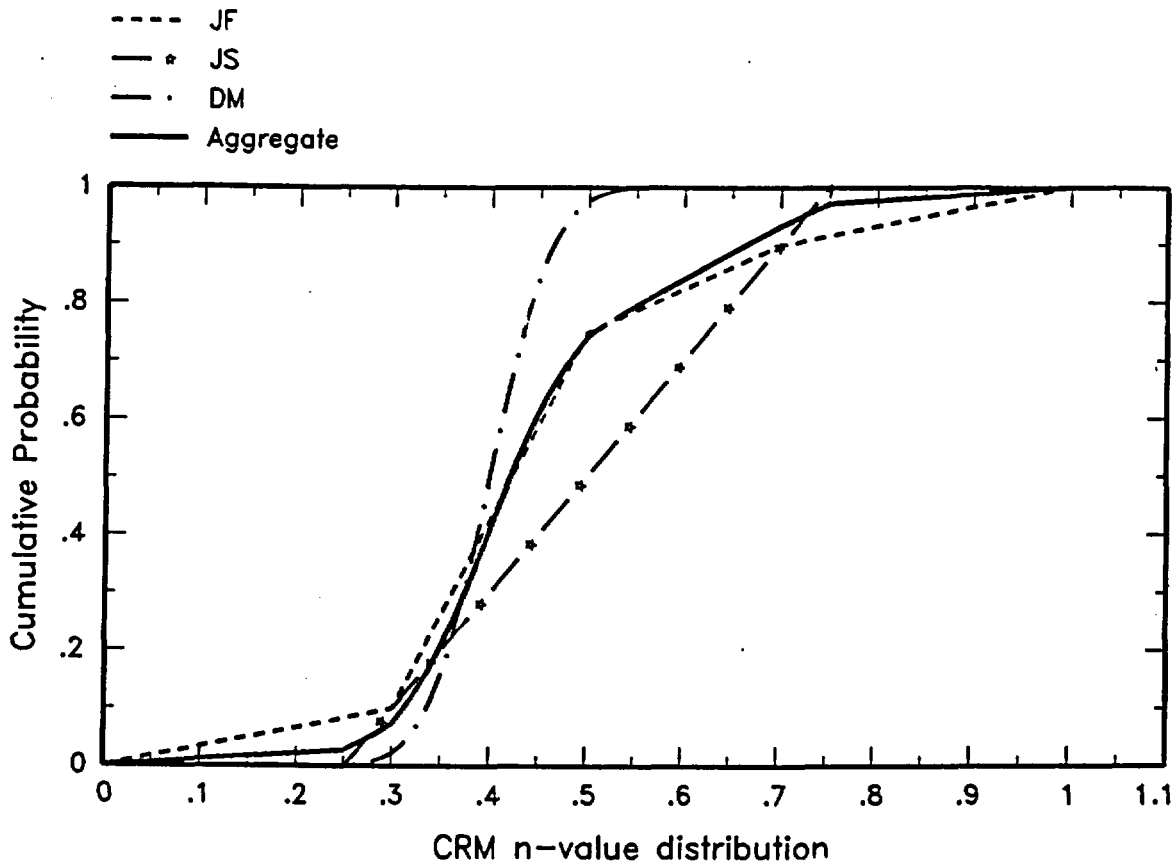


Distribution for David Shoesmith



Distribution for John Scully

high T, pH
w/ window of
susceptibility
for pit growth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1
1.1
CRM n-value distribution

(2)

Use of WPDEE Results in TSPA-VA WP Degradation analysis and Sensitivity Analysis Results

Joon H. Lee
Duke Engineering & Services

Waste Package Degradation
Expert Elicitation Project Workshop
February 2, 1998
Washington, D.C.

B&W Federal Services
Duke Engineering & Services, Inc.
Fluor Daniel, Inc.
Fraenstome Cogema Funis
Integrated Resources Group
INTERA, Inc.
JAI Corporation
JK Research Associates, Inc.
Lawrence Berkeley Laboratory
Lawrence Livermore National Laboratory
Los Alamos National Laboratory
Morrison-Knudsen Corporation
Science Applications International Corporation
Sandia National Laboratories
TRW Environmental Safety Systems Inc.
Woodward-Clyde Federal Services
Winston & Strawn
Cooperating Federal Agency:
U.S. Geological Survey

Outline of the Presentation

- Objectives
- Conceptual model for waste package degradation modeling for TSPA-VA
- Base case waste package degradation model for TSPA-VA
- Abstraction of CRM corrosion models from WPDEE and YMP
  - three alternative general corrosion models
  - three alternative localized corrosion models
- Analysis results for the sensitivity of waste package degradation to alternative CRM corrosion models
  - parameters and assumptions employed in the stochastic waste package degradation model
- Concluding remarks

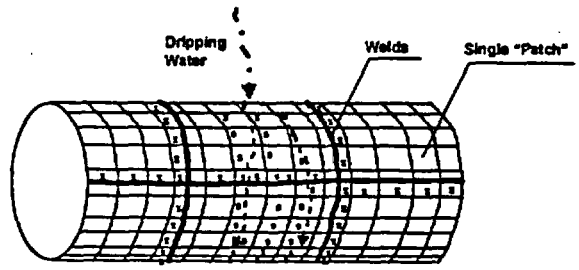
Objectives

- Provide to the WPDEE panel how the WPDEE results and other data/information are used in the stochastic waste package degradation model
- Present the analysis results for the sensitivity of waste package degradation to alternative CRM corrosion models

Schematic of the Conceptual Model for WP Degradation Modeling and Abstraction

* T, RH, in-drift water dripping across repository from drift-scale T-H model abstraction

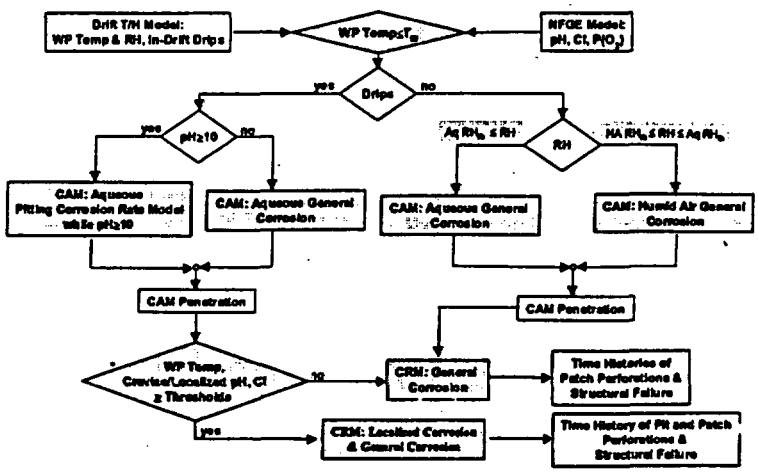
* pH, [Cl] of dripping water, $P(O_2)$, across repository from NFGE model abstraction



s - Patches with drips; Potential salt deposits; CRM localized corrosion

x - Patches with welds

Logic Diagram for the Base Case TSPA-VA Waste Package Degradation Model

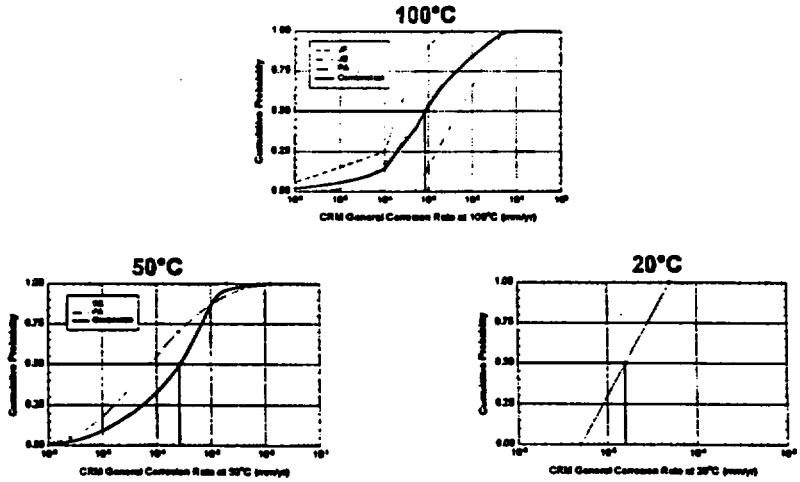


Abstraction of CRM General Corrosion Models

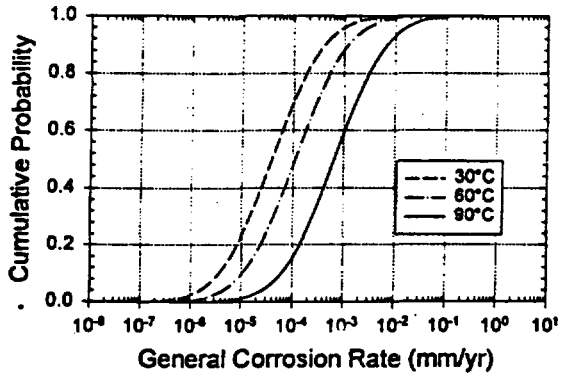
Abstraction of CRM General Corrosion Model(I)

- Based on the combined/aggregate distributions of the CRM general corrosion rates at 25, 50 and 100°C from the WPDEE → from EE
- Randomly sampled a total of 100,000 points from each of the three combined cumulative distribution functions (CDFs) at the three temperatures
- Fit the re-sampled distributions to an Arrhenius functional form

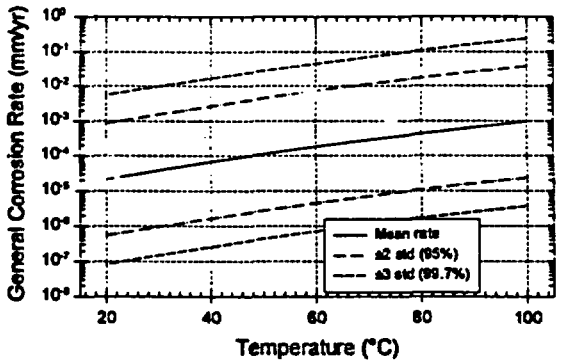
WPDEE Results for CRM General Corrosion Rate



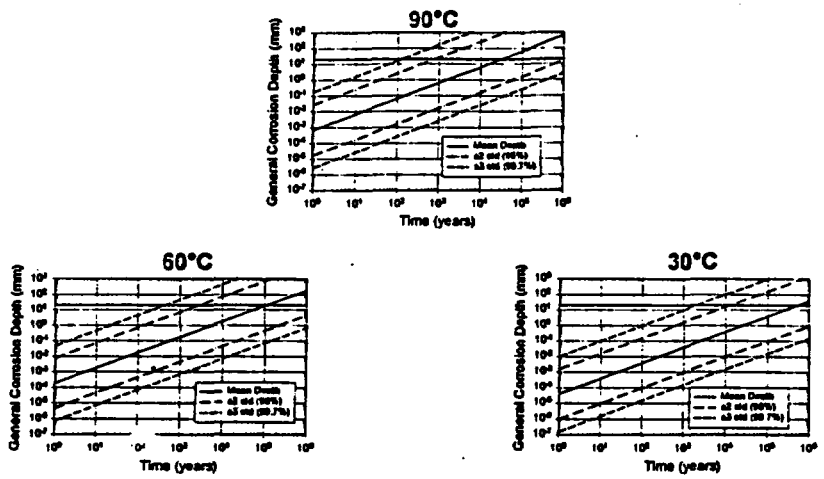
Cumulative Distribution Functions (CDFs) of Re-sampled CRM General Corrosion Rate from WPDEE



General Corrosion Rate vs. Temperature of CRM General Corrosion Model(I)



General Corrosion Depth predicted by CRM General Corrosion Model(I)



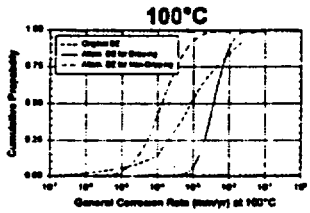
Abstraction of CRM General Corrosion Model(II)

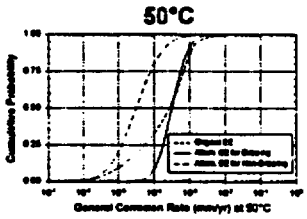
- Assumed CRM general corrosion rates with dripping higher than without drips (exposed to humid-air conditions all the time)
- Split the original combined distributions given for the three temperatures at the median (50th percentile) assuming that, for each temperature,
  - the first half of the distributions (up to 50th percentile) represents the general corrosion rates for no-drip conditions
  - the second half (from the 50th to 100th percentile) represents dripping conditions

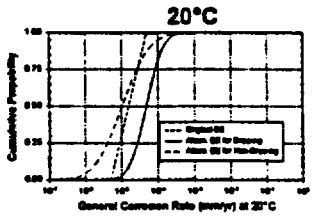
Abstraction of CRM General Corrosion Model(II)
(continued)

- Truncated the second half distribution for dripping conditions at each temperature at 10 μm/yr
  - the truncation to reflect maximum general corrosion rates of Alloy C-22 (2 μm/yr) and Alloy 625 (4 μm/yr) from short-term electrochemical polarization measurements in very aggressive conditions at LLNL
- Randomly sampled a total of 100,000 points from each of the three split cumulative distribution functions at the three temperatures for dripping or no-drip conditions
- Fit the re-sampled distributions to an Arrhenius functional form for no-drip or dripping conditions
- The split and truncation of the original distributions were "arbitrary" and to capture potential differences between dripping and no-drip conditions

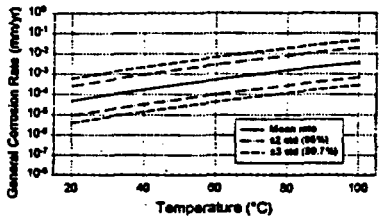
CDFs for CRM General Corrosion Rates Split for Non-dripping and Dripping Conditions



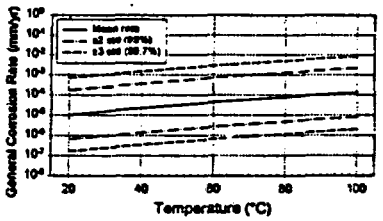




General Corrosion Rate vs. Temperature of CRM General Corrosion Model(II)

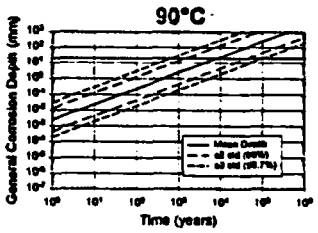


Dripping Conditions

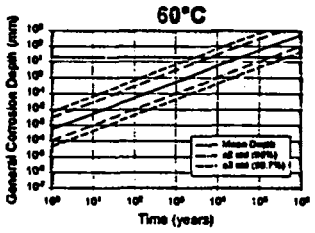


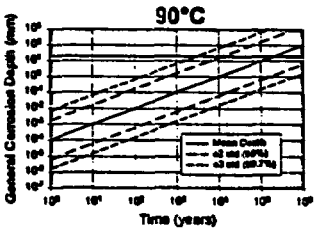
Non-Dripping Conditions

General Corrosion Depth predicted by CRM General Corrosion Model(II)

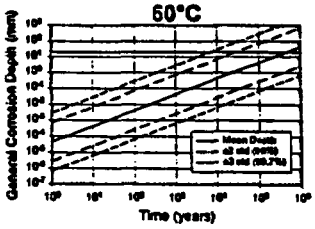


Dripping Conditions





Non-Dripping Conditions



Abstraction of CRM General Corrosion Model(III)

- CRM general corrosion model developed by the YMP after completion of the WPDEE Rev 0 Report
  - based on the 6-month data from the Long-Term Corrosion Test Facility, short-term electrochemical polarization measurement data at LLNL, and the published literature data

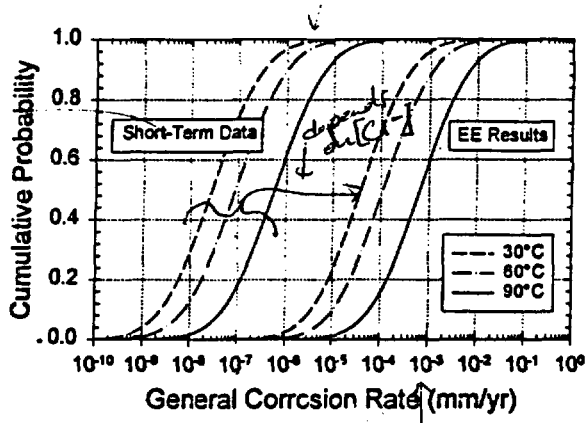
$$\text{Rate} = b_0 + b_1/T + b_2\,pH + b_3\,C_{NaCl} + b_4\,C_{FeCl3}$$

  - applicable conditions:
    $pH = 6\text{-}7$; $C_{NaCl} = 0.01\text{-}1$ wt.%; $C_{FeCl3} = 0$ wt.%
- The model "reduced" to a simpler function form (function of temperature only)
  - effects of the uncertain/variable water chemistry conditions represented by incorporating the suggested water-chemistry parameter ranges

Abstraction of CRM General Corrosion Model(III)
(continued)

- Estimated the uncertainty in the coefficients (b_i's) using the same data used for the model
- Generated distributions for general corrosion rates using the model at different temperatures by varying the model coefficients and the water chemistry parameters assuming pH=uniform (6,7) and C_{NaCl} (wt.%) = log-uniform (0.01,1)
- Fit the resulting general corrosion rate distributions to an Arrhenius functional form

Cumulative Distribution Functions (CDFs) of CRM General Corrosion Rate from Short-Term Data and WPDEE Results



Simulated diluted data

~~simulated~~ ~~actual data~~

1 mm/yr

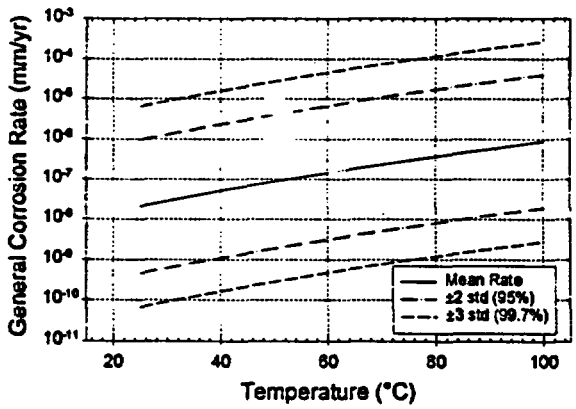
[Cl⁻] = 0.01 - 1 wt

pH = 6-7

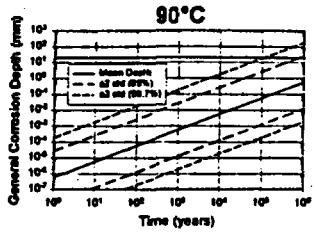
⇒ need to understand context of this p

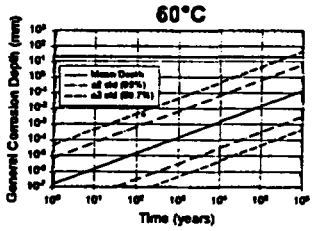
— under dropping!

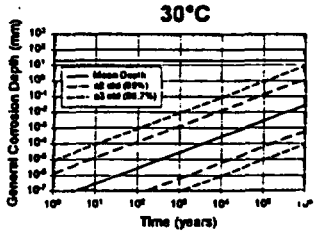
General Corrosion Rate vs. Temperature of CRM General Corrosion Model(III)



General Corrosion Depth predicted by CRM General Corrosion Model(III)







Abstraction of CRM Localized Corrosion Models

CRM Localized Corrosion Model(I)

- Logarithmic pit growth law from WPDEE

  depth = k * exp[Q (1/T - 1/373.15)] * log (t) - x_0

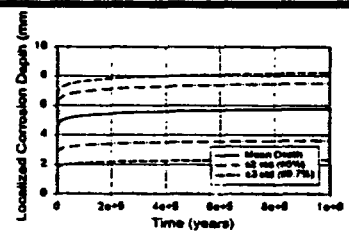
  t = time

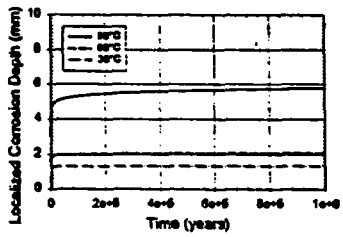
  k, Q and x_0 = constants; the values and uncertainties from WPDEE

Shoesmith Model
fit to data, exclude
extremely long t in ...

⇒

Localized Corrosion Depth Predicted by CRM Corrosion Model(I)





CRM Localized Corrosion Model(II)

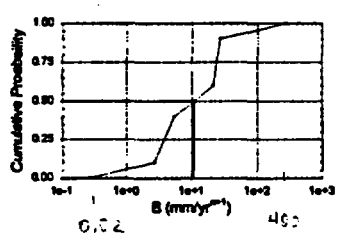
- **Exponential pit growth law from WPDEE**

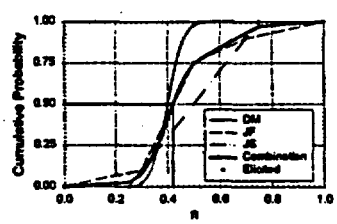
  depth = B * t^n

  t = time

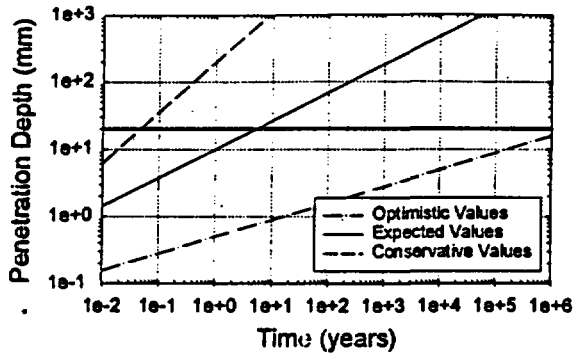
  B and n = constants; the values and uncertainties from WPDEE

Constants 'B' and 'n' of CRM Exponential Pit Growth Law





Localized Corrosion Depth Predicted by CRM Corrosion Model(II)



Optimistic values: B=0.5 mm/yr^n; n=0.25
Expected values : B=10 mm/yr^n; n=0.42
Conservative values : B=200 mm/yr^n; n=0.75

Abstraction of CRM Localized Corrosion Model(III)

- CRM localized corrosion model developed by the YMP after completion of the WPDEE Rev 0 Report depth = (rate) x $t^{1/2}$
  - based on the 6-month data from the Long-Term Corrosion Test Facility, short-term electrochemical polarization measurement data at LLNL, and the published literature data
  - the rate term identical to CRM general corrosion model(III), but with different applicable water chemistry ranges in crevice/pits
  - suggested applicable conditions:
    pH = 1.63 - 6; C_{NaCl} = 0.01 - 10 wt.%; C_{FeCl3} = 0.01- 4 wt.%
- The ~~model~~ rate term "reduced" to a simpler function form (function of temperature only)
  - effects of the uncertain/variable water chemistry conditions represented by incorporating the suggested water-chemistry parameter ranges

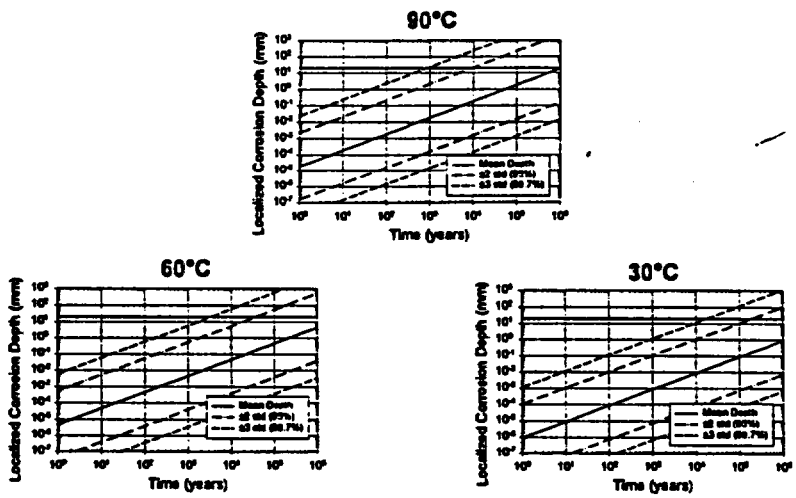
Abstraction of CRM General Corrosion Model(III)
(continued)

- Estimated the uncertainty in the coefficients (b_i's) using the same data used for the model
- Generated distributions for localized corrosion rates using the model at different temperatures by varying the model coefficients and the water chemistry parameters assuming pH = uniform (1.63,6), C_{NaCl}(wt.%) = log-uniform (0.01,10), and C_{FeCl3} (wt.%) = log-uniform (0.01,4)
- Fit the resulting localized corrosion rate distributions to an Arrhenius functional form

Composite distribution

What is saturation limit of $FeCl_3$ in H_2O?

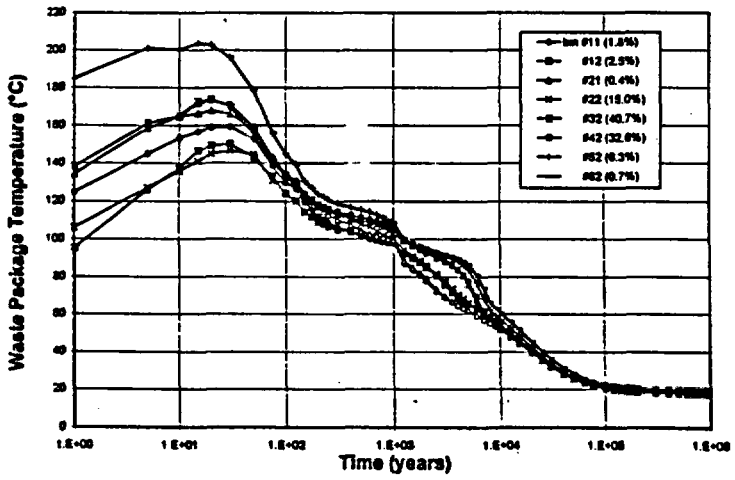
Localized Corrosion Depth Predicted by CRM Corrosion Model(III)



— not sure of time?
n=1!
⇒ needs to be changed

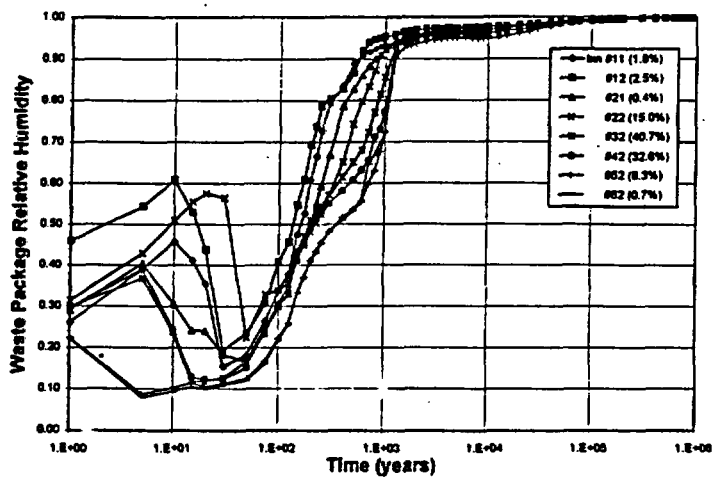
Sensitivity of WP Degradation to CRM Corrosion Models

Time-histories of Temperature of CSNF WP Groups
(CC area; base case; climate change at 1000 yrs; no backfill)



Time-histories of Relative Humidity of CSNF WP Groups

(CC area; base case; climate change at 1000 yrs; no backfill)

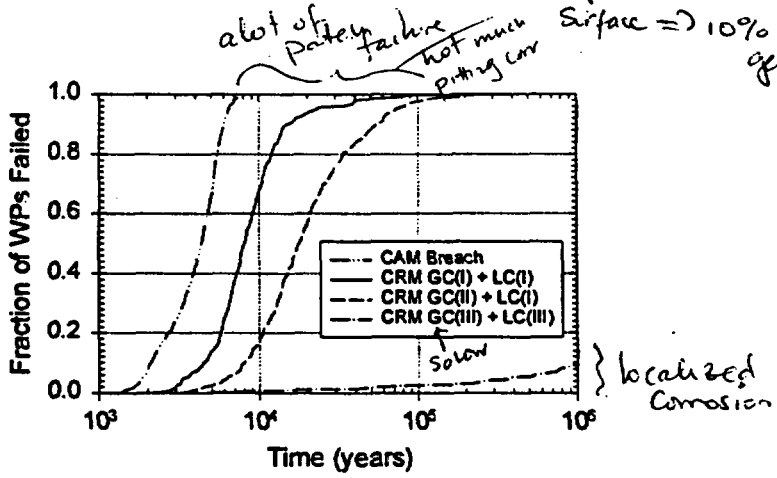


Sensitivity of WP Failure to CRM Corrosion Models

(base case; climate change at 1,000 years; no backfill; 10% WP dripped on)

all 400 WP dripped on

Surface ⇒ 10% WP surface undergo general + local. corr.



model III = sampled distrib.

• 1st pit through = failed WP

* model can have all WP not dripped on
* WP corr by general / HA corr if no drips

Concluding Remarks

- CRM corrosion models have potentially significant impacts on long-term performance of waste packages,
- This warrants very careful evaluation and assessment of CRM corrosion rates for the use in the performance assessment calculations of long-term waste package degradation
- Additional assessments from the panel for the CRM corrosion rates will be incorporated in the TSPA-VA waste package degradation analysis

Backups

Parameters and Assumptions Used in the Stochastic WP Degradation Modeling

- 400 WPs per simulation; 964 patches per WP with a single patch area of 310 cm^2; a pit density of 10 pits/cm^2
- Multiple histories for T and RH of WP groups in a given repository location
- CAM corrosion
  - T and RH thresholds for the initiation of CAM humid-air and aqueous corrosion from WPDEE CDF tables
    - the thresholds distributed among WPs to be modeled
    - individual WP assigned with different T and RH thresholds
  - TSPA-1995 models used for CAM humid-air and aqueous general corrosion
    - the model parameters sampled stochastically for a WP and the patches within the WP
    - an uniform corrosion depth assumed for individual patches

Parameters and Assumptions Used in the Stochastic WP Degradation Modeling (continued)

- CAM corrosion (continued)
  - Variations in CAM corrosion modeled with the localization factor (or pitting factor) with a mean of 1.5 and a standard deviation of 0.25
    - the same localization factor distribution applied equally to all the patches
- CRM corrosion
  - Once a CAM patch penetrated, an aqueous condition assumed for the ("same size") patch of CRM underneath the failed CAM patch
  - Assume general corrosion active for the CRM patch in the absence of water drip, and both the localized corrosion and general corrosion active for the CRM patch if dripped on
    - CRM general and localized corrosion modeled as a function of temperature
    - the model parameters sampled stochastically for a WP and the patches within the WP

Parameters and Assumptions Used in the Stochastic WP Degradation Modeling (continued)

- CRM corrosion (continued)
  - CRM patches penetrated by general corrosion if no drips, and by pitting/crevice and general corrosion if dripped on
- Representation of variability and uncertainty in WP degradation
  - Incorporate explicitly the effects of temporally and spatially varying exposure conditions
    - T, RH, WP surface dripped on
    - effects from other sources not explicitly accountable represented by splitting the uncertainties in the individual model parameters
    - half of the uncertainty distributed among WPs (Package-to-package variability) and other half among patches (patch-to-patch variability)

(3)

Rationale for Selection of C-22 as the Base Case Alloy

February 2, 1998

David Stahl, (Ph.D.) Manager

Waste Package Materials Department

Outline

- Basis for Change
- Design Impacts
- Corrosion Performance
- Weldability
- Summary

Basis for Change

- Expert panel concluded that crevice/pitting corrosion is the most probable degradation mode for the inner barrier
  - Note however that the elicitation process yielded large uncertainty in general corrosion rate which made that the dominant long-term mechanism
- Original selection process did not include local corrosion resistance as a selection criterion

  Alloy 625 selected as ref. mat'l

- Original selection was also based on 1000 years as waste package lifetime → going to 3000 yrs + maybe more

Design Impacts

- Structural and thermal analyses not complete but no change in design is expected because of similarities in properties of Alloy C-22 and Alloy 625

- By comparison, the two CRM waste package (Alloy C-22 over titanium alloy) design represents a significant change in analysis

  have begun to evaluate this design.

- Analysis documenting selection of Alloy C-22 completed in December 1997 and base-line change approved January 29, 1998

Corrosion Resistance

- Alloy C-22 is much more resistant to crevice/pitting corrosion than Alloy 625
- Susceptibility to crevice/pitting is a function of crevice chemistry, pH, temperature and crevice geometry
- For a given crevice condition, critical temperature for local corrosion is important
  - This is the temperature below which corrosion does not occur

Corrosion Resistance (Continued)

- In a relatively aggressive solution containing 24,300 ppm chloride:
  - Critical crevice corrosion temp.
    - C-22 102 deg C
    - 625 50 deg C
  - Critical pitting corrosion temp.
    - C-22 >150 deg. C
    - 625 90 deg. C

Note: J-13 water has only 7.2 ppm chloride

Corrosion Resistance (Continued)

- Alloy C-22 has excellent phase stability under low temperature (~450 deg C) aging while Alloy 625 suffers from embrittlement

- Alloy C-22 is less susceptible to stress corrosion cracking than alloy 625 under similar conditions

- C-22 is a newer alloy. C-22 was developed in 1985 and Alloy 625 was developed in the 1950s, however, costs are about the same.

Weldability

- Discussion with manufacturers has indicated that weldability of Alloy C-22 is not significantly different than Alloy 625 (perhaps up to 5% increase in welding time)

- Framatome welding engineers do not forsee great difficulty in the closure weld

- However, Alloy C-22 is <u>not</u> as amenable to weld cladding deposition, as opposed to shrink fit.

  under bead cracking, perhaps due to dilution of alloying constituents

Summary of Change to Alloy C-22

- Basis for change was presented
- Design impacts are minimal
- Corrosion performance is superior
- Weldability and cost are similar
- Analysis for material change was performed and base-line change was approved

(4)

Recent Corrosion Resistance Material Test Results

R. Daniel McCright

Waste Package Degradation Expert Elicitation Panel Meeting

2 February 1998

Source of Corrosion Resistant Material Data

- Long-term Corrosion Test Facility constructed at LLNL in 1996-97
- Total of 24 vessels operating, 6 contain Ni-base corrosion resistant candidate alloys
- Ni-base candidate materials include Alloys 825, G-3, 625, C-4, and C-22
- Emphasis in this presentation is on Alloy C-22
- 6 vessels containing Ni-base alloys operate at 2 temperatures (60 and 90 C) and three different water chemistries
  - low ionic strength water (code SDW) – dilute water
  - high ionic strength water (code SCW) – conc. water
  - acidified, high ionic strength water (code SAW) – acidified (H_2SO_4), conc. water
- These 6 vessels began operation in February to April 1997
- Six-month exposure data available from all 6 vessels, one-year data available from one vessel

Nickel Material Under Test in Long Term Corrosion Test

UNS Number	Common Name	Nominal Composition
N08825	Alloy 825, Incoloy 825	40 Ni 22 Cr 3 Mo 31 Fe
N06985	Alloy G-3, Hastelloy G-3	48 Ni 23 Cr 7 Mo 20 Fe
N06625	Alloy 625, Inconel 625	62 Ni 23 Cr 9 Mo 5 Fe
N06455	Alloy C-4, Hastelloy C-4	60 Ni 16 Cr 16 Mo 3 Fe
N06022	Alloy C-22, Hastelloy C-22	57 Ni 22 Cr 13 Mo 3 W 4 Fe

About the Three Water Chemistries

- Low Ionic Strength Water -- Essentially 10 x [average of J-13 water + perched water compositions]
- High Ionic Strength Water -- Essentially 1000 x [average of J-13 water + perched water compositions]
- Acidified, high ionic strength water -- like the above but pH adjusted to 2.7 target pH by H_2SO_4 addition
  ↳ pH simulates crevice or MIC env.
- Solutions made up by adding different 'salts' (e.g. $NaHCO_3$, KNO_3, NaCl, etc.) to get desired target composition to deionized water
- Solubility of some compounds exceeded in the more concentrated environments (e.g. $CaCO_3$ precipitation)
- Metal test specimens placed on racks so that some are fully immersed in water and some are exposed to wet vapor above water line

Target Compositions for the Three Water Chemistries

	J-13 Well Water (measured)	Low Ionic Strength Water (~10x J-13)	High Ionic Strength Water (~1000x J-13)	Acidified High Ionic Strength Water
pH	7.41	9.3-9.5	9.8-9.9	2.7 - 2.8
Na	45.80 mg/l	409 mg/l	40,900	37,690
Si	28.5	27-49*	27-49*	27-49*
Ca	13.0	0.5	<1	1000
K	5.04	34	3400	3400
Mg	2.01	1	<1	1000
F	2.18	14	1400	0
Cl	7.14	67	6700	24,250
NO_3	8.78	64	6400	23,000
SO_4	18.4	167	16,700	38,600
HCO_3	128.9	947	70,000	0
$CaCO_3$		470 (precipitate)	47,500 (ppt)	
$MgCO_3$		70 (precipitate)	7300 (ppt)	

* measured OCP of alloys in these sol'ns!

Seems to high ← V_{OCP} = +500 mV → +100 mV

* No chem. potentio stat. sol'ns sat. w/oxygen

Some Actual Water Chemistries

Constituent	Low Ionic Strength	High Ionic Strength	Acidified High Ionic Strength
pH	9.02/9.29 → 9.6-9.8	9.40/9.65 → 9.8-9.9	2.74/2.71 → stable
Na	440/430 mg/L +	44,000/45,000 mg/L +	43,000/42,000 mg/L +
Si	20/21	52/55	27/42
Ca	3/1	1/2	55/55
K	36/36	3600/3700	3700/3500
Mg	1.3/1	0.1/0.3	52/51
F	13/16	1290/1410	<10/<10
Cl	127/101	8410/8400	27,500/26,900
NO_3	63/65	8120/7580	24,300/24,000
SO_4	174/180	14,200/14,000	42,400/41,000
HCO_3	750/660 *	60,270/56,600 *	na/na → just evolve bicarbonate after time

→ establish carbonate, bicarbonate eqn.

+ first figure is concentration in 60 C vessel, second in 90 C vessel
+ these analyses performed near time of initial operation
* bicarbonate calculated from total inorganic carbon analysis

CO_2 enriched air above water } may affect corr. behavior of steel

don't replenish chem. only water

- most. corr. stay same if run for long time. [Cl^-],
- pH changes, creeping up over time

6-Month General Corrosion Data for Alloy C-22

	Temperature (°C)	Low Ionic Strength Water	High Ionic Strength Water	Acidified High Ionic Strength Water
in water	60	0.04 μm/yr	0.08 μm/yr	0.04 μm/yr
in water	90	0.06	0.08	-0.02
in vapor	60	0.05	0.06	0.06
in vapor	90	0.06	0.07	0.05

deposits on coupon, can't clean off. original error in measurements.

10^{-5} mm/yr

+ corrosion rates are averages of 8-12 specimens in each condition → what's upper + lower limit
+ negative value indicates weight gain

General Corrosion Rates of Alloy C-22 After 5 Months and 1 Year

		6-month exposure (4296 hours)	1-year exposure (8376 hours)
In water	60 C, acidified high ionic strength water	0.04 μm/yr	0.03 μm/yr
In vapor	60 C, above the acidified high ionic strength water	0.03	0.04

→ Peter ⇒
- wants to know how much the weight gain due to corrosion deposits + then weigh after

+ corrosion rates are averages of 12 specimens in each condition
+ above data suggest that rates do not change with time

Commentary on Corrosion Test Results from Alloy C-22

- Thus far, no evidence of localized attack - pitting or crevice attack, even in intentionally creviced area (metal/Teflon crevice)
- No evidence of preferential attack around welds
- Corrosion rate appears insensitive to temperature, pH, other water chemistry, and whether specimen in the water or in the saturated vapor for ranges tested
  - 60 - 90 C
  - pH 2.7 - 9.9
  - 10 x - 1000x 'J-13' (70 - 7000 ppm chloride ion)
- Therefore, a 'grand cannonical' average of 128 test specimens for all conditions tested is <u>0.05 μm/yr</u>
- For the one data set available, corrosion rate appears unchanged with time
- Behavior of this material has followed expectations

at 90°C ⇒ teflon will creep

A Simple Cumulative Frequency Table Calculated from C-22 Corrosion Rate Data

Percentile	Corrosion Rate (μm/yr)
5%	-0.05
10%	-0.01
25%	0.02
50%	0.05
75%	0.08
90%	0.10
95%	0.12
99%	0.25

compiled from128 coupons: 3 water chemistries x 2 temperatures x 2 locations (vapor and water) -- 6 mo. corrosion data

Comparison of Corrosion Rates of Nickel Base Alloys

Ni-Cr-Mo Alloys	Environment	Corrosion Pate (μm/yr)
C-22	90 °C Acidified High Ionic Strength Water	-0.02
C-4	"	0.04
625	"	-0.06
Ni-Fe-Cr-Mo Alloys		
G-3	"	0.01
825	"	0.24*

* showed crevice corrosion in this test environment

Technique for Characterizing Test Specimens

- General procedure is ASTM G-31
- Follow a 'planned interval' test approach
- Written some specific YMP-QA Technical Implementation Procedures (TIPs) for our circumstances
  - TIP CM-01 through CM-11
  - These cover pre-exposure specimen measurement, weighing, specimen identification, handling, make-up of test waters
- Micrometers, weights calibrated to NIST traceable standards
- Post-exposure specimens usually covered by a light, white scale, presumably Ca-rich or Si-rich -- cleans off rather easily } other more stubborn oxides, haven't characterized
- Specimen cleaning follows ASTM G-1
  - Specifically for the Ni-base alloys: most often use C.6.1 (150 mL conc. HCl diluted to make 1000 mL of solution - 1 to 3 minutes); occasionally use C.7.5 (100 mL conc. HNO_3 + 20 mL HF - 5 to 20 minutes)

Sample Calculation of General Corrosion Rate from Weight Loss Measurement

- 'Formula' from ASTM G-31: corrosion rate = kw/Atd, where
  - k is proportionality constant for desired units, here μm/yr
  - w is weight change (in gm),
  - A is exposed specimen area (in cm^2),
  - t is exposure time (in hrs),
  - d is density (in gm/cm^3)
- As an example, use sample DWA 042 from Rack 26-1 (90 C acidified high ionic strength water, vapor phase)
- For this sample, weight loss was 0.0006 g , surface area was 28.111 cm^2, time was 4344 hours, density is 8.8 gm/cm^3, k is 8.76×10^7
- Calculated corrosion rate is 0.05 μm/yr

Sources of Experimental Error

- **Instrumental:**
  - Balance accuracy: 0.2 mg (0.0002 g)
  - Micrometer accuracy: 0.0005 in or ~0.0013 cm
  - Calibrate both at each 'sitting'
  - Typical weight change 0.1 mg to 1.3 mg on 25 g 'weight loss' specimens and 0.1 mg to 3.8 mg on 50 g 'crevice' specimens
  - Significant error for calculated corrosion rates near zero, only 5 -15 % for highest rates measured in this series
  - Error should become less for longer exposure times
- **Operator:**
  - Each operator recalibrates at start of 'sitting'
  - Tried to eliminate this as a source
- **Specimen cleaning:**
  - This is an 'art'
  - Some deposits hard to eliminate (Ni alloys easier than Ti)
  - Much harder to estimate, perhaps ~ 20%

Summary/Conclusions

- General corrosion rates of Alloy C-22 are low, mostly less than 0.1 μm/yr, for exposure periods up to one year in a range of environments simulating Yucca Mountain geochemical conditions
- Thus far, general corrosion rate of Alloy C-22 appears to be insensitive to pH, T, and water chemistry over range of conditions tested
- Thus far, general corrosion rate of Alloy C-22 does not appear to change with exposure time
- However, single-metal tests of C-22 and galvanically-coupled tests (carbon steel/C-22) are continuing for much longer time periods for more definitive conclusions

(5)

Model Development for Crevice Corrosion & Pitting of High-Level Waste Containers

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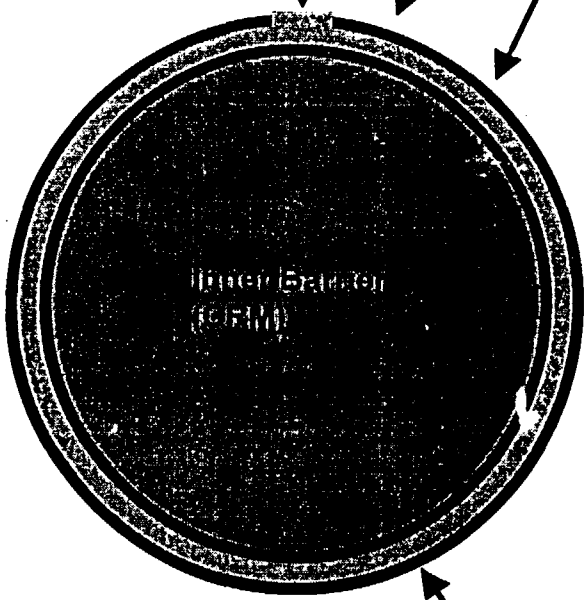
Repository

- Proposed deep geological repository at Yucca Mountain
  - At western boundary Nevada Test Site (near Beatty)
  - Underground in welded tuff - unsaturated zone
    - 600-1300 ft below ground level
    - 800-1200 ft above water table
- Long-term stability of the waste package is required
  - Substantially complete containment of spent fuel for 300-1000 years
  - Radioactivity will decay to a level comparable to a natural deposit of uranium ore in 10,000 years
- Construction of containers
  - Outer barrier: 10 cm of Alloy 516 (CAM)
  - Inner barrier: 2 cm of Alloy 825, 625 or C-22 (CRM)

Choice now

Conceptual representation of WP under attack



→ real possibility

S. ppression of pH (Wang)

$FeCl_3$ (wt. %)	pH
1	1.92
2	1.86
3	1.71
4	1.63
10	0.70

← hydrolysis reactions

Suppression of pH (Jones)

Salt	1 N	3 N	Saturated
$FeCl_2$	2.1	0.8	0.2
$NiCl_2$	3.0	2.7	2.7
$CrCl_3$	1.1	-0.3	-1.4

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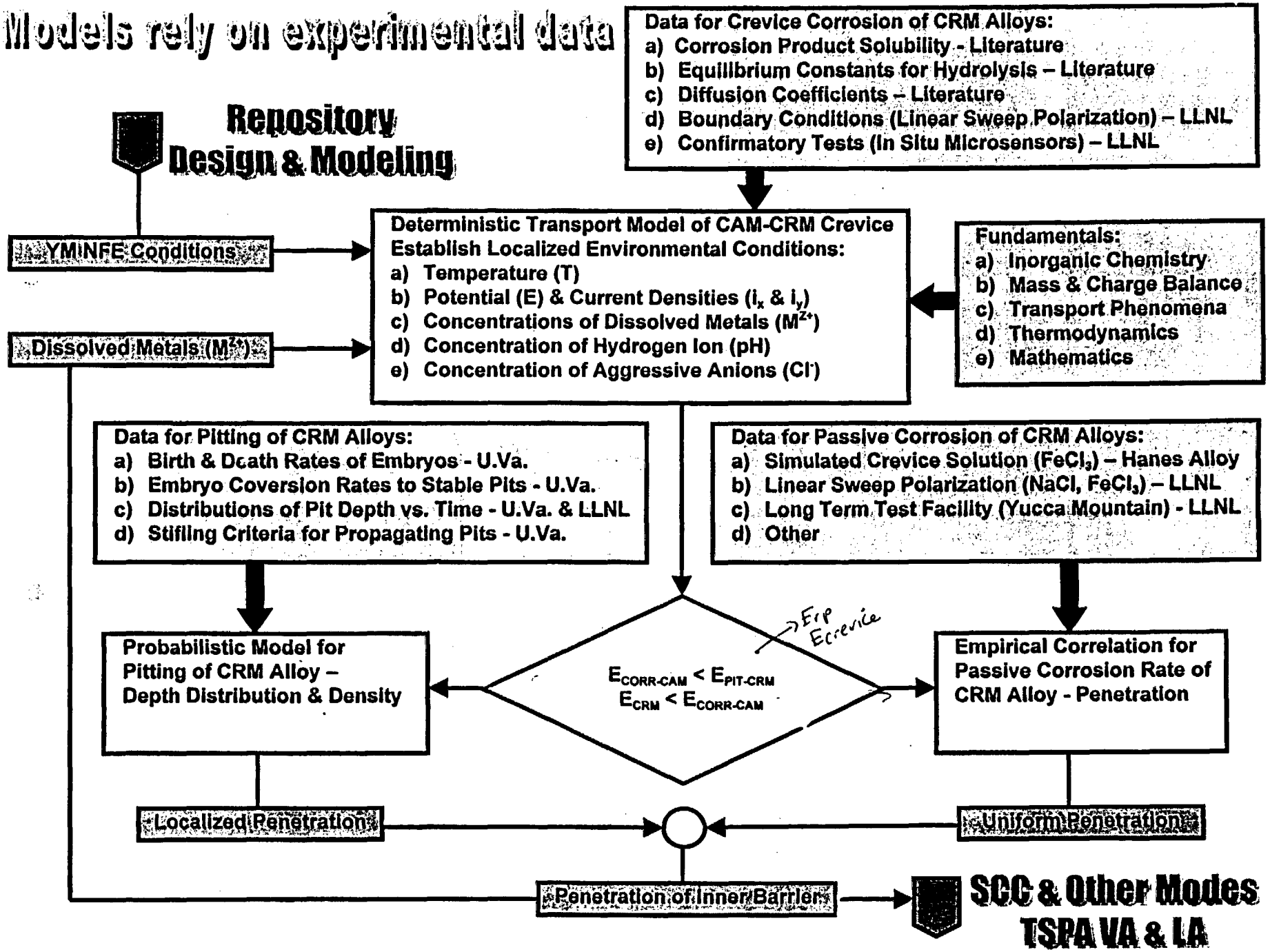
Crevice corrosion should be accounted for by TSPA

- Crevices will be formed
  - Between waste package and supports
  - Between CAM and CRM
  - Beneath dust, scale and biofilms
- The crevice environment will be more severe than the NFE
  - Suppression of pH due to the accumulation of H^+ from the hydrolysis of dissolved metal
  - Field-driven electromigration of Cl^- (and other anions) into crevice must occur to balance cationic charge associated with H^+
- The crevice environment sets the stage for other modes of attack
  - General corrosion ⇒ passive corrosion
  - Pitting (initiation & propagation)
  - Stress corrosion cracking (initiation & propagation)
- The development of an adequate crevice corrosion model is prudent

Models rely on experimental data



Corrosion research for waste package

- Long Term Corrosion Test Facility
  - Four generic test solutions
    - Simulated Acidified Well Water (SAW)
    - Simulated Dilute Well Water (SDW)
    - Simulated Concentrated Well Water (SCW)
    - Simulated Cement-Modified Water (SCMW)
  - Four generic sample configurations
    - Weight loss
    - Crevice
    - Galvanic couples
    - U-bend

Corrosion research for waste package (cont'd.)

- Other corrosion testing & characterization
  - Atmospheric (TGA)
  - Electrochemical - Acid
  - Mechanical (Slow-Strain Rate Testing)
- Corrosion modeling for Total System Performance Assessment (TSPA)
  - Simple correlations of experimental data
  - Mechanistic models - needed for long-term predictions
    - Deterministic transport model for crevice
    - Probabilistic model for pit initiation and growth
    - Film rupture model for stress corrosion cracking

Corrosion research for waste package (cont'd.)

Composition of Waters in Long Term Corrosion Test Facility

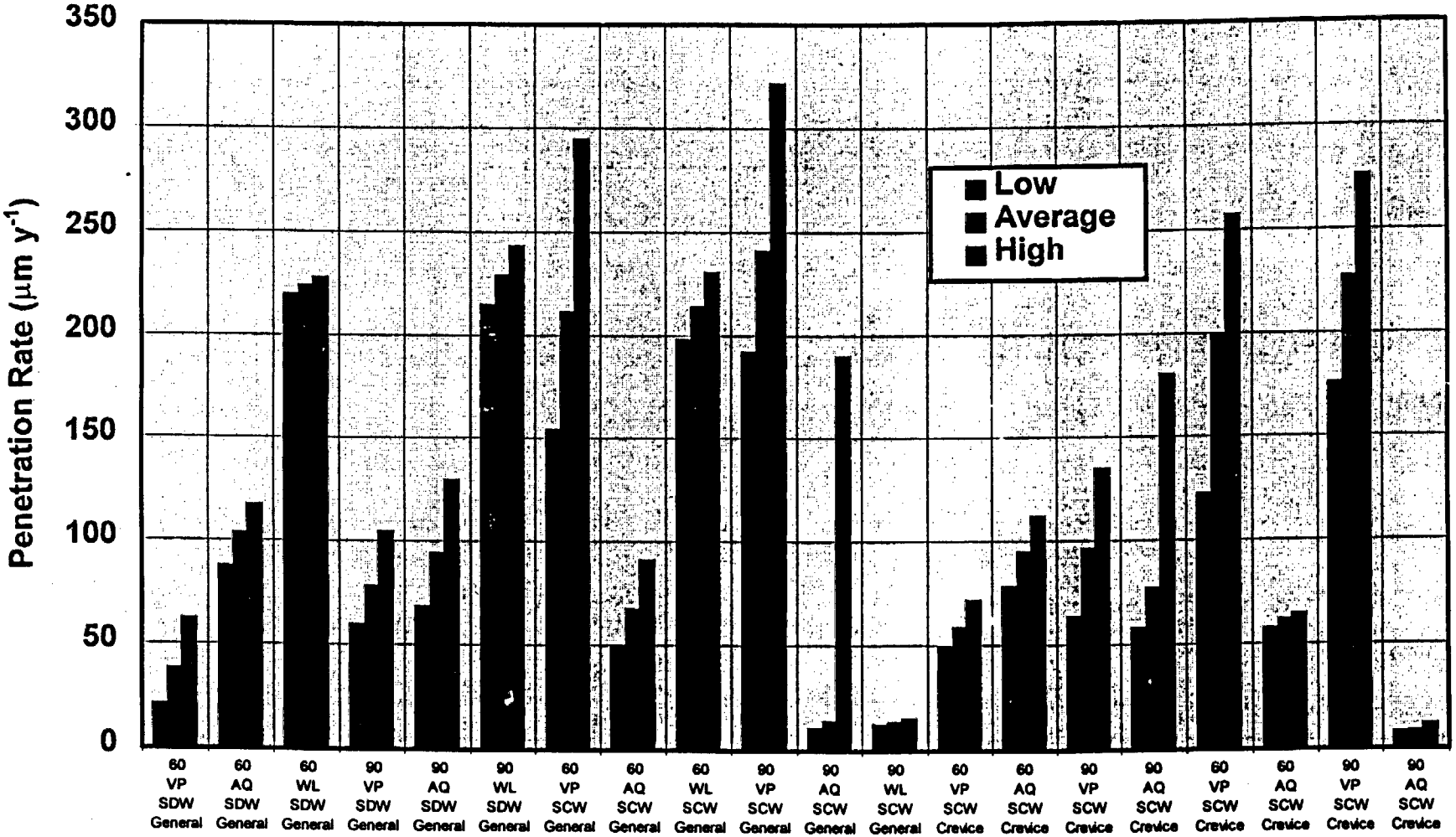
Media	Temp.	pH	Ca^{2+}	Mg^{2+}	K^+	Na^+	Si	SO_4^{2-}	Cl^-	NO_3^-	F^-	HCO_3^-	Equiv. NaCl
	°C		ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
SDW	60	9.5	3.5	1.2	36	430	17	170	68	62	14	720	112.095
SDW	90	9.9	3.4	ND	38	460	16	180	74	64	15	700	121.986
SCW	60	9.2	16	29	4600	36000	18	13000	7400	7000	330	44000	12198.587
SCW	90	9.2	15	3.4	4[illegible]	44000	58	13000	7500	7200	1400	51000	12363.433
SAW	60	2.7	58	52	4300	43000	30	41000	28000	23000	0	0	46156.815
SAW	90	2.7	58	53	4300	43000	50	40000	27000	24000	0	0	44508.357
SCMW	60	7.8	400	4	85	10	10	1200	11	10	< 0.1	< 1	18.133

assume all free Cl^- is from NaCl

– wants to see what is correlated w/ NaCl

Cl^-, NO_3^- ⇒ cancel each other out may preclude corrosion

Observed Penetration Rates for A516 (6 month data)



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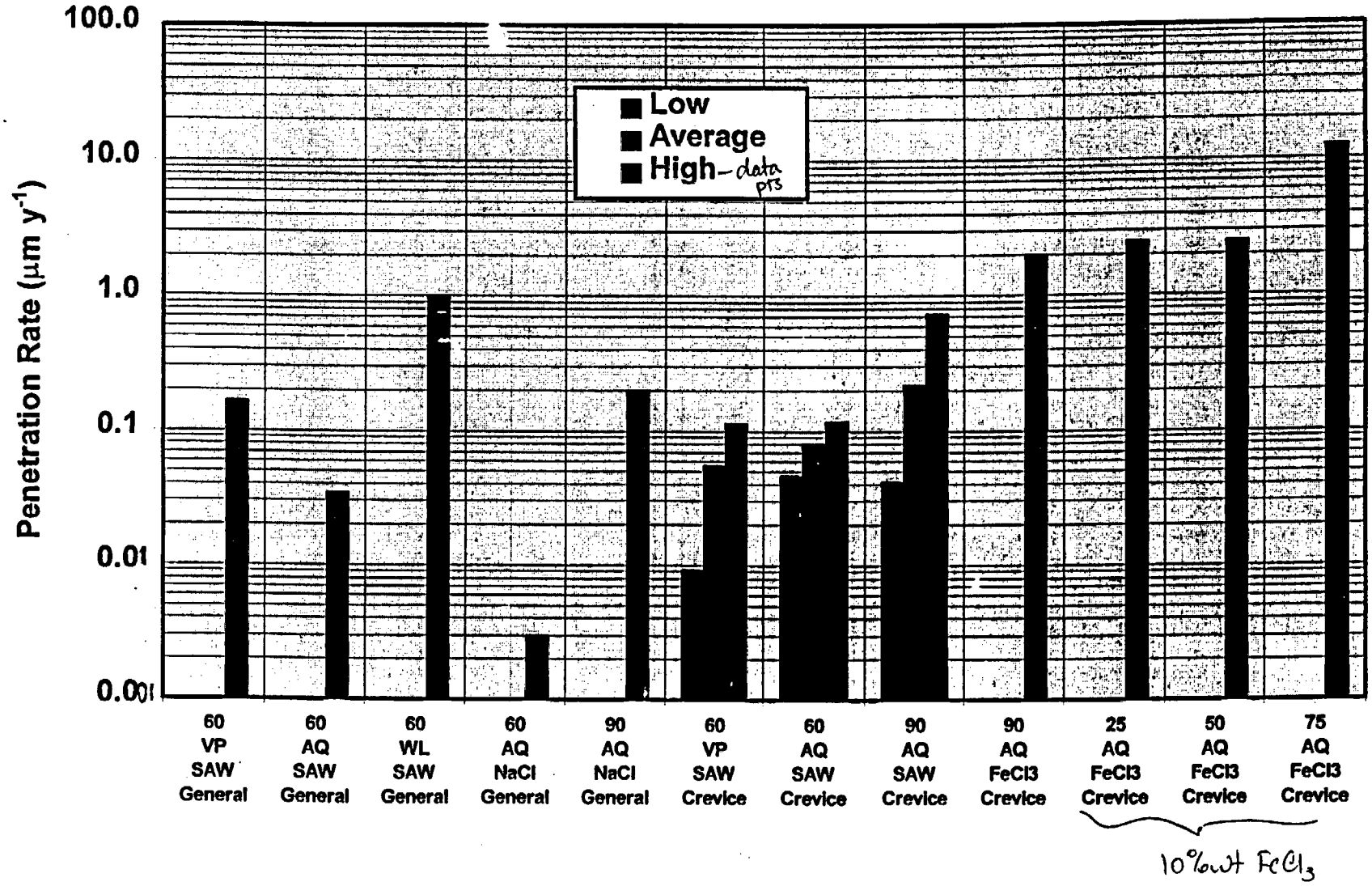
Observed Penetration Rates for C-22 (all sources)



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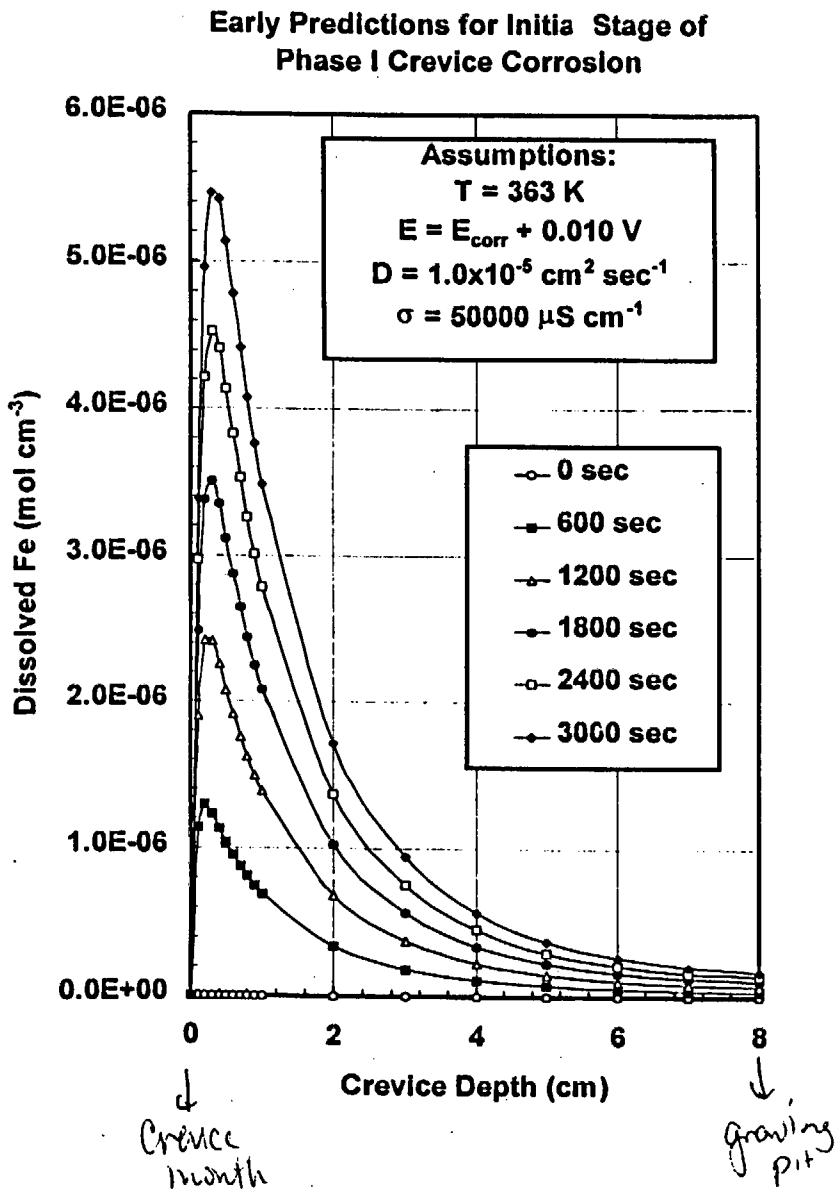
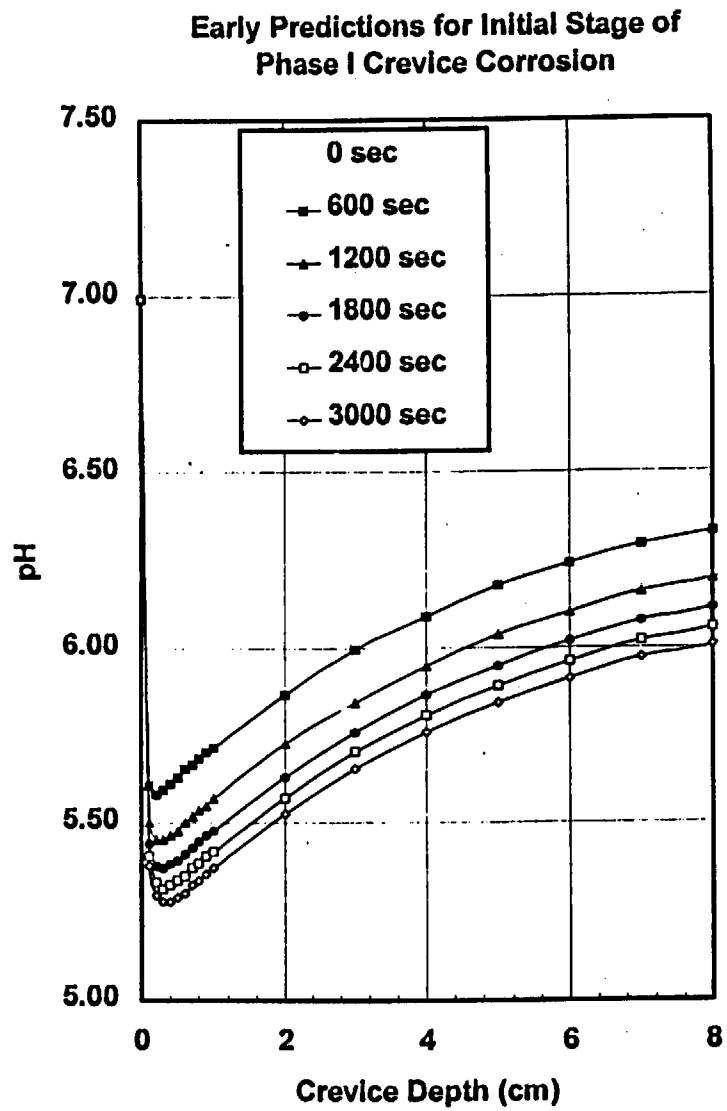
Phase I sets stage for attack of inner barrier





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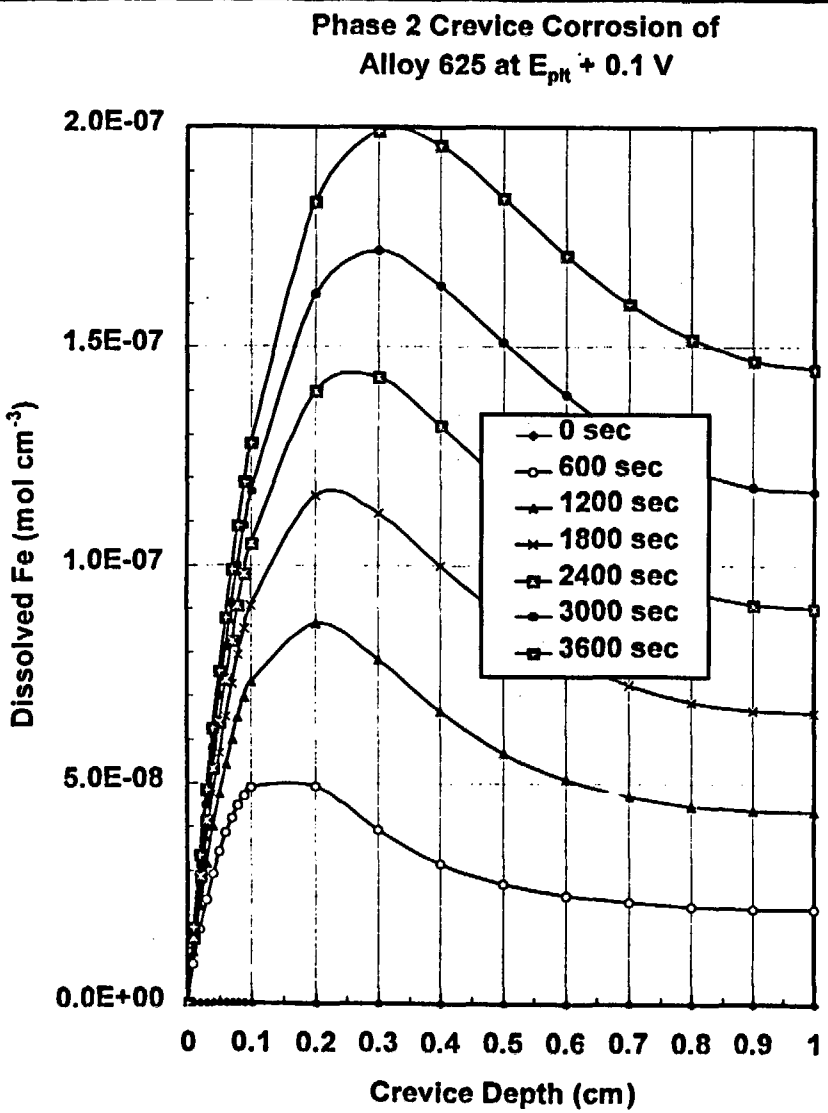
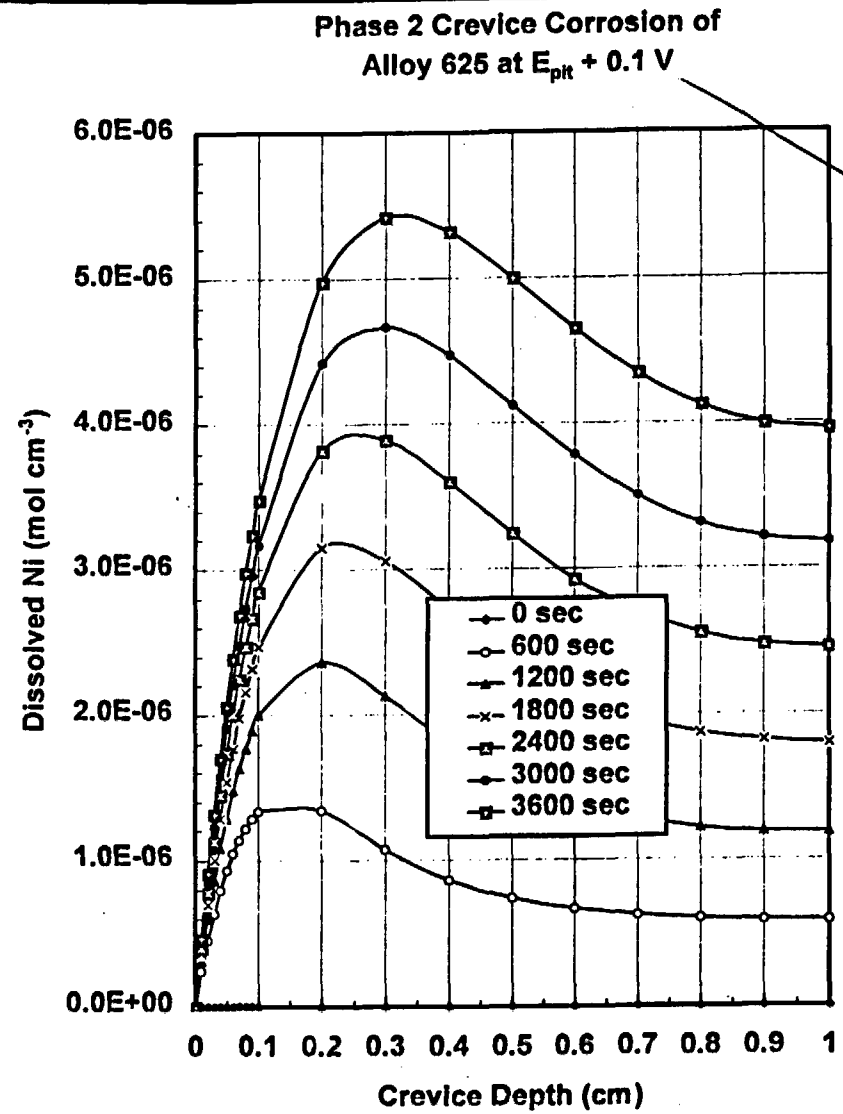
Metal dissolution during Phase II crevice corrosion





if we lower potential we don't get these dissolution

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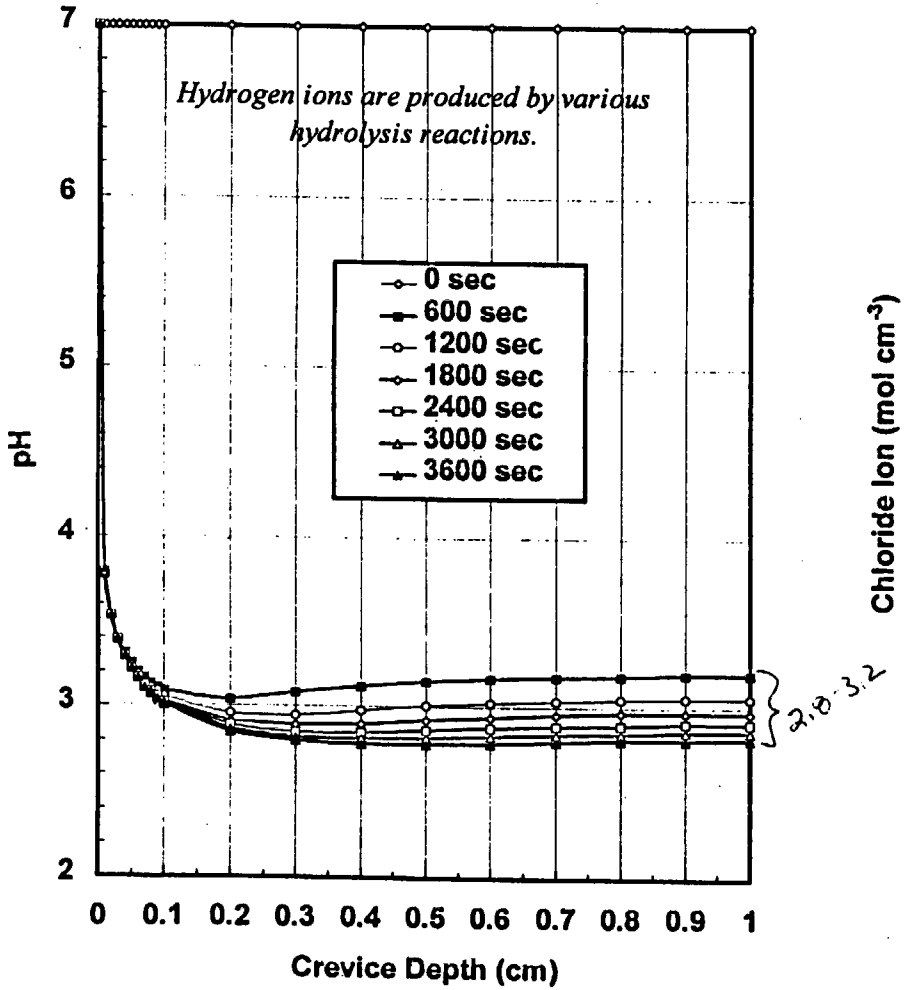
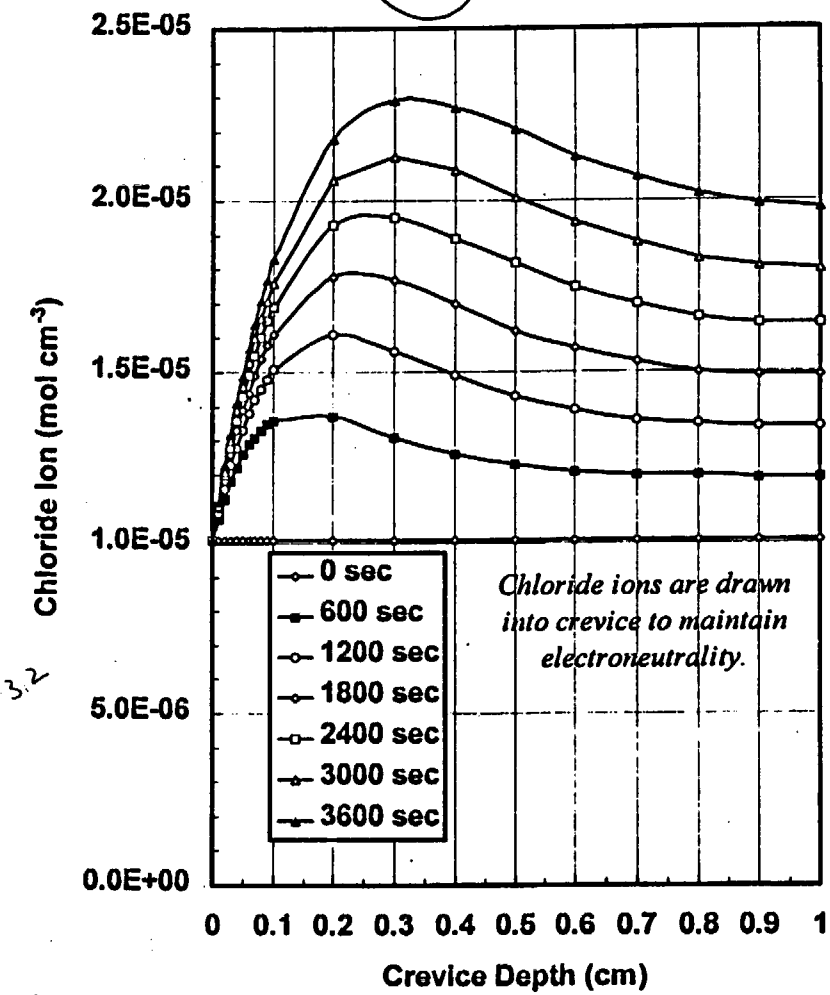
Suppression of pH during Phase II crevice corrosion

Crevice w/ only 625, not 516/625 crevice





Both low pH & high chloride exacerbate corrosion of CRM.

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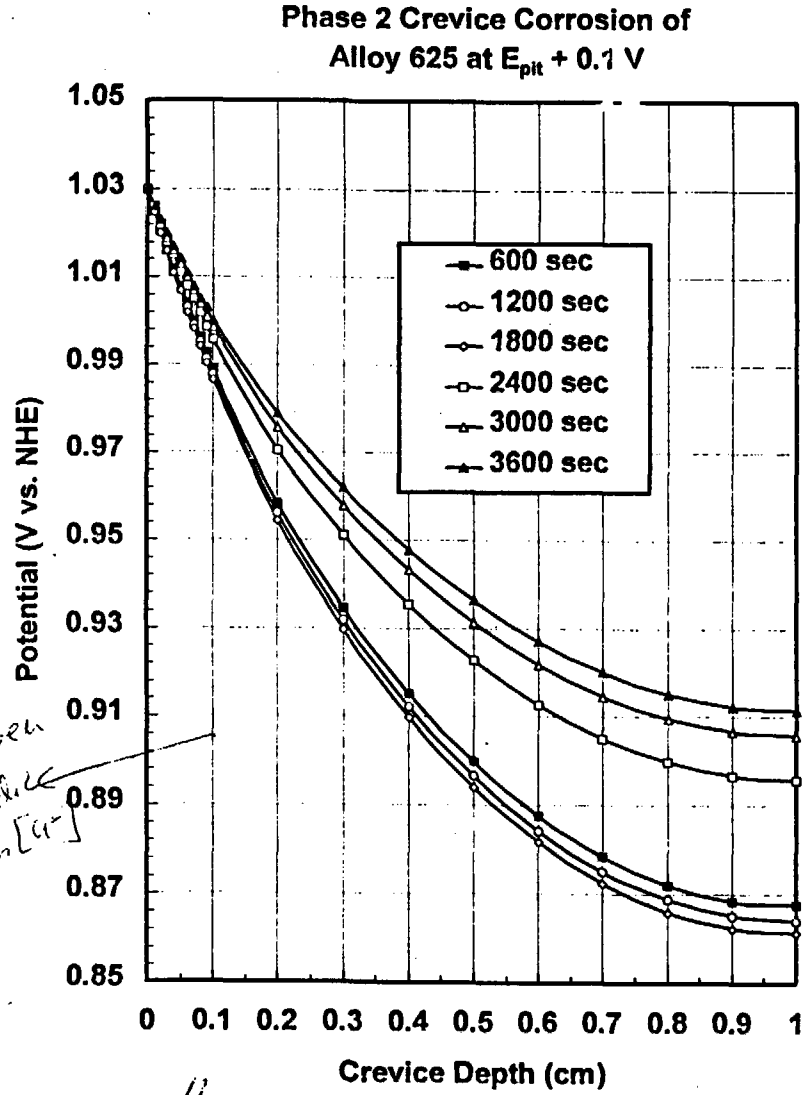
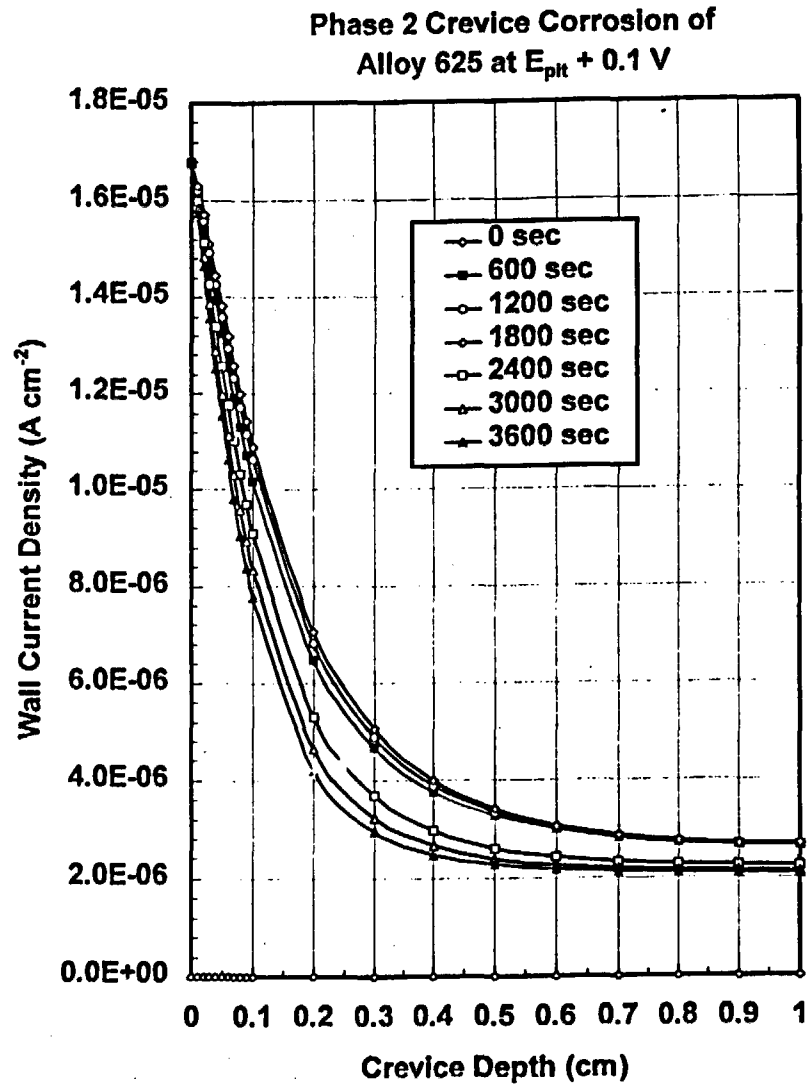
Potential & current during Phase II crevice corrosion





increases down
horizontal axis
is dep. on [Cl-]

Consistent w/ CANDRA work

Potential becomes less damaging inside crevice.

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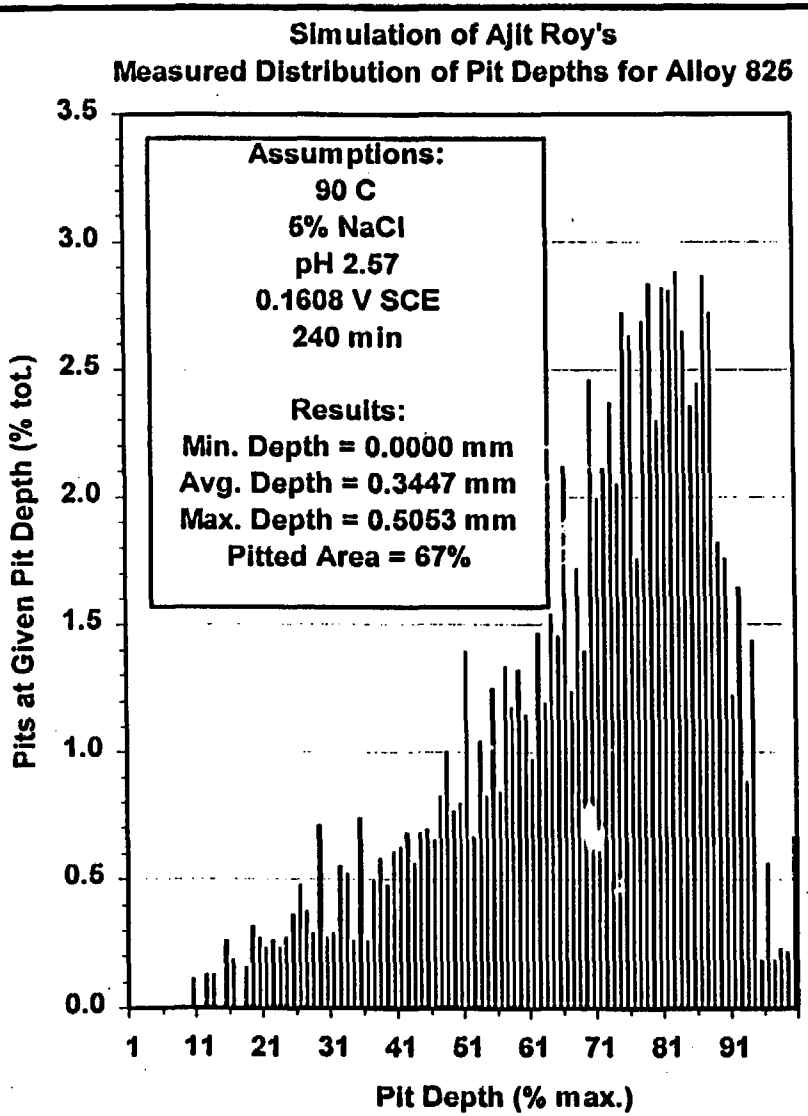
Confirmatory experiment for transport model

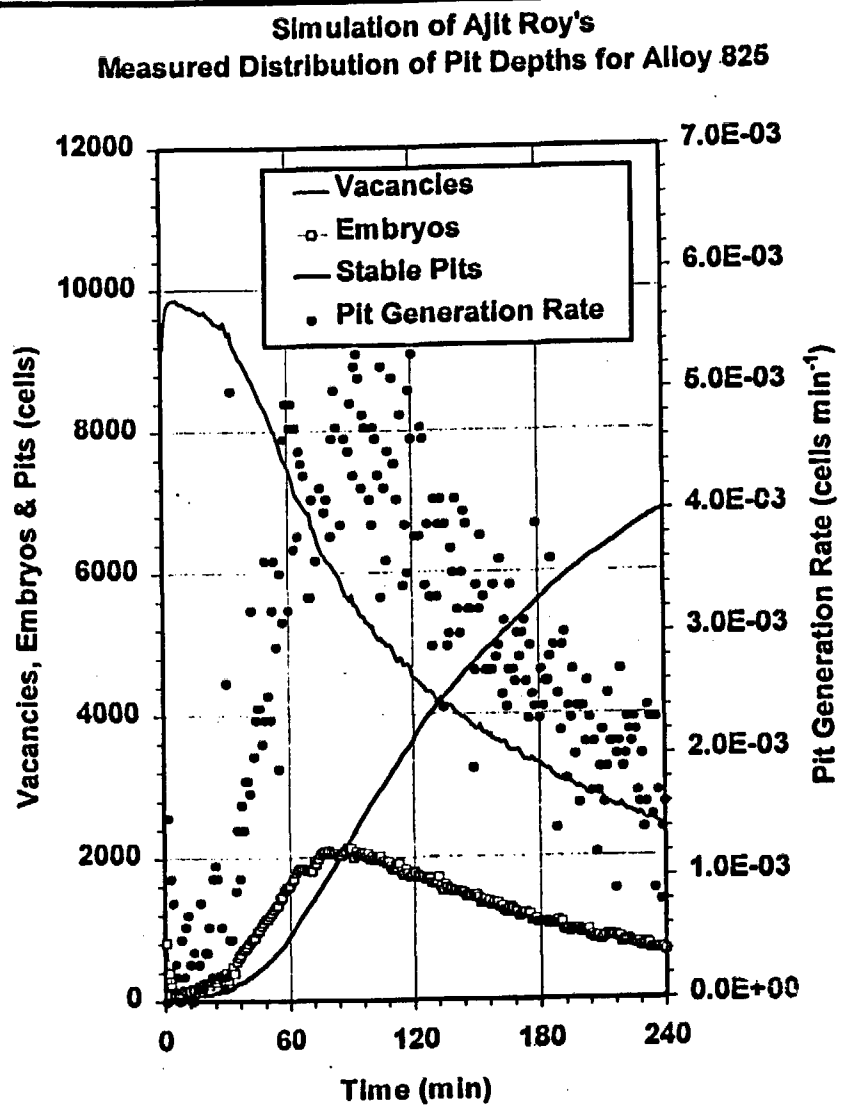
- Use of microsensors to map conditions in crevice
  - Fiber Optic Microprobes
    - pH, Fe(II)/Fe(III), Ni(II), Cr(III)/Cr(VI), etc.
  - Microelectrodes
    - Potential, O_2, Cl^-, NO_3^-, SO_4^{2-}, Fe(II)/Fe(III), Ni(II), Cr(III)/Cr(VI)
  - Minature Ion Selective Electrodes
    - pH, Cl^-, NO_3^-, SO_4^{2-}, etc.
- Use of other in situ optical techniques
  - Interferometry & ellipsometry (penetration)
  - Elastic light scattering & reflectance (surface roughness)
  - Raman spectroscopy (concentrated dissolved species) ⇒ to see what surface species form
- Post-test examination of crevice walls
  - Optical & scanning electron microscopy
  - Scanning tunneling & atomic force microscopy

Probabilistic pitting model developed for YMP

- Container surface is divided into hypothetical "cells" where probabilities for the transition from one pitting state to another can be assigned
- Nucleation or death of a pit "embryo" is determined by comparing random numbers (generated by power residue method) to:
  - Birth probability (λ)
  - Death probability (μ)
- An "embryo" becomes a "stable pit" after a critical age (τ) is reached
  - The depth of a "stable pit" is calculated from its age

Penetration of inner barrier can be quantified





Develop model for accelerated conditions, then apply to less severe, long term conditions.

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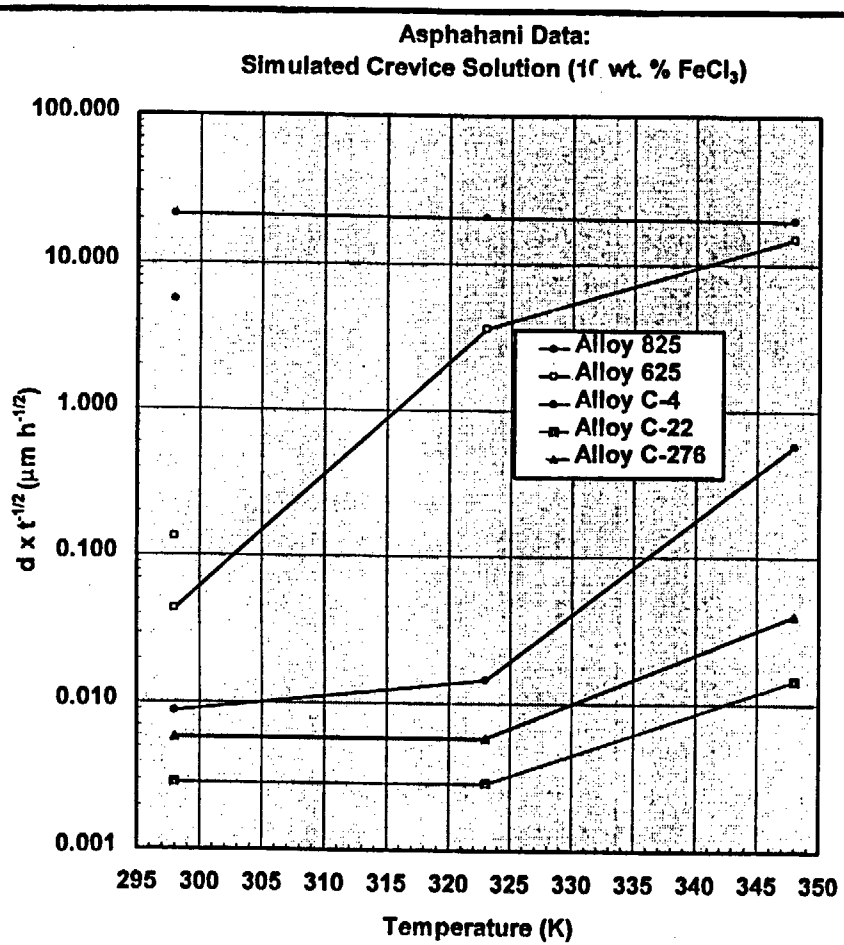
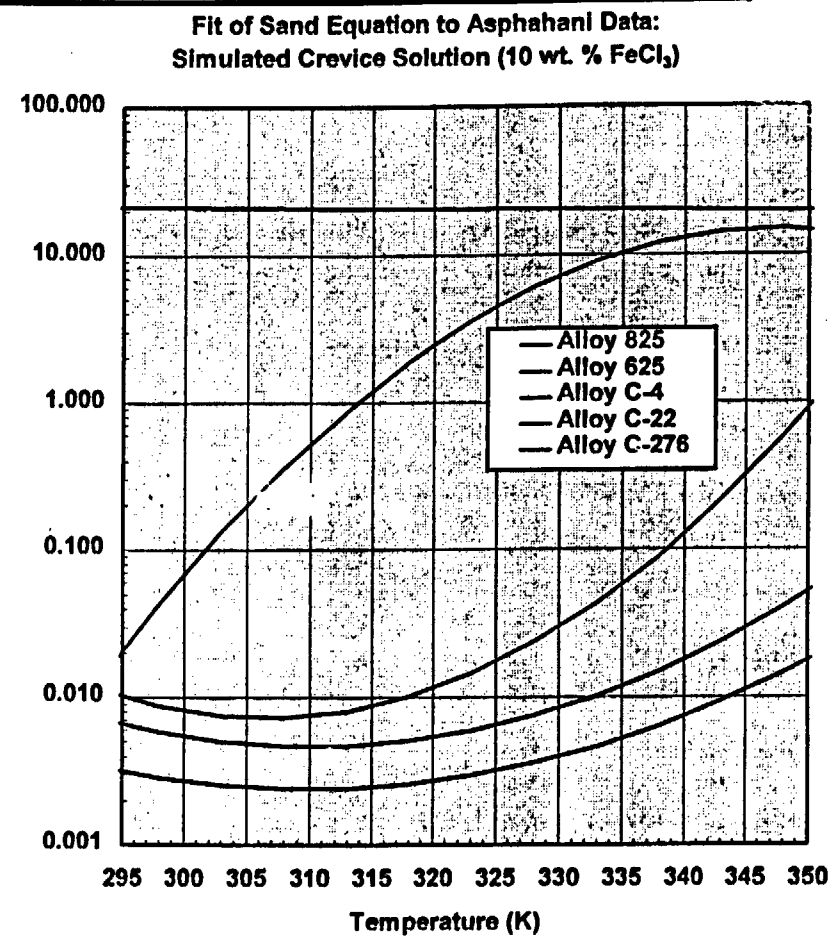
Empirical model: simulated crevice solution data





$$\Psi = \frac{d}{\sqrt{t}}$$

Rates are indicative of passive corrosion - passive film remains intact.

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Empirical model: simulated crevice solution data

- **Alloy 825 (worst)**

$$\ln(\Psi) = \ln(2.1164 \times 10^{1}) - 5.9141 \times 10^{-6}(T - T_0)^2 - 1.1235 \times 10^{-3}(T - T_0)$$

- **Alloy 625**

$$\ln(\Psi) = \ln(4.3493 \times 10^{-2}) - 2.4010 \times 10^{-3}(T - T_0)^2 + 2.3662 \times 10^{-1}(T - T_0)$$

- **Alloy C-4**

$$\ln(\Psi) = \ln(8.6758 \times 10^{-3}) + 2.5403 \times 10^{-3}(T - T_0)^2 - 4.2970 \times 10^{-2}(T - T_0)$$

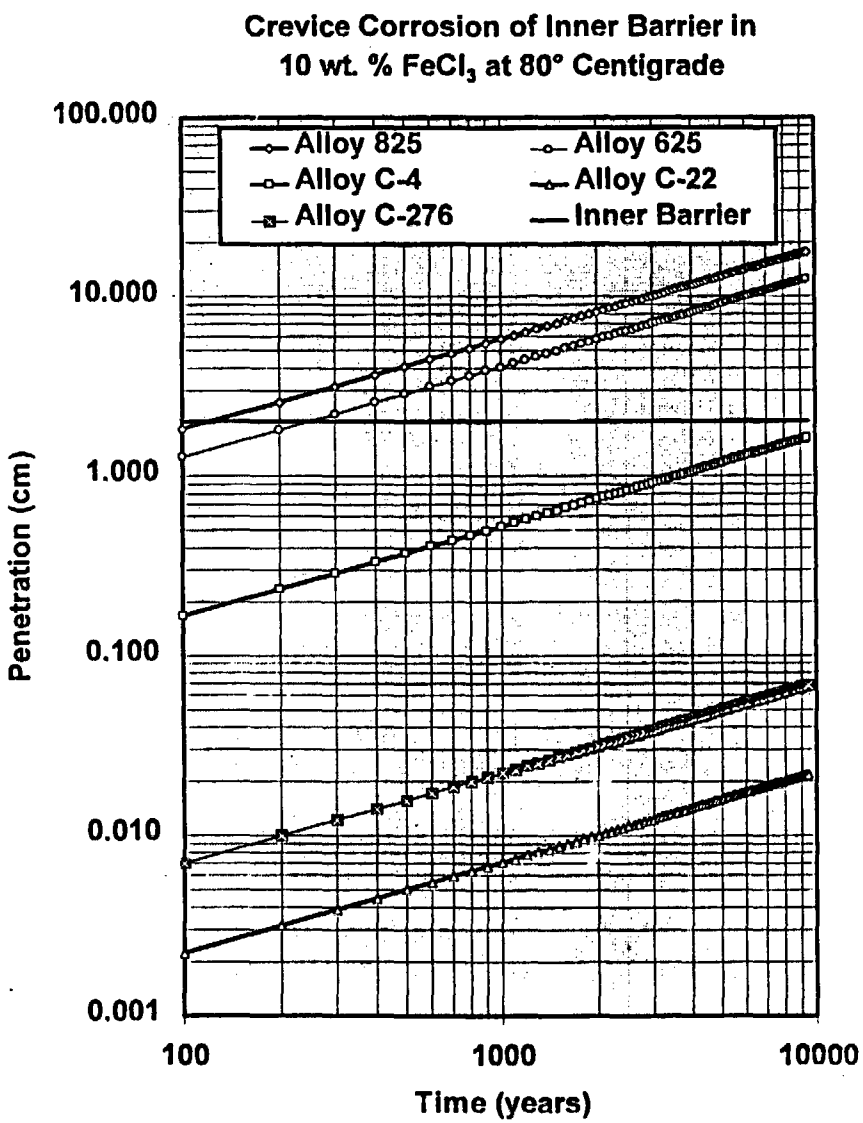
- **Alloy C-276**

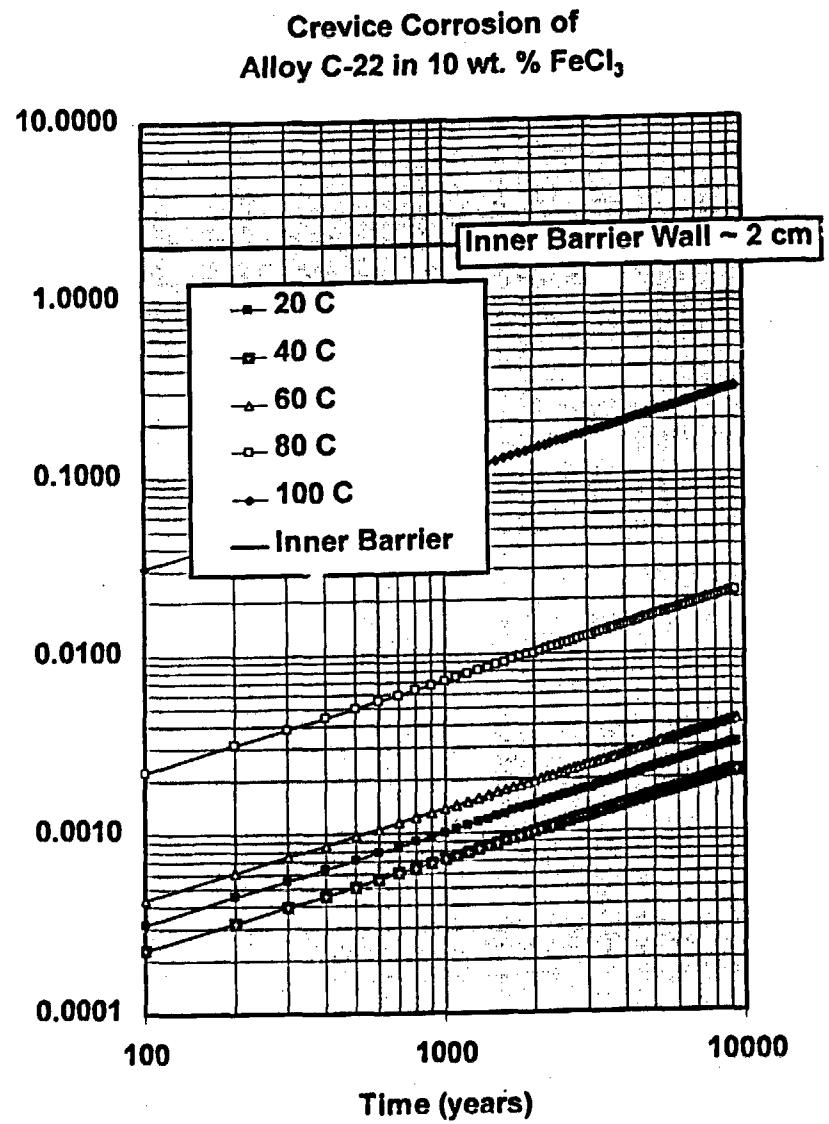
$$\ln(\Psi) = \ln(5.8219 \times 10^{-3}) + 1.5234 \times 10^{-3}(T - T_0)^2 - 3.7309 \times 10^{-2}(T - T_0)$$

- **Alloy C-22 (best)**

$$\ln(\Psi) = \ln(2.8539 \times 10^{-3}) + 1.2375 \times 10^{-3}(T - T_0)^2 - 2.9369 \times 10^{-2}(T - T_0)$$

Empirical model: simulated crevice solution data





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Empirical model: long term testing (6 month data)

- **General linear expression**

$$\ln\left(\frac{\Delta p}{\Delta t}\right) = b_0 + b_1\left(\frac{1000}{T+273}\right) + b_2(pH) + b_3(C_{NaCl}) + b_4(C_{FeCl_3})$$

- **Results of correlation**

$$\ln\left(\frac{\Delta p}{\Delta t}\right) = 13.409 - \left(\frac{5558.7}{T+273}\right) - 0.87409(pH) + 0.56965(C_{NaCl}) + 0.60801(C_{FeCl_3})$$

- **Standard error and regression coefficient**

$$s_{y/1234} = 1.5092$$

$$r_{y/1234} = 0.65628$$

- **Uncertainty in parameters**

$$\beta_j = b_j \pm (t_{a/2,n-k-1}) \times s_{b_j} \qquad s_{b_j} = s_{y/123\ldots k}\sqrt{ne_{jj}}$$

Data used in regression: long term test facility

	Comments	Exp sure	dp/dt	Temp.	pH	NaCl	$FeCl_3$	Air
		hours	microns/yr	°C	none	wt. %	wt. %	Sat.
1	Long Term Test - SAW	4296	2.53×10^{-2}	60	2.7	4.616	0	1
2	Long Term Test - SAW	4296	5.07×10^{-2}	60	2.7	4.616	0	1
3	Long Term Test - SAW	4296	1.13×10^{-1}	60	2.7	4.616	0	1
4	Long Term Test - SAW	4296	1.64×10^{-1}	60	2.7	4.616	0	1
5	Long Term Test - SAW	4296	6.03×10^{-2}	60	2.7	4.616	0	1
6	Long Term Test - SAW	4296	3.45×10^{-2}	60	2.7	4.616	0	1
7	Long Term Test - SAW	4296	3.47×10^{-2}	60	2.7	4.616	0	1
15	Long Term Test - SAW	4296	8.58×10^{-2}	60	2.7	4.616	0	1
16	Long Term Test - SAW	4296	1.13×10^{-1}	60	2.7	4.616	0	1
17	Long Term Test - SAW	4296	7.70×10^{-2}	60	2.7	4.616	0	1
18	Long Term Test - SAW	4296	2.81×10^{-2}	60	2.7	4.616	0	1
19	Long Term Test - SAW	4296	1.87×10^{-2}	60	2.7	4.616	0	1
20	Long Term Test - SAW	4296	9.31×10^{-3}	60	2.7	4.616	0	1
21	Long Term Test - SAW	4296	1.04×10^{-1}	60	2.7	4.616	0	1
22	Long Term Test - SAW	4296	8.11×10^{-2}	60	2.7	4.616	0	1
23	Long Term Test - SAW	4296	1.17×10^{-1}	60	2.7	4.616	0	1
24	Long Term Test - SAW	4296	6.56×10^{-2}	60	2.7	4.616	0	1
25	Long Term Test - SAW	4296	6.61×10^{-2}	60	2.7	4.616	0	1
26	Long Term Test - SAW	4296	4.71×10^{-2}	60	2.7	4.616	0	1
27	Long Term Test - SAW	4344	2.45×10^{-1}	90	2.7	4.616	0	1
28	Long Term Test - SAW	4344	7.31×10^{-1}	90	2.7	4.616	0	1
29	Long Term Test - SAW	4344	1.76×10^{-1}	90	2.7	4.616	0	1
30	Long Term Test - SAW	4344	4.16×10^{-2}	90	2.7	4.616	0	1
31	Long Term Test - SAW	4344	1.07×10^{-1}	90	2.7	4.616	0	1

Data used in regression: Roy & Asphahani

	Comments	Exposure	dp/dt	Temp.	pH	NaCl	$FeCl_3$	Air
		hours	microns/yr	°C	none	wt. %	wt. %	Sat.
8	Linear Polarization - NaCl	~1	3.00×10^{-4}	60	2.69	1	0	1
9	Linear Polarization - NaCl	~1	3.00×10^{-3}	60	6.53	5	0	1
10	Linear Polarization - NaCl	~1	2.01×10^{-2}	90	6.53	5	0	1
11	Linear Polarization - NaCl	~1	3.02×10^{-2}	90	6.83	10	0	1
12	Linear Polarization - NaCl	~1	2.01×10^{-1}	90	2.69	1	0	0
13	Linear Polarization - NaCl	~1	2.01×10^{-1}	90	2.67	1	0	0
14	Linear Polarization - NaCl	~1	2.01×10^{-1}	90	2.69	5	0	0
32	Linear Polarization - $FeCl_3$	~1	3.00×10^{-3}	90	2.14	0	0.61	0
33	Linear Polarization - $FeCl_3$	~1	6.00×10^{-3}	90	2.16	0	0.61	0
34	Linear Polarization - $FeCl_3$	~1	2.01×10^{-1}	90	1.72	0	3.05	0
35	Linear Polarization - $FeCl_3$	~1	2.01	90	1.72	0	3.05	0
36	Asphahani - $FeCl_3$	100	2.50	25	0.7	0	10	1
37	Asphahani - $FeCl_3$	100	2.50	50	0.7	0	10	1
38	Asphahani - $FeCl_3$	100	12.7	75	0.7	0	10	1

Summary - models for long-term predictions

- Crevice corrosion
  - A detailed model has been developed
    - Potential & current distributions (limited by E_{mix} in crevice)
    - Transient concentration profiles of reactive species
    - Suppressed pH due to hydrolysis of Fe, Ni, Cr & Mo
  - Several useful conclusions can be drawn from this model
    - The pH will be fairly uniform inside the crevice (pH ~ 2-3)
    - The potential (E) will decrease with increasing depth
    - Chloride (Cl^-) concentration will increase
- Pitting corrosion
  - Expressions for (λ μ γ τ) are now functions of E, T, pH, and Cl^-
    - No pitting of Alloy 825 predicted at E_{corr} of carbon steel
  - Reliable quantitative predictions require additional measurements
    - Pit distributions for Alloys 625 and C-22 (Ajit Roy, LLNL)
    - Birth & death rates of metastable pits (John Scully, U.Va.)

Acknowledgements

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- Jia-Song Huang - Stress Corrosion Testing
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- John Estill - Lead Technician
- Ken King - Technician
- Steve Gordon - Technician
- Dennis Fleming - Technician
- Bev Lum - Technician

Summary - models for long-term predictions

- Crevice corrosion
  - A detailed model has been developed
    - Potential & current distributions (limited by E_{mix} in crevice)
    - Transient concentration profiles of reactive species
    - Suppressed pH due to hydrolysis of Fe, Ni, Cr & Mo
  - Several useful conclusions can be drawn from this model
    - The pH will be fairly uniform inside the crevice (pH ~ 2-3)
    - The potential (E) will decrease with increasing depth
    - Chloride (Cl^-) concentration will increase
- Pitting corrosion
  - Expressions for (λ μ γ τ) are now functions of E, T, pH, and Cl^-
    - No pitting of Alloy 825 predicted at E_{corr} of carbon steel
  - Reliable quantitative predictions require additional measurements
    - Pit distributions for Alloys 625 and C-22 (Ajit Roy, LLNL)
    - Birth & death rates of metastable pits (John Scully, U.Va.)

Data used in regression: Roy & Asphahani

	Comments	Exposure	dp/dt	Temp.	pH	NaCl	$FeCl_3$	Air
		hours	microns/yr	°C	none	wt. %	wt. %	Sat.
8	Linear Polarization - NaCl	~1	3.00×10^{-4}	60	2.69	1	0	1
9	Linear Polarization - NaCl	~1	3.00×10^{-3}	60	6.53	5	0	1
10	Linear Polarization - NaCl	~1	2.01×10^{-2}	90	6.53	5	0	1
11	Linear Polarization - NaCl	~1	3.02×10^{-2}	90	6.83	10	0	1
12	Linear Polarization - NaCl	~1	2.01×10^{-1}	90	2.69	1	0	0
13	Linear Polarization - NaCl	~1	2.01×10^{-1}	90	2.67	1	0	0
14	Linear Polarization - NaCl	~1	2.01×10^{-1}	90	2.69	5	0	0
32	Linear Polarization - $FeCl_3$	~1	3.00×10^{-3}	90	2.14	0	0.61	0
33	Linear Polarization - $FeCl_3$	~1	6.00×10^{-3}	90	2.16	0	0.61	0
34	Linear Polarization - $FeCl_3$	~1	2.01×10^{-1}	90	1.72	0	3.05	0
35	Linear Polarization - $FeCl_3$	~1	2.01	90	1.72	0	3.05	0
36	Asphahani - $FeCl_3$	100	2.50	25	0.7	0	10	1
37	Asphahani - $FeCl_3$	100	2.50	50	0.7	0	10	1
38	Asphahani - $FeCl_3$	100	12.7	75	0.7	0	10	1

Data used in regression: long term test facility

	Comments	Exposure	dp/dt	Temp.	pH	NaCl	$FeCl_3$	Air
		hours	microns/yr	°C	none	wt. %	wt. %	Sat.
1	Long Term Test - SAW	4296	2.53×10^{-2}	60	2.7	4.616	0	1
2	Long Term Test - SAW	4296	5.07×10^{-2}	60	2.7	4.616	0	1
3	Long Term Test - SAW	4296	1.13×10^{-1}	60	2.7	4.616	0	1
4	Long Term Test - SAW	4296	1.64×10^{-1}	60	2.7	4.616	0	1
5	Long Term Test - SAW	4296	6.03×10^{-2}	60	2.7	4.616	0	1
6	Long Term Test - SAW	4296	3.45×10^{-2}	60	2.7	4.616	0	1
7	Long Term Test - SAW	4296	3.47×10^{-2}	60	2.7	4.616	0	1
15	Long Term Test - SAW	4296	8.58×10^{-2}	60	2.7	4.616	0	1
16	Long Term Test - SAW	4296	1.13×10^{-1}	60	2.7	4.616	0	1
17	Long Term Test - SAW	4296	7.70×10^{-2}	60	2.7	4.616	0	1
18	Long Term Test - SAW	4296	2.81×10^{-2}	60	2.7	4.616	0	1
19	Long Term Test - SAW	4296	1.87×10^{-2}	60	2.7	4.616	0	1
20	Long Term Test - SAW	4296	9.31×10^{-3}	60	2.7	4.616	0	1
21	Long Term Test - SAW	4296	1.04×10^{-1}	60	2.7	4.616	0	1
22	Long Term Test - SAW	4296	8.11×10^{-2}	60	2.7	4.616	0	1
23	Long Term Test - SAW	4296	1.17×10^{-1}	60	2.7	4.616	0	1
24	Long Term Test - SAW	4296	6.56×10^{-2}	60	2.7	4.616	0	1
25	Long Term Test - SAW	4296	6.61×10^{-2}	60	2.7	4.616	0	1
26	Long Term Test - SAW	4296	4.71×10^{-2}	60	2.7	4.616	0	1
27	Long Term Test - SAW	4344	2.45×10^{-1}	90	2.7	4.616	0	1
28	Long Term Test - SAW	4344	7.31×10^{-1}	90	2.7	4.616	0	1
29	Long Term Test - SAW	4344	1.76×10^{-1}	90	2.7	4.616	0	1
30	Long Term Test - SAW	4344	4.16×10^{-2}	90	2.7	4.616	0	1
31	Long Term Test - SAW	4344	1.07×10^{-1}	90	2.7	4.616	0	1

Empirical model: long term testing (6 month data)

- **General linear expression**

$$\ln\left(\frac{\Delta p}{\Delta t}\right) = b_0 + b_1\left(\frac{1000}{T+273}\right) + b_2(pH) + b_3(C_{NaCl}) + b_4(C_{FeCl_3})$$

- **Results of correlation**

$$\ln\left(\frac{\Delta p}{\Delta t}\right) = 13.409 - \left(\frac{5558.7}{T+273}\right) - 0.87409(pH) + 0.56965(C_{NaCl}) + 0.60801(C_{FeCl_3})$$

- **Standard error and regression coefficient**

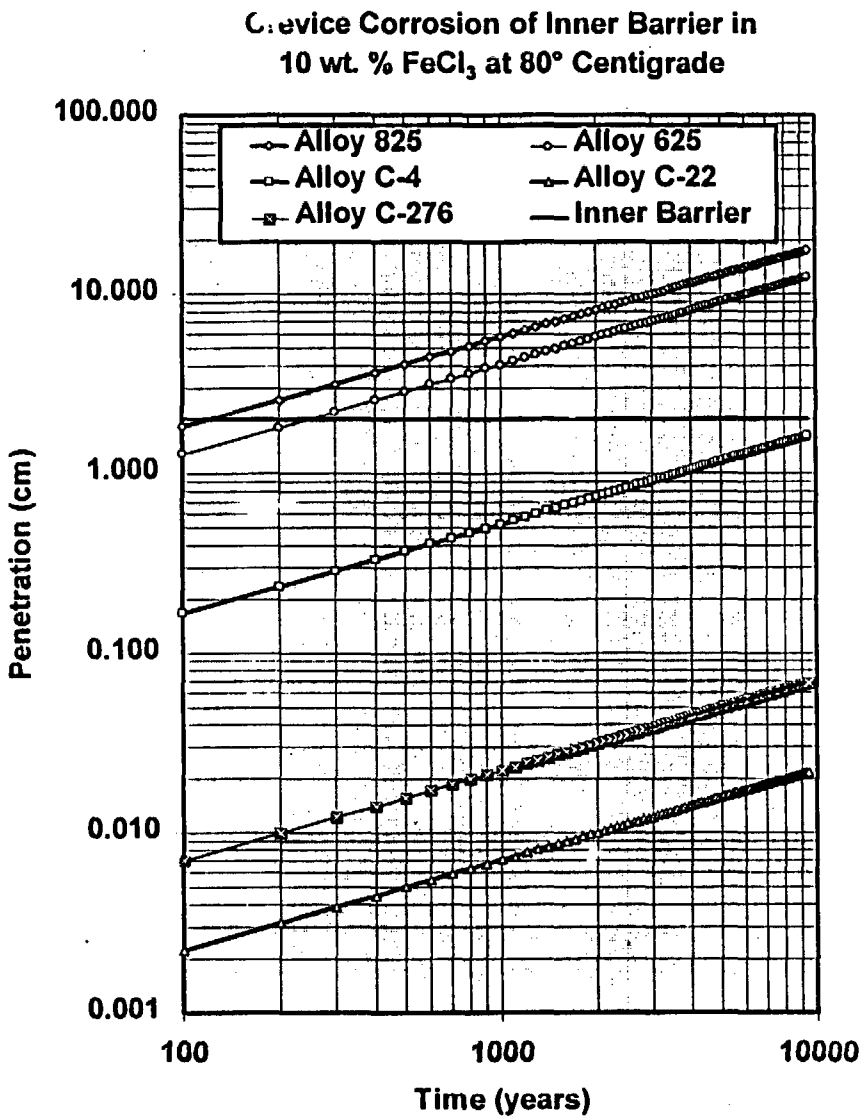
$$s_{y/1234} = 1.5092$$

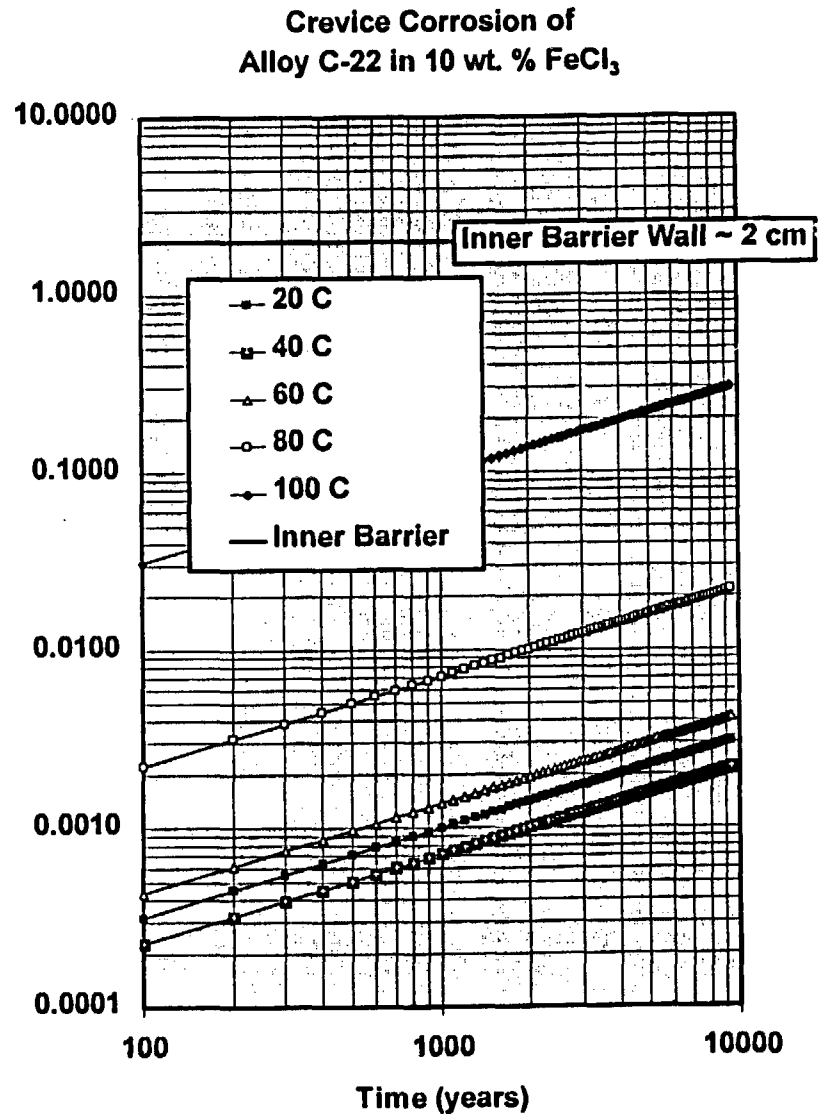
$$r_{y/1234} = 0.65628$$

- **Uncertainty in parameters**

$$\beta_j = b_j \pm \left(t_{a/2,n-k-1}\right) \times s_{b_j} \qquad s_{b_j} = s_{y/123\ldots k}\sqrt{ne_{jj}}$$

Empirical model: simulated crevice solution data





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Empirical model: simulated crevice solution data

- **Alloy 825 (worst)**

$$\ln(\Psi) = \ln(2.1164 \times 10^{1}) - 5.9141 \times 10^{-6}(T - T_0)^2 - 1.1235 \times 10^{-3}(T - T_0)$$

- **Alloy 625**

$$\ln(\Psi) = \ln(4.3493 \times 10^{-2}) - 2.4010 \times 10^{-3}(T - T_0)^2 + 2.3662 \times 10^{-1}(T - T_0)$$

- **Alloy C-4**

$$\ln(\Psi) = \ln(8.6758 \times 10^{-3}) + 2.5403 \times 10^{-3}(T - T_0)^2 - 4.2970 \times 10^{-2}(T - T_0)$$

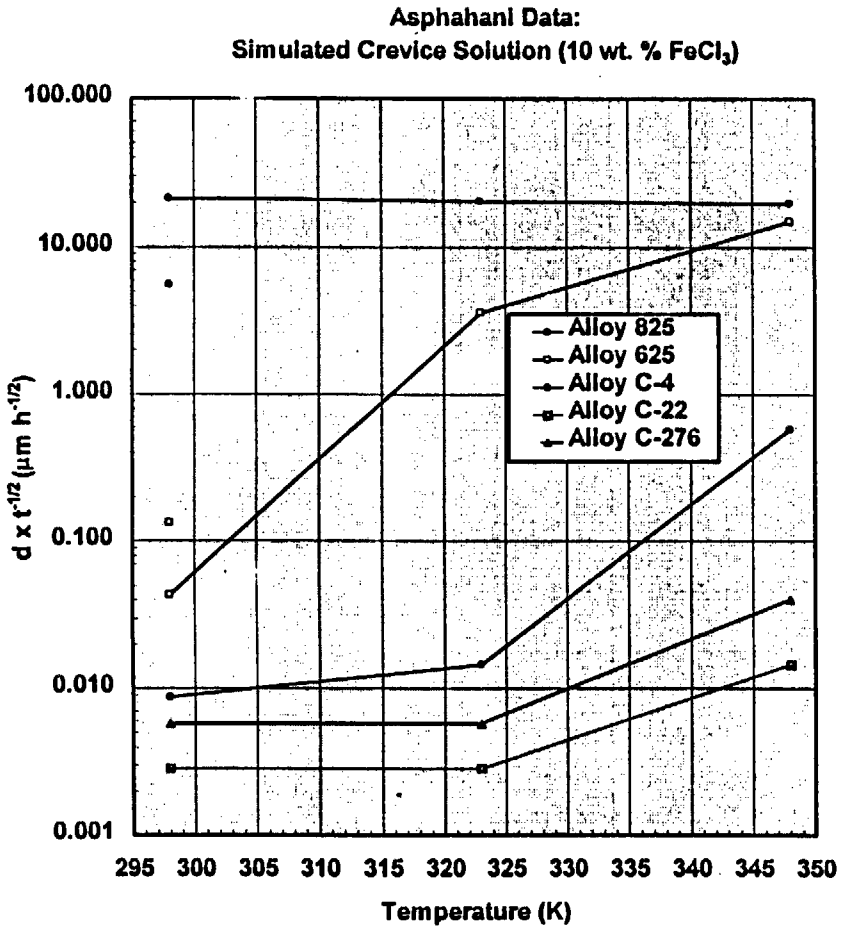
- **Alloy C-276**

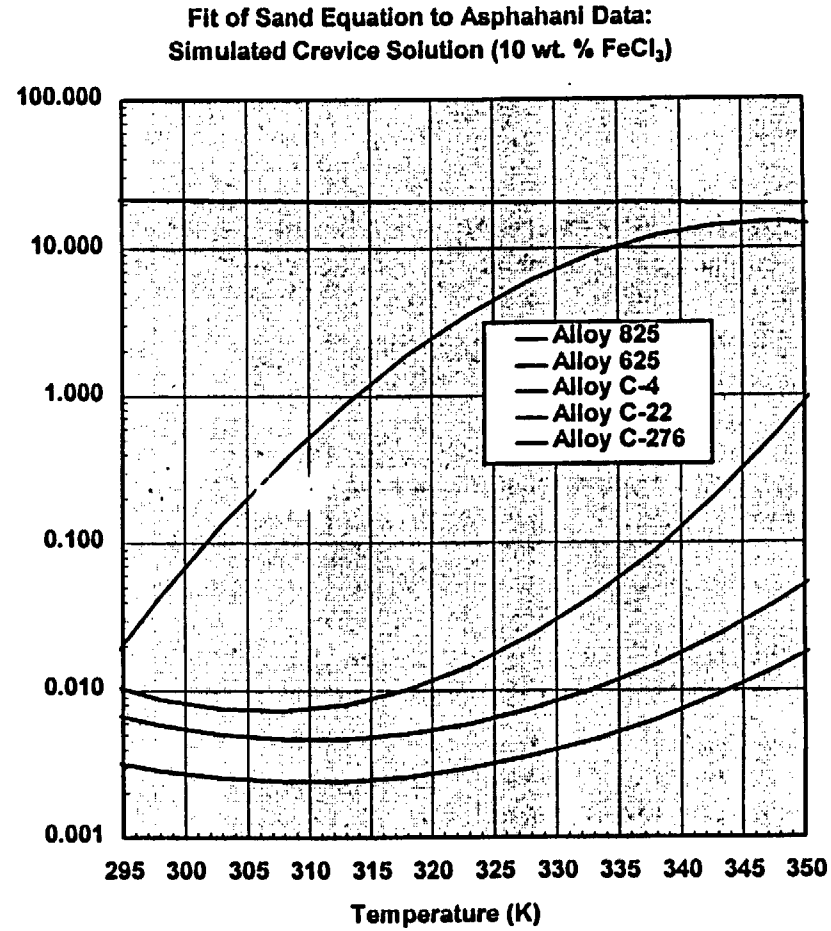
$$\ln(\Psi) = \ln(5.8219 \times 10^{-3}) + 1.5234 \times 10^{-3}(T - T_0)^2 - 3.7309 \times 10^{-2}(T - T_0)$$

- **Alloy C-22 (best)**

$$\ln(\Psi) = \ln(2.8539 \times 10^{-3}) + 1.2375 \times 10^{-3}(T - T_0)^2 - 2.9369 \times 10^{-2}(T - T_0)$$

Empirical model: simulated crevice solution data



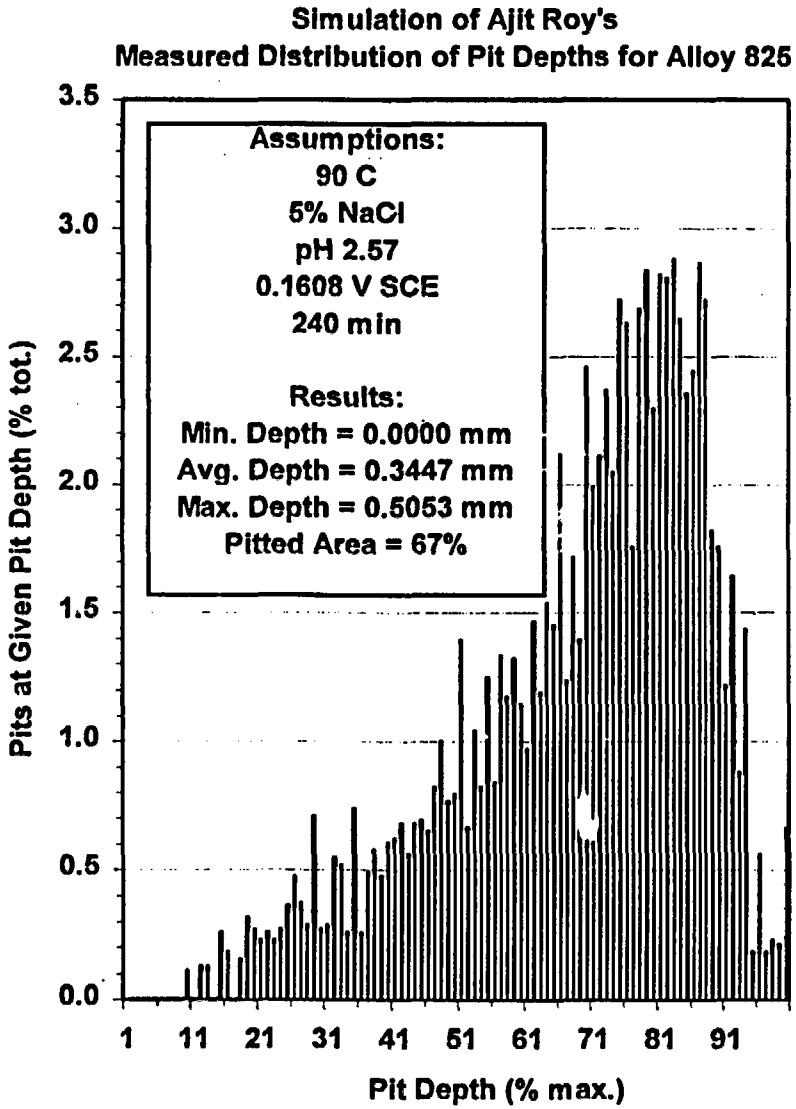


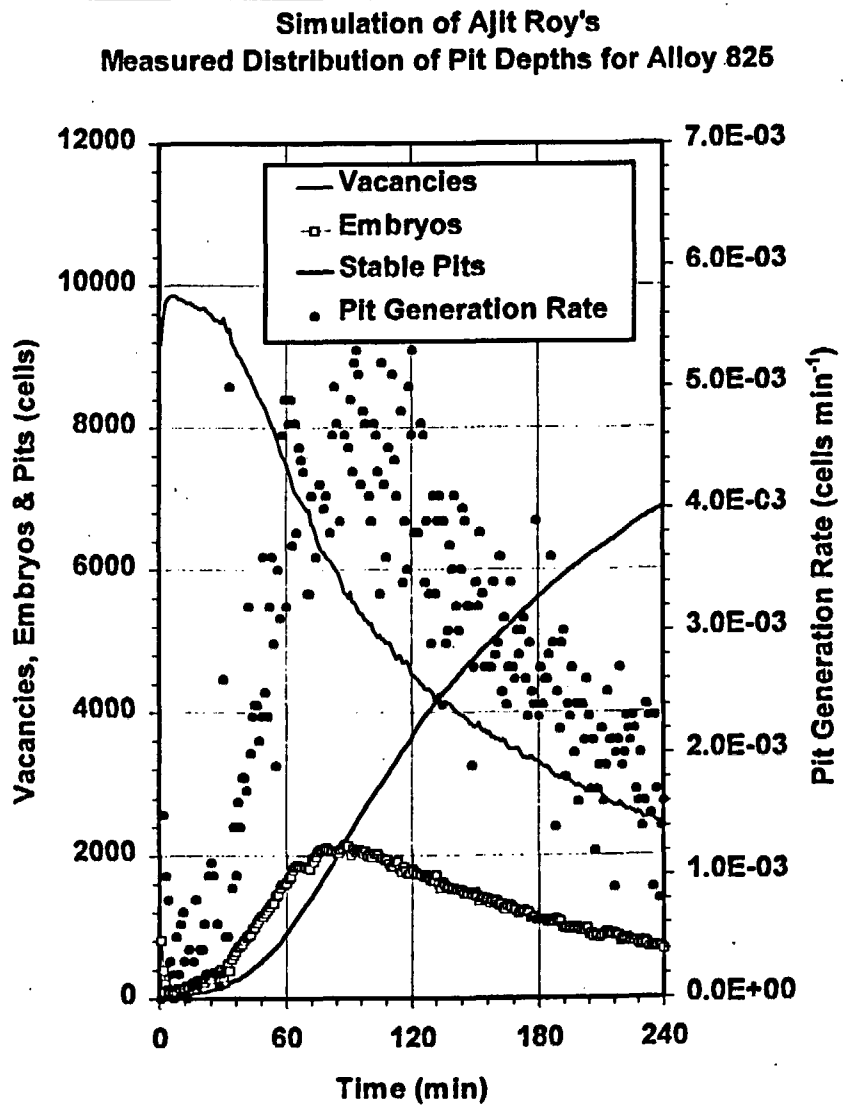
$$\Psi = \frac{d}{\sqrt{t}}$$

Rates are indicative of passive corrosion - passive film remains intact.

J.C. Farmer, LLNL, January 1998

Penetration of inner barrier can be quantified





Develop model for accelerated conditions, then apply to less severe, long term conditions.

J.C. Farmer, LLNL, January 1998

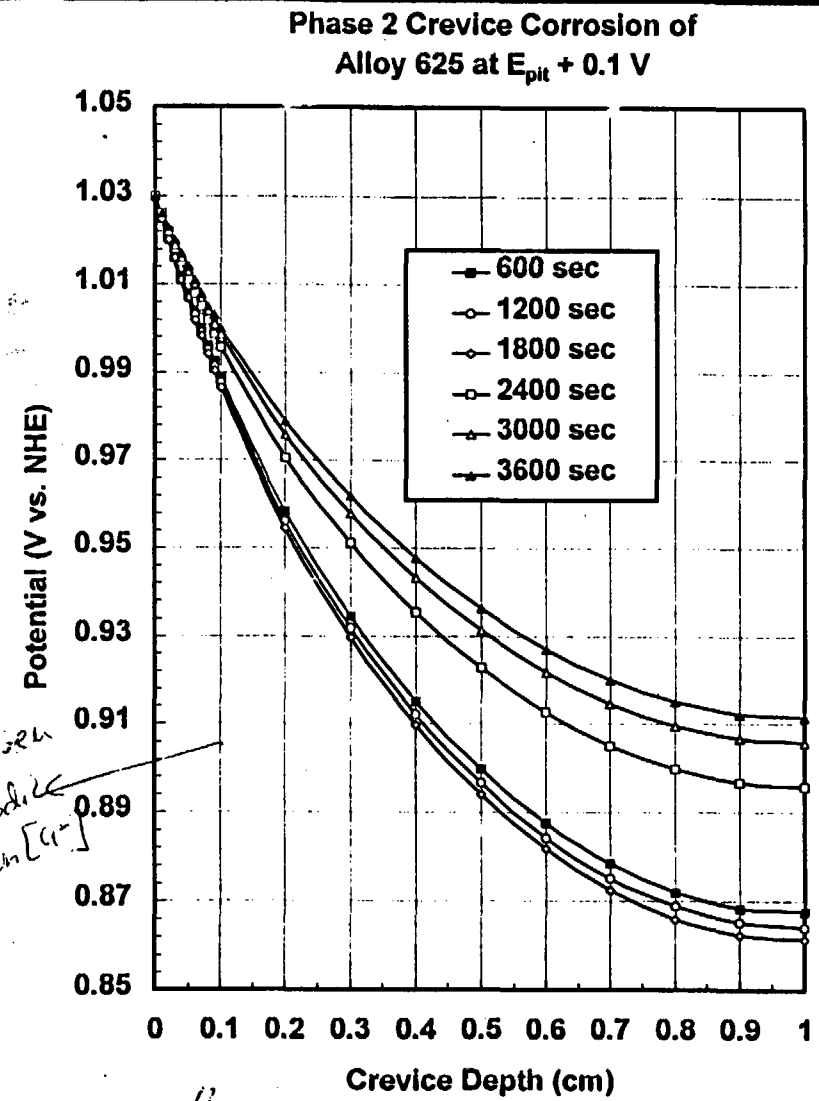
Probabilistic pitting model developed for YMP

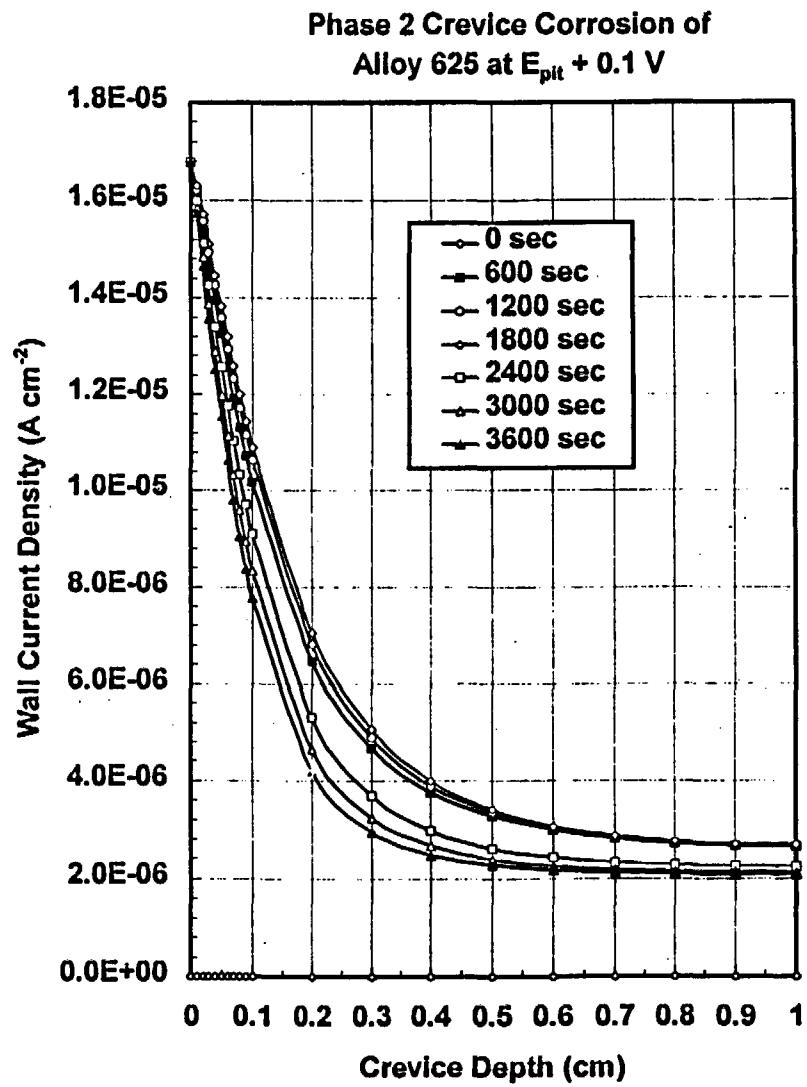
- Container surface is divided into hypothetical "cells" where probabilities for the transition from one pitting state to another can be assigned
- Nucleation or death of a pit "embryo" is determined by comparing random numbers (generated by power residue method) to:
  - Birth probability (λ)
  - Death probability (μ)
- An "embryo" becomes a "stable pit" after a critical age (τ) is reached
  - The depth of a "stable pit" is calculated from its age

Confirmatory experiment for transport model

- Use of microsensors to map conditions in crevice
  - Fiber Optic Microprobes
    - pH, Fe(II)/Fe(III), Ni(II), Cr(III)/Cr(VI), etc.
  - Microelectrodes
    - Potential, O_2, Cl^-, NO_3^-, SO_4^{2-}, Fe(II)/Fe(III), Ni(II), Cr(III)/Cr(VI)
  - Minature Ion Selective Electrodes
    - pH, Cl^-, NO_3^-, SO_4^{2-}, etc.
- Use of other in situ optical techniques
  - Interferometry & ellipsometry (penetration)
  - Elastic light scattering & reflectance (surface roughness)
  - Raman spectroscopy (concentrated dissolved species) ⇒ to see what surface species form
- Post-test examination of crevice walls
  - Optical & scanning electron microscopy
  - Scanning tunneling & atomic force microscopy

Potential & current during Phase II crevice corrosion





cross driven horizontal is, dep. on [Cl-]

Consistent w/ CNWRA work

Potential becomes less damaging inside crevice.

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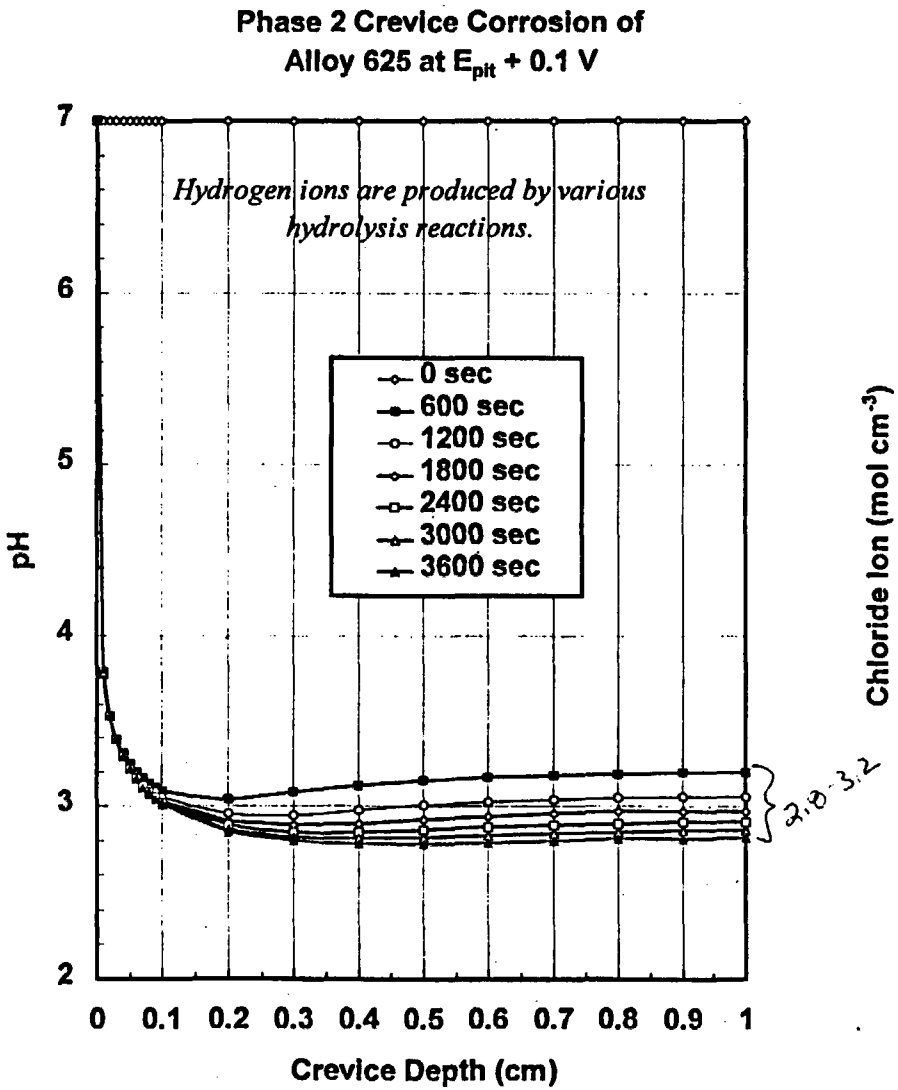
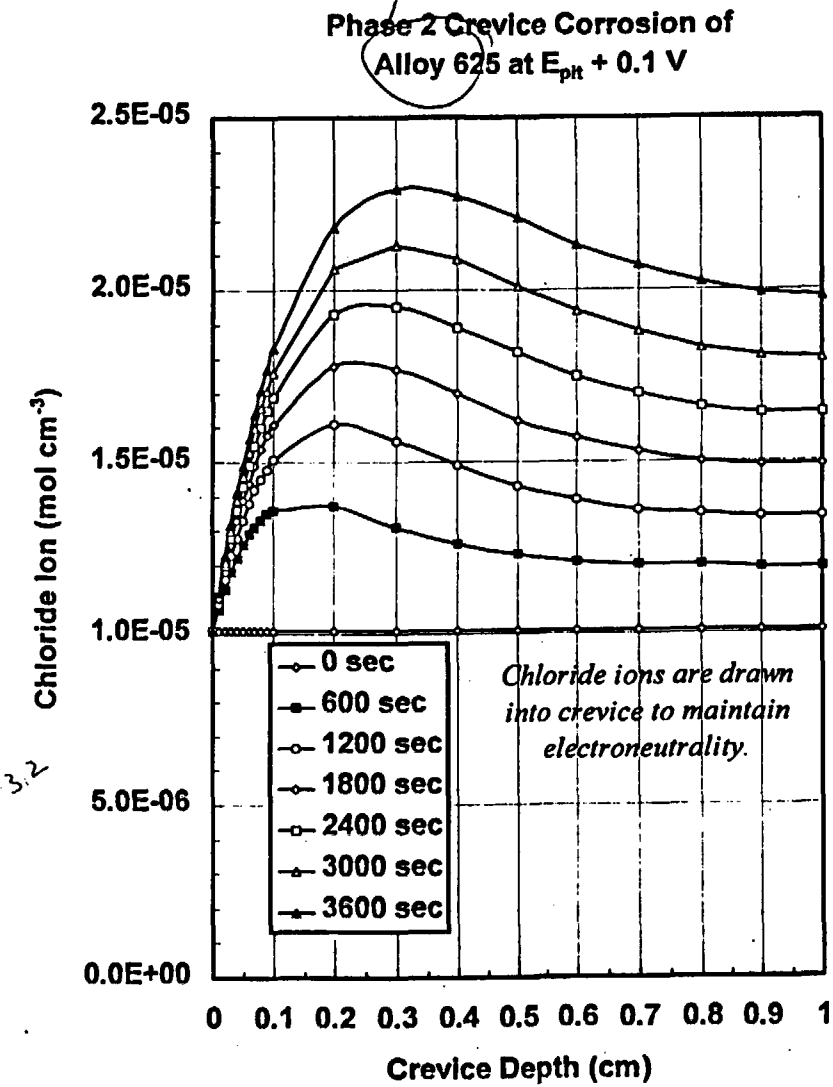
Suppression of pH during Phase II crevice corrosion





Crevice w/ only 625, not 516/625 crevice

Both low pH & high chloride exacerbate corrosion of CRM.

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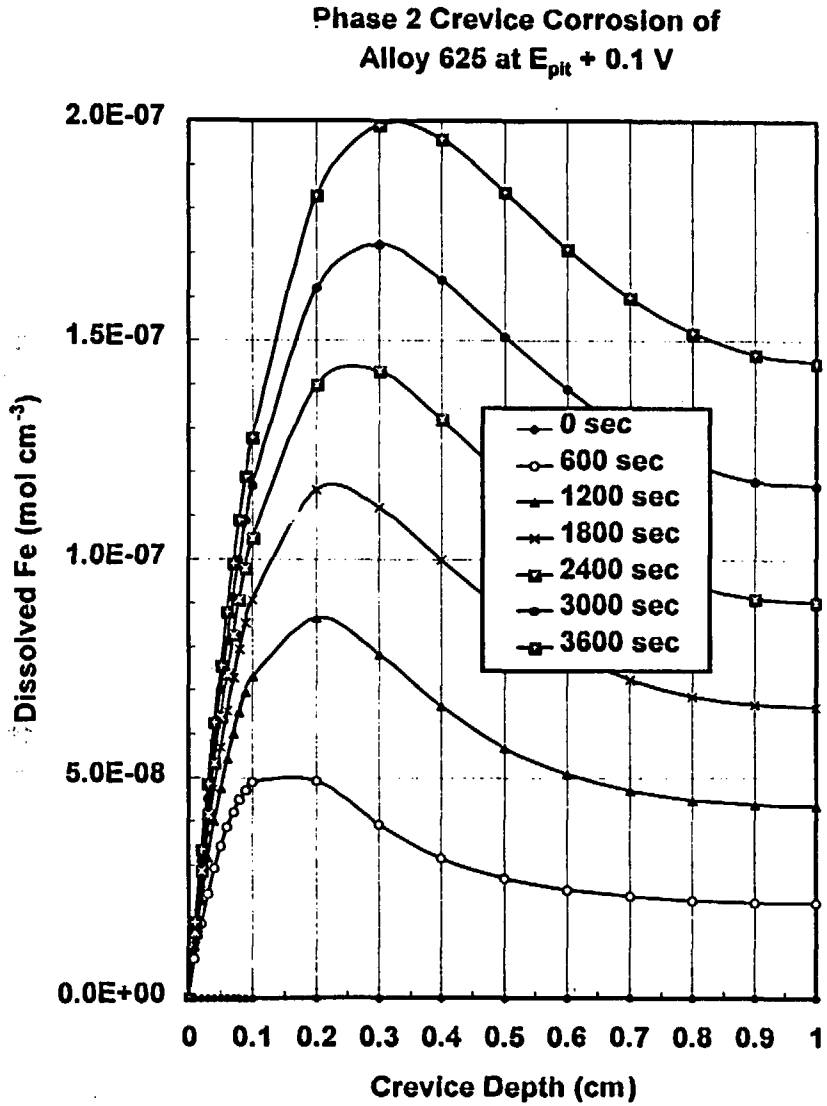
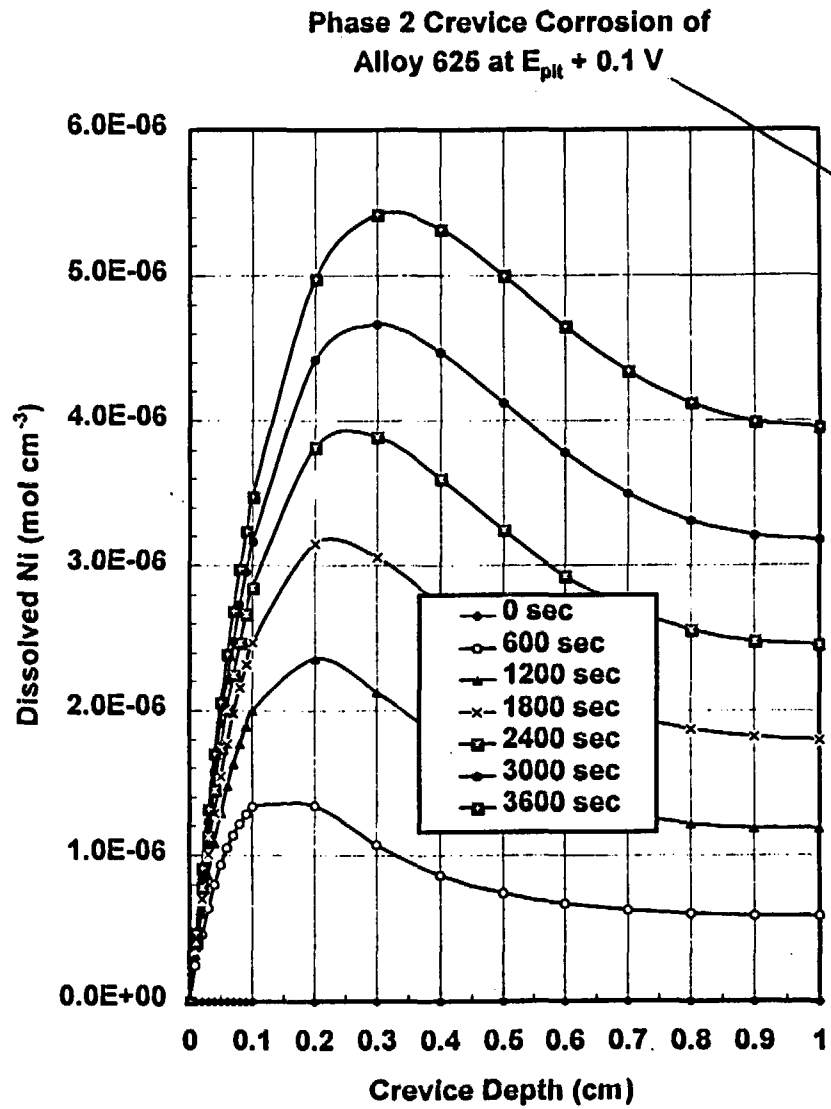
Metal dissolution during Phase II crevice corrosion





If we lower potential we don't get these dissolution

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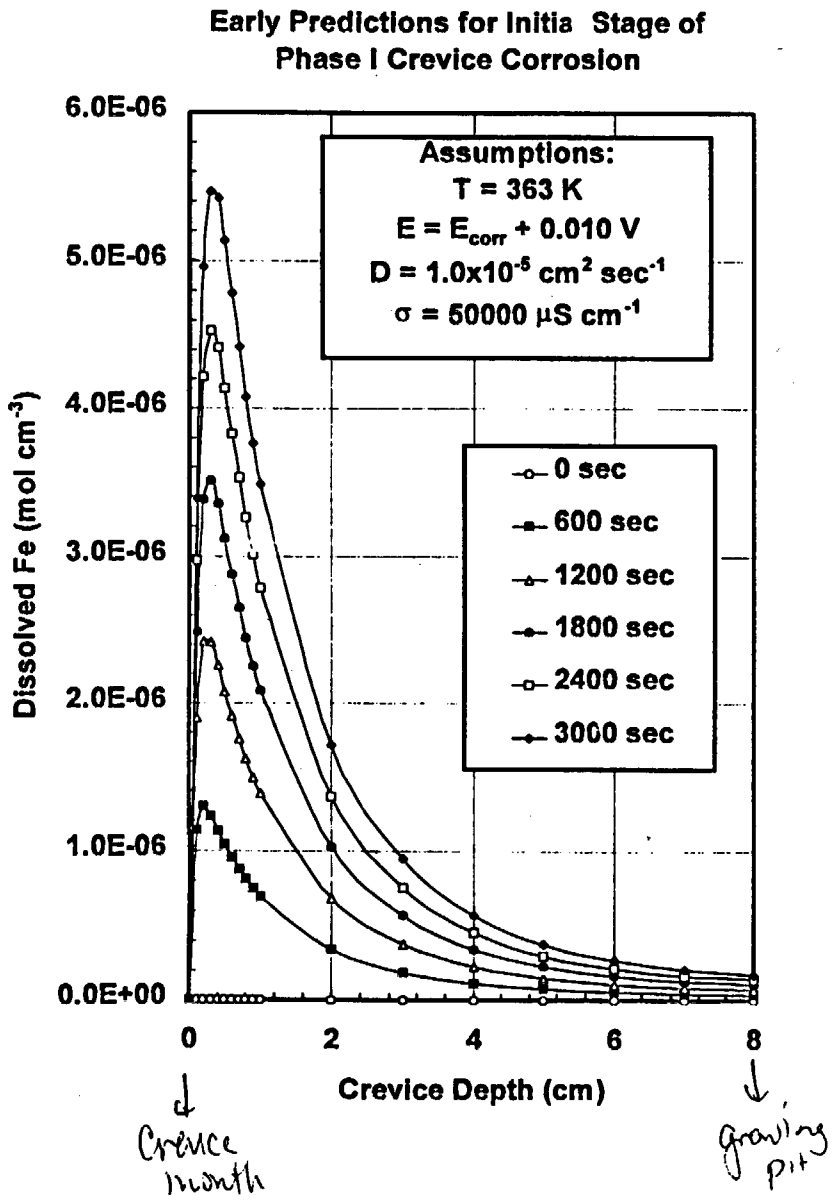
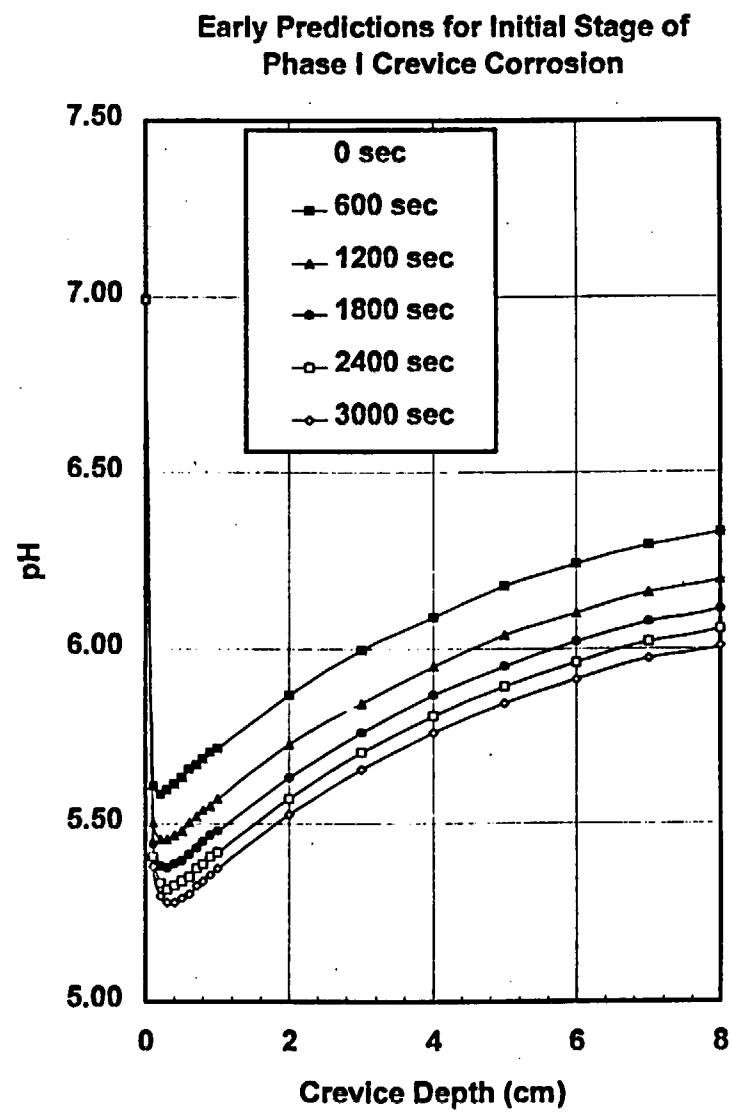
Phase I sets stage for attack of inner barrier





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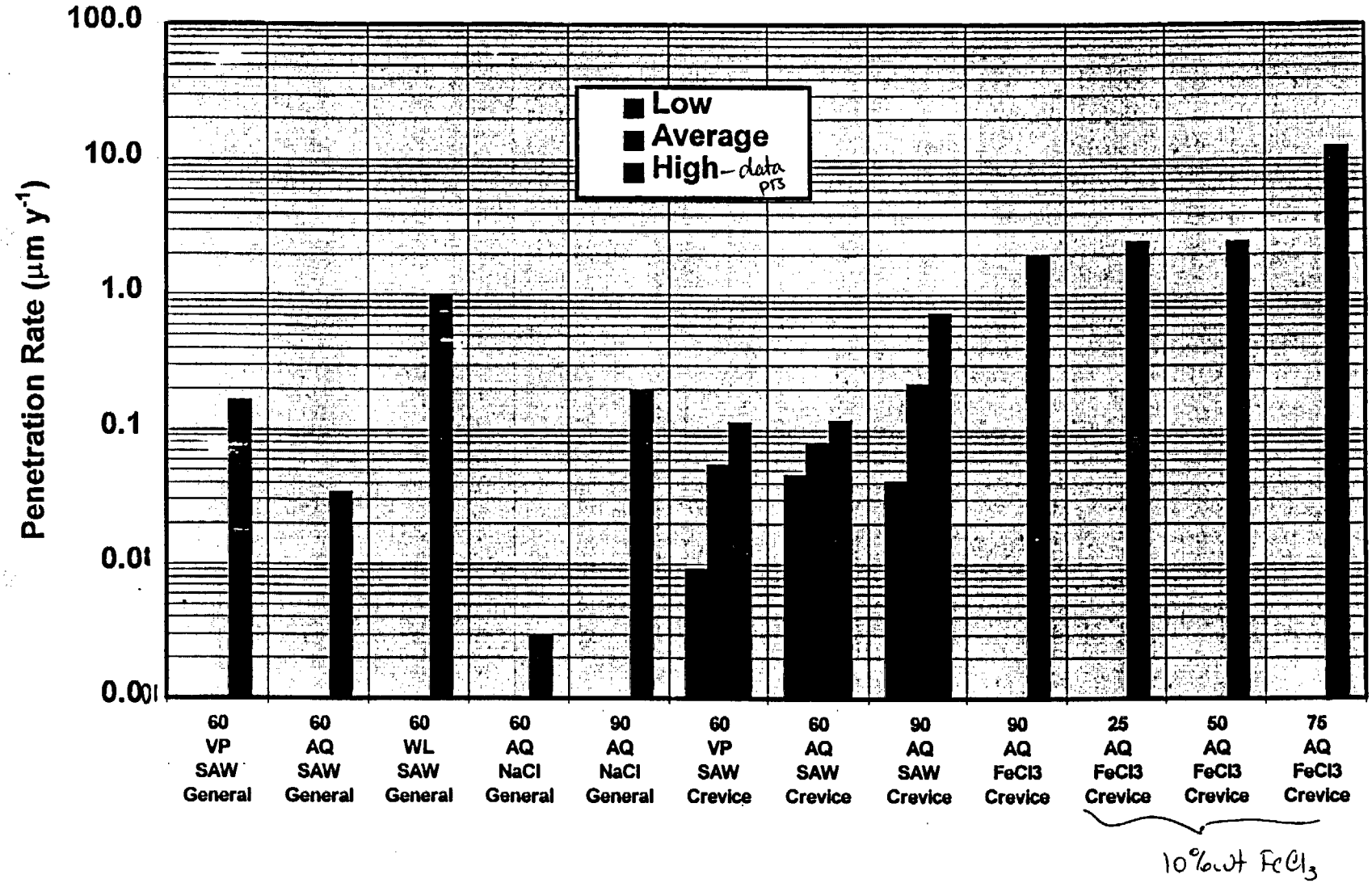
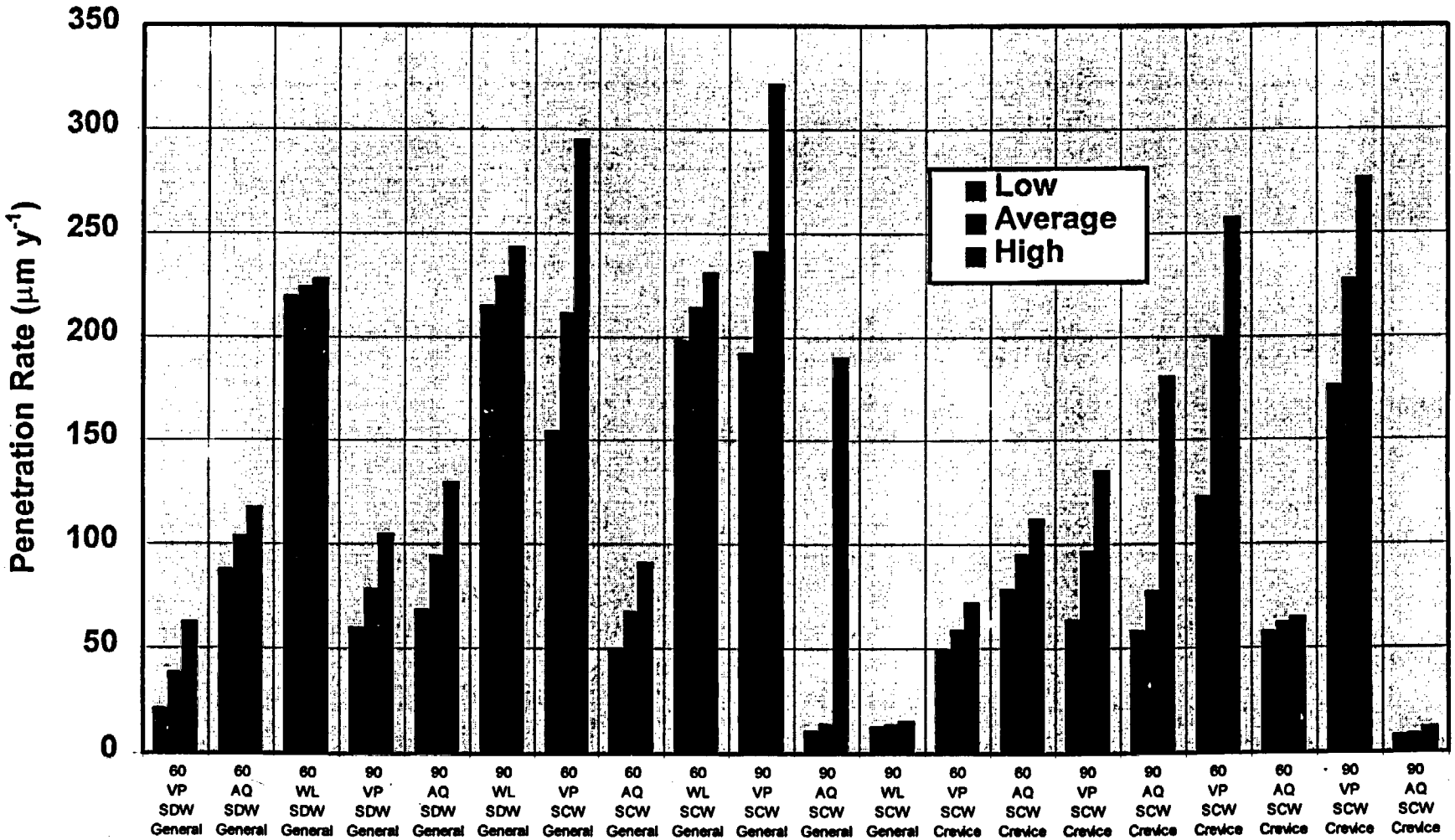
Observed Penetration Rates for C-22 (all sources)



J.C. Farmer, LLNL, January 1998

Observed Penetration Rates for A516 (6 month data)

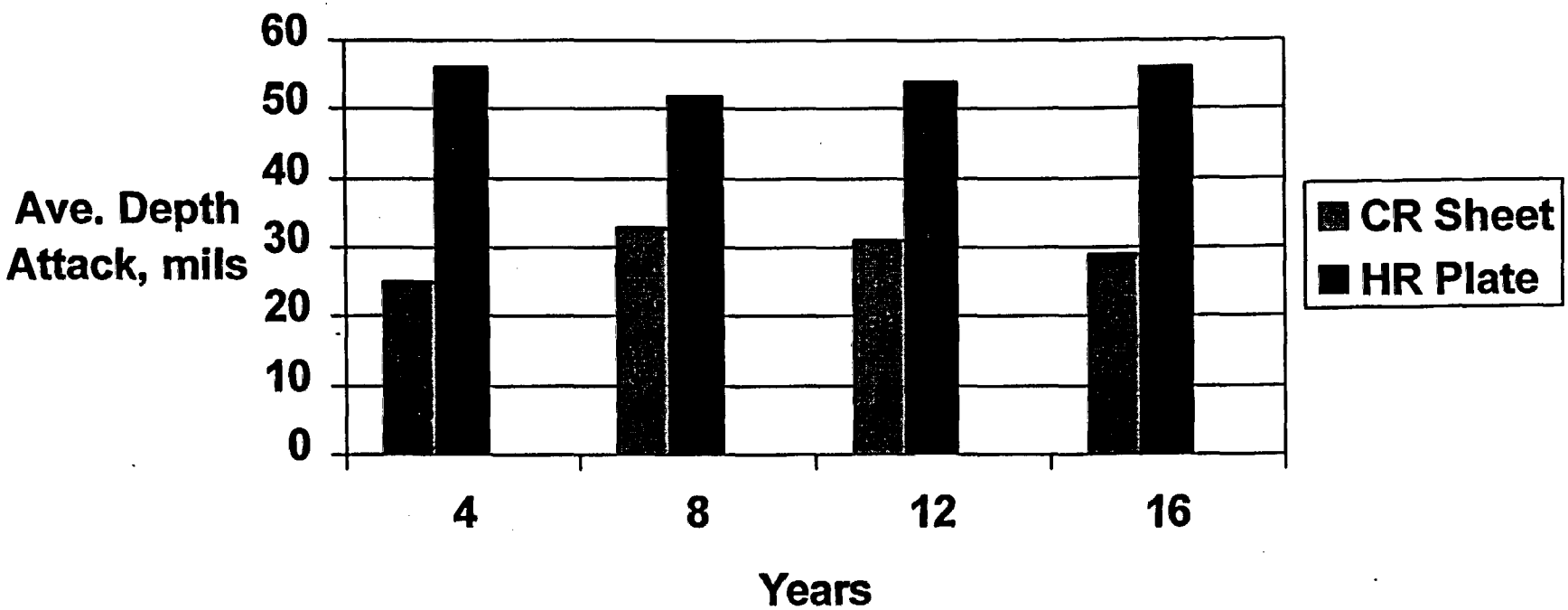


J.C. Farmer, LLNL, January 1998

Nickel Alloys
High-velocity (>120 fps) Seawater

Alloy	Corrosion Rate, mpy
625/C-276	<1
400/K-500	<1
718/725/925	<1
T-304/T-316	<1
Steel	>300

Ni-Cu alloy 400 Corrosion Tropical Quiet Seawater



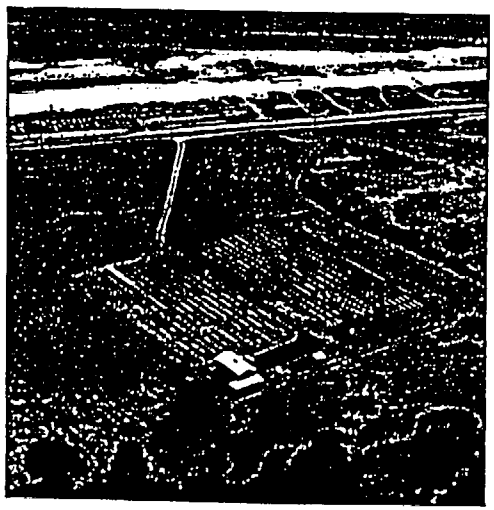
Nickel Alloys
Quiet Seawater Corrosion - 3 Yrs

Alloy	Max. Depth of Attack, mils
625	Nil
825	1
K-500	34
400	42
T-316 SS	62

MARINE ATMOSPHERIC TESTING

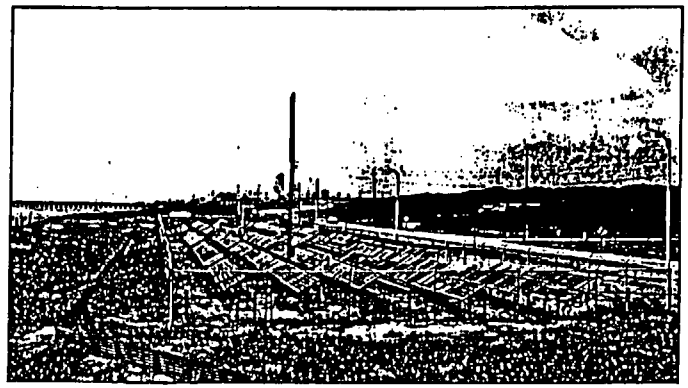
The **LaQUE CENTER FOR CORROSION TECHNOLOGY, INC.** is a world leader in marine atmospheric exposure testing. Its Kure Beach, NC, test sites, established in 1935, are considered the world standard for natural marine atmospheric exposures. In 1988, ASM International designated the Kure Beach atmospheric test sites as a Historical Landmark for its pioneering efforts in marine atmospheric testing.

Kure Beach, 18 miles south of Wrightsville Beach, is located at latitude 34° N, longitude 77.5°W. Four acres of test areas, free of potential sources of industrial air contamination, are available for specimens and various equipment to be exposed to the ravages of the marine atmosphere.

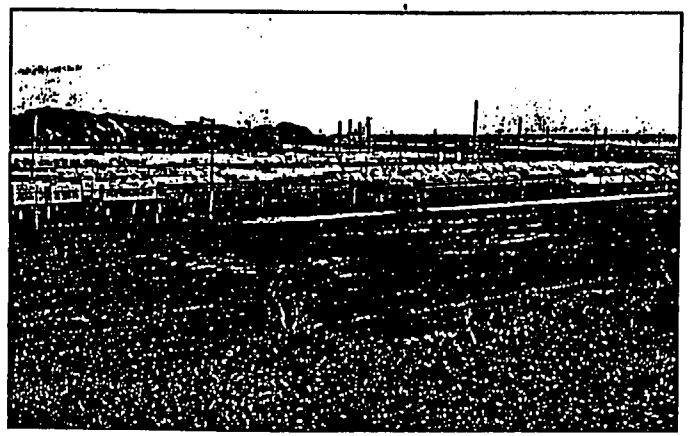


Available for test exposures is almost a 1000 foot long area of oceanfront at an average distance of about 80 feet (25 meters) from the normal high tide level. A larger test area is located about 800 feet (250 meters) from the surf.

TWO DISTINCT AREAS FOR TESTING -



25 Meter Lot - Test specimens face the surf in an easterly direction at an average distance of 25 meters from the mean tide level. Natural salt spray produces a severely corrosive environment heavily laden with chlorides.



250 Meter Lot - Test specimens face southward for maximum solar exposure. Airborne chlorides are considerably lower in comparison with the 25 meter lot, producing a less aggressive atmospheric exposure.

Nickel Alloys
Corrosion Resistance

- Quiet Seawater
- Velocity Effects
- Crevice Corrosion
- Galvanic Effects
- Effect of Temperature
- Effects of Chlorination
- Stress Corrosion
- Corrosion Fatigue

"C" Alloy
Chemical Composition
Minor Elements

Alloy	Si	C	Cu
C-4	0.04	0.005	
59	0.04	0.005	
C-2000	0.04	0.005	1.6
C-22	**0.04**	**0.005**	
C-276	0.04	0.005	
686	0.04	0.005	
C	0.7	0.05	

not good for thermal state perhaps

"C" Alloy
Chemical Composition

Alloy	Ni	Cr	Mo	Fe	Other
C-4	64	16	16	2	Ti
59	59	23	16	1	
2000	58	23	16		1.6Cu
C-22	**58**	**22**	**13**	**3**	**3W**
C-276	56	16	16	5	4W
686	55	21	16	3	4W
C	55	16	16	6	4W

Alloy 625 – resistance in seawater military applications
Chemical Composition

Ni	Cr	Mo	Fe	Other
61	22	9	2	Cb

Nickel Alloys
Composition

	Alloy	Ni	Cu	Other
Monel	400	66	31	Fe
ppt-hardened 400	K-500	65	30	Al, Ti

"C" Family of Nickel Alloys Date Introduced

C - 1930's

[625 - 1960's]

C-276 - 1965

C-4 - 1970's

C-22 - 1982

Alloy 59 - 1990

Alloy 686 - 1993

C-2000 - 1995

C ⇒ Sensitive to weld issues

Nickel Alloys
Summary

- Chemical Composition of “C” Alloys
- Corrosion in Seawater
- Corrosion in Marine Atmospheres

Long Term Corrosion of Nickel Alloys

Ralph Moeller

Bud Ross

Nickel Development Institute

THE NICKEL DEVELOPMENT INSTITUTE

FORUM FOR THE
USE OF NICKEL ALLOYS FOR RADWASTE CONTAINERS

HOLIDAY INN CITY CENTER
TUCSON, AZ
Feb. 22, and 23, 1995

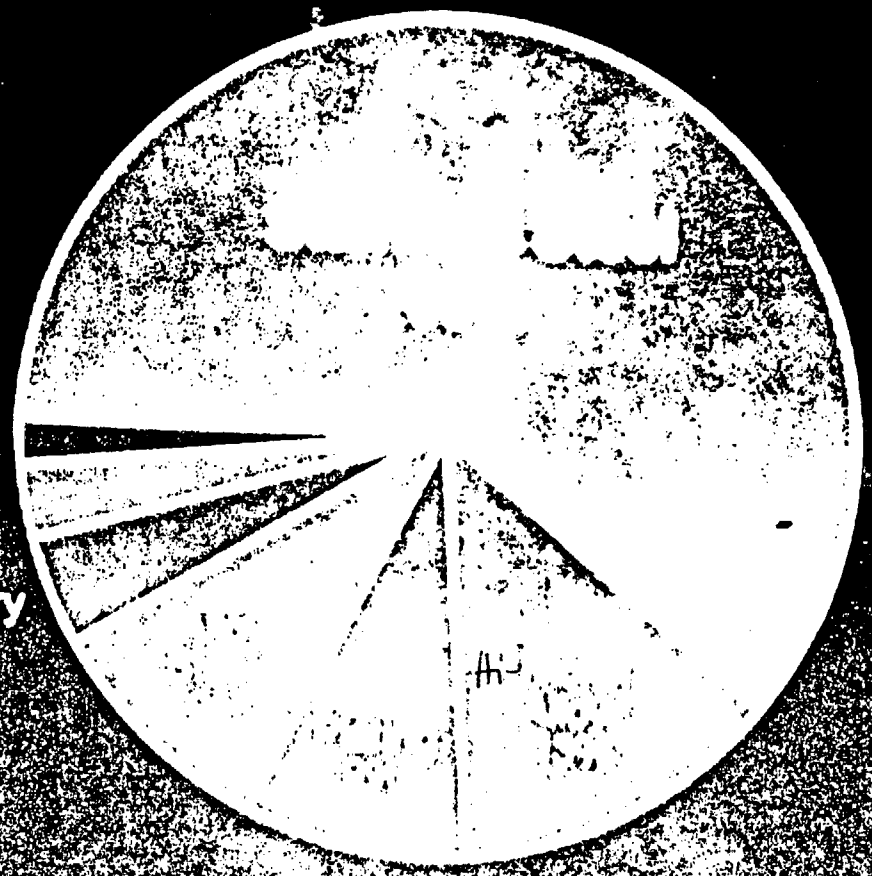
Ralph H. Moeller MDP 94-10

NiDI Materials Workshops

Purpose

- To promote the technical and cost advantages of nickel steels and alloys to specifiers, engineers and others involved in selecting materials
- To establish a dialogue and help resolve materials – related engineering problems, now and in the future

FIRST USE OF NICKEL
Western World 1991



NiDI Global Programs

- 65 Market Development
- 20 Market Exploration
- 21 Technical Research – 1 is use + testing of C276 in Canada
- Over 75 Consultants

What is NiDI?

- A Non-profit Trade Organization
- Represents the Nickel Industry
- Established in 1984
- 16 Sponsors Worldwide ⇒ Ni producers around World
- Based in Toronto

NiDI

NICKEL DEVELOPMENT INSTITUTE

Nickel Alloys
Summary

- High Strength
- High Velocity Resistance
- Outstanding Corrosion Resistance
- NI-Mo-Cr-W For Critical Areas
- Overlays or Cladding
- Will Boifoul

Nickel Alloys
Marine Applications

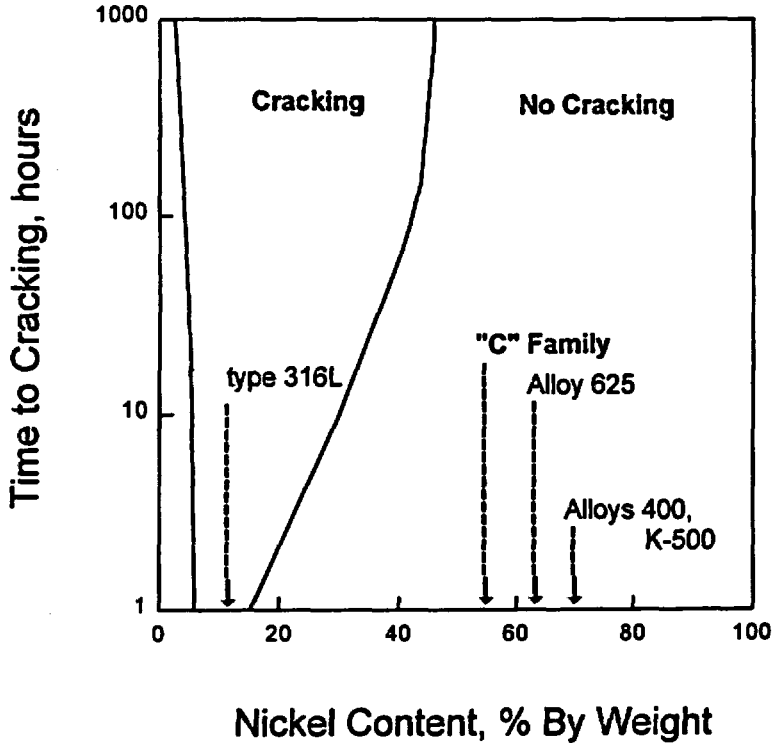
Alloys	Applications
400, K-500, 625	Pumps
K-500, 625 Overlays	Propeller Shafts
625, C-family	Exhaust Systems
625, C-family	Piping Syetms
625, C-family	Heat Exchangers
400, 625	Sheathing
400, K-500, 718, 925, 725, 625, C-family	Fasteners

Nickel Alloys
Marine Atmospheres

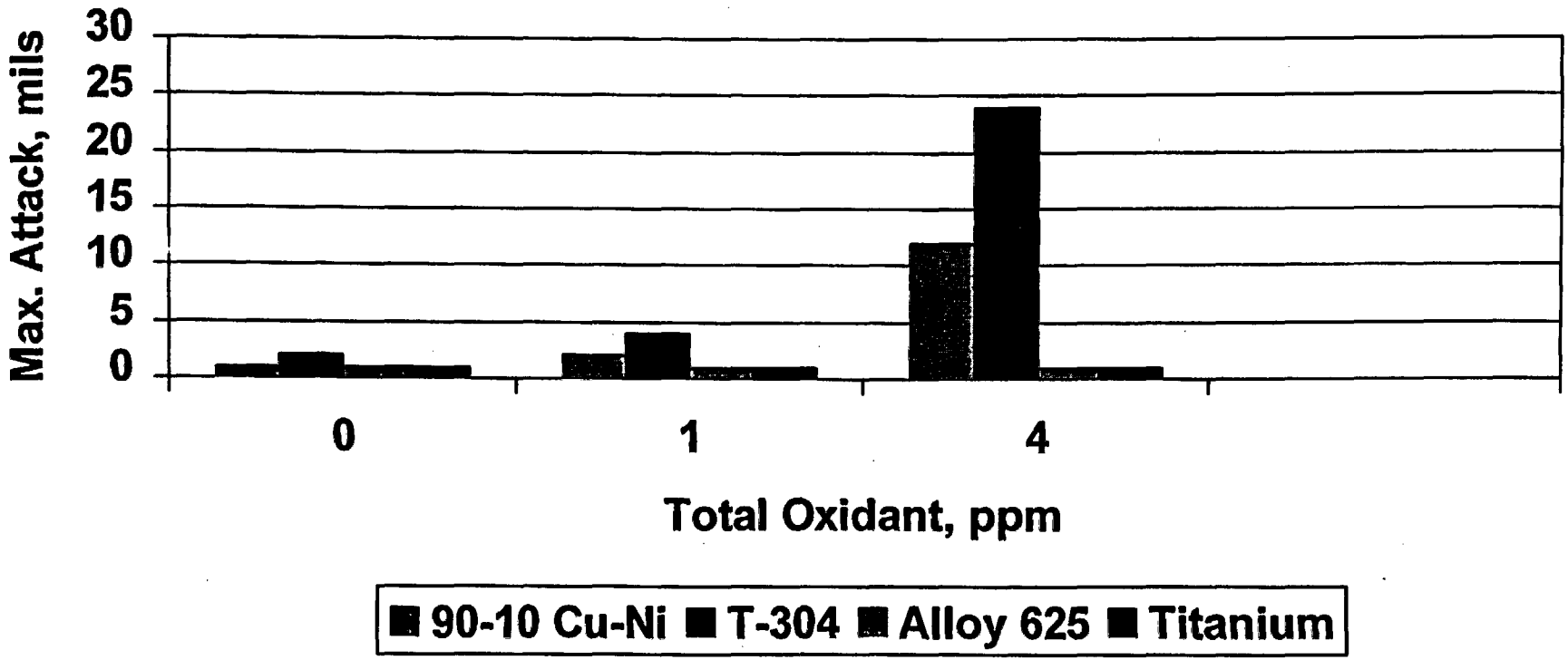
Alloy	Test Lot	Time, yr	Ave. Corrosion Rate, mm/yr (mpy)	Pitting Attack, mm (mils)
Alloy 200	25-m (80-ft)	20	<0.0025 (<0.1)	Nil
Alloy 200	**250-m (800-ft)**	**36**	**0.00025 (0.010)**	**0**
Alloy 400	25-m (80-ft)	20	<0.0025 (<0.1)	<0.025 (1)
Alloy 400	**250-m (800-ft)**	**36**	**0.0003 (0.012)**	**0.1 (4)**
Alloy K-500	**250-m (800-ft)**	**36**	**0.0002 (0.008)**	**0.2 (8)**
Alloy 600	25-m (80-ft)	20	<0.0025 (<0.1)	Nil
Alloy 600	**250-m (800-ft)**	**36**	**0.000008 (0.0003)**	**0.1 (4)**
Alloy 800	25-m (80-ft)	20	<0.0025 (<0.1)	<0.025 (1)
Alloy 825	25-m (80-ft)	20	<0.0025 (<0.1)	<0.025 (1)
Alloy 625	25-m (80-ft)	21	0.001 (0.04)	---
Alloy 625	250-m (800-ft)	21	0.001 (0.04)	---
Alloy C	**250-m (800-ft)**	**56**	**Nil - mirror finish**	**0**

Effect of Nickel
Chloride-ion Stress Corosion Cracking

Boiling 42% Magnesium Chloride Test



Ni-Cr-Mo-Cb alloy 625 - Effect of Chlorination in <1 fps Seawater

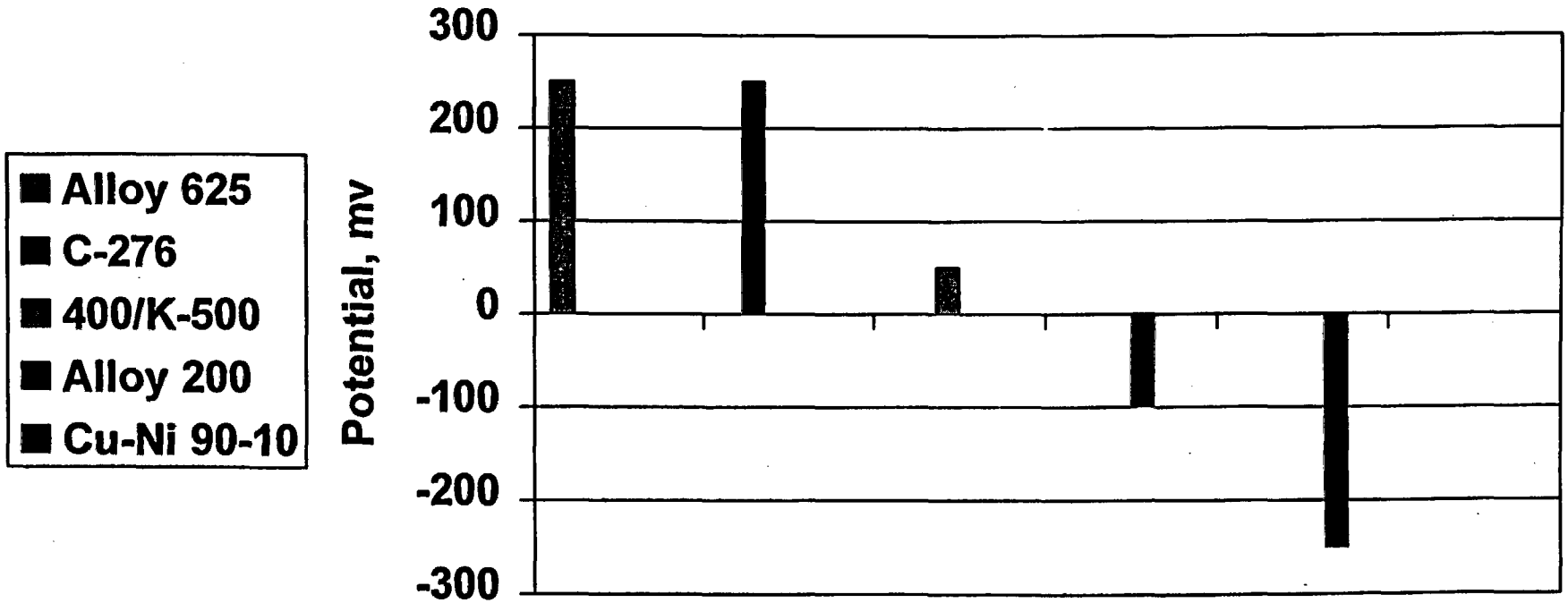


Ni-Cr-Mo-Cb alloy 625 - Effect of Temperature in Seawater

(90 Days)

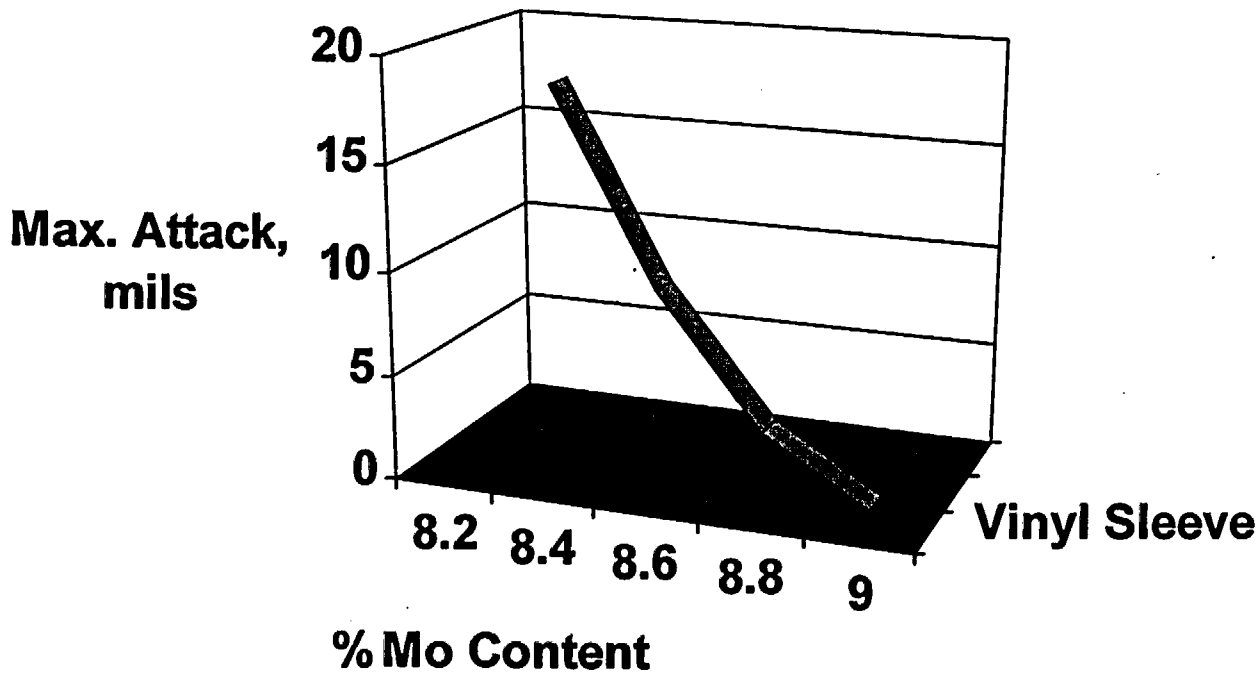
Temperature, F	Corrosion Rate, mpy	Max. Depth Attack, mils
55	0	0
85	0	0
122	0	0
135	0	0
165	0	0
225	0	0

Nickel Alloys
Galvanic Series in 3 fps Seawater

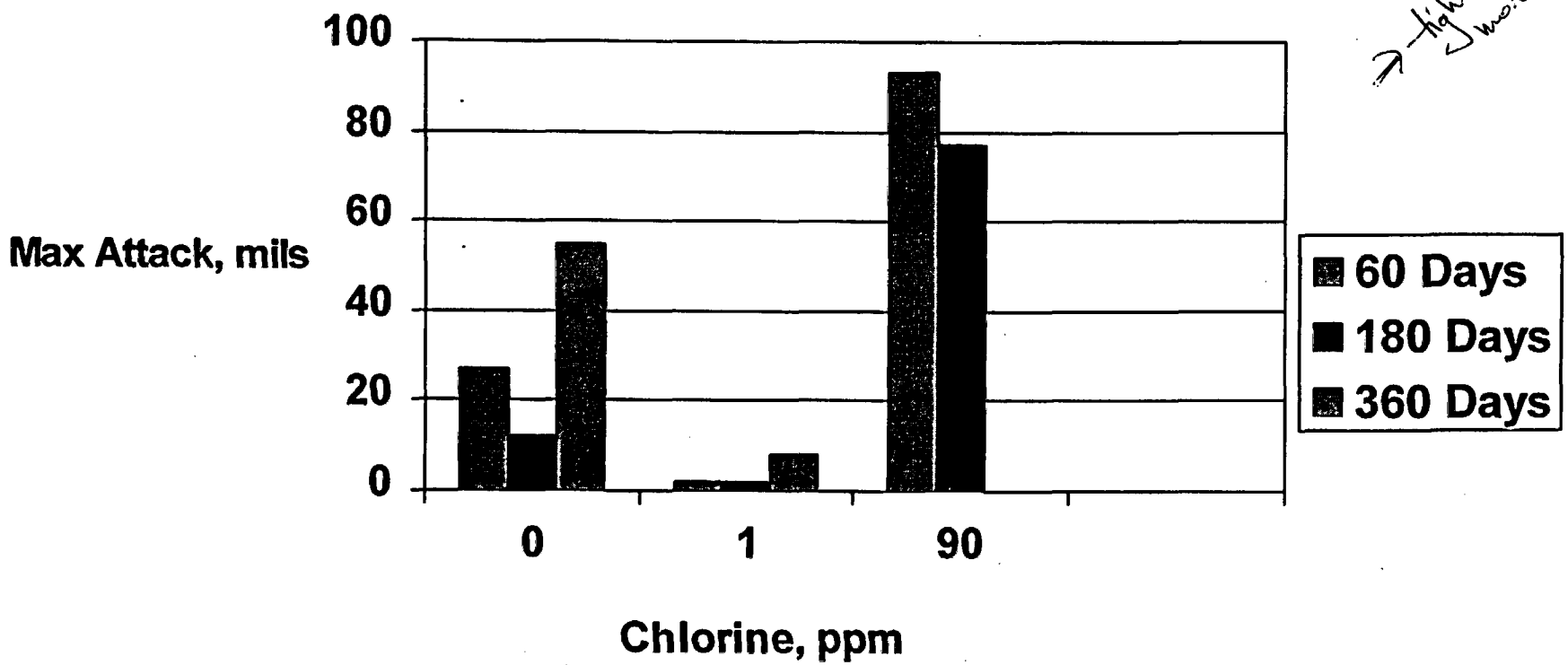


ref. electrode - Ag/AgCl$_3$?

Effect of Mo Content
Alloy 625 Pipe in Seawater
(60 Days)



Alloy 625 Pipe - Vinyl Sleeve Corrosion in Seawater - 3 fps



tight crevice
more susceptible

Ni-Cr-Mo-Cb alloy 625 in 2 fps Ambient Seawater

Time, Years	Corrosion Rate, mpy	Max. Depth Attack, mils
1	0	0
7	0	0
10.8	0	Crevice Etch
11.3	0	2

Nickel Alloys Crevice Corrosion in Seawater - 30 Days at 86 F

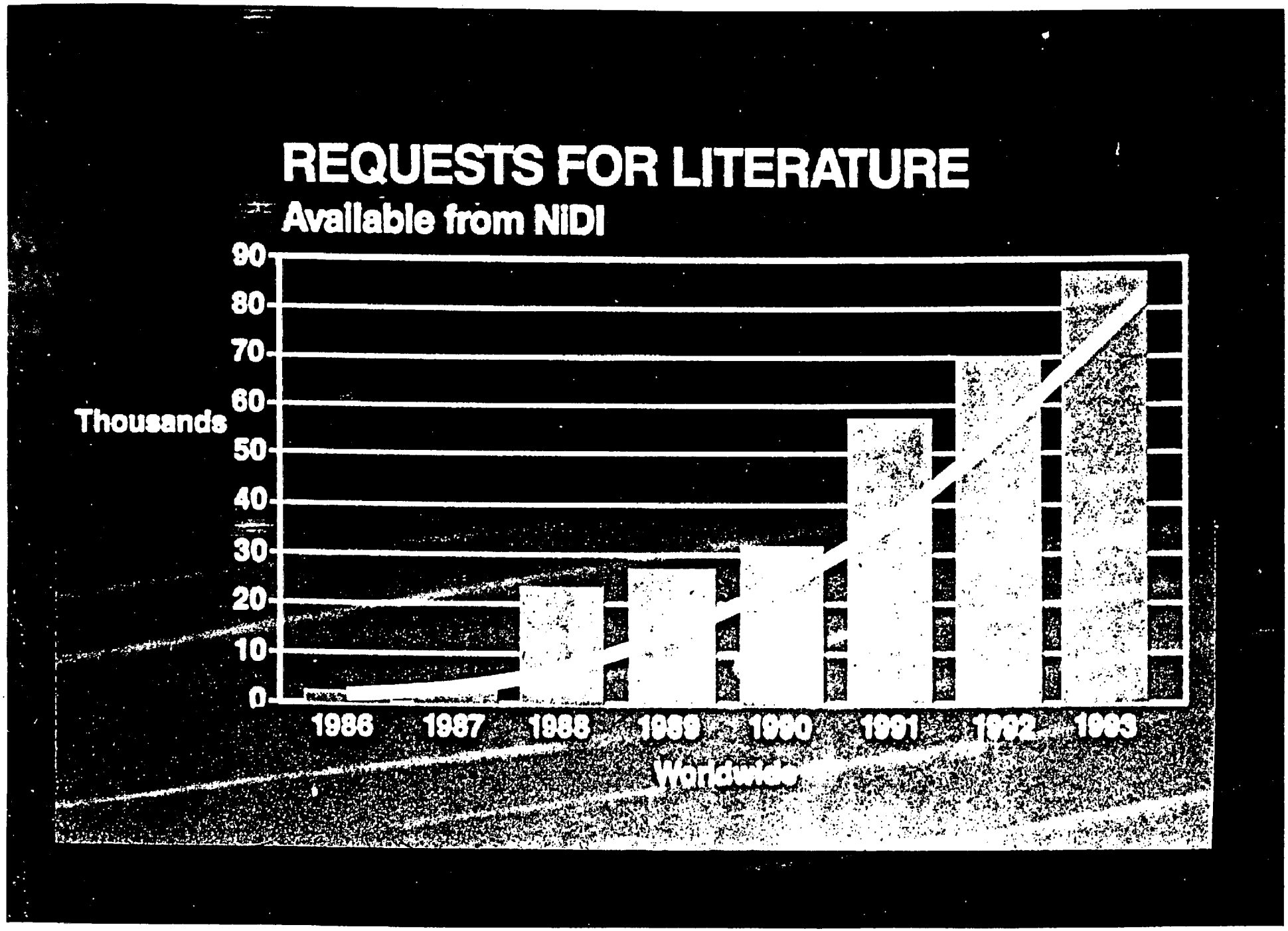
Alloy	Max. Depth Attack, mils	Initiation Time, hrs
T-316	76	24 – 102
G-3	9	102
625	0	0
C-276	0	0

PROGRAM ACTIVITY

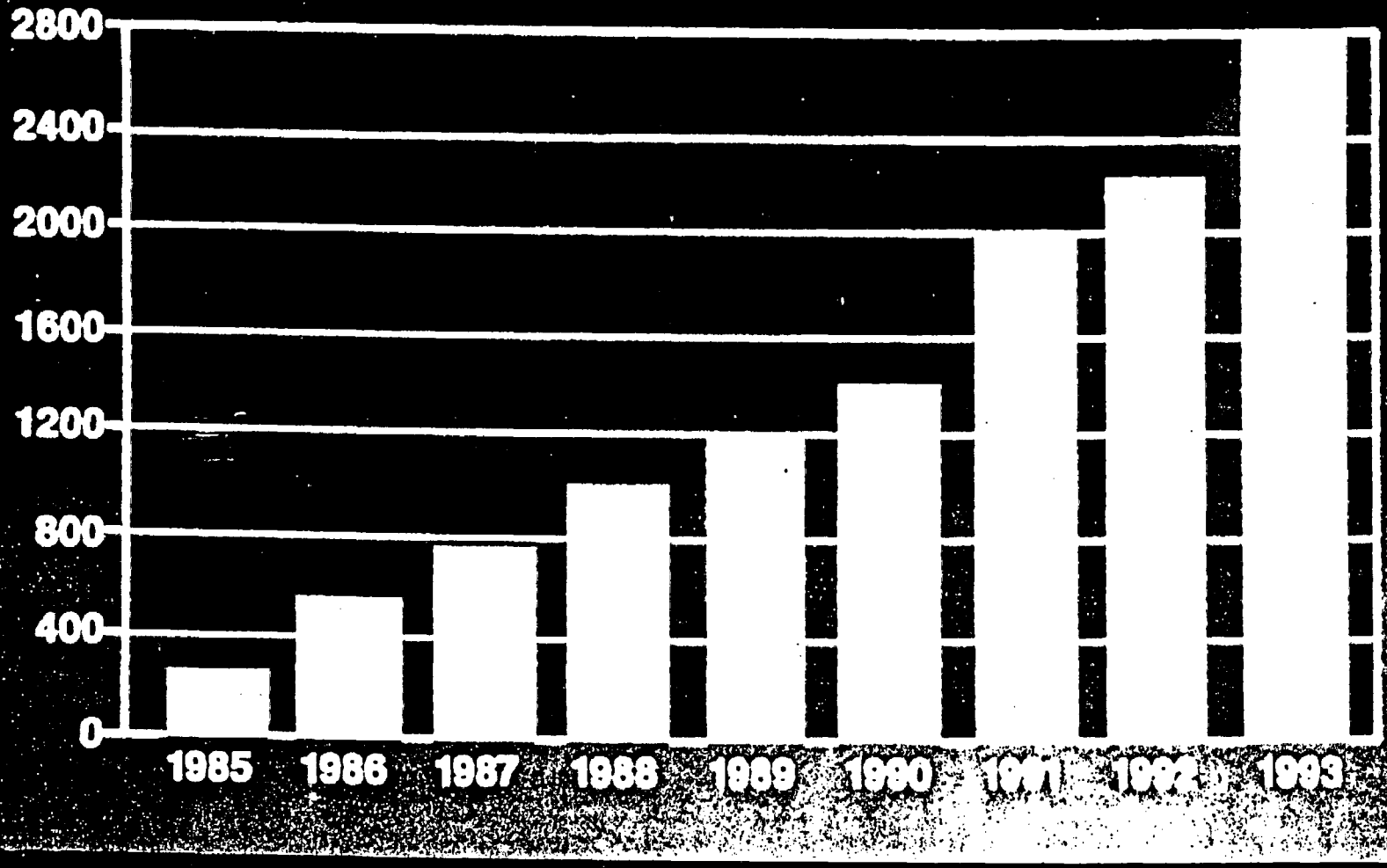
SUPPORT SERVICES

- Technical Literature
- *Nickel* Magazine
- *Communique* Periodical
- Technical Service

Prime aim: To support NIDI's development programs


REQUESTS FOR LITERATURE
Available from NIDI
Thousands
90
80
70
60
50
40
30
20
10
0
1986
1987
1988
1989
1990
1991
1992
1993
Worldwide

NiDI TECHNICAL SERVICE ENQUIRIES
Worldwide



NiDI Research

Objective

To support specific market development projects

Results

Nickel stainless steel proven as more hygienic than competitive non-metallics used in food preparation and handling

LOCALIZED CORROSION OF ALLOY C-276 UNDER NUCLEAR WASTE DISPOSAL CONDITIONS

A commercial report prepared for
The Nickel Development Institute (NiDI), Toronto

by

D. W. Shoesmith, B.M. Ikeda and M.G. Bailey

AECL
Whiteshell Laboratories
Pinawa, Manitoba, Canada R0E 1L0
1996 May

Assessment of Localized Corrosion of Alloys 825, 625, and C-22 for HLW Containers

Presented by

Gustavo A. Cragnolino

Center for Nuclear Waste Regulatory Analyses

San Antonio, TX

Waste Package Degradation Expert Elicitation Workshop

February 2, 1998

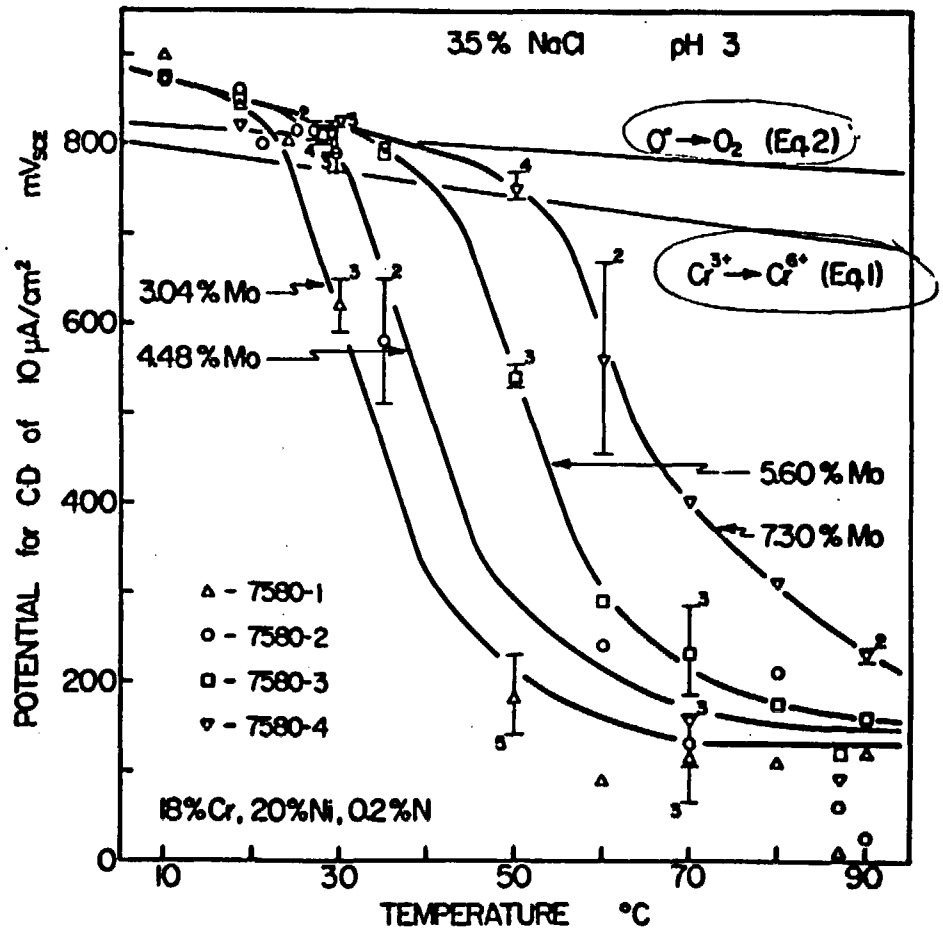
Prediction of Localized Corrosion of CRM

Approach

- Repassivation potential (E_{rp} or E_{rcrev}) is the critical potential used to define susceptibility to pitting or crevice corrosion in chloride solutions for Ni-Cr-Mo alloys
- Effect of environmental variables on E_{rp} or E_{rcrev}
  - Decrease with increasing chloride concentration above a critical concentration
  - Decrease with increasing temperature above the critical temperature of a given alloy
  - Does not depend on pH within the range of ~ 1.0 to 8.2

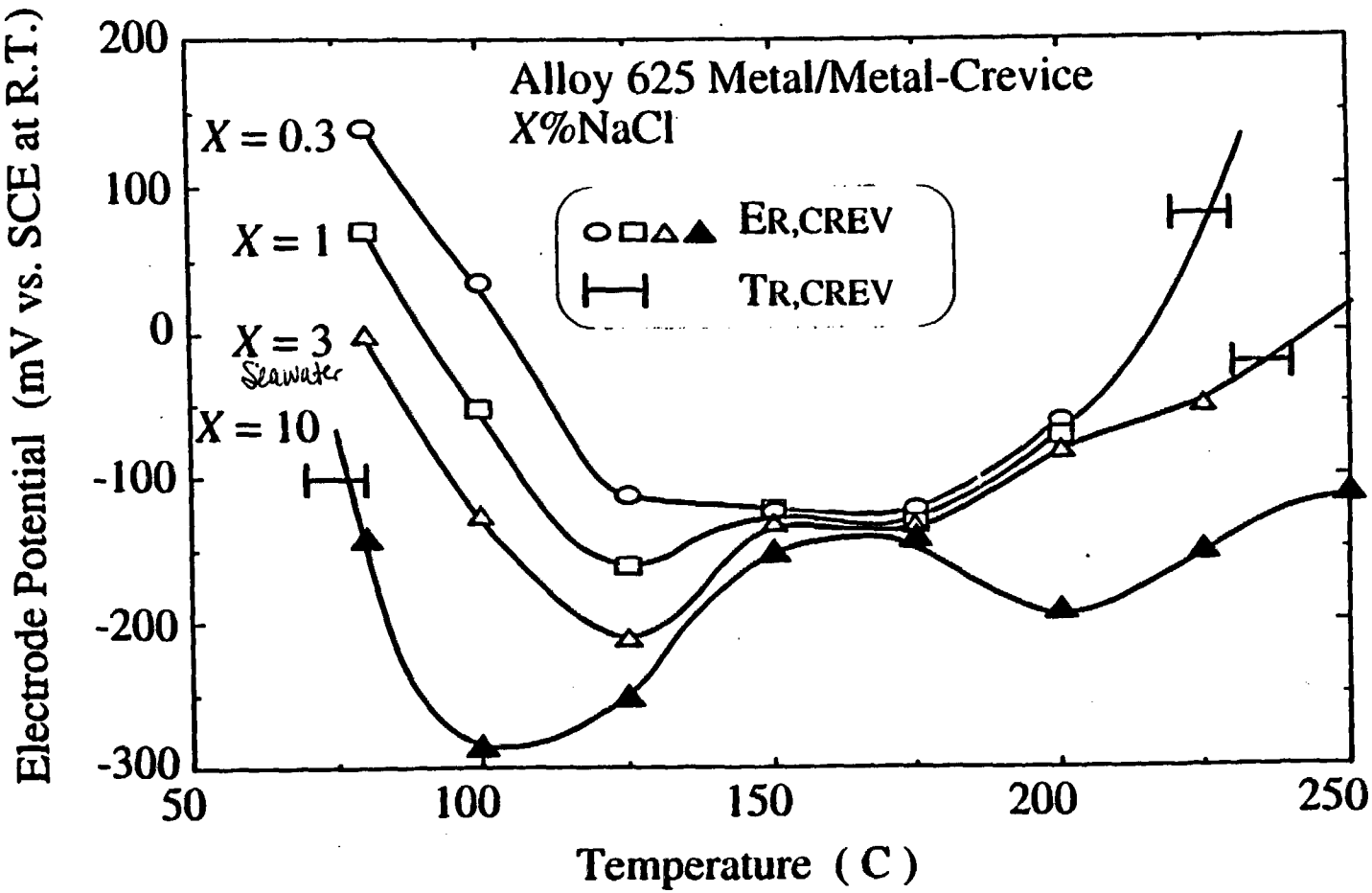
ideas not new - Brigham

Relationship Between Critical Potential and Critical Temperature for Localized Corrosion (From Brigham, 1972)

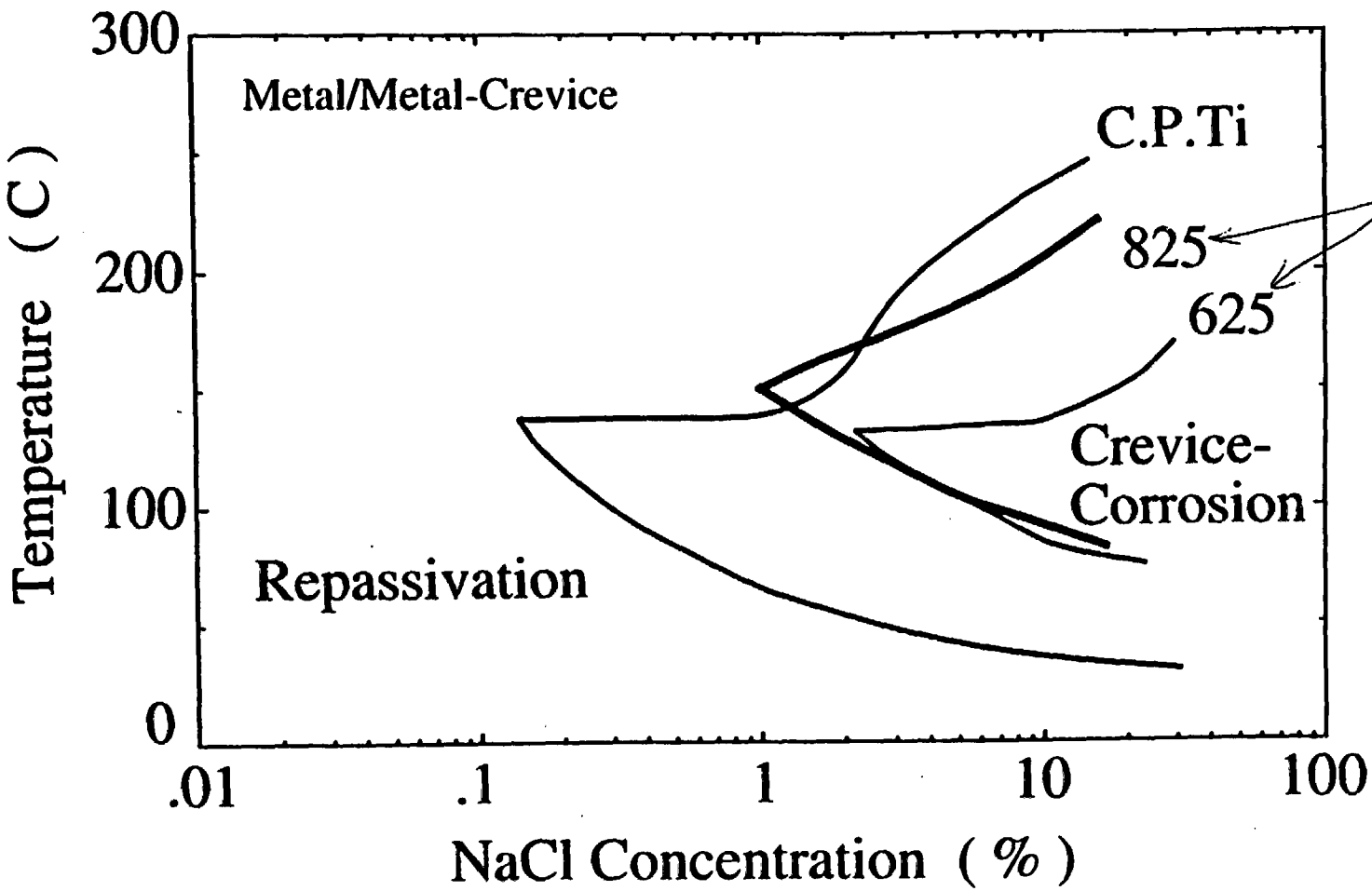


Can plot tabular data on this plot for C22

Relationship Between Potential and Temperature for Crevice Corrosion of Alloy 625 (From Tsujikawa, 1996)

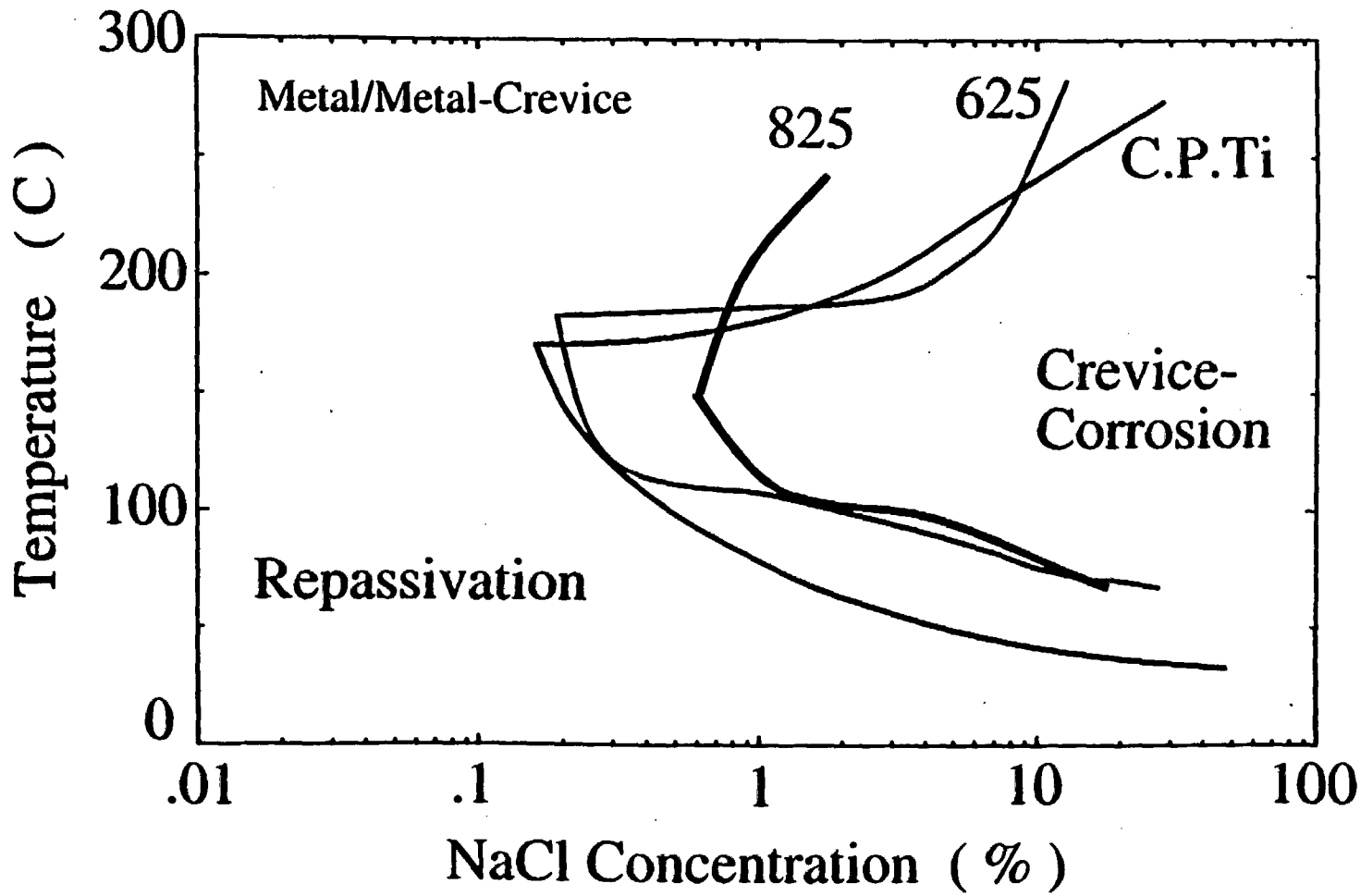


Crevice Corrosion Domains for Alloys 825 and 625, and Ti at -0.2 V_{SCE} (From Tsujikawa, 1996)

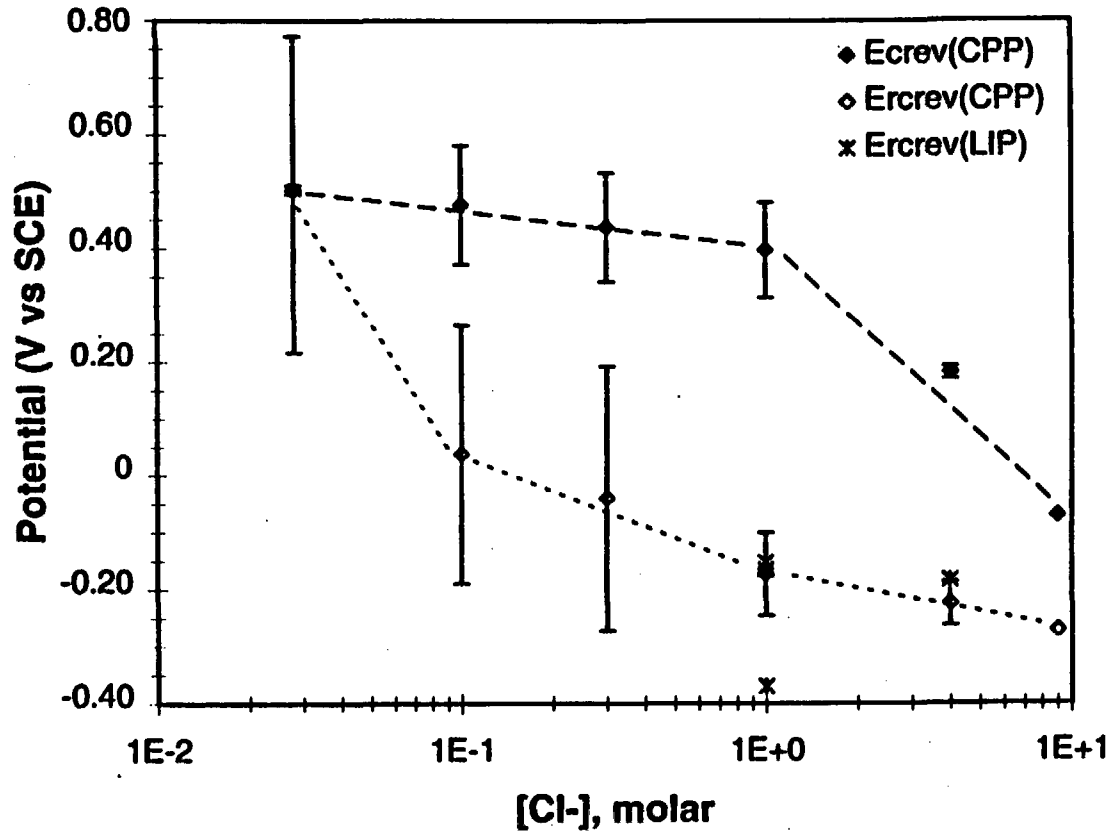


doesn't agree necessarily w/ data, but approac

Crevice Corrosion Domains for Alloys 825 and 625, and Ti at -0.1 V_{SCE} (From Tsujikawa, 1996)



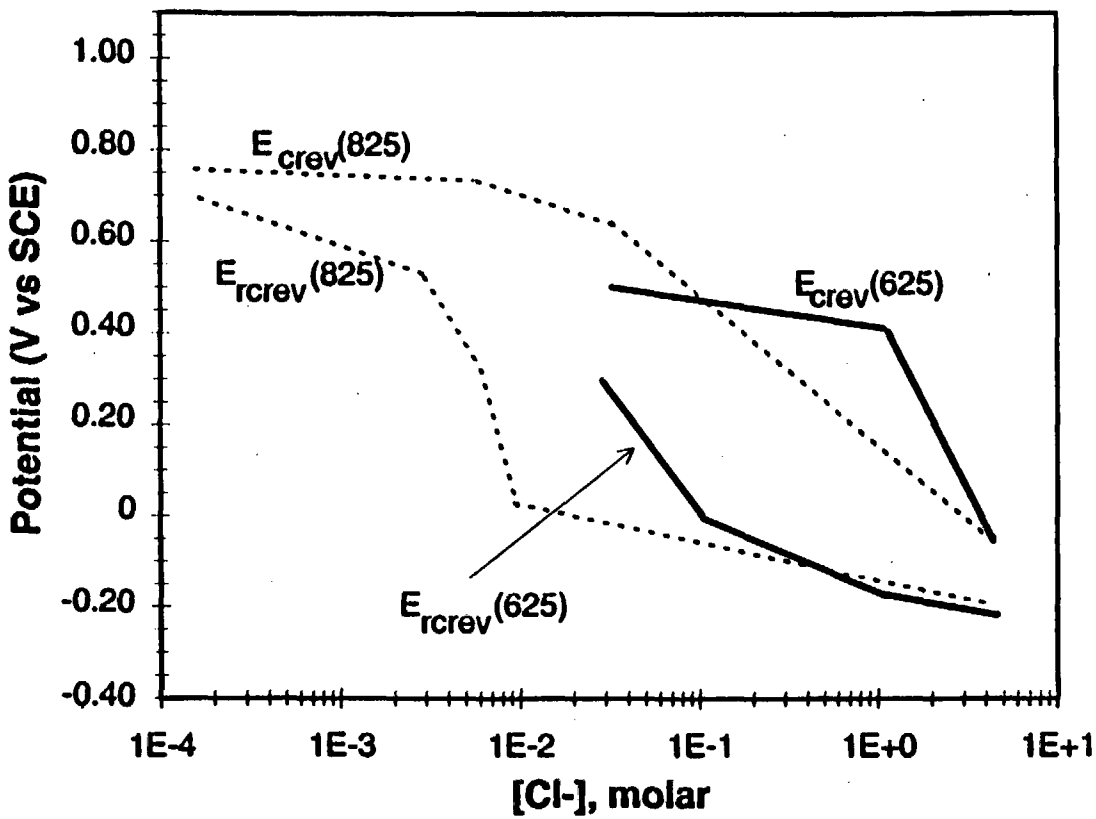
Critical Potentials for Alloy 625 in Chloride Solutions at 95 °C (From Gruss et al, 1998)



- explanation of method
- Characteristics of plot
→ Same # measurement
- explanation of LIP test + sub. data
LIP data ≅ CPP data

CPP: Cyclic potentiodynamic polarization LIP: Lead-in-pencil

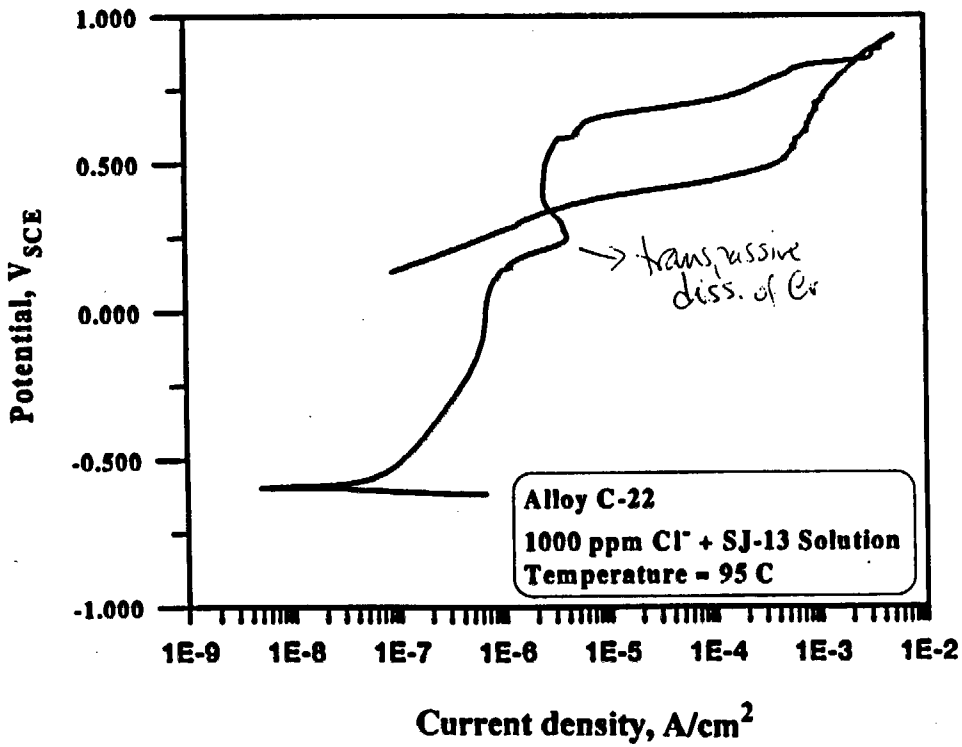
Critical Potentials for Alloys 825 and 625 in Chloride Solutions at 95 °C



- characteristics of plot
- relation to env. in WP w/r.t. [Cl-]
- CO_2/Bicarbonate effect
- threshold [Cl-] and potential define regime

low T ⇒ any differences may be ~~negligible~~ negligible at higher T

Repassivation Potential Measurements of Alloy C-22 in Cl^- solutions



- Hysteresis in CPP measurements do not correspond to visual evidence of localized corrosion
- Several authors have reported low values of E_{rp} or E_{rcrev} that are not consistent with resistance to localized corrosion in field and salt brine tests

Results of Cyclic Potentiodynamic Polarization Tests of Alloy C-22 at 95 °C

– cylindrical specimens

– no crevice formers on them

Solution	pH	E_p (mV_{SCE})	E_{rp} (mV_{SCE})	Appearance
0 ppm Cl^- + SJ-13 solution	8.34	737	588	dark spots
6 ppm Cl^- + SJ-13 solution	8.28	727	507	bronze; spots; pits?
6 ppm Cl^- + SJ-13 solution	8.27	681	531	dark spots
6 ppm Cl^- + SJ-13 solution	8.41	729	559	gold spots; no pits
6 ppm Cl^- + SJ-13 solution	8.38	722	557	gold color w/dark spots; no pits
6 ppm Cl^- + SJ-13 solution	7.88	761	513	yellowish; many small pits
300 ppm Cl^- + silicate	8.90	716	355	gold colored; no pits
1,000 ppm Cl^- (as KCl) + SJ-13 solution	8.27	666	346	bronze color
1,000 ppm Cl^- + SJ-13 solution	8.29	542	346	bronze; spots faded away
1,000 ppm Cl^- + SJ-13 solution	8.42	661	332	bronze; spots faded away
1,000 ppm Cl^- + SJ-13 solution	8.43	679	326	uniform gold color
1,000 ppm Cl^- + SJ-13 solution	8.45	682	378	uniform gold color; no pits
1,000 ppm Cl^- + 0.01 M $S_2O_3^{2-}$	4.00	860	689	deep pits; green color in pits
10,000 ppm Cl^- + SJ-13 solution	7.94	618	406	uniform gold color
10,000 ppm Cl^- + 1,000 ppm SO_4^{2-} + SJ-13 solution	8.33	619	363	uniform gold color

Results of Cyclic Potentiodynamic Polarization Tests of Alloy C-22 at 95 °C

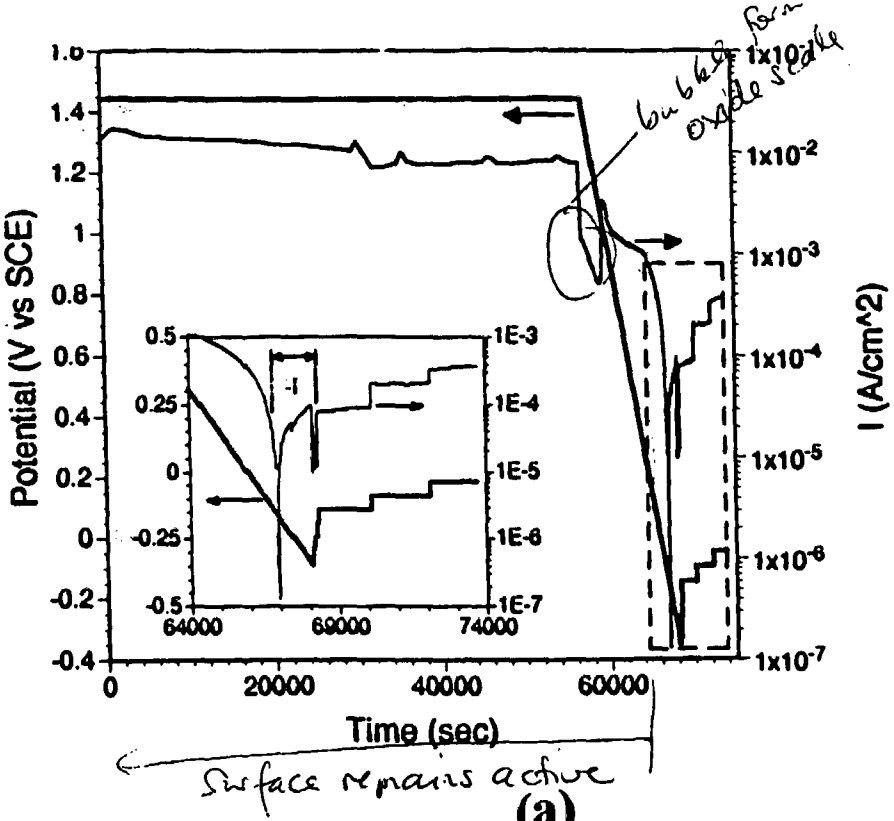
Solution	pH	E_p (mV_{SCE})	E_{rp} (mV_{SCE})	Appearance
1 molal Cl^- + 0.01 M $S_2O_3^{2-}$? why pits? peculiarly aggressive - interaction w/ film on the surface	4.00	550	550	thick bronze color; maybe a few small pits
4 molal Cl + 85 ppm HCO_3 + 20 ppm SO_4^{2-} + 10 ppm NO_3^- + 2 ppm F^-	7.40	792	392	bronze; small pits
4 molal Cl^-	4.00	911	−119	many small fine pits; a few larger pits; grain boundaries appear visible
4 molal Cl^-	1.00	785	785	a few small spots
4 molal Cl^-	9.00	560	337	bronze film uneven in thickness; many spots
6.2 molal Cl^-	4.00	656	626	bronze; spots
6.2 molal Cl^-	4.00	667	632	bronze; spots; shallow pits
6.2 molal Cl^- + 0.01 M $S_2O_3^{2-}$	4.00	662	642	bronze; spots; small areas of shallow attack
9.1 molal Cl^- (as LiCl)	4.00	717	642	spots; no pits
14 molal Cl^- (as 40% $MgCl_2$)	—	21	−254	pits; etched; grains visible

worst possible conditions

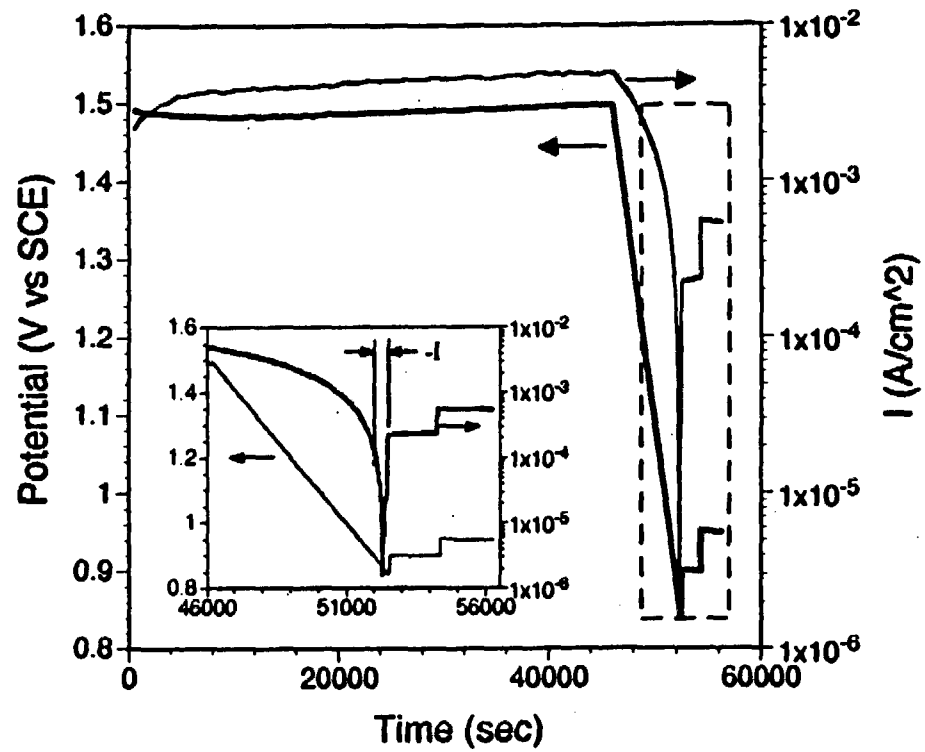
Repassivation of Alloys 625 (a) and C-22 (b) in 1M Cl^- Solution at 95 °C and pH 8.2

controlled by carbonate in solution

(Lead-in-Pencil Electrode)



(a)



(b)

Note differences in the potential scale between (a) and (b)

– explains LIP test + relate to CCS in put

Repassivation Potentials of Alloys 625 and C-22 in Cl^- Solutions of pH 8.2
(Lead-in-Pencil Electrode)

Specimen No.	$[Cl^-]$, M	T, °C	E_{rerev}, V_{SCE}
625-1	4.0	95	-0.183
625-2	4.0	60	-0.167
625-3	1.0	95	-0.367
625-4	1.0	95	-0.166
625-5	1.0	95	-0.153
625-6	1.0	60	1.001
625-7	0.028 100 ppm	60	0.857
625-8	0.028	60	0.873
C22-1	4.0	95	0.916
C22-2	4.0	95	0.911
C22-3	4.0	95	0.900
C22-4	4.0	60	0.911
C22-5	1.0	95	0.829
C22-6	1.0	60	0.986
C22-7	0.028	95	0.854

T_{crit} for alloy 625 as f(Cl^-)

effect of T

O_2 evol. rxn

regime of O_2 evolution

T_{crit} for alloy C22 is higher than 90°C

Comparative Assesment of Localized Corrosion of Alloys 825, 625, and C-22 in Cl^- solutions at 95 °C

- Alloy 625 is more resistant than 825 only at intermediate Cl^- concentrations (0.028 to 0.1 M)
- E_{rcrev} of alloys 825 and 625 are almost identical at high Cl^- concentrations (0.1 to 4 M)
- E_{rcrev} of alloy C-22 is considerably higher (it may correspond to the potential for the O_2 evolution reaction instead of crevice repassivation)
- Crevice corrosion of alloy C-22 was observed in a CPP test in 4M Cl^- solution of pH 2.5, in which $E_{crev} = 0.62\ V_{SCE}$ and $E_{rcrev} = 0.59\ V_{SCE}$

Needs Some Investigation

In air saturated solution

E_{corr} = 100 - 2[illegible] mV (SCE) (RT)

Prediction of Localized Corrosion Susceptibility of Alloy C-22

- Conduct tests at temperatures above 100 °C to measure E_{rcrev} establishing effect of Cl^- concentration, temperature, and pH
- Determine a parametric equation for

$$E_{rcrev} = f([Cl^-], T, pH)$$

or a critical repassivation temperature (T_{crev}) to be used in the TPA code to predict the mode of corrosion within the environmental range of interest