Tests to Explore Specific Aspects of the Corrosion Resistance of C-22

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Main/Legacy - 20

Preliminary Tests in Aggressive Environments

- Purpose of tests was to determine in a preliminary fashion whether species such as lead, mercury, arsenic or sulfides could aggravate corrosion of C-22 (e.g., SCC, pitting or crevice corrosion).
- Tests explored acid and caustic environments with and without lead, mercury, arsenic and sulfides.
- Tests of U-bends, mostly at 250 °C.
- Tests of static disks at 163°C

Species Concentration in Simulated 1000x J-13 Concentrate

Species	Concentration (ppm)
Ca^{2+}	30
Cl^{-}	6123
F^{-}	1550
C	1546
Si	8404
K^{+}	4792
NO^{3-}	6729
Na^{+}	44082
SO_4^{2-}	15711
Li^{+}	36
B	17

U-Bend Tests - Matrix and Results

Sample ID	Temperature (°C)	pH_{RT}	pH_T	Weld?	Minerals?# (10g/Vessel)	Tuff? (10g/Vessel)	Accelerant •	Potential	Duration (days)	Results
1	250	2.6*	5.6	no	yes	no	none	---	32	tarnished
2	250	2.6*	5.6	no	no	no	none	---	32	slight pitting
3	250	12.5	9.6	no	yes	no	none	---	32	tarnished
4	250	12.5	9.6	no	no	no	none	---	32	tarnished
5	RT	2.6*	2.6	no	yes	no	H_2	---	61	none
11	200	12.5	9.8	no	yes	yes	none	---	35	none
12	250	0.53†	1.6	no	no	no	Pb	---	15	through specimen crack
14	250	11.92	9.6	no	no	no	S	---	21	tarnished
15	250	1.32†	4.53	no	no	no	Hg	---	8	very severe pitting
W-1	250	2.6*	5.6	yes	yes	no	none	---	32	tarnished
W-2	250	2.6*	5.6	yes	no	no	none	---	32	slight pitting
W-3	250	12.5	9.6	yes	yes	no	none	---	32	tarnished
W-4	250	12.5	9.6	yes	no	no	none	---	32	tarnished
W-5	RT	2.6*	2.6	yes	yes	no	H_2	---	61	none
W-13	200	12.5	9.8	yes	yes	yes	none	+200mV	35	none
W-14	250	12.11	9.6	yes	no	no	Pb	---	29	tarnished
W-15	250	0.59†	1.6	yes	no	no	S	---	29	severe pitting

* with sulfuric acid; † with hydrochloric acid;

• Hydrogen Gas Saturated and Over-Laid; Lead Acetate at 5000 ppm Pb;
Sodium Sulfite at 3200 ppm S; Mercury Acetate at 6300 ppm Hg;

mineral mixture consists of 70% pyrite (FeS_2), 20% galena (PbS)
5% cinnabar (HgS) and 5% realgar (As_2S_2)

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U-Bend Tests - Matrix and Results (Cont.)

Sample ID	Temperature (°C)	pH_{RT}	pH_T	Accelerant	Duration (days)	Concentration in Post Test Solution (mg/L or ppm)					% Weight Lost	Results
						Cr	Ni	Fe	Mo	Pb		
1	250	2.6	5.6	none	32	3	70	120.5	NM	3.1	0.14	tarnished
2	250	2.6	5.6	none	32	21	39	3.2	NM	0.6	0.10	slight pitting
3	250	12.5	9.6	none	32	1	1.2	0.35	NM	0	0.00	tarnished
4	250	12.5	9.6	none	32	43	1.4	0.45	NM	0.65	0.00	tarnished
5	RT	2.6	2.6	H_2	61	3.4	19	82	0.7	5.85	0.00	none
11	200	12.5	9.8	none	35	0.8	0.7	1.1	3.1	7.3	0.00	none
12	250	0.53	1.6	Pb	15	16	3217	857	31	NM	0.88	through specimen crack
14	250	11.92	9.6	S	15*	2	0.8	6.3	21	NM	0.00	tarnished
15	250	1.32	4.53	Hg	8	5.1	413	65	151	12.1	0.54	very severe pitting
W-1	250	2.6	5.6	none	32	3	70	120.5	NM	3.1	0.12	tarnished
W-2	250	2.6	5.6	none	32	21	39	3.2	NM	0.6	0.13	slight pitting
W-3	250	12.5	9.6	none	32	1	1.2	0.35	NM	0	0.00	tarnished
W-4	250	12.5	9.6	none	32	43	1.4	0.45	NM	0.65	0.00	tarnished
W-5	RT	2.6	2.6	H_2	61	3.4	19	82	0.7	5.85	0.00	none
W-13	200	12.5	9.8	none	35	0.8	0.7	1.1	3.1	7.3	0.00	none
W-14	250	12.11	9.6	Pb	29	117	0.3	1.8	91	1311	0.00	tarnished
W-15	250	0.59	1.6	S	29	15	2574	507	0.1	4.4	0.42	severe pitting

* mid-test sample, not post-test solution

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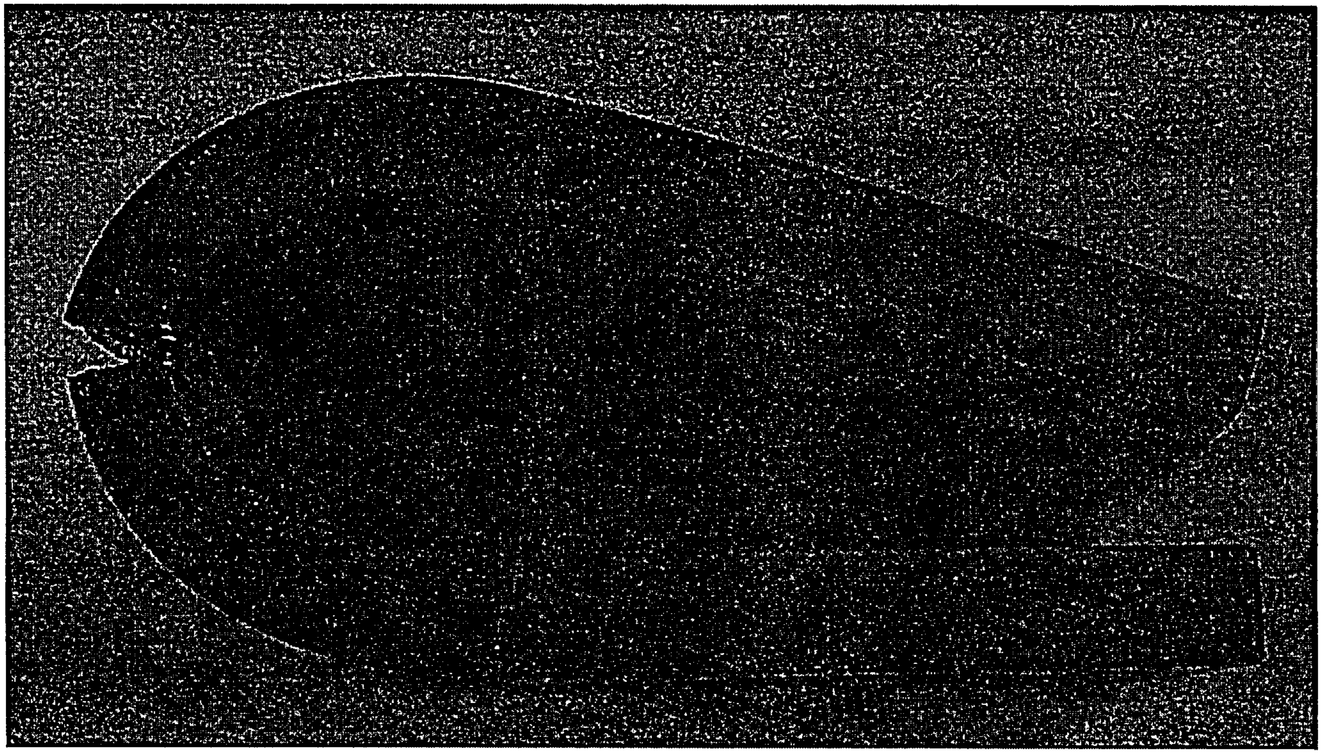
Sample 12 (Lead-Acid)



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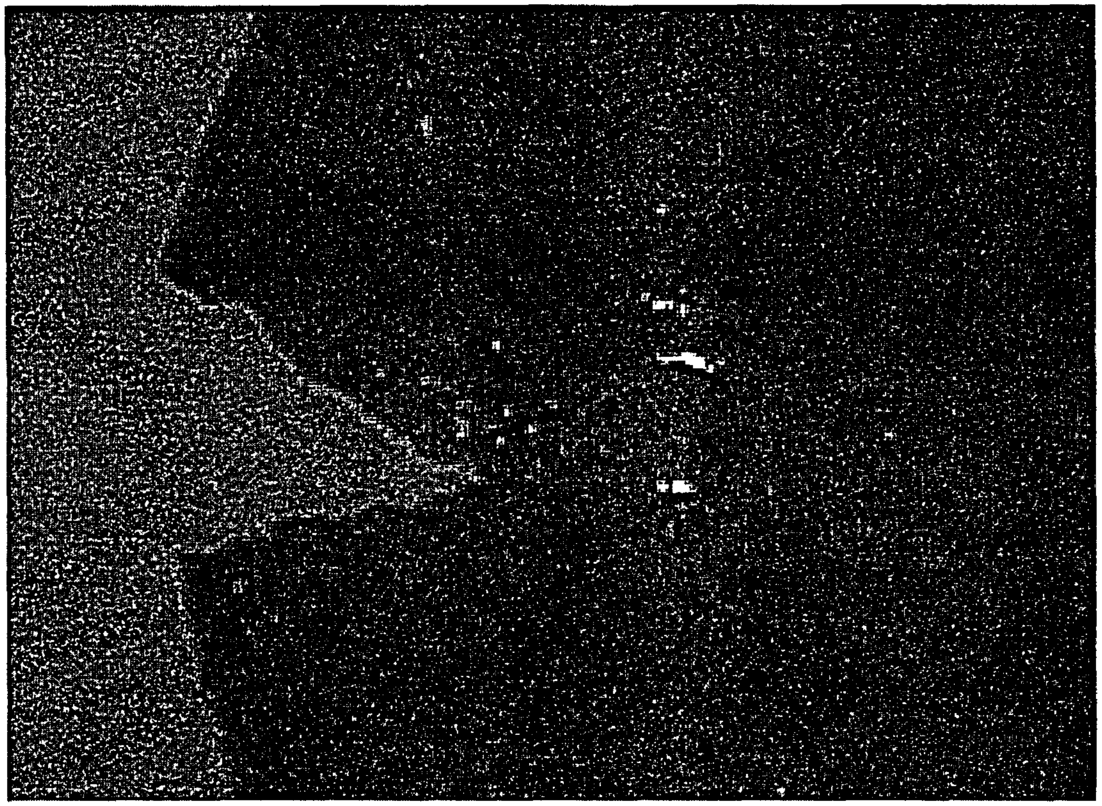

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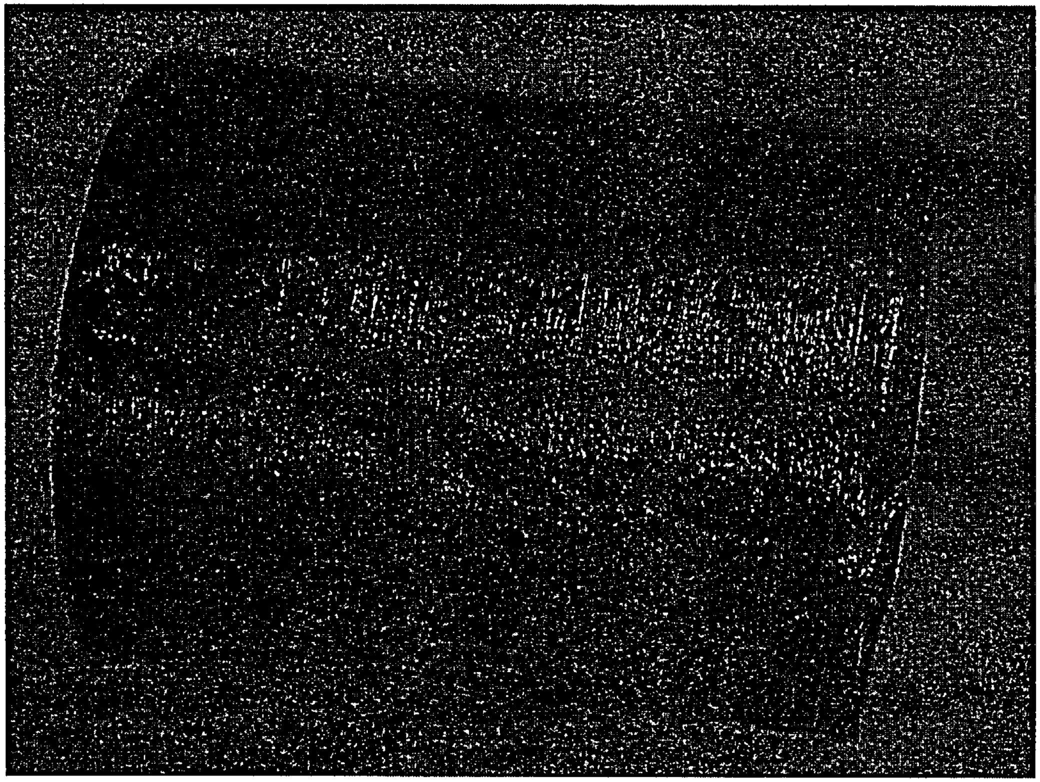

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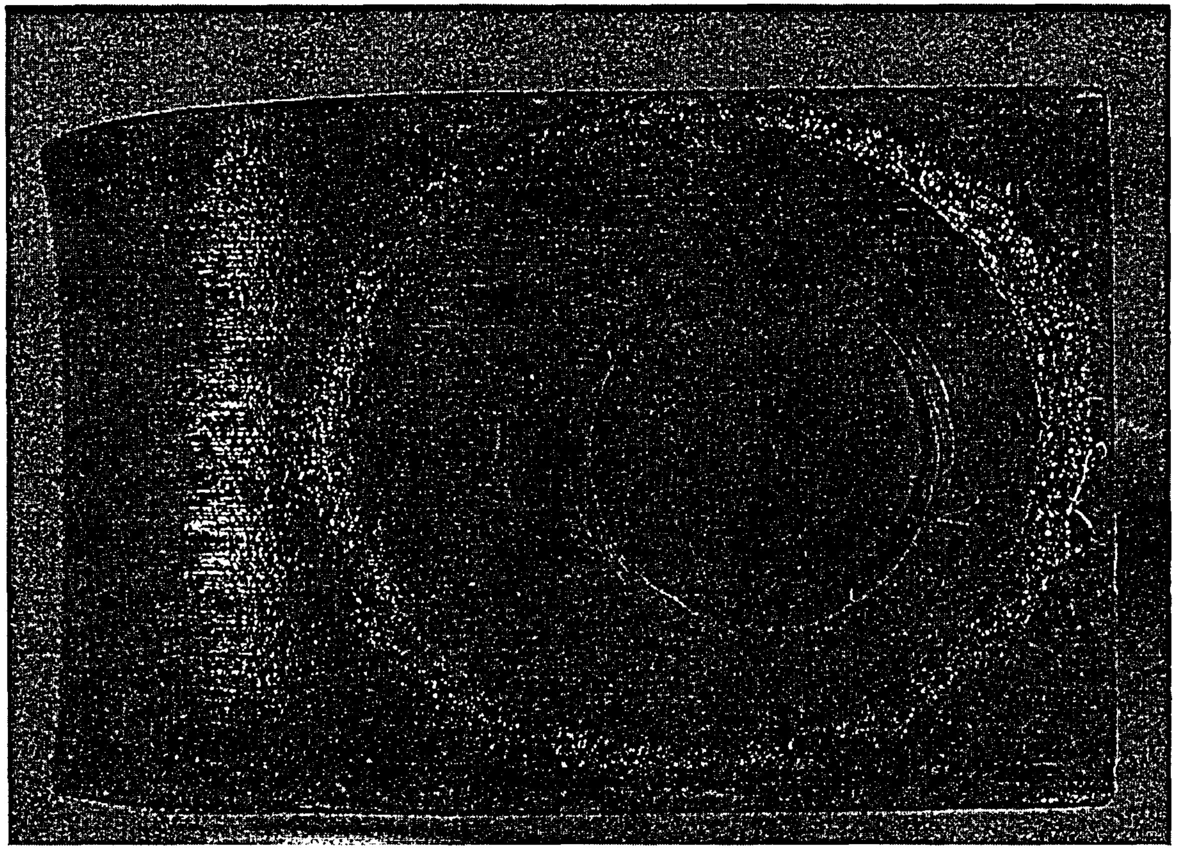

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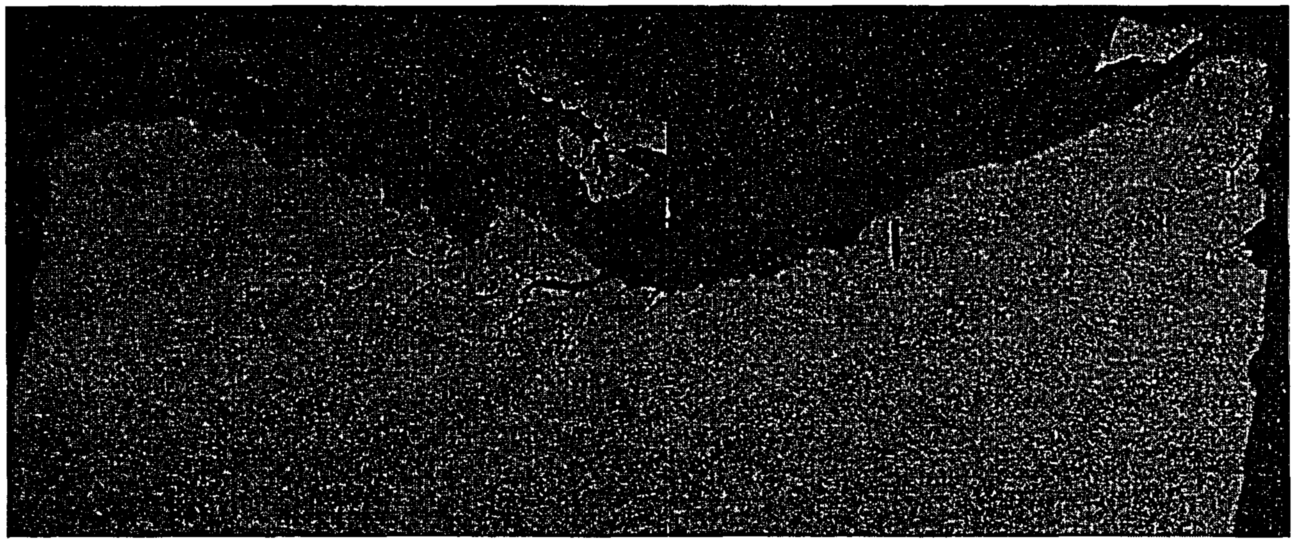

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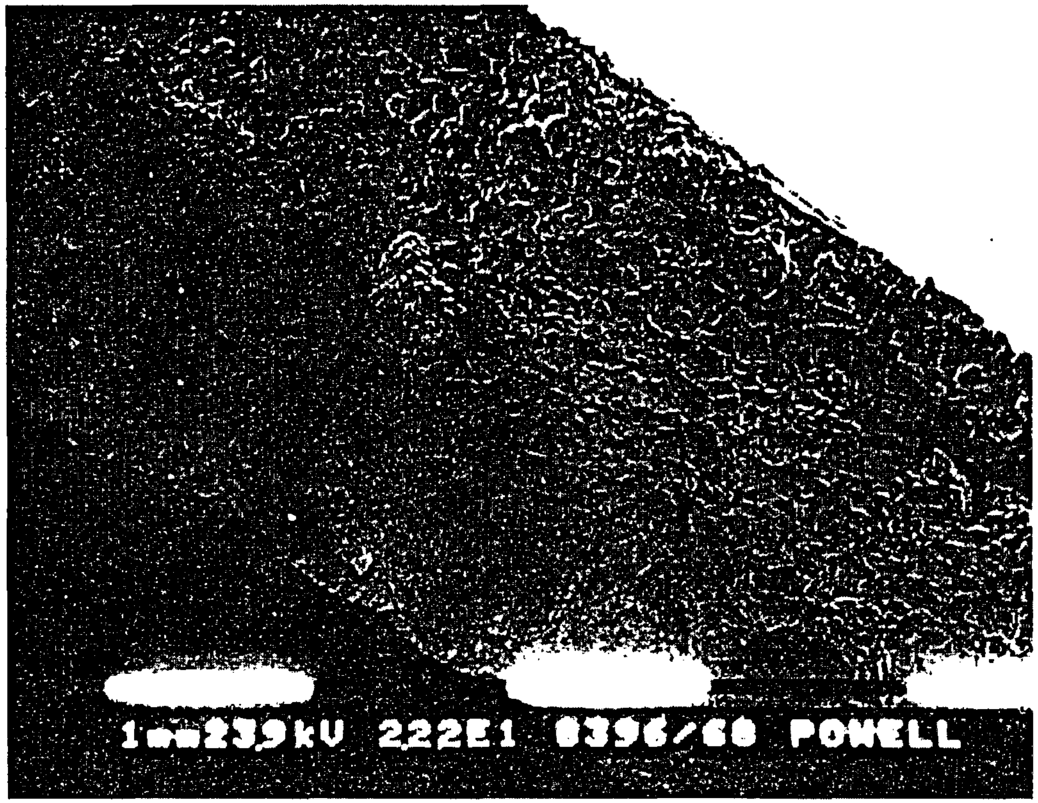
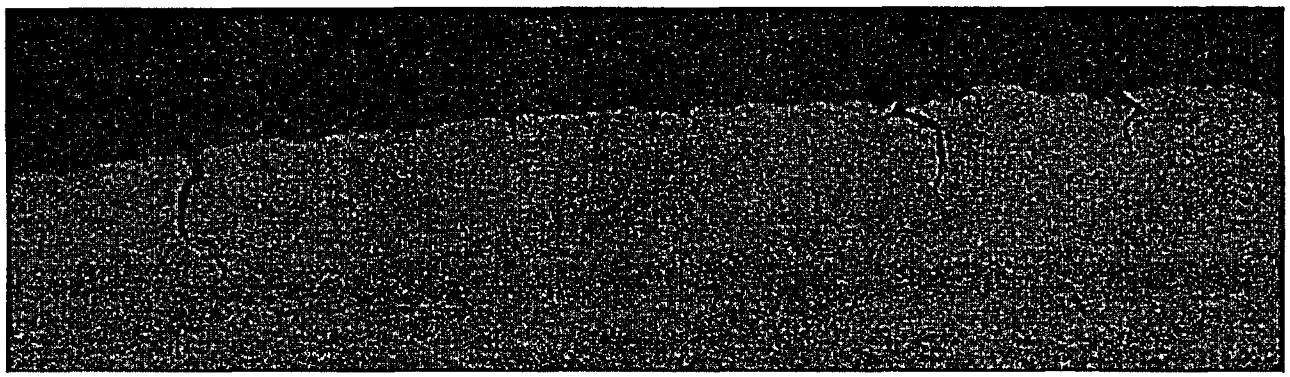
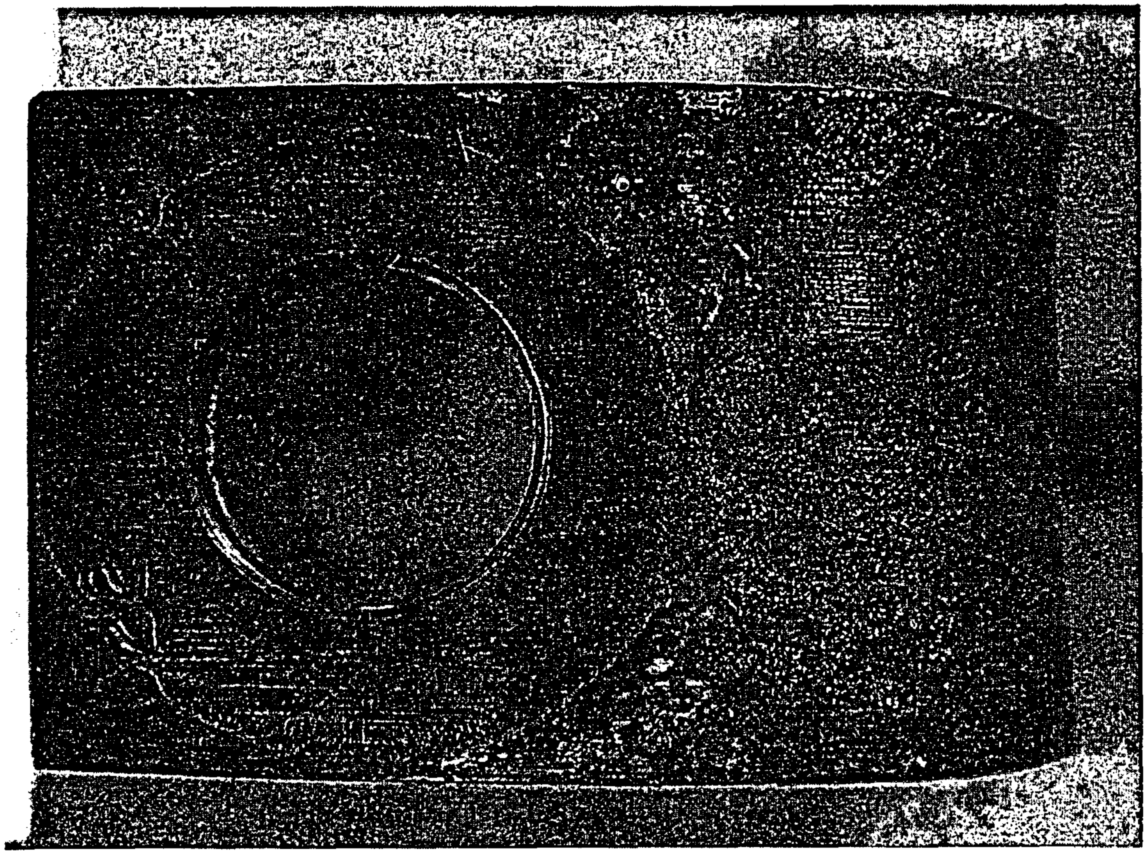


Sample 12 (Lead-Acid)



Sample 15 (Mercury-Acid)



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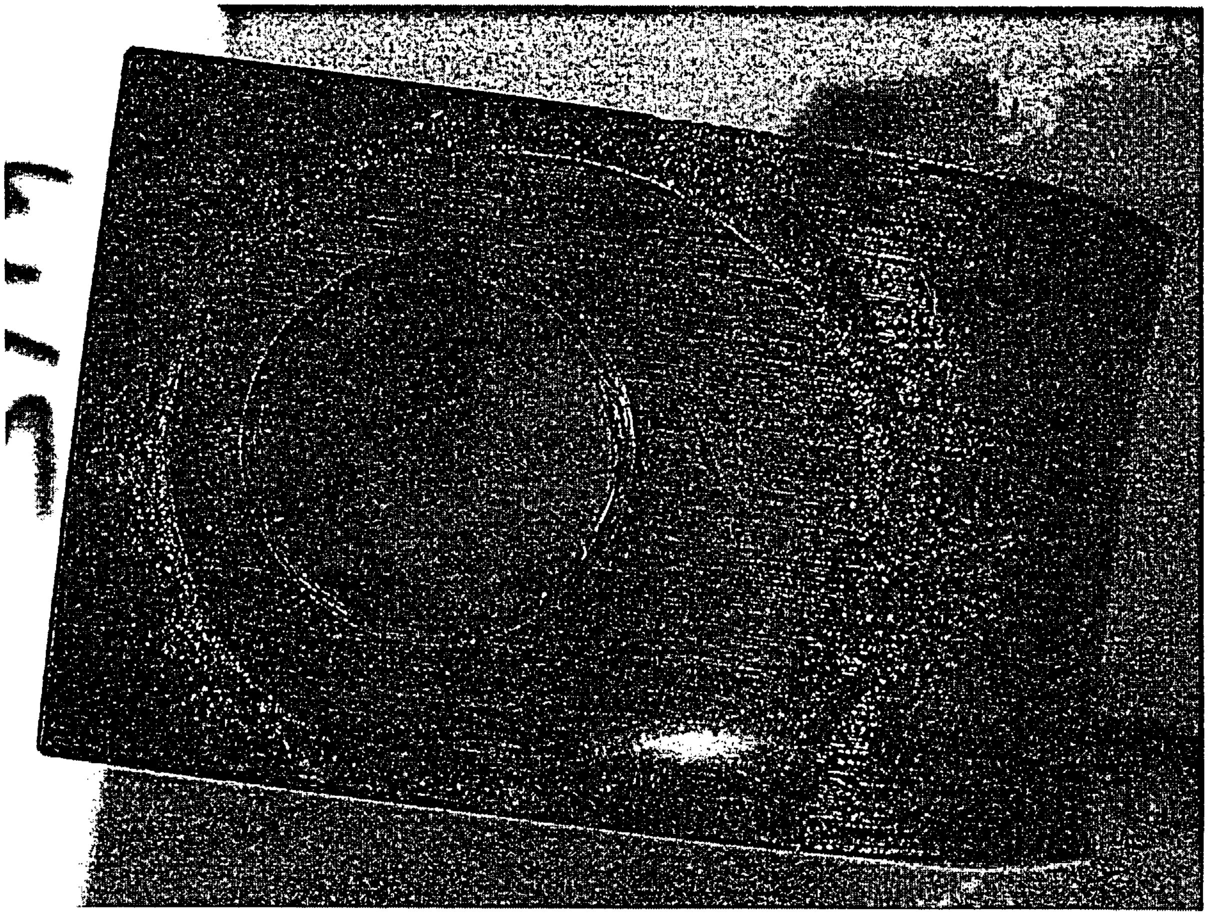
Sample W-15 (Sulfur-Acid)



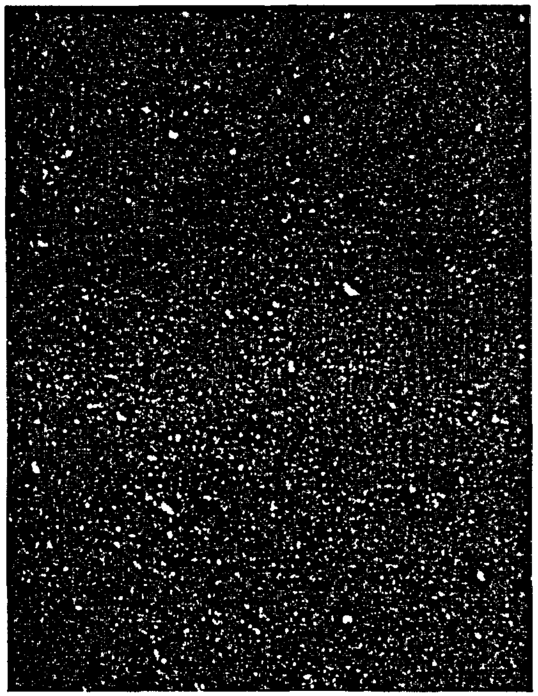
Concentrations of Main Alloying Elements After Testing

Tests of C-22 Unstressed Disks, 20 mL of solvent, 163°C, 15 days

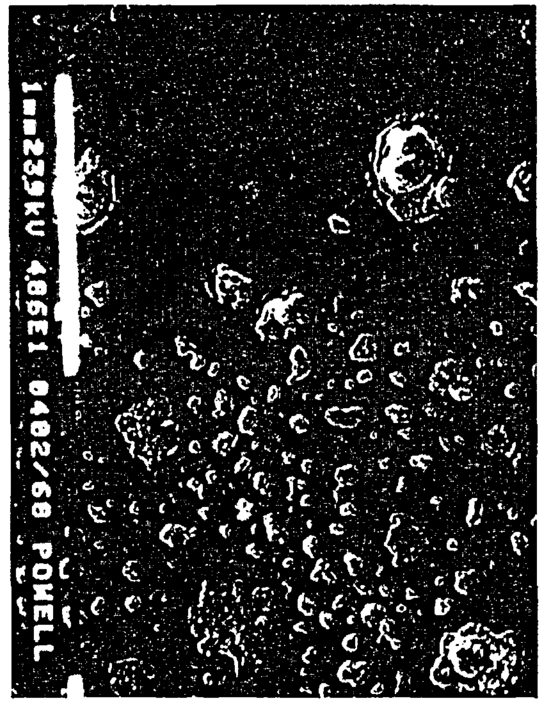
Additives to 1000x J-13 Water	pH_{RT}	Concentrations (mg/L or ppm)			
		Cr	Ni	Fe	Mo
2.25% H_2O_2	12.89	3.8	0.7	1.5	3.3
3.86% $Pb(OAc)_2$	13.15	4.3	0.5	0.2	4.1
4.34% $CuCl_2$	13.21	2.7	0.4	0.4	2.1
4.50% $Na_2CO_3 \cdot 1.5H_2O_2$ + 1.93% Na_2SiO_3	13.25	4.4	0.8	2.5	3.3
3.50% As_2O_3	12.90	1.8	0.7	1.3	1.4
4.50% $FeCl_3$	13.17	1.2	0.3	0.4	2.3
none	13.20	2.8	1.0	2.1	2.3
4.0% $Hg(OAc)_2$	13.15	75.9	0.7	4.2	60.9
3.86% $Pb(OAc)_2$ + H_2SO_4	2.52	250.4	1868.8	7.0	22.0
4.0% $Hg(OAc)_2$ + H_2SO_4*	2.65	421.5	1727.5	48.8	266.3

* Test duration only 7 days

Sample C20 (Lead-Acid)



Stereomicroscope



SEM

Main Findings - Tests of U-Bends

30-day tests were conducted on stressed U-bend samples in modified 1000x concentrated J-13 water at 250°C

- Acidified solution (pH_{RT} 0.5) without additives:
  - The corrosion is mild and involves shallow general corrosion and pitting, possibly with some deposition.
- Acidified solution (pH_{RT} 0.5) with mercury:
  - Strong general corrosion, pitting, and deposition of corrosion products are observed.
  - No accumulation of mercury is observed on corroded surface.

Main Findings - Tests of U-Bends (Cont.)

- Acidified solution (pH_{RT} 0.5) with lead:
  - Cracking occurs first in a transgranular mode.
  - When this cracking relieves the stress (at about the halfway point), crack growth continues in an intergranular mode.
  - Numerous secondary cracks, mostly intergranular, are observed.
  - Corrosion product deposition is observed, mostly in the transgranular (TG) region. The deposit-covered TG region is enriched in silicon and depleted with respect to nickel and tungsten.
  - Pitting may precede the transgranular cracking.
  - A large amount of lead concentrates at the crack surface.
- The corrosion mechanism in the presence of lead appears to be different than the mechanism in the presence of mercury.

Main Findings - Tests of Unstressed Disks

In 15-day tests on unstressed disks in J-13 water concentrated X1000 at 163°C, corrosive attack was identified in specimens exposed to moderately acidic environment (pH_{RT} 2.5) in the presence of lead.

- The surfaces of the specimens were strongly pitted.
- Extensive deposition of corrosion products was observed.
- A very large amount of lead concentrated on the pitted surface.
- Ongoing tests indicate that mercury aggravates pitting.

Main Findings - Tests of Unstressed Disks: Chemical Analysis of Dissolved Species

- In moderately acidic media (pH_{RT} 2.5) both lead and mercury caused extensive dissolution of C-22 ingredients, in particular nickel.
- In basic concentrated J-13 (pH_{RT} 13) mercury, but not lead, caused moderately significant dissolution of chromium and molybdenum.
- In general, surface characterization and wet analysis agree with respect to lead and mercury exhibiting large specific effects of enhancing C-22 corrosion.

Conclusions from Preliminary Tests

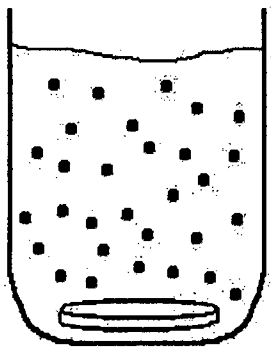
- The preliminary tests indicate that, in some environments, small amounts of aggressive species that could be present in the repository water, such as lead and mercury, can strongly aggravate pitting, crevice corrosion and SCC of C-22.
- It is concluded that the qualification program for alloy C-22 may need to evaluate the possible presence and effects of aggressive species such as lead, mercury, arsenic, and sulfides.

Concentration versus Inventory

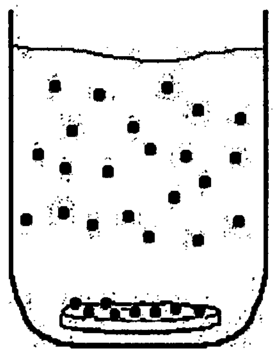
- Aggressive species concentrations may be less important than their inventories (total mass in the environment)
- If C-22 adsorbs aggressive species, surface concentrations will be high, even if environmental concentrations are low
- High surface concentrations could be deleterious
- Geological measurements indicate that aggressive species inventories are high, even though concentrations may be low

Concentration Hypothesis

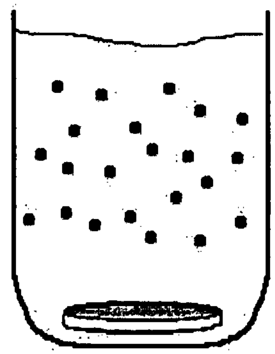
High concentrations of aggressive species are required for accelerated corrosion



Pb concentrated in solution



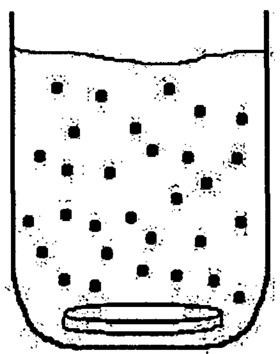
Little or no lead sorbed to the surface



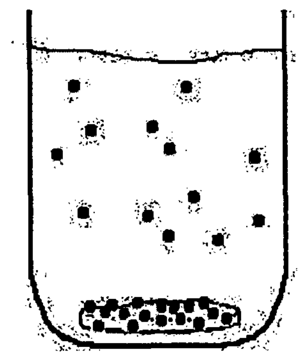
Most Pb remains in solution and does not contribute to corrosion

Adsorption Hypothesis

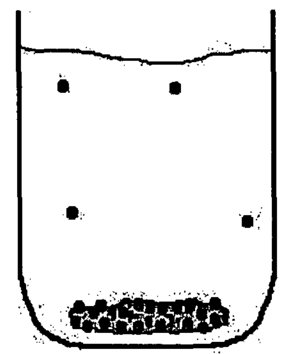
High inventories of aggressive species are required for accelerated corrosion



Pb concentrated in solution



All Pb is eventually scavenged by the C-22



All Pb contributes to corrosion — very little remains in solution

Lead Adsorption Testing

- Unstressed C-22 Disks
- J-13 x1000, minus lead precipitating species
- 160°C
- 14 day incubation
- Several levels of lead (<0.01 to 275 ppm in 15 ml)
- Measured lead
  - original solution
  - decanted solution

Results of Lead Adsorption Tests

Initial Pb		Pb in Decanted Solution		Percent Sorbed on C-22*	Appearance
Concentration	Inventory	Concentration	Inventory		
ppm	µg	ppm	µg		
<0.01	< 0.01	<0.01	< 0.01	—	Almost unchanged
35	0.518	4.7	0.07	87	Light tarnish
125	1.88	0.9	0.014	99	Light tarnish
275	4.12	14.4	0.216	95	Tarnish

* Calculated based on fraction of initial inventory absent from the decanted solution

Lessons from Nuclear Power Plant Experience

Numerous materials selected on basis of good general corrosion resistance have turned out to be susceptible to SCC. Examples include:

- Austenitic stainless steels (SS) for BWR structural materials
- Inconel 600 for PWR steam generator (SG) tubes
- X750 in AH heat treatment for bolting and similar hardware
- A286 for reactor internals bolting
- 17-4 PH SS for high temperature valve parts and bolting
- Martensitic SS for bolting and other hardware
- Zircaloy fuel rod cladding

These case histories highlight that, despite apparently careful selection and qualification, significant corrosion in service can occur.

Example 1: BWR Stainless Steel Cracking

- Extensive cracking has occurred at welds in austenitic SS in BWR piping and internals. Lengthy and expensive inspections and repairs have been required.
- Austenitic SS was chosen based on its good general corrosion resistance. Selection failed to adequately consider:
  - Effects of sensitization at welds
  - Effects of oxidizing potentials caused by radiolytically produced oxidants
  - Effects of residual stresses and local cold work due to grinding

Example 2: Inconel 600 SG Tube Cracking

- Extensive cracking has occurred of Inconel 600 SG tubes and has required extensive plant changes, water chemistry upgrades, inspections and SG replacements.
- Selection of Inconel was based on its good general corrosion resistance and resistance to chlorides, but failed to consider:
  - Large variation in susceptibility to SCC as a function of processing history and compositional variations (1000x!)
  - Effects of low potentials, cold work and residual stresses on SCC from primary side
  - Effects of oxidizing potentials, concentration of impurities (leading to high and low pH), and trace aggressive species (such as lead) on intergranular attack (IGA) and SCC from secondary side.
  - Effects of minor elements in the metal, such as boron, on susceptibility to SCC.

Example 3: Failures of High Strength Materials

- Many failures have occurred of high strength materials such as X750, A286, 17-4 PH, and martensitic SS. These have resulted in extensive inspections and replacements.
- Materials were selected based on their good general corrosion resistance. Selection failed to consider:
  - Susceptibility to SCC in long time exposure to reactor environments of material heat treated based on aerospace applications.
  - Effects of local residual stresses and cold work on susceptibility to SCC.
  - Effects of time at temperature on material properties (embrittlement) and susceptibility to SCC.
  - Needs for detailed quality control to assure that desired material conditions (proper heat treatment) are achieved.

Example 4: SCC of Zircaloy Cladding

- Many failures occurred due to SCC of zircaloy fuel rod cladding associated with "pellet clad interaction."
- Zircaloy was selected for fuel rod cladding because of its good general corrosion resistance and low neutron cross section. Selection failed to consider:
  - Effects of fission products such as iodine and cesium on possible SCC.
  - Effects of high strains and stresses caused by clad creep down onto pellets and subsequent pellet expansion.

Summary of Lessons Learned from Nuclear Power Plant Experience

- Reasons for unexpected failures include:
  - Full range of realistic service environments not considered (potential, pH, aggressive species)
  - Realistic range of material conditions and compositions not evaluated
  - Realistic range of total stresses (including residual stresses) and applied strains not adequately considered
  - Long term susceptibility in realistic environments not adequately tested (need for accelerated testing)
  - Aggravating effects of fabrication details, surface damage, and local residual stresses not adequately considered
  - Long term material aging effects not adequately addressed

Summary of Lessons Learned from Nuclear Power Plant Experience (Cont.)

- Main lesson - all of the above factors need to be addressed.
- Several of these factors may have not been suitably addressed to date for C-22.

Testing Status of Alloy C-22

While significant numbers of tests have been and are being performed of Alloy C-22, some aspects may require more attention:

- Tests thus far reported do not appear to have addressed possible effects of trace aggressive impurities such as lead, mercury, arsenic and sulfides on SCC and other modes of corrosion.
- Tests thus far do not appear to have addressed full range of water chemistries and concentrations that could occur, especially in heated crevices and under deposits.
- Tests thus far do not appear to have addressed full range of base material composition variations (including trace deleterious impurities) and conditions (e.g., welding, cold work and sensitization).

Objectives of the Experimental Program

- Identify the mechanisms of possible corrosion phenomena
  - Pitting
  - Crevice corrosion
  - Under deposit corrosion
  - IGA/SCC
- Determine the effects of crevices and deposits on the near field chemistry (pH, aggressive species concentrations and potentials) and the resultant effects of those chemistry changes on corrosion phenomena

Objectives of the Experimental Program (continued)

- Develop a scientifically based method for predicting the long term performance of Alloy C-22 using temperature accelerated experiments
- Evaluate the ability of Alloy C-22 to scavenge and concentrate aggressive species (lead, mercury, *etc.*)
- Determine the correct measure of aggressive species activity: inventory or concentration