Bases for Predicting Occurrences of Rapid Corrosion on the Surfaces of Containers of C-22 at Yucca Mountain

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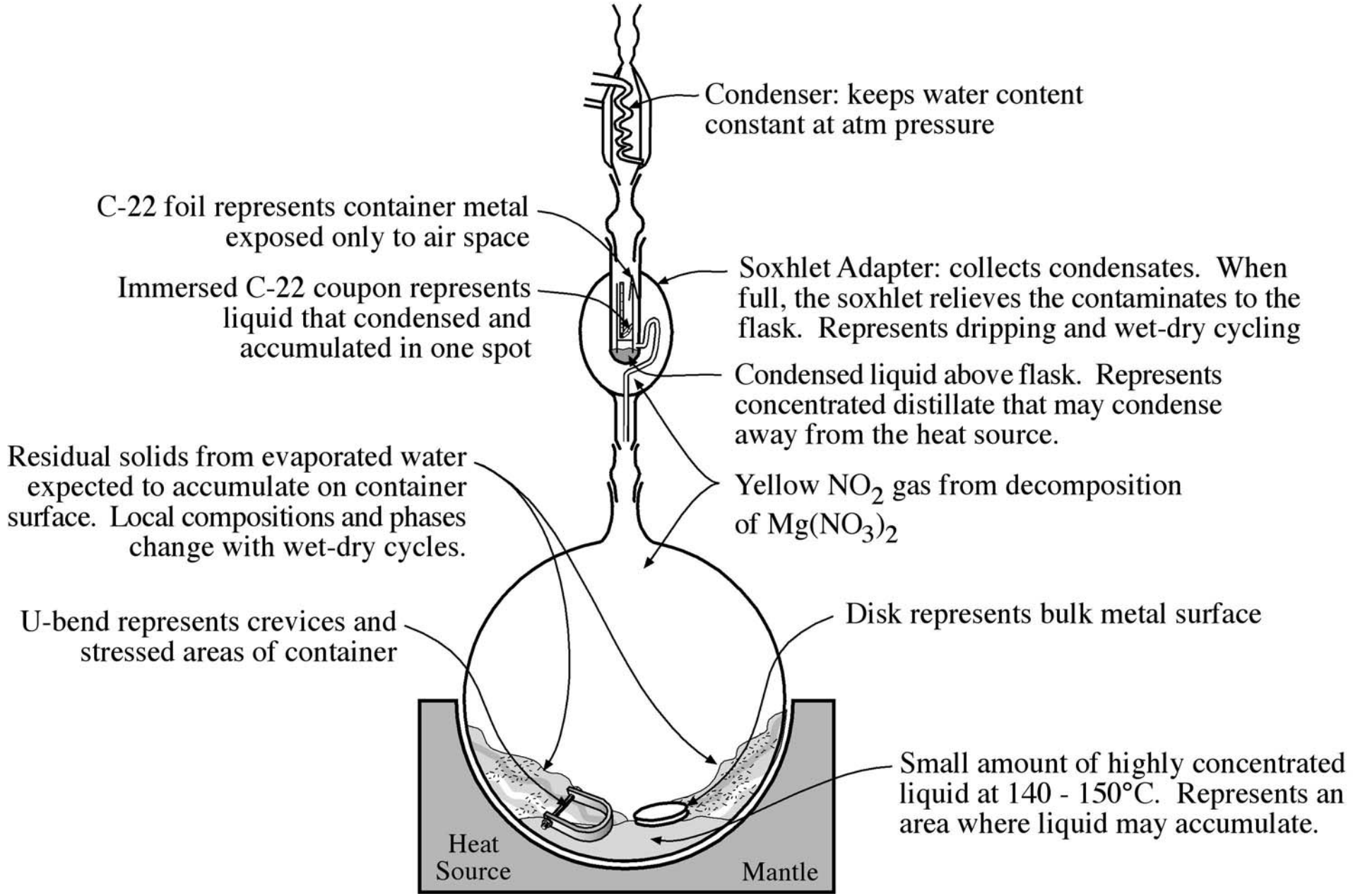
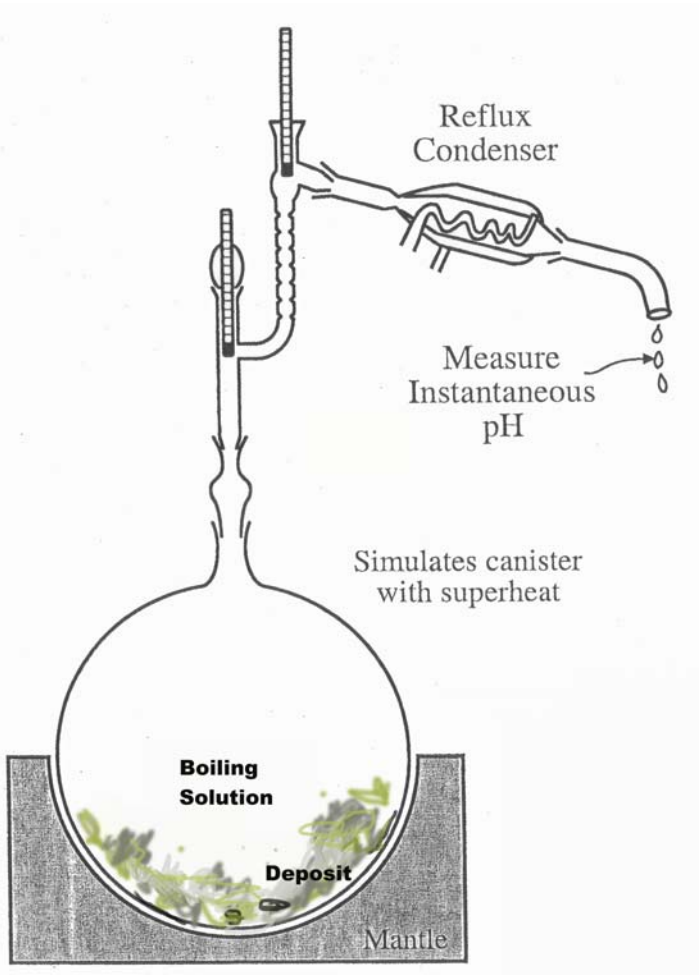
Composition of Pore Waters in Unsaturated and Saturated Zones at Yucca Mountain

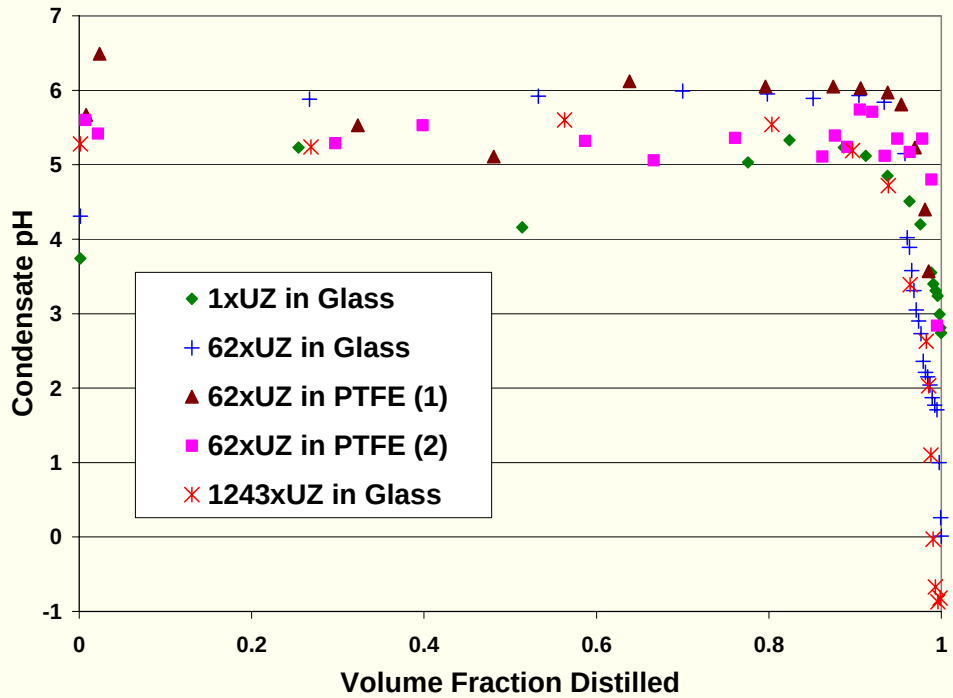
ppm ion	Concentration (mg/L)					
	Saturated Zone Water (J-13)			Unsaturated Zone Pore Water (UZ)		
	1x	150x	250x re-wet	1x	62x	1243x
Na^{+}	45.2	162.2	12294	8.56	476.8	6223
K^{+}	5.2	592.8	1336	4	268.4	2644
Mg^{2+}	2.1	1.12	0.08	11.8	550	5546
Ca^{2+}	5.8	0.06	3.31	57.3	1713	15643
SiO_2	10.4	1040	3317	10.4	503.36	540.8
HCO_3^{-}	105.0	4410	9271	20.3	9.95	44.66
SO_4^{2-}	18.5	2109	4608	83.9	1543	2097.5
Cl^{-}	7.2	813.6	1850	76.6	4259	52165
NO_3^{-}	7.9	1034.9	1990	10.7	591.7	2578.7
F^{-}	2.3	236	554.3	2.16	38.2	432
pH	8.07	10.18	10.59	7.55	7.65	6-6.5

Corrosion Cell for Direct Applicability to Container



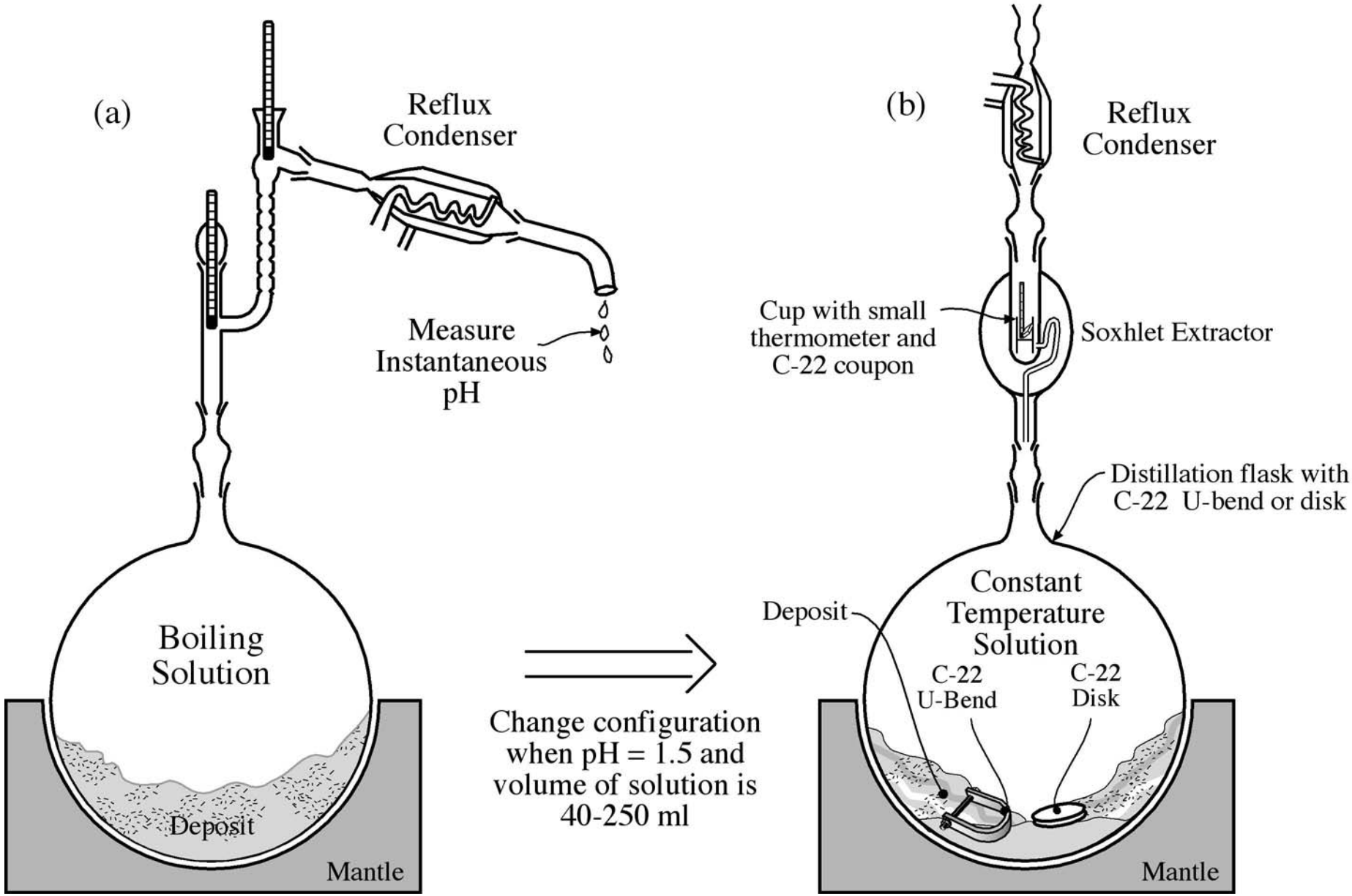
Distillation of UZ-pore Waters



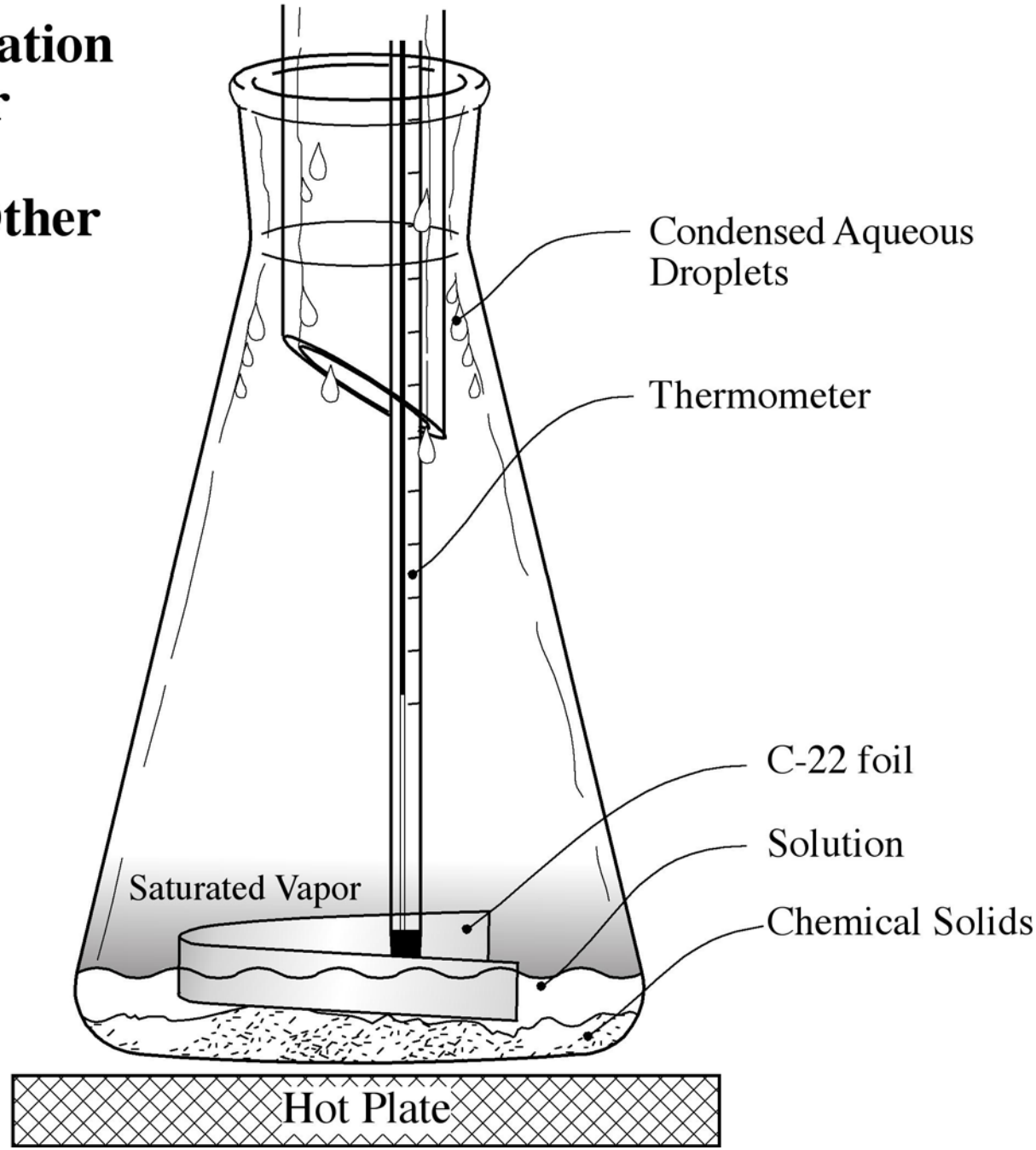


Original Solution	Measured pH_{RT} of final dist.	Test temp °C	Corrosion rate of C-22
62xPore	0.59	130	406
1243xPore	-0.54	90	603

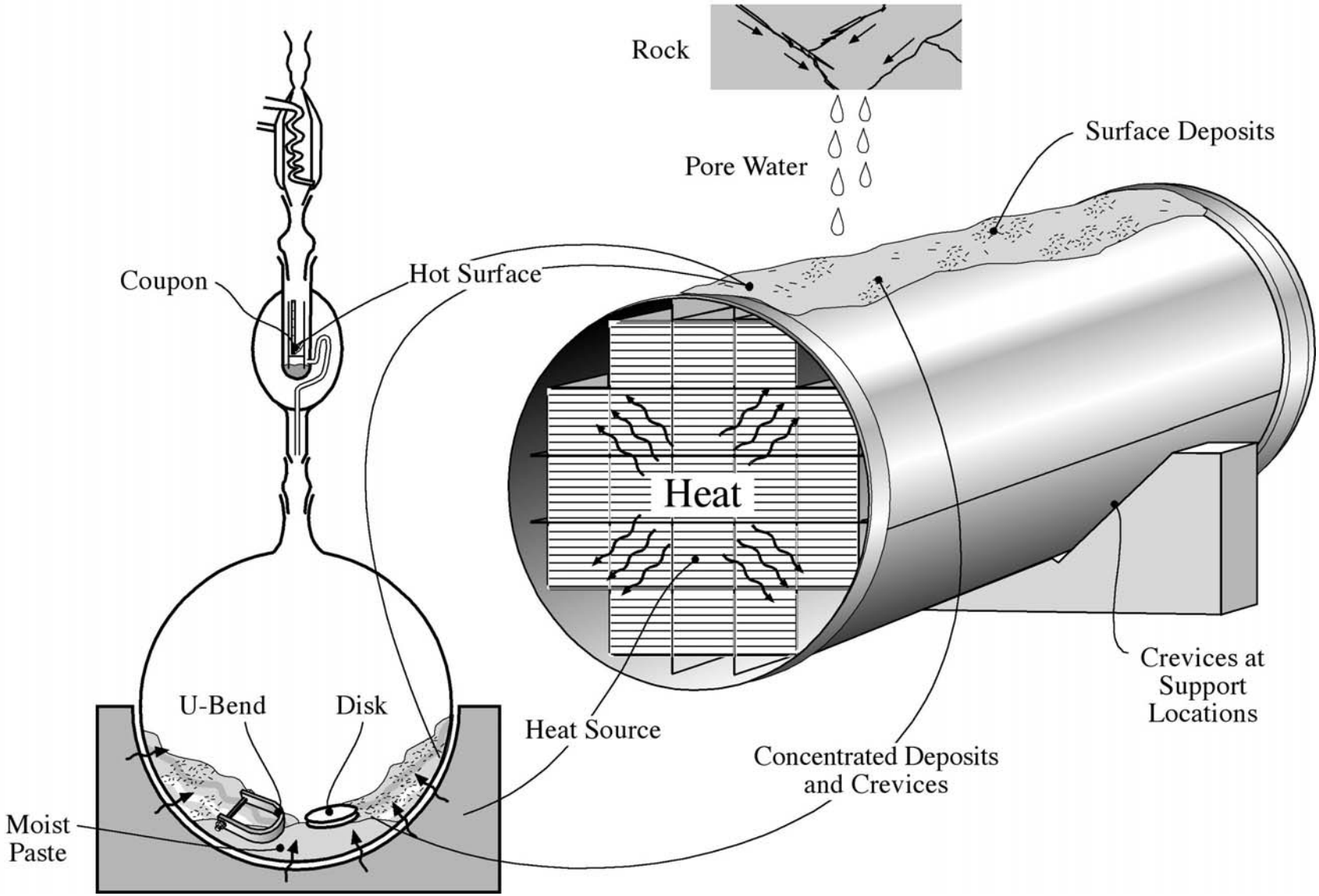
Experimental Configurations for Concentrating Solutions and Then for Corrosion Testing



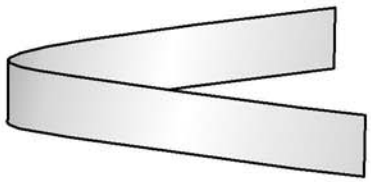
Experimental Configuration of Erlenmeyer Flask for Exposing Alloy C-22 Specimens to UZ and Other Solids and Liquids

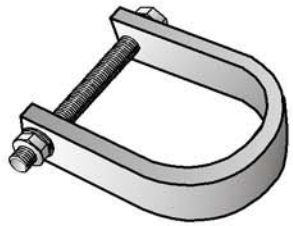


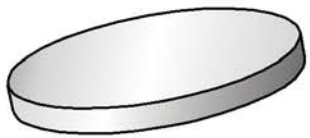
Direct Application of Experiments to Heated Container

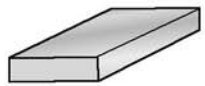


Samples for Testing

Foil  76.2 x 12.7 x 0.051 mm

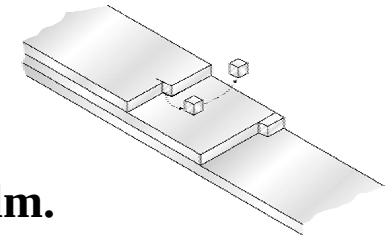
U-Bend  45 x 12.7 x 3.18 mm
Bent around 6.4 mm mandrill

Disk  25.4 ϕ x 3.18 mm

Small Sohxlet Coupon  10 x 5 x 3.18 mm

		Composition, $^{w}/_{o}$				
Sample	**Heat**	**Ni**	**Mo**	**Cr**	**W**	**Fe**
Alloy 22 foil	227703129	54.65	13.51	21.52	3.18	4.04
Alloy 22 sheet (U-bends, disk, coupons)	22713264	56.89	13.37	21.50	2.91	3.97

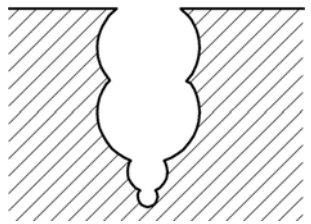
Modes of Corrosion Observed



1. Terrace-ledge-kink TLK

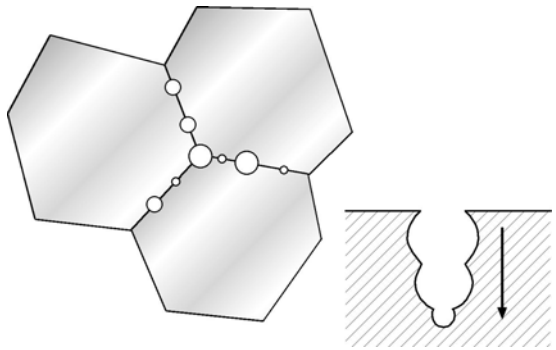
- Indicates that dissolution is occurring without significant passive film.
- High rates occur when no inhibitive species to block kink sites.

2. Continuous localized corrosion with re-nucleation (non structural)



- Sequesters acidic solutions and continues acidification by hydrolysis.
- Stops as solution is saturated with metal ions.
- Provides a mode for “drilling” through the C-22 wall.

3. Preferential localized corrosion with re-nucleation at grain boundaries (structural)

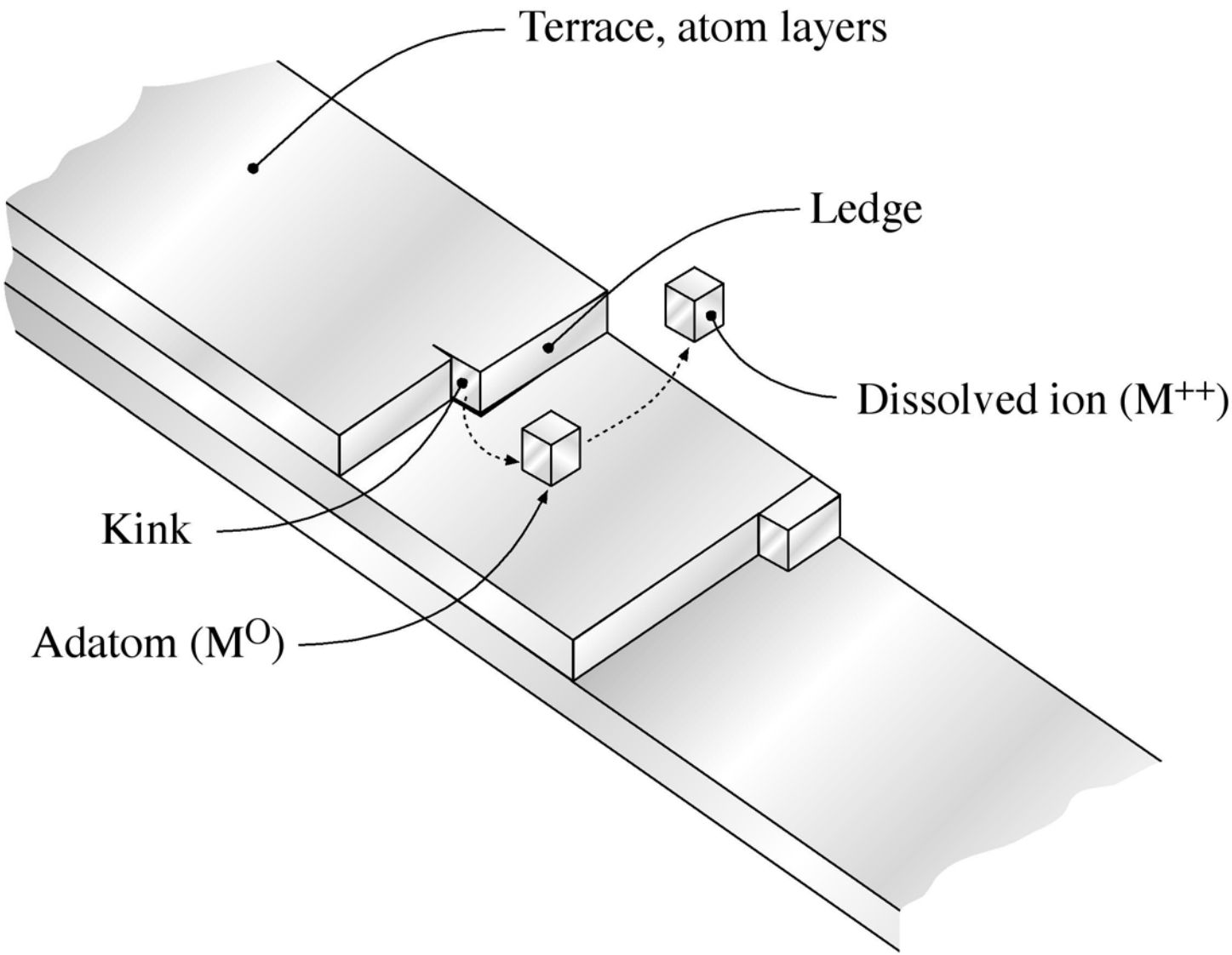


- Variation on #2 but starts at grain boundaries.
- Multiple events destroy integrity of grain boundaries.

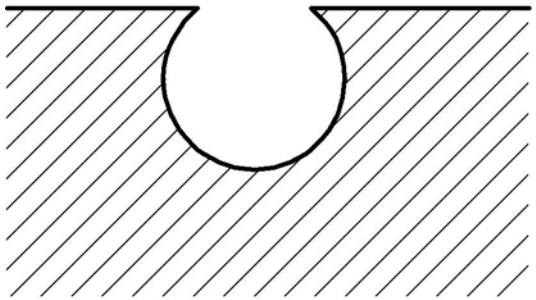
4. SCC

- Only one event found.
- Not the general case.

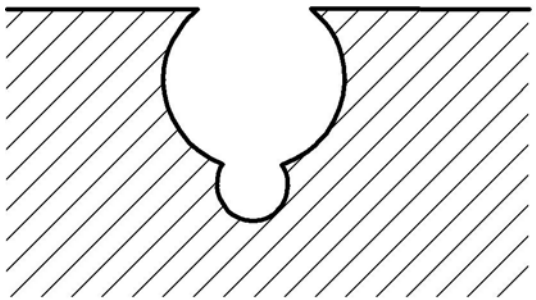
Terrace-Ledge-Kink (TLK) Dissolution



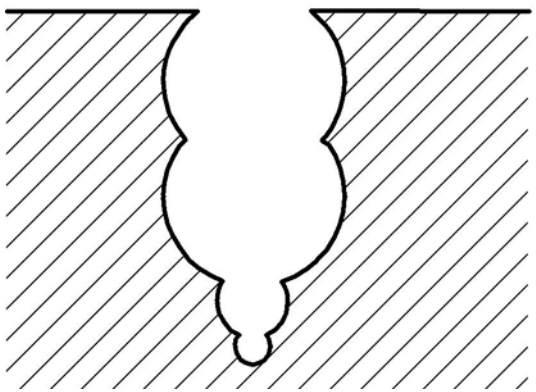
Continuous Growth by Re-nucleation (Non-structural)



Initial

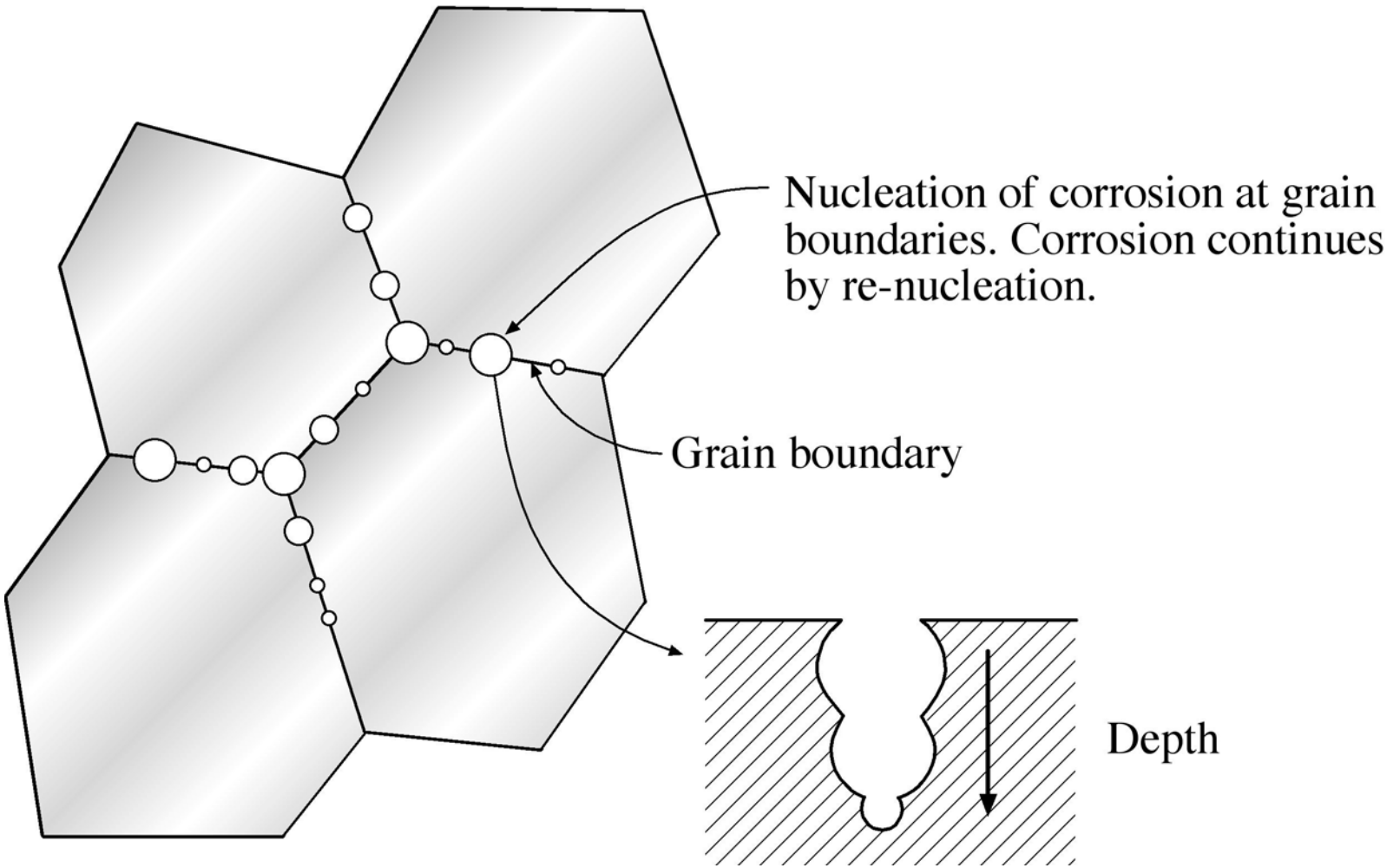


Re-nucleates at bottom



Process of re-nucleation and growth continues and does not stop

Corrosion Preferentially at Grain Boundaries



Qualitative Description of Environments

1. Paste at bottom of testing flask

- **Difficult to analyze because heterogeneous and salts are hygroscopic.**
- **Continued wetting from Soxhlet changes chemistry and physical nature.**
- **Xray signal shows paste is dominated by NaCl and anhydrous/ hydrated $CaSO_4$ but these are probably "spectators."**
- **Corrosion seems dominated by mixture of HNO_3+HCl. A wet paste has pH=2-3; w/o liquid the pH is=8.**

2. Liquid at bottom of testing flask

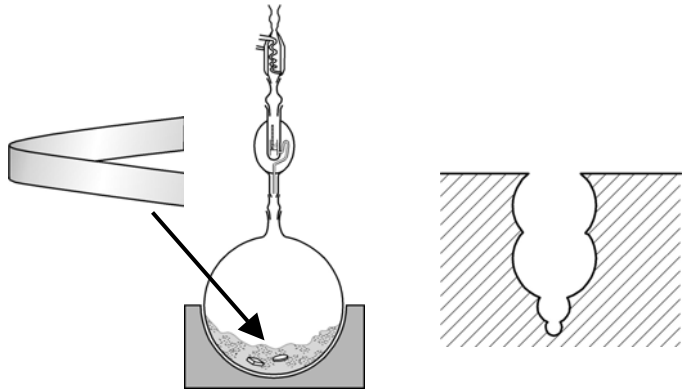
- **Boils at 145-150°C, therefore mixture of concentrated acids.**
- **Indirect comparison with Soxhlet suggests a pH=0.**

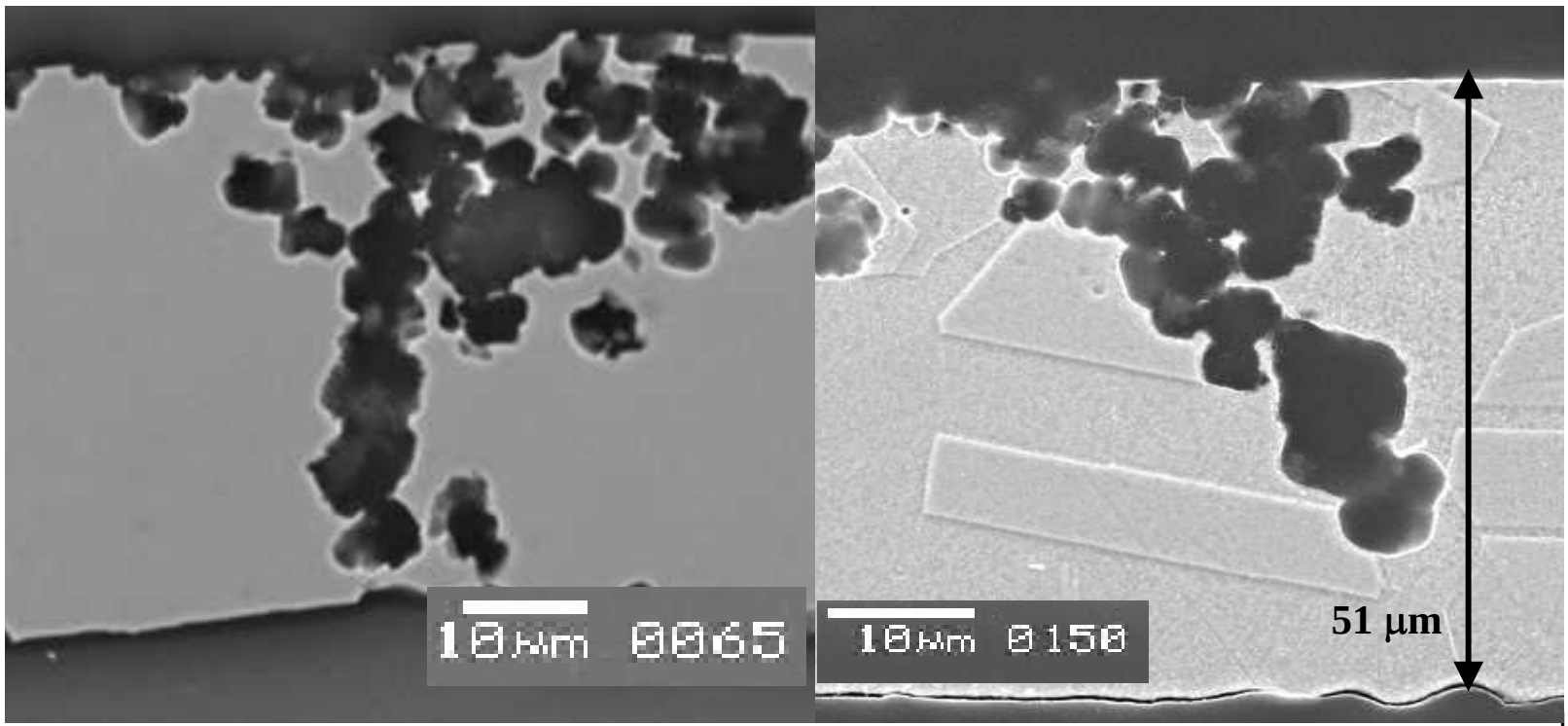
3. Soxhlet

- **Specimens immersed in liquid.**
- **Temperature is constant near 75°C but cycles 75-100°C.**

Initially, 1243x UZ pore water (F 15)

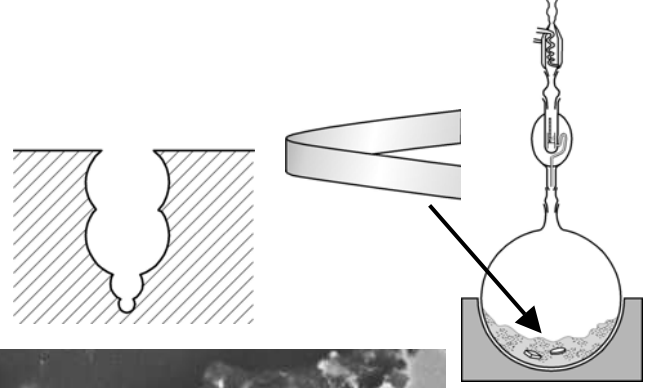
- **Paste environment, bottom of flask**
- **150°C**
- **Specimen of C-22: 76.2x12.7x 0.051 mm**
- **<5 days test**
- **>3.7mm/year penetration rate**

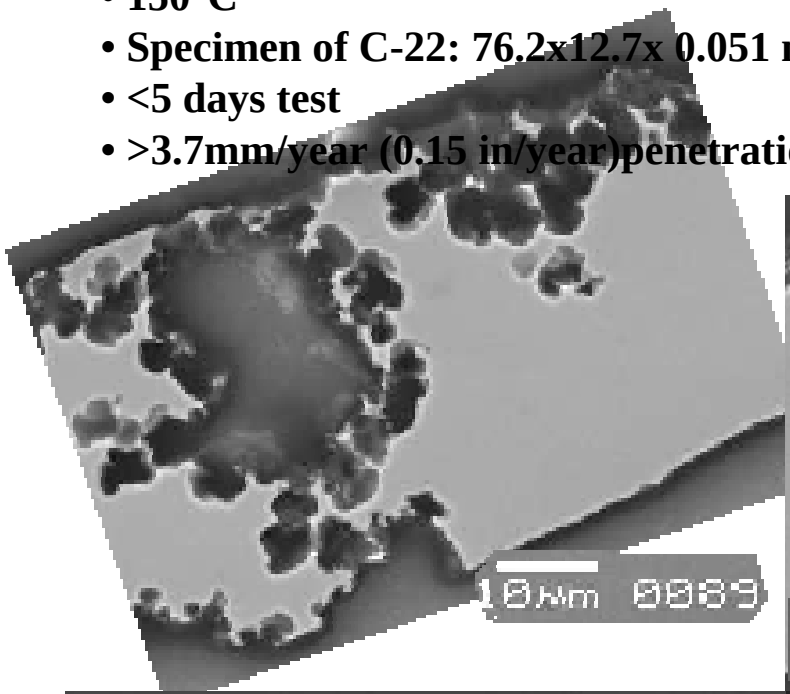


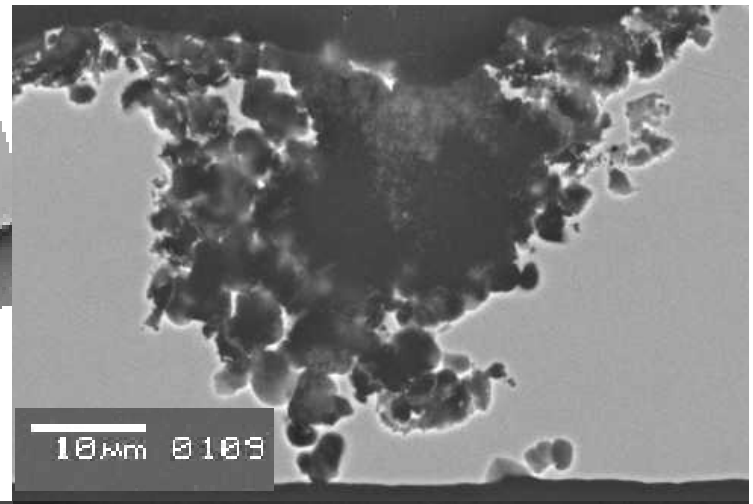


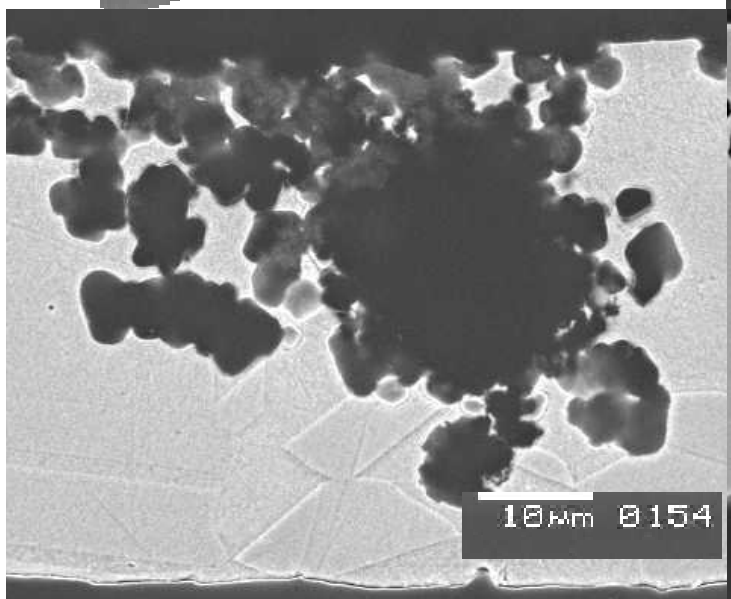
Initially 1243x UZ pore water (F 15)

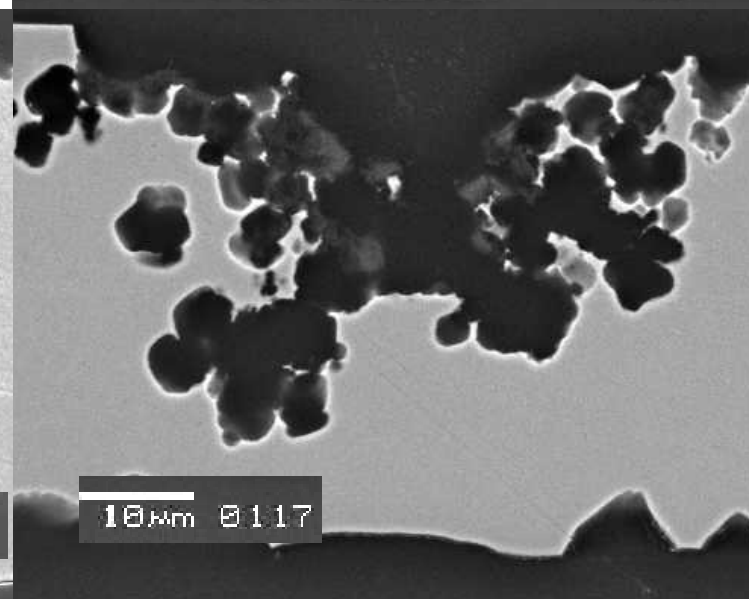
- **Paste environment, bottom of flask**
- **150°C**
- **Specimen of C-22: 76.2x12.7x 0.051 mm**
- **<5 days test**
- **>3.7mm/year (0.15 in/year)penetration rate**





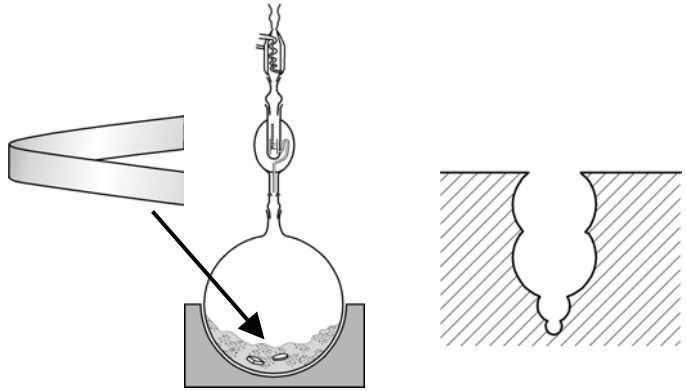


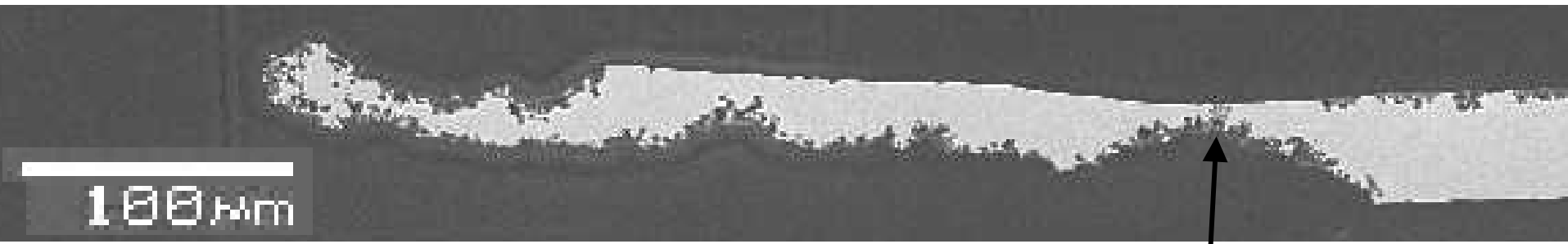


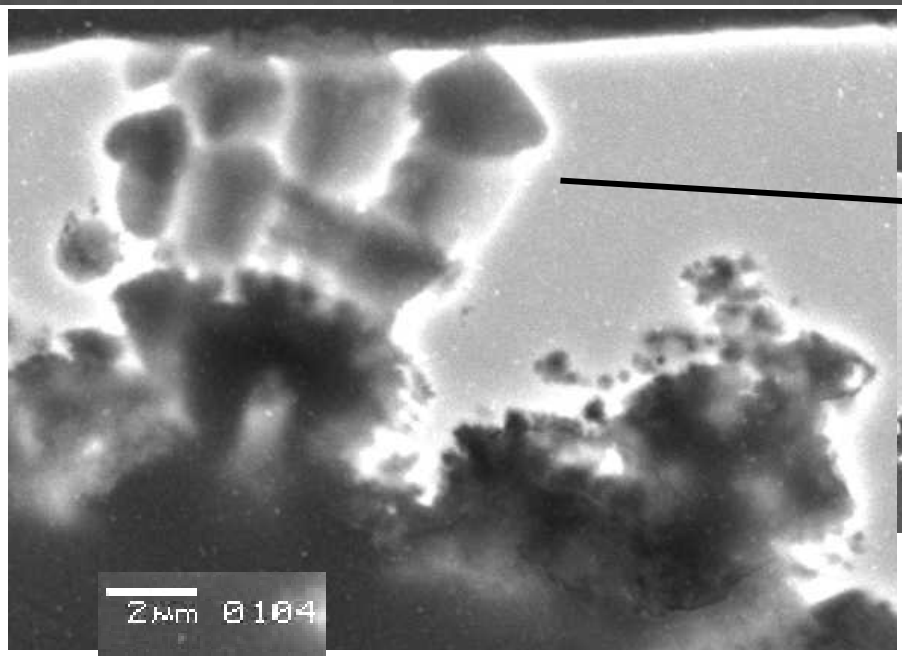


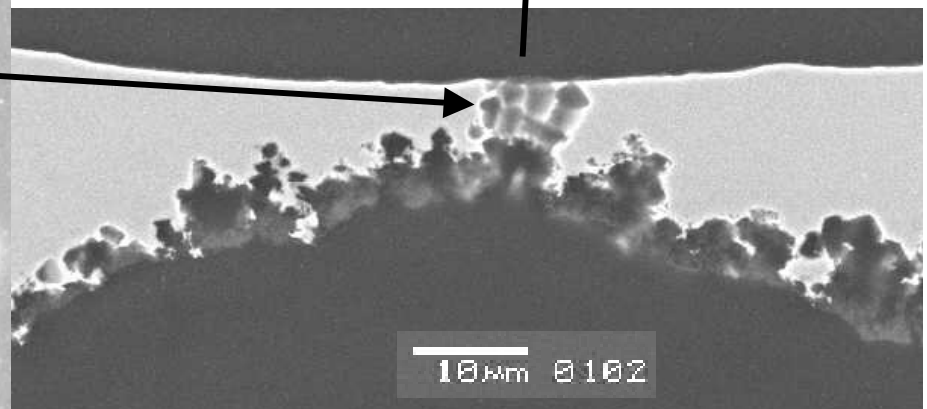
Initially 1243x UZ pore water (F 15)

- **Paste environment, bottom of flask**
- **150°C**
- **Specimen of C-22: 76.2x12.7x 0.051 mm**
- **<5 days test**
- **>3.7mm/year (0.15 in/year)penetration rate**



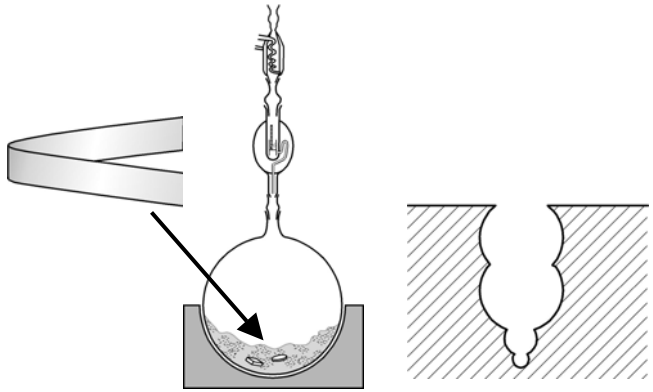


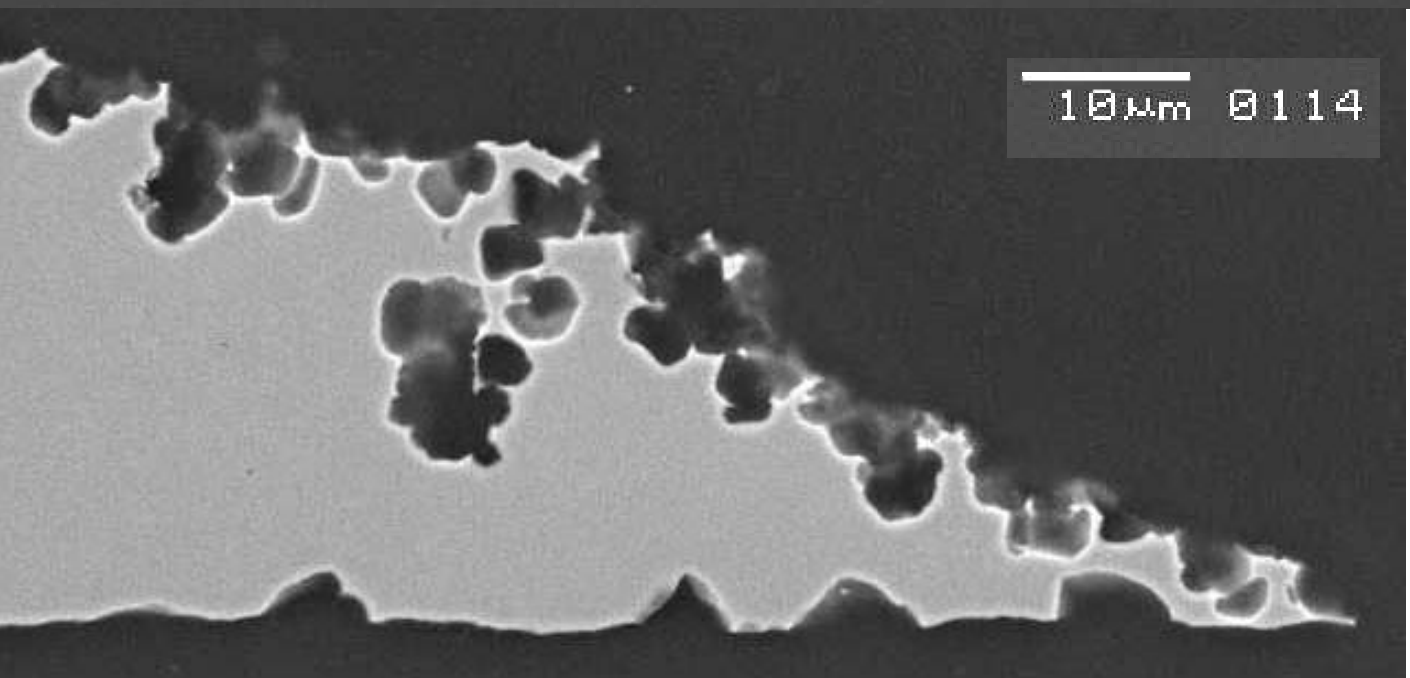




Initially 1243x UZ pore water (F 15)

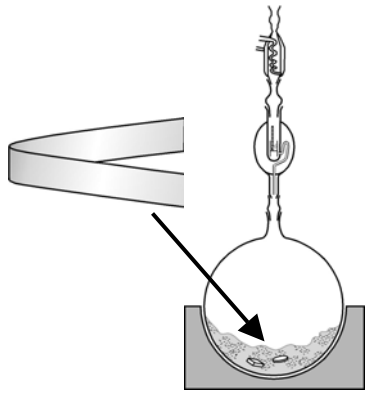
- **Paste environment, bottom of flask**
- **150°C**
- **Specimen of C-22: 76.2x12.7x 0.051 mm**
- **<5 days test**
- **>3.7mm/year (0.15 in/year)penetration rate**

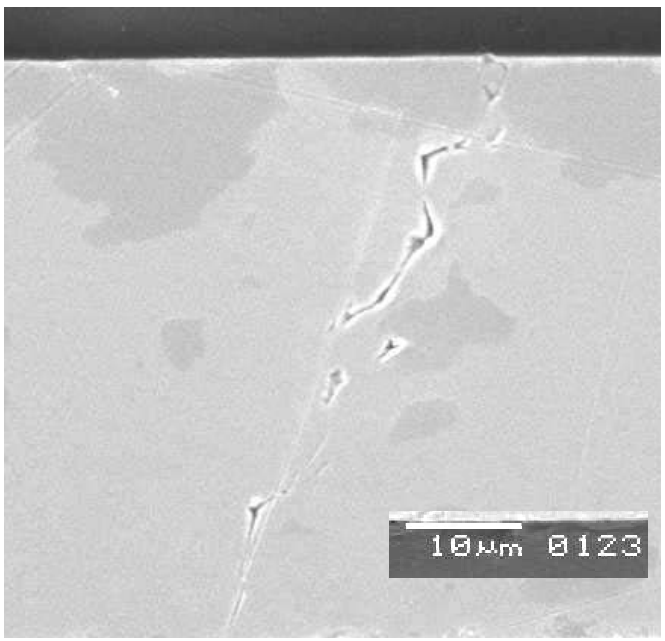


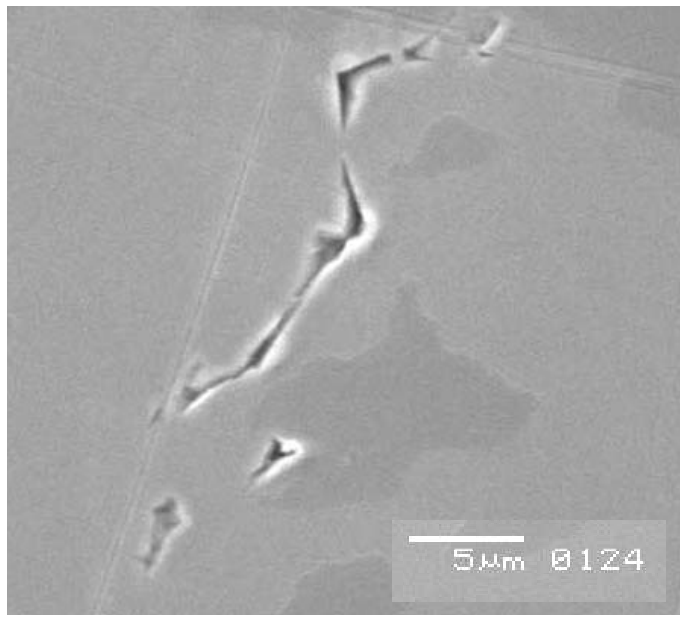


Initially 1x UZ pore water (F 14)

- **Paste environment, bottom of flask**
- **120°C**
- **Specimen of C-22: 76.2x12.7x 0.051 mm**
- **8 days**
- **Minimal general corrosion, one SCC observed.**

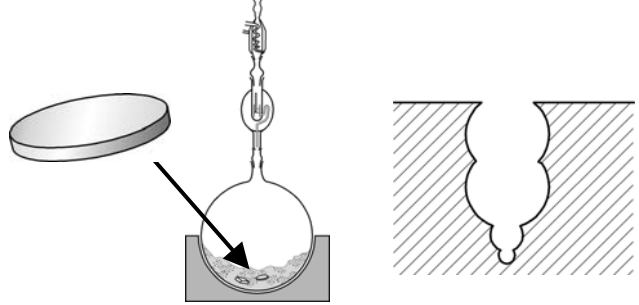


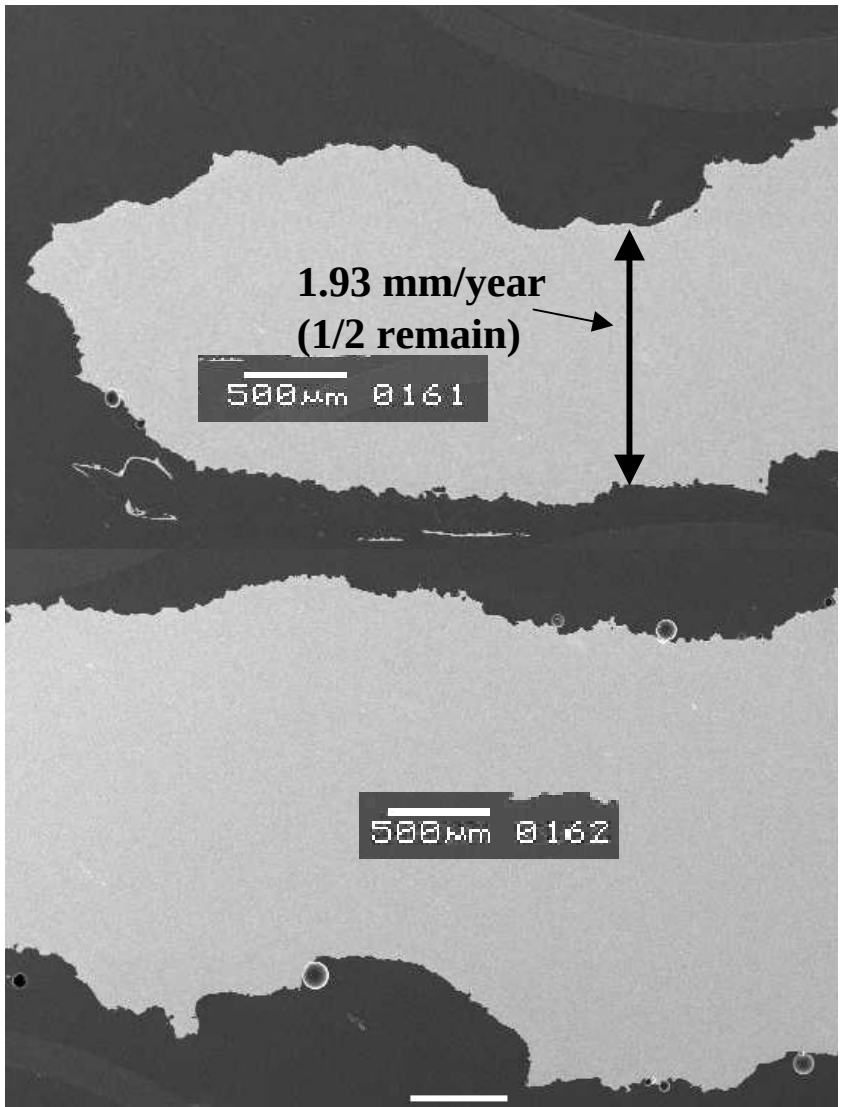


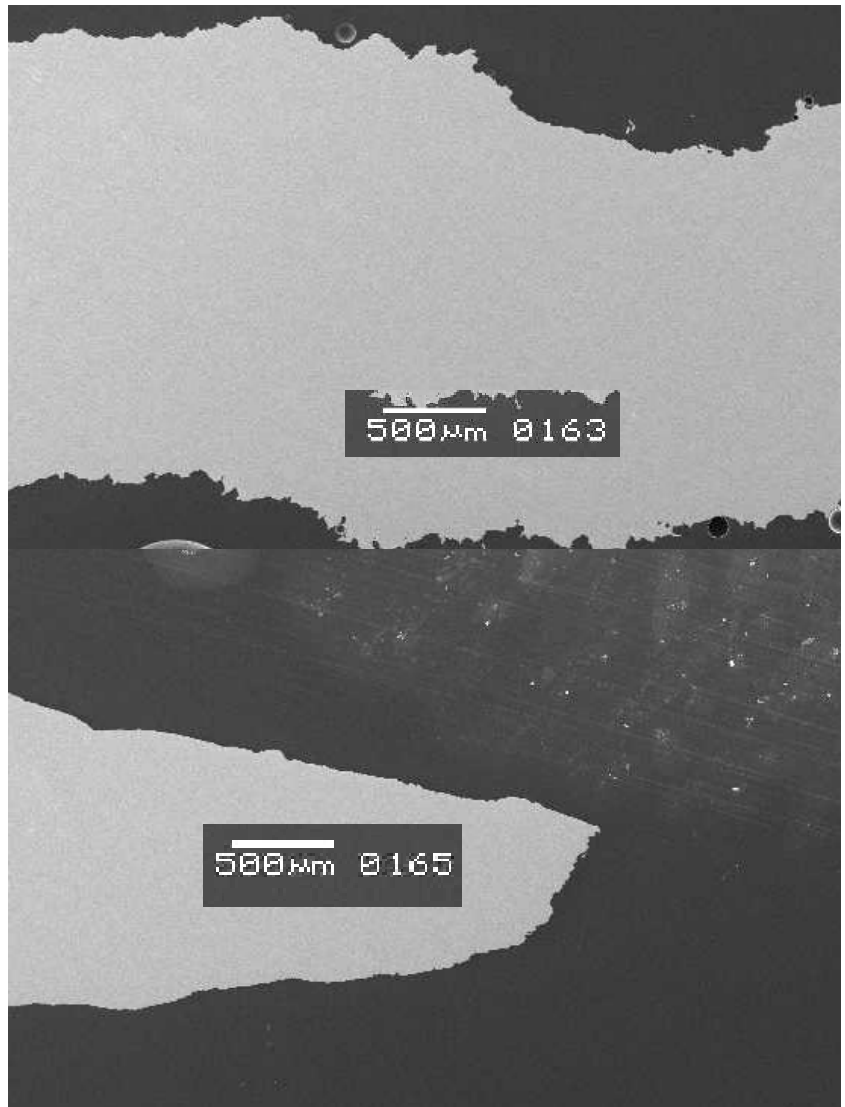


Initially 1243xUZ pore water (α-22 disc)

- **Paste environment, bottom of flask**
- **145°C**
- **Specimen of C-22: 2.54 diam x 3.18 mm**
- **Six months test: 1.93 mm/yr**

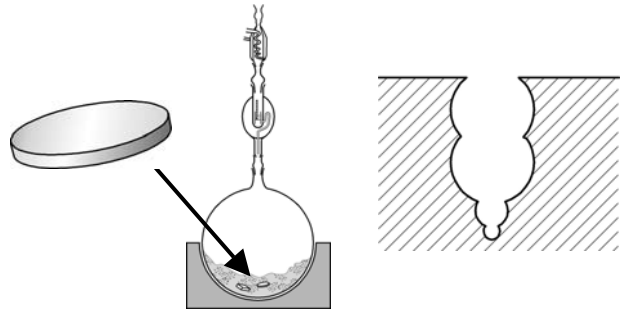


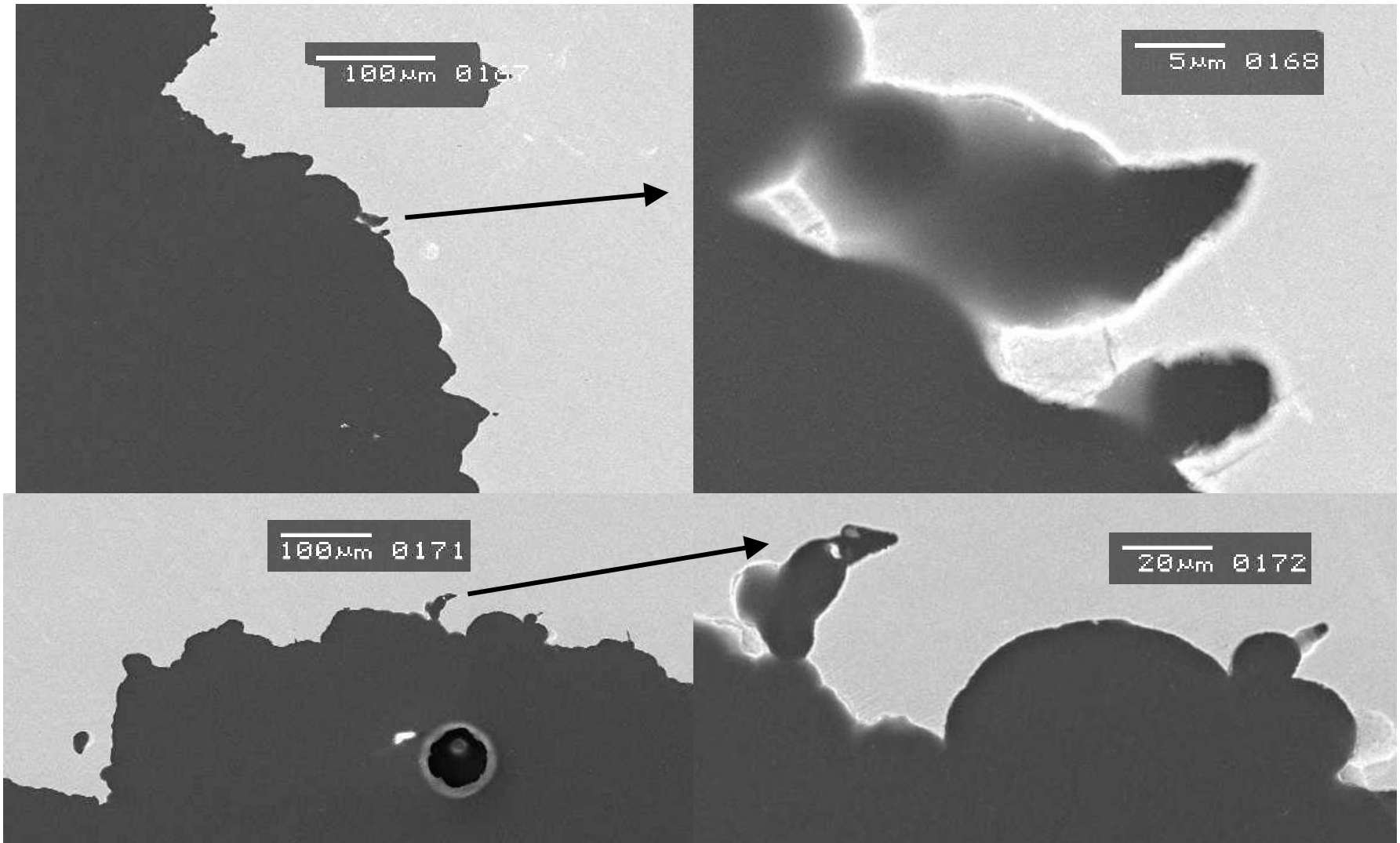


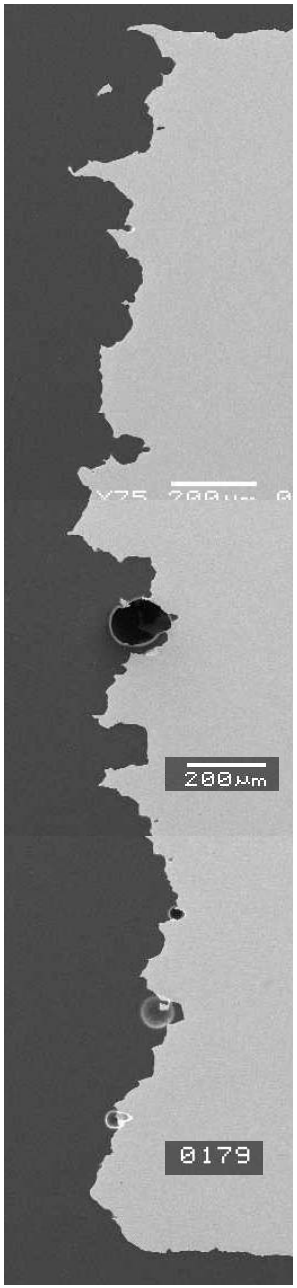


Initially 1243xUZ pore water (α-22 disc)

- **Paste environment, bottom of flask**
- **145°C**
- **Specimen of C-22: 25.4 ϕ x 3.18 mm**
- **Six months test**
- **1.93 mm/yr**

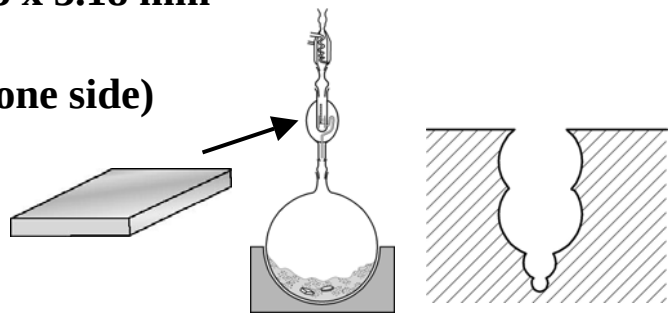


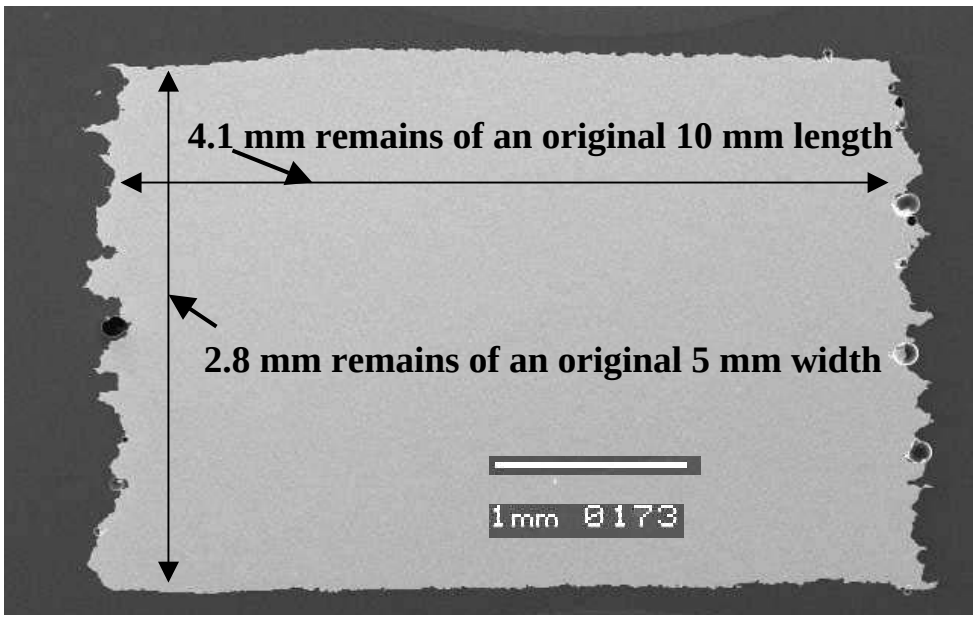


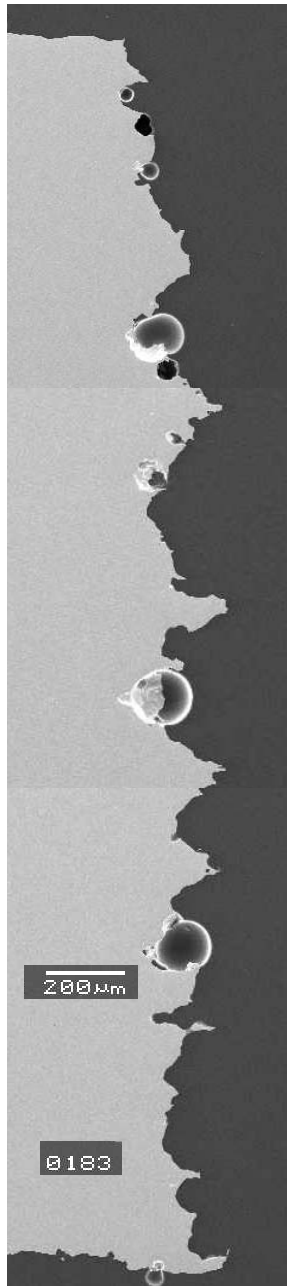


Initially 1243x UZ pore water(α-22 Soxhlet)

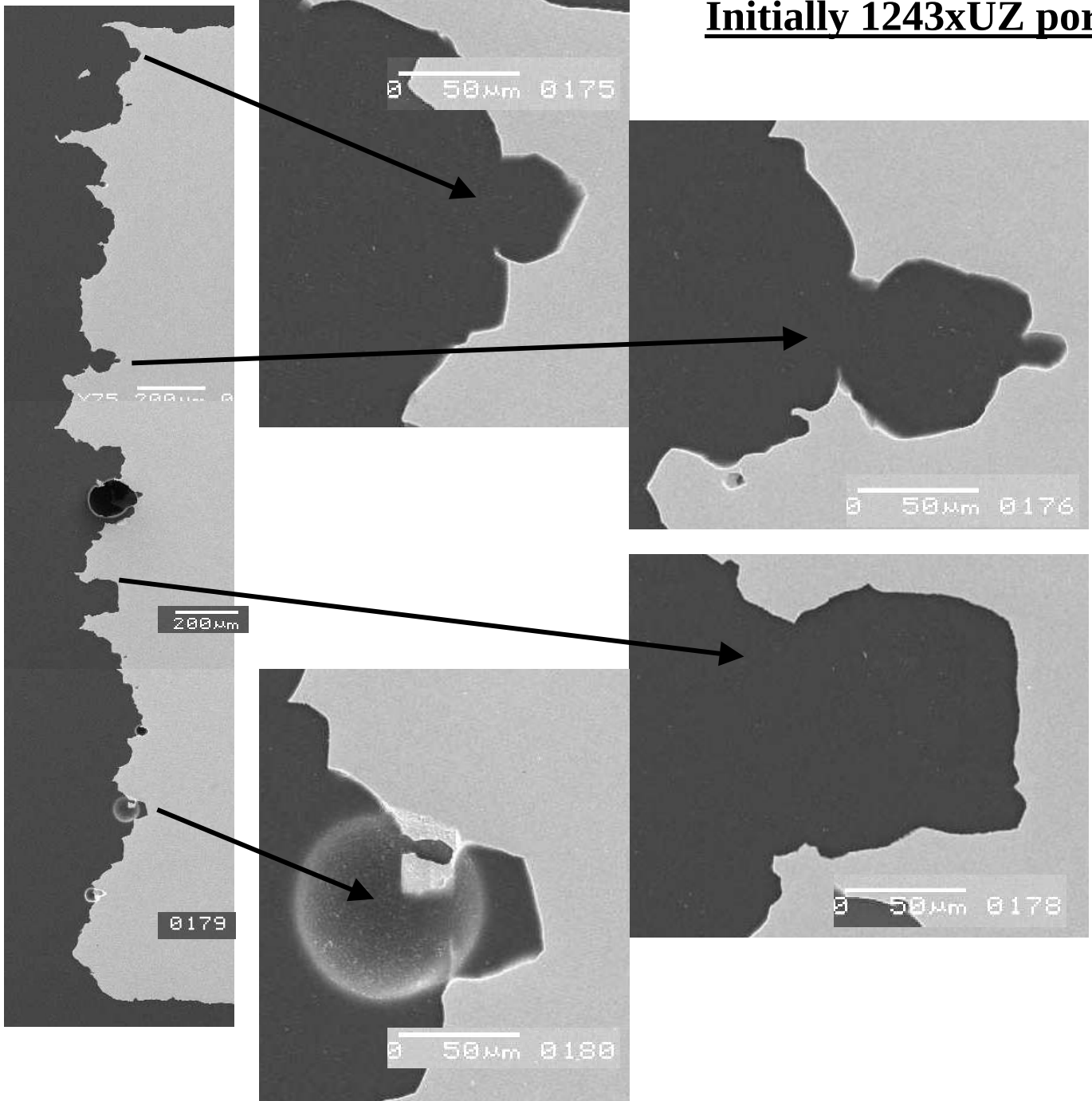
- **Specimen completely immersed in Soxhlet, pH 0.53**
- **75°C**
- **Specimen of C-22: 10 x 5 x 3.18 mm**
- **Six months test**
- **5.5 mm/yr penetration (one side)**



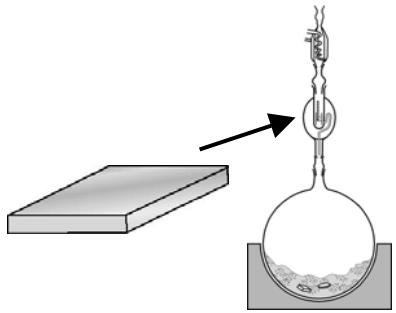


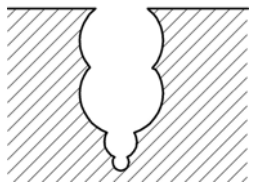


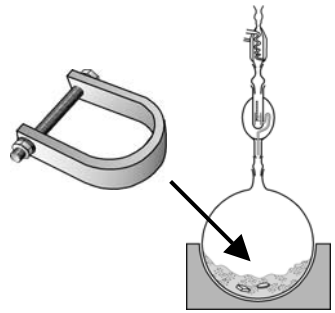
Initially 1243xUZ pore water (α-22 Soxhlet)



- **Specimen immersed, pH 0.53**
- **75°C**
- **Specimen of C-22: 10 x 5 x 3.18 mm**
- **Six months test**
- **5.5 mm/yr**

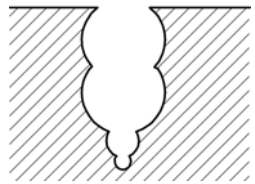


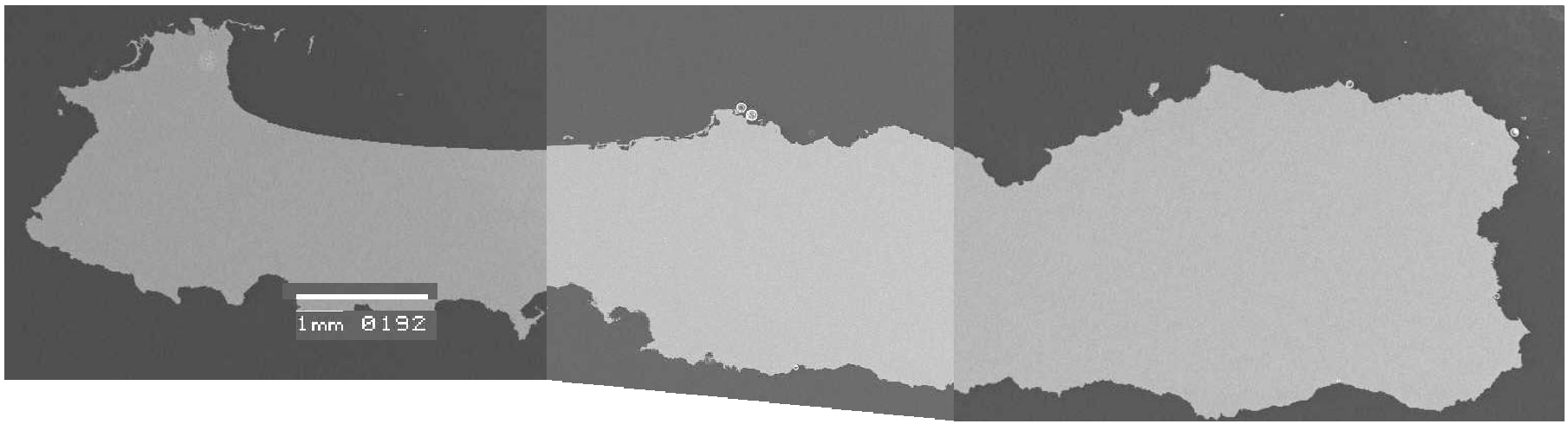




Initially 1243x UZ pore water (α-22 U-bend)

- **Specimen immersed in paste**
- **145°C**
- **Specimen of C-22: 55 x 13 x 3.18 mm (around 6.35 mm mandrill)**
- **Six months test**
- **2.1 mm/yr penetration (one side)**





Initially 1243x UZ pore water (α-22 U-bend)

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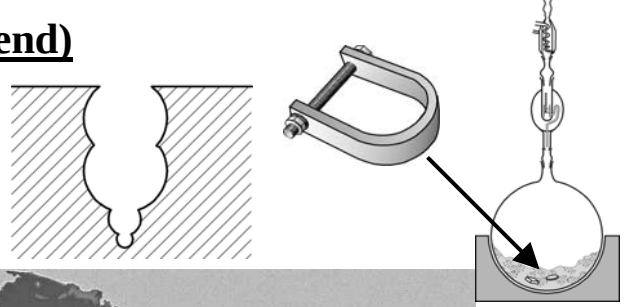
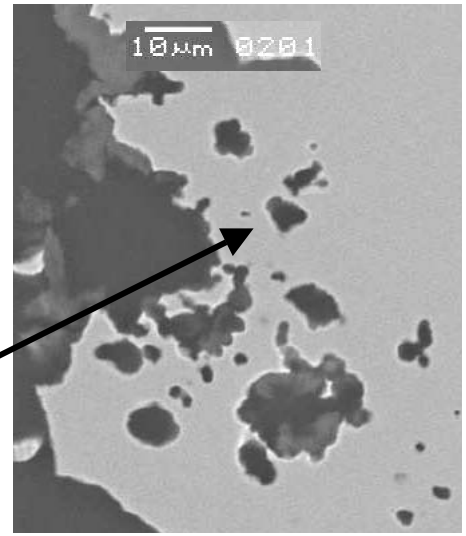
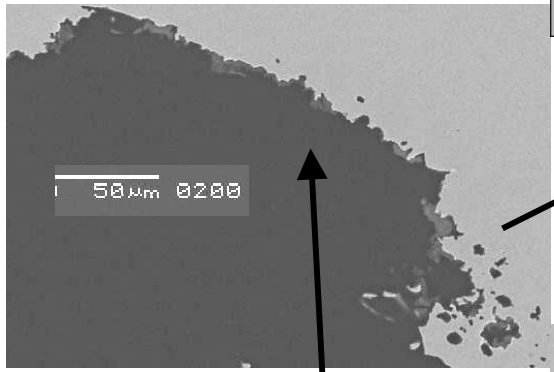
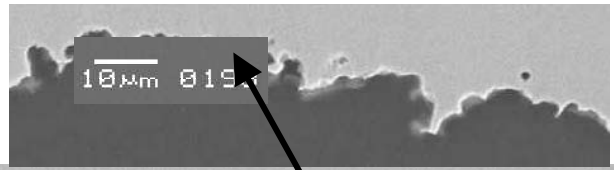
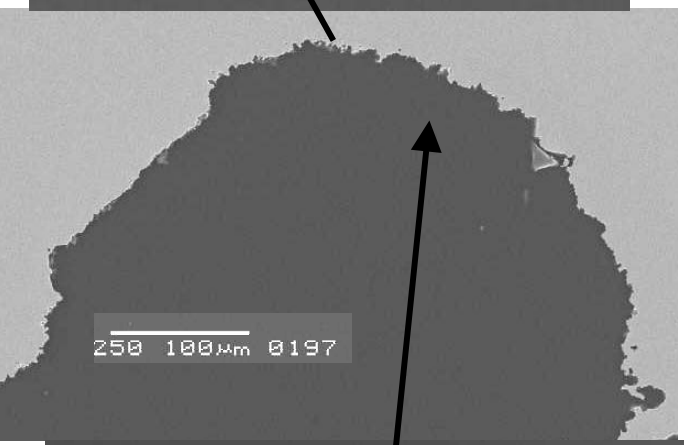
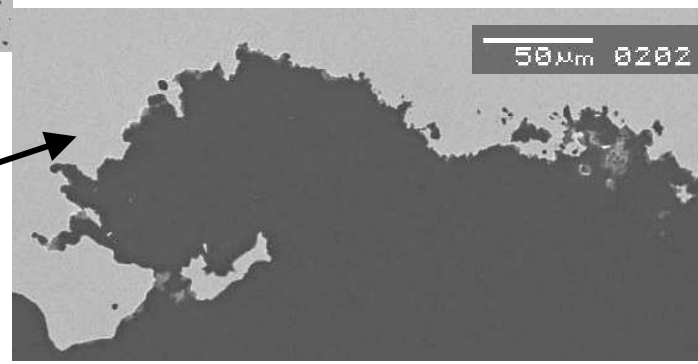


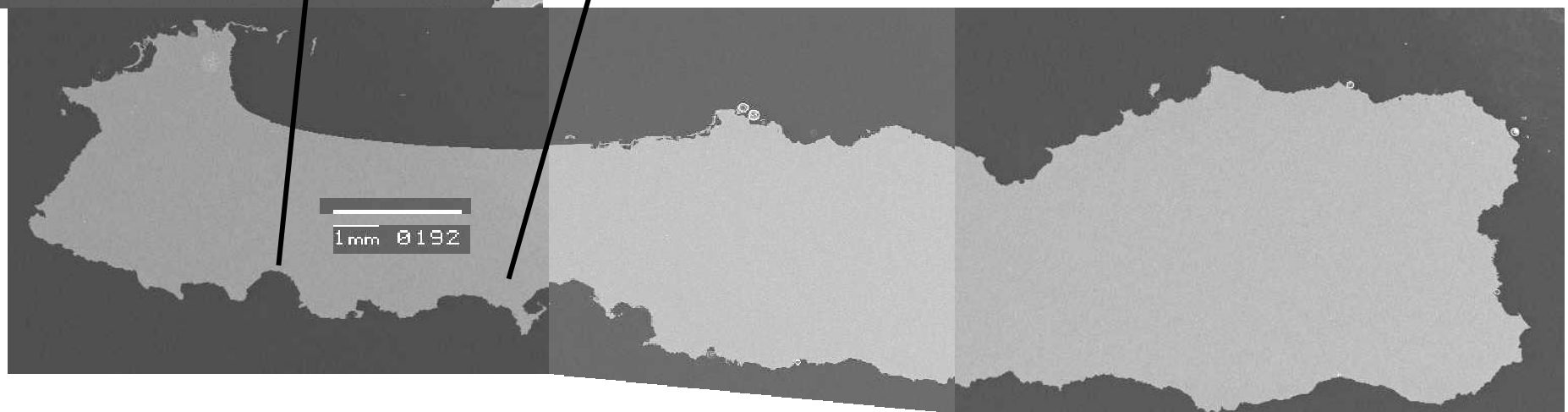


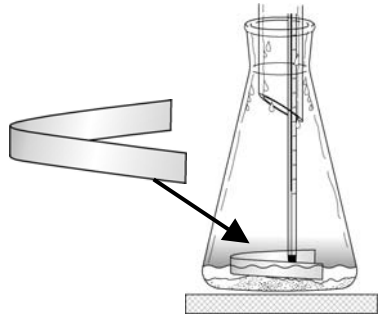


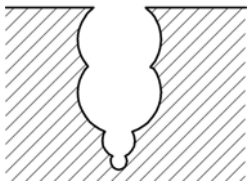






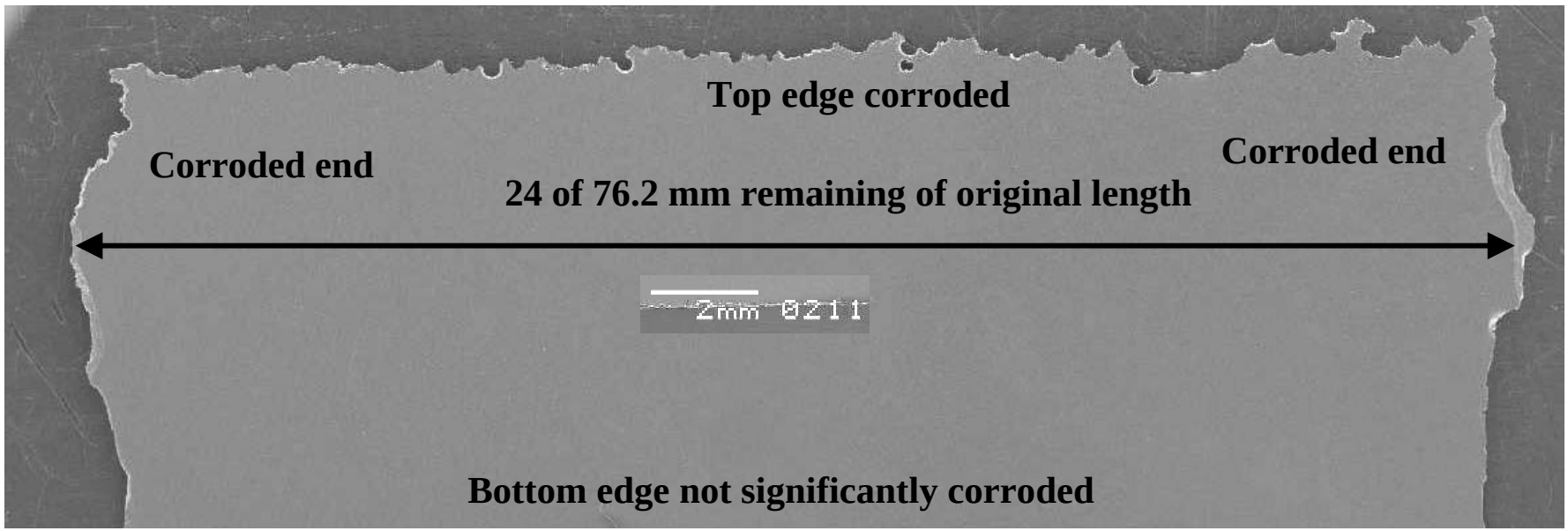






Saturated $FeCl_3$, Erlenmeyer (F 59)

- **C-22 specimen on edge and half submerged**
- **128°C**
- **Six days; extensive corrosion in last 3 1/2 hours, lost both ends**
- **76.2 x 12.7 x 0.051 mm**
- **Rate: >1.6 mm/year(one side)**



Saturated $FeCl_3$, Erlenmeyer (F 59)

- **C-22 specimen on edge and half submerged**
- **128°C six days, extensive corrosion in last 3 1/2 hours, lost both ends**
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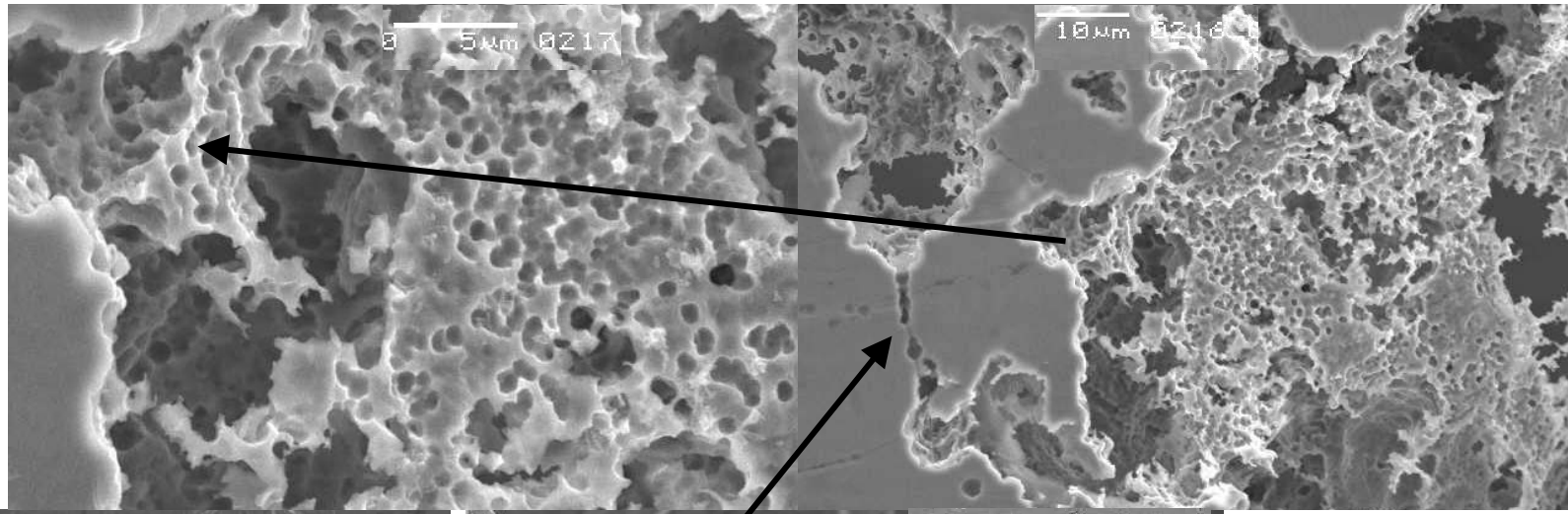
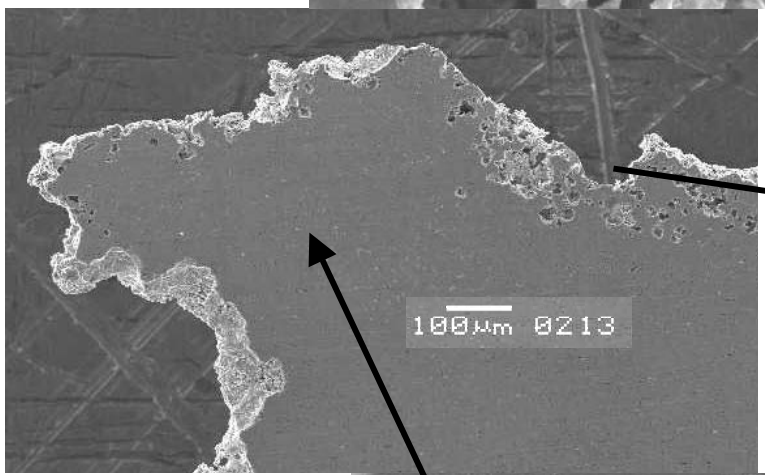
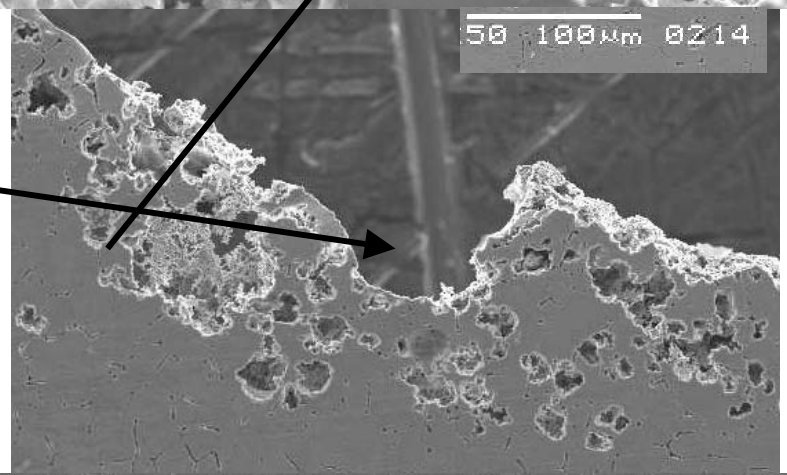
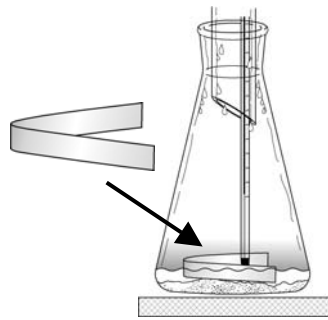
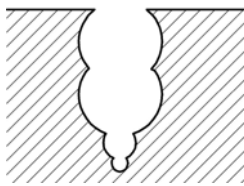
  > 1.6 mm/year

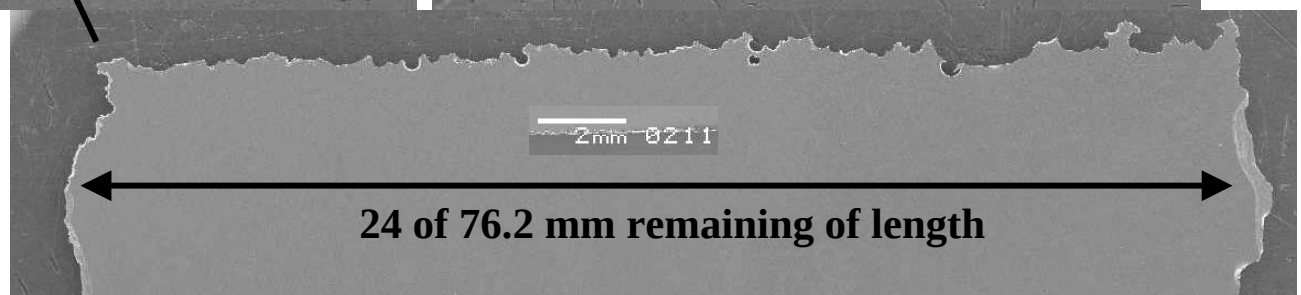












Saturated $FeCl_3$, Erlenmeyer (F 59)

- C-22 specimen on edge and half submerged
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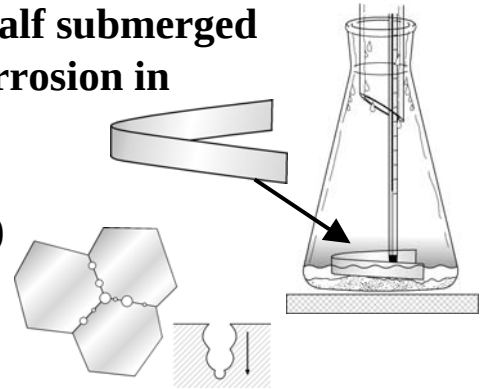

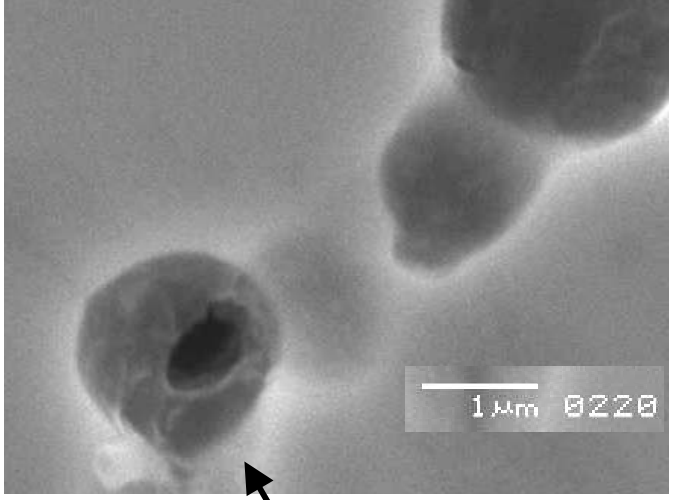

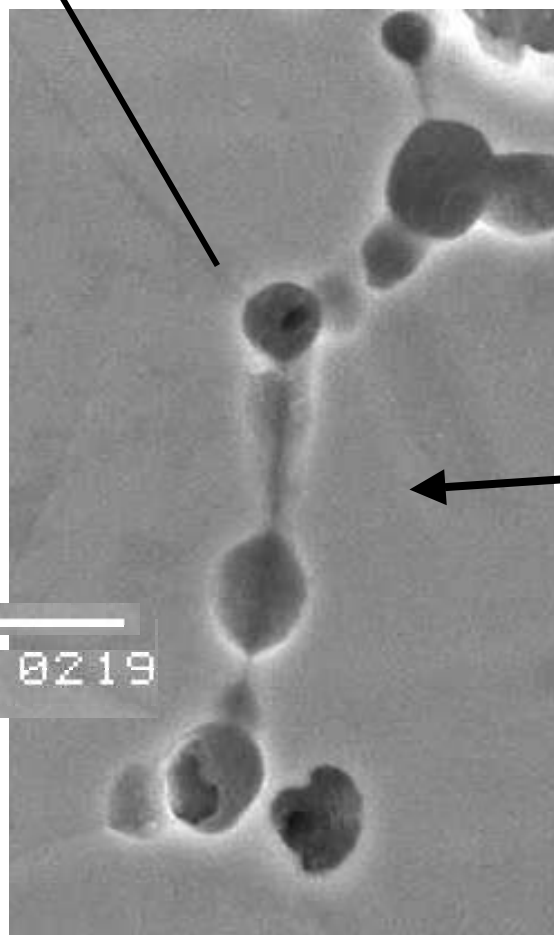

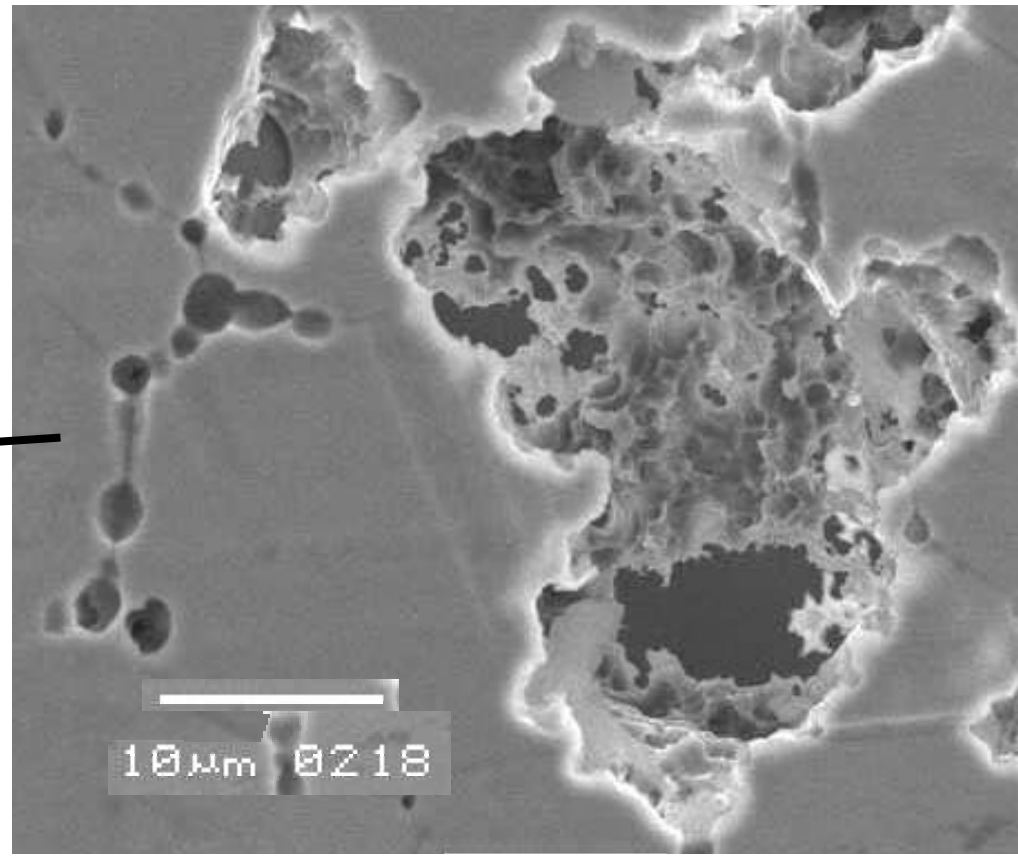

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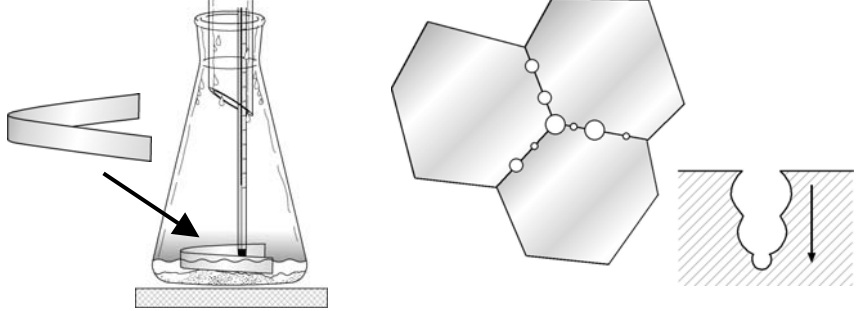
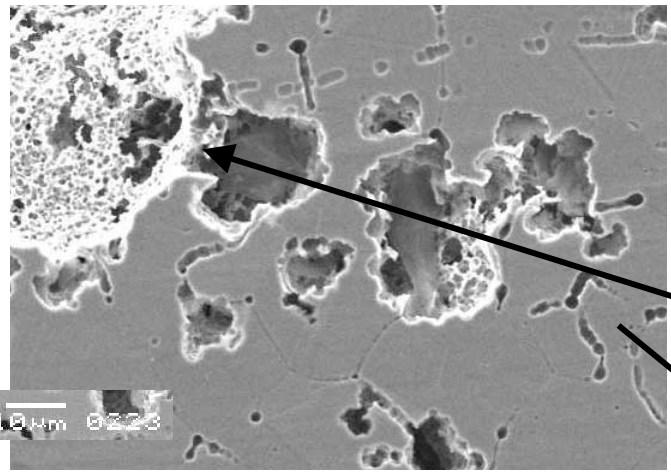
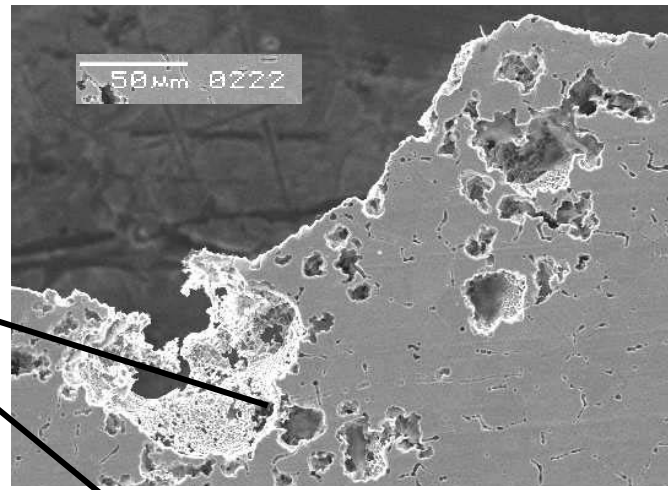
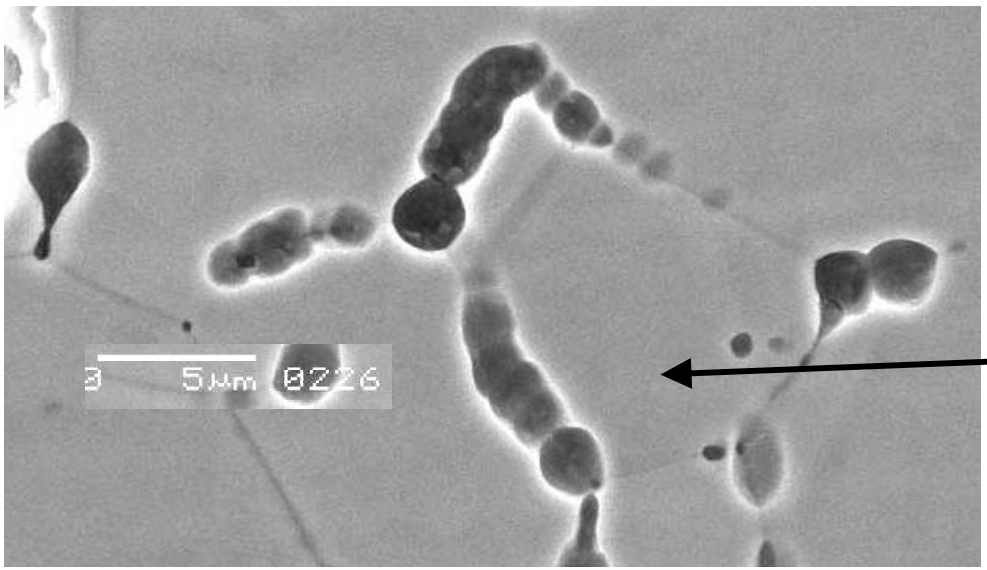
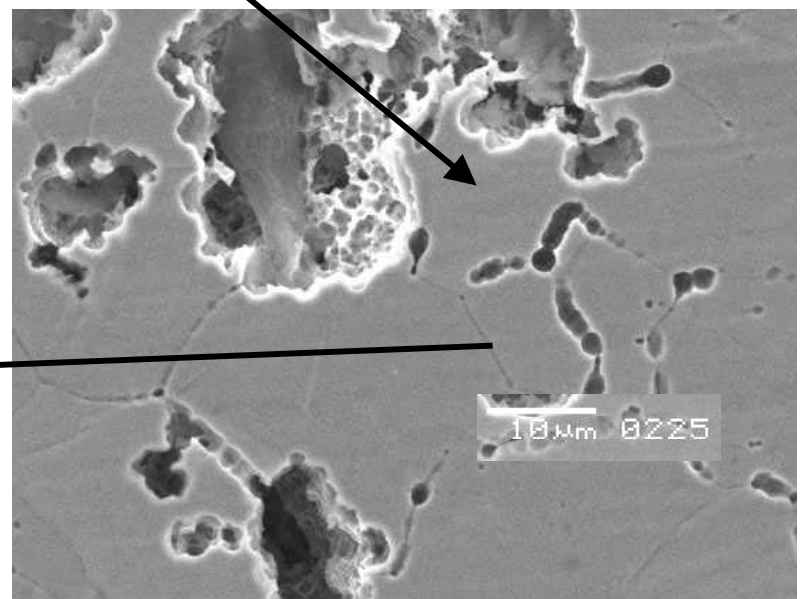




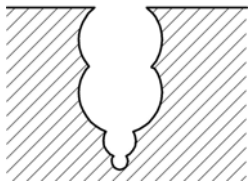


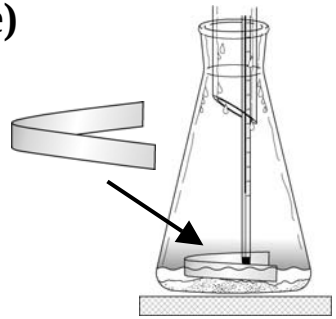


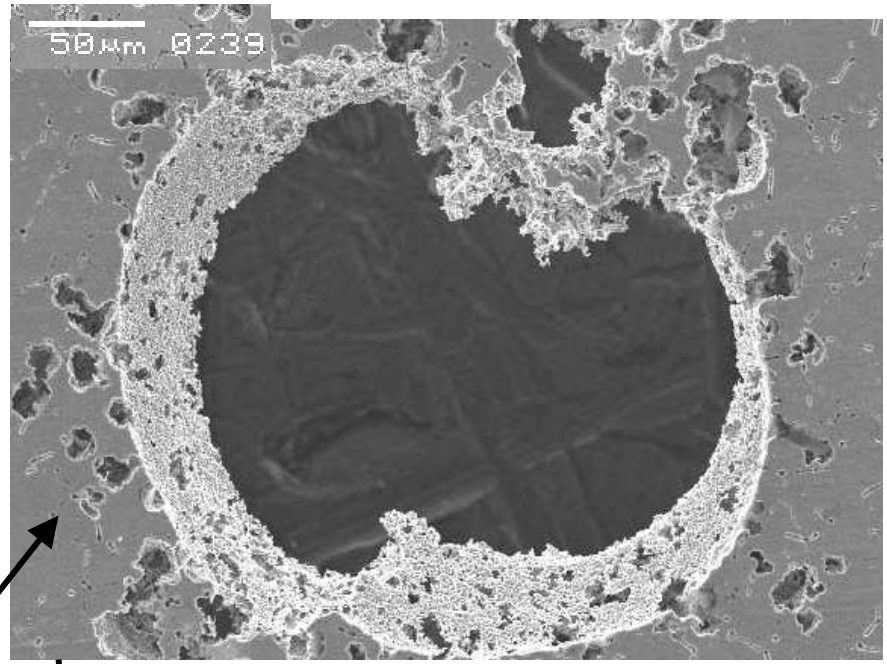


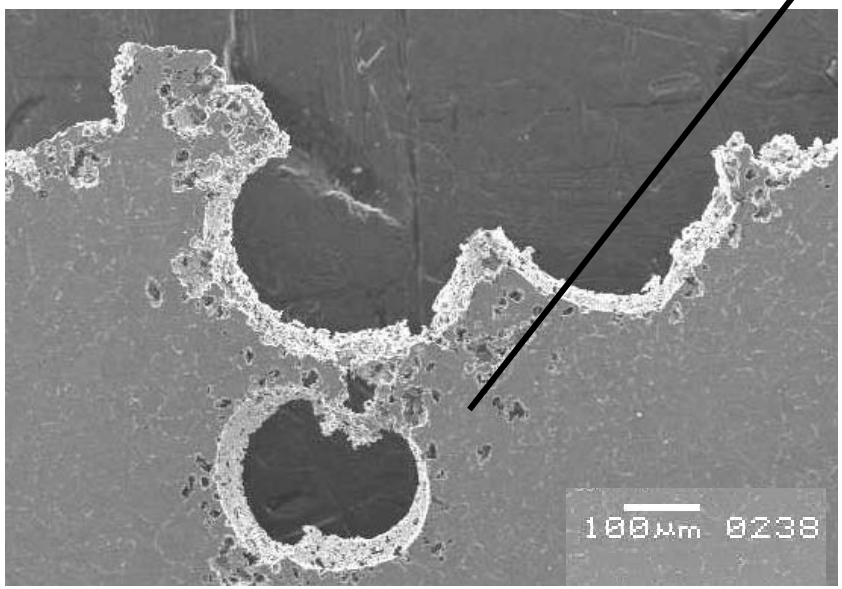
Saturated $FeCl_3$, Erlenmeyer (F 59)

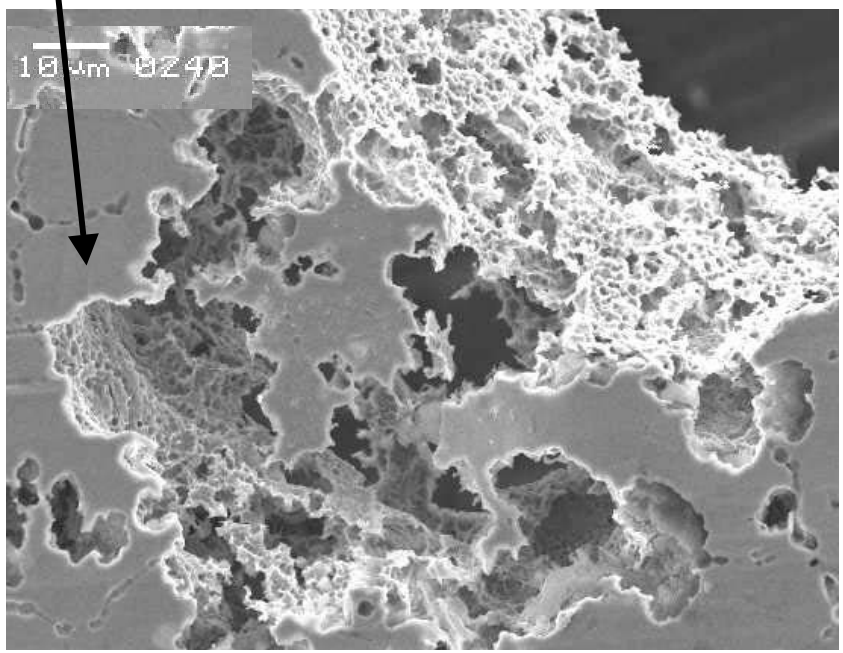
- **C-22 specimen on edge and half submerged**
- **128°C**
- **Six days; extensive corrosion in last 3.5 hours, lost both ends**
- **76.2 x 12.7 x 0.051 mm**
- **Rate: >1.6 mm/year(one side)**





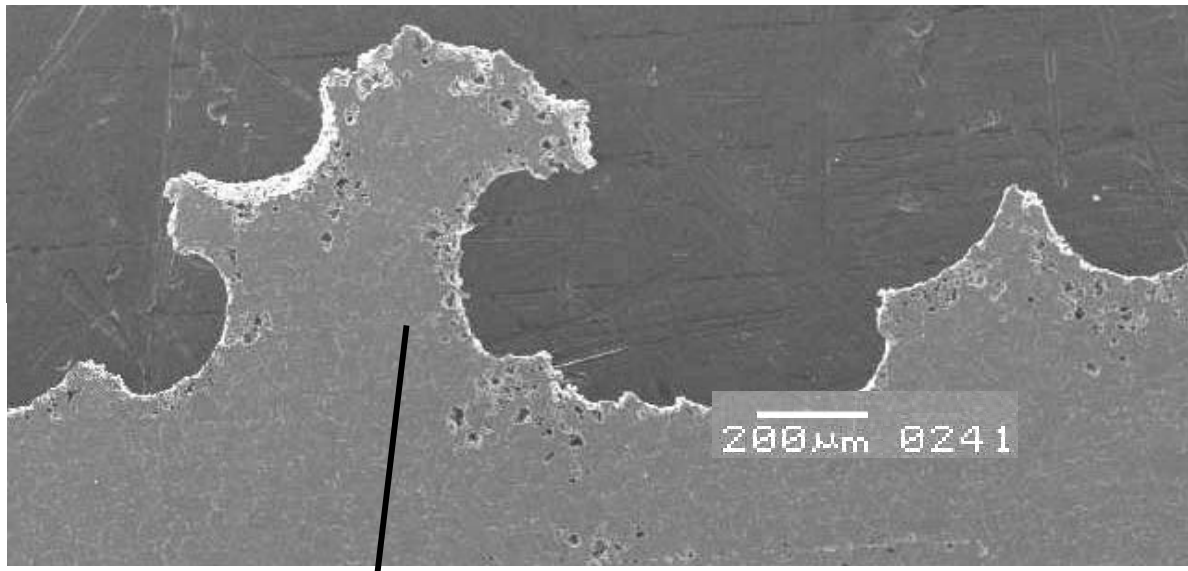


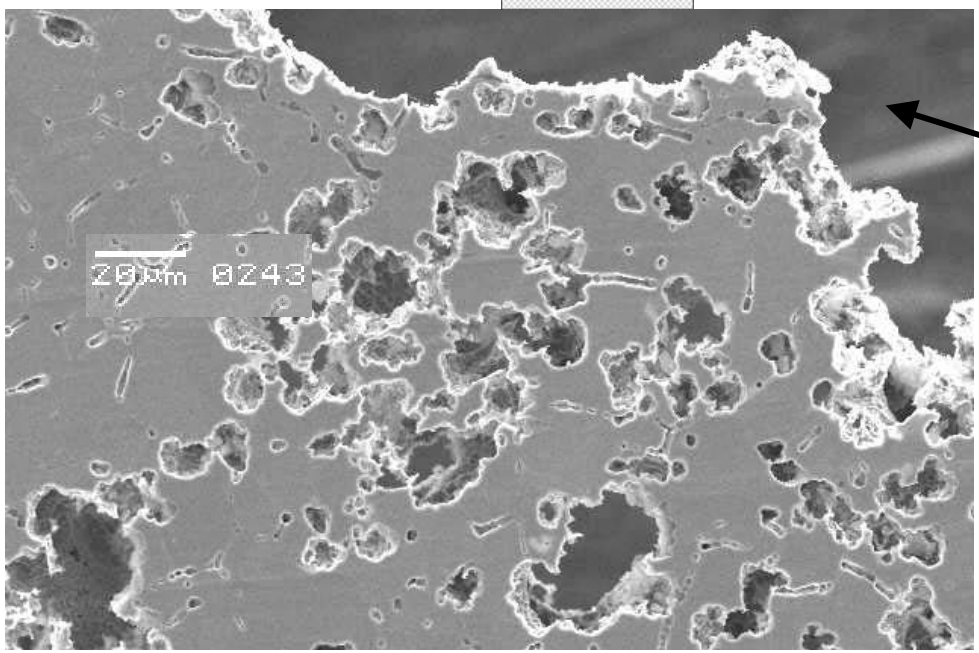


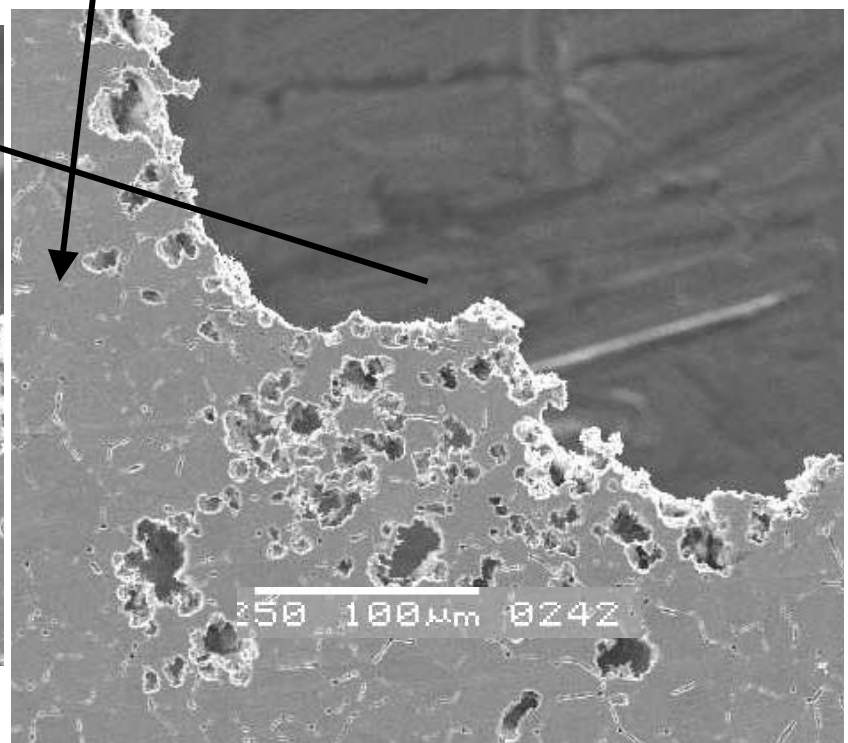


Saturated $FeCl_3$, Erlenmeyer (F 59)

- C-22 specimen on edge and half submerged
- 128°C
- Six days; extensive corrosion in last 3.5 hours, lost both ends
- 76.2 x 12.7 x 0.051 mm
- Rate: >1.6 mm/year(one side)

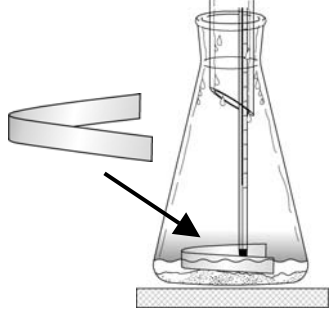


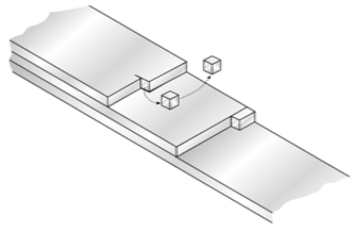


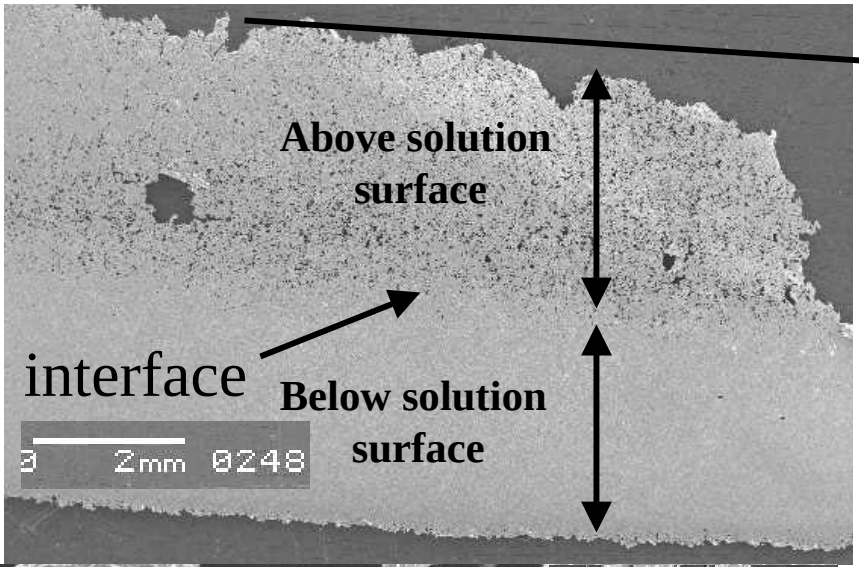


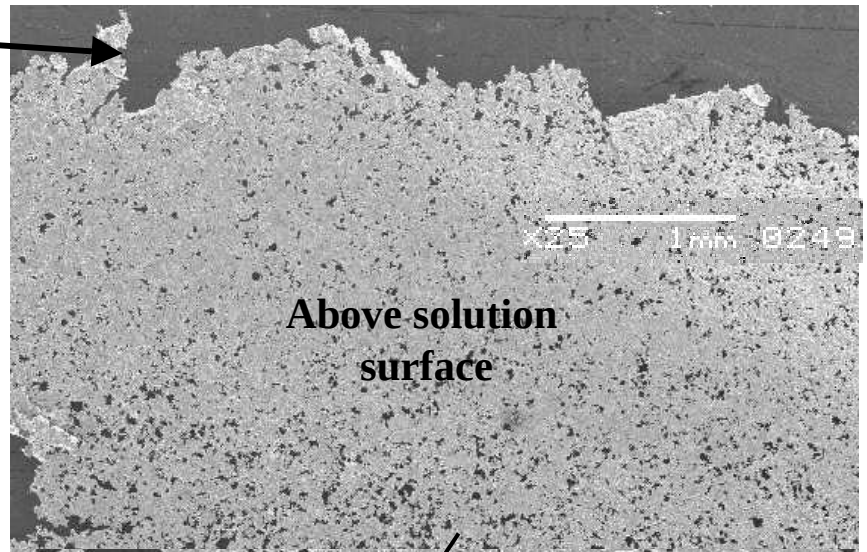
Boiling Conc. HCl, Erlenmeyer (F 62)

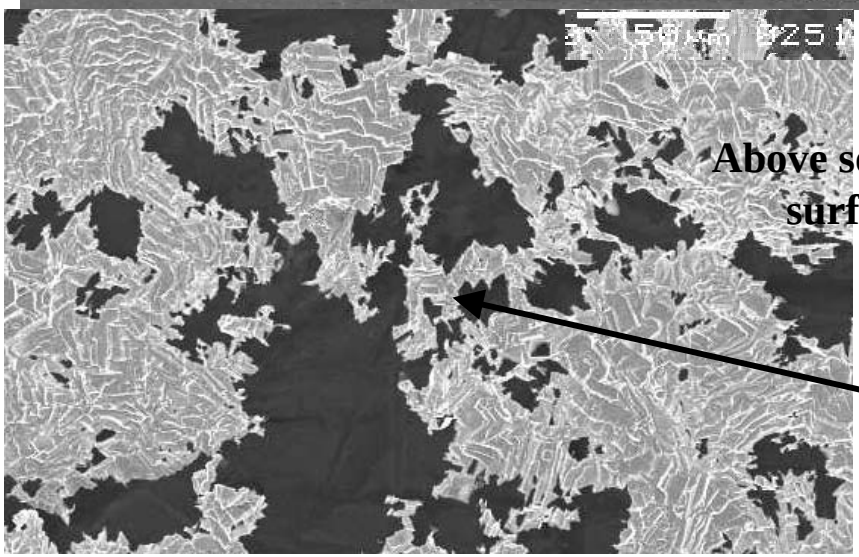
- C-22 specimen on edge and half submerged
- 110°C, • 42 hours
- U bend • 76.2 x 12.7 x 0.051 mm
- Rate of top >5.32 mm/yr (one side)

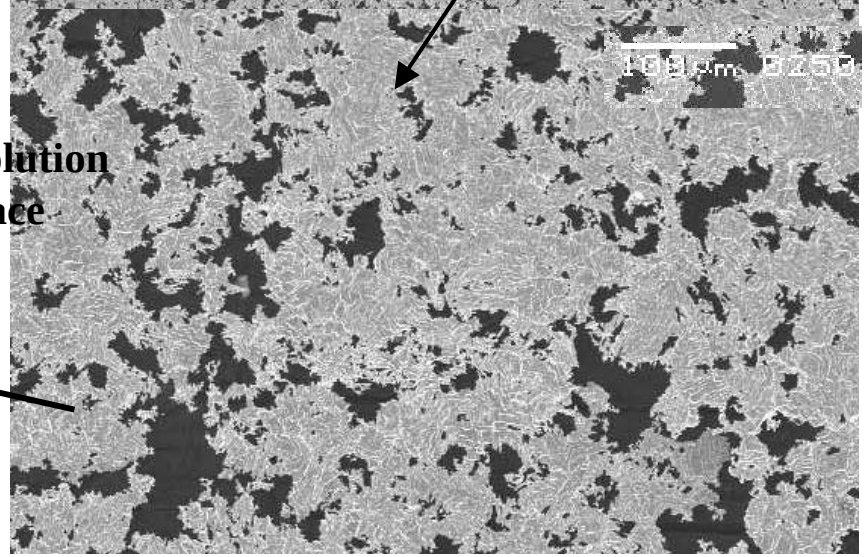






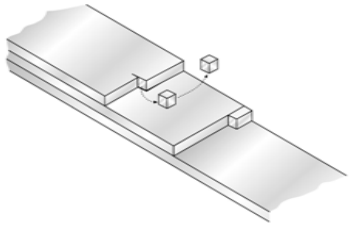


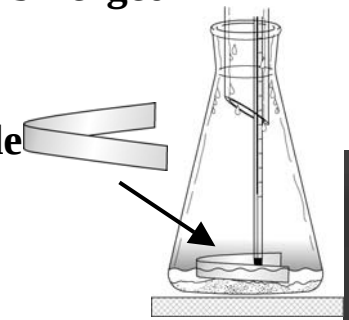


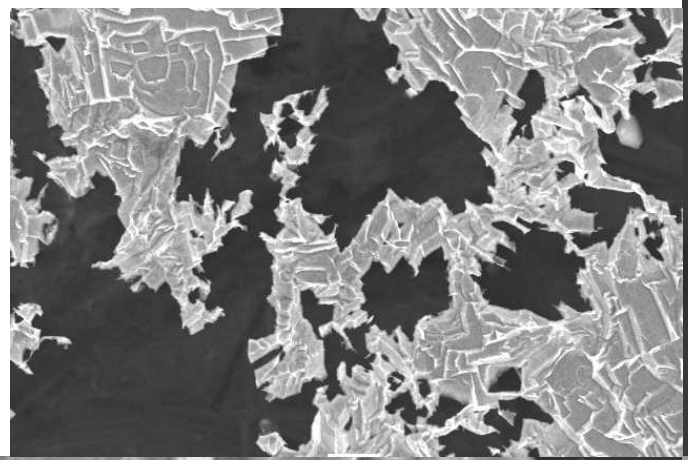


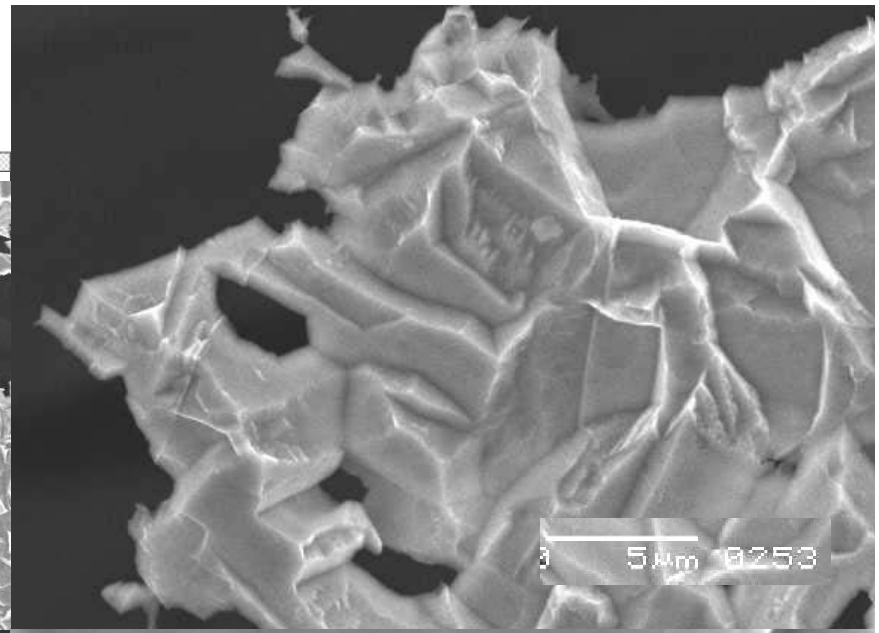
Boiling Conc HCl, Erlenmeyer (F 62 top)

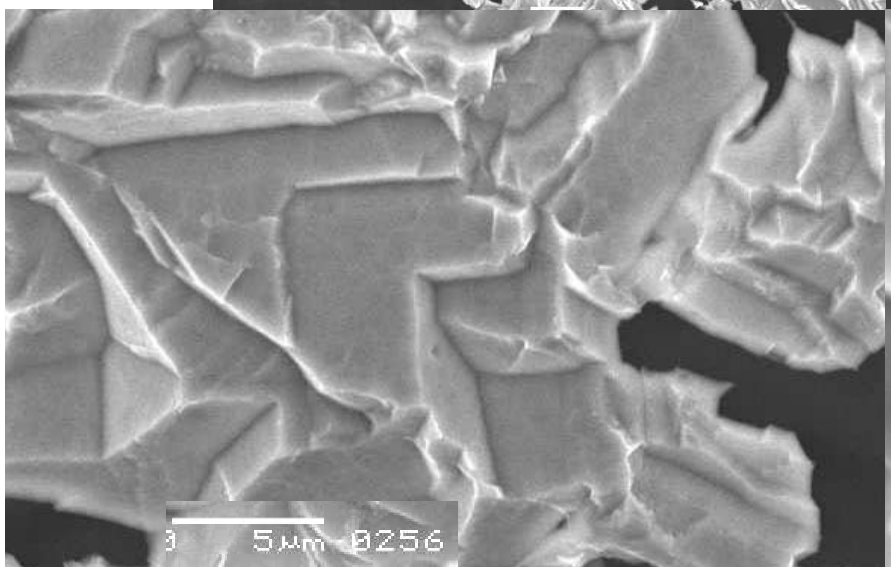
- C-22 specimen on edge and half submerged
- 110°C, • 42 hours
- U bend • 76.2 x 12.7 x 0.051 mm
- Rate of top: >5.32 mm/yr (one side

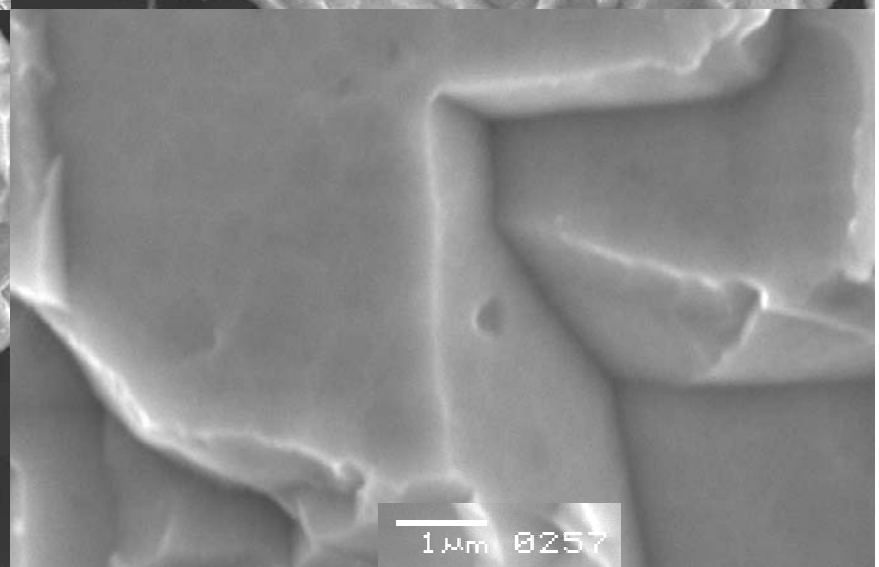






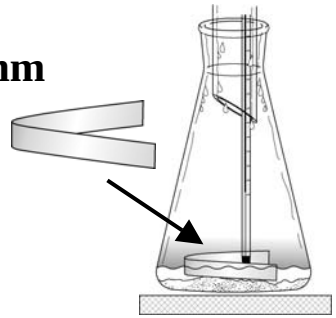


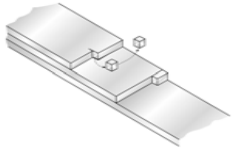


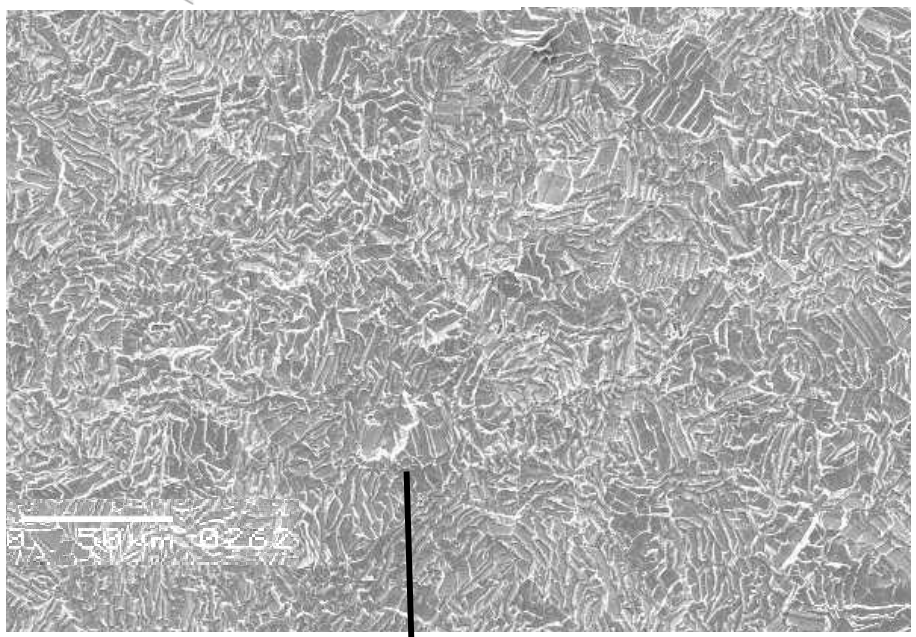


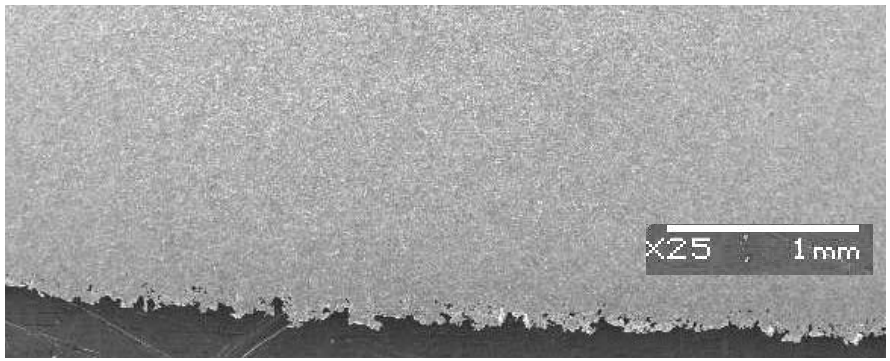
Boiling Conc HCl, Erlenmeyer (F 62 bottom)

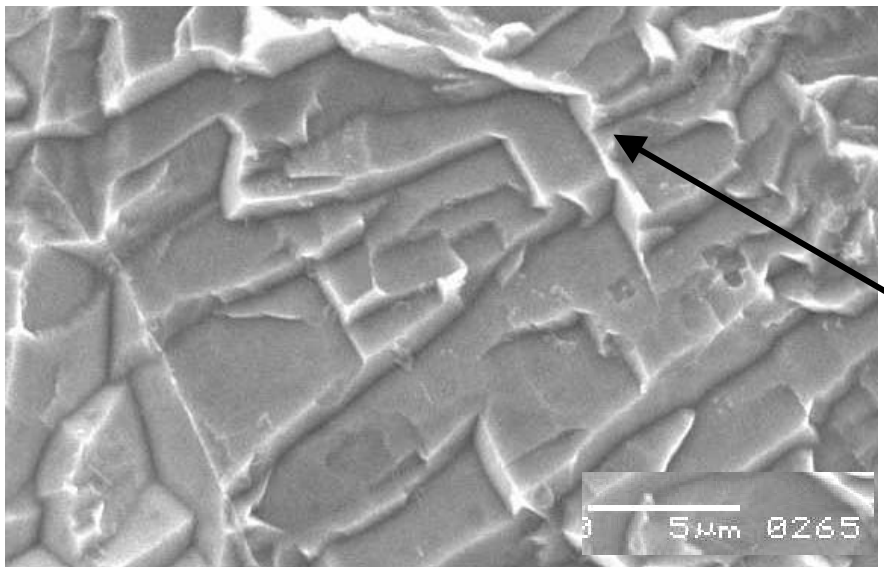
- **C-22 specimen on edge and half submerged**
- **110°C, • 42 hours**
- **U bend, 76.2 x 12.7 x 0.051 mm**
- **Rate of bottom:**
  > 2.0 mm/yr (one side)

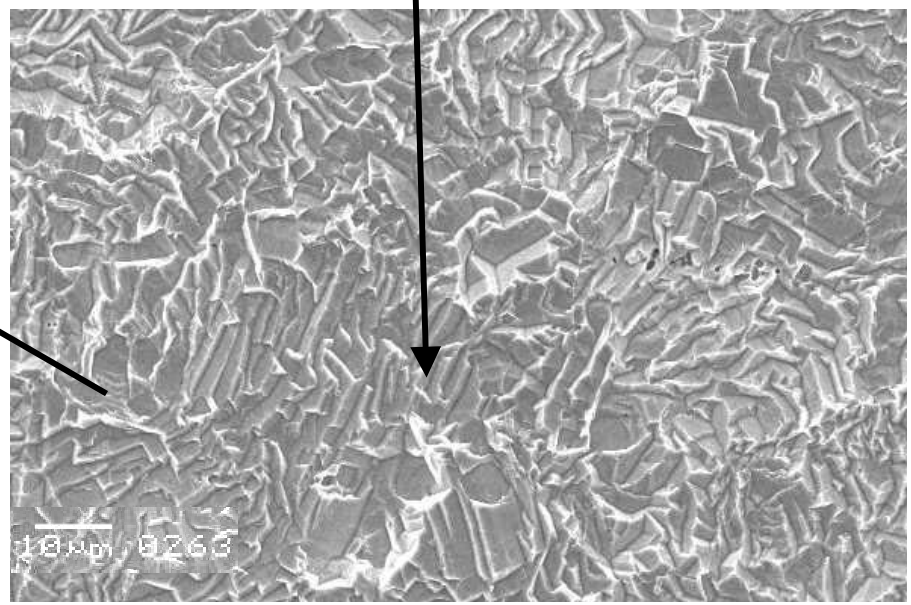






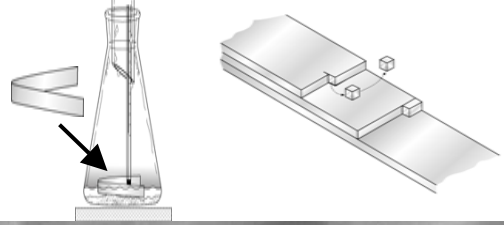




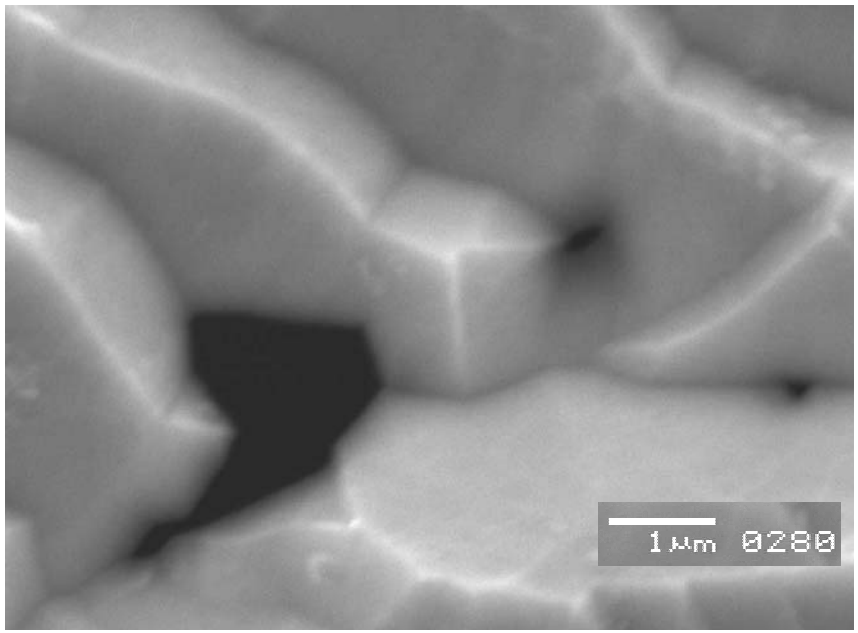


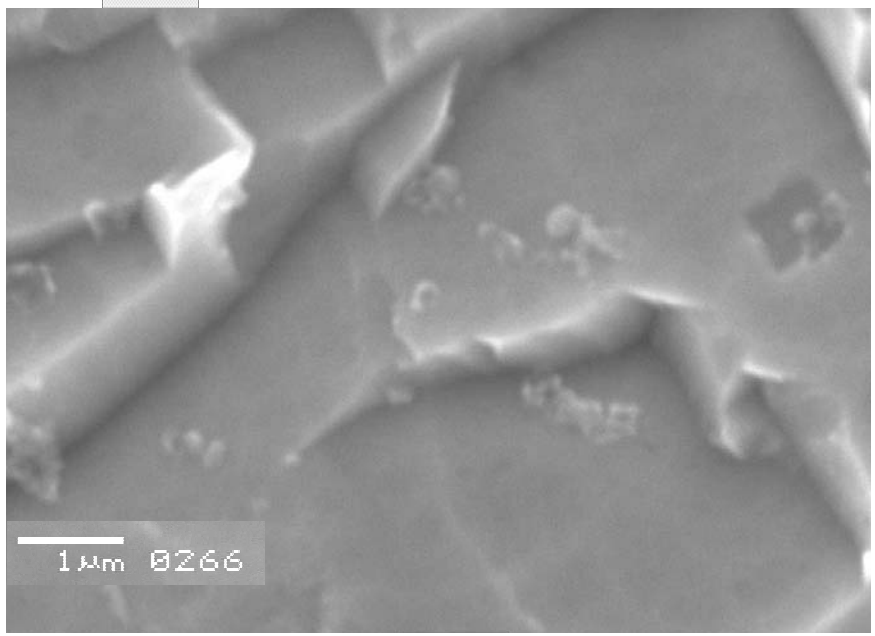
Boiling Conc. HCl, Erlenmeyer (F 62)

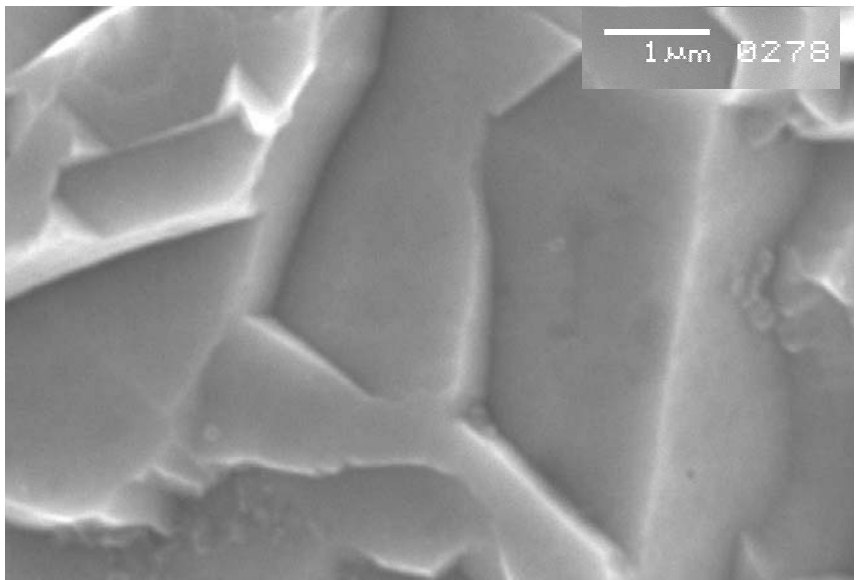
- **C-22 specimen on edge and half submerged**
- **110°C, 42 hours**
- **U bend, 76.2 x 12.7 x 0.051 mm**

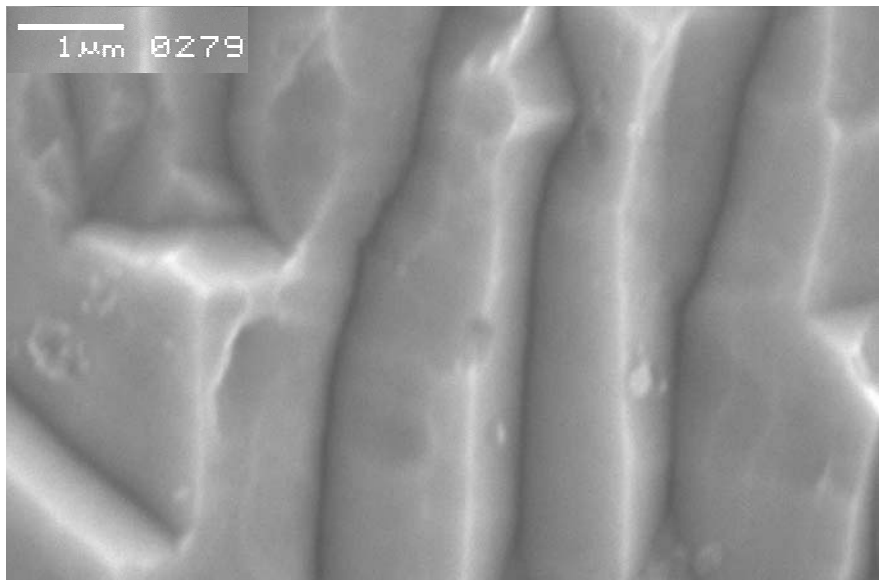


Depth



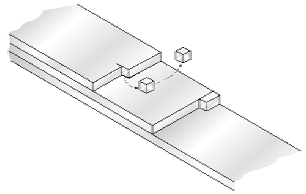


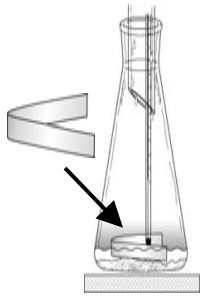


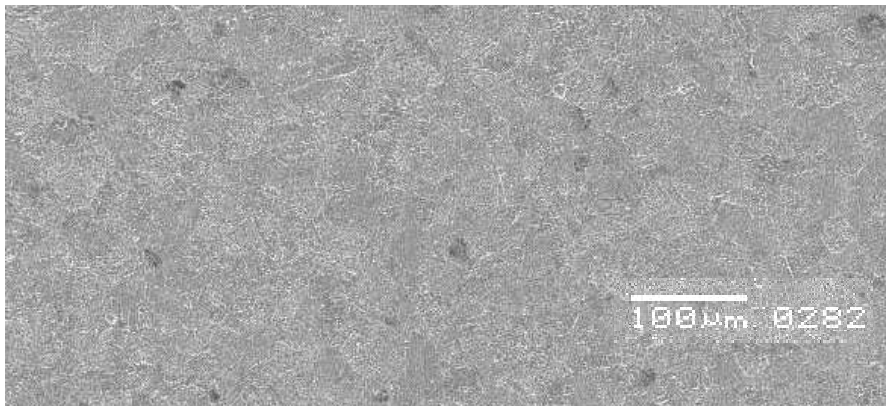


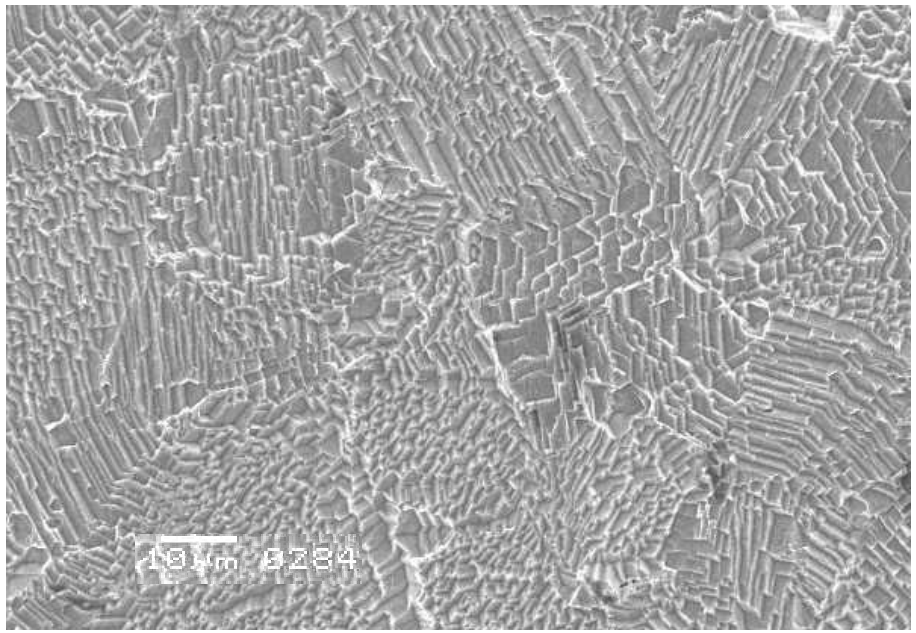
Boiling Conc HCl, Erlenmeyer (F 61 fully immersed)

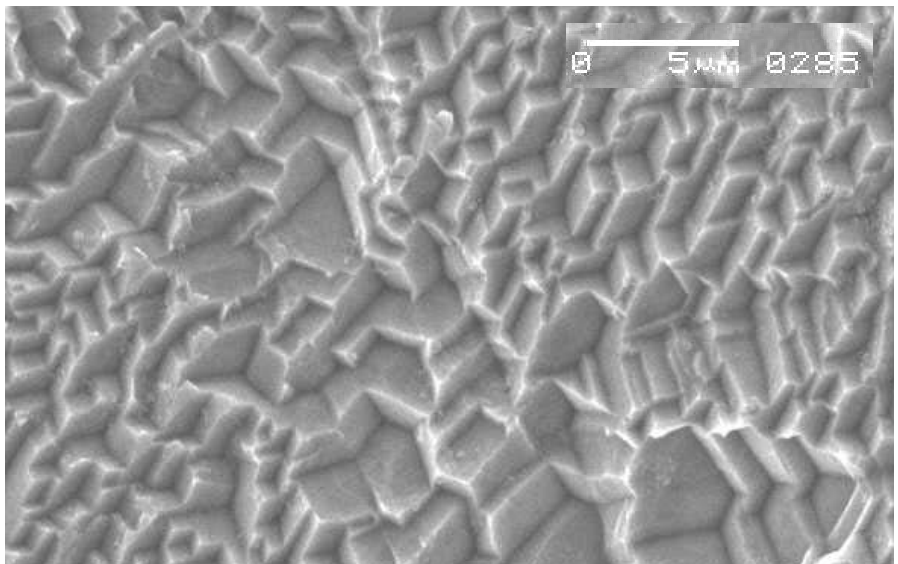
- C-22 specimen fully immersed
- 110°C, 42 hours
- U bend, 76.2 x 12.7 x 0.051 mm

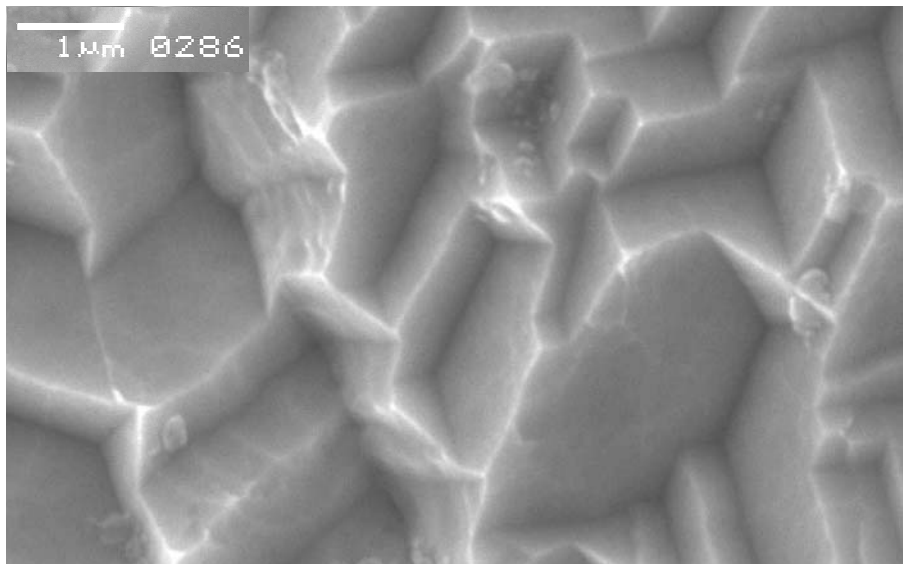












Morphology of Corrosion

1. **The corrosion observed in these SEM examinations exhibit different morphologies even within a single general morphology.**

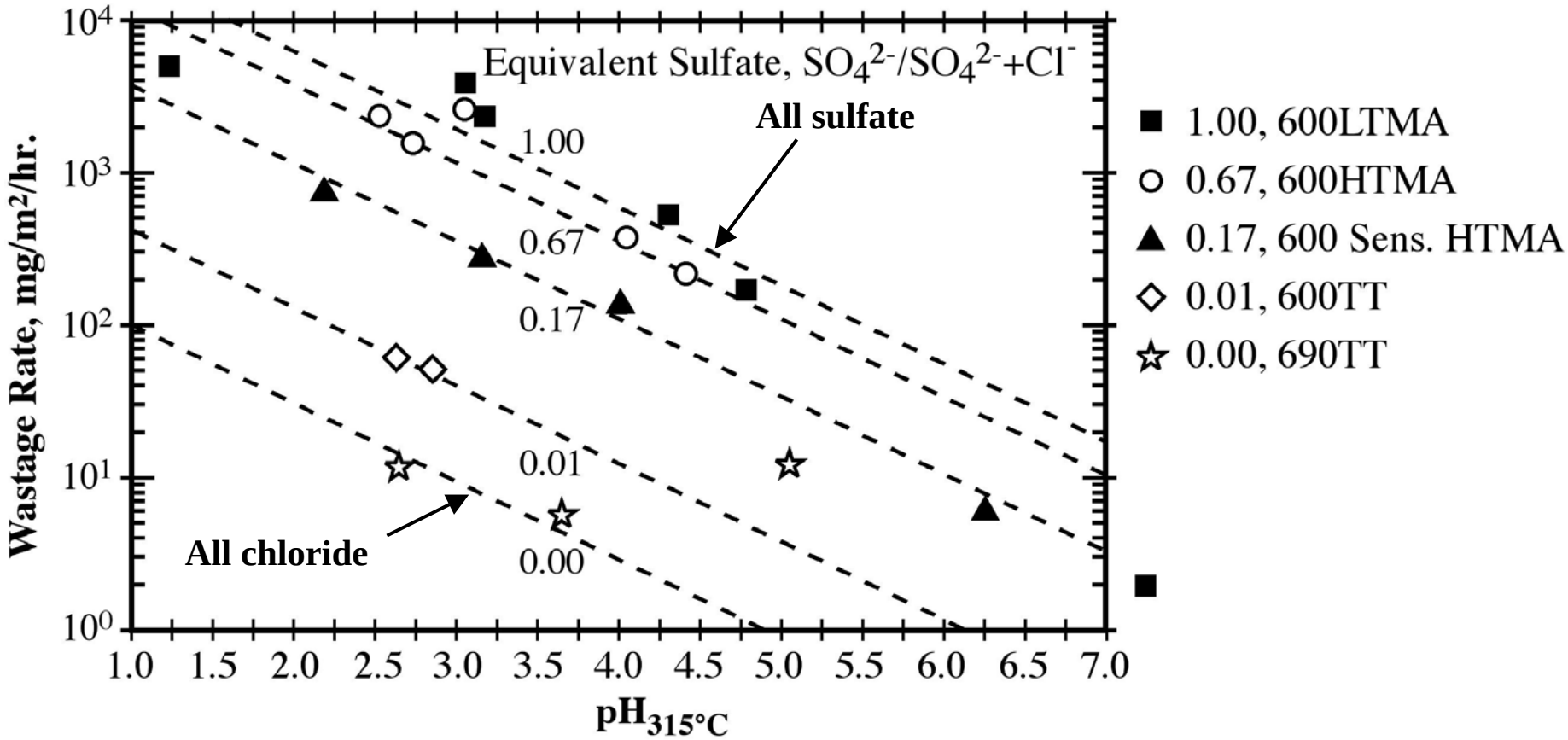
2. **The differences in morphologies seem to result from various effects of adsorbed ions on the velocity of recession of terraces or on the local chemistry of concentrated solutions in advancing localized corrosion.**

3. **Thus, the mix of anions in solutions should be expected to exert important influences on the shape of localized corrosion.**

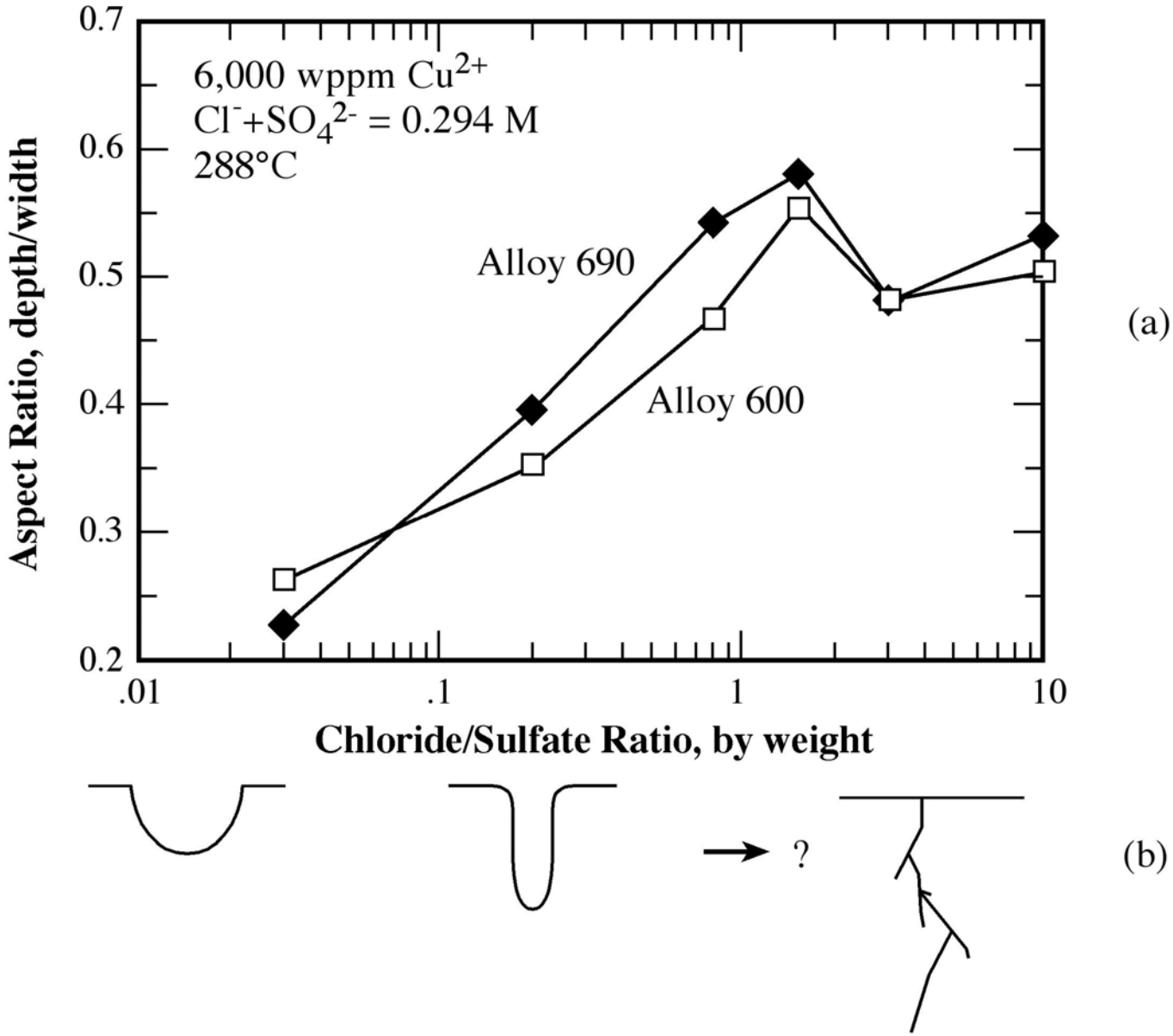
4. **The work of Cullen shows that the SO_4^{2-} ion does not block the recession of terraces as does the Cl^- ion. This difference leads to the variations in the acuity of localized corrosion.**

5. **For a given overall corrosion, the rate of penetration could be quite different.**

Effects of pH, Chloride/Sulfate, Alloy on General Corrosion for Alloys 600 and 690 (Work by Cullen)

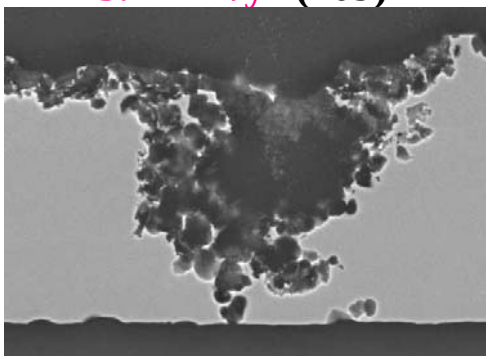


Effect of Chloride/Sulfate Ratios on the Aspect Ratio of Pits for Alloys 600 and 690 (Work by Was)

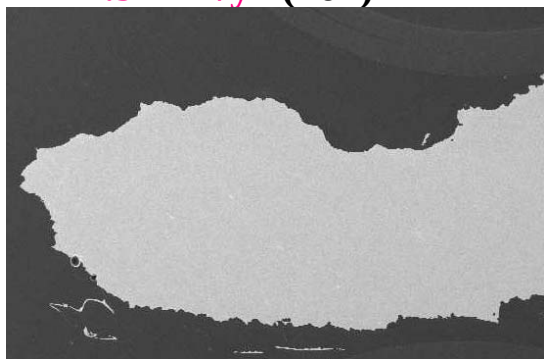


Summary of modes and rates of corrosion

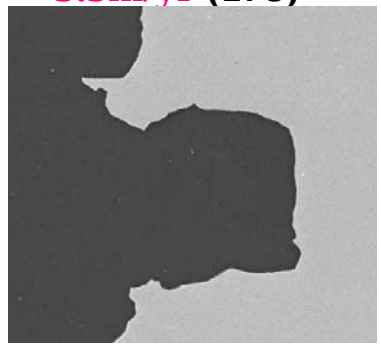
1243x UZ foil paste 150°C, >3.7 mm/yr (109)



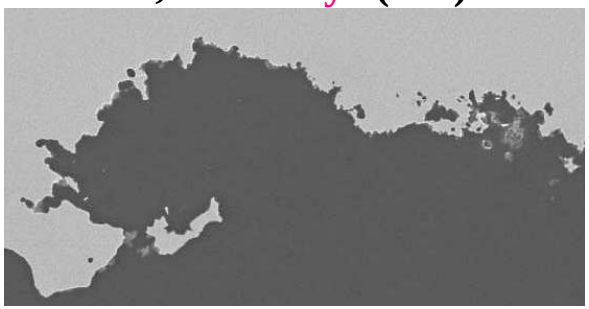
1243x UZ disc, 145°C, 1.9 mm/yr (161)



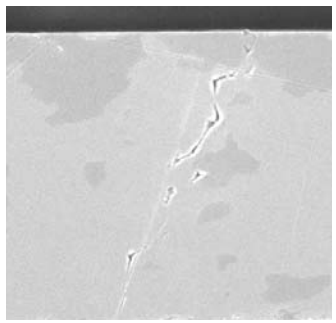
1243x UZ sox 75°C, 5.5m/yr (178)



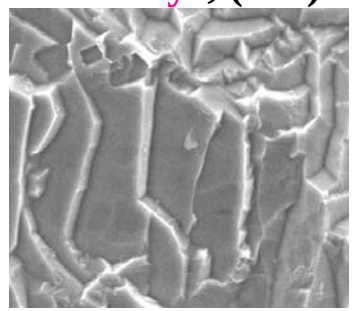
1243x UZ U bend, 145°C, 2.1 mm/yr (202)



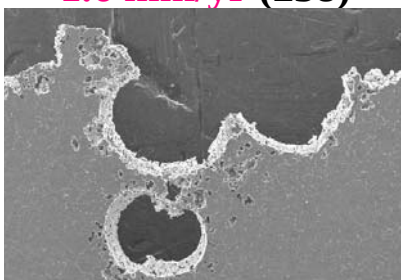
1x UZ, 120°C (123)



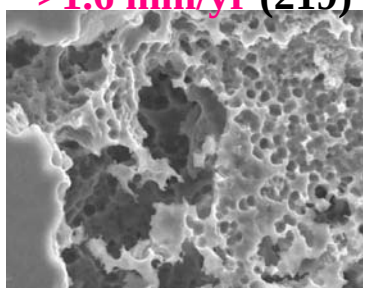
Boil, conc HCl, 110°C, 2-6 mm/yr, (264)



Sat'd $FeCl_3$, 128°C, >1.6 mm/yr (238)



Sat'd $FeCl_3$, 128°C, >1.6 mm/yr (219)



Sat'd $FeCl_3$, 128°C, >1.6 mm/yr (217)

Warnings

1. **There is an abundance of warnings as well as solid quantitative data that demonstrate that corrosion of the C-22 alloy is inevitable and rapid.**

2. **A good paradigm for the warnings about C-22 can be found with Alloy 600 that was widely used in the nuclear industry as tubing in steam generators and as structural components. Alloy 600 has broadly failed in these applications, and present failures could easily have been predicted from past occurrences.**

3. **There are now abundant warnings that that C-22 alloy is not adequate nor is the present design of the repository adequate. Such warnings are founded on warnings, some of which are 15 years old.**

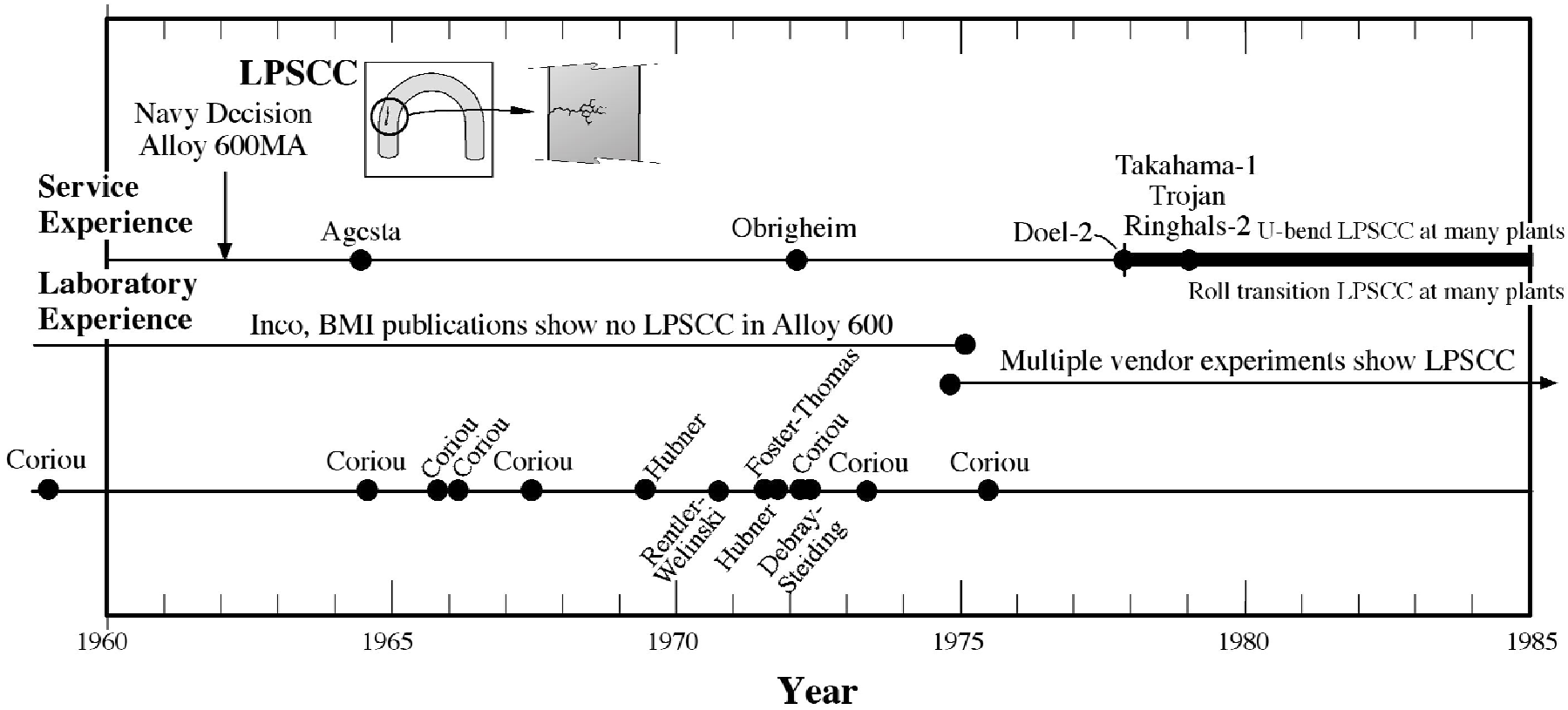
4. **Further, there is abundant evidence that the YM site itself is not adequate.**

5. **The analogies of warnings from the present nuclear industry are abundant and apply directly to whether the present design at YM is adequate. The answer is that it is not.**

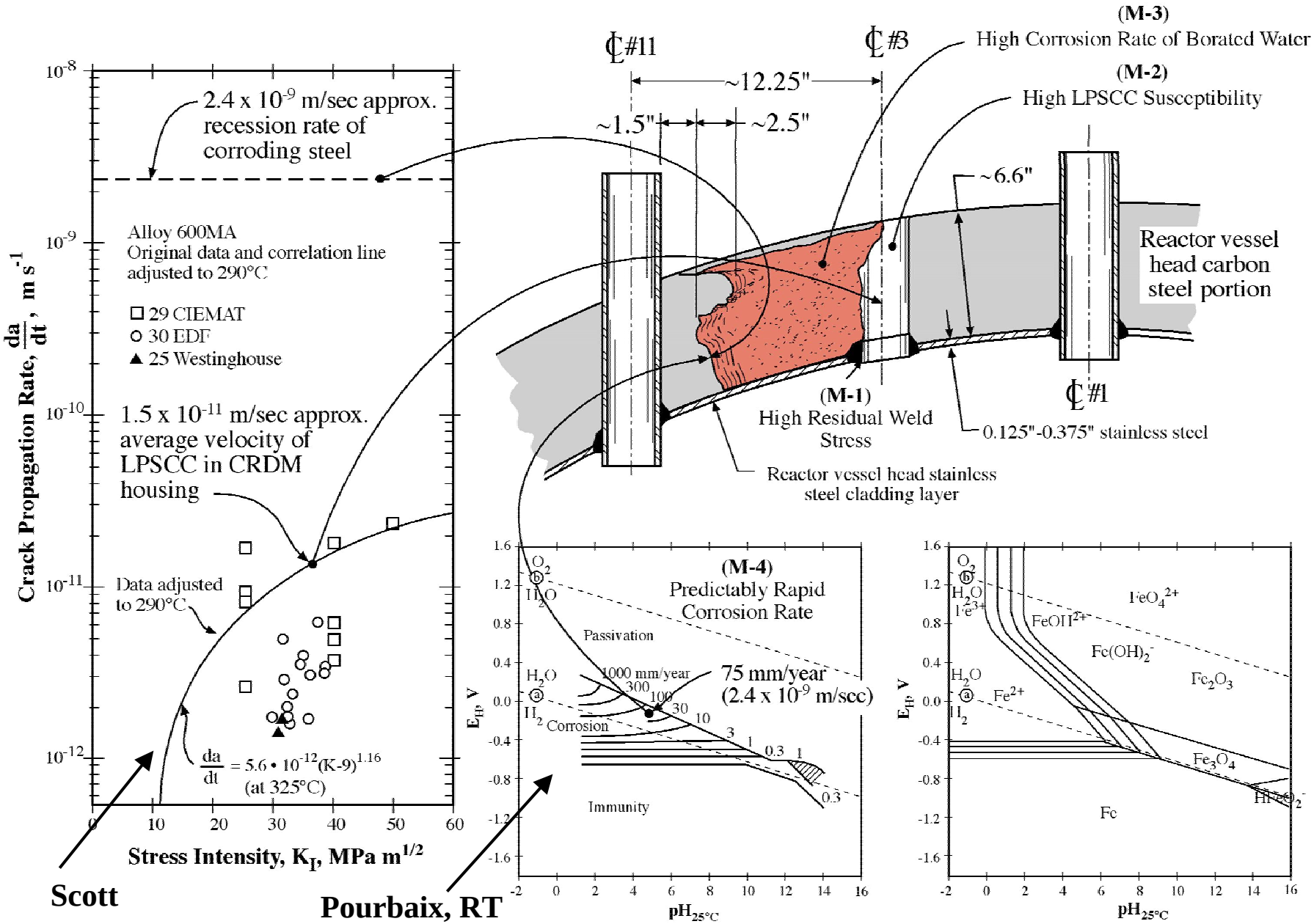
6. **Some of the warnings from experience of the water cooled nuclear reactor industry apply directly to the design and development of the Yucca Mountain facility. These should be carefully assessed,e.g. as they apply to heated surfaces.**

7. **Finally, the incapacity to inspect the YM containers requires assurances of reliable performance that are higher than those of normal industrial expectations.**

Chronology of LPSCC: service and laboratory experience
--Reticence to act on observations



Mi sequence for Davis Besse type of failure



"Knowns" about Corrosion of C-22

1. **Deposits. which are reasonably expected due to concentration by a heated surface from pore water from the UZ, produce corrosive environments.**

2. **Relatively simple experiments can model reasonably expected conditions on container surface. However, the inherent complexities prevent precise modeling.**

3. **A range of chemistries from concentrating the pore water can be expected including HNO_3, HCl, HF species in high concentrations.**

4. **Corrosion produced by these environments can proceed at rates of 1 to 6 mm/yr compared to a wall of C-22 of 20 mm and a backup of Type 316 SS of about 20 mm.**

5. **Temperatures over which these high corrosion rates can occur are in the range of 70 to 150°C.**

6. **There is no evidence that the corrosion is self-stifling.**

7. **The corrosion observed proceeds without stress.**

8. **Accelerated corrosion is observed in the paste of deposits, in the liquid layer above the paste, in the saturated vapor above the paste, and in liquid formed from re-fluxing.**

Facts Relevant to the Corrosion-Related Integrity of the Container

Significant pore water in unsaturated zone (81 L/m^3)

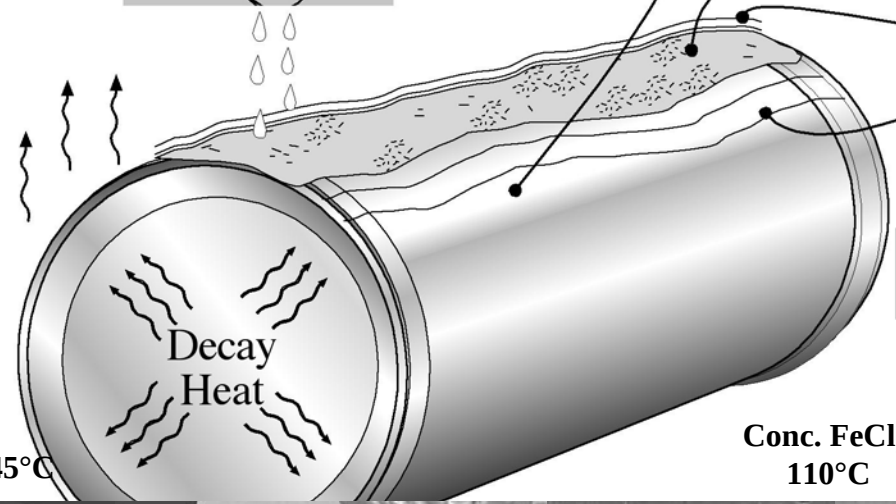
Rock extensively fractured (preferred water pathway)

Surface temperature in range of 90-250°C

Concentration of pore water to acidic solutions due to hot surface

Increasingly thick and increasingly circumferential deposits

Decay heat to rock causes water movement and rock instability

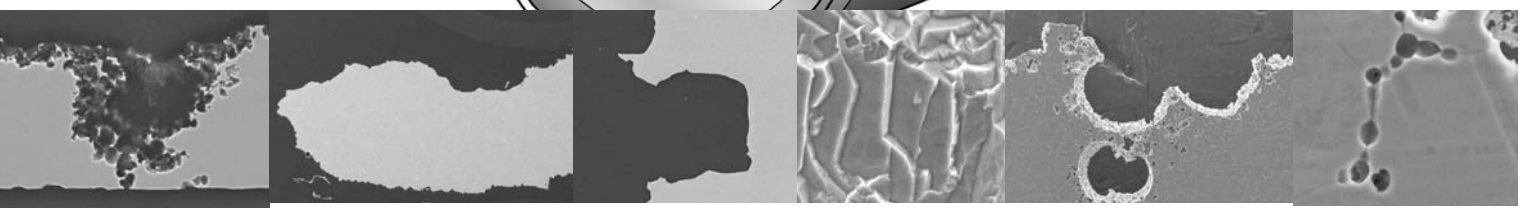


UZ pore water produces acidic (HNO_3, HCl, HF) species when concentrated

1243x UZ 150°C

1243x UZ 145°C

Conc. $FeCl_3$ 110°C



Non-stifled corrosion of multiple modes without stress. Rates from 1 - 6 mm/year compared with C-22 wall thickness of 20mm

1243x UZ sox 75°C

Conc. HCl 110°C

Porous rock - minimal barrier to release of radioactivity

Saturated zone produces alkaline species when concentrated by heat

"Inevitabilities" about early corrosion of C-22 waste containers

1. **C-22 sustains rapid corrosion in environments that are reasonably expected to develop on the heated surface.**

2. **A significant amount of water is present above the containers in the UZ.**

3. **The pore water in the UZ contains chemicals that produce acidic environments on the surfaces of heated containers.**

4. **The extensively fractured rock above the containers provides easy access of pore water to the surface of the container as the UZ is heated.**

5. **Continued formation of deposits on containers will increase surface temperatures and accelerate concentration as well as sequestering corrosive chemicals.**

6. **Stress is not necessary for the rapid penetration of C-22.**

7. **Other alloys beneath the C-22 are unlikely to provide significant barriers to the corrosive environments that perforate C-22. Penetrating C-22 will be slow step.**

8. **The lack of capacity to inspect containers over time exacerbates the seriousness of the present state of inevitability.**

Primary Conclusions

1. **There is now ample and compelling evidence that the container of the present design, in the present location, and with present materials will not work. Further "band-aids" cannot reliably provide significant assurance of satisfactory performance.**

2. **Penetration of the corrosive chemicals that can reasonably be expected to accumulate on the surface could perforate to the fuel in asearly as ten years and is especially accelerated during the "thermal pulse."**

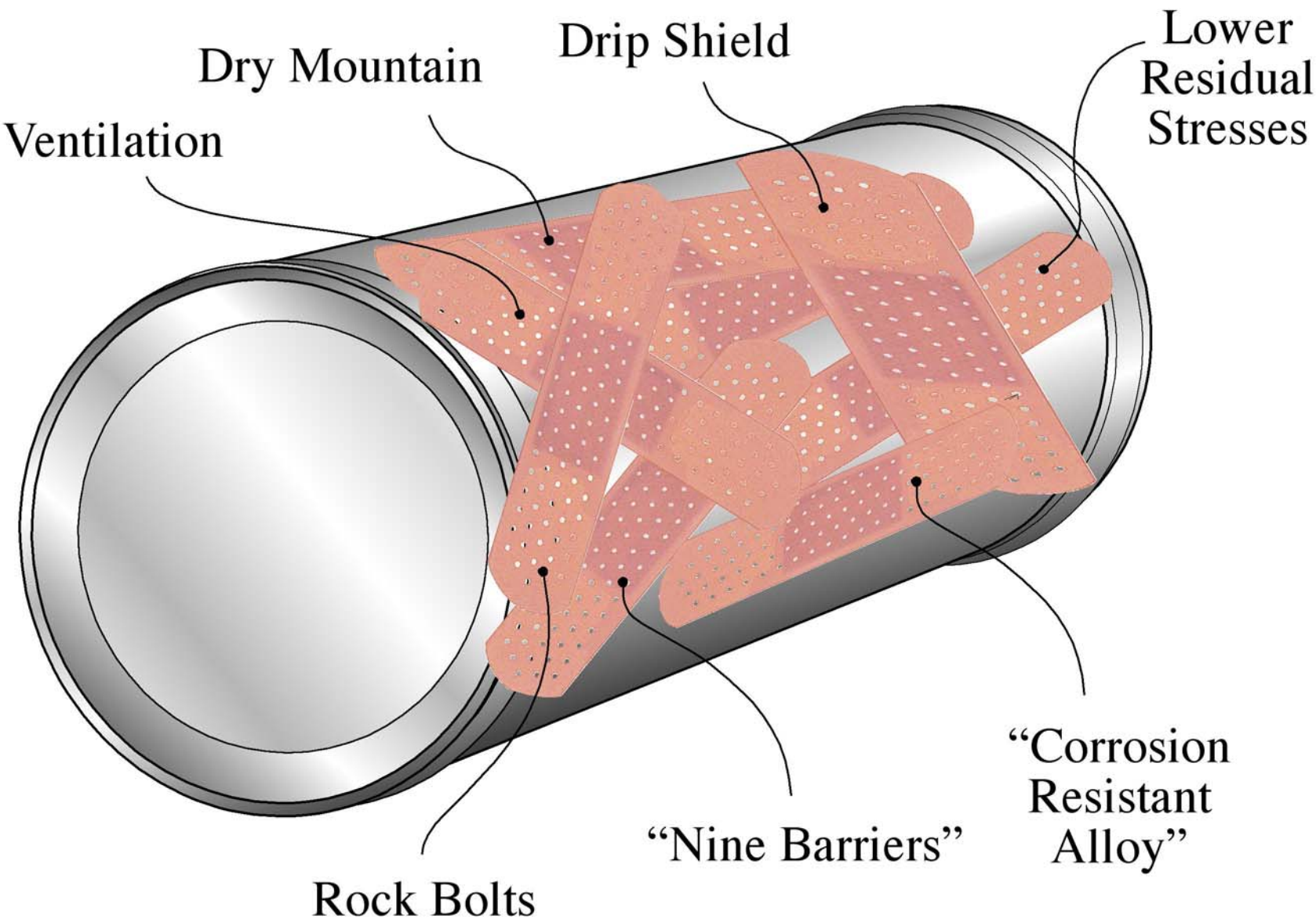
3. **There are no reliable barriers that have been identified to prevent release of radioactivity to the atmosphere through the porous saturated zone.**

4. **While the possibility of such failure is clear, the detailed avenues and rates for such failures cannot be readily bounded. It is probably not possible to develop a quantitative bounding model in view of the complexities that must be considered.**

5. **The principal factors that are critical to the lack of integrity of the vessel have been know for relatively long times: The importance of the hot surface was identified in the late 1980s; the porosity of the saturated zone was known by the same time; the fact that C-22 could not sustain concentrated acids has also been known.**

6. **Clear warnings that failures of the containers are inevitable are already available. However, quantifying such warnings is difficult in view of the complexity.**

Patch-on-Patch Design



What? Me worry?