



REVIEW OF INDUSTRIAL CORROSION PROBLEMS IN SALINE ENVIRONMENTS

Conditions when corrosion problems expected are well understood.

CREVICE CORROSION

- For Ti-2, high temperatures ($>70^{\circ}\text{C}$) and/or low pH (<3) required
- Conditions inevitably continuously oxidizing
- At flanges or under certain gasket materials
- In heat exchangers at tube-to-tubesheet joints, under salt deposits, in the presence of hydrolyzable salts (e.g., Mg, Ca, Zn, Al chlorides)
- Not observed under biofilms or antifouling paints
- Problems avoided by selection of Ti-12 or Ti-7 (0.2wt.% Pd)

PITTING

- Not failure process in seawater applications
- Observed in hot salt evaporators for $T > 130^{\circ}\text{C}$
- Shallow pitting when embedded Fe particles present



SEAWATER APPLICATIONS

Titanium is fully resistant to natural seawater regardless of chemistry variations and pollution effects.

Corrosion rates (over 20 a) $\ll 0.3 \mu\text{m}\cdot\text{a}^{-1}$

**** (Similar rates measured for Ti buried in soils)**

Since 1959, Ti-2 has become the material of choice for heat transfer applications

- **Wall thickness steadily reduced from 1.24 mm to 0.7 mm**
- **Not one failure has been reported in this application over 35 a of service**
- **120,000 km of welded Ti tube used in seawater-cooled power plant condenser service with no reported failures due to seawater corrosion in 25 a**
- **15,000 km of welded Ti tube used in Japanese desalination plants (since 1974)**



SEAWATER APPLICATIONS

- **6,000 tonnes (last 10 years) of welded tube and tube plate used in Japanese power plant condensers**
- **Fatigue strength and toughness of titanium are unaffected by seawater exposure**
- **Lean Ti alloys (e.g., Ti-2, Ti-12) are immune to SCC in seawater**
- **Various test exposures of titanium alloy samples in the sea for periods as long as 20 years have demonstrated immunity to microbially induced corrosion despite extensive micro- and macrogrowth on metal surfaces**



MICROBIAALLY INDUCED CORROSION

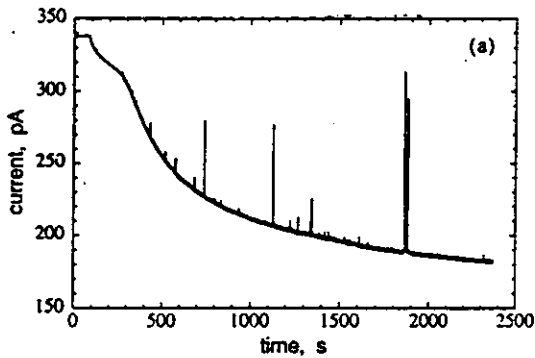
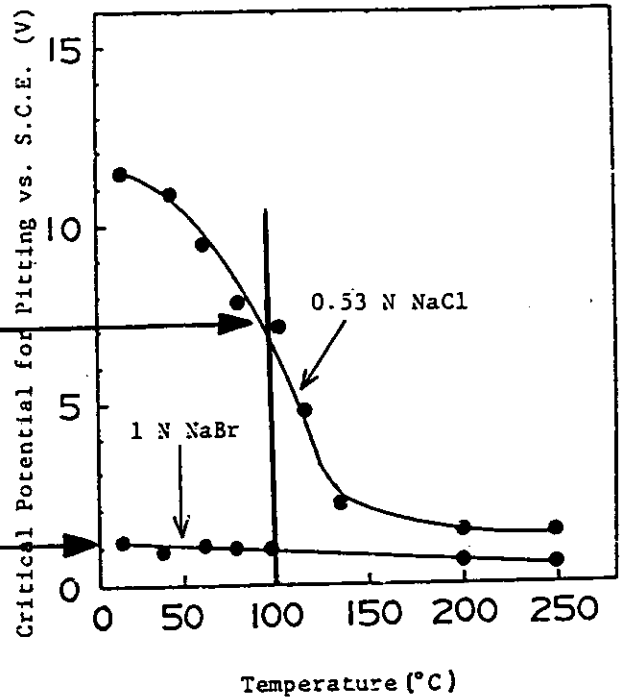
- **“The resistance of titanium alloys to MIC in operating systems and laboratory experiments has been repeatedly demonstrated.” (5 references). B.J. Little et al. (Corrosion 93; paper 308)**
- **A review of the literature and service experience fails to reveal a single titanium alloy component failure related to MIC. This record exists despite its extensive use in plate/frame and shell-tube heat exchangers, vessels, pumps, valves and piping systems handling highly biologically active processes and raw cooling water streams over the past 30 a.....”**
- **Various test exposures of titanium alloy samples in the sea for periods as long as 20 years have demonstrated immunity to attack despite extensive micro- and macrogrowth on metal surfaces.”**

R.W. Schutz (Materials Performance 30, 58 (1991))

Ti-2 SUSCEPTIBLE TO
PITTING IN BROMIDE BUT
NOT CHLORIDE

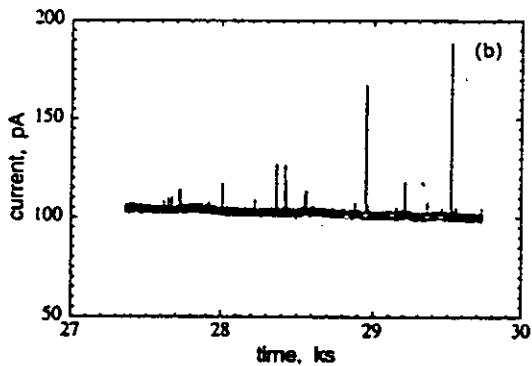
PITTING POTENTIAL IN Cl^-

PITTING POTENTIAL IN Br^-

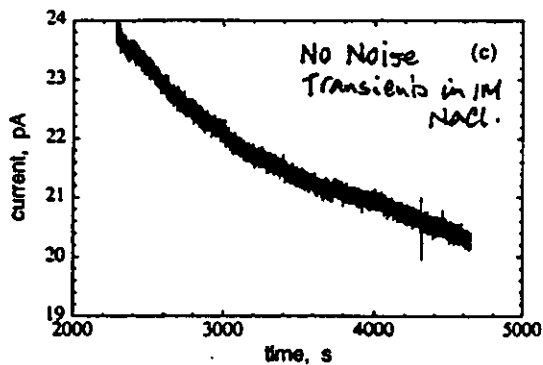


1.5 mol.L⁻¹ HCl
0.9 V (vs SCE)

NO METASTABLE PITTING
EVENTS OBSERVED ON Ti
MICROELECTRODES IN
NEUTRAL CHLORIDE SOLUTION.



1.5 mol.L⁻¹ HCl
0.9 V (vs SCE)



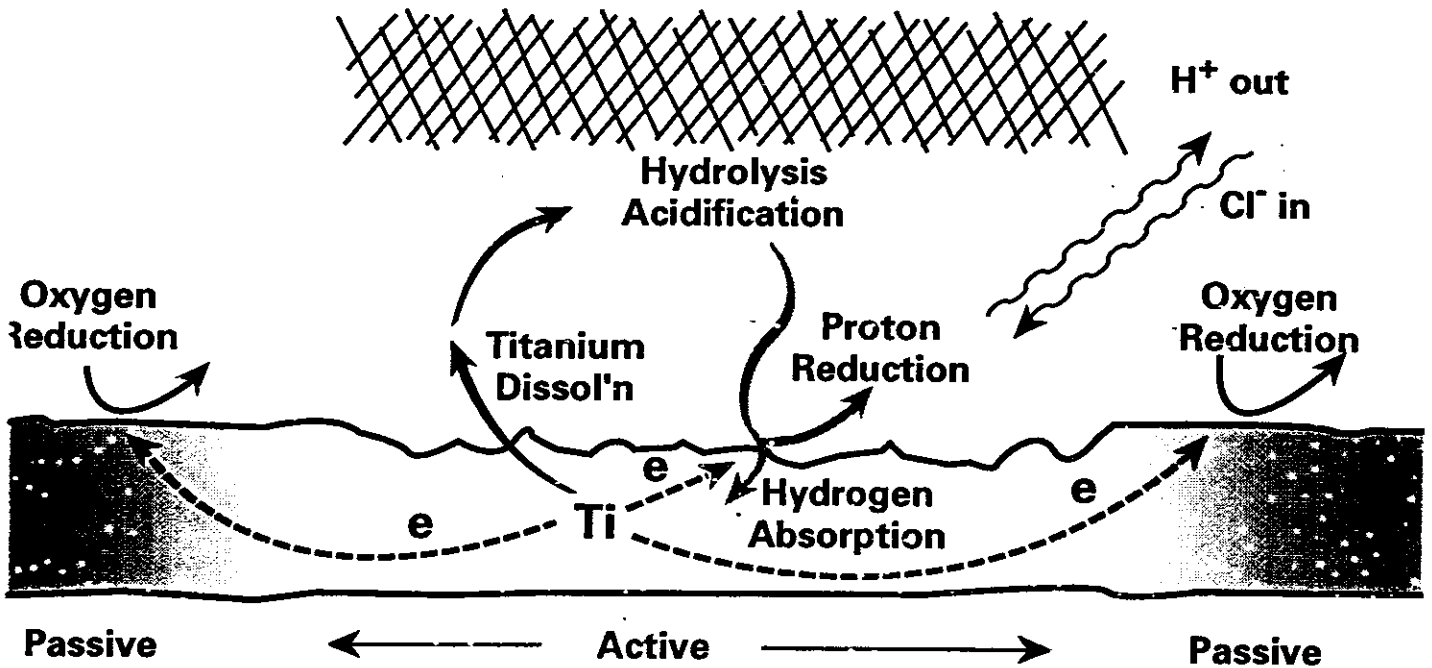
1 mol.L⁻¹ NaCl
0.5 V (vs SCE)



EFFECT OF WELDING ON THE CORROSION OF TITANIUM ALLOYS

- **The welding of Ti-2 and Ti-12 is a common and well-established process with QA procedures for producing qualified welds**
- **Poor welding of Ti-12 can change the microstructure and precipitate intermetallics, but these changes are not detrimental to the corrosion performance of the weld or the heat affected zone**
- **Susceptibility to HIC is reduced by welding, partly due to an increased randomization of the microstructure in the heated zones**

Crevice Corrosion is the most likely localized Corrosion process under Disposal Vault Conditions

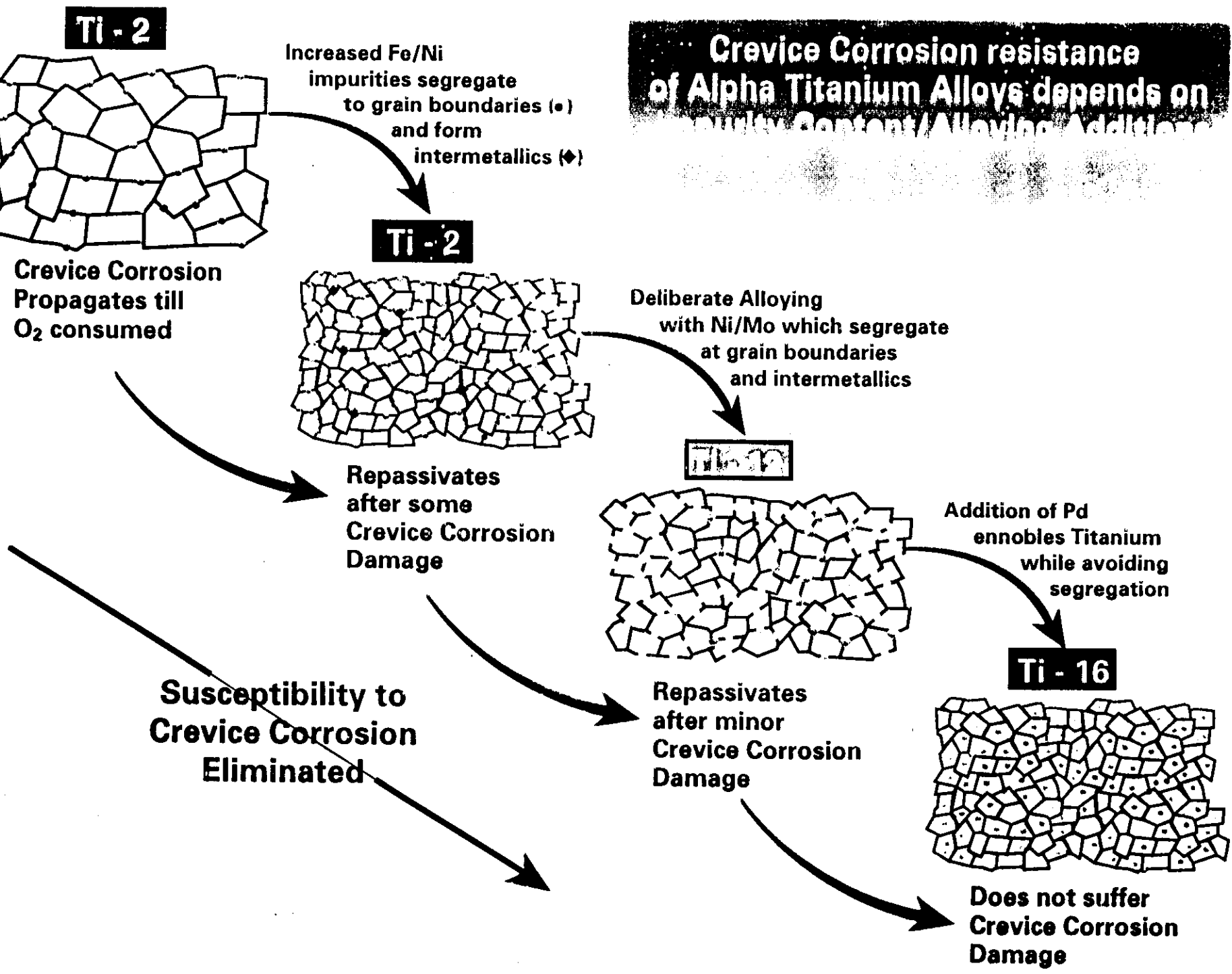


Factors Controlling Crevice Corrosion

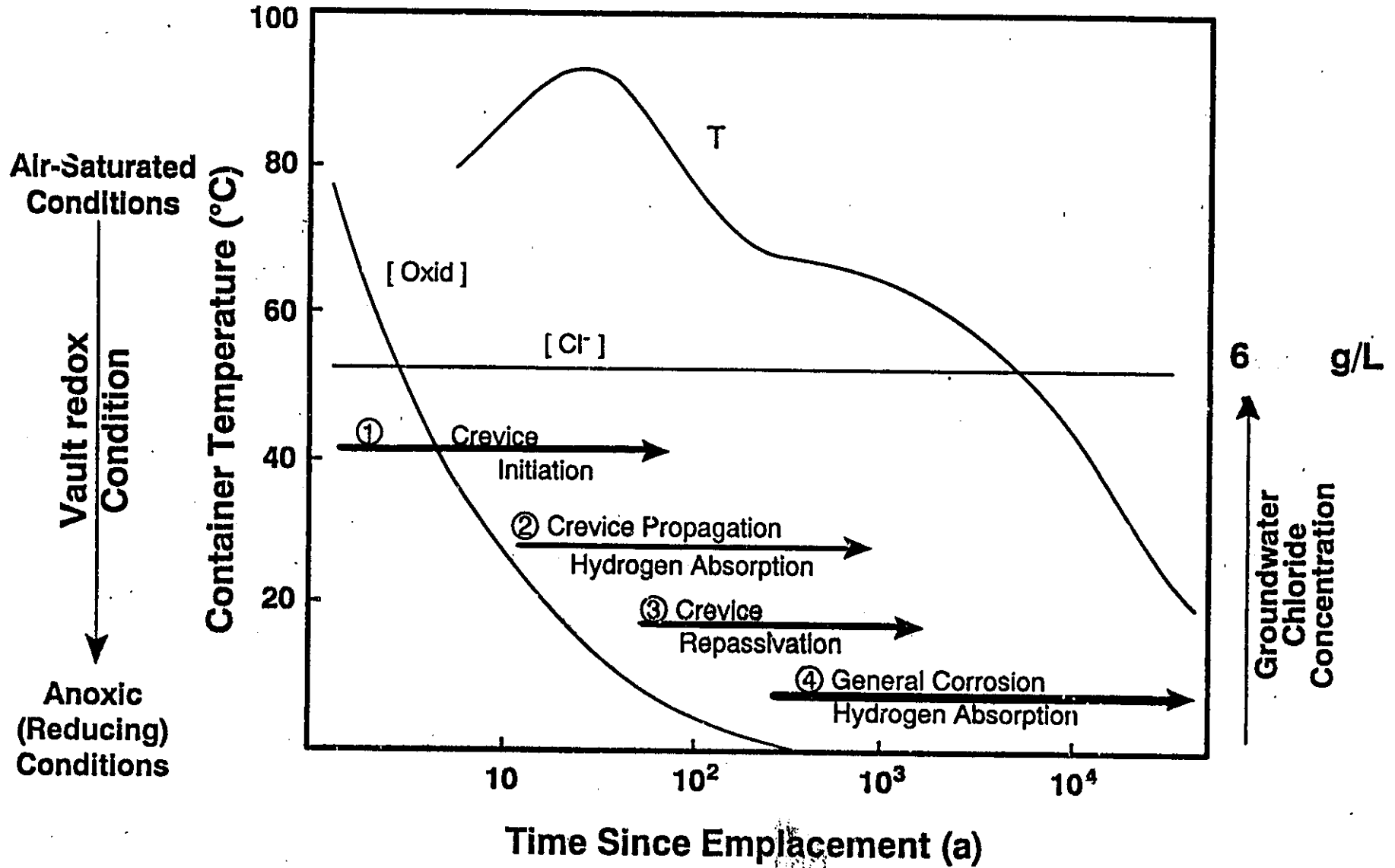
- Vault Temperature
- Availability of Oxygen
- Groundwater Salinity
- Materials Properties

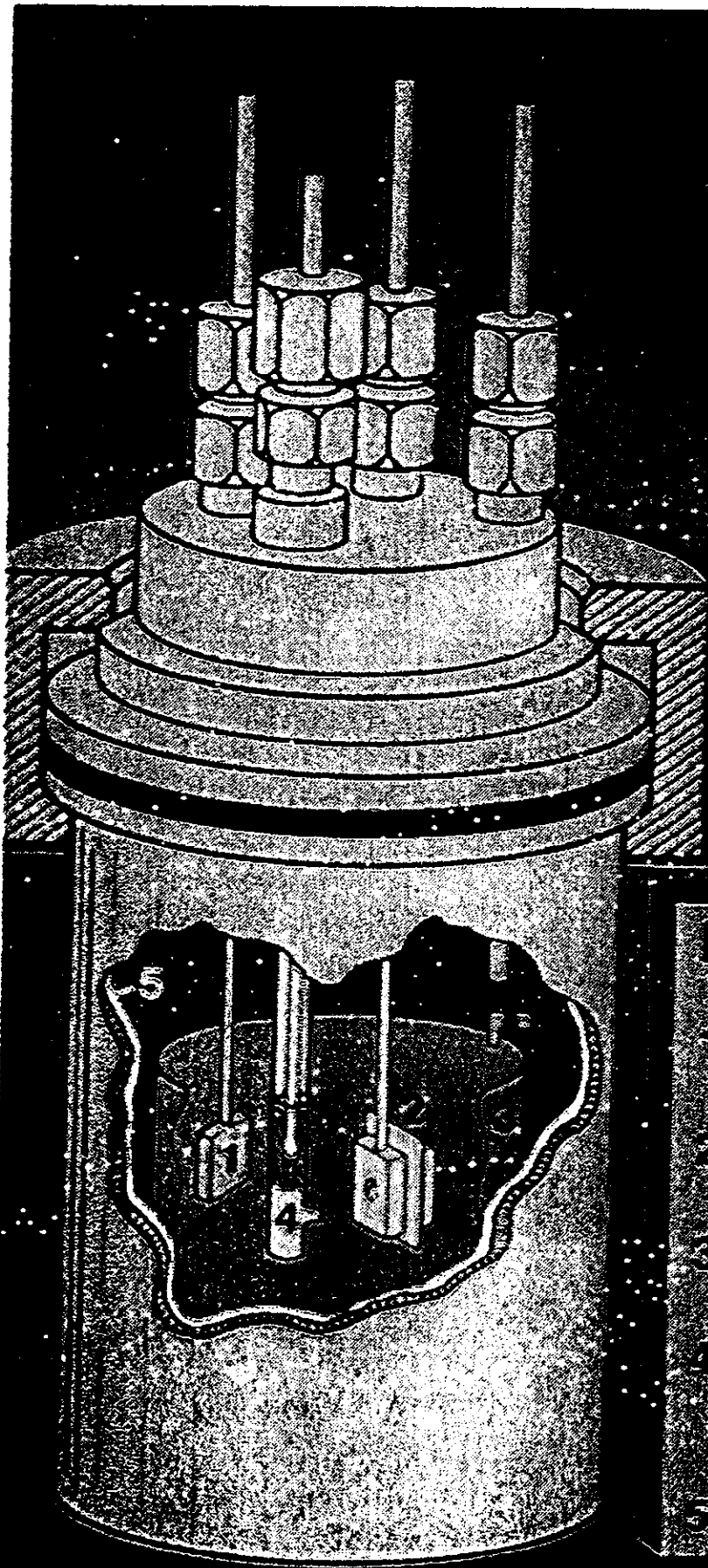
Container failure is assumed to occur when the crevice corroded front exceeds the corrosion allowance. Then, mechanical integrity is assumed to be lost and the container will collapse or buckle.

Crevice Corrosion resistance of Alpha Titanium Alloys depends on Impurity Content/Alloying Additions



Anticipated periods for Various Corrosion Processes

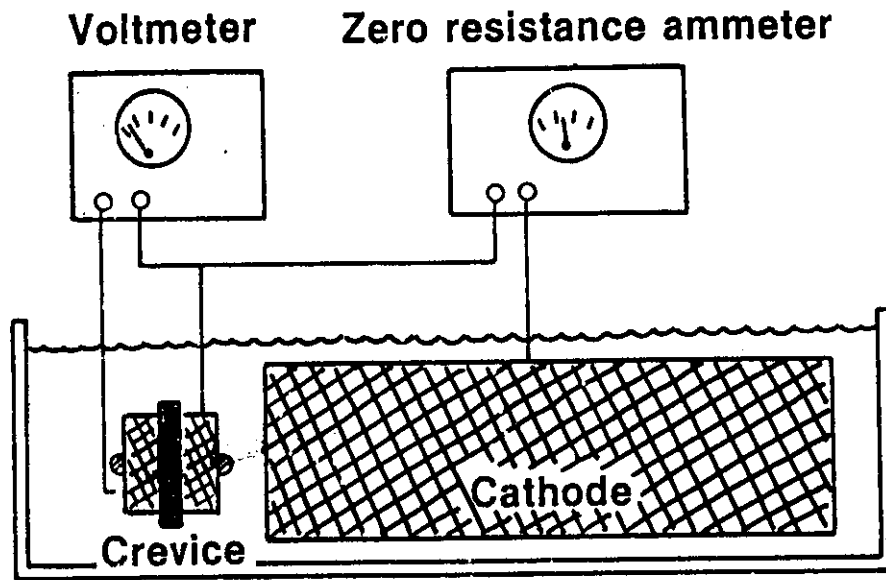




LEGEND

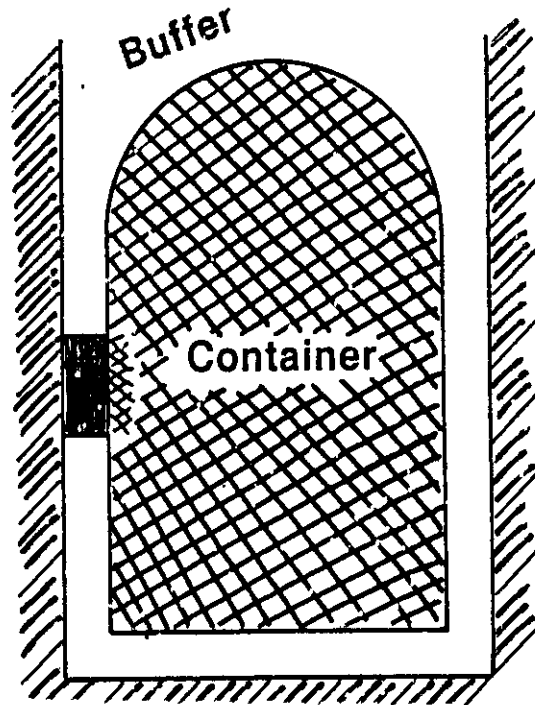
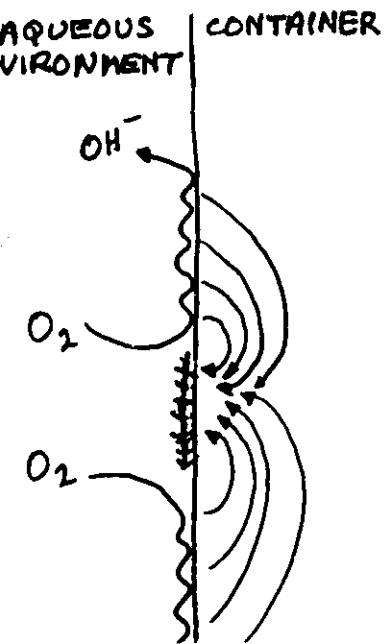
- 1 Planar electrode
- 2 Creviced electrode
- 3 Counter electrode
- 4 Reference electrode
(Ag/AgCl in 0.1N KCl)
- 5 PTFE liner

A GALVANIC COUPLING IS USED TO STUDY CREVICE CORROSION.



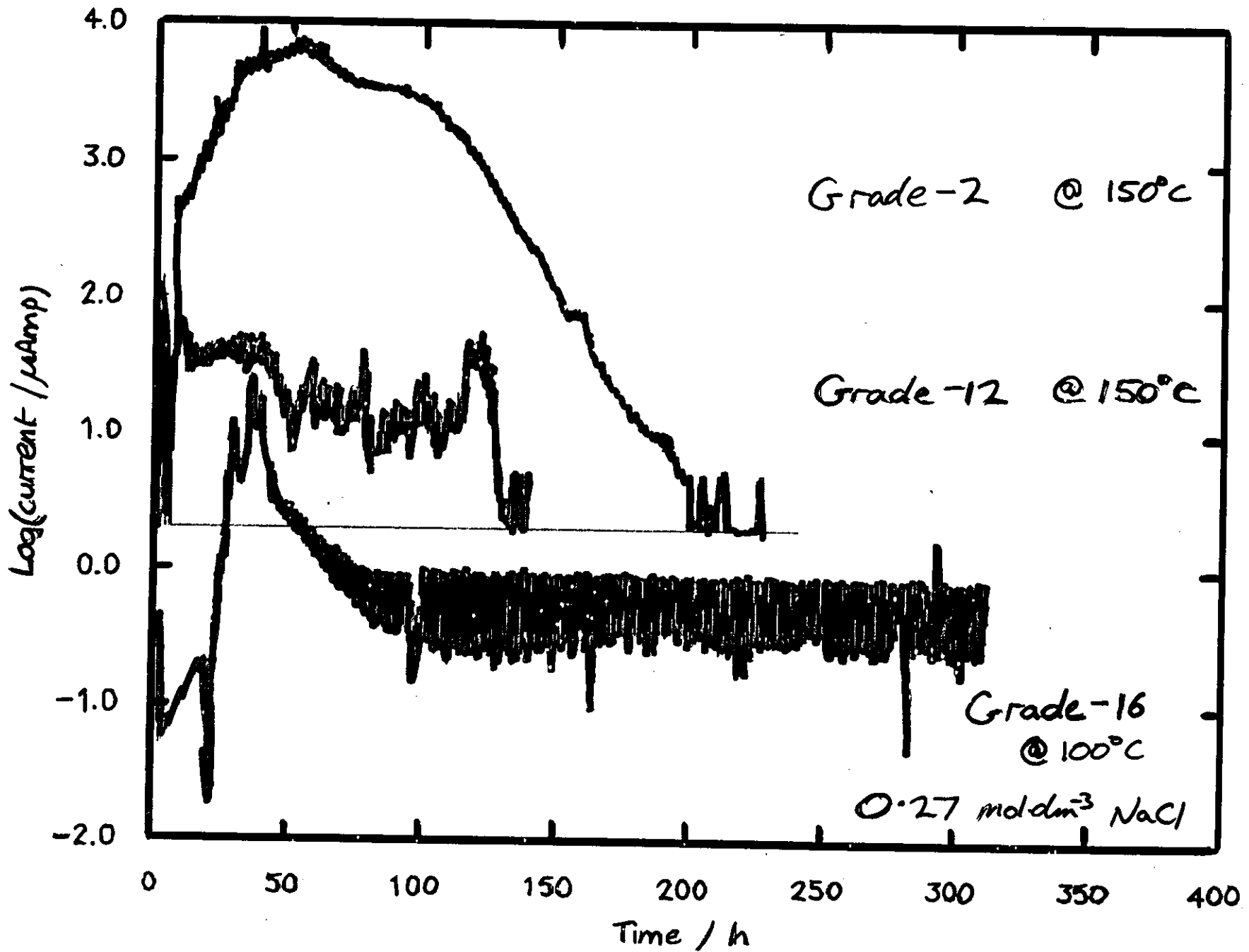
RATIO OF CREVICED
AREA TO CATHODIC
AREA

1 : 40



OUR EXPERIMENT SIMULATES
A SMALL CREVICED AREA
ON A LARGE GENERAL
UNCREVICED AREA.

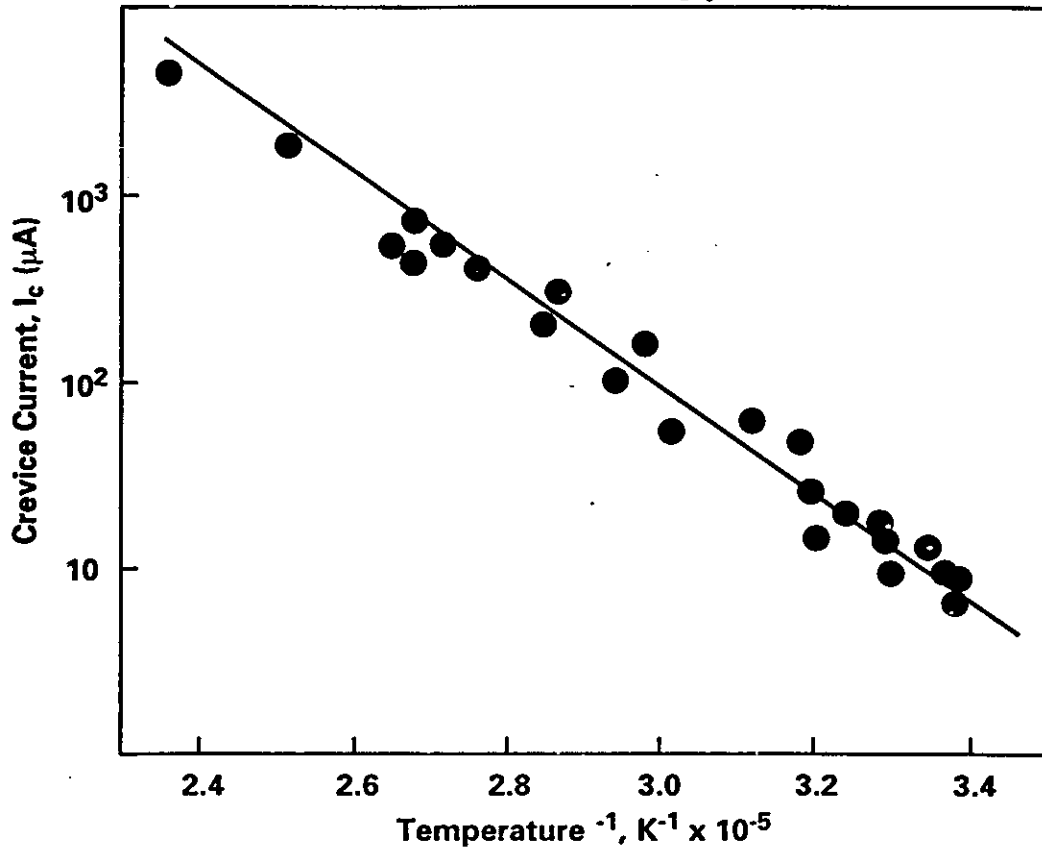
crevice-corrosion resistant than grade-2 titanium.



DEPENDENCE OF THE CREVICE CORROSION
CURRENT FOR Ti-2 ON TEMPERATURE

(0.27 mol.L⁻¹ NaCl)

94-3321.07d



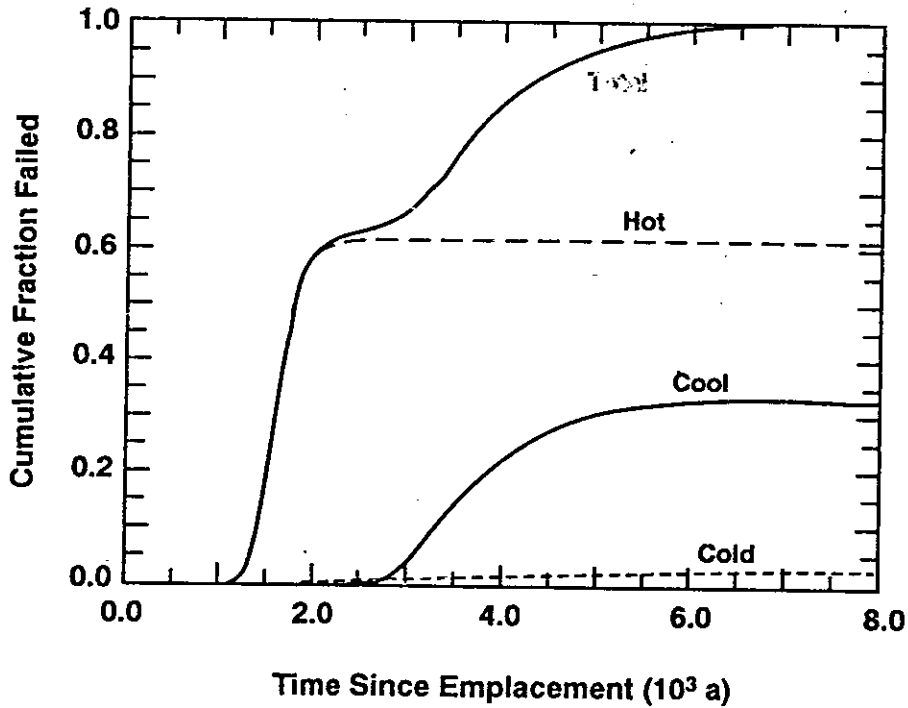
ACTIVATION ENERGY ~ 55 kJ.mol⁻¹

CREVICE CURRENT FOR Ti-12 ALMOST
INDEPENDENT OF TEMPERATURE.

REPASSIVATION OF Ti-12 OCCURS FOR
 $T \lesssim 70^{\circ}\text{C}$.

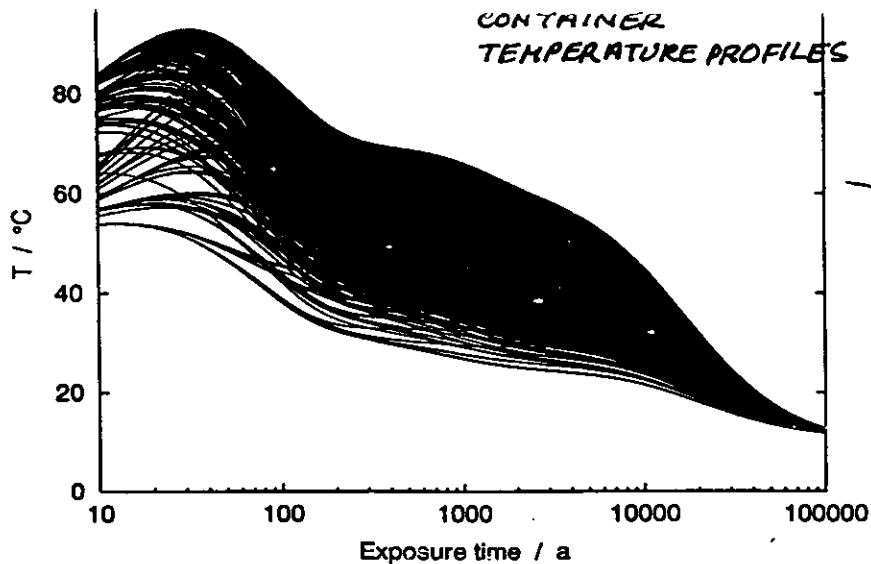
Assessment of Container Lifetimes

EIS



Long-lived Ti containers (nominal 6.35-mm wall thickness)

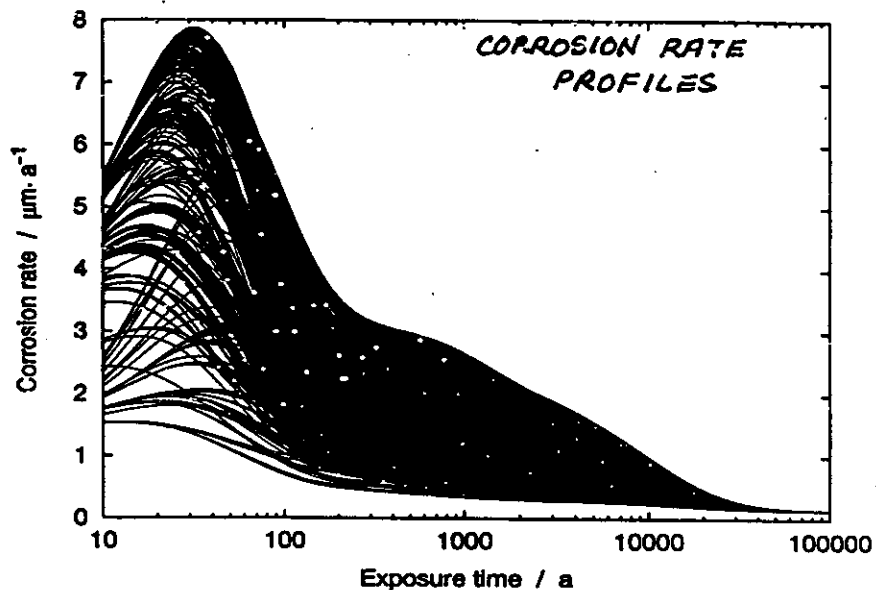
	Extent of CC (mm)	Remaining UC allowance (mm)	Film growth law (nm/a)	Fractional H uptake	Failure mode	Container lifetime (a)
Ti-12	1.3	3.0	0.44	0.1	HIC	1.4 x 10 ⁶
			31.5	0.1	HIC	2.0 x 10 ⁴
Ti-16	0	4.3	0.44	0.1	HIC	1.4 x 10 ⁶
			1.4	0.1	HIC	4.5 x 10 ⁵



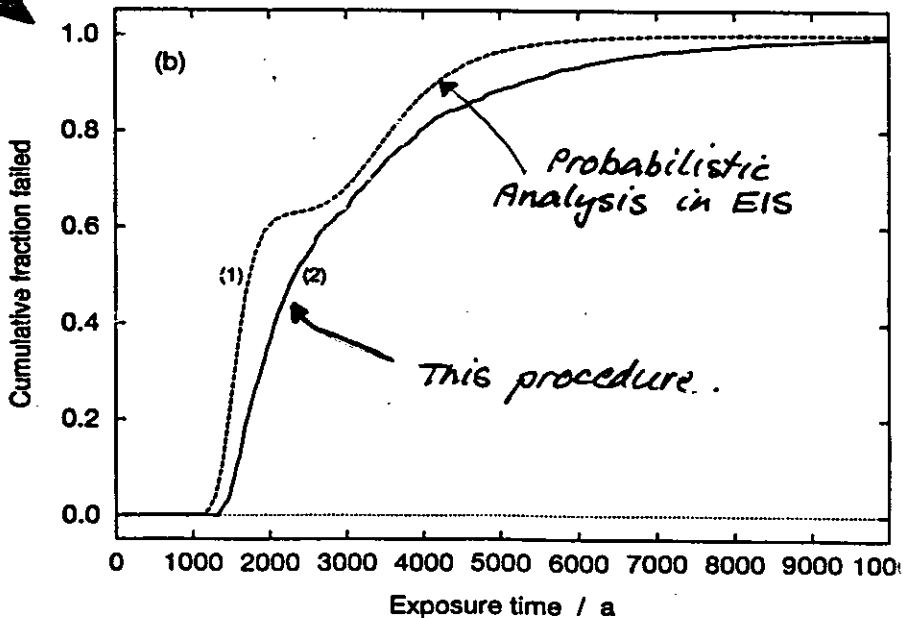
Crevice Propag'n
Rate at 100°C
= $10 \pm 5 \mu\text{m} \cdot \text{a}^{-1}$

$$E_A^\ddagger = 55 \text{ kJ} \cdot \text{mol}^{-1}$$

Calculate the
time to
penetrate the
corrosion
allowance



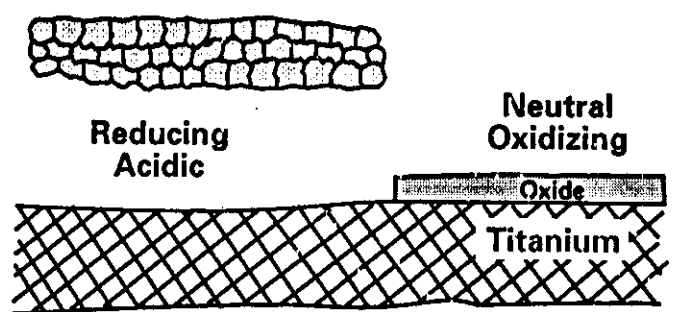
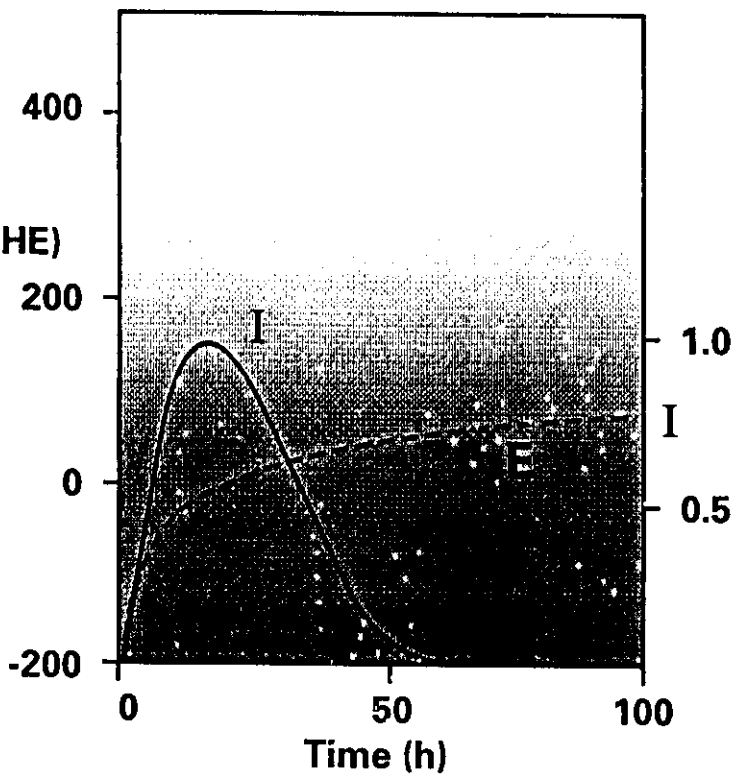
Every site within
the creviced area
corrodes at the
same rate.



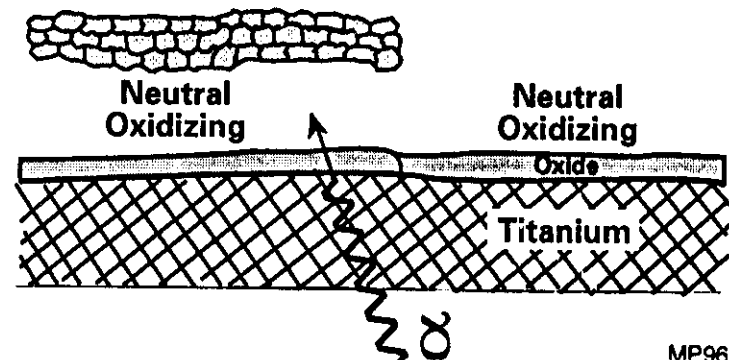
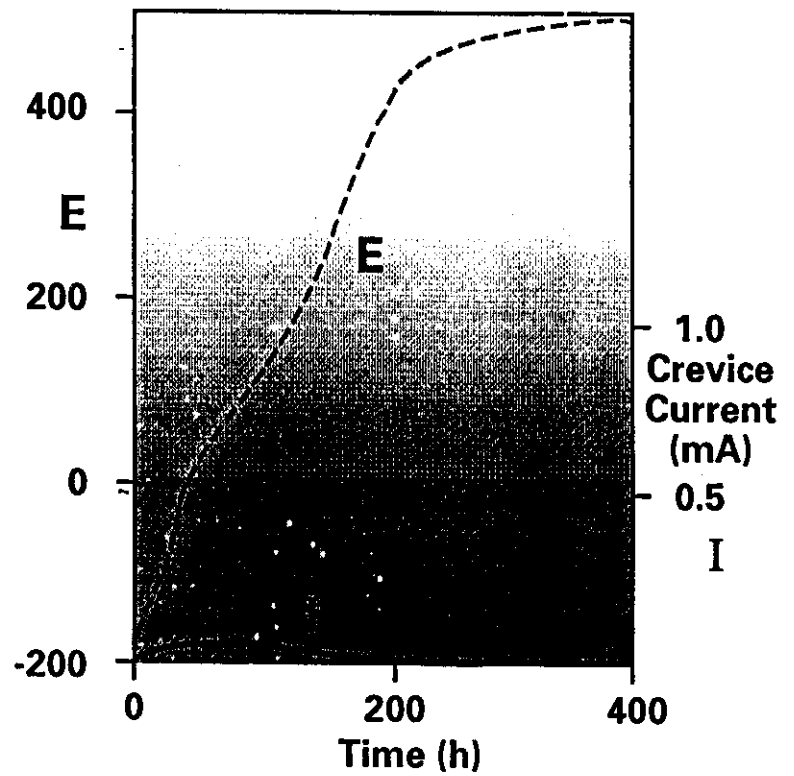
The presence of radiation causes the Repassivation of Crevices on Ti - 2

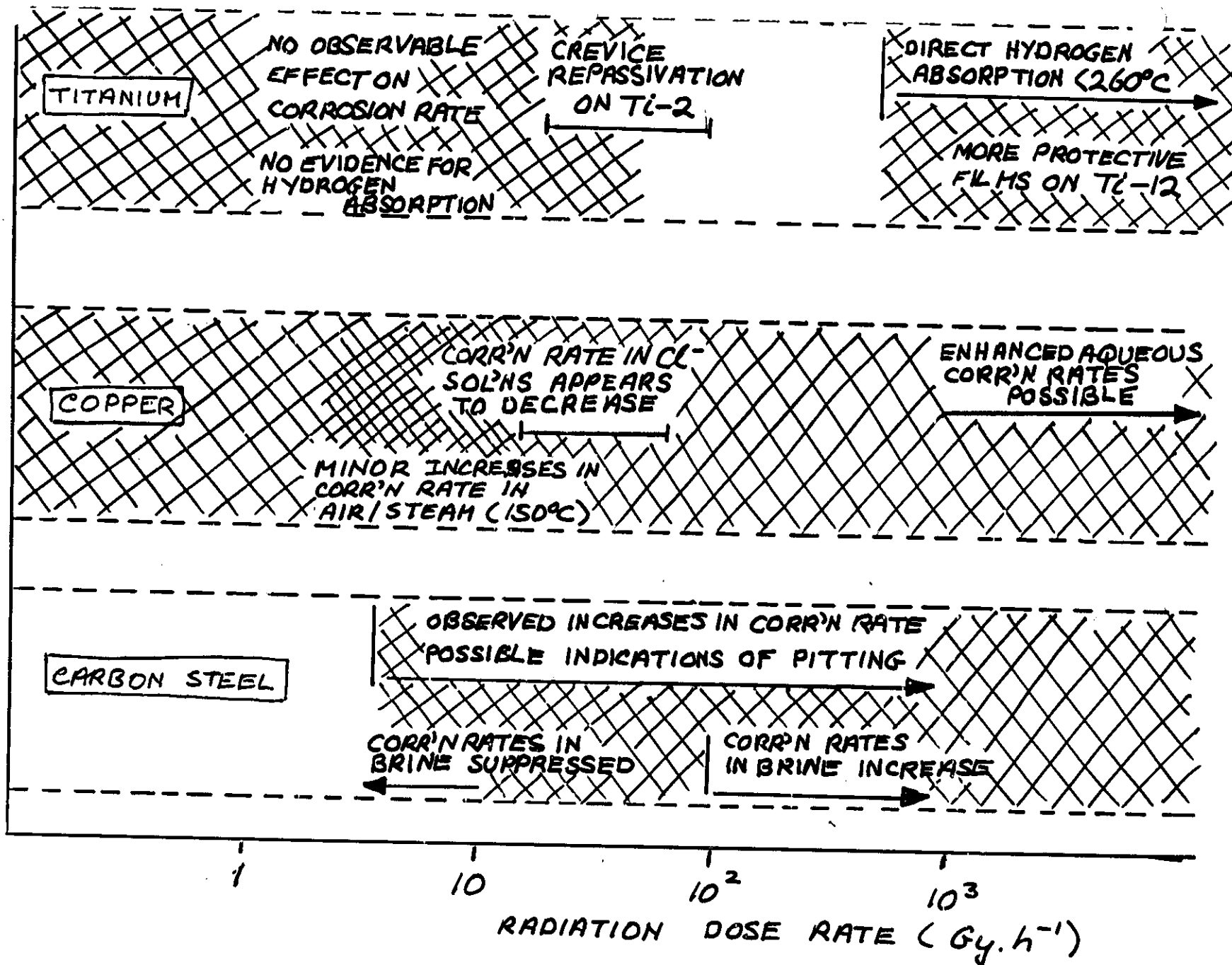
(0.27 mol · L⁻¹ NaCl; 150°C)

No Radiation

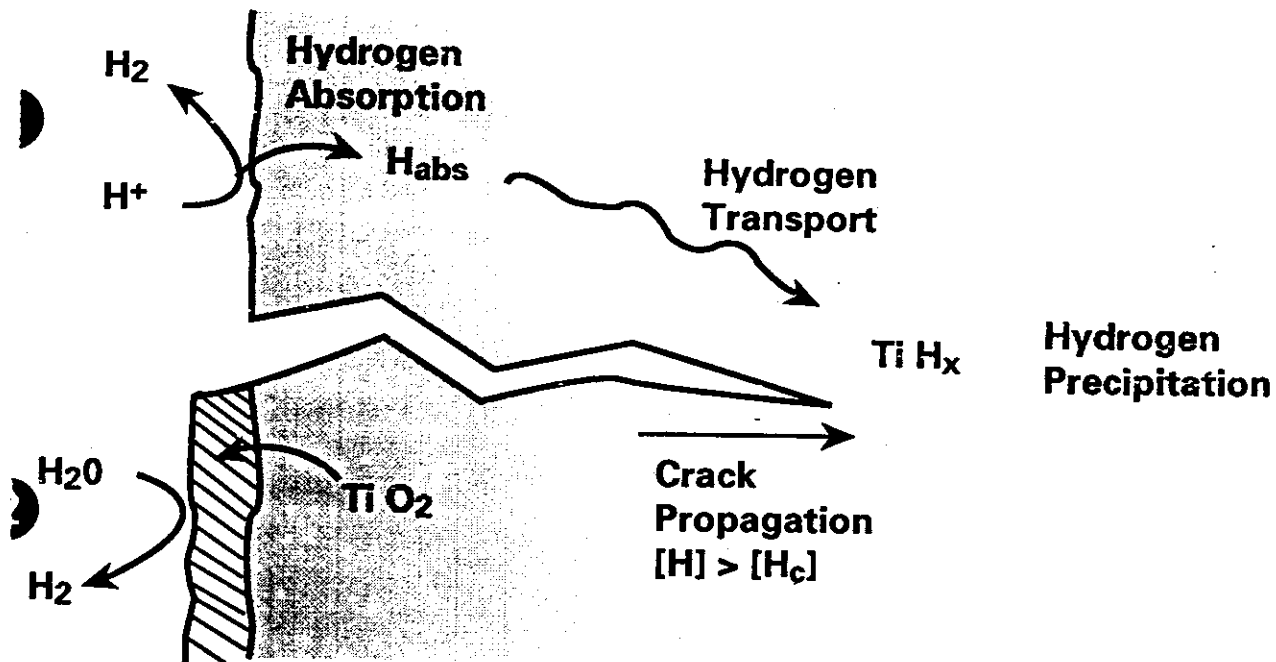


Radiation (24 Gy · h⁻¹)





The second possible Localized Corrosion Process is Hydrogen - Induced Cracking (HIC)

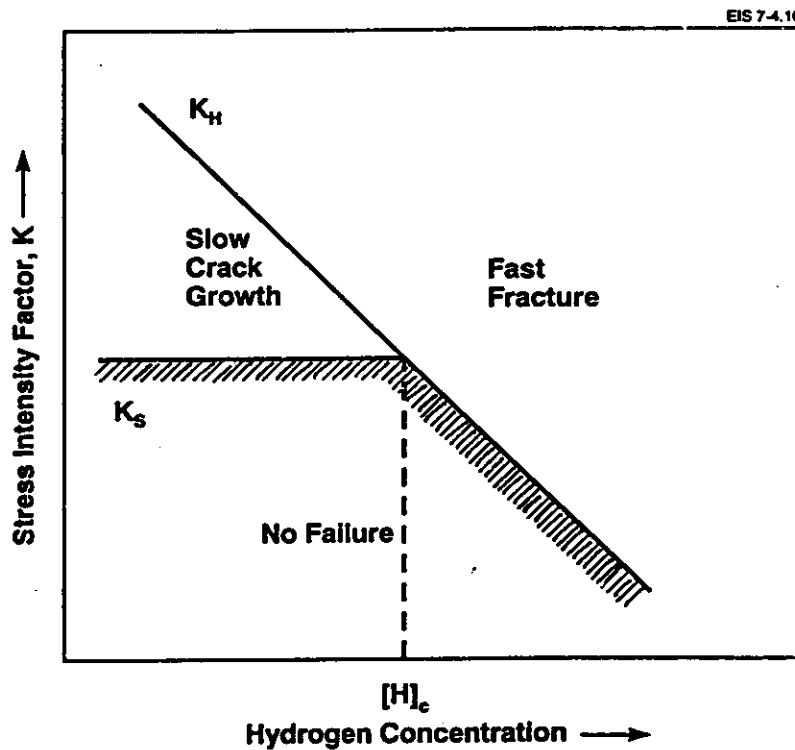
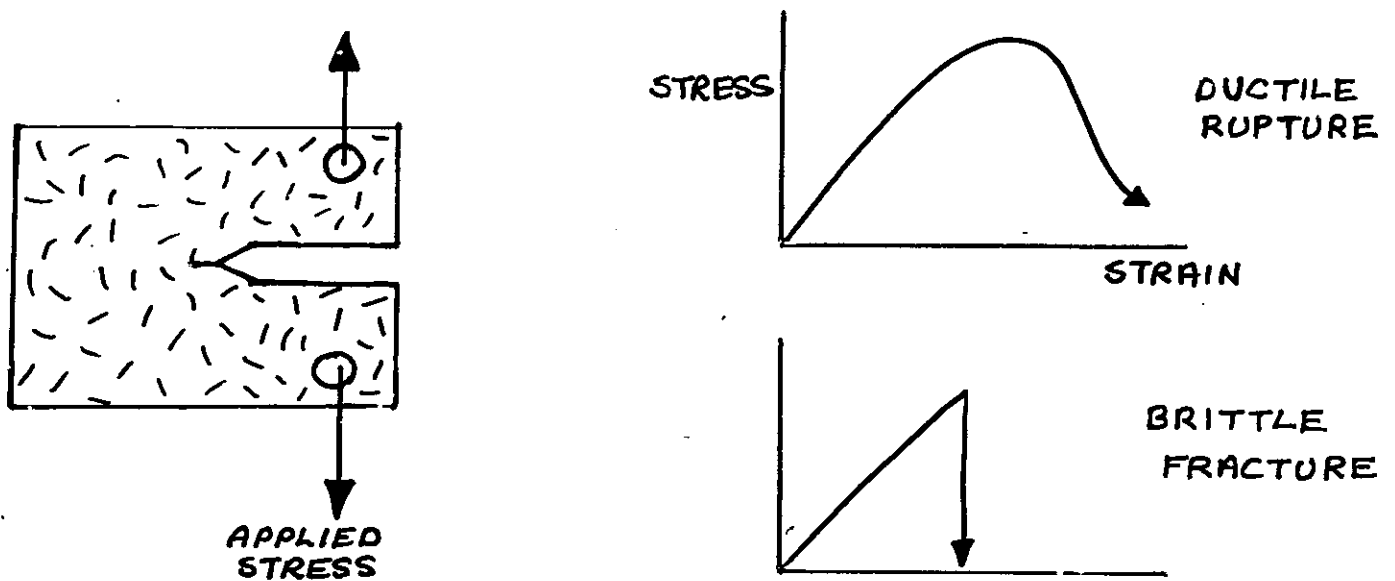


- 1 Hydrogen absorption rapid under acidic crevice conditions.
- 2 Hydrogen absorption slow or negligible under passive conditions.

Crack propagation occurs when the concentration of hydrogen in the metal is greater than the critical amount ($[H_c]$) required to make the material susceptible to HIC.

The container is then assumed to fail rapidly, since tensile stresses are assumed to be always sufficient to drive crack growth.

THE CRITICAL HYDROGEN CONCENTRATION IS DETERMINED USING SLOW STRAIN RATE TESTS ON COMPACT TENSION SPECIMENS PRELOADED TO A KNOWN HYDROGEN LEVEL.

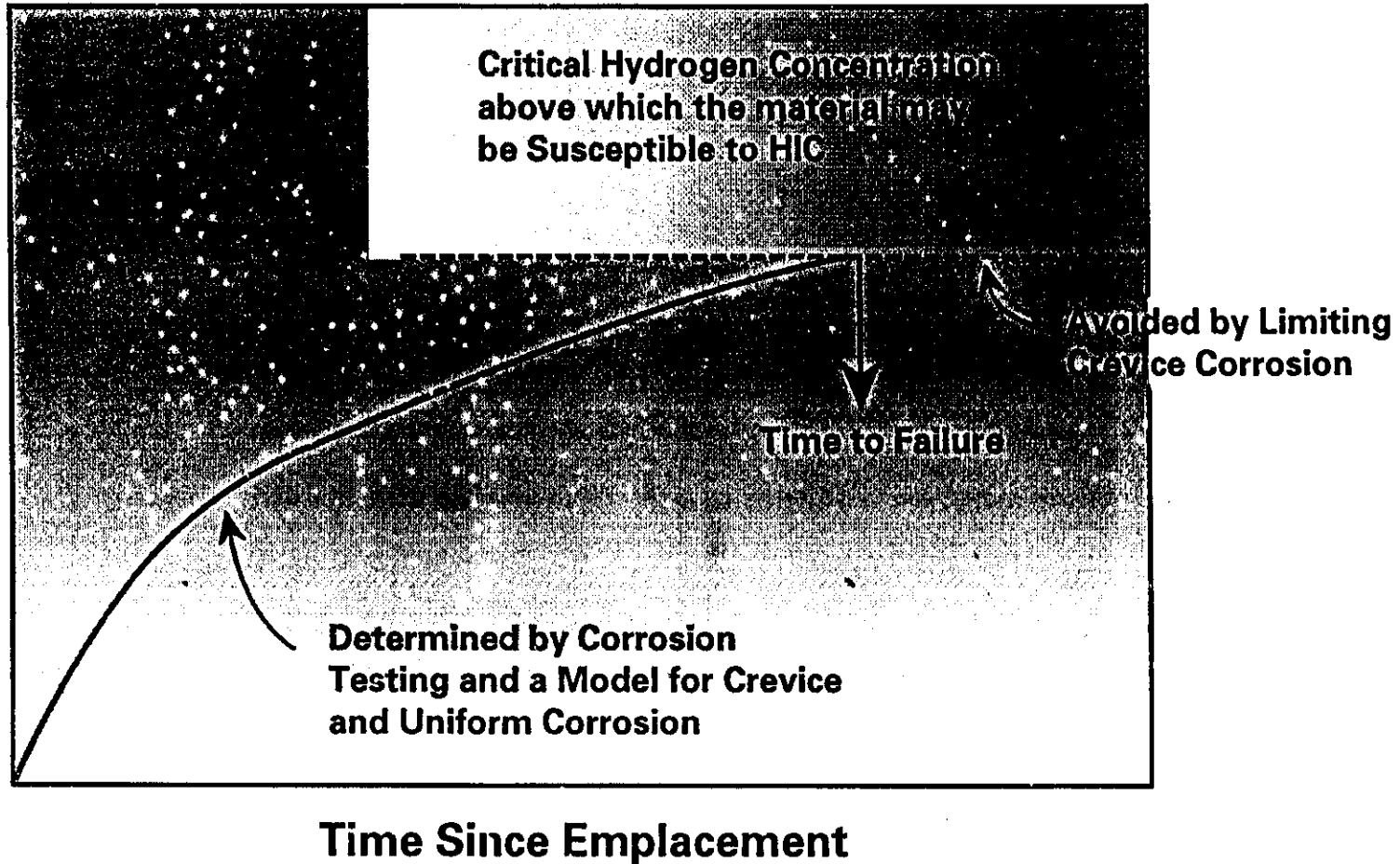


THE FRACTURE TOUGHNESS OF Ti-2 (AND Ti-12) ARE NOT SIGNIFICANTLY AFFECTED UNTIL THE HYDROGEN CONTENT EXCEEDS A CRITICAL VALUE.

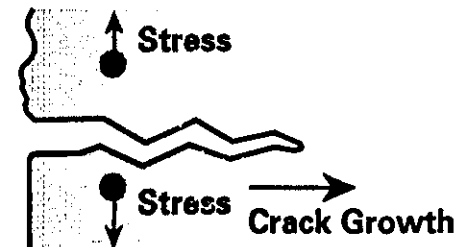
Clarke et al. CORR. SCI. 36, 487-509 (1994).

Criteria for Failure by Hydrogen Induced Cracking

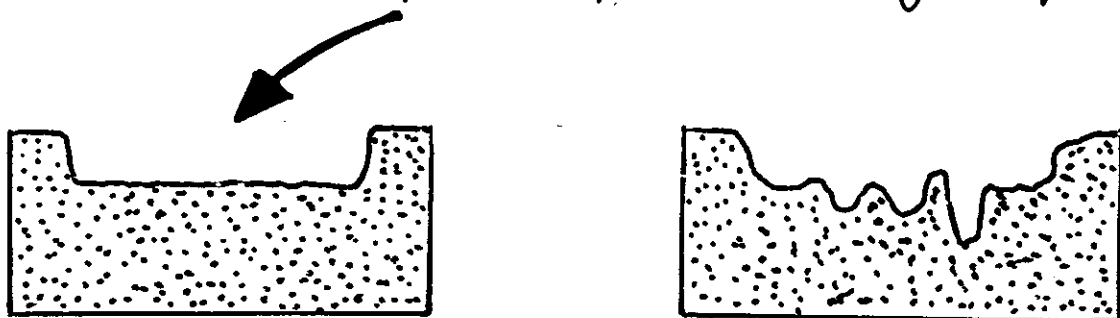
↑
Amount of
Hydrogen
absorbed by
the material



Since Crack Growth Rates could be fast and difficult to predict, we assume Failure occurs as soon as the material becomes susceptible



- The use of a propagation rate based on weight change measurements means
 - penetration within the crevice is assumed to proceed in the form of an averaged front.



Depth profiles on crevice-corroded specimens show this is not the case.

- Our procedure underestimates the early penetration rates within the creviced area.

ADOPT DAMAGE FUNCTION APPROACH.

- More empirical
- Avoids non-conservative underestimation of rate of penetration during the early stages of crevice propagation
- Determined by measuring the maximum depth of penetration as a function of exposure time or the amount of oxygen consumed.

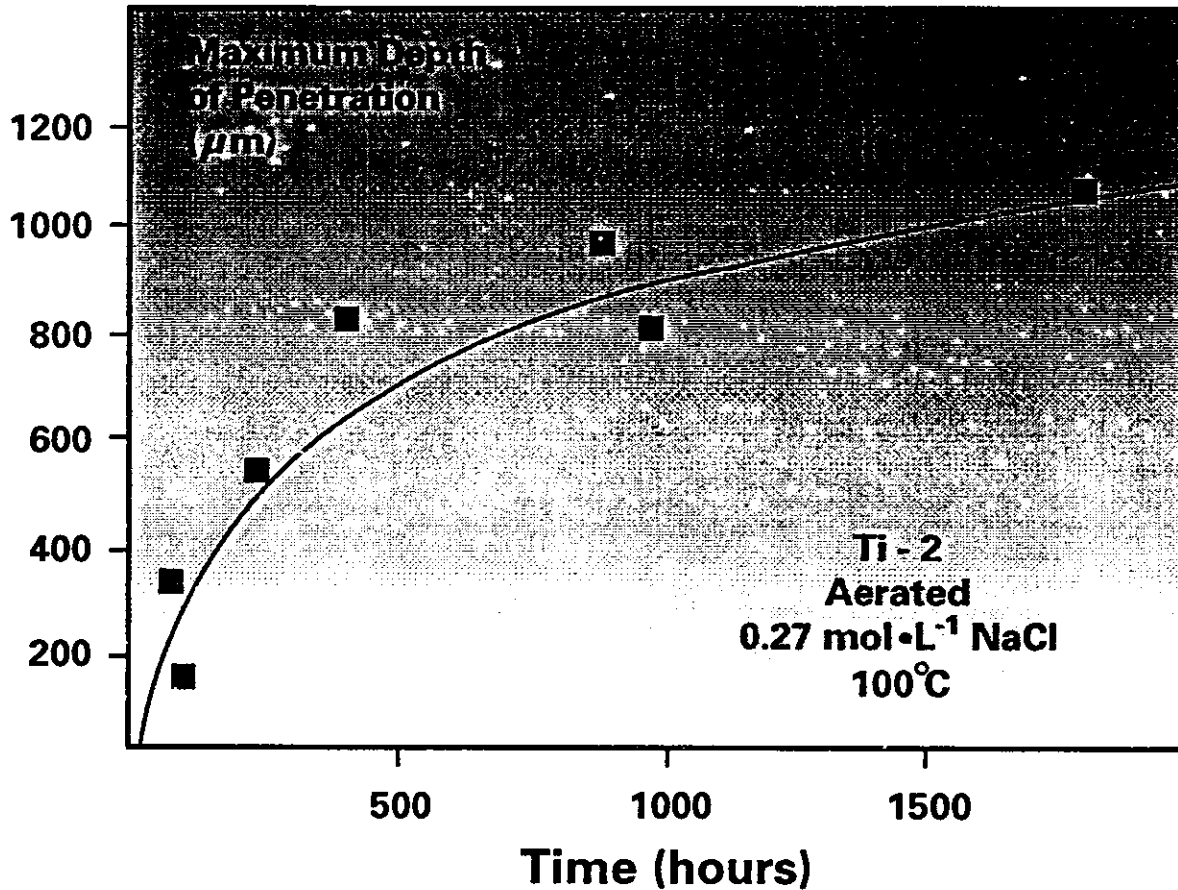


The measurement of corrosion penetration rates is a widely accepted procedure in determining lifetimes of corrodible structures and fitness for service guidelines.

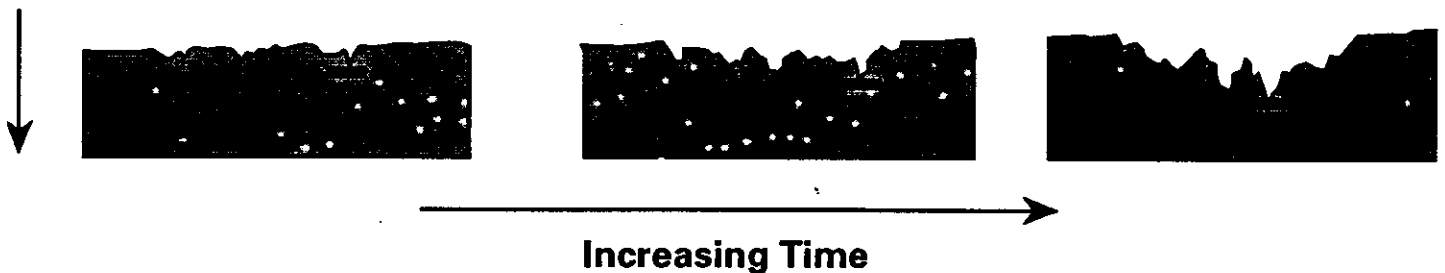
- **statistical analyses of pit depths.**
- **measurement of crack growth rates.**
- **This approach has been peer-reviewed in many publications, conference presentations and international workshops.**
- **A model based on the inability to initiate crevice corrosion has been developed for Ti-16 (0.06 wt % Pd), and is referenced in the Vault Model Report.**

A Totally Independent Procedure has Been used to check our Model Predictions

Development of a Damage Function



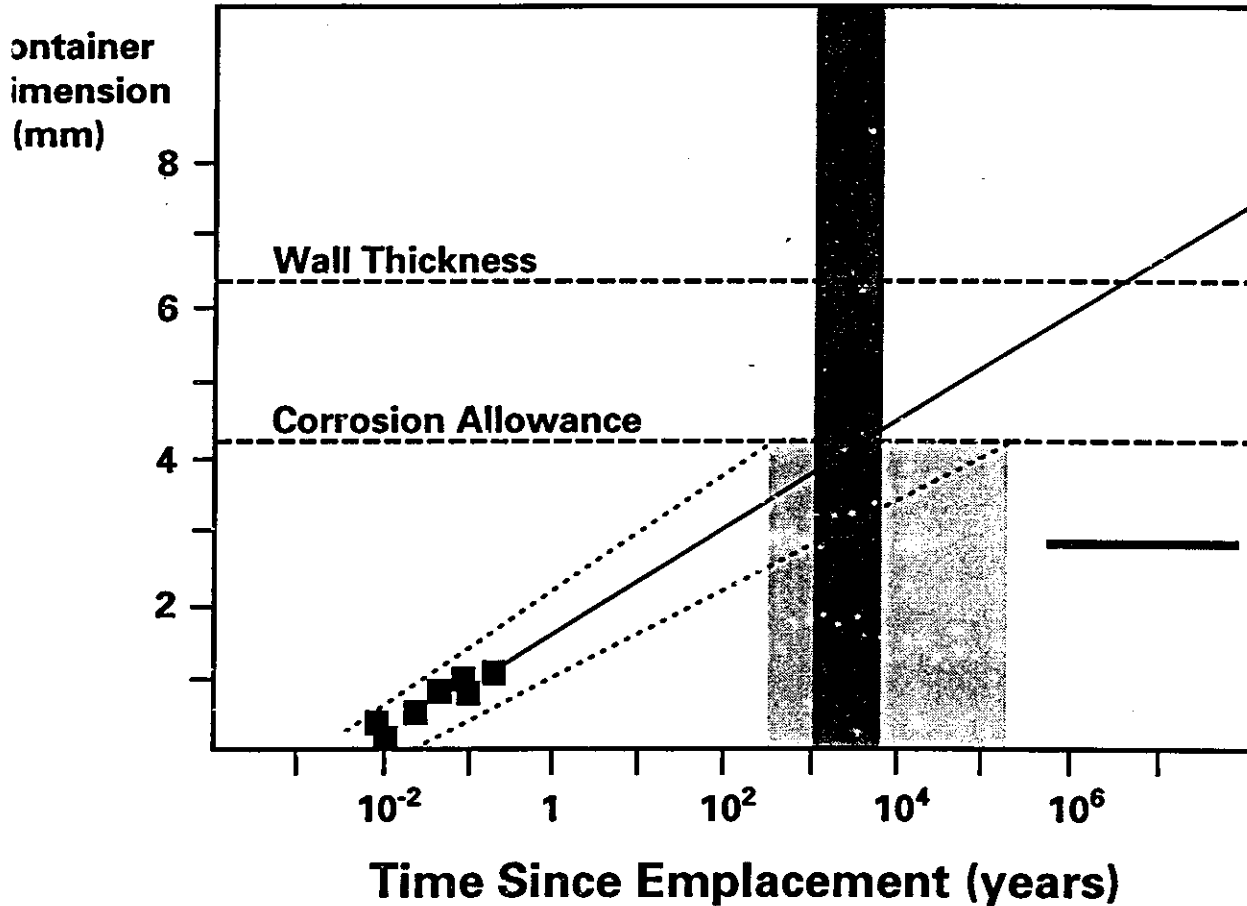
Maximum Depth






The Form of this Damage Function is common to many materials

- Pitting of Copper
- Underdeposit Corrosion/
Pitting of Carbon Steel
- Pitting of Stainless Steel

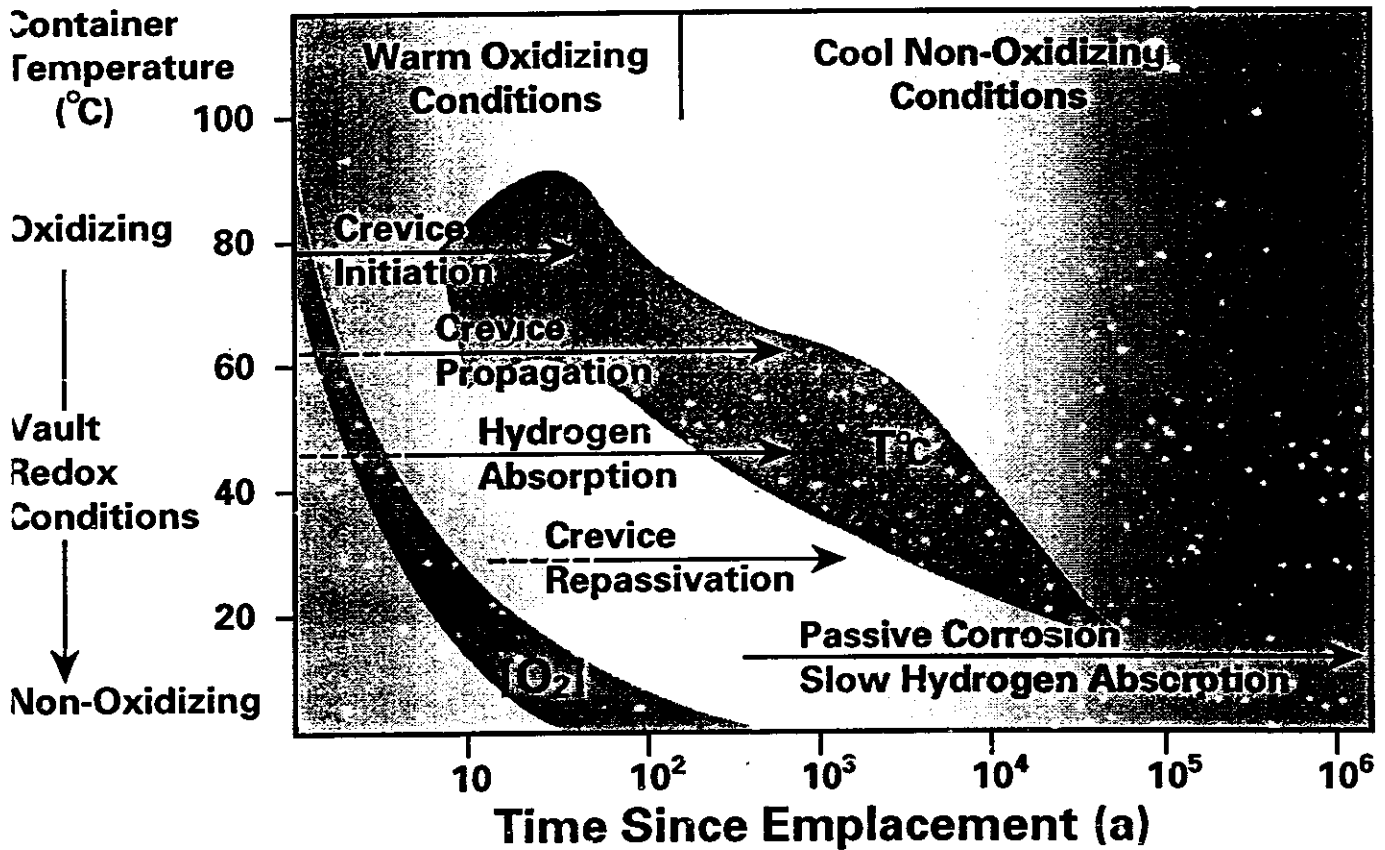
**Predictions of Container Lifetimes using
a Damage Function approach are consistent
with those of the Vault Model**



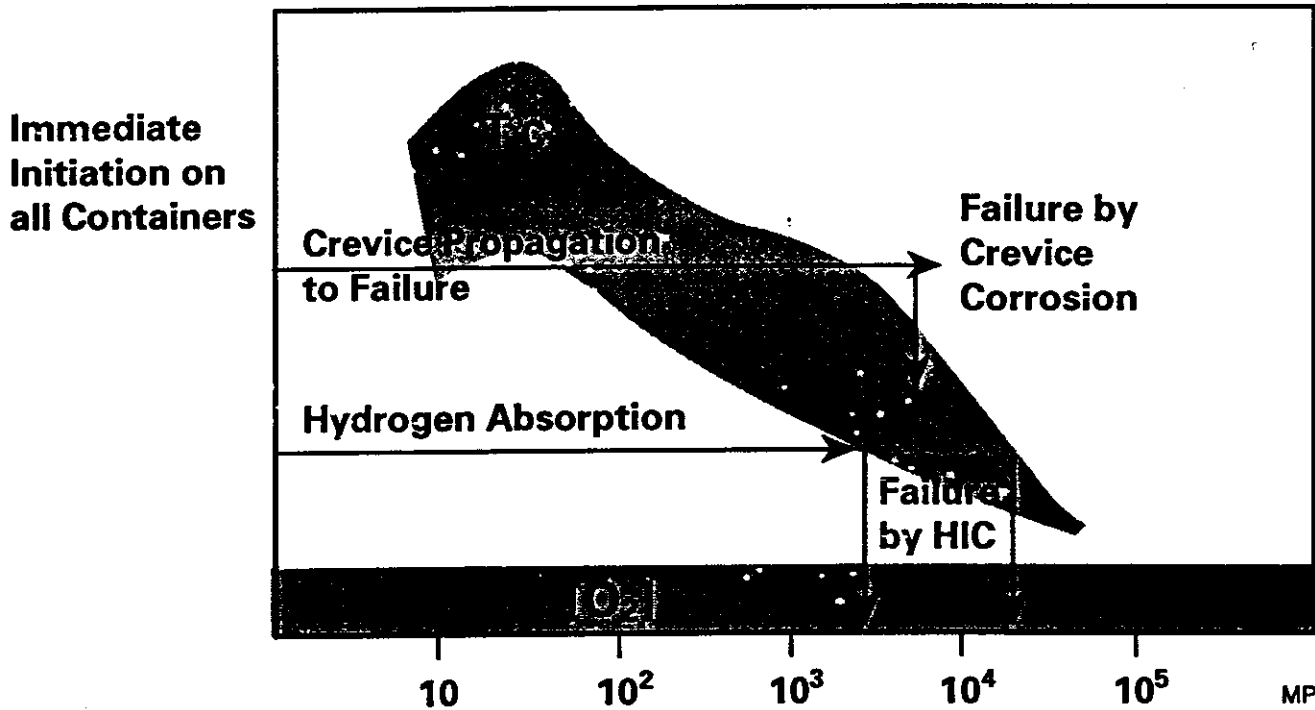
		Lifetimes
	Predictions from Vault Model	1200a - 7000a
	Predictions from Extrapolated Damage Function at 100°C	350a - 230000a
	Depth of penetration when all the O₂ available in a borehole has been consumed	

Evolution of Vault Conditions

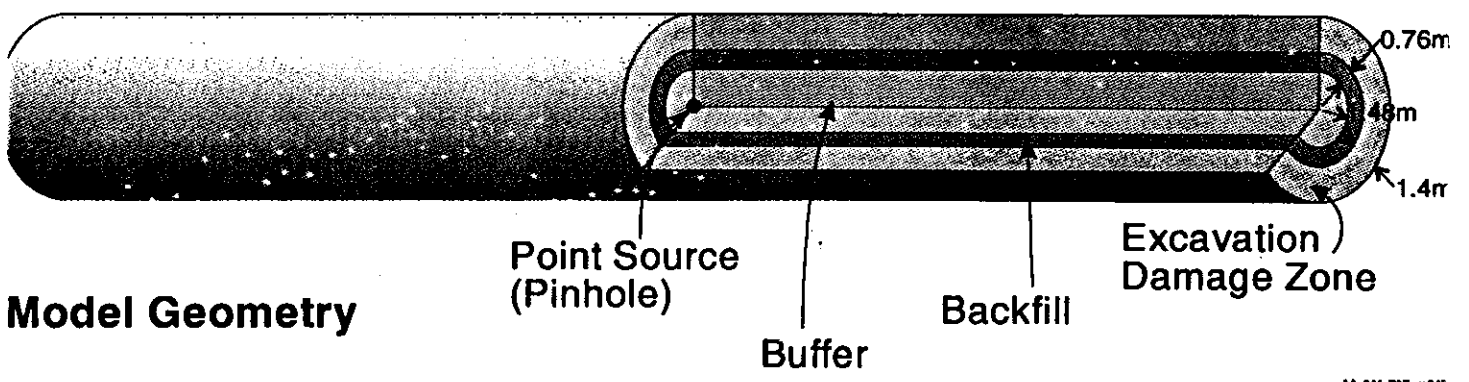
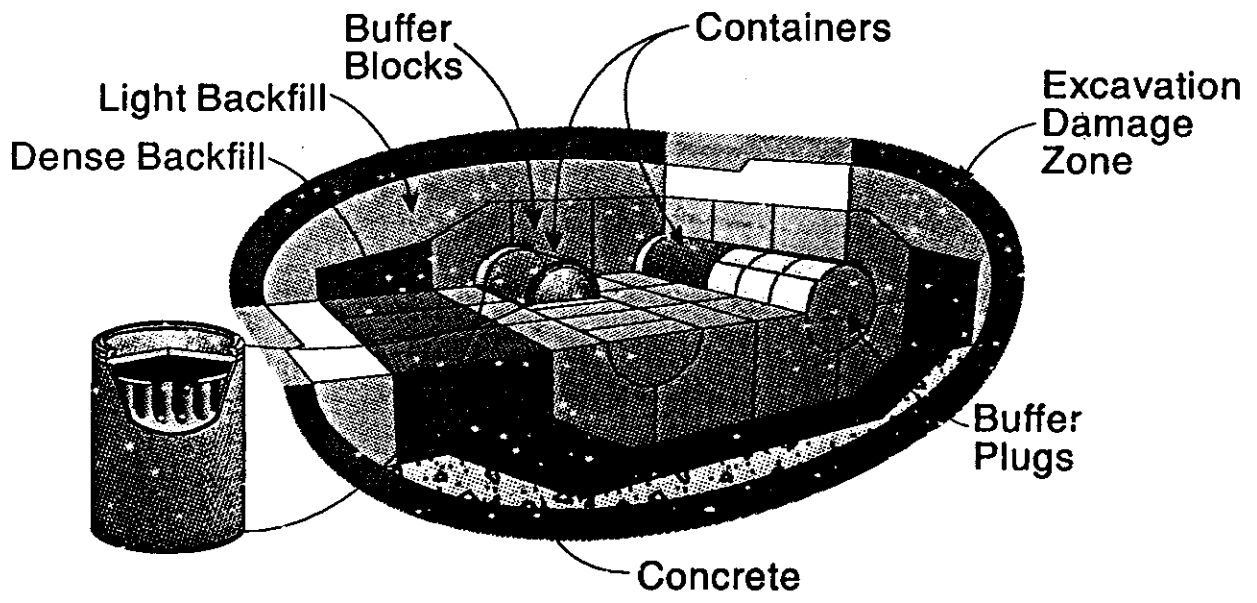
The Potential Corrosion Scenario



The Modelled Corrosion Scenario



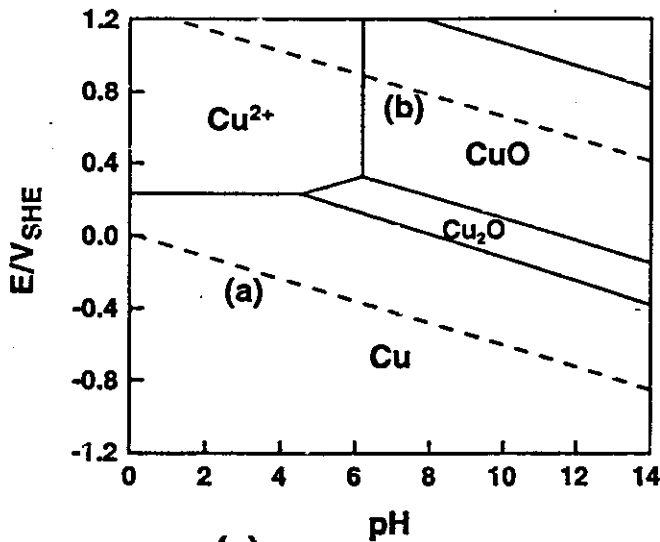
Physical Layout of Disposal Room



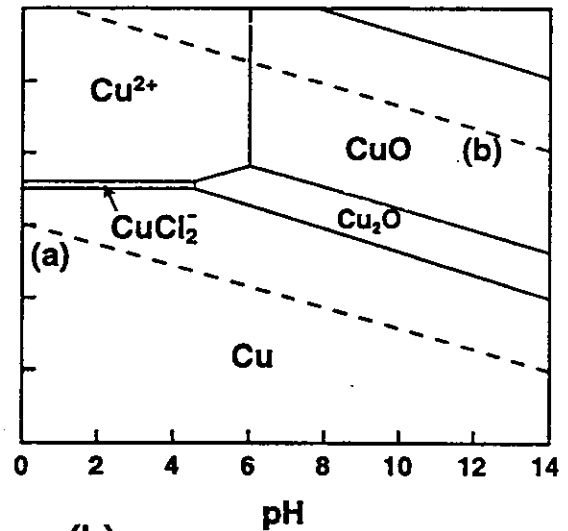
Model Geometry

THERMODYNAMIC POTENTIAL - pH DIAGRAMS FOR THE
 $\text{Cu}/\text{H}_2\text{O}/\text{Cl}^-$ SYSTEM FOR VARIOUS CHLORIDE CONCN'S.

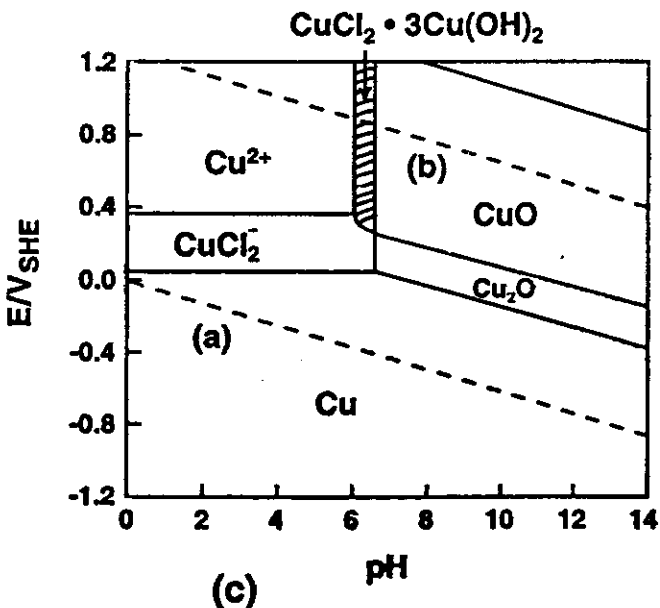
THE PHASES OBSERVED IN COPPER/CLAY CORROSION
 EXPERIMENTS ARE THOSE PREDICTED THERMODYNAMICALLY



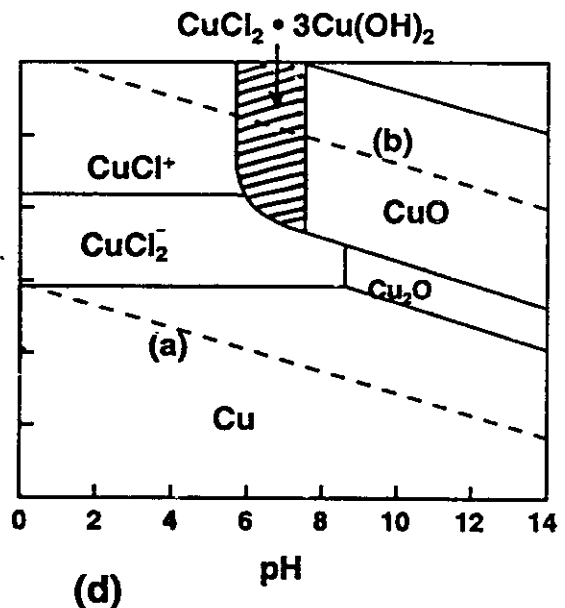
(a) $[\text{Cl}^-] = 10^{-3} \text{ mol. L}^{-1}$



(b) $10^{-2} \text{ mol. L}^{-1}$

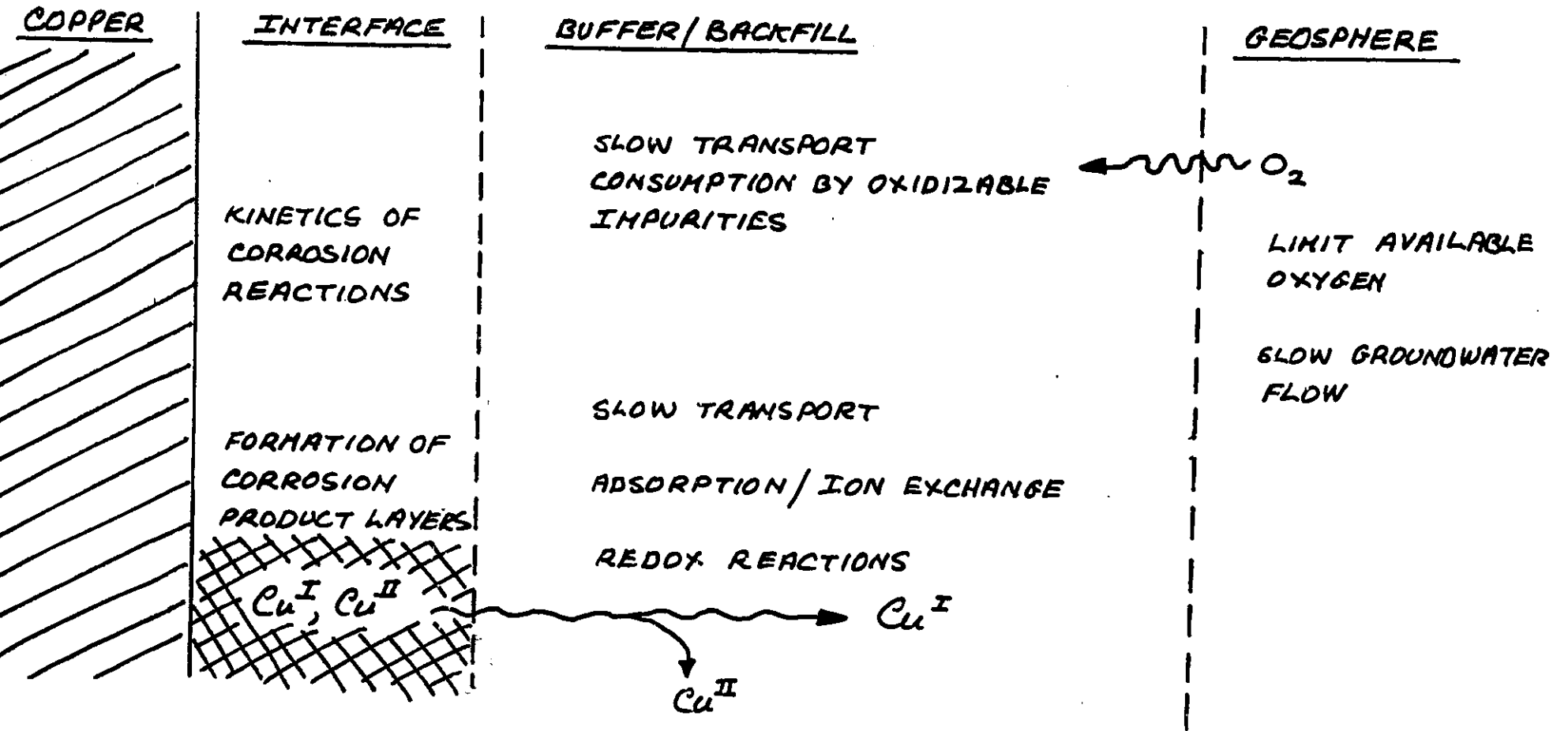


(c) $10^{-1} \text{ mol. L}^{-1}$

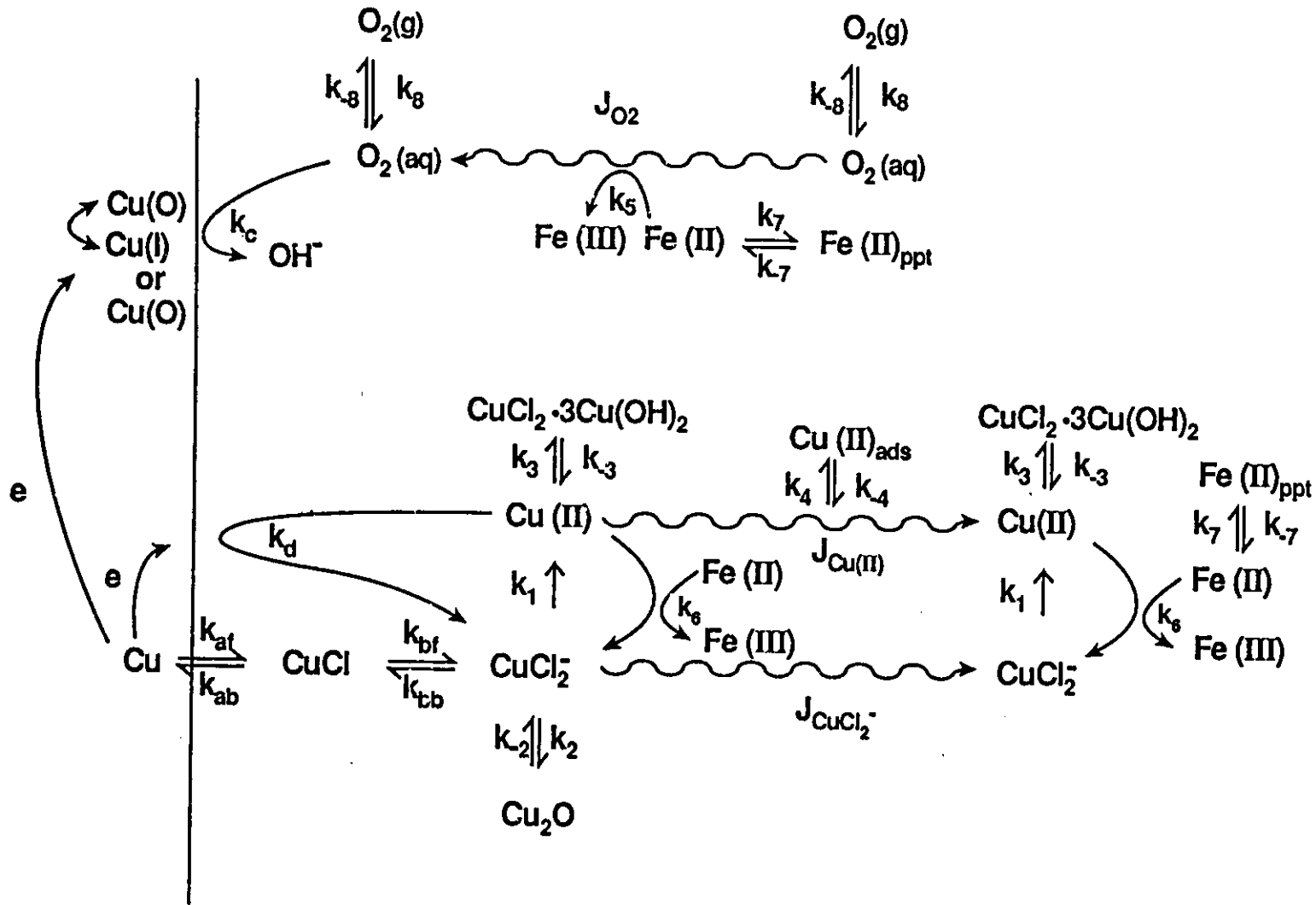


(d) 1.0 mol. L^{-1}

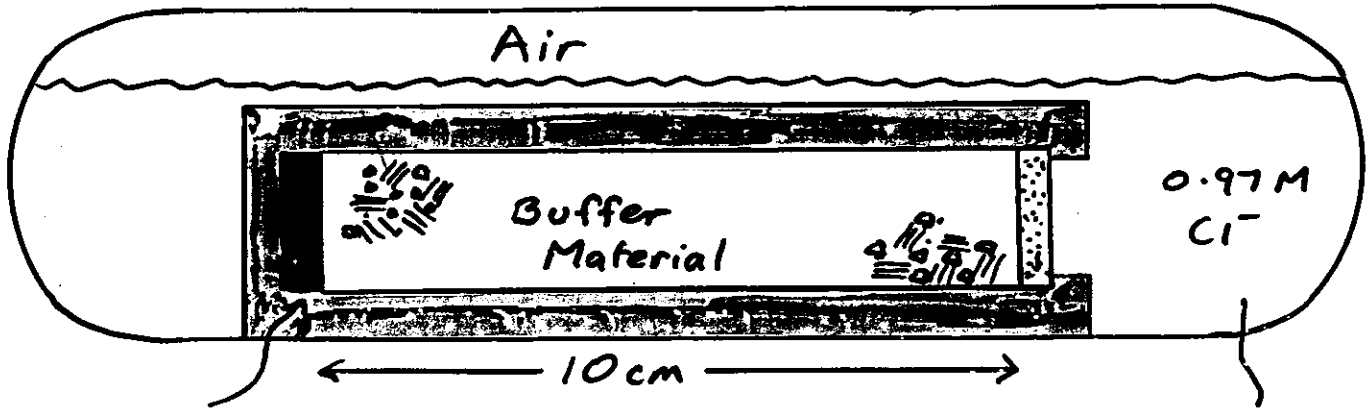
IMPORTANT PROCESSES IN THE CORROSION OF COPPER CONTAINERS



MECHANISM FOR THE CORROSION OF COPPER NUCLEAR WASTE CONTAINERS IN COMPACTED BUFFER MATERIAL IN CONTACT WITH O₂-CONTAINING CHLORIDE SOLUTION



CORROSION TESTS IN COMPACTED BUFFER



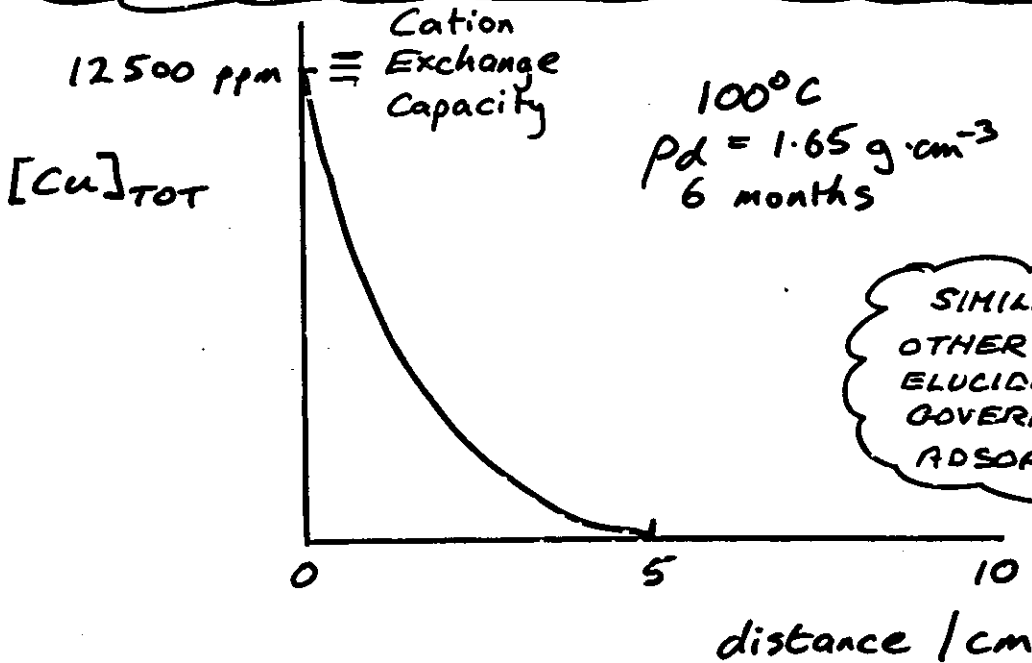
Cu disc

Standard
Canadian
Shield
Saline
Solution

Study profiles & wt. losses

$f(T, t, p_d, \gamma\text{-rad})$

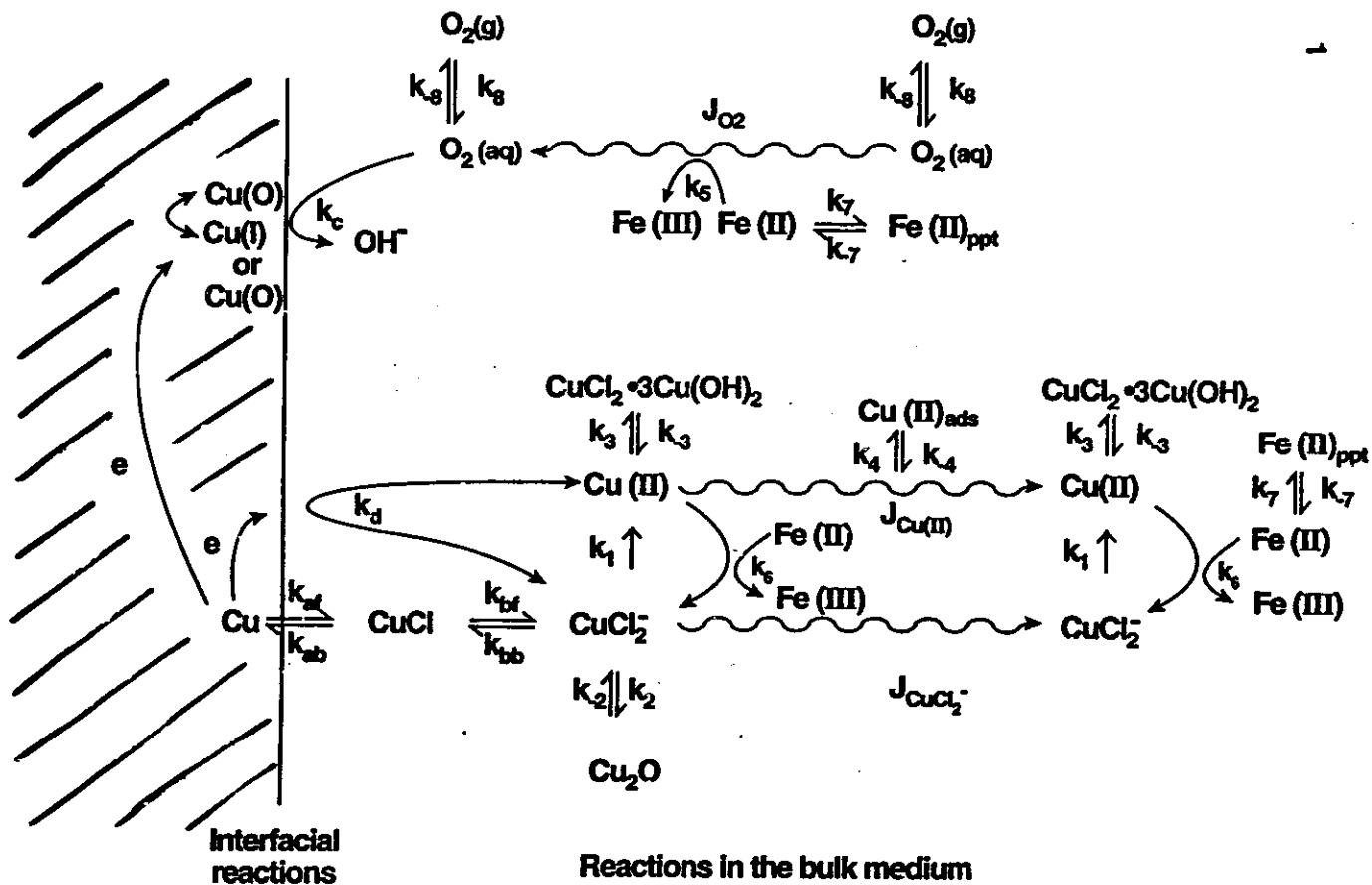
CONCENTRATION PROFILE OF COPPER ESTABLISHES THE BASIS FOR ADSORPTION-TRANSPORT MODELLING.



SIMILAR STUDIES WITH OTHER METALS WILL ELUCIDATE THE FACTORS GOVERNING TRANSPORT ADSORPTION PROCESSES

$$Q_{TOT}^{Cu} = Q_{Buffer}^{Cu} + Q_{Pore\ Water}^{Cu}$$

CORROSION OF COPPER CONTAINERS



	Buffer Material	Light Backfill	EDZ
	$[O_2] = 1.9 \times 10^{-3} M$ $A_{blotite} = 0$ $\epsilon_p \tau = 0.009$	$[O_2] = 5.8 \times 10^{-3} M$ $A_{blotite} = 0$ $\epsilon_p \tau = 0.015$	$[O_2] = 2.3 \times 10^{-4} M$ $A_{blotite} = 50 \text{ dm}^{-1}$ $\epsilon_p \tau = 4 \times 10^{-5}$
	$[O_2] = 1.9 \times 10^{-3} M$ $A_{blotite} = 7.9 \text{ dm}^{-1}$ $\epsilon_p \tau = 0.009$	$[O_2] = 1.6 \times 10^{-7} M$ $A_{blotite} = 0.5 \text{ dm}^{-1}$ $\epsilon_p \tau = 1.4 \times 10^{-5}$	

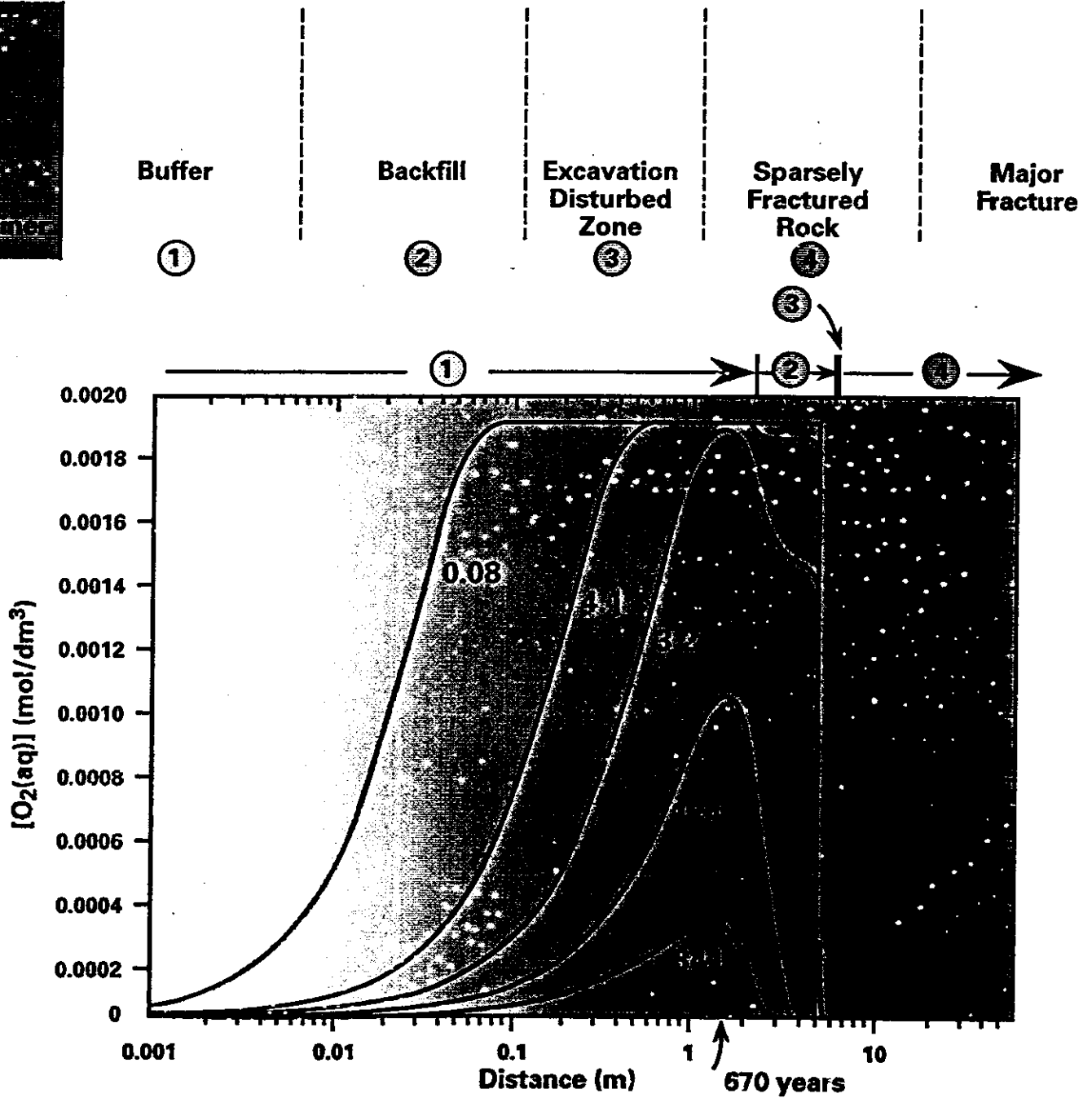
$$I_{CORR}/4F = \partial[O_2(0,t)]/\partial x$$

$$\partial[Fe(II)(0,t)]/\partial x = 0$$

$$[O_2] = 1.6 \times 10^{-7} M$$

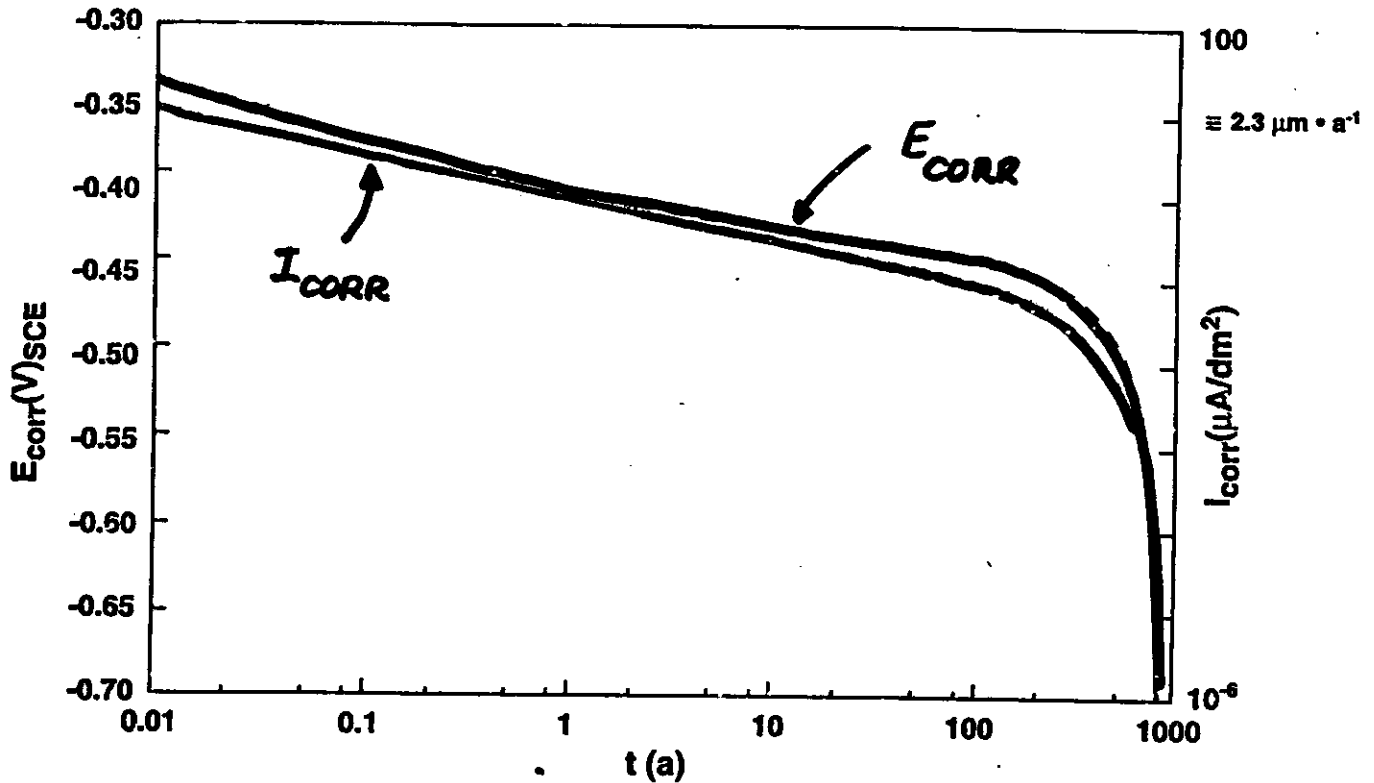
$$[Fe(II)] = \cdot \times 10^{-5} M$$

**The rate of consumption of oxygen for the in-room
Emplacement Configuration has been calculated using
a one dimensional representation of the
layers around the container**



(Calculation for 75°C; oxidation of organic material not included)

PREDICTED CORROSION POTENTIAL AND CORROSION CURRENT.



- Uniform corrosion effectively stops after O_2 consumed.
- Max wall penetration $\sim 38 \mu\text{m}$ (10^4 ya)
- Subsequent corrosion due to traces of O_2 in groundwater negligible upto 10^6 years.
- $E_{\text{corr}} \ll E_B, E_{\text{RP}}$; pitting should not occur.

TOTAL CORROSION ALLOWANCE REQUIRED FOR 10^6 years CONTAINMENT $\approx 7\text{mm}$.

CONTAINER DESIGN WALL THICKNESS 25mm.

Lifetime Predictions for Copper Containers



Detailed Modelling

Uniform corrosion

11 μ m

Pitting

Extreme-value statistical analysis

Max. pit depth after 10⁶a:

6.0mm

Total wall penetration

<7mm

Container lifetime

>10⁶a

Simple Modelling

Uniform corrosion

All O₂ trapped in vault (27 mol/container),
evenly distributed as Cu(I) over container

170 μ m

Pitting

Pitting factor of 5

Pit depth 0.85mm

Total wall penetration

<2mm

Container lifetime

>10⁶a

Evolution of Vault Conditions and Predicted Container Lifetimes

