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ANALYSIS OF CORROSION DATA FOR CARBON STEELS IN SIMULATED SALT REPOSITORY BRINES AND ACID CHLORIDE SOLUTIONS AT HIGH TEMPERATURES*

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SUMMARY

Carbon steel is currently the leading candidate material for fabrication of a container for isolation of high level nuclear waste in a salt repository. Since brine entrapped in the bedded salt can migrate to the container by several transport processes, corrosion is an important consideration in the long-term performance of the waste package. A detailed literature search was performed to compile relevant corrosion data for carbon steels in anoxic acid chloride solutions, and simulated salt repository brines at temperatures between ~20 and 400°C. The hydrolysis of Mg^{2+} ions in simulated repository brines containing high magnesium concentrations causes acidification at temperatures above 25°C, which, in turn, influences the protective nature of the magnetite corrosion product layer on carbon steel. The corrosion data for the steels were analyzed, and an analytical model for general corrosion was developed to calculate the amount of penetration (i.e., wall thinning) as a function of time, temperature, and the pressure of corrosion product hydrogen that can build up during exposure in a closed system (e.g., a sealed capsule). Both the temperature and pressure dependence of the corrosion rate of steels in anoxic acid chloride solutions indicate that the rate-controlling partial reaction is the cathodic reduction of water to form hydrogen. Variations in the composition and microstructure of the steels or the concentration of the ionic species in the chloride solutions (provided that they do not change the pH significantly) do not appear to strongly influence the corrosion rate.

The amount of corrosive penetration of a carbon steel container and the buildup of hydrogen pressure were calculated for three waste package configurations for emplacement time periods up to 1000 years. For an unlimited quantity of brine, the results indicated that only the waste package with the lowest temperature-time profile satisfied the suggested corrosion limit of ~25 mm after a 1000 years; however, the hydrogen pressure exceeded the lithostatic pressure of the repository environment within this time period. Since it is unlikely that the hydrogen pressure will exceed the lithostatic pressure within a repository, the total amount of corrosion will be greater than predicted by this analysis.

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*Work supported by the U. S. Department of Energy, Salt Repository Project, under Contract W-31-109-Eng-28.

The expected corrosion performance of selected waste package configurations on the basis of our corrosion data base and analysis was compared with similar results from a recent BMI-ONWI[†] study. For conditions in which the amount of corrosion is not limited by the quantity of available brine, the expected corrosion after 1000 years predicted by the two models differed significantly. The lower penetration obtained in the BMI-ONWI study resulted from the relatively low corrosion rates employed during the first 100 years of the emplacement period when the container interface temperatures are high.

Models for thermally induced brine migration to the container indicate that the relatively small quantity of available brine would limit the amount of corrosion penetration. However, experimentally observed rates of non-thermal brine migration, if they persist over long time periods, would be sufficient to support unacceptably high corrosion rates of carbon steels on the basis of our review and analysis of corrosion data for these materials in anoxic acid chloride solutions. The use of a corrosion-resistant cladding on carbon steel and/or the development of methods to immobilize the brine in the vicinity of the container would be required to achieve adequate corrosion performance of a carbon steel waste container in a salt repository.

[†] Battelle Memorial Institute, Office of Nuclear Waste Isolation.

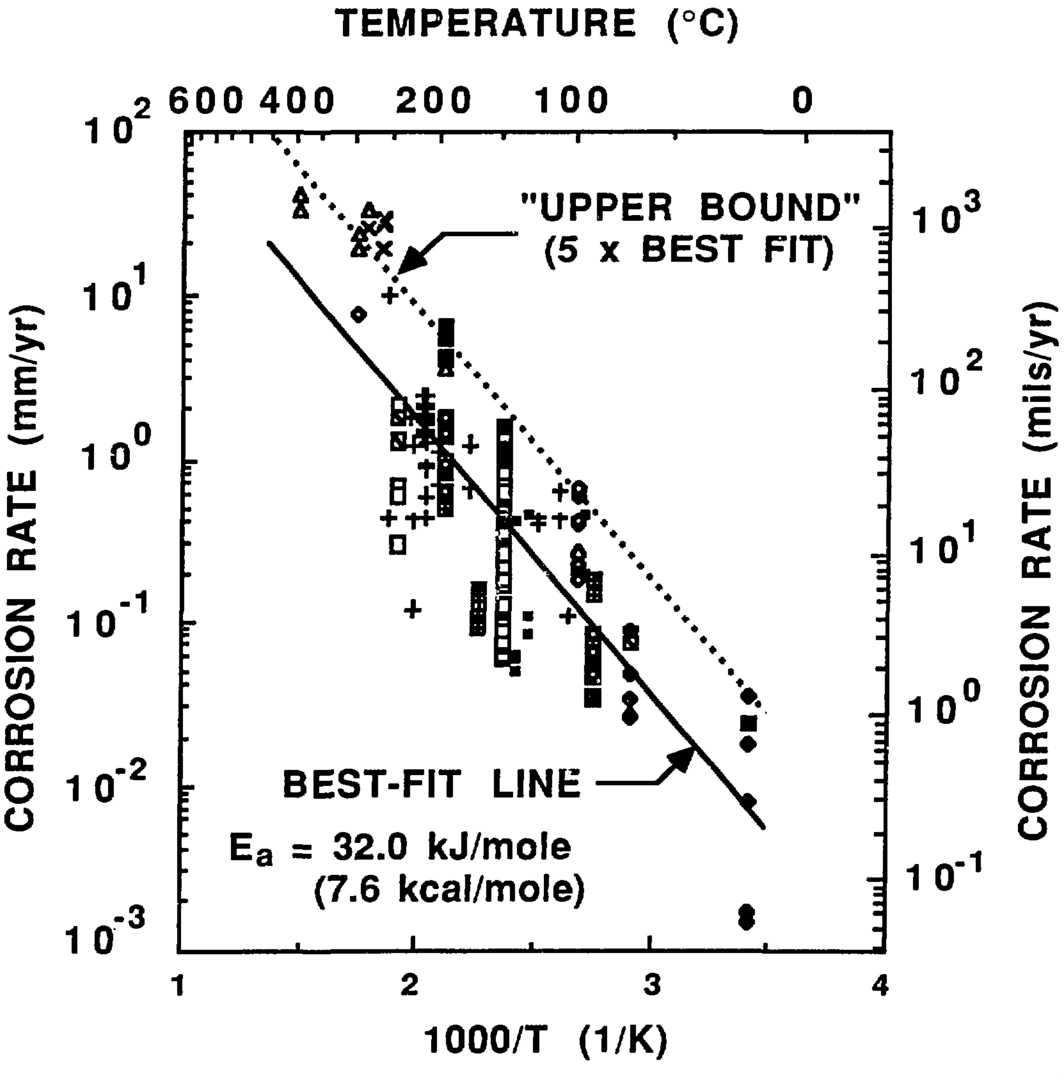
ANALYSIS OF CORROSION DATA FOR CARBON STEELS IN SIMULATED SALT REPOSITORY BRINES AND ACID CHLORIDE SOLUTIONS AT HIGH TEMPERATURES

- <u>METHODOLOGY</u>
  - COMPILED LITERATURE DATA ON CORROSION OF LOW-CARBON STEELS IN BRINES, CONCENTRATED SEAWATER, AND ACID CHLORIDE SOLUTIONS AT 20 TO 400°C.
  - DETERMINED THE TEMPERATURE DEPENDENCE OF THE CORROSION RATES:
    - ACIDIC SOLUTIONS (OXIC AND ANOXIC)
    - NEAR-NEUTRAL AND BASIC SOLUTIONS (ANOXIC)
  - DEDUCED THE RATE CONTROLLING PARTIAL PROCESS FROM THE TEMPERATURE AND HYDROGEN PRESSURE DEPENDENCES OF THE CORROSION RATES.
  - DERIVED AN EQUATION FOR CORROSIVE PENETRATION IN ANOXIC ACID CHLORIDE SOLUTIONS AS A FUNCTION OF TIME, TEMPERATURE, HYDROGEN PRESSURE BUILDUP, AND THE RATIO OF CONTAINER AREA TO NEAR-FIELD CONTAINER VOLUME.
  - COMPARED CALCULATED CORROSION PENETRATIONS WITH DATA FROM AUTOCLAVE TESTS IN SIMULATED SALT REPOSITORY BRINES.

ANALYSIS OF CORROSION DATA FOR CARBON STEELS IN SIMULATED SALT REPOSITORY BRINES AND ACID CHLORIDE SOLUTIONS AT HIGH TEMPERATURES

- APPLICATION OF MODEL TO WASTE CONTAINERS
  - COMPUTED CORROSION PENETRATIONS AND HYDROGEN PRESSURE BUILDUP FOR SEVERAL WASTE-PACKAGE CONFIGURATIONS FOR TIMES OUT TO 1000 YEARS AND UNLIMITED BRINE AVAILABILITY.
  - COMPARED BRINE CONSUMPTION RATES DURING CARBON-STEEL CORROSION WITH THERMALLY DRIVEN BRINE SUPPLY RATES TO THE WASTE PACKAGE.

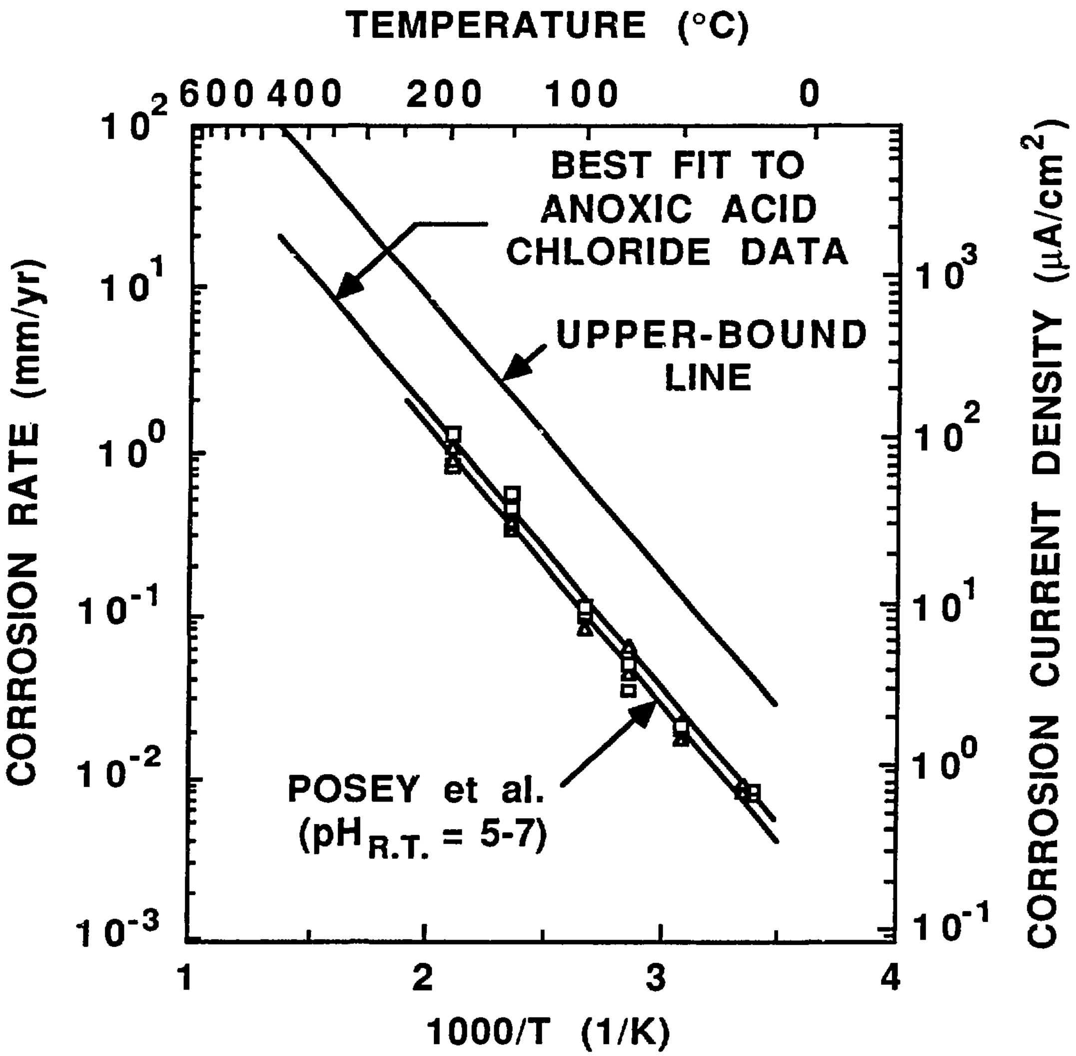
CORROSION RATE OF CARBON STEELS IN ANOXIC ACID CHLORIDE SOLUTIONS AS A FUNCTION OF TEMPERATURE



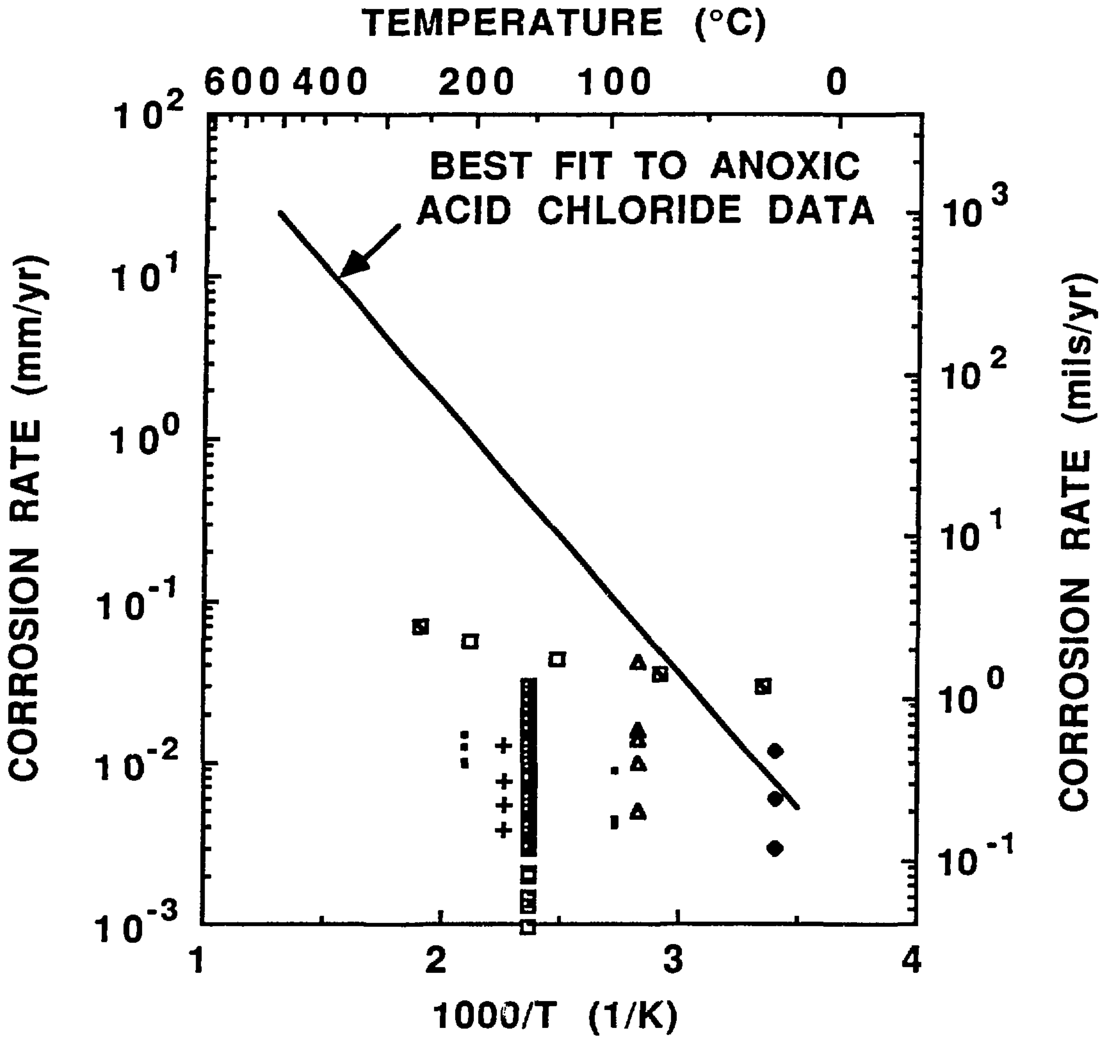
KEY TO DATA ON CORROSION OF CARBON STEELS IN ANOXIC ACID CHLORIDE SOLUTIONS

Symbol/Solution		Author
▪	PBB3 Brine	Westerman et al.
□	PBB1/PBB3	Westerman et al.
◘	Surrogate salt/PBB3	Westerman et al.
×	10x or Acid Seawater	Vaia et al. Wootten et al.
△	$NiCl_2$, $FeCl_2$, or HCl	Vaia et al. Potter and Mann
■	Q and Z Brines	Smailos et al. Mirschinka and Odoj
+	Salton Sea Geothermal Brines	Quong and Owen McCright et al. Carter and McCawley DeBerry et al.
▪	East Mesa and Krafla Geothermal Brines	Smith and Ellis McCawley et al. Shannon
■	Brine A	Braithwaite and Molecke Westerman
◆	$CaCl_2$ Solution	Korzh et al.
▫	Acid NaCl Solution	Shannon
◇	$MgCl_2$ or $NaCl/MgCl_2$ Solution	Pathania and McVey Butler and Beynon

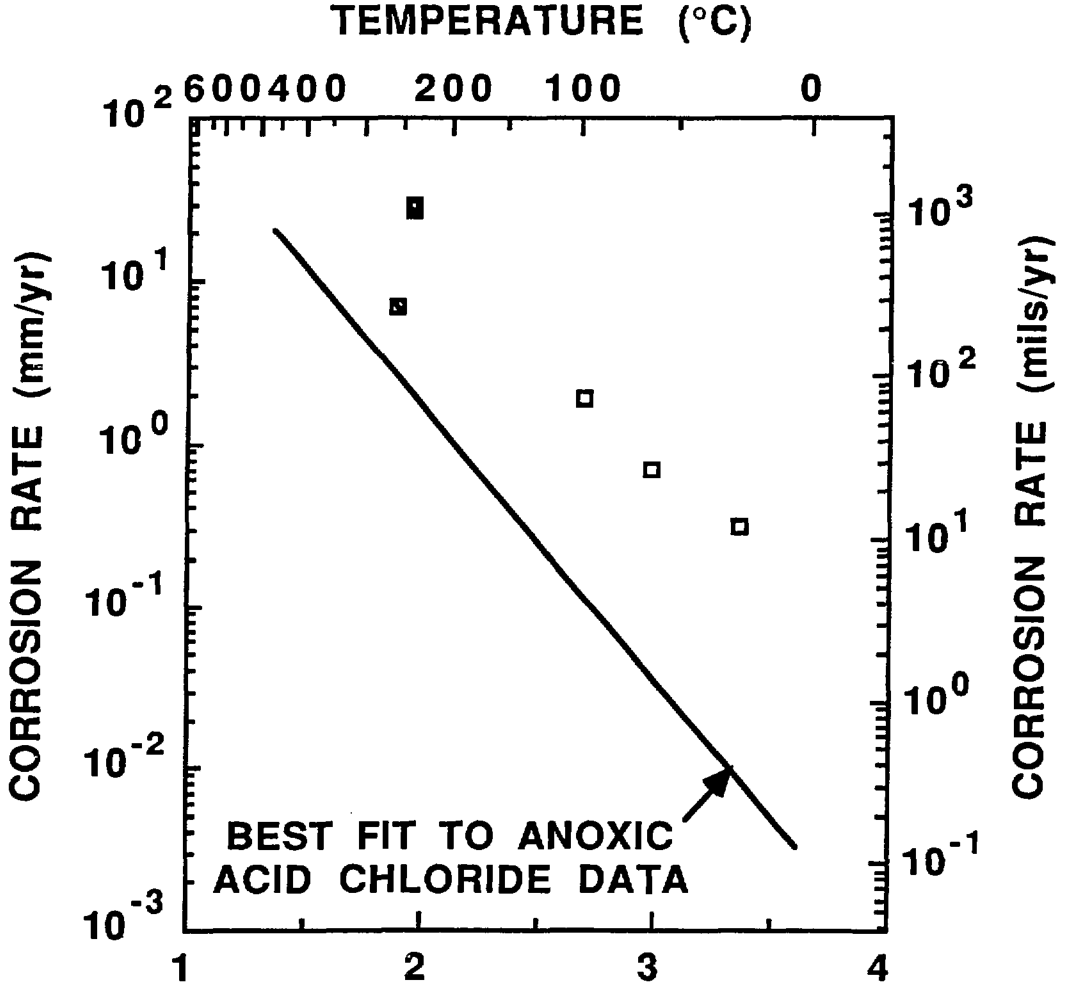
COMPARISON OF BEST FIT TO ANOXIC ACID CHLORIDE CORROSION DATA FOR CARBON STEELS TO ELECTROCHEMICAL DATA OF POSEY et al. (ORNL/TM-6308)



CORROSION RATE OF CARBON STEELS IN OXIC AND ANOXIC NEUTRAL AND BASIC CHLORIDE SOLUTIONS AS A FUNCTION OF TEMPERATURE



CORROSION RATE OF CARBON STEELS IN OXIC ACID CHLORIDE SOLUTIONS AS A FUNCTION OF TEMPERATURE



ELECTRODE PROCESSES

ANODIC DISSOLUTION

$$Fe \longrightarrow Fe^{2+} + 2\,e^-$$

$$K_{eq} = [\,e^-\,]^2\,[\,Fe^{2+}]$$

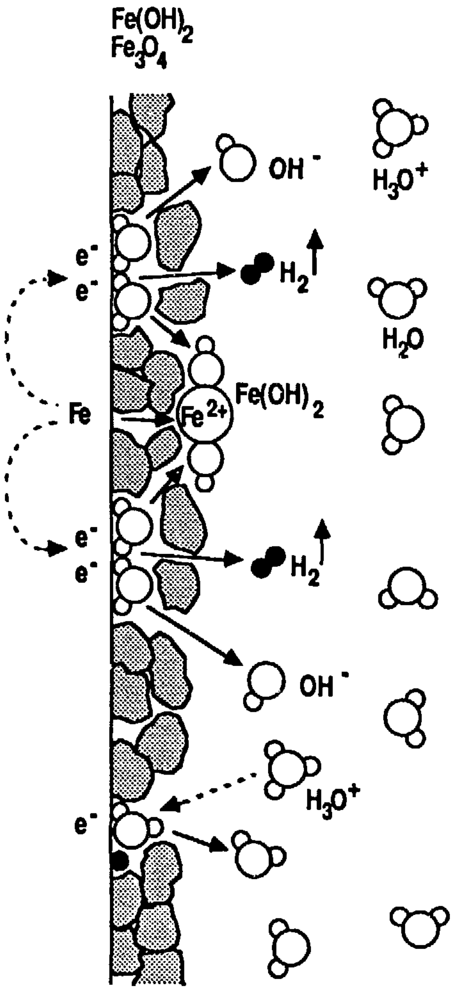
$$\text{Corr. rate} = \frac{M_{Fe}\;i_a}{Z\,\rho\,F}$$

$$\approx \frac{J_{Fe}}{\rho} = -\,\frac{D\,[\,Fe^{2+}\,]}{\rho\;\Delta x}$$

$$= -\,\frac{D\;K_{eq}}{\rho\;\Delta x\,[\,e^-\,]^2}$$

$$\text{i.e., Corr. rate} \propto \frac{1}{[\,e^-\,]^2}$$

DISSOLUTION CONTROL



$$|\,i_a\,| = |\,i_c\,|$$

CATHODIC REDUCTION

$$H^+ + e^- \longrightarrow H^\circ$$

$$H_2O + e^- \longrightarrow H^\circ + OH^-$$

$$H^\circ + H^\circ \longrightarrow H_2$$

OVERALL REACTIONS:

$$2\,H_2O + 2\,e^- \longrightarrow H_2 + 2\,OH^-$$

$$2\,H^+ + 2\,e^- \longrightarrow H_2$$

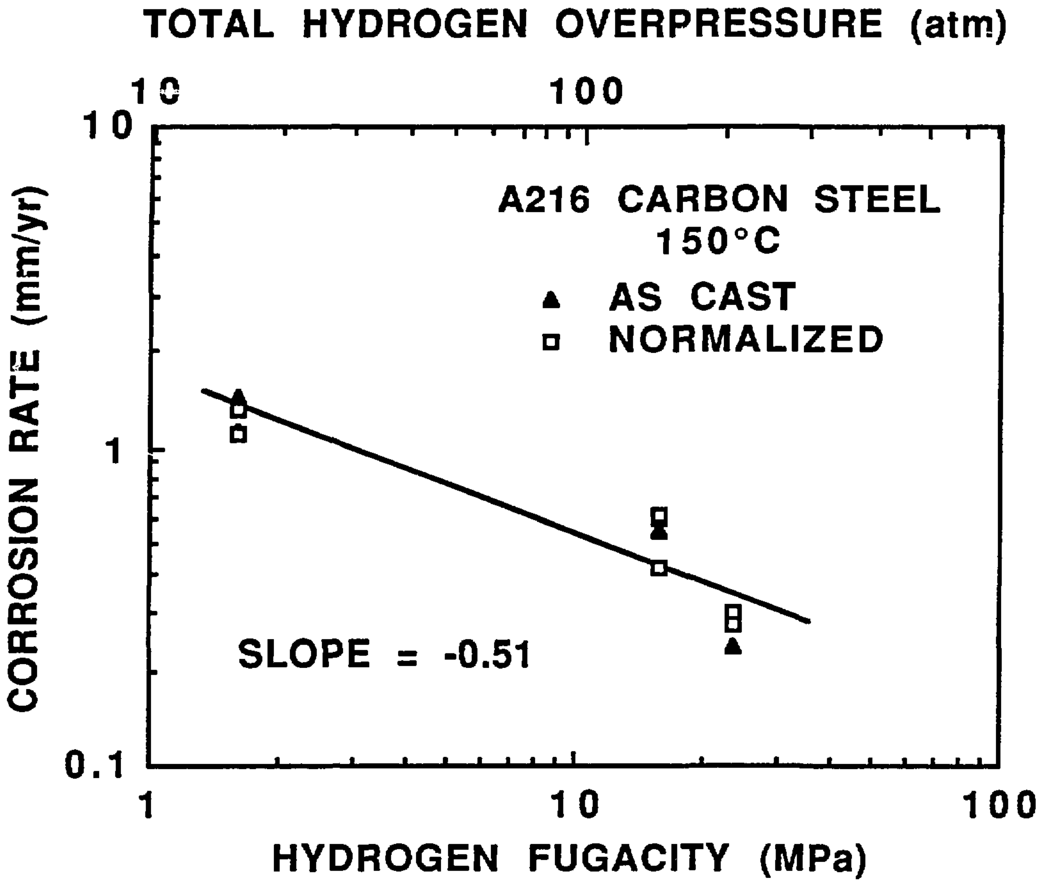
$$K_{eq} = \frac{[OH^-]^2\;(p_{H_2})}{[\,e^-]^2}$$

$$\frac{1}{[\,e^-]} = \frac{K_{eq}^{1/2}\,[H^+]}{K_w\;(p_{H_2})^{1/2}}$$

$$\text{i.e., Corr. rate} \propto \frac{1}{[\,e^-\,]} = \frac{K\;[H^+]}{(p_{H_2})^{1/2}}$$

REDUCTION CONTROL

VARAITION OF CORROSION RATE WITH HYDROGEN FUGACITY FOR PNL SEALED CAPSULE TESTS



MODELING OF IRON CORROSION IN ACID CHLORIDE SOLUTIONS

Variation of Corrosion Rate (mm/yr) with Temperature T and Hydrogen Fugacity f:

$$\frac{dx}{dt} = -3866 \cdot \exp(-3844/T)$$

$$\frac{dx}{dt} = 5.40 \cdot f^{-0.5} \quad (\text{at } T = 150°\text{C})$$

Simultaneous Variation of Corrosion Rate with Temperature and Pressure, in Differential Form:

$$d \ln\left(\frac{dx}{dt}\right) = \left[\frac{\partial \ln (dx/dt)}{\partial T}\right]_f \cdot dT + \left[\frac{\partial \ln (dx/dt)}{\partial f}\right]_T \cdot df$$

Substituting Differential Form of Above Equations into this Relation and Integrating between Appropriate Limits:

$$\ln\left(\frac{dx}{dt}\right) = -3844/T - 0.5 \ln f + 9.081$$

$$\boxed{\frac{dx}{dt} = 8640 \cdot f^{-0.5} \cdot \exp(-3844/T), \quad (\text{mm/yr})}$$

MODELING OF IRON CORROSION IN ACID CHLORIDE SOLUTIONS

Corrosion Rate (mm/yr) as a Funtion of Temperature T and Hydrogen Fugacity f:

$$\frac{dx}{dt} = 8640 \cdot f^{-0.5} \cdot \exp(-3844/T)$$

Moles of Iron n Dissolved per unit Time t:

$$\frac{dn}{dt} = \frac{A\rho}{M} \cdot \frac{dx}{dt}$$

From Ideal Gas Law:

$$\frac{dp}{dt} = \frac{RT}{V} \cdot \frac{dn}{dt} = \frac{RT\rho}{M} \cdot \frac{A}{V} \cdot \frac{dx}{dt}$$

Substituting Expression for dx/dt (assuming $f \approx p$):

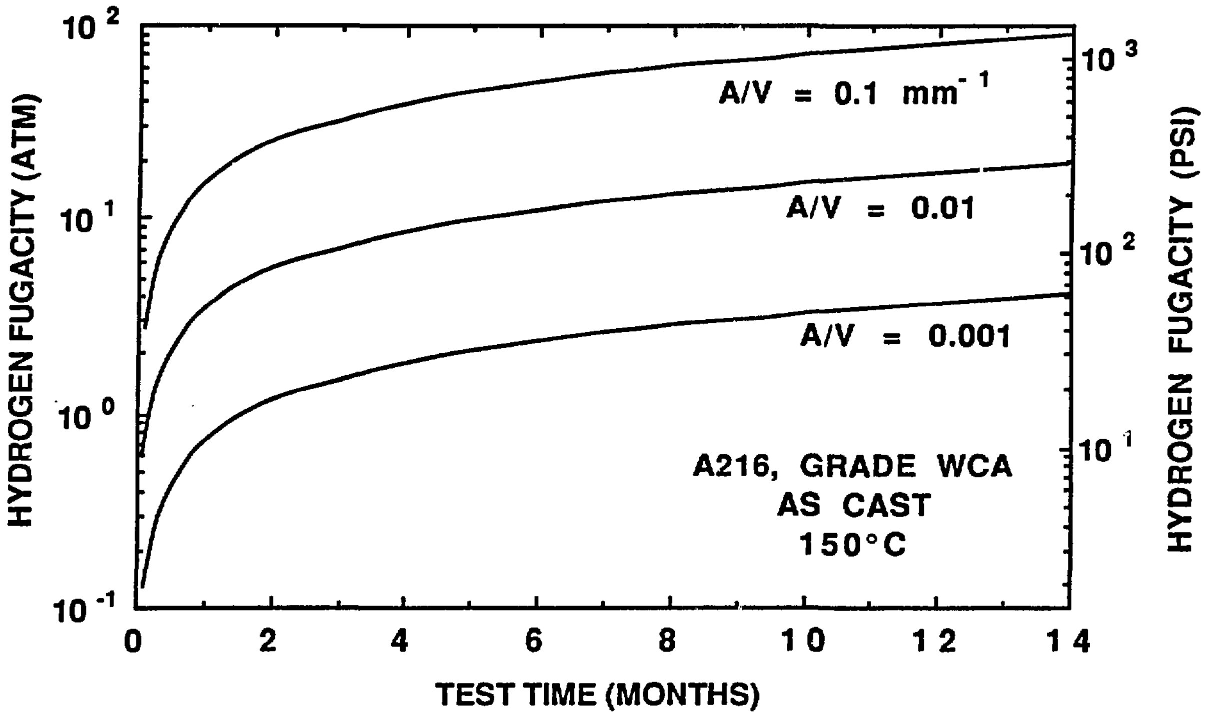
$$\frac{dp}{dt} = 8640 \cdot \frac{RT\rho}{M} \cdot \frac{A}{V} \cdot p^{-0.5} \cdot \exp(-3844/T)$$

Solving for Hydrogen Pressure p and Integrating to Obtain Expression for p as a Function of Time t:

$$\frac{2}{3}\, p^{3/2} = 8640 \cdot \frac{RT\rho}{M} \cdot \frac{A}{V} \cdot \exp(-3844/T) \cdot t$$

$$\boxed{p = 551.7 \cdot \left(\frac{RT\rho}{M}\right)^{2/3} \cdot \left(\frac{A}{V}\right)^{2/3} \cdot \exp(-2562.7/T) \cdot t^{2/3}}$$

CALCULATED HYDROGEN FUGACITY VS. TEST TIME FOR SEALED-CAPSULE TESTS AT 150°C



MODELING OF IRON CORROSION IN ACID CHLORIDE SOLUTIONS (Cont'd.)

Substituting Expression for p into Previous Expression for dx/dt (assuming $f \approx p$):

$$\frac{dx}{dt} = \frac{8640}{(551.7)^{1/2}} \cdot \left(\frac{RT\varrho}{M}\right)^{-1/3} \cdot \left(\frac{A}{V}\right)^{-1/3} \cdot \frac{\exp(-3844/T)}{\exp(-1281.3/T)} \cdot t^{-1/3}$$

$$dx = 367.7 \cdot \left(\frac{RT\varrho}{M}\right)^{-1/3} \cdot \left(\frac{A}{V}\right)^{-1/3} \cdot \exp(-2562.7/T) \cdot t^{-1/3}\, dt$$

Integrating from x = 0 to x and t = 0 to t:

$$\boxed{x = 551.7 \cdot \left(\frac{RT\varrho}{M}\right)^{-1/3} \cdot \left(\frac{A}{V}\right)^{-1/3} \cdot \exp(-2562.7/T) \cdot t^{2/3}}$$

x = mm

A/V = mm^{-1}

T = °K

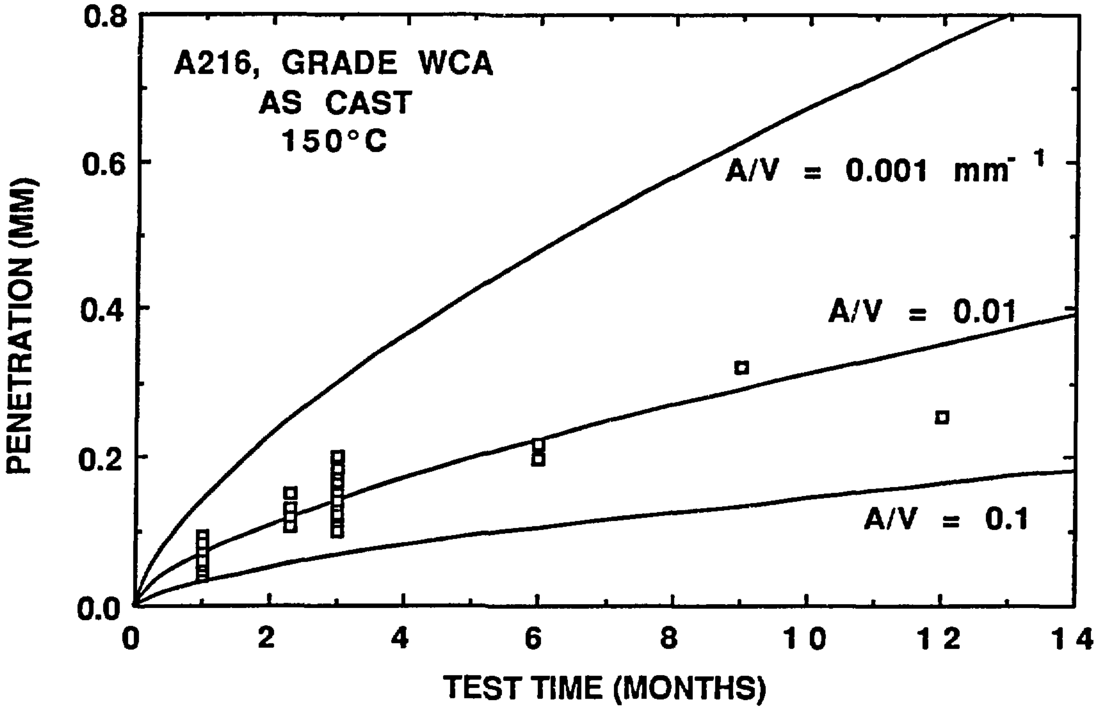
t = yr

R = 82,050 mm^3 atm/mole °K

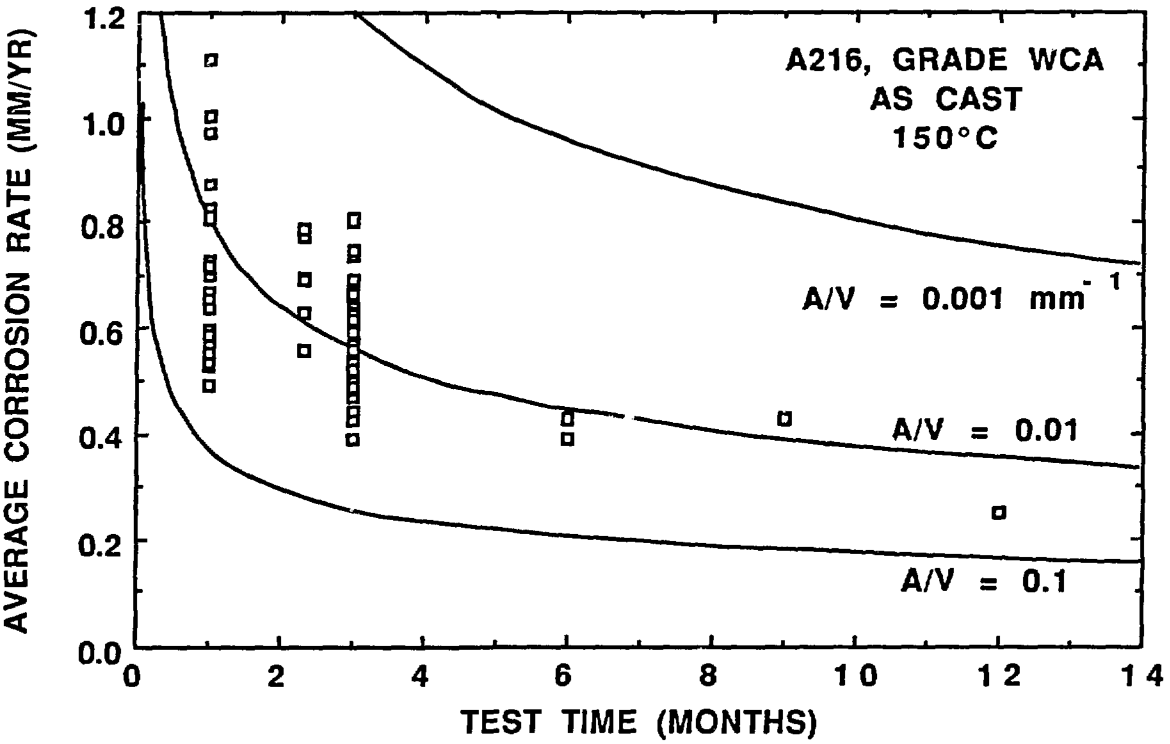
ϱ = 0.00787 g/mm^3

M = 55.85 g/mole

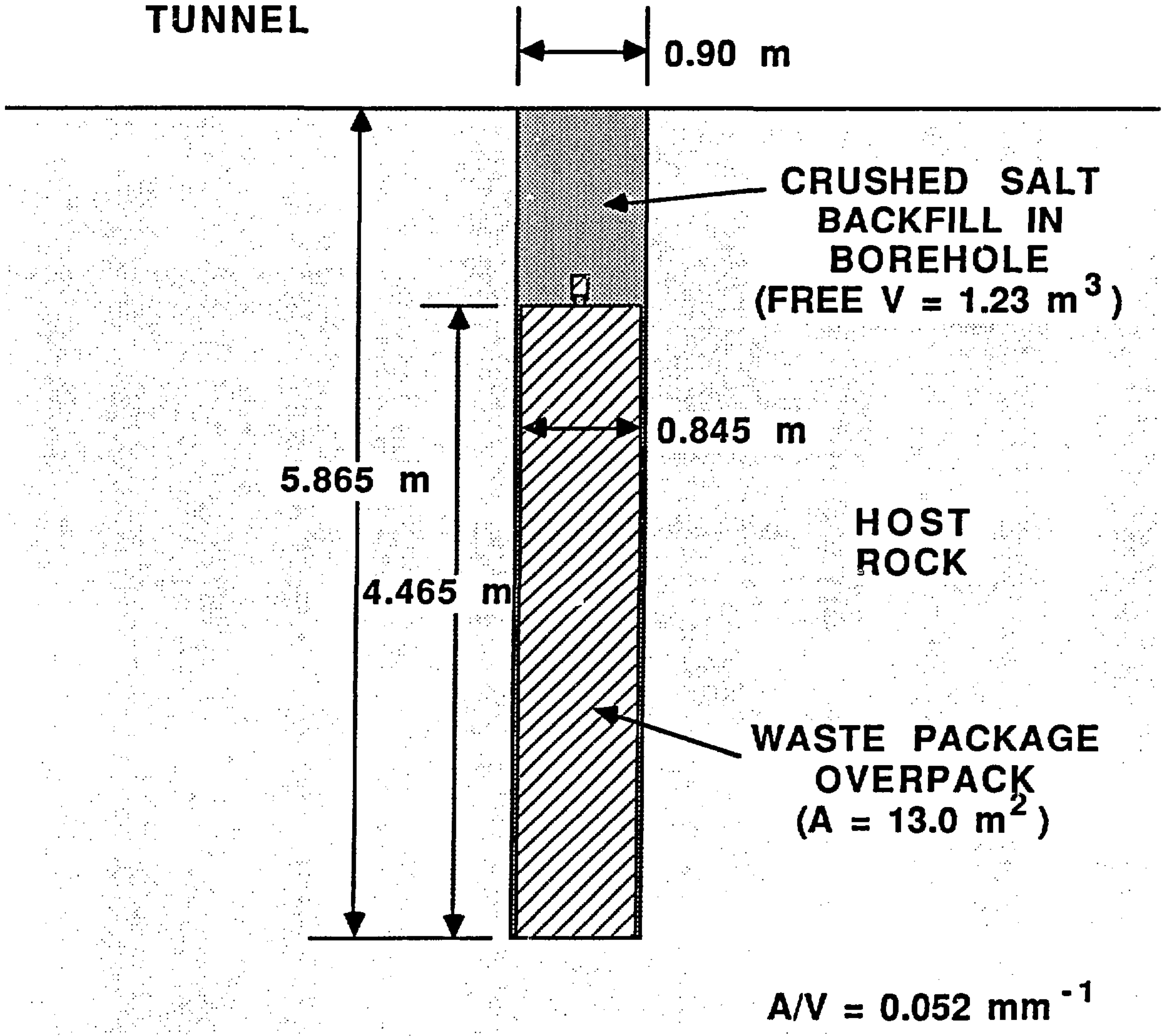
CALCULATED CORROSION PENETRATION VS. TEST TIME FOR SEALED-CAPSULE TESTS COMPARED WITH DATA OF WESTERMAN ET AL.



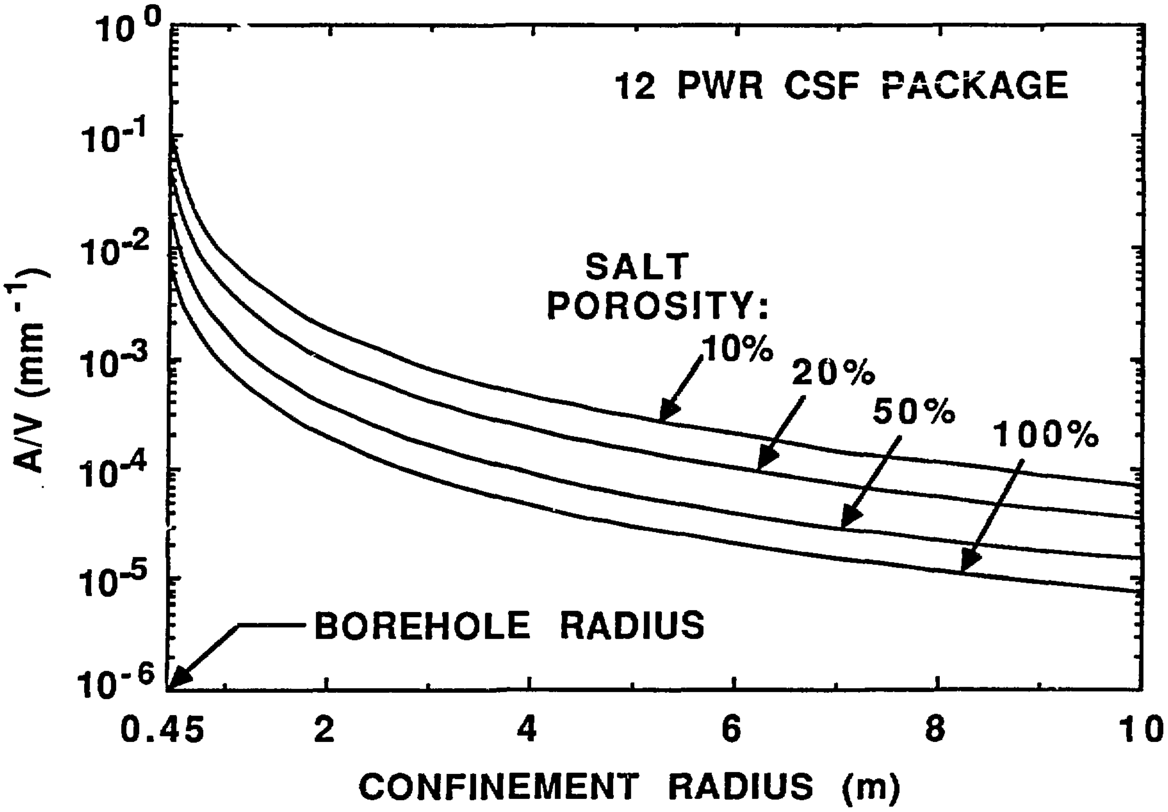
CALCULATED AVERAGE CORROSION RATE VS. TEST TIME FOR SEALED-CAPSULE TESTS AT 150°C COMPARED WITH DATA OF WESTERMAN ET AL.



DIMENSIONS OF WASTE PACKAGE OVERPACK AND REPOSITORY BOREHOLE
(12 PWR CSF)



A/V RATIO VS. RADIUS OF HYDROGEN CONFINEMENT REGION FOR 12 PWR CSF WASTE PACKAGE

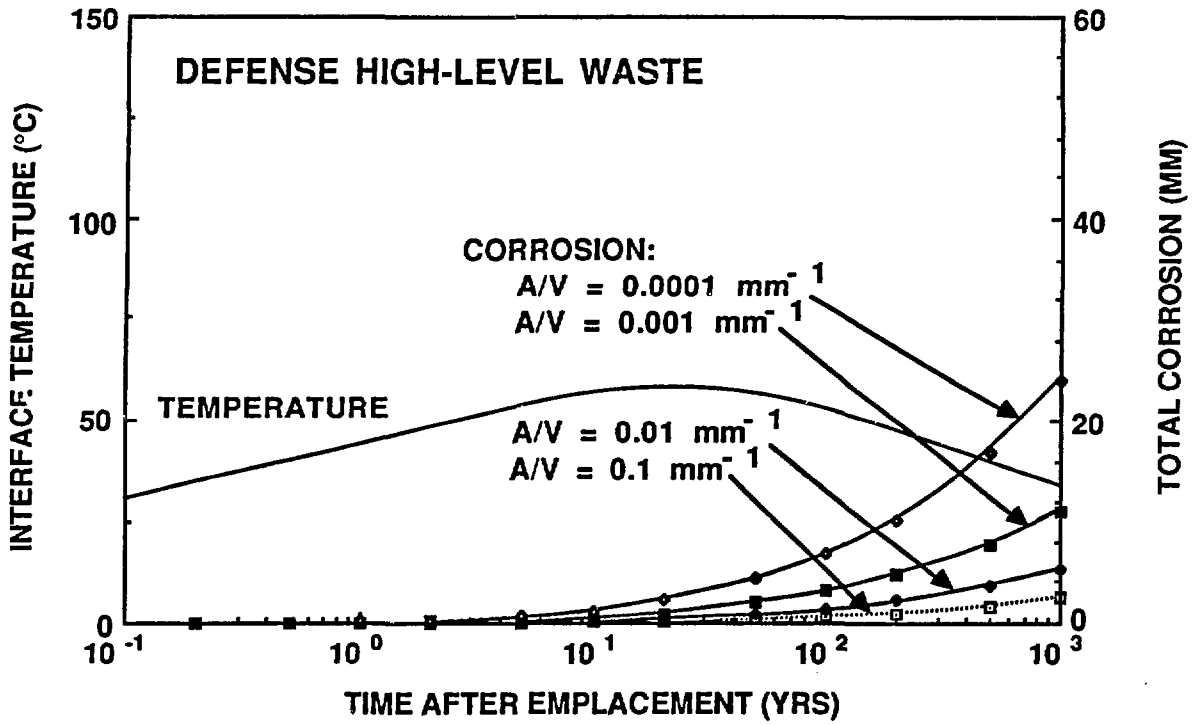


CALCULATED PENETRATIONS FOR SELECTED A/V RATIOS, TEMPERATURES, AND EXPOSURE TIMES

A/V (mm^{-1})	Temp. (°C)	Penetration (mm) after Indicated Exposure Time (yrs) 1	3	10	30	100	300	1000	Final H_2 Press. (atm)
0.1	100	**0.08**	**0.16**	*0.35*	*0.73*	*1.6*	*3.4*	*7.6*	3,270
	125	**0.11**	**0.24**	*0.53*	*1.1*	*2.5*	*5.1*	*11.4*	5,250
	150	**0.16**	*0.34*	*0.76*	*1.6*	*3.5*	*7.3*	*16.4*	8,010
	175	**0.23**	*0.47*	*1.05*	*2.2*	*4.9*	*10.1*	*22.5*	11,670
	200	*0.30*	*0.62*	*1.4*	*2.9*	*6.4*	*13.4*	*29.9*	16,370
0.01	100	**0.16**	**0.34**	**0.75**	**1.6**	*3.5*	*7.3*	*16.3*	704
	125	**0.25**	**0.51**	**1.1**	**2.4**	*5.3*	*11.0*	*24.1*	1,130
	150	**0.35**	**0.73**	**1.6**	*3.4*	*7.6*	*15.8*	*35.3*	1,730
	175	**0.49**	**1.0**	**2.3**	*4.7*	*10.5*	*21.7*	*48.5*	2,510
	200	**0.64**	**1.3**	*3.0*	*6.2*	*13.9*	*28.9*	*64.5*	3,530
0.001	100	**0.35**	**0.73**	**1.6**	**3.4**	**7.6**	**15.8**	*35.2*	152
	125	**0.53**	**1.1**	**2.5**	**5.1**	**11.4**	**23.8**	*53.0*	244
	150	**0.76**	**1.6**	**3.5**	**7.3**	**16.4**	*34.1*	*76.0*	372
	175	**1.0**	**2.2**	**4.9**	**10.1**	**22.5**	*46.9*	*105*	542
	200	**1.4**	**2.9**	**6.5**	**13.4**	*29.9*	*62.3*	*139*	759
0.0001	100	**0.76**	**1.6**	**3.5**	**7.3**	**16.3**	**34.0**	**75.8**	33
	125	**1.1**	**2.4**	**5.3**	**11.0**	**24.6**	**51.2**	**114**	53
	150	**1.6**	**3.4**	**7.6**	**15.8**	**35.3**	**73.4**	**164**	80
	175	**2.3**	**4.7**	**10.5**	**21.7**	**48.5**	**101**	**225**	117
	200	**3.0**	**6.2**	**13.9**	**28.9**	**64.5**	**134**	*299*	164

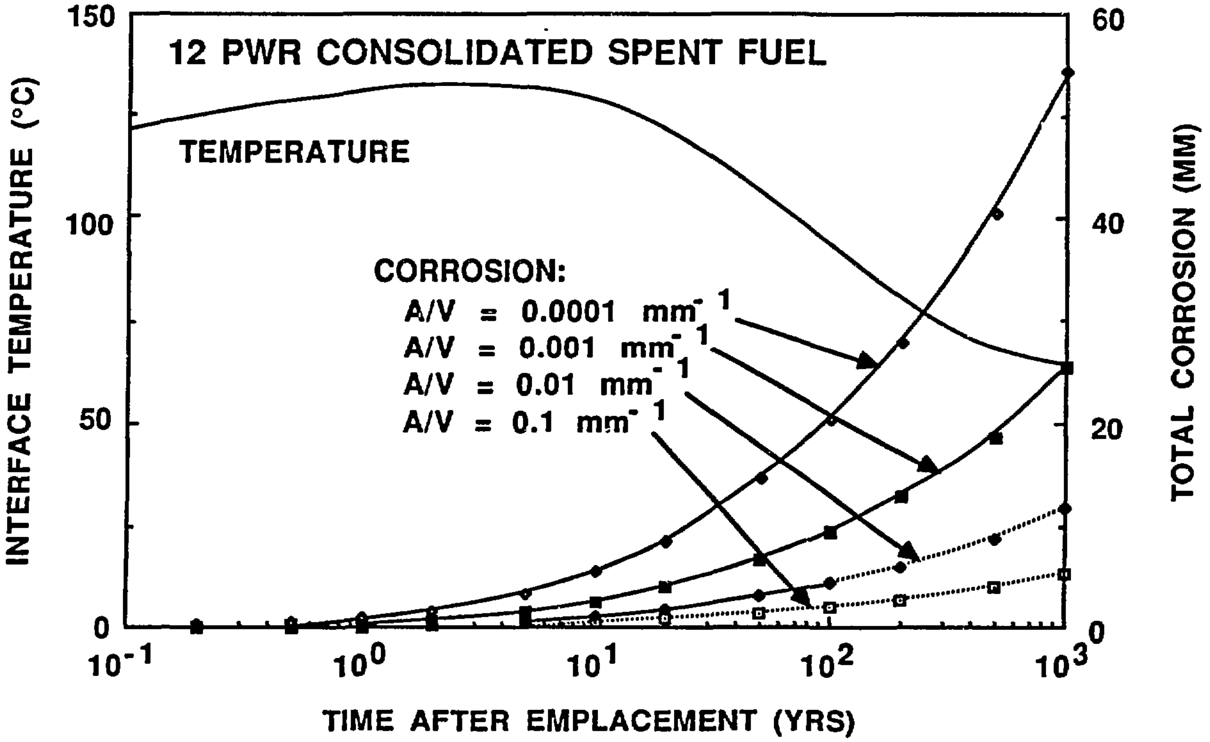
[a] The penetration values inside the shaded areas fall within the 25-mm corrosion allowance for waste package containers. For the penetration values printed in bold-faced type, the calculated hydrogen pressure lies below the lithostatic pressure of 148 atm; for the values printed in italics, the hydrogen pressure exceeds 148 atm.

CALCULATED CORROSION OF CARBON-STEEL CONTAINER IN ACID CHLORIDE BRINE ASSUMING CLOSED SYSTEM[a] (DEFENSE HIGH-LEVEL WASTE)



[a] The calculated hydrogen pressure exceeds the lithostatic pressure of 148 atm for the dotted portion of the penetration curves.

CALCULATED CORROSION OF CARBON-STEEL CONTAINER IN ACID CHLORIDE BRINE ASSUMING CLOSED SYSTEM[a] (12 PWR CONSOLIDATED SPENT FUEL)



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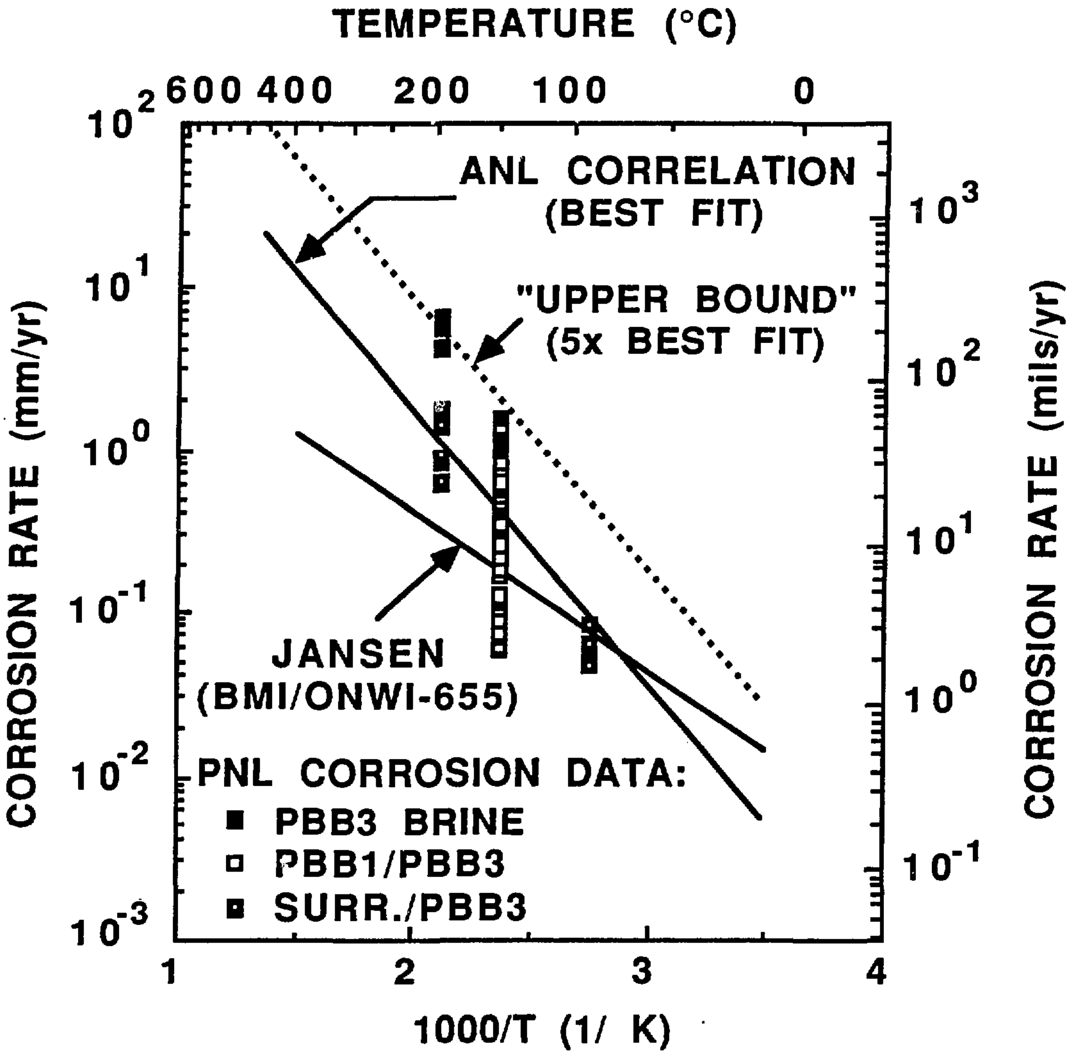
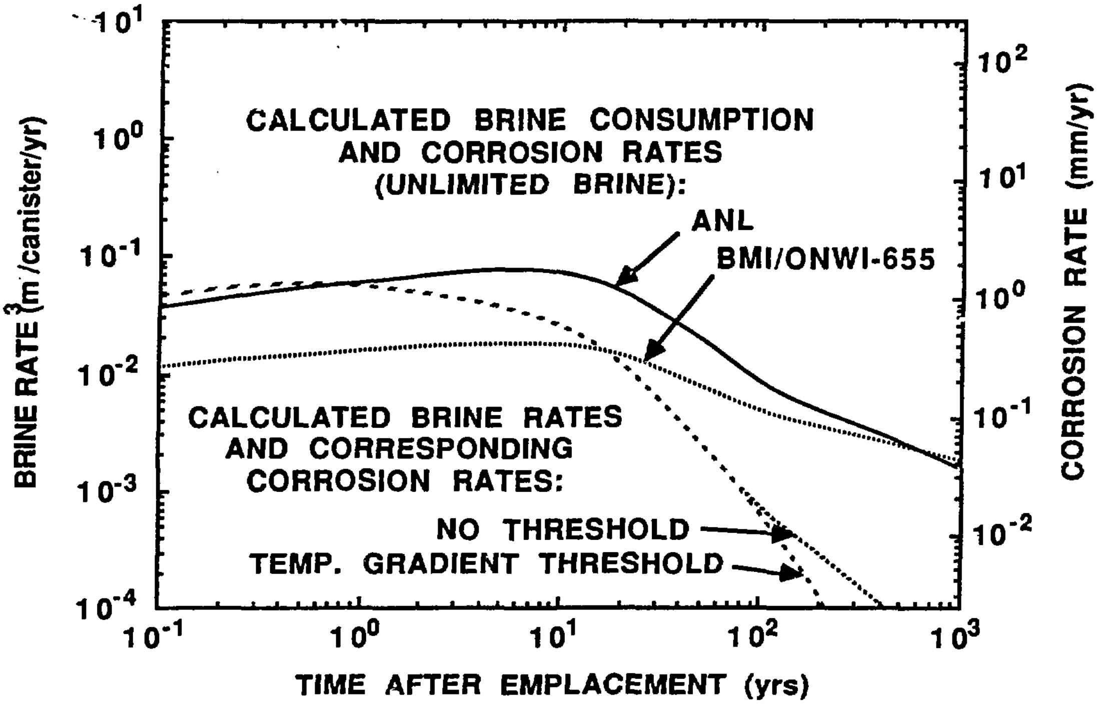
[a] The calculated hydrogen pressure exceeds the lithostatic pressure of 148 atm for the dotted portion of the penetration curves.

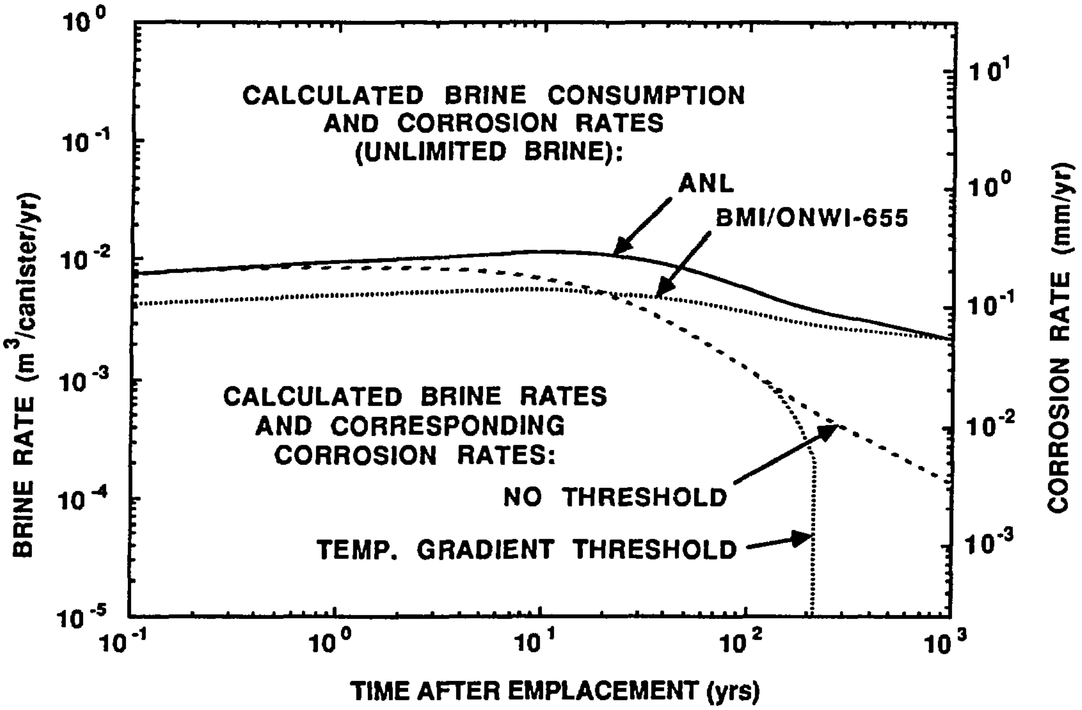
COMPARISON OF ANL DATA CORRELATION FOR CORROSION RATE OF CARBON STEELS IN ANOXIC ACID CHLORIDE SOLUTIONS WITH CORRELATION OF BMI/ONWI-655



CALCULATED BRINE CONSUMPTION RATES AND CORROSION RATES FOR THE CHLW WASTE PACKAGE. THE CALCULATED THERMALLY INDUCED BRINE SUPPLY RATES ARE SHOWN FOR COMPARISON



CALCULATED BRINE CONSUMPTION RATES AND CORROSION RATES FOR THE SFPWR WASTE PACKAGE. THE CALCULATED THERMALLY INDUCED BRINE SUPPLY RATES ARE SHOWN FOR COMPARISON



SUMMARY AND CONCLUSIONS

- THE CORROSION OF CARBON STEELS IN ACID CHLORIDE SOLUTIONS OBEYS AN ARRHENIUS DEPENDENCE ON TEMPERATURE WITH AN ACTIVATION ENERGY OF 32 kJ/mole.
- THE RATE LIMITING STEP IN THE CORROSION OF CARBON STEELS IN ANOXIC, MODERATELY ACID CHLORIDE SOLUTIONS APPEARS TO BE THE CATHODIC REDUCTION OF WATER.
- A MODEL DEVELOPED ASSUMING THE TEMPERATURE DEPENDENCE DESCRIBED ABOVE AND A SQUARE ROOT DEPENDENCE OF CORROSION RATE ON HYDROGEN PRESSURE WAS FOUND TO AGREE WELL WITH PNL DATA.
- APPLICATION OF THIS CORROSION MODEL TO SELECTED WASTE PACKAGE CONFIGURATIONS INDICATED THAT, IN ALMOST ALL CASES, A SUGGESTED CORROSION ALLOWANCE OF 25 mm WOULD BE EXPENDED WELL BEFORE THE END OF A 1000-YEAR EMPLACEMENT TIME.
- CALCULATED RATES OF <u>THERMALLY</u> INDUCED BRINE MIGRATION MAY POTENTIALLY LIMIT THE AMOUNT OF CORROSION PENETRATION TO ACCEPTABLE LEVELS, BUT EXPERIMENTALLY OBSERVED <u>NONTHERMAL</u> MIGRATION RATES, IF THEY PERSIST OVER LONG TIME PERIODS, WILL SUPPORT UNACCEPTABLY HIGH CORROSION RATES OF THE WASTE CONTAINER.