



U.S. Department of Energy
Office of Civilian Radioactive Waste Management

Waste Package Corrosion Process Components

Presented to:

Nuclear Waste Technical Review Board

Presented by:

Gregory E. Gdowski

Lawrence Livermore National Laboratory

Bechtel SAIC Company, LLC

June 20-21, 2001

Las Vegas, NV

**YUCCA
MOUNTAIN
PROJECT**

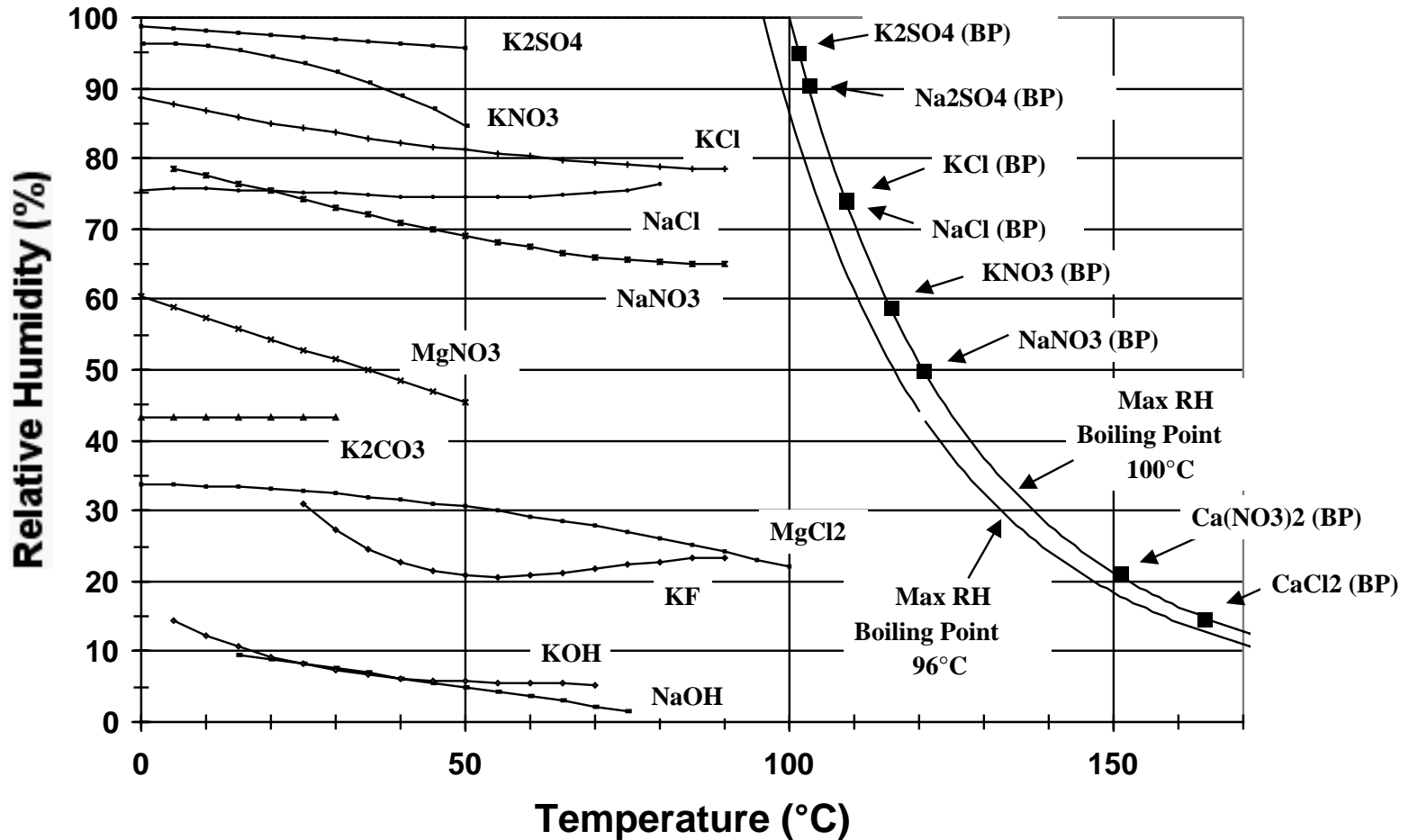
Outline

- **Environments on Waste Package**
- **Phase Stability**
- **General Corrosion**
- **Passive Film Stability**
- **Localized Corrosion**
- **Summary**

Environment on Waste Package

- **Range of water chemistries affect salt development**
 - **Previously [Total System Performance Assessment-Site Recommendation (TSPA-SR)] considered only carbonate base brines**
 - **Now consider [Supplemental Science and Performance Analyses (SSPA)] near-neutral pH brines, and hence possibility of soluble calcium (Ca) and magnesium (Mg)**
- **Considered potential effect of soluble lead (Pb) in natural systems (SSPA)**
- **Also considered other sources of soluble salts (SSPA)**
 - **Entrained matter in ventilation air**
 - **Rock dust**

Deliquescence Points for Pure Salts



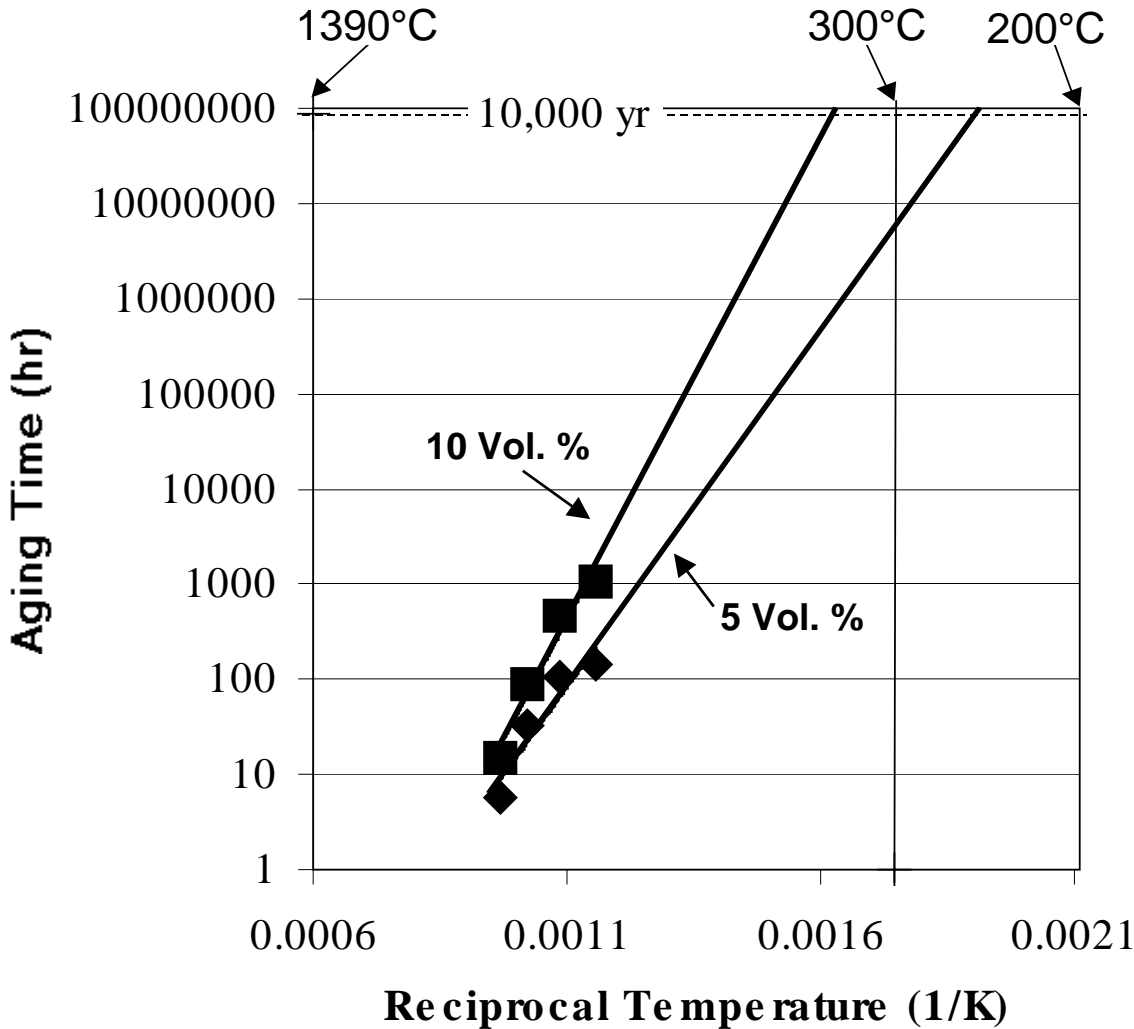
L. Greenspan, *J. of Research of the National Bureau of Standards* 81A (1977) 89-96

F.C. Kracek, *International Critical Tables of Numerical Data, Physics, Chemistry and Technology*, Volume 3, pp. 351-385, 1928.

Alloy 22 Phase Stability in Supplemental Science and Performance Analyses

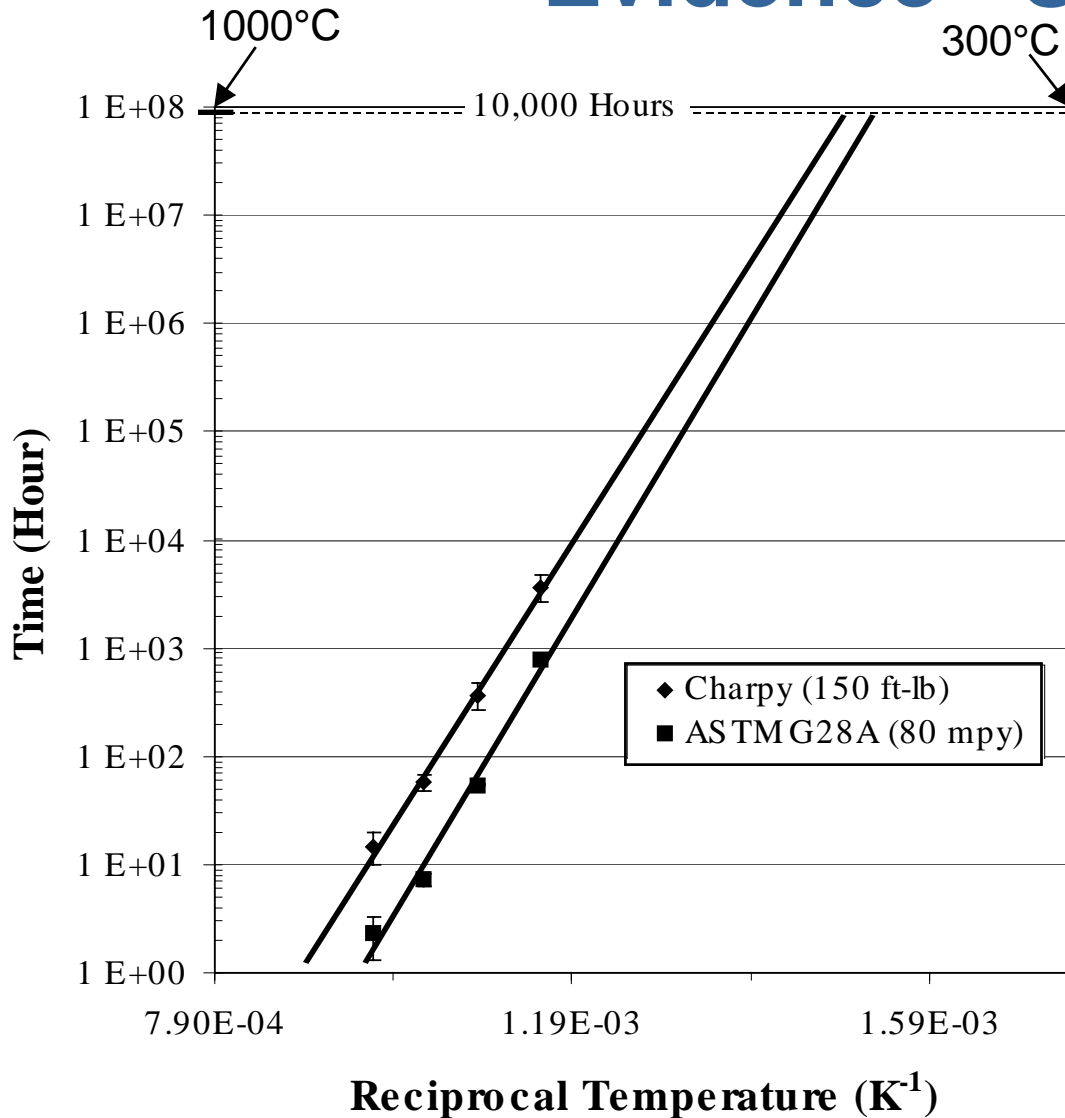
- **New data increases confidence in TSPA-SR**
 - Theoretical modeling of base metal does not show phase instabilities under repository conditions
 - Long-range ordering (LRO) not expected below 300°C
 - Preliminary weld data do not indicate instabilities below approximately 200°C (see Slide 6)
- **Alternative lines of evidence**
 - Aging time to cause a measured degradation in mechanical and corrosion properties does not appear likely at temperatures below 300°C (see Slide 7)
 - Two-phase metastable structures in Josephinite stable for more than 100 million years

Phase Stability - New Data for Phase Precipitation in Alloy 22 Welds - SSPA



Volume fraction data for tetrahedrally-close-packed (TCP) precipitates from half-inch thick, Alloy 22, double-V, Gas-Tungsten-Arc Welds (GTAW). Extrapolation of these preliminary data indicate that further nucleation and growth of the phases that form during welding of Alloy 22 is possible in 10,000 years at temperatures between 200 and 300°C and higher.

Phase Stability - Alternative Line of Evidence - SSPA



Uncertainty in data for direct examination of TCP phase precipitation in Alloy 22 led to bounding argument. Degradation of properties caused by precipitation can be measured with greater precision. Using the aging time to cause a measured degradation in the mechanical and corrosion properties, significant TCP phase precipitation does not appear likely at temperatures below 300°C.

Alloy 22 General Corrosion Model - TSPA-SR

- **Dry oxidation [below critical relative humidity (RH)] negligible**
- **Aqueous-phase corrosion requires dripping water**
- **Humid-air corrosion (above critical RH) same rate as aqueous-phase corrosion**
- **Deliquescence point of sodium nitrate (NaNO_3) defined critical RH**
- **Passive film assumed stable**

Alloy 22 General Corrosion Model - TSPA-SR

(Continued)

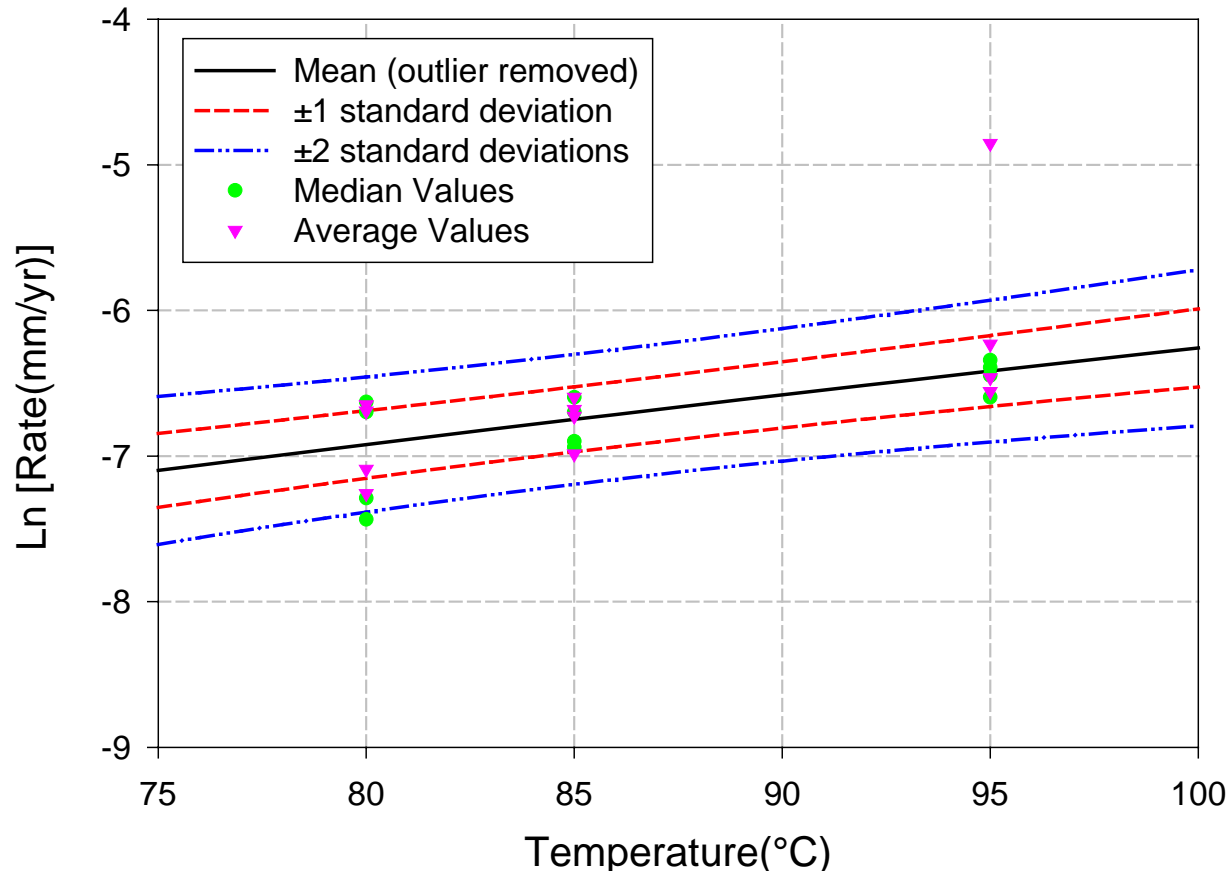
- **Models based on weight loss data for Alloy 22 (2-year data) and for Titanium Grade 7 (1-year data) from Long-Term Corrosion Testing Facility**
 - Rate independent of temperature and water chemistry
 - Sampled the fraction of uncertainty and variability of the total variance
 - Enhancement factors for aging and microbiologically induced corrosion (MIC)

Alloy 22 General Corrosion Model Improvement for SSPA

- **Temperature dependent general corrosion rate**

- **Added a temperature dependency term to the general corrosion rate distribution that was based on weight loss measurements**
 - ◆ **Assumed that the rate distribution is representative for an exposure temperature of 60°C**
- **Assumed an Arrhenius relationship; $R = A \exp[-E/RT]$**
- **Temperature dependence term was derived from the passive current density (potentiodynamic tests) conducted at 80 to 95°C**
 - ◆ **$E = 36 \text{ kJ/mol}$**
- **Similar temperature dependence for passive dissolution rate was derived from potentiostatic tests conducted at 25 to 80°C**
 - ◆ **$E = 32 \text{ kJ/mol}$**
- **Assumed all variance from weight loss data is due to uncertainty**

Temperature Dependency Term from Potentiostatically Measured Passive Current Density of Alloy 22 - SSPA

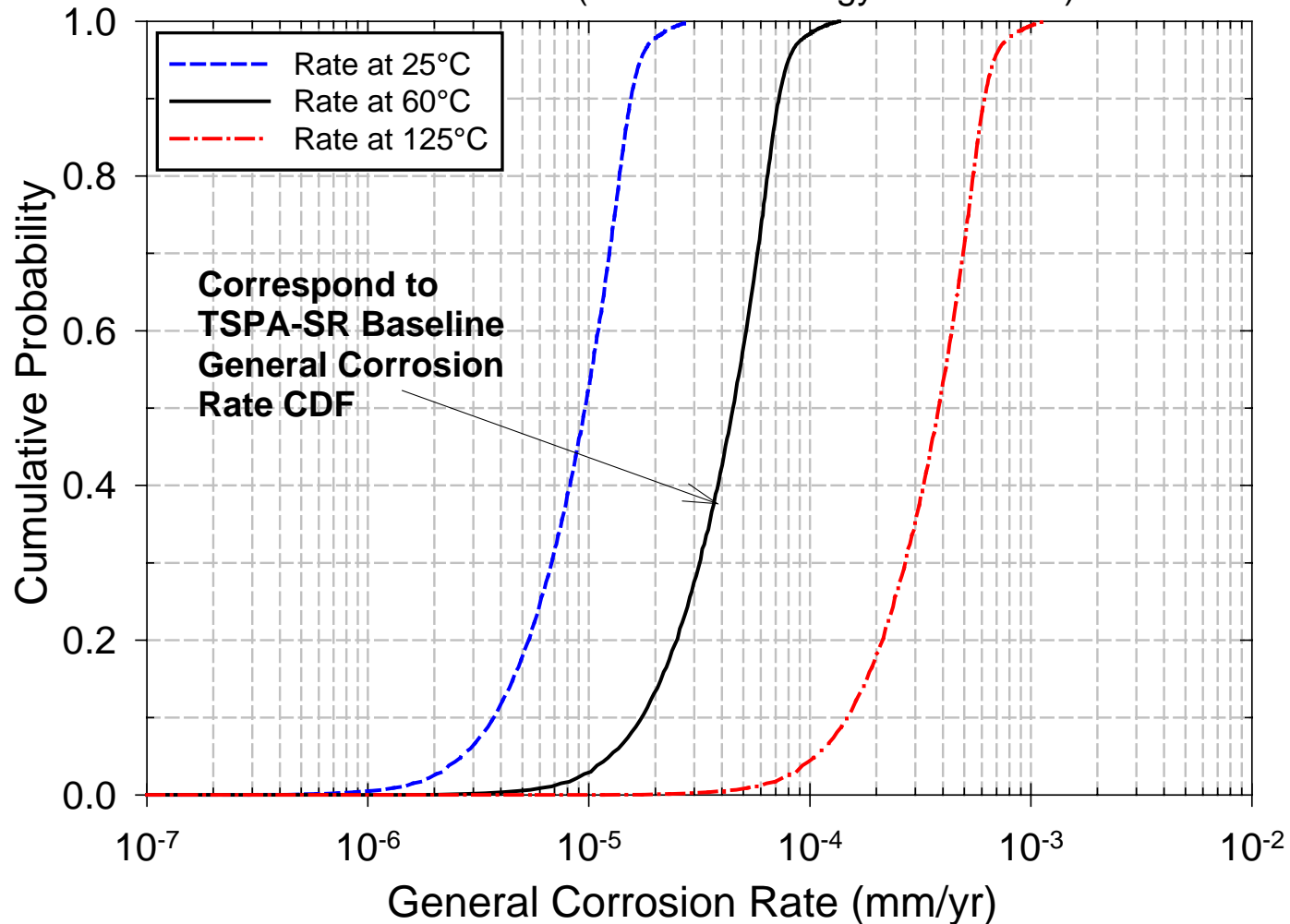


Activation energy calculated from these data = 36 kJ/mole

Project data from University of Virginia obtained in 5M LiCl buffered with 10:1 or 100:1 chloride to sulfate anion ratio, pH 2.75-7.75

Waste Package Outer Barrier General Corrosion Rate CDFs vs. Temperature

Waste Package Outer Barrier (Alloy 22) General Corrosion Rate
Arrhenius Relation (Activation Energy 36 kJ/mole)



Alloy 22 Passive Film Stability - SSPA

- **Generalized Corrosion Model**
 - Based on Point Defect Model and Mixed Potential Model
 - Provide a mechanistic basis for extrapolation of short-term corrosion data
- **Localized corrosion**
 - The current model will be extended to evaluate breakdown of the passive film
- **As a function of growth conditions, new studies aimed at**
 - Quantifying growth rate of passive film*
 - Characterizing passive film structure*
 - Evaluating any potential breakdown mechanisms*

***These will be further discussed by G. Gordon**

Generalized Corrosion Model - SSPA

● Point Defect Model

- Extensively developed for describing growth and breakdown of passive films on numerous metal and alloys
- Tested against experimental data and found to hold for a wide variety of systems
- Provides analytic relationships between anodic partial current and barrier layer thickness and potential
 - ◆ Requires $i_{\text{corr}}(E)$, which corresponds to the passive current density
- Requires identification of the principal crystallographic defect in the barrier oxide layer

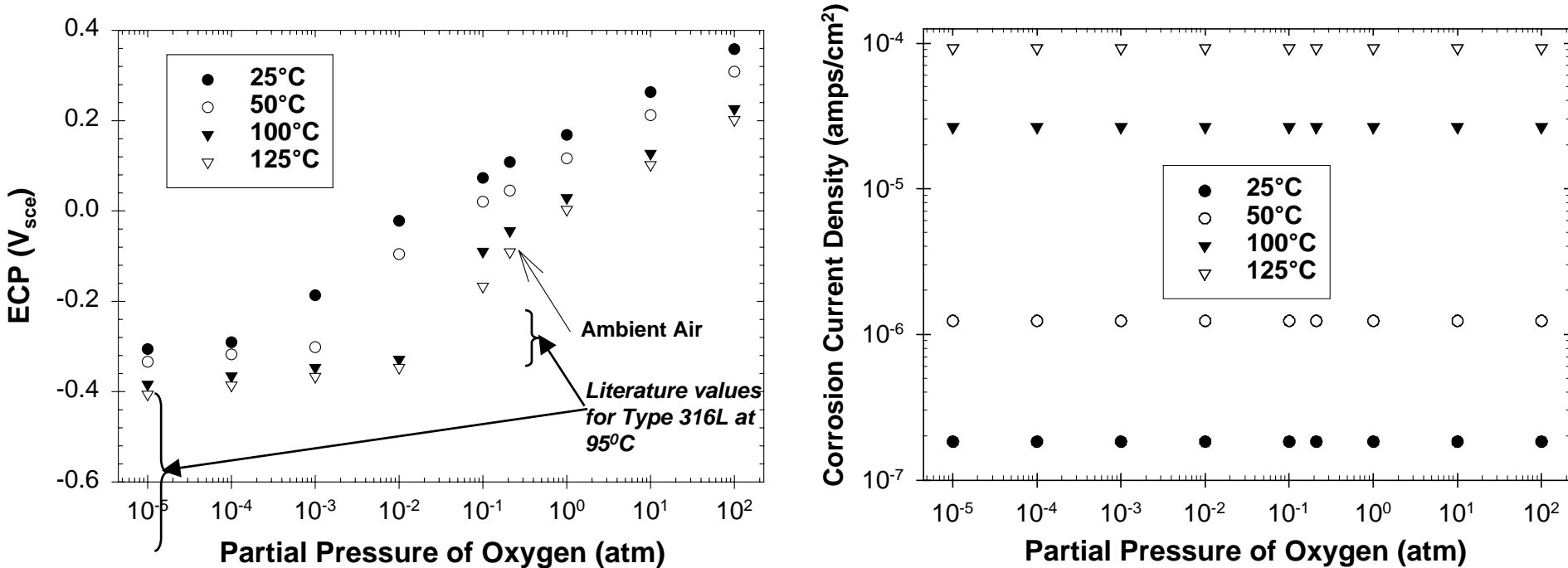
Generalized Corrosion Model - SSPA

(Continued)

- **Mixed Potential Model**
 - Based on the physical condition that charge conservation must be obeyed in the system
 - Corrosion potential, E_{corr}
 - Corrosion current density, $i_{\text{corr}}(E)$

Passive Film Stability Modeling Simulations - SSPA

(Continued)



NOTE: The following parameter values were assumed: Stainless Steel, pH= 3, saturated NaCl solution, electrolyte film thickness = 0.01 cm.

• Characterization of redox couples in solutions

- Introduced by the environment
- Introduced by degradation of engineered barrier system components

• Experimental studies to evaluate the effect of these redox couples

Localized Corrosion Consideration - SSPA

- **In TSPA-SR, localized corrosion threshold based on corrosion potential and threshold potential as a function of contacting solution pH**
 - **Threshold potentials not exceeded, and no localized corrosion initiated; $E(\text{corr}) < E(\text{crit})$**
- **Mechanistic modeling of localized corrosion**
- **Corrosion and threshold potential dependence on solution composition and temperature**
- **Determine Alloy 22 susceptibility**
 - **Eh-pH diagrams**

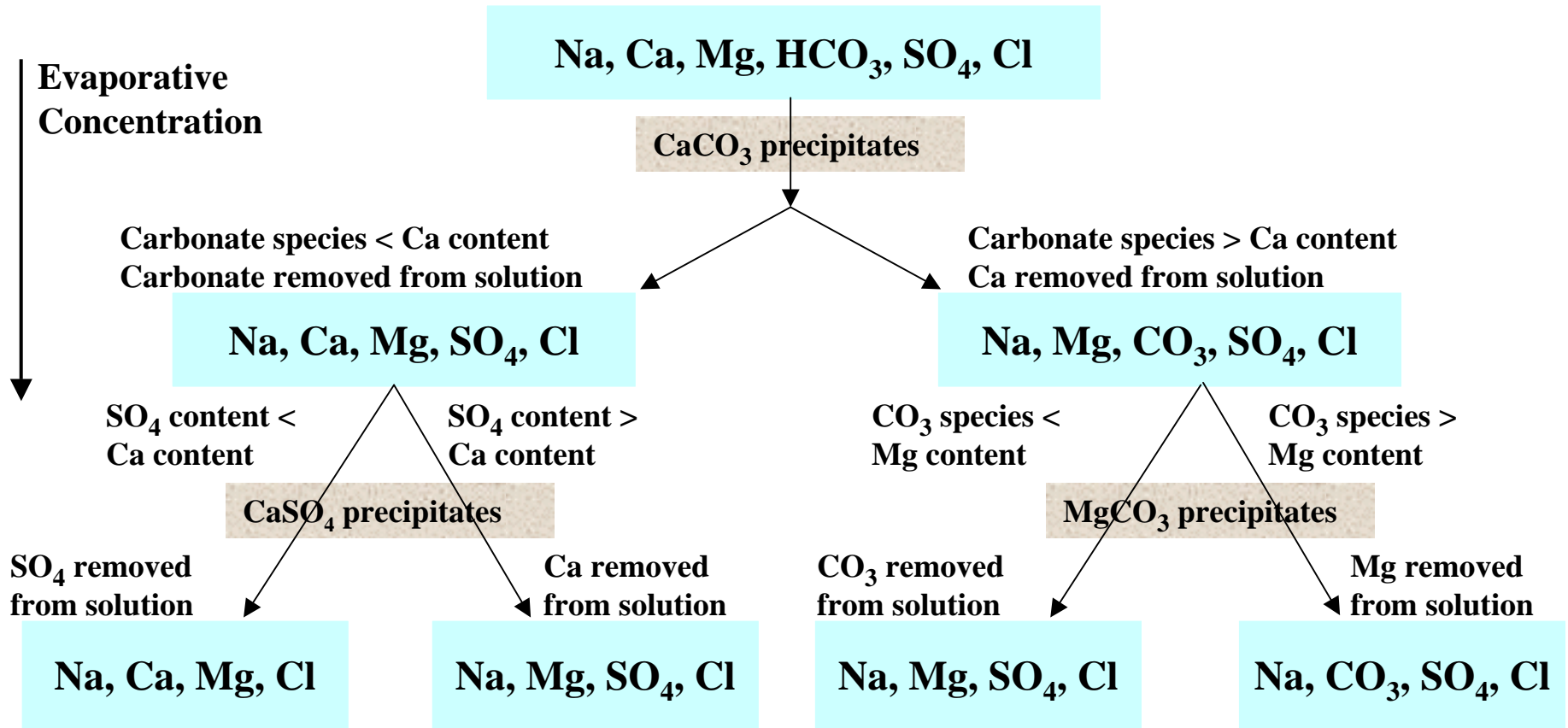
Summary

	TSPA-SR	SSPA
Bounding Waters	High pH sodium carbonate brine	Include near-neutral pH brine (Mg, Ca containing)
Phase Instability	Base metal Long-range ordering not expected <260°C Welds not considered	Theoretical modeling indicates not expected Not expected <300°C Not expected <200°C
General Corrosion	No temperature dependence	Temperature dependence for general corrosion incorporated
Passive Film Stability	Assumed stable	Mechanistic modeling Characterization and growth kinetic studies
Localized corrosion	Threshold potential not exceeded	Extend studies to higher temperature aqueous solutions

Backup

Brine Evolution from Dilute Natural Waters

J.I. Drever, *The Geochemistry of Natural Waters*, Prentice-Hall, Inc., 1997.



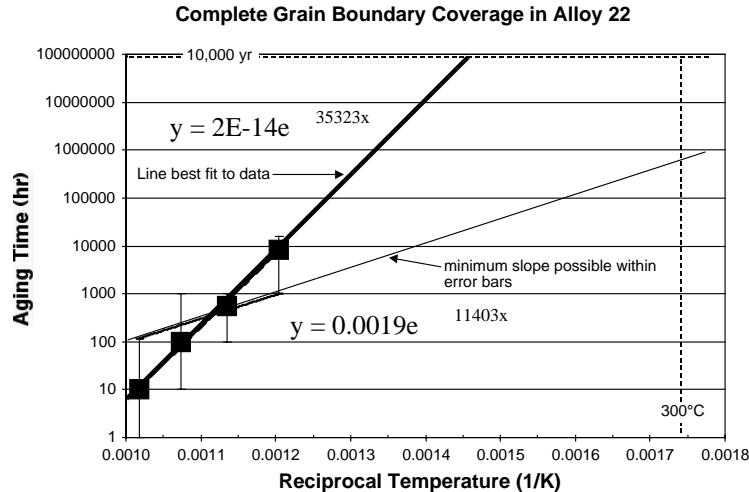
Death Valley, CA (Na)*
 Bristol Dry Lake, CA (Na, Ca)
 Cadiz Lake, CA (Na, Ca)
 Carson Sink, NV (Na)

Saline Valley, CA (Na)*
 Danby Lake, CA (Na)
 Salton Sea, CA (Na)

Surprise Valley, CA
 Mono Lake, CA
 Owens Lake, CA
 Soda Lake, CA
 Pyramid Lake, NV
 Winnemucca Lake, NV

* dominant cation(s) in brine

Alloy 22 Phase Stability - TSPA-SR

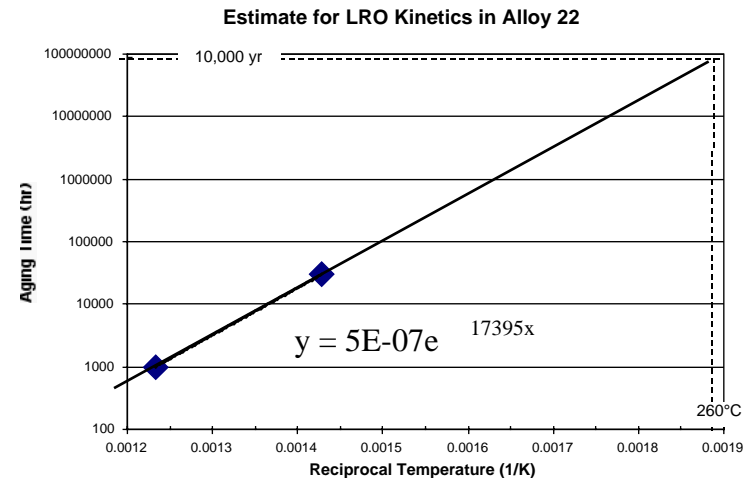


TCP Phase Precipitation

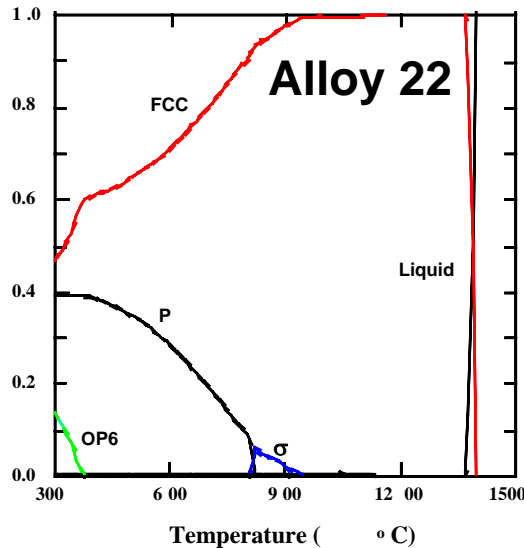
Available data do not indicate that TCP phases will form under repository conditions. A bounding argument was created to account for uncertainties in the data. A 2.5x corrosion enhancement factor was used to represent this bounding structure.

Long-Range Ordering

Long-range ordering is not expected below approximately 260°C.

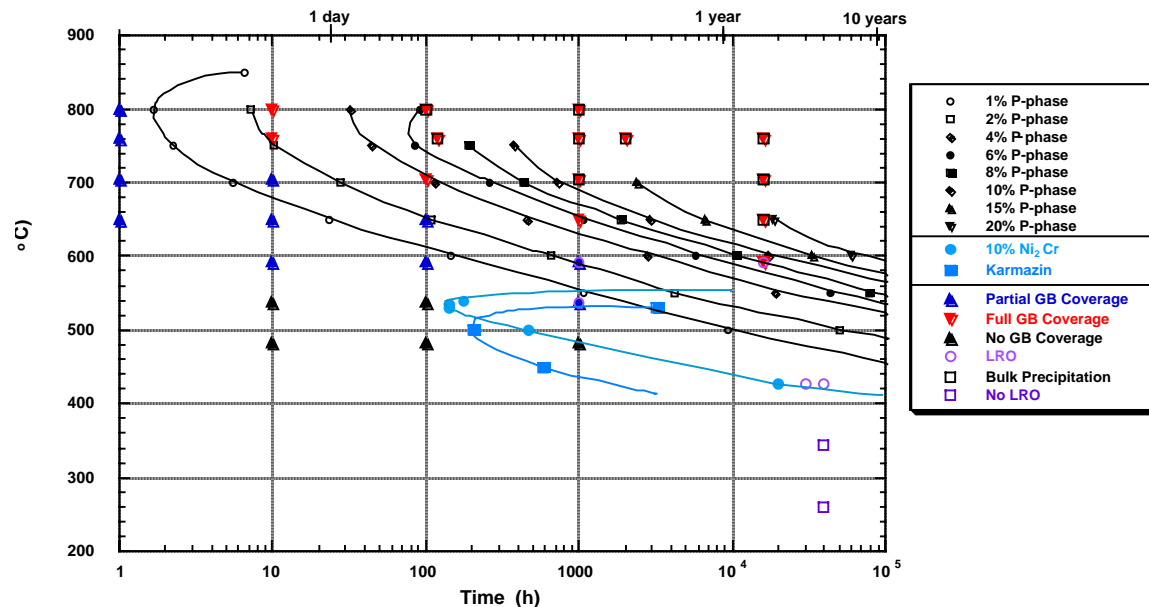


Alloy 22 Phase Stability- New Data - SSPA

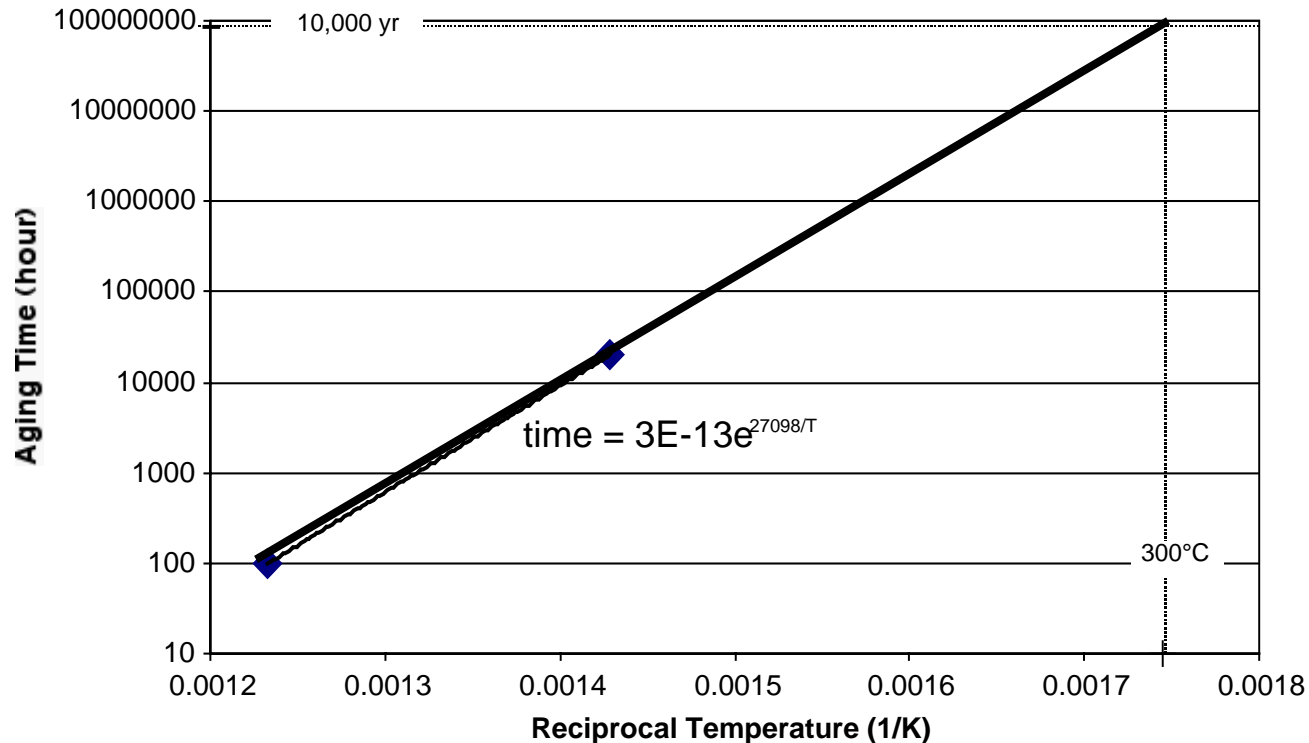


At low temperatures, three phases are predicted to be thermodynamically stable (μ and P phase are similar and are not treated separately here): OP6 (which refers to the LRO phase), P and the FCC solid solution phase. The s phase is only stable at higher temperatures.

Kinetic modeling of TCP phase precipitation and LRO agree reasonably well with available data. Extrapolation of these data do not indicate phase instabilities will occur under repository conditions.



New Experimental Data for Long Range Ordering - SSPA



The critical temperature for LRO during an isothermal anneal of Alloy 22 is greater than that assumed in from preliminary data in TSPA-SR.

Temperature Dependence of General Corrosion - SSPA

Median General Corrosion Rate vs. Temperature
Arrhenius Relation (Activation Energy 36 kJ/mole)

