U.S. DEPARTMENT OF ENERGY
OFFICE OF CIVILIAN RADIOACTIVE WASTE MANAGEMENT

PRESENTATION TO
THE NUCLEAR WASTE TECHNICAL REVIEW BOARD

SUBJECT: CORROSION MODELING AND TESTING

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Outline of presentation

- Conditions outside one specific spent-fuel container
- Documentation of existing models
- Modeling and testing for vapor-phase environment
  - Rates of uniform oxidation
- Modeling and testing for aqueous environment
  - Pit initiation and propagation
  - Crack initiation and propagation
- Status of corrosion research at LLNL
  - Corrosion and pitting potential measurements
  - Identification of corrosion products
  - Monitoring of crack initiation and propagation

Conditions expected outside <u>one</u> <u>specific</u> spent-fuel container

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- Time immediately following emplacement
  - Temperature <u>expected</u> to remain above boiling point
  - Radiolytic formation of NO_2 in <u>dry</u> air
  - Radiolytic formation of HNO_3 and <u>some</u> NH_3 in <u>moist</u> air
  - <u>Possible</u> formation of salt crust on container surface
- After very long periods of time
  - Temperature <u>expected</u> to drop below boiling point
  - <u>Possible</u> formation of concentrated electrolyte
  - Radiolytic formation of H_2O_2 in aqueous phase
  - Radiolytic formation of HNO_3 in vapor phase

Documentation of existing models and data

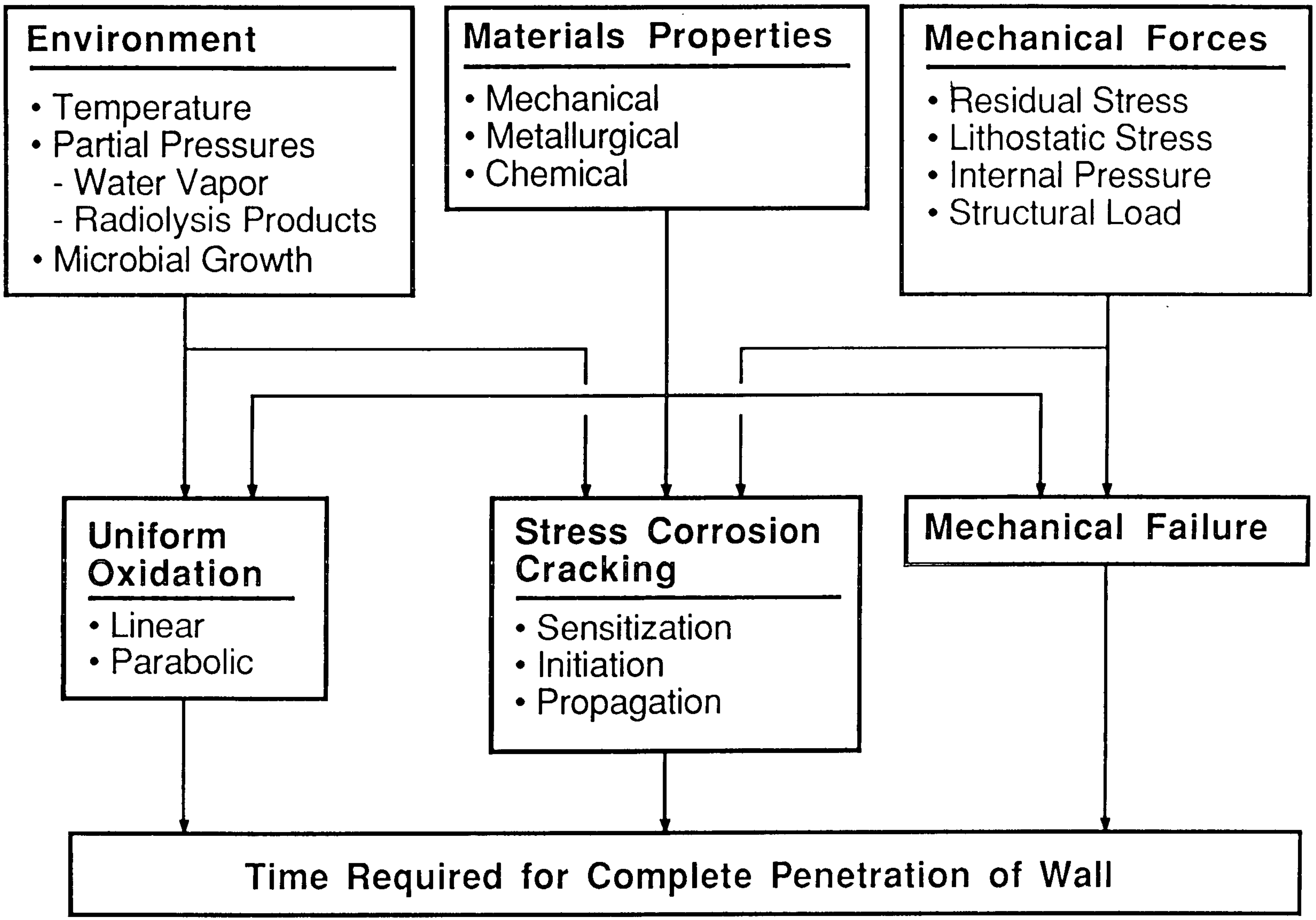
Corrosion Models for Performance Assessment of High-Level Radioactive Waste Containers, SMiRT-10 Conference Seminar No. 11 on Structural Mechanics and Materials Properties in Radioactive Waste Repository Technology, Anaheim, California, August 21-22, 1989, to be published in Nuclear Engineering Design (1990).

A Review of Models Relevant to the Prediction of Performance of High-Level Radioactive Waste Disposal Containers, Paper No. 519, Corrosion 89, National Association of Corrosion Engineers (1989).

Localized Corrosion and Stress Corrosion Cracking of Candidate Materials for High-Level Radioactive Waste Disposal Containers in U.S.: A Critical Literature Review, Materals Research Society Symposium Proceedings, Vol. 127, pp. 359-371 (1989).

Survey of Degradation Modes of Candidate Materials for High-Level Radioactive-Waste Disposal Containers, Overview and Vols. 1-8, UCID-21362 (1988).

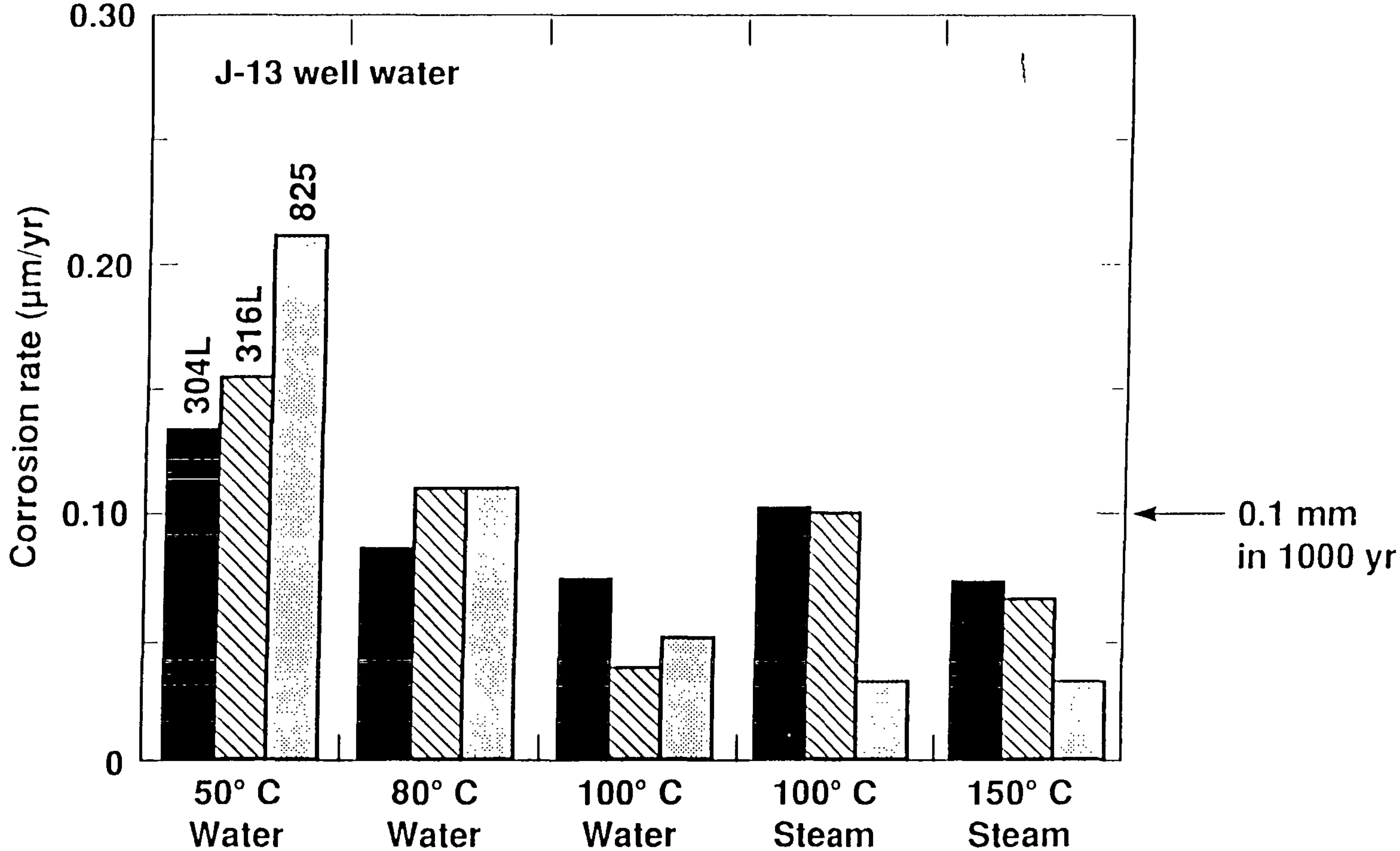
Containers exposed to vapor-phase environments



Models and testing for vapor-phase oxidation

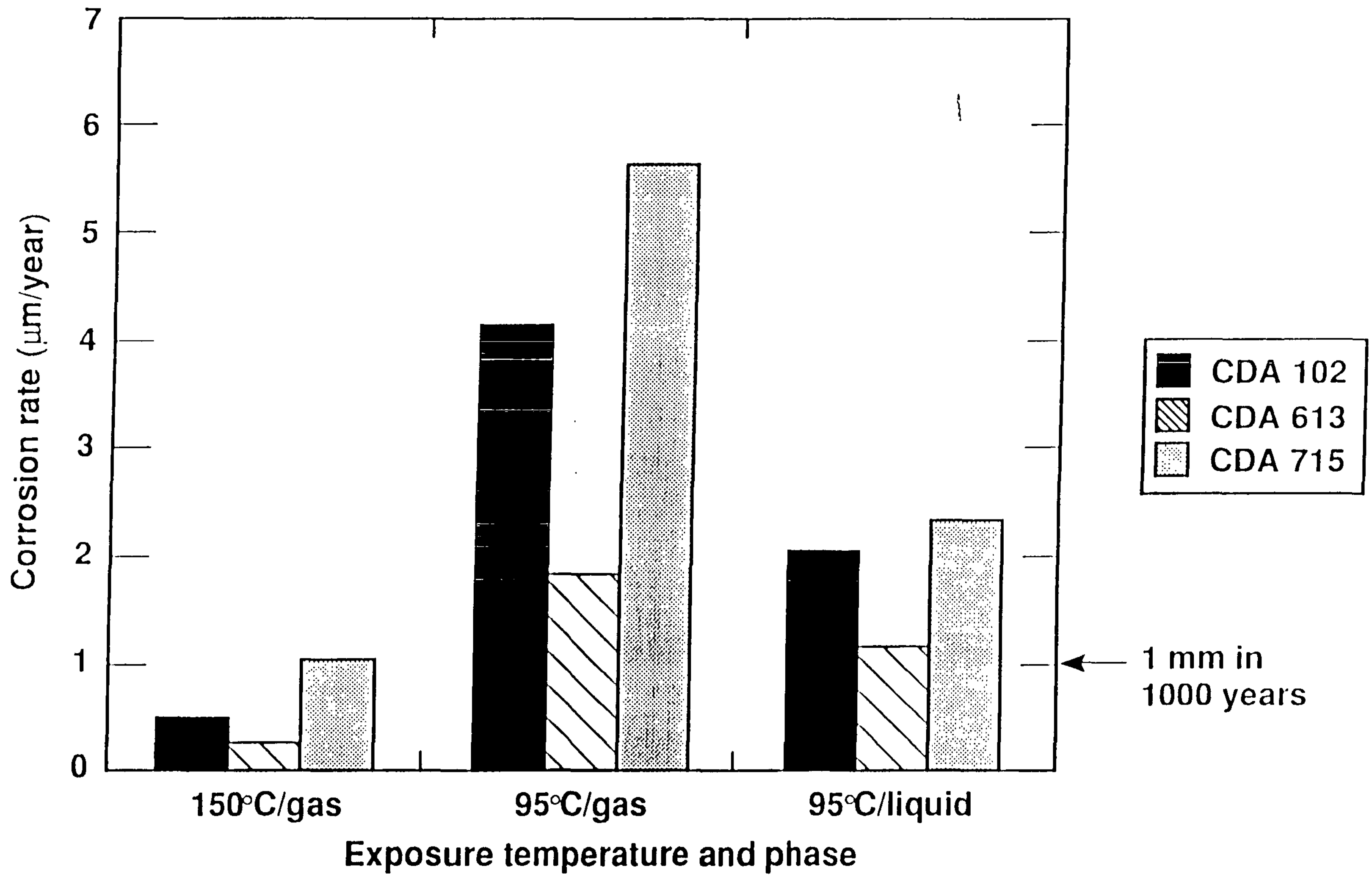
- Models for vapor-phase oxidation
  - Parabolic growth law: adherent protective oxide film
  - Linear growth law: spalling non-protective oxide film
- Testing to support models
  - Coupons exposed to steam and water
  - Periodic measurement of weight gain
  - Experiments at temperatures ranging from 50 to 150°C
  - Determination of the effects of γ irradiation
  - Identification of corrosion products by X-ray diffraction

Container life is not limited by uniform corrosion and oxidation of the austenitic alloys



From McCright et al., UCID–21044, December 1987 (Table 2)

Container life may be limited by uniform corrosion of the copper-based alloys in saturated steam at 95°C



From McCright et al., UCID-21044, December 1987 (Table 13)

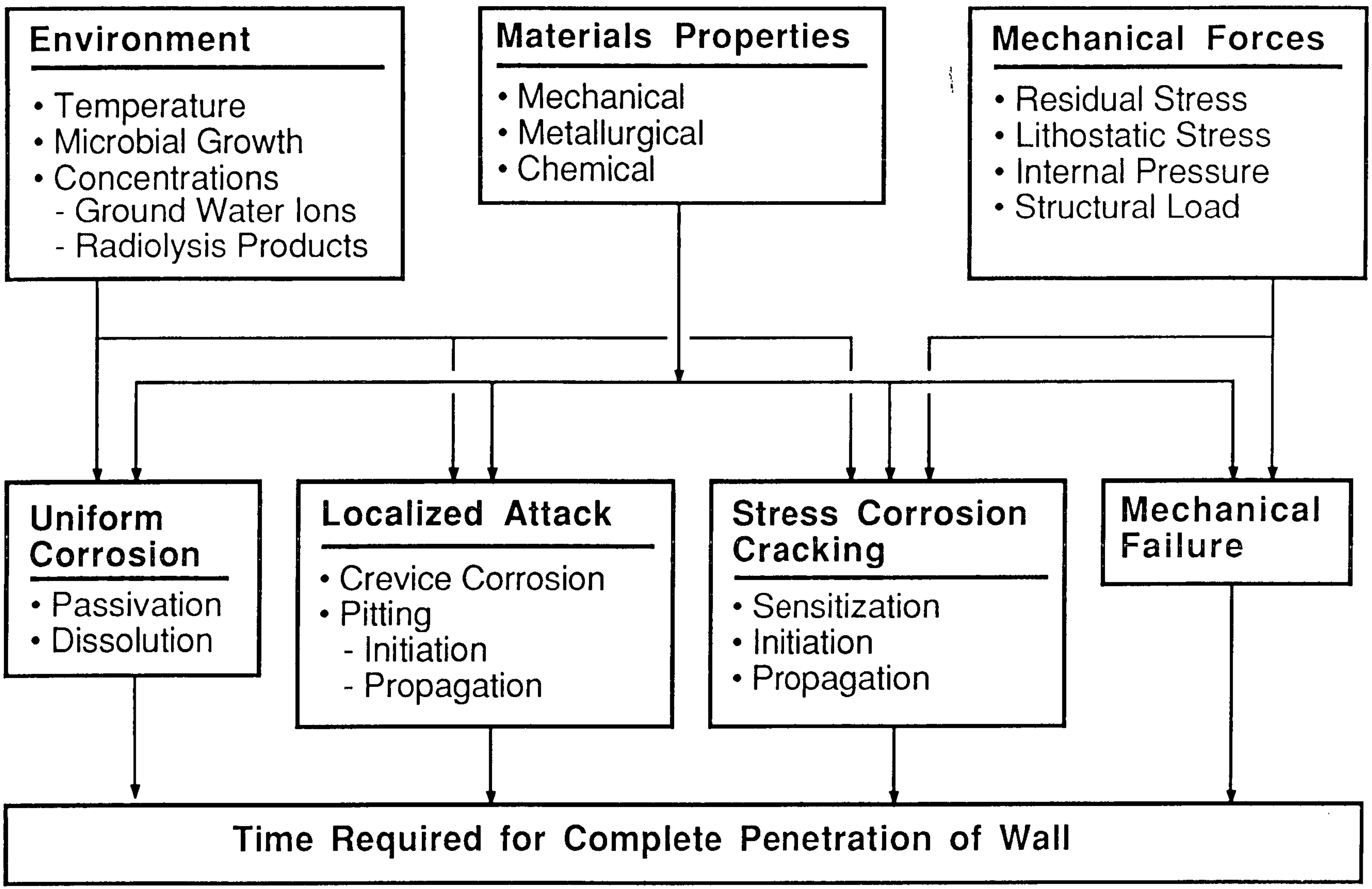
X-Ray diffractometry of corrosion product on copper from target cave of 100-MeV electron LINAC

Observed		Known Spectrum of $Cu_2NO_3(OH)_3$	
d(Å)	Peak Area	d(Å)	Relative Intensity
7.90	0.2		
6.85	100.0	6.91	100
5.606	0.3	5.597	5
5.510	0.2		
5.398	0.2		
4.554	0.5	4.550	13
		4.188	10
4.096	4.0	4.121	40
3.610	2.5	3.631	30
3.440	58.9	3.454	70
3.184	0.3		
3.027	1.6	3.047	10
3.000	3.4	3.006	20
2.927	0.3		
2.842	0.2	2.843	5
2.781	9.6	2.795	40

Observed		Known Spectrum of $Cu_2NO_3(OH)_3$	
d(Å)	Peak Area	d(Å)	Relative Intensity
2.712	0.3	2.725	5
2.656	27.4	2.669	80
2.511	5.4	2.532	20
2.450	37.7	2.460	70
		2.441	10
2.376	0.3	2.331	10
2.298	2.6	2.303	20
		2.283	5
2.254	13.3	2.264	50
2.218	0.8		
2.187	0.3	2.193	5
2.145	8.5	2.155	40
2.085	3.2	2.093	20
2.069	18.4	2.077	60
2.014	0.3	2.006	10
2.001	0.4	1.980	5
1.937	0.1	1.942	5

Van Konynenburg, 1989

Containers exposed to aqueous environments



Pitting models

- Initiation on passive surfaces of austenitic alloys

    1. Halide nuclei theory (Okada, 1984)
    2. Point defect model (Chao et al., 1981)
    3. Critical suppression of pH (Galvele, 1976)
    4. Electrostriction model (Sato, 1971)
    5. Inclusion model (Manning et al., 1980)
    6. Stochastic theory (Shibata and Takeyama, 1977)

- Propagation of pits in austenitic alloys

    1. Quasi-steady-state mass-transport model assuming active surface at base of pit (Pickering and Frankenthal, 1972; Galvele, 1976)

    2. Transient mass-transport model assuming highly resistive salt film at base of pit (Beck and Alkire, 1978)

- Predictive models for pitting of copper-based alloys do not exist

- Time will be required for the development of such models

Halide nuclei theory of pit initiation (Okada, 1984)

- Two independent approaches were used to derive the same expressions for the critical pitting potential (E_c) and the incubation time (τ)
  - General evolution criterion proposed by Glansdorff and Prigogine for irreversible thermodynamics
  - Application of perturbation theory
- The expressions relating Ec and τ to chloride concentration and temperature are simple linear functions

$$E_c = \text{constant} - (RT/F)\ln[Cl^-]$$

$$\ln(\tau) = \text{constant} - 2n\ln[Cl^-] - 2FE/RT$$

The linear relationship existing between E_c and $\ln[Cl^-]$ is well established

- Equations deduced from the point defect model (Chao et al., 1981) have the same functional forms as those deduced from the halide nuclei theory (Okada, 1984)

- Similar results have been derived from a model based upon pH suppression inside cracks in the passive film (Galvele, 1976)

- The following relationship between chloride concentration, temperature and pH has been observed (Matamala, 1987)

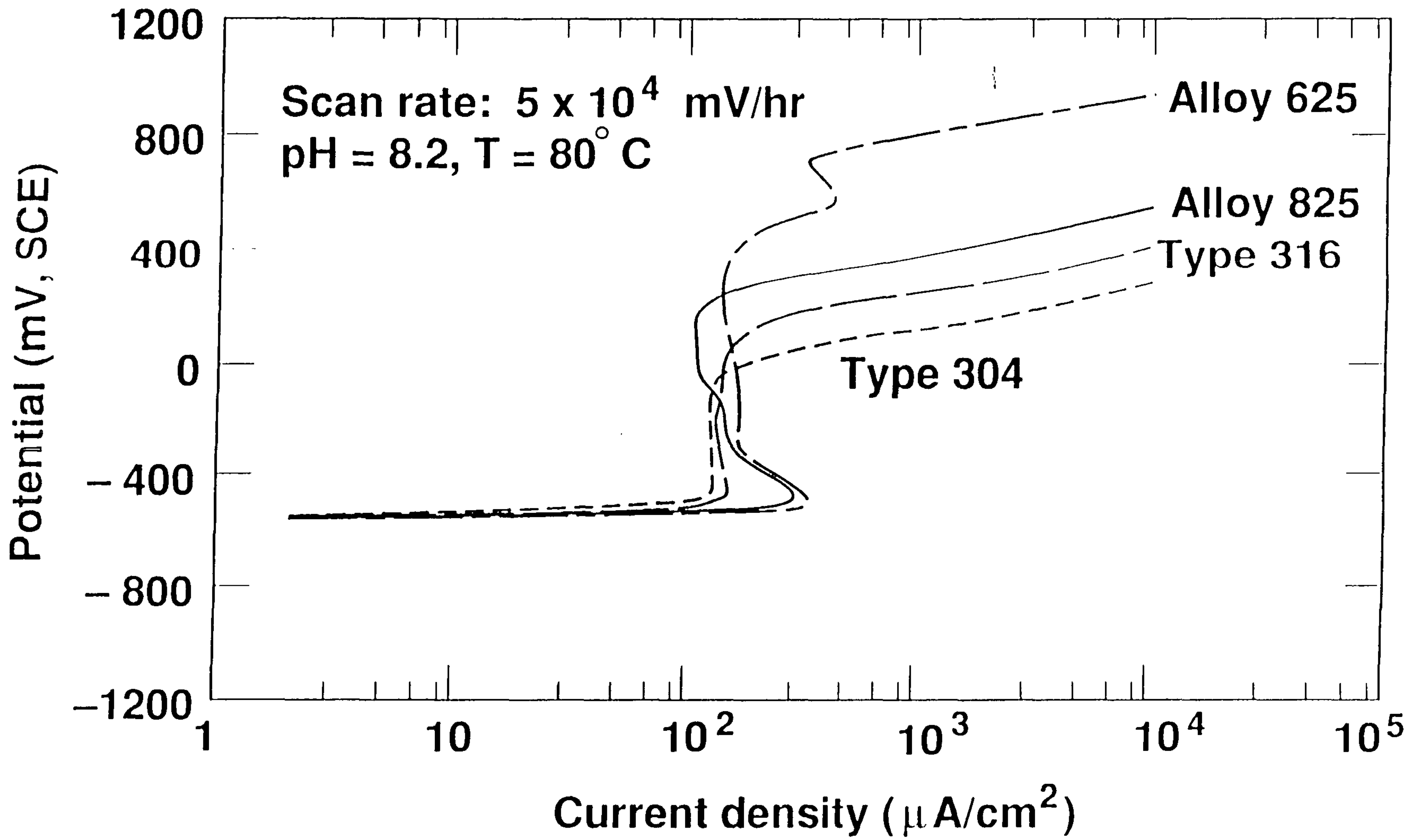
$$Ec = 2570 - 5.81 \cdot T + 0.07 \cdot T \cdot pH - 0.49 \cdot T \cdot \log[Cl^-]$$

- This type of functionality has also been observed experimentally in cases involving pit initiation at sulfide inclusions (Manning, 1980)

Experiments supporting predictive models for the initiation of pits

- Critical pitting potential (E_c)
  - Potentiodynamic linear-sweep polarization
- Incubation time (τ)
  - Potentiostatic polarization
- Application of statistics
  - Factorial designs to determine the dependence of E_c and τ on chloride, pH and temperature
  - Stochastic theory to determine probability density functions for E_c and τ (Shibata and Takeyama, 1977)

Pitting potentials were determined by linear sweep anodic polarization



Slow scan tests in deaerated seawater. From Scarberry et al., Paper No. 245, Corrosion 79, Atlanta, Ga., March 12-16, 1979.

Factorial designs minimize the number of experiments required to determine the coefficients in linear equations

- Most general form of the equation for pitting potential

$$Ec = a_0 + a_1 \cdot \ln[Cl^-] + a_2 \cdot pH + a_3 \cdot T + a_{12} \cdot \ln[Cl^-] \cdot pH + a_{13} \cdot \ln[Cl^-] \cdot T + a_{23} \cdot pH \cdot T + a_{123} \cdot \ln[Cl^-] \cdot pH \cdot T$$

- Important two-and three-factor interactions are included
- Only eight experiments are required to determine eight parameters
- A similar approach can be used to determine parameters in the equation for the incubation tim

Factorial design for determining parameters in the pitting potential equation

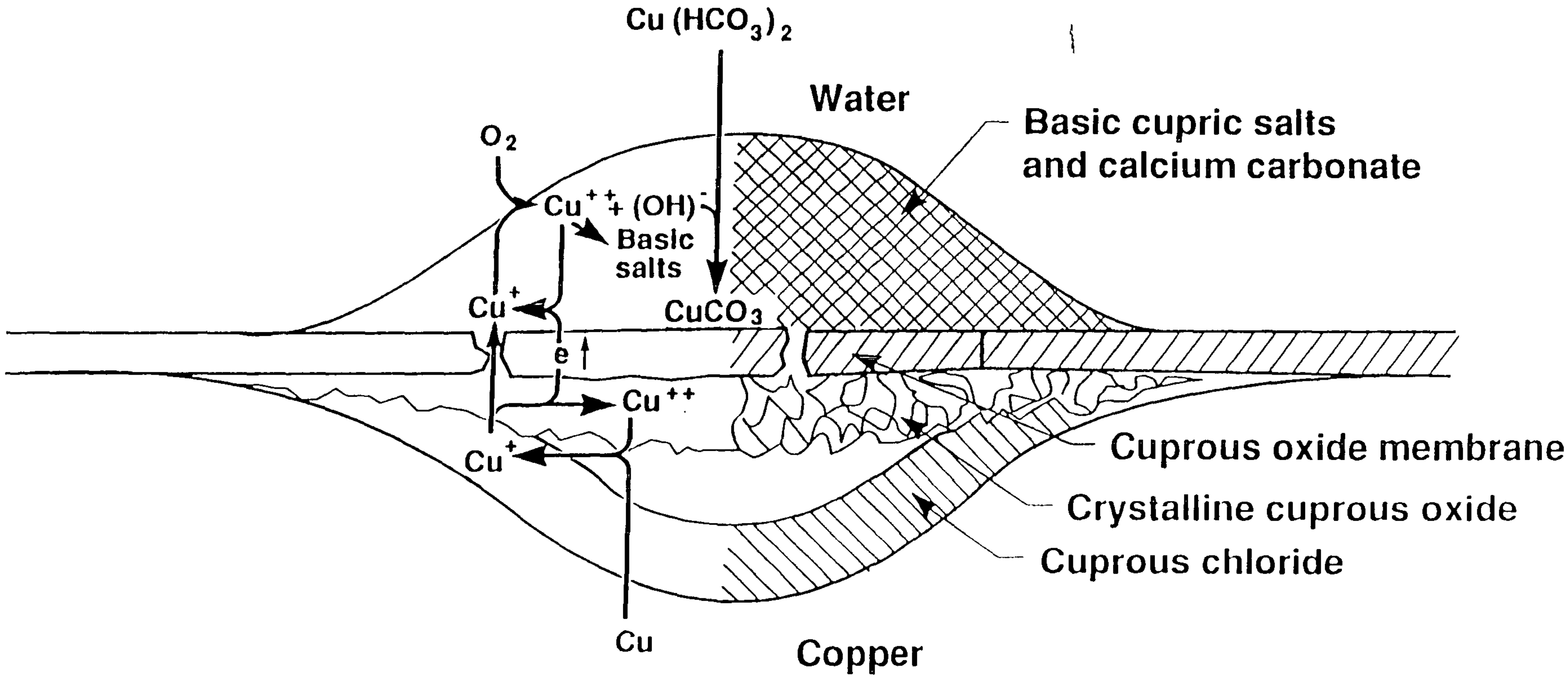
Expt.	ln[Cl⁻]	pH	T	ln[Cl⁻]•pH	ln[Cl⁻]•T	pH•T	ln[Cl⁻]•pH•T
#1	-	-	-	+	+	+	-
#2	+	-	-	-	-	+	+
#3	-	+	-	-	+	-	+
#4	+	+	-	+	-	-	-
#5	-	-	+	+	-	-	+
#6	+	-	+	-	+	-	-
#7	-	+	+	-	-	+	-
#8	+	+	+	+	+	+	+

Note: (+) high level of variable; (-) low level of variable.

Experiments supporting predictive models for the propagation of pits

- Determination of pit depth (x or a_p) as a function of time (t)
  - Exposure of specimens to environment
  - Optical microscopy to measure focal distance at base of pit
  - Optical microscopy of metallographic cross-section
- Fractional coverage of surface by pits
  - Optical microscopy with video camera
  - Use of digital image processing for quantification
- Overall loss of material due to pitting
  - Weight loss measurements

Lucey has proposed a mechanism for the pitting of copper which involves a porous cuprous oxide membrane



Reaction occurring within the mound above a pit:

$4CuCl + Ca(HCO_3)_2 + O_2 \rightarrow CuCO_3 \ Cu(OH)_2 + CaCO_3 + 2CuCl_2$.

From Lucey, Brit. Corr. J., Vol. 7, January 1972, p. 36

Stress corrosion cracking models

- Initiation of cracks

  1. Linear-elastic fracture mechanics model for initiation of fatigue crack at pit (Hagn, 1983)

  2. Crack-tip-opening displacement model for initiation of stress corrosion crack at pit (Buck and Ranjan, 1984)

  3. Spontaneous initiation (Andresen and Ford, 1985)

- Propagation of cracks

  1. Anodic dissolution of active crack tip (Turnbull and Thomas, 1982)

  2. Periodic fracture of passive film at crack tip (Andresen and Ford, 1982-1988)

  3. Film-induced cleavage of base metal (Paskin et al., 1980-83)

Buck and Ranjan (1984) developed the CTOD model for SCC initiation

- Assumptions of the CTOD (crack-tip-opening displacement) model
  - Stress corrosion cracking (SCC) initiates at pits
  - Corrosion at base of pit obeys Butler-Volmer kinetics

    Active surface at base of pit

    Pit depth varies linearly with time
  - Displacement at mouth of pit (δ) sufficient to prevent blunting of base by corrosion

    Due to applied stress (s)

    Elastic and plastic contributions
  - Propagation rate of microcrack at base of pit (da_m/dt) proportional to displacement

The CTOD model predicts the <u>conditions</u> and <u>time</u> required for the initiation of SCC at a pit

- Criteria for initiation

$$\delta - (\delta_o + \delta_c) > 0 \quad \text{and} \quad (\sigma^2 - \sigma_o^2)\, a_p - (K_{ISCC})^2/\pi > 0$$

- Incubation time (t_{inc}) is the time required for initiation

$$t_{inc} = (1/\pi)[(K_{ISCC})^2/(\sigma^2 - \sigma_o^2)][\exp(-\beta FE/RT)/(V_M i_{corr}/zF)]$$

- mechanical stress - *- electrochemical corrosion -*

- Mechanical effects (residual stress) are taken into account by the first factor

- Environmental effects are taken into account by the second factor

Experiments supporting predictive models for initiation of SCC

- Threshold stress intensity factor for SCC (K_{ISCC})
  - Modified Wedge-Opening-Loading (WOL) fracture specimen (Novak and Rolfe, 1969)
- Effects of environment on incubation time (t_{inc})
  - Load specimen in screw-driven tensile machine (Buck and Ranjan, 1984)
  - Vary chemistry of environment, electrochemical polarization and temperature
  - Measure time required for reduction in stress at constant displacement
  - Monitor stress with load cell

The model developed by Andresen and Ford (1982-1988) involves film fracture at the crack tip

- The crack propagation rate is proportional to the charge density associated with repassivation and the crack tip strain rate

$$da/dt = [MQ_f/z\rho F][(d\varepsilon_{ct}/dt)/\varepsilon_f]$$

- The charge density can be calculated from the current transient immediately following film fracture

$$i = m\,t^{-n}$$

- Effects of environment and material chemistry on propagation rate can be represented by the single parameter (n)

$$da/dt = f(n)(d\varepsilon_{ct}/dt)^n$$

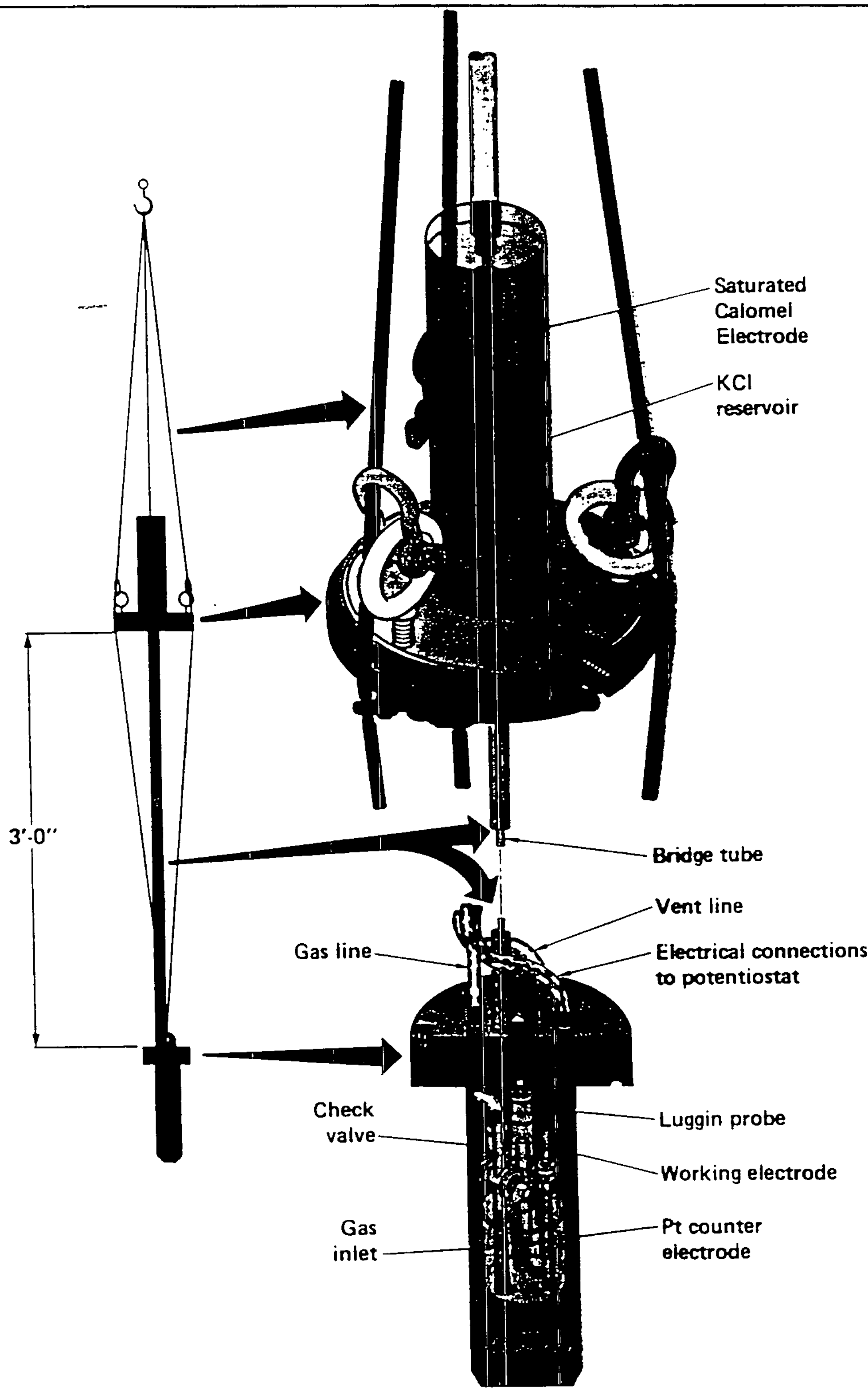
Andresen-Ford model (cont.)

- An empirical relationship between the crack tip strain rate and stress intensity has been established for the case of constant load

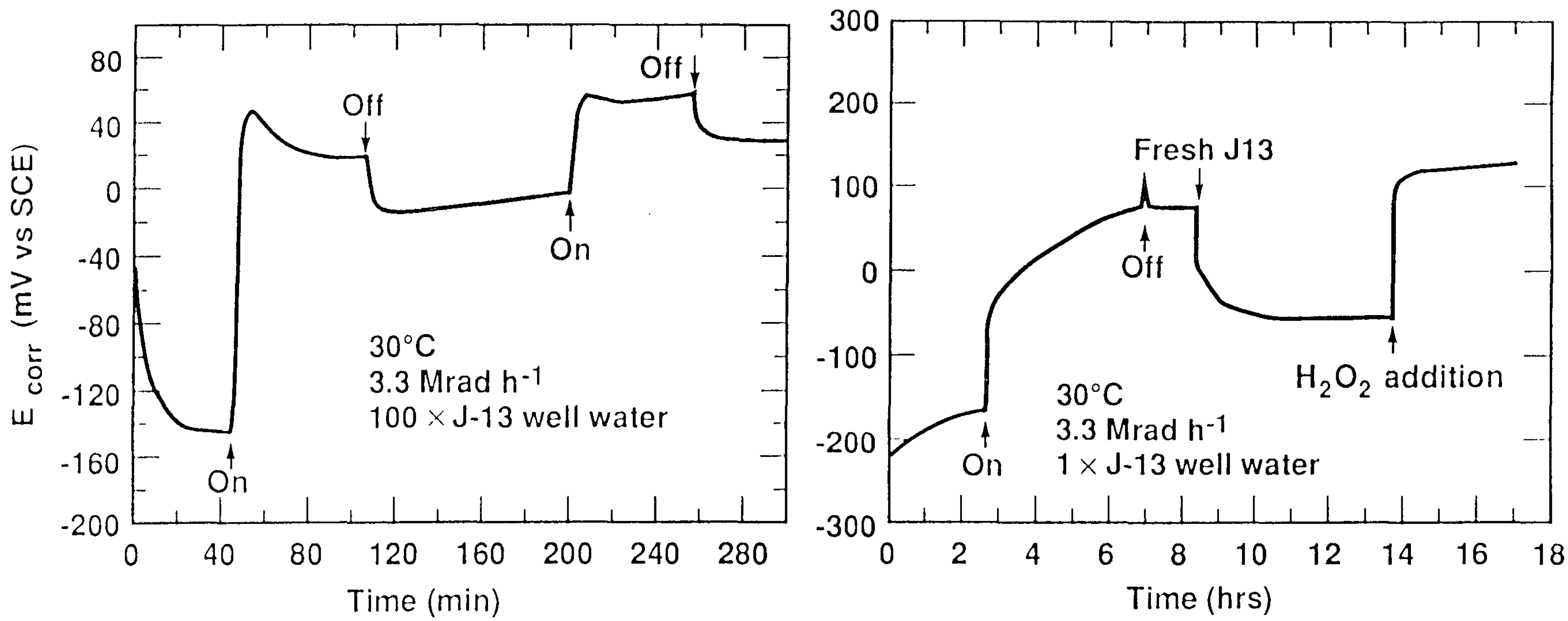
$$d\varepsilon_{ct}/dt = 6 \times 10^{-14} K^4$$

- This model has been used to successfully predict rates of crack propagation in Type 304 stainless steel used in boiling water reactors (BWR's)

Schematic of electrochemical apparatus for gamma irradiation studies

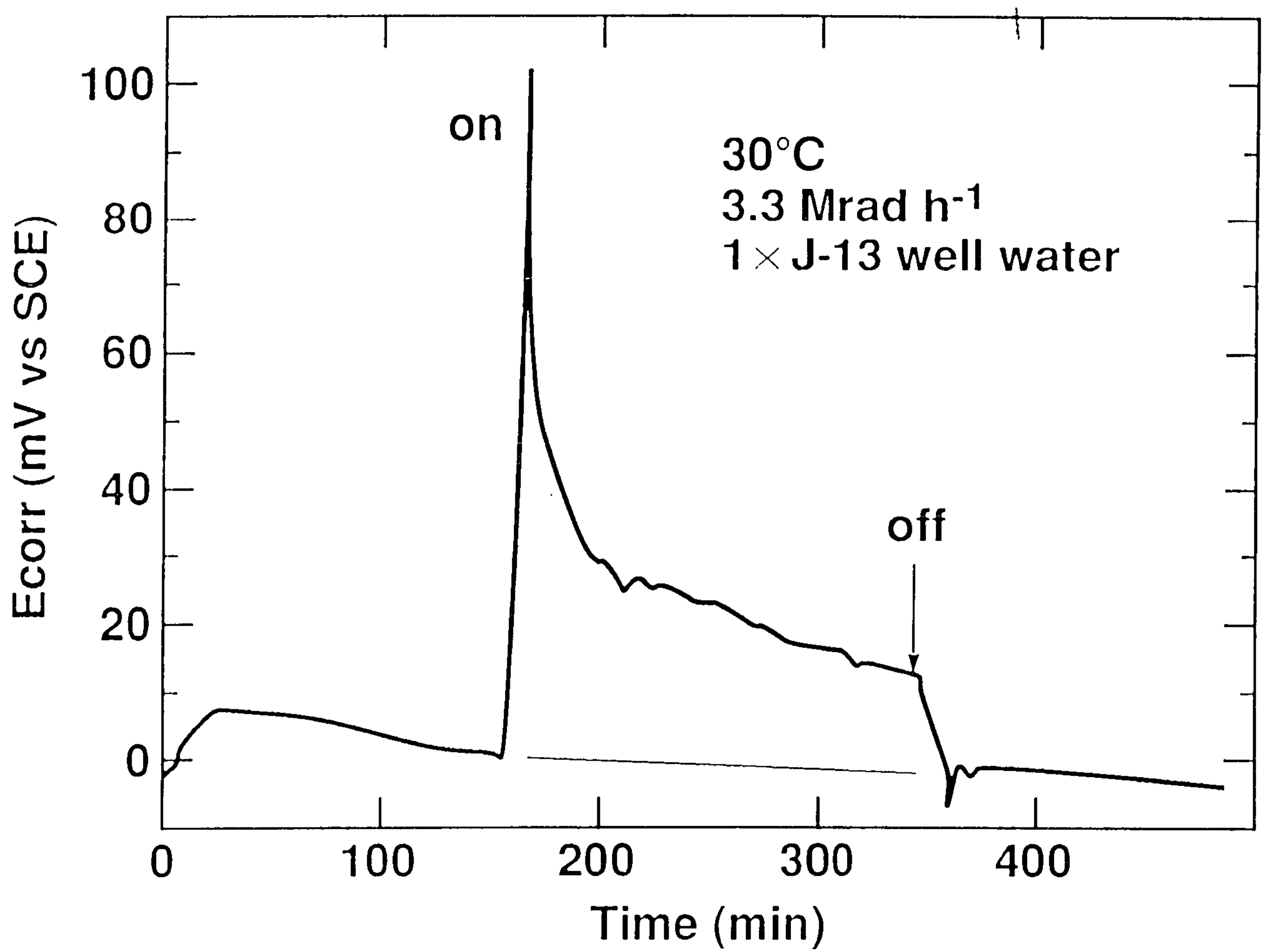


Effect of gamma irradiation on the corrosion potential of 316L in J-13 well water



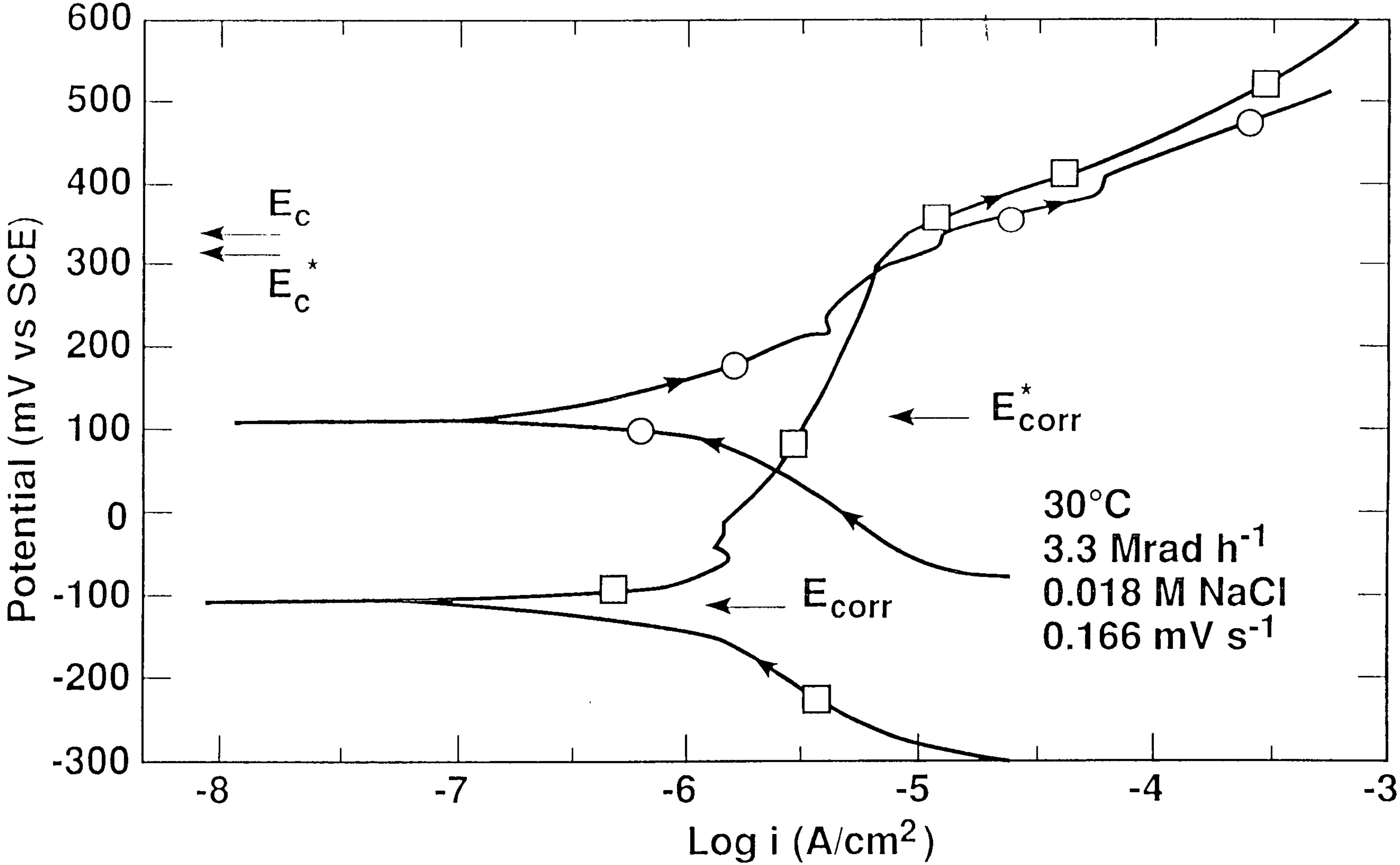
From Glass et al., Corrosion Science, Vol. 26, No. 8, 1986, pp. 577-590

Effect of gamma irradiation on corrosion potential of CDA 102



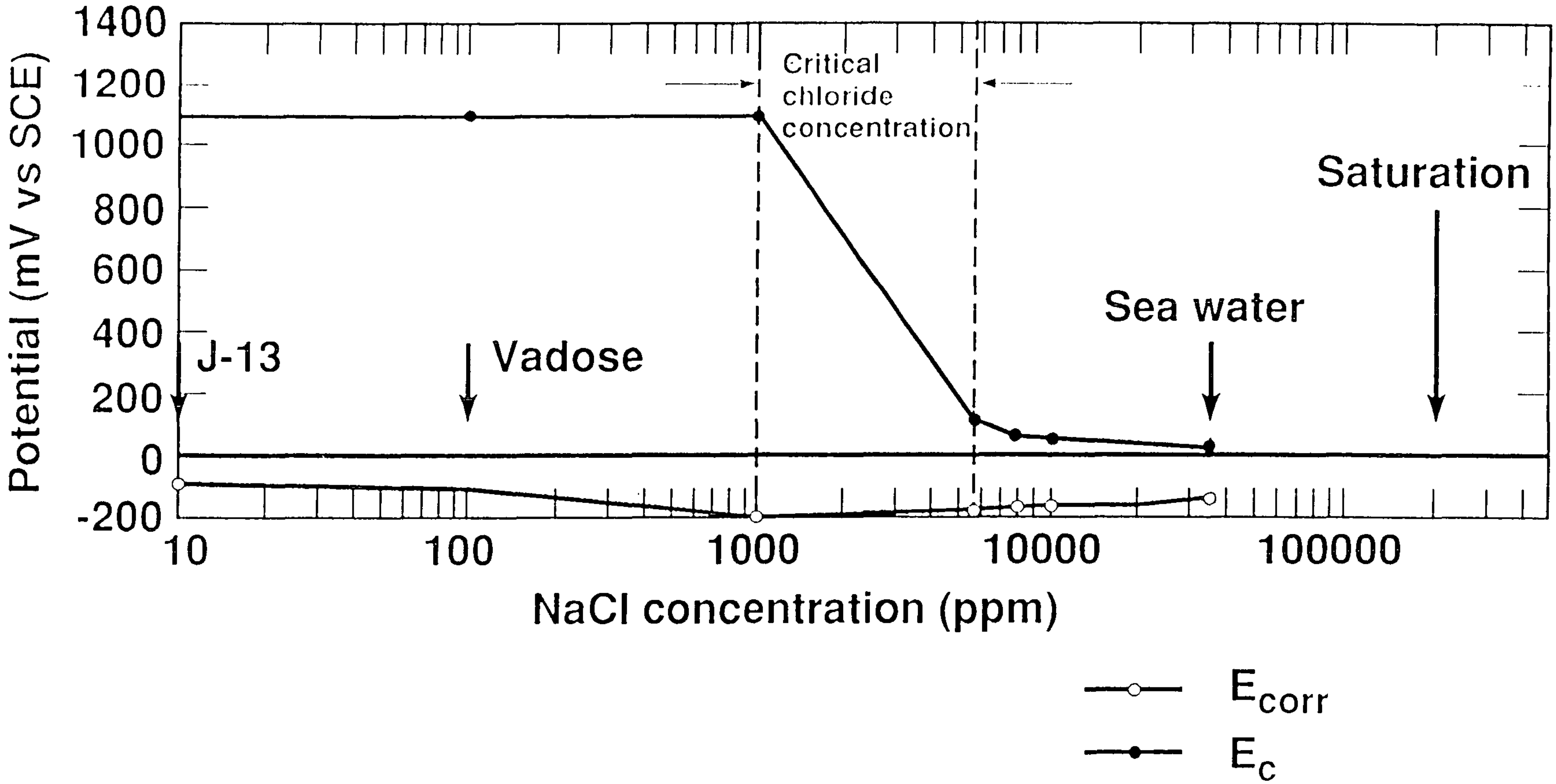
From Glass et al., Paper No. 258, Corrosion 86, NACE, Houston, Texas, March 17-21, 1986

Effect of gamma irradiation on the pitting potential of 316L in NaCl solution



From Glass et al., Corrosion Science, Vol. 26, No. 8, 1986, pp. 577-590

Effect of chloride on pitting potential of 316L determined by potentiodynamic polarization



ASTM G5 Procedure. Farmer, 1989

Implementation of QAP (quality assurance plan)

Sub-Activity Description	Identification Number of Plan	Planning Document	Status of Lab Work
Corrosion Modeling	E-20-16a	Approved	Planned
Linear Polarization	E-20-18a	Approved	In Progress
Long-Term Tests	E-20-18b	Approved	Planned
Measurement of K_I	E-20-18c	Approved	Planned
Measurement of K_{ISCC}	E-20-18d	Approved	Planned
SEM and STEM	E-20-18e	Approved	Planned
Radiation Effects	E-20-18f	Approved	In Progress
SCC in J-13 Water	E-20-18g	Approved	Planned
CERT Testing	E-20-18h	Approved	Planned

Summary

- Description of conditions outside one specific container
  - Predicted temperature profile
  - Chemical species formed by γ radiolysis and their effects on container materials
  - Role of ions found in ground water on localized attack of container materials
- Review of models and testing for vapor-phase and aqueous corrosion
  - Uniform oxidation
  - Pit initiation and propagation (E_{corr}, E_c, τ)
  - Crack initiation and propagation (t_{inc}, K_{ISCC}, da/dt)