### A

## REVIEW OF INDUSTRIAL CORROSION PROBLEMS IN SALINE ENVIRONMENTS

Conditions when corrosion problems expected are well understood. <u>CREVICE CORROSION</u>

- For Ti-2, high temperatures (>70°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°C
- Shallow pitting when embedded Fe particles present

page 18



## SEAWATER APPLICATIONS

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

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

\*\*(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 microand macrogrowth on metal surfaces

### A

### MICROBIALLY 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))



### A

# 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



**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.



#### 100 Т 80 Air-Saturated ŝ Conditions **Container Temperature** [Oxid] 60 g/Ĺ [Cr] 6 Vault redox Condition (f)Crevice 40 Initiation Groundwater Chloride Concentration **②** Crevice Propagation Hydrogen Absorption 20 (3) Crevice Repassivation **(4)** General Corrosion Anoxic Hydrogen Absorption (Reducing) **Conditions** 10<sup>2</sup> 10<sup>3</sup> 104 10 Time Since Emplacement (a)

Anticipated periods for Various Corrosion Processes









ACTIVATION ENERGY ~ 55 kJ. mol-1

CREVICE CURRENT FOR 'T'-12 ALMOST INDEPENDENT OF TEMPERATURE.

REPASSIVATION OF TE-12 OCCURS FOR TE 70°C.



**Assessment of Container Lifetimes** 

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 31.5	0.1 0.1	HIC HIC	1.4 x 10 <sup>6</sup> 2.0 x 10 <sup>4</sup>
Fi-16	0	4.3	0.44 1.4	0.1 0.1	HIC HIC	1.4 x 10 <sup>6</sup> 4.5 x 10 <sup>5</sup>





MP96-028.33

Ϊ.



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



Hydrogen absorption rapid under acidic crevice conditions.



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<sub>c</sub>]) 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 MYDROGEN 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



### **Time Since Emplacement**

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

show this is not the case.

Our procedure underestimates the early penetration rates within the crediced area.

#### ADOPT DAMAGE FUNCTION APPROACH.

- More empirical
- Avoids non-conservative underestimat of rate of penetration during the early stages of crevice propagatic

- 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.



— Pitting of Stainless Steel

MP96-028.9



#### **Evolution of Vault Conditions**





### **Physical Layout of Disposal Room**

.

THERMODYNAMIC POTENTIAL - pH DIAGRAMS FOR THE Cu/H20/CC SYSTEM FOR VARIOUS CHLORIDE CONC'NS.

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





IMPORTANT PROCESSES IN THE CORROSION OF COPPER

CONTAINERS



MECHANISM FOR THE CORROSION OF COPPER NUCLEAR WASTE CONTAINERS IN COMPACTED BUFFER HATERIAL IN CONTACT WITH O1 - CONTAINING CHLORIDE SOLUTION



CORROSION TESTS IN COMPACTED BUFFER





reactions





 $l_{\text{CORR}}/4F = \partial [O_2(0,t)]/\partial x$  $\partial [Fe(II) (0,t)]/\partial x = 0$ 

[O<sub>2</sub>] = 1.6x10<sup>-7</sup>M [Fe(II)] = `x10<sup>-5</sup>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)



TOTAL CORROSION ALLOWANCE REQUIRED FOR 10<sup>6</sup> years CONTRINMENT <57mm. CONTRINER DESIGN WALL THICKNESS 25mm.

## **Lifetime Predictions for Copper Containers**



#### Detailed Modelling Uniform corrosion

11µm

#### Pitting

and the

Extreme-value statistical analysis Max. pit depth after 10<sup>6</sup>a: 6.0mm

Total wall penetration <7mm

Container lifetime >10<sup>6</sup>a <u>Simple Modelling</u> <u>Uniform corrosion</u> All O<sub>2</sub> trapped in vault (27 mol/container), evenly distributed as Cu(I) over container

170µm

Pitting Pitting factor of 5

Pit depth 0.85mm

<u>Total wall penetration</u> <2mm

Container lifetime >10<sup>6</sup>a



**Time Since Emplacement (a)**