RPP-34720-VA
Revision 0

Electrochemical Studies of Hanford Double-Shell Tank Waste

Prepared for the U.S. Department of Energy
Assistant Secretary for Environmental Management

Contractor for the U.S. Department of Energy
Office of River Protection under Contract DE-AC27-99RL14047

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Hanford Group, Inc.

P.O. Box 1500
Richland, Washington

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Electrochemical Studies of Hanford Double-Shell Tank Waste

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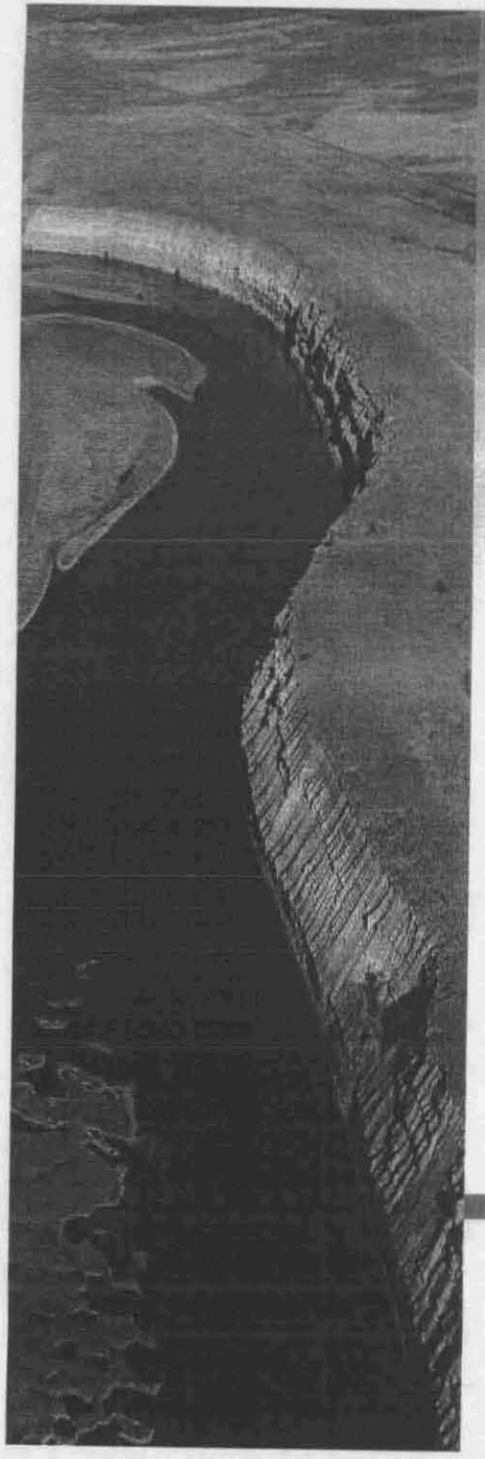

Electrochemical Studies of Hanford Double-Shell Tank Waste

Gary A. Cooke and James B. Duncan

August 23, 2007

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Analytical Technical Services
Analytical Process Development

This work was performed for the U.S. Department of Energy, Office of River Protection, under Contract DE-AC27-99RL14047

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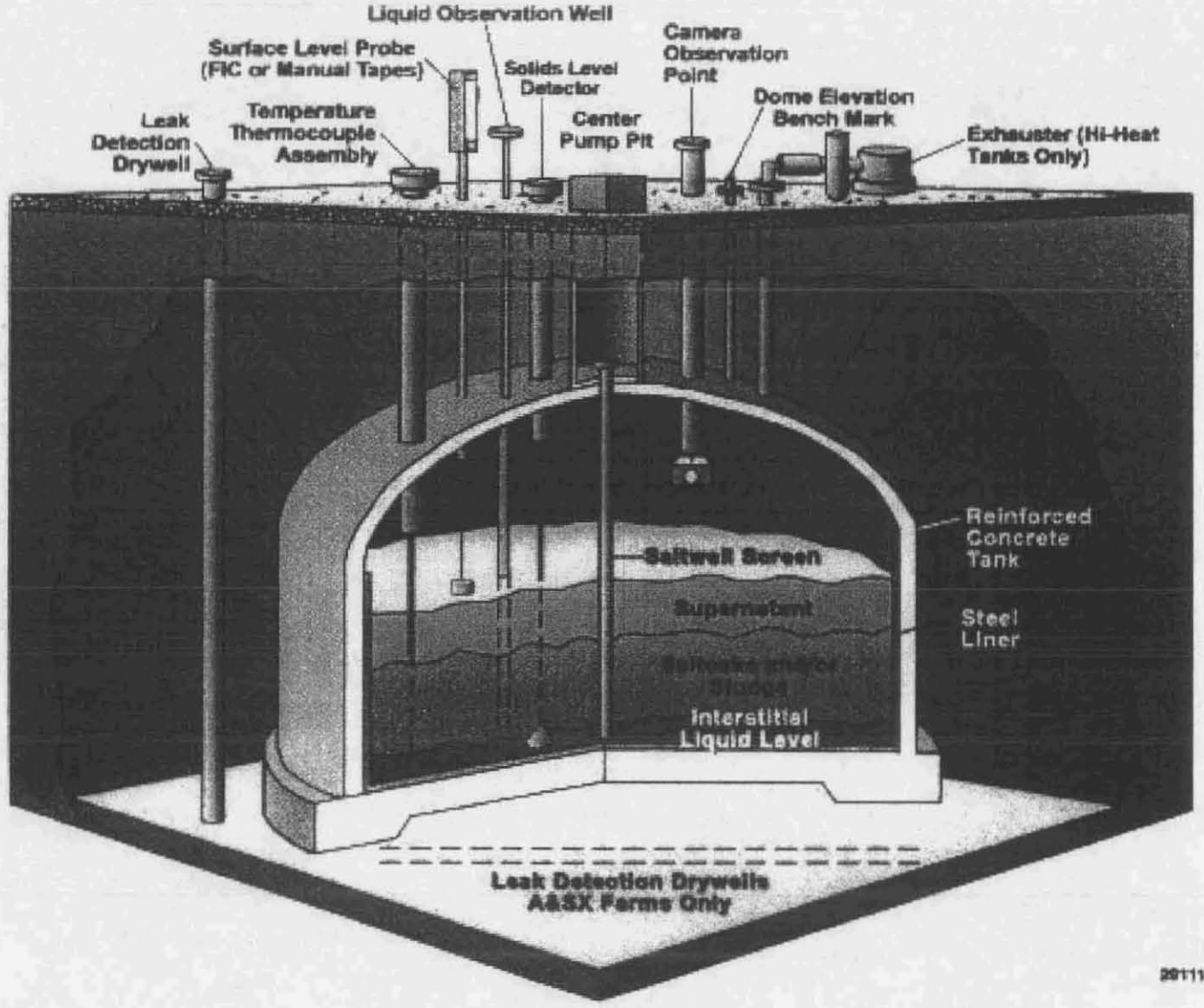
Single-Shell Tank



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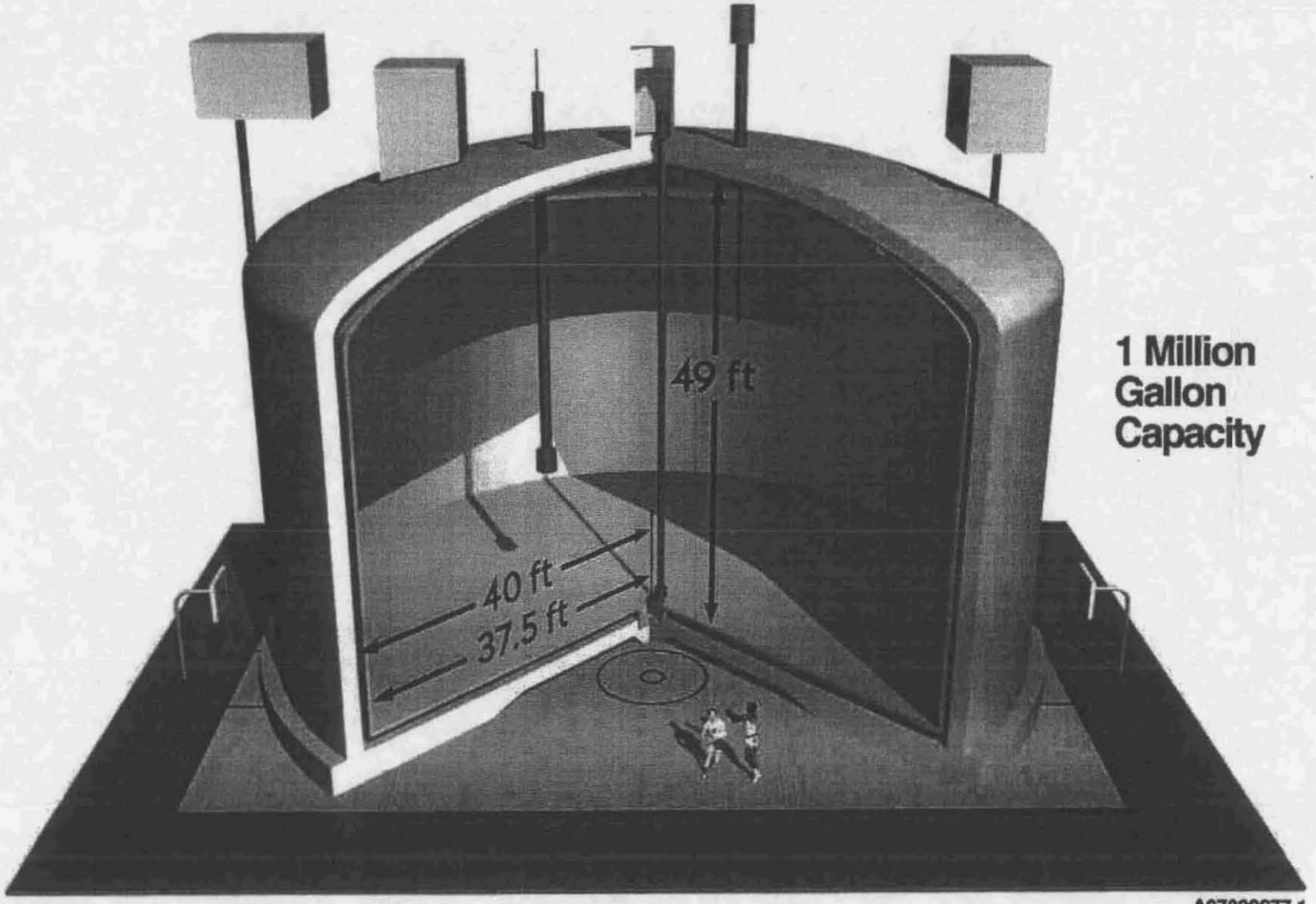
Hanford Double-Shell Tank



1 Million Gallon Capacity

A97020277.1

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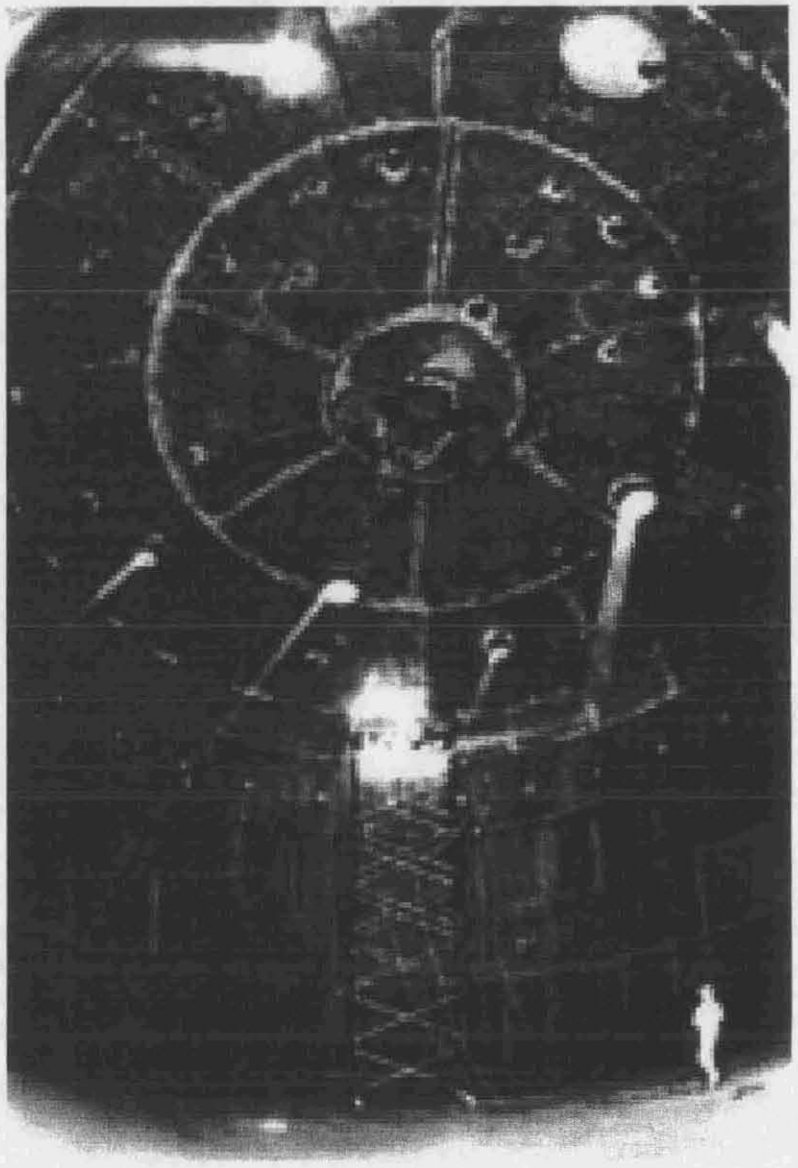
Hanford Underground Storage Tanks

- **149 Single-Shell Tanks (SST)**
  - Built 1943-1964
  - 55,000 to 1 M gal capacity
- **28 Double-Shell Tanks (DST)**
  - Built 1966-1986
  - 1.25 M gal capacity, each
- **ca. 54 M gal of waste**



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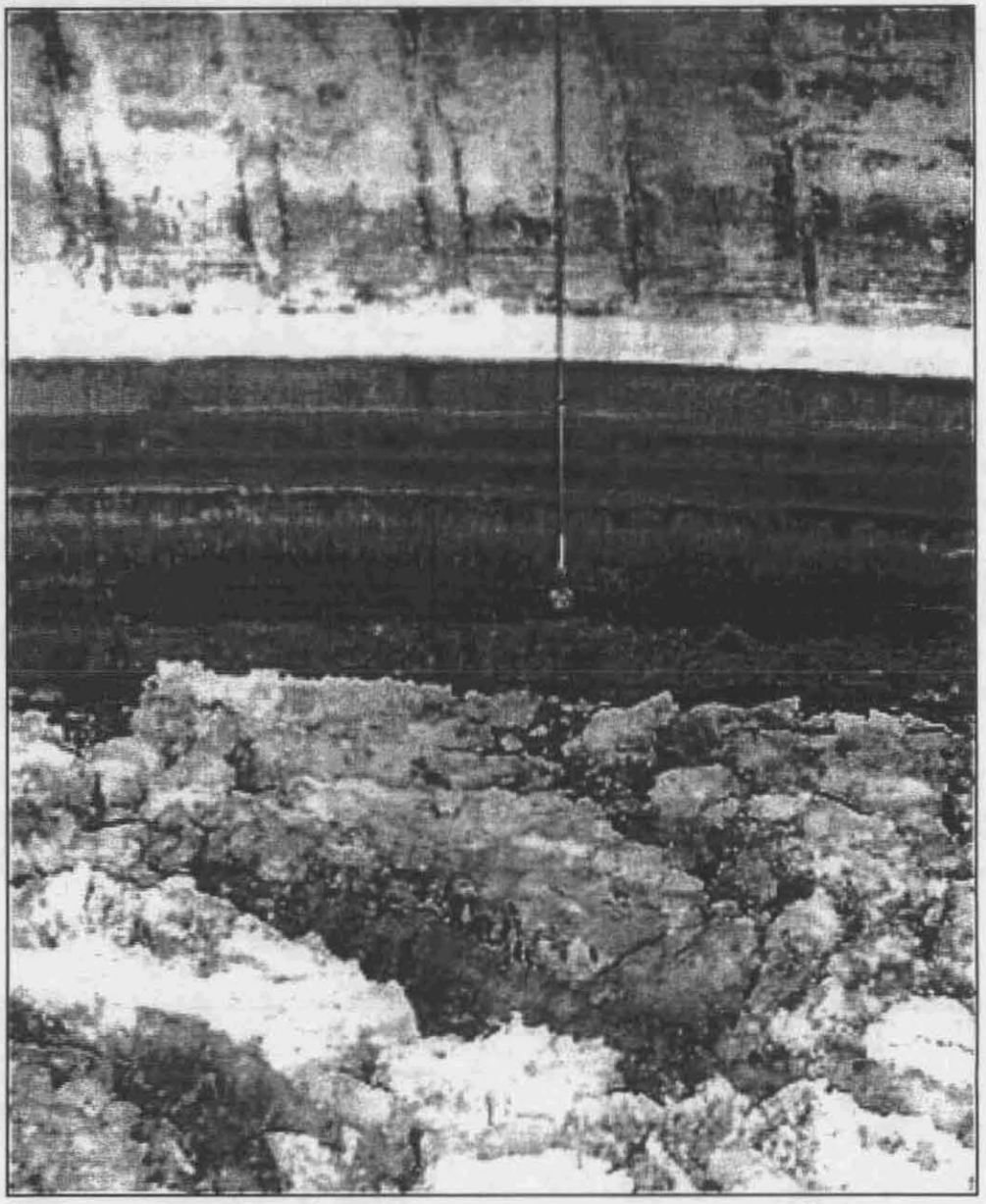
Hanford Tank Waste

Approximate waste composition by volume:

- **Sludge: 21%**
- **Saltcake: 46%**
- **Supernate: 33%**



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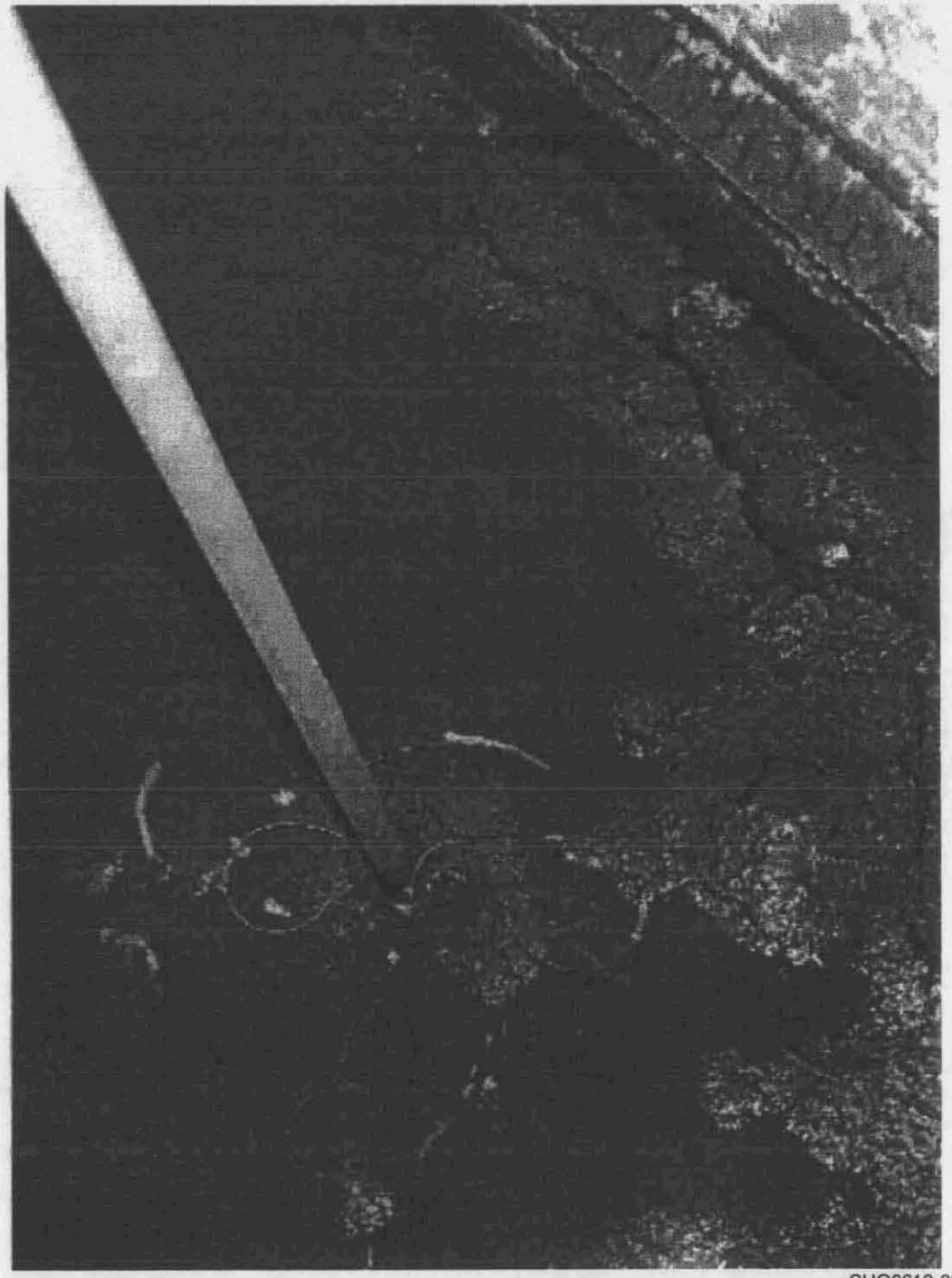
Sludge

- Wet mud
- Water insoluble
- White to black (usually dark brown)
- 50-80% H_2O
- High in Fe, Al, Si, Mn, ^{90}Sr, TRU



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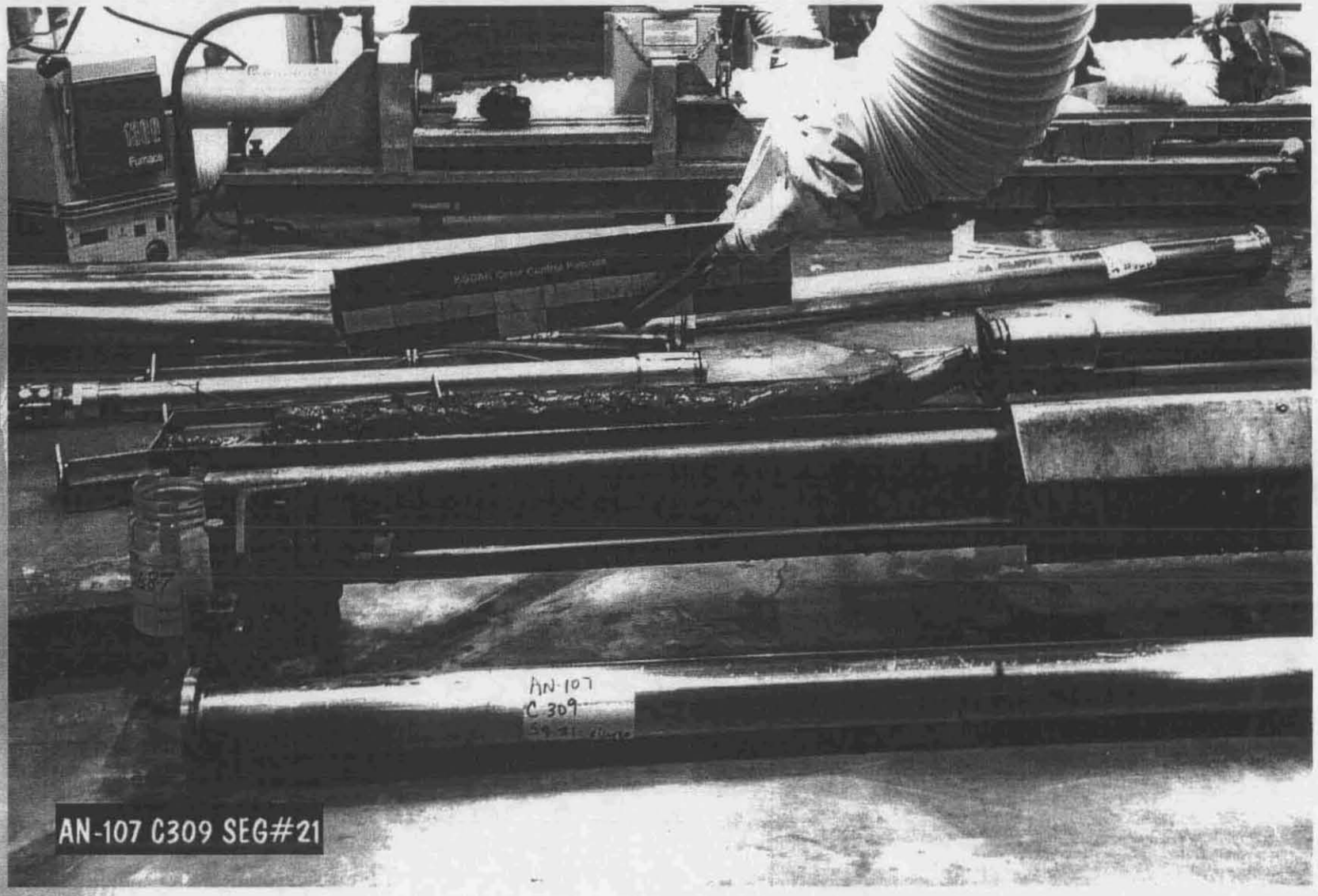
Typical Sludge Extrusion



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Saltcake

- Water soluble
- White to black (usually light brown)
- 10-50% H_2O
- High in Na, Al, anions, ^{137}Cs

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Supernatant Liquid

- Pale yellow or green to coffee-colored (usually bright yellow)
- 50–90% H_2O
- Na^+ 10 M

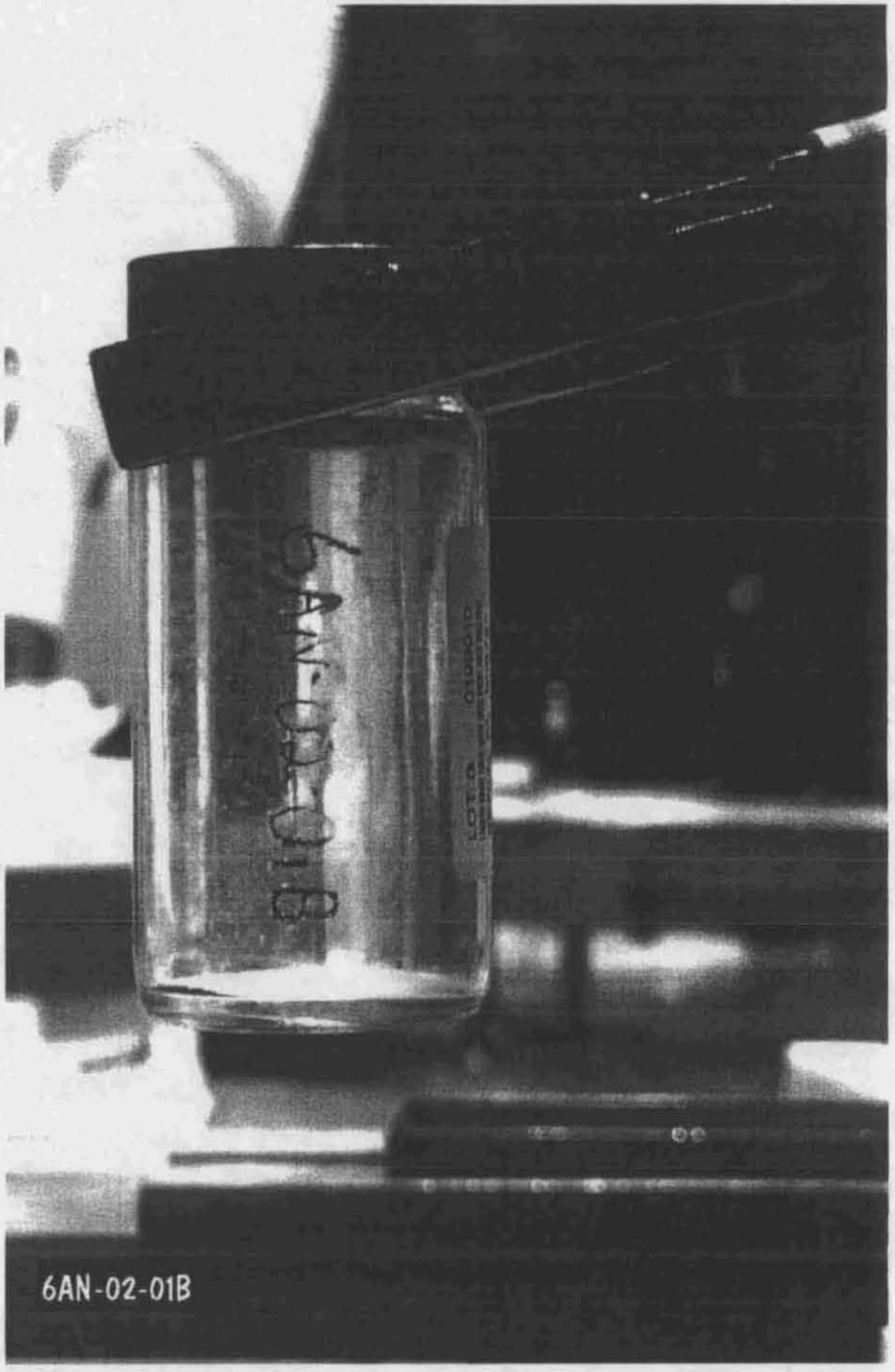
  NO_3^- 3 M

  NO_2^- 2 M

  OH^- 1 M

  $Al(OH)_4^-$ 0.5 M

  (all with wide variations)



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222-S Laboratory Support For Corrosion Control

- Chemistry Control
- Caustic Demand
- Field Analysis for Caustic Additions
- Analysis of Corrosion Products
- Analysis of Corroded Steel
- Electrochemical Corrosion Studies

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Current Hanford DST Waste Chemistry Limits (T<167°F)[a]

For $[NO_3^-]$ Range	Variable	T < 167 °F
$[NO_3^-] \leq 0.1$ M	$[OH^-]$	$0.01\ M \leq [OH^-] \leq 8.0\ M$
	$[NO_2^-]$	$0.011\ M \leq [NO_2^-] \leq 5.5\ M$
	$[NO_3^-]/([OH^- + [NO_2^-])$	< 2.5
$1.0\ M < [NO_3^-] \leq 3.0\ M$	$[OH^-]$	$0.1([NO_3^-] \leq [OH^-] < 10\ M$
	$[OH^-] + [NO_2^-]$	$\geq 0.4([NO_3^-])$
$[NO_3^-] > 3.0\ M$	$[OH^-]$	$0.3\ M < [OH^-] < 10\ M$
	$[OH^-] + [NO_2^-]$	$\geq 1.2\ M$
	$[NO_3^-]$	$\leq 5.5\ M$

[a] HNF-SD-WM-TSR-006, Rev 5, *Tank Farms Technical Safety Requirements*, "Corrosion Mitigation Program," CH2M HILL Hanford Group, Inc., Richland, Washington

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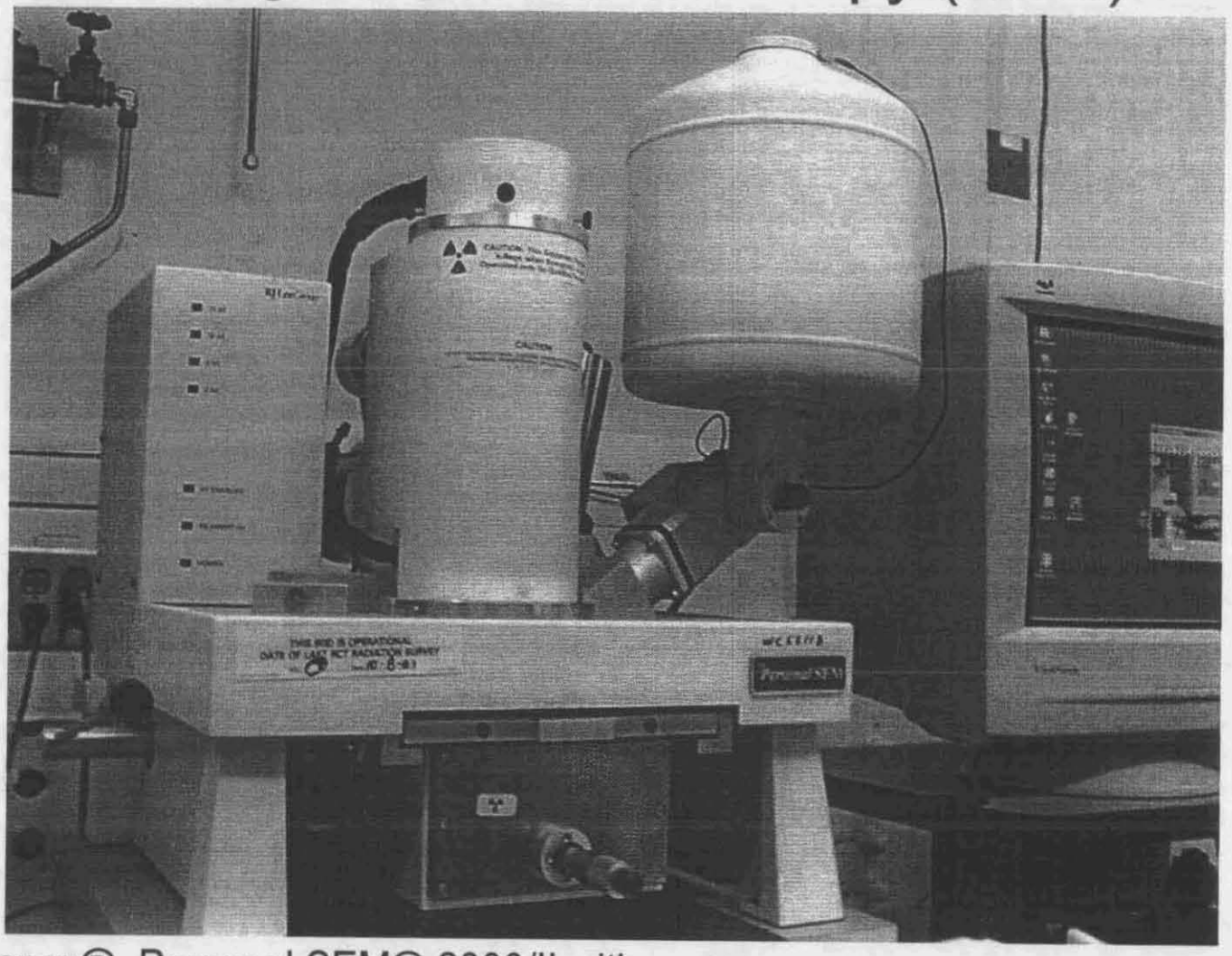
Scanning Electron Microscopy (SEM)



Aspex®, Personal SEM® 2000/II with

Noran Light Element Energy Dispersive Spectrometer (EDS)

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[redacted]

W314 Cross-Site Transfer Pipe

- 3-in.-diameter stainless steel inner pipe inside 6-in.-diameter carbon steel outer pipe
- Line was being removed from service and samples were retrieved for corrosion analysis
- 3-in.-diameter pipe was not corroded, inside was coated with insoluble tank waste
- 6-in.-diameter pipe showed surface corrosion on inside with pits generally less than 60 μ deep

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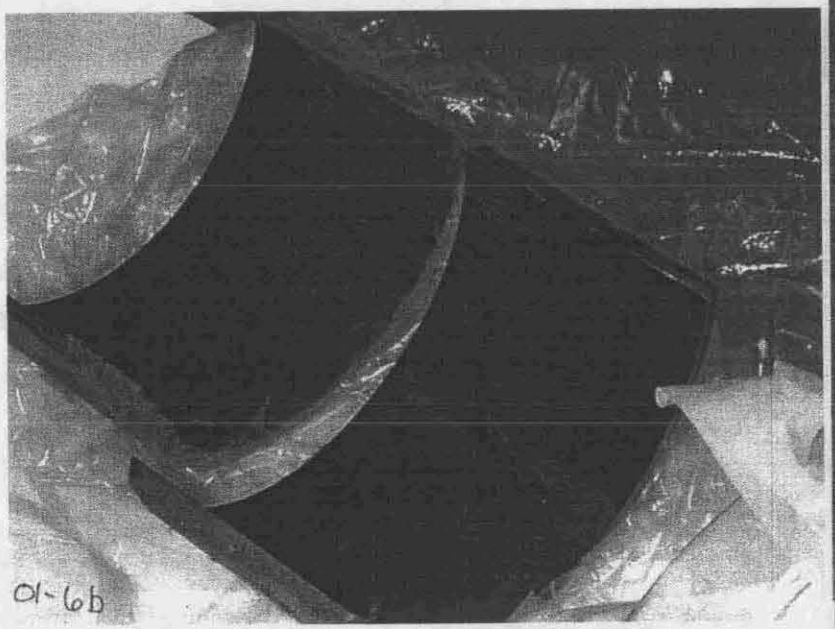
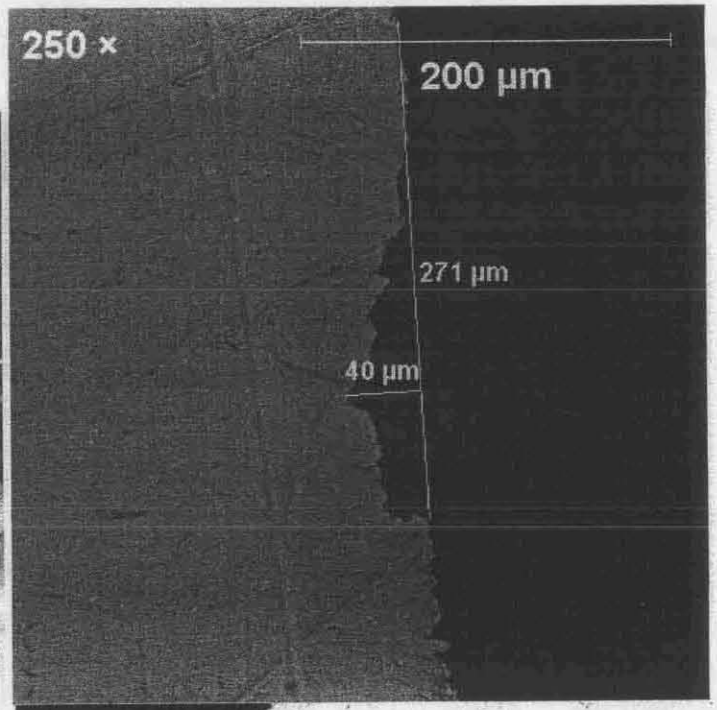
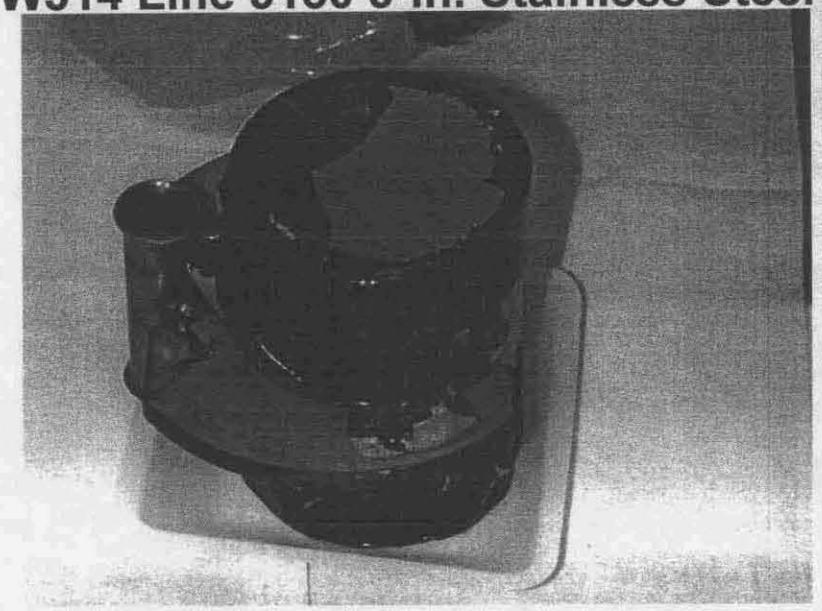
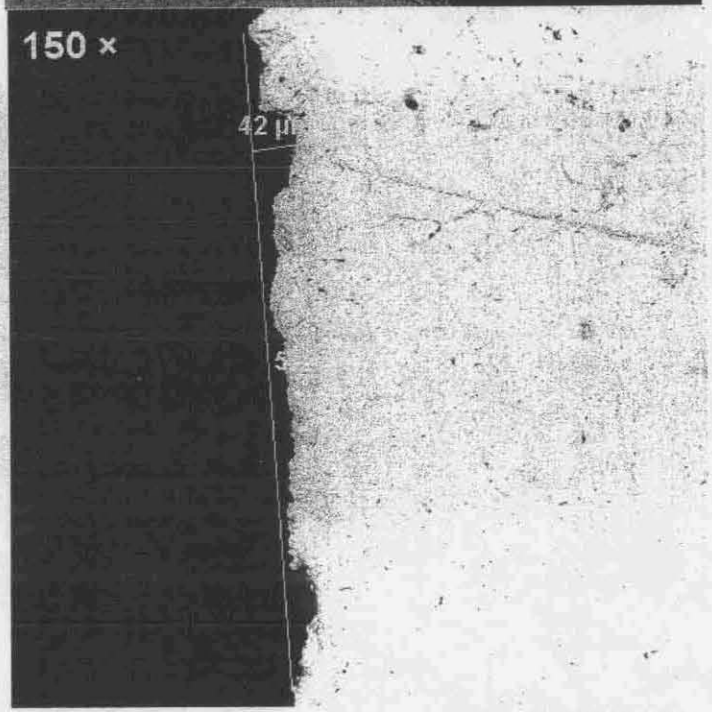
W314 Line 3150 6-in. Carbon Steel





W314 Line 3150 3-in. Stainless Steel





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SL-167 Transfer line in AW-6 Clean-out Box (COB)

- Flushing of outer encasement line returned dark particulate due to previous standing water
- SEM analysis revealed iron-rich and lead-rich particulate dominating.
- X-ray diffraction (XRD) determined that Fe-rich material was magnetite
- Pipe was lined with scale from manufacturing and lead paint

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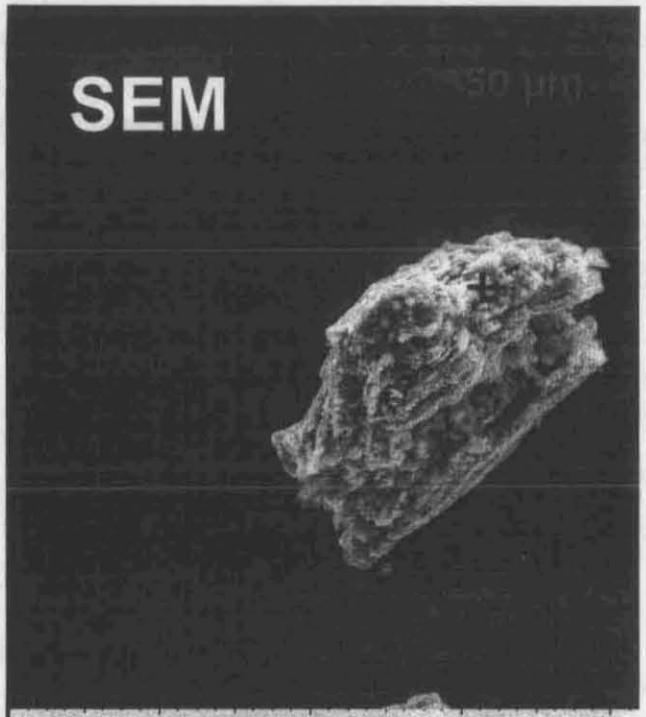

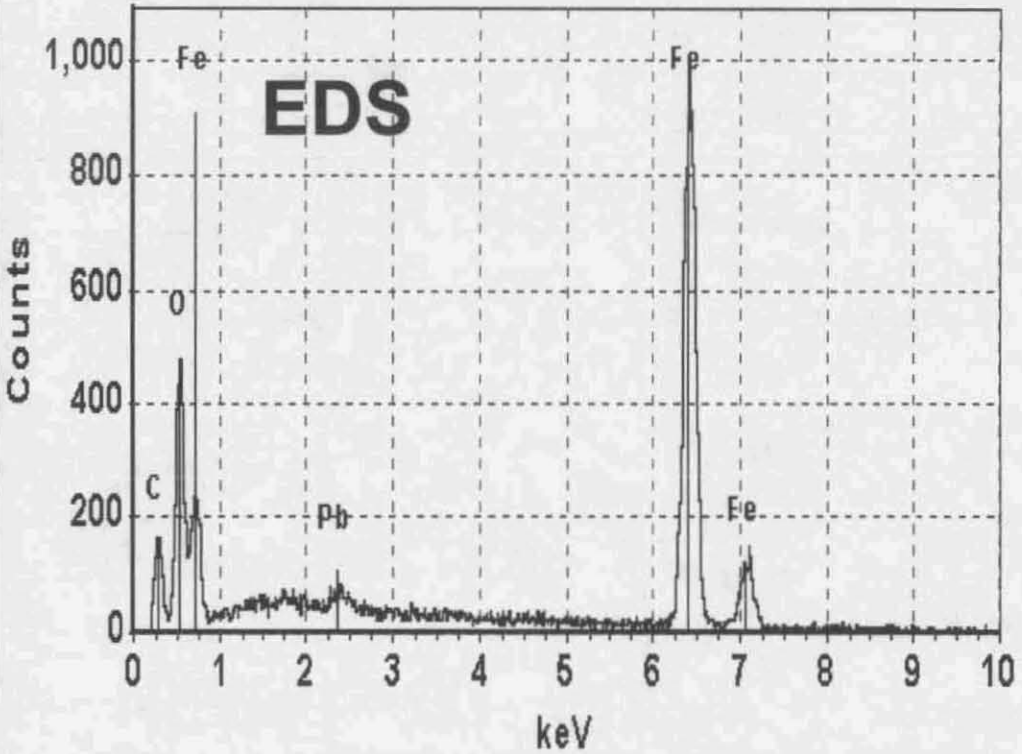

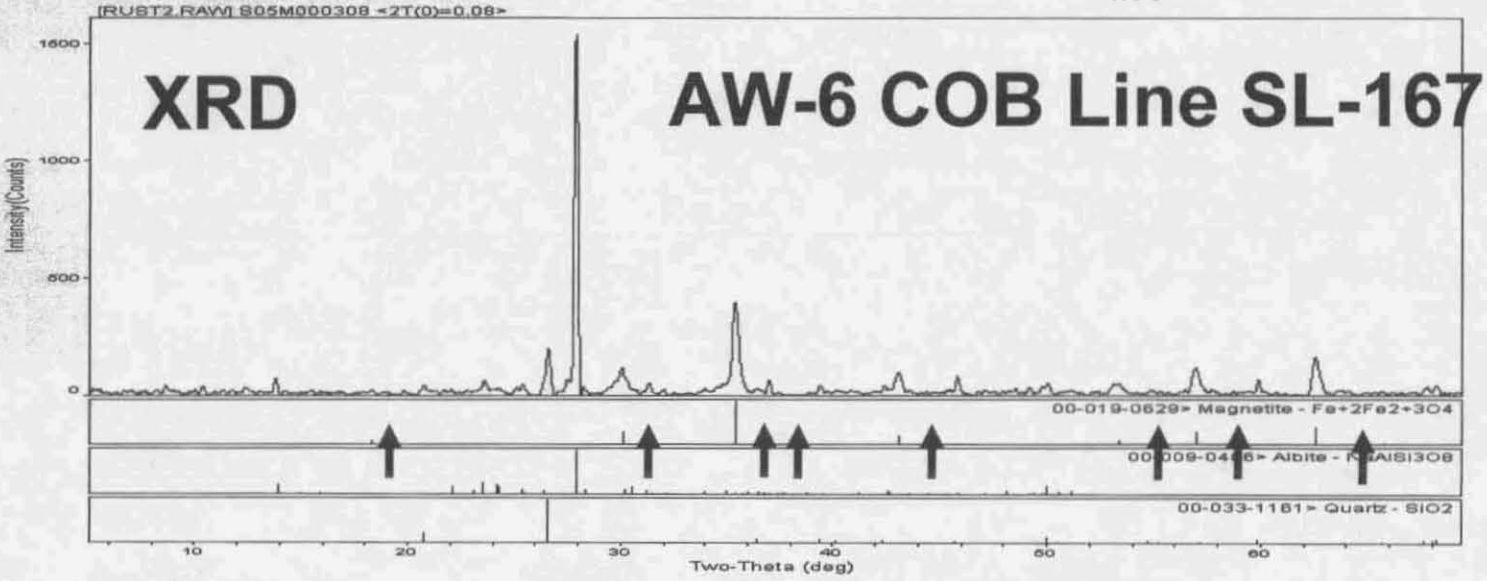

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[WC77311|H1662341]<f:\SPECTRAL\RWW> Friday, Jun 24, 2005 02:39p (MDI/JADE7)

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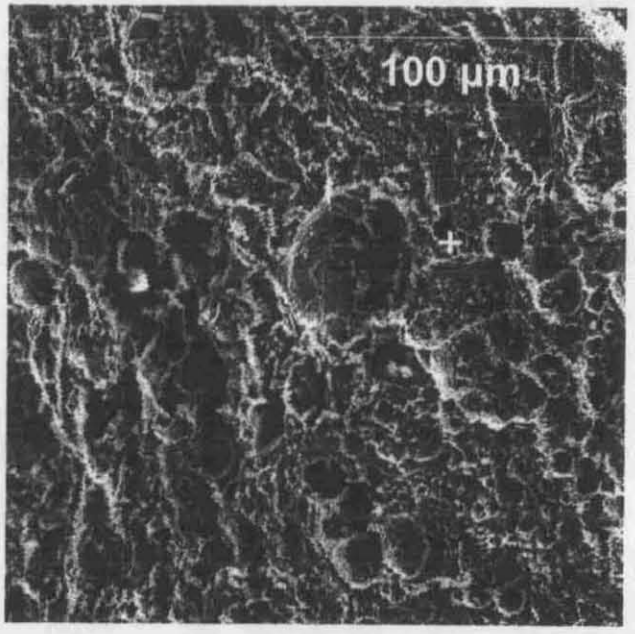
Tank AP-105 Drill String Pipe

- 2-in.-diameter drill pipe, left suspended in tank headspace vapors showed evidence of corrosion
- Cleaning with ammonium citrate revealed little weight loss or wall thinning (< 5 mil).
- Pitting corrosion was slight and shallow



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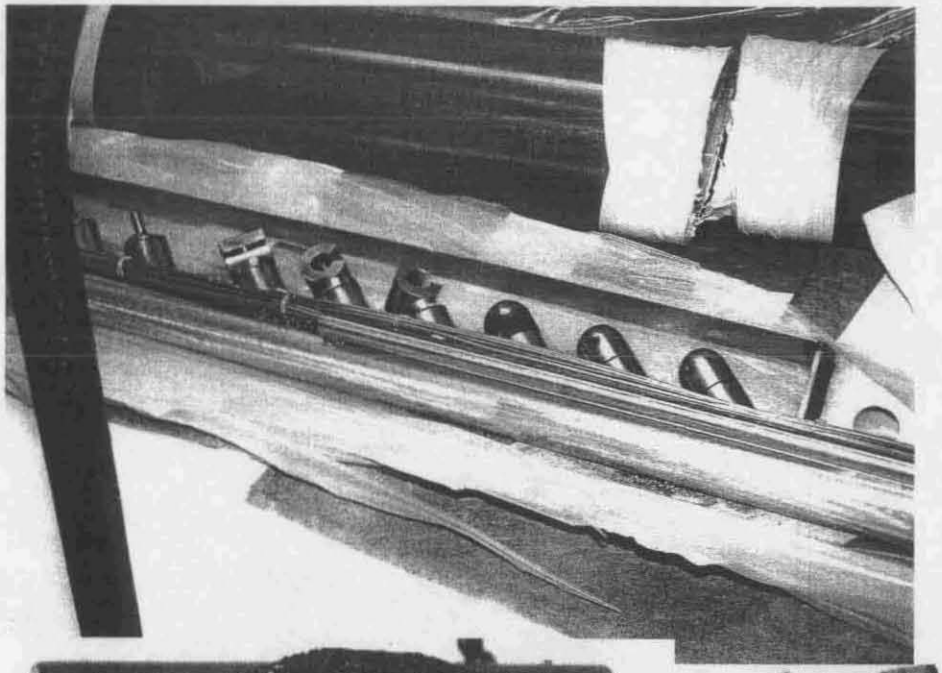
Electrochemical Noise Probe Corrosion Coupons

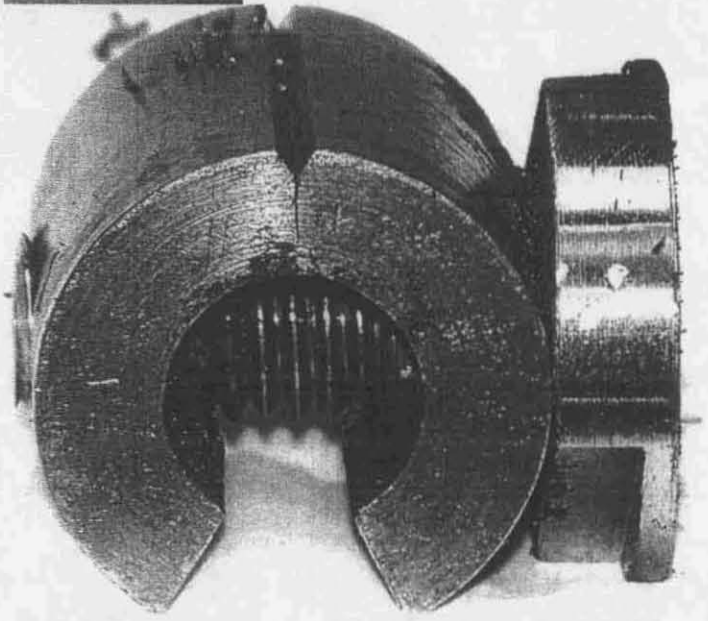
- Electrochemical noise probes are being deployed in selected DSTs
- Probes include C-ring and bullet specimens for examination of corrosion
- Stress corrosion cracking does not appear to be occurring
- Crevice corrosion in the vapor space may be significant

AN-107 Probe removed August 2006 Vapor Space Detector



Vapor space detector showed most evidence for corrosion

Precracked C-ring shows corrosion associated with bolt and base



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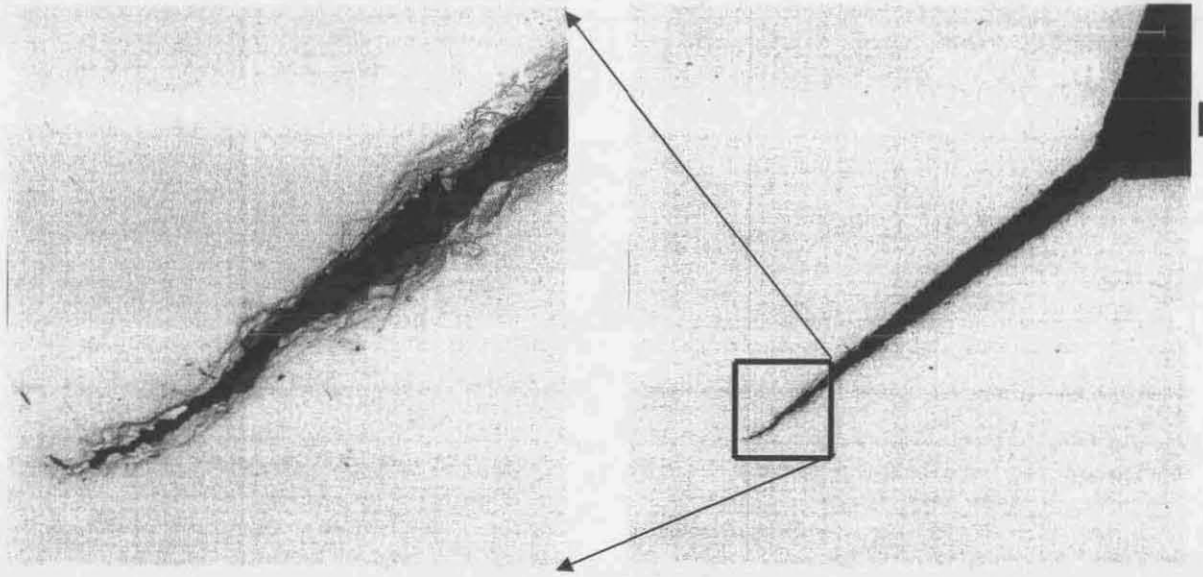
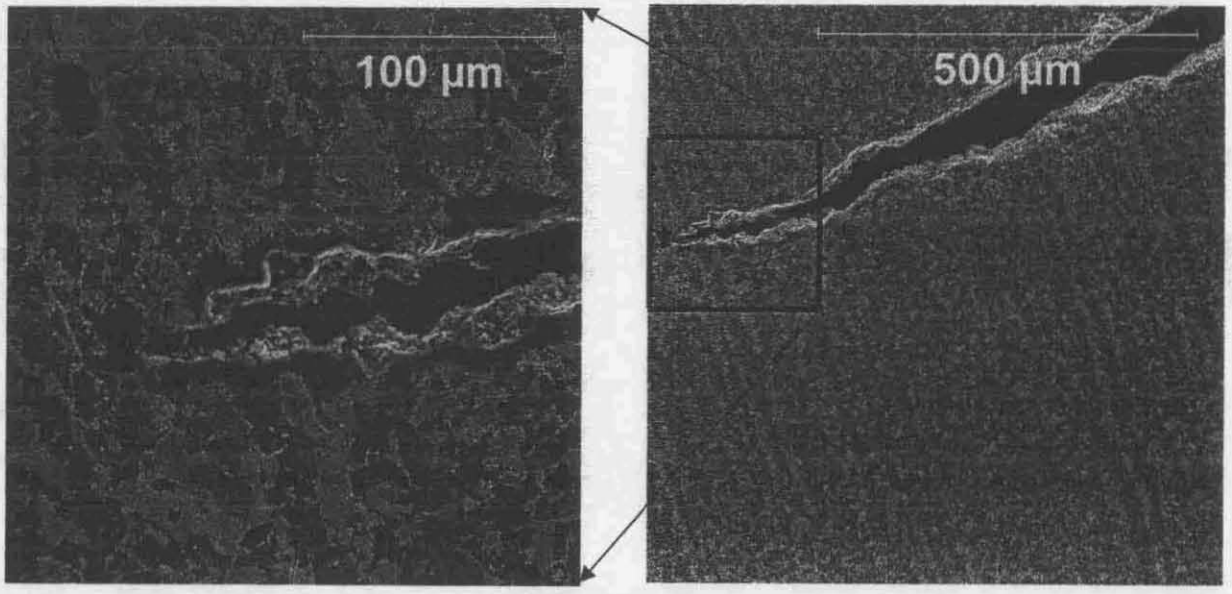
Detector 4 (sludge) precracked C-ring shows no evidence for stress corrosion cracking



Polished



Etched

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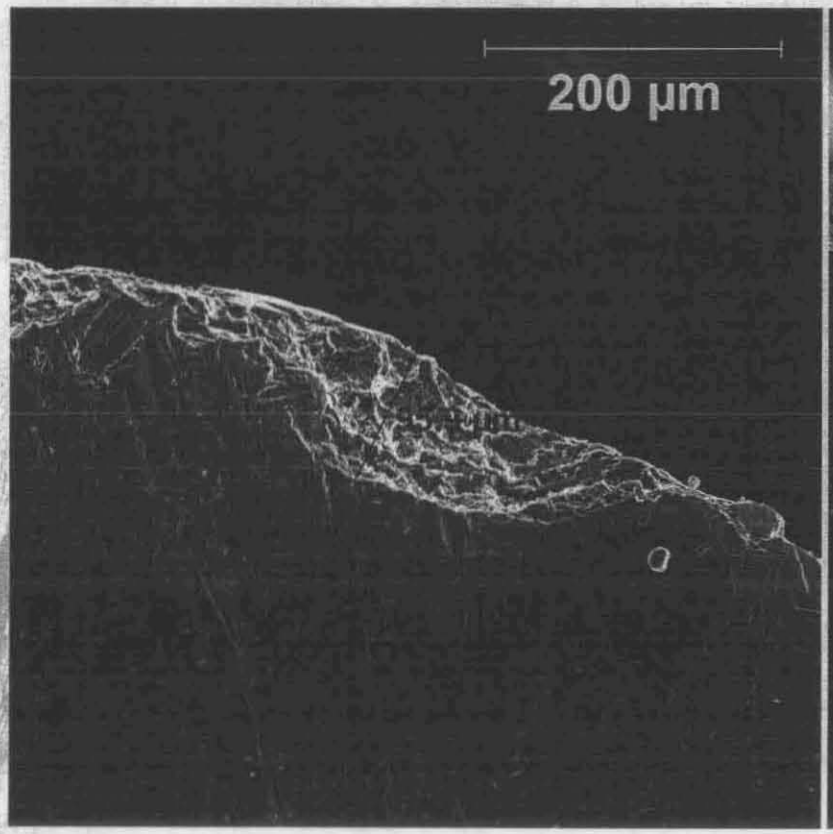
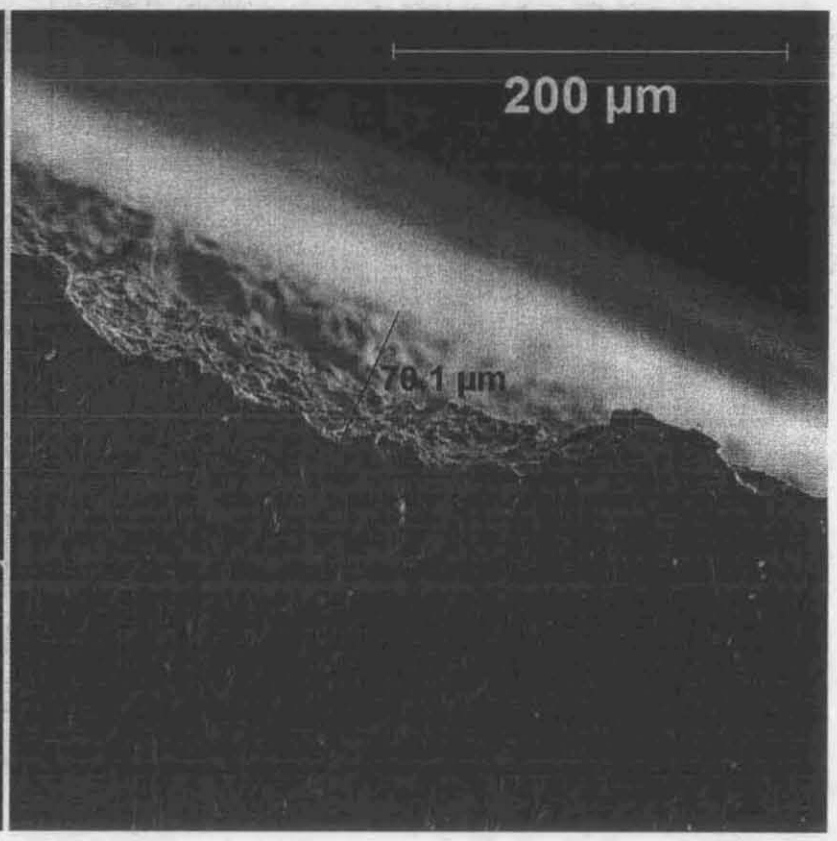
Crevice corrosion most obvious in vapor space but also found in submerged sections of AN-107 probe.

SEM Image of pitted area from end of bolt on unstressed C-ring, in AN-107 vapor space



SEM Image of pitted area from underside of bullet, in AN-107 sludge layer



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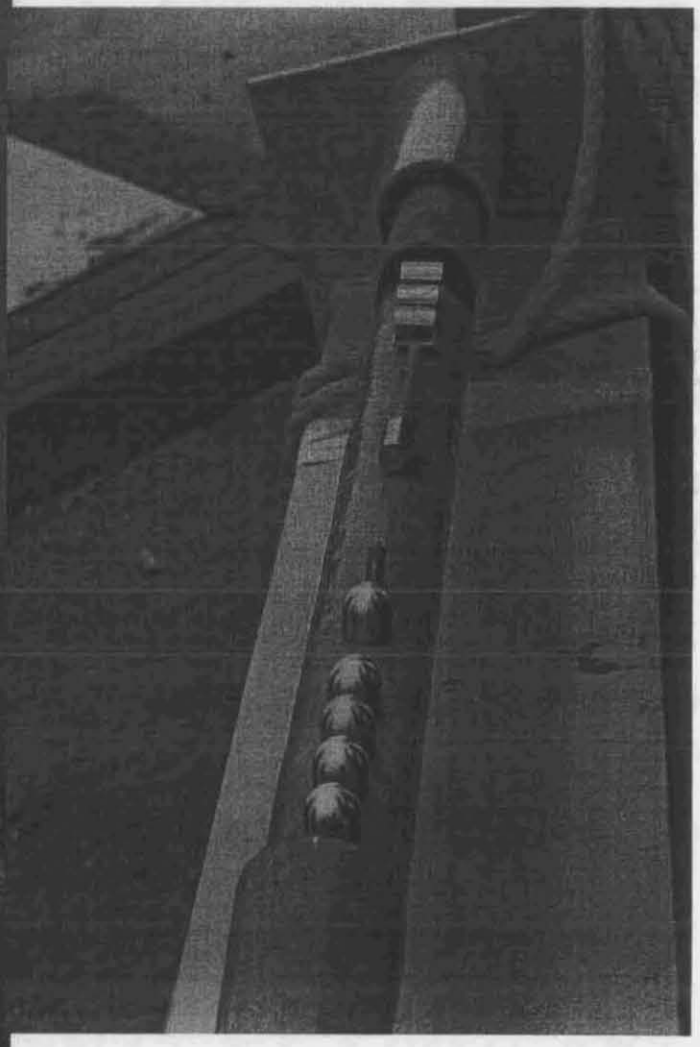
Installation of Fiberglass AN-107 Corrosion Probe, September 20, 2006



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Microbial Induced Corrosion SL-167 Encasement at COB AW-6

- From a visual standpoint, the corrosion observed in SL-167 COB is a microbially influenced corrosion (MIC) process
- MIC is initiated by allowing water to contact the carbon steel surface for a period of time that would allow microbial colonies to initiate the corrosion process
- It would appear from the literature that there are nonoxidizing biocides available to mitigate MIC in the tank farms without deleterious effects on carbon steel

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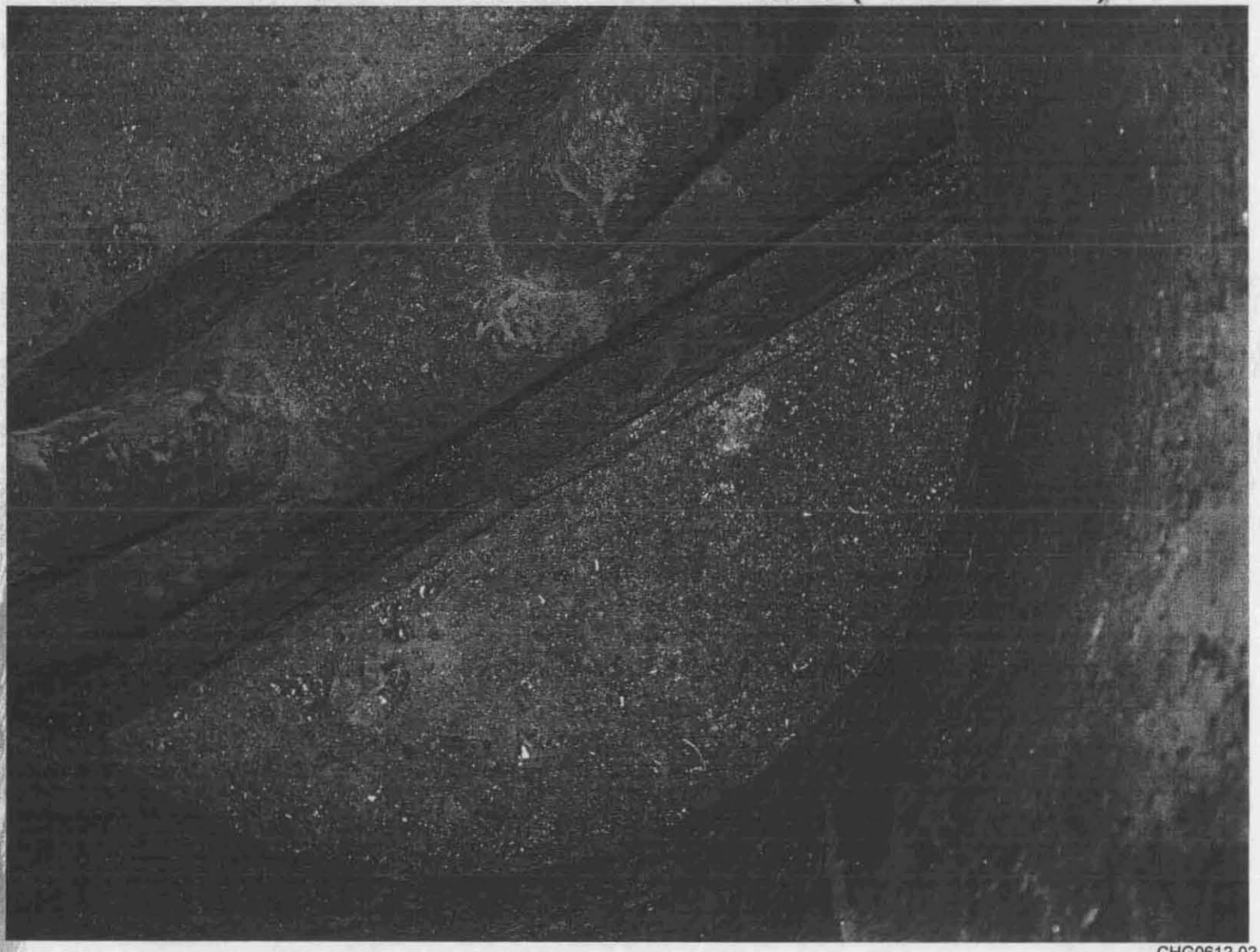
Microbial Induced Corrosion
SL-167 Encasement at COB AW-6 (Continued)



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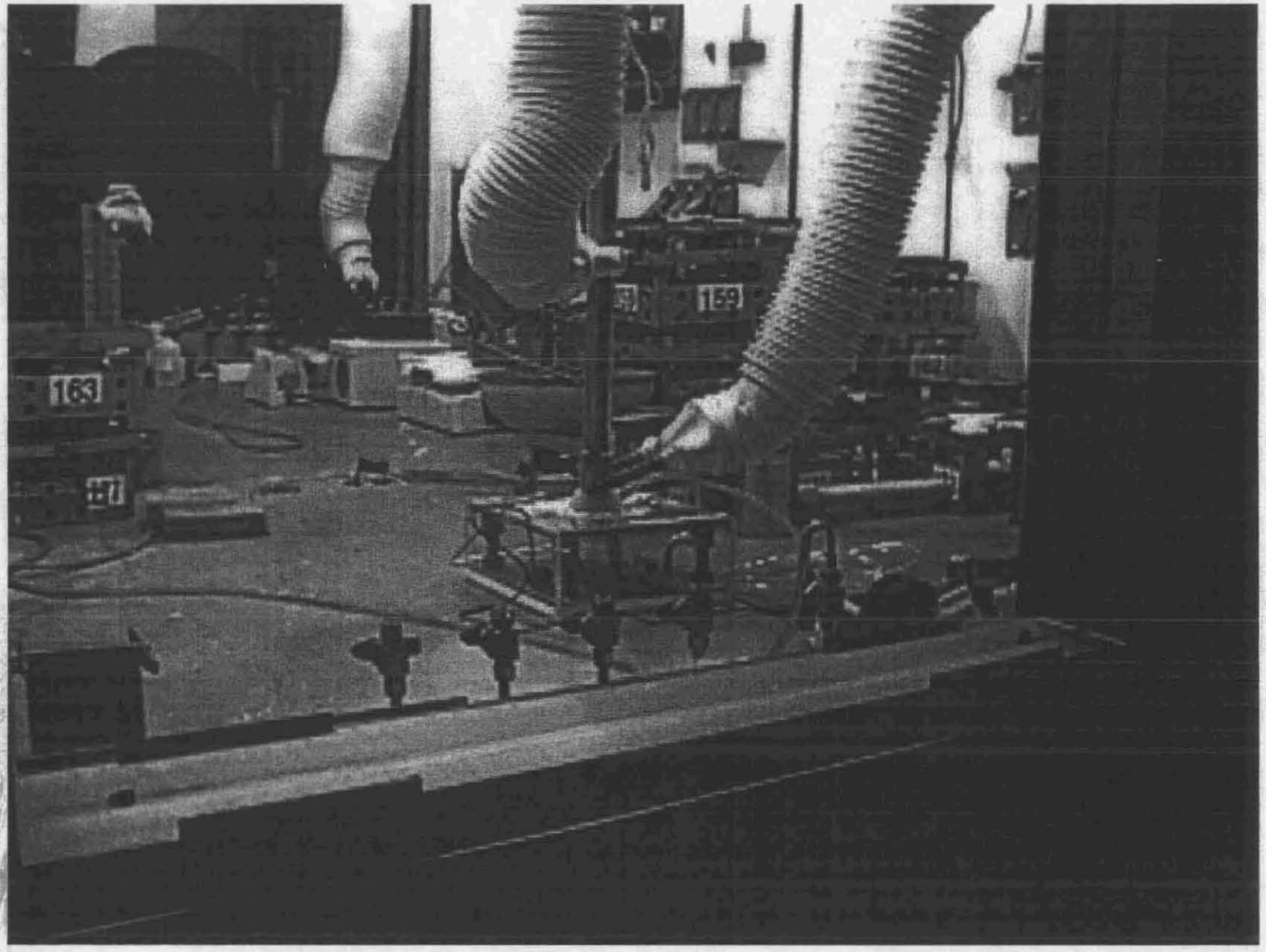

Anaerobic Extrusion, AY-102

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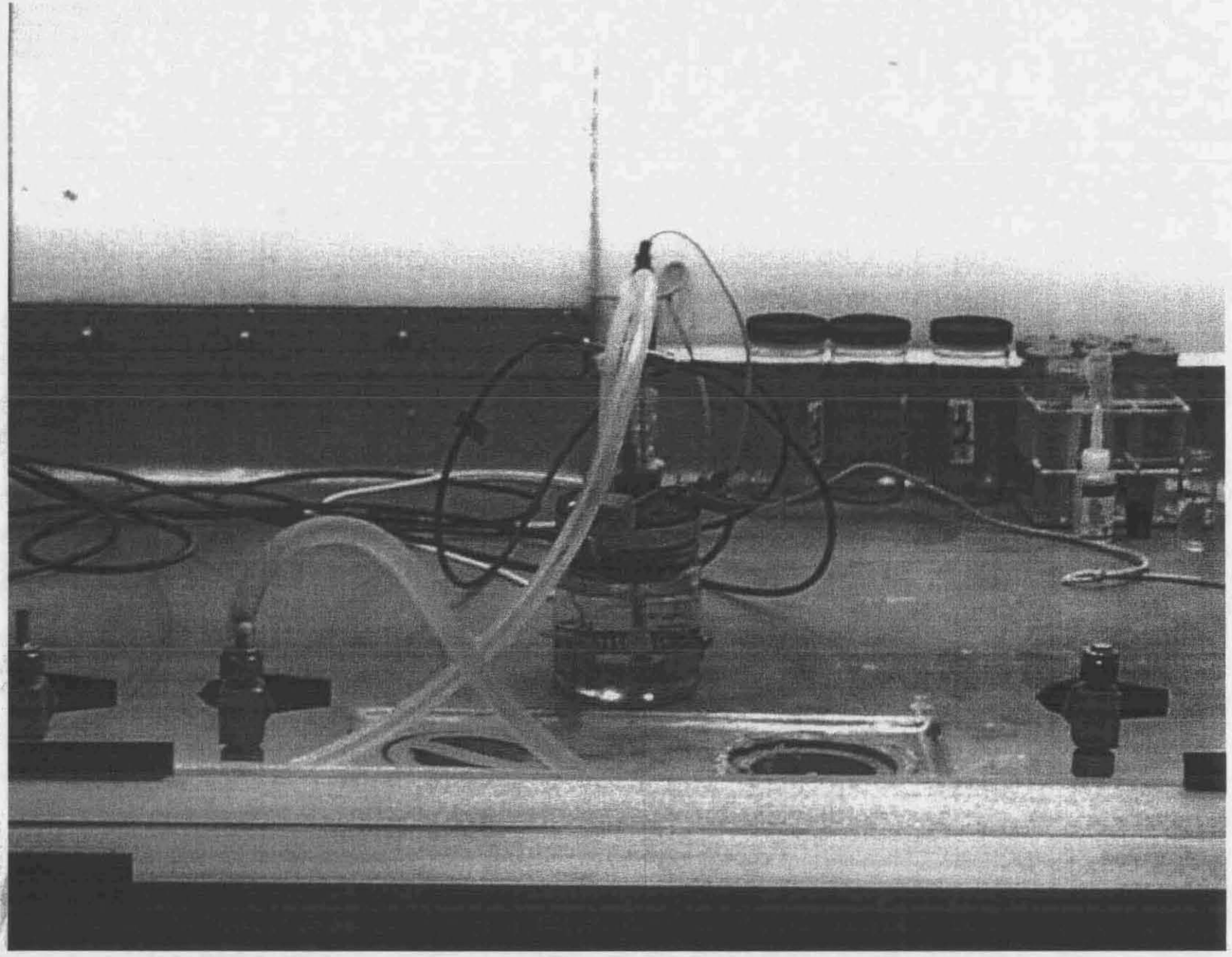

ASTM G-5 Electrochemical Corrosion, 222-S 11A Cell 3

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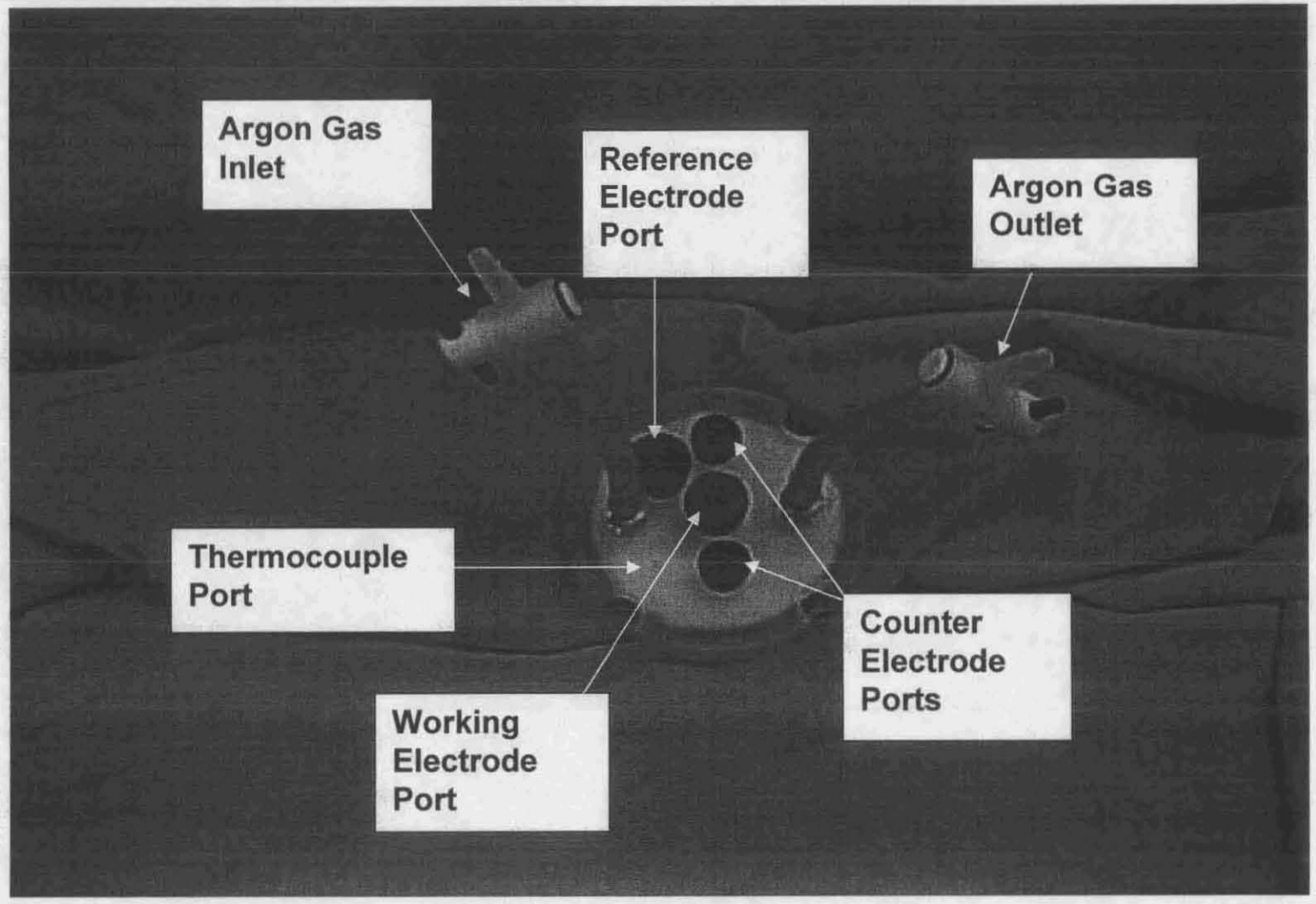
Sample Jar/Electrochemical Cell Lid



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[redacted]

RESULTS OF ELECTROCHEMICAL CYCLIC POLARIZATION SCANS FOR SY-102 SUPERNATE

Sample	Without Argon Purge			With Argon Purge		
	OCP (Breakdown potential) mV	Corrosion Rate (mpy)	χ^2	OCP[a] (Breakdown potential) mV	Corrosion Rate (mpy)	χ^2
2SY-04-05	-350 (450)	0.039	49.3	-540 (500)	0.014	83.7
2SY-04-06	-430 (480)	0.039	20.3	-360 (490)	0.018	47.9
2SY-04-06 DUP	-428 (450)	0.028	44.3	-580 (450)	0.012	44.1
2SY-04-07	-430 (450)	0.038	23.5	-560 (460)	0.013	59.1
2SY-04-08	-390 (460)	0.039	16.8	-583 (450)	0.019	31.4

[a] OCP = open circuit potential

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[redacted]

SY-102 SUPERNATE CHEMISTRY COMPARED TO HANFORD DST CHEMISTRY CONTROL PARAMETERS

$[NO_3^-]$> 3M, T<167 °F			
	$0.3M \leq [OH^-] < 10M$	$[OH^-] + [NO_2^-] \geq 1.2M$	$[NO_3^-] \leq 5.5M$
2SY-04-05	0.57	**1.06**	3.74
2SY-04-06	0.58	**1.08**	3.79
2SY-04-06 DUP	0.57	**1.07**	3.79
2SY-04-07	0.55	**1.04**	3.71
2SY-04-08	0.80	1.58	3.18

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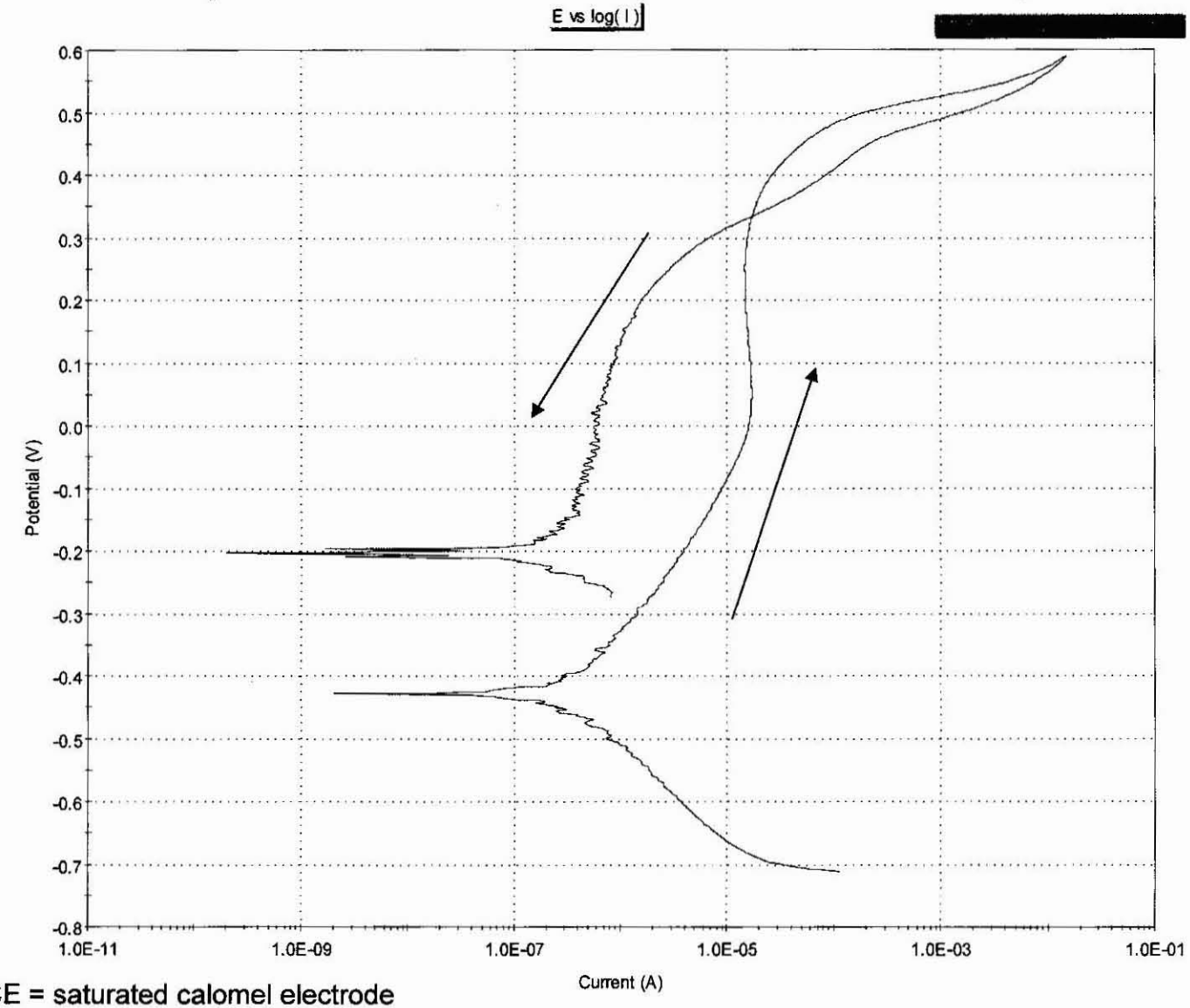
[redacted]

Cyclic Potentiodynamic Polarization Scan
SY-102 Supernate Reversed at 2.5 mA/cm^2, vs. SCE



SCE = saturated calomel electrode

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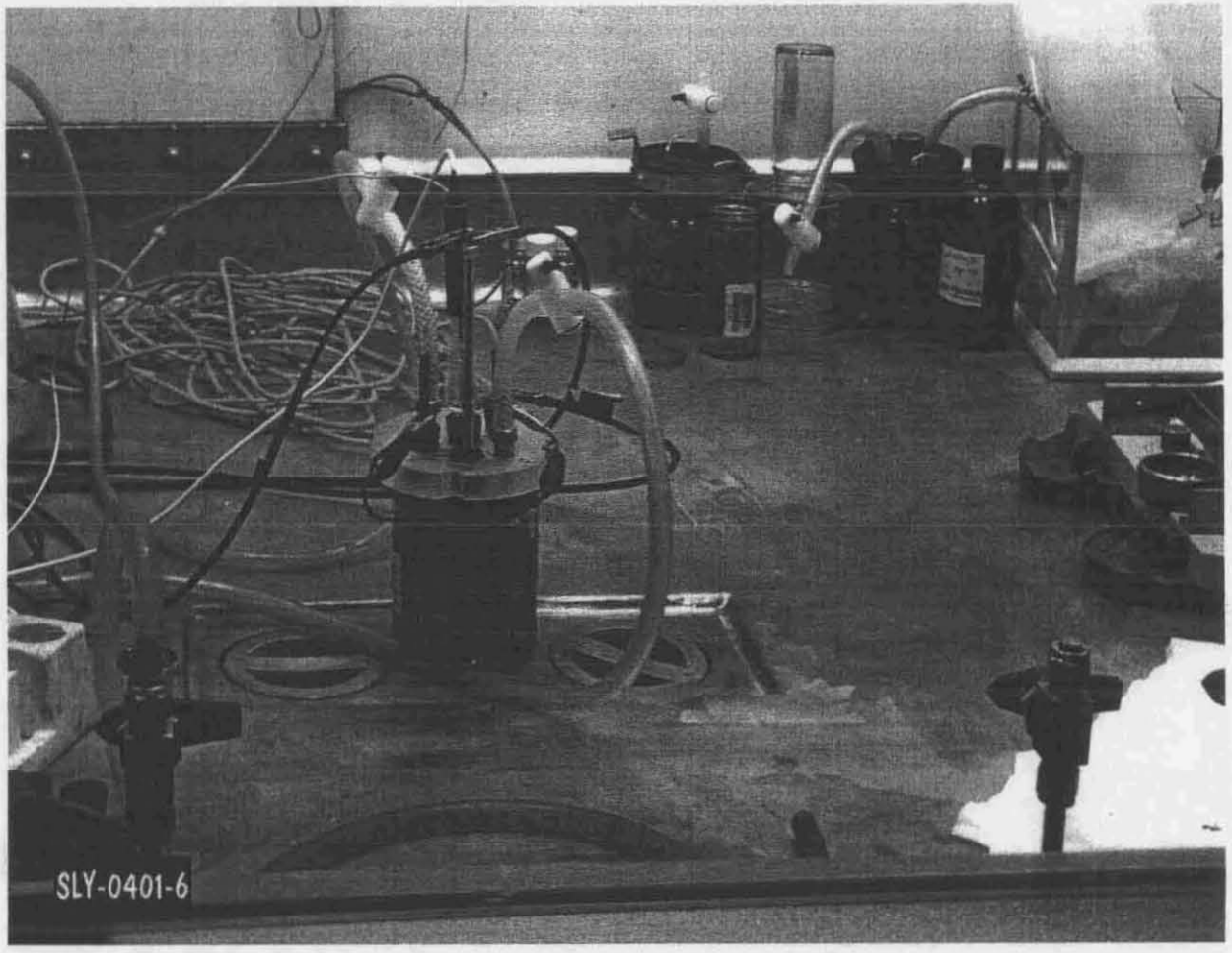
Sample Jar/Electrochemical Cell



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[redacted]

SAMPLE 19/R1 AND 19R3 CHEMISTRY COMPARED TO HANFORD DST CHEMISTRY CONTROL PARAMETERS

$[NO_3^-] < 1M$, $T < 167\ ^oF$			
	$0.01M \leq [OH^-] < 8.0M$	$0.11M \leq [NO_2^-] \leq 5.5M$	$[NO_3^-] / ([OH^-] + [NO_2^-] < 2.5$
19/19R1	**0.009**	0.94	0.04
19R3	**0.003**	0.98	0.04

CHG0612-02.31

[redacted]

SLUDGE INTERSTITIAL LIQUID CHEMICAL ANALYSIS, AZ-102

Segment	% Water	pH	Calculated OH^- (M)	NO_2^- (M)	NO_3^- (M)
19/19R1	32	11.97	0.009	0.94	0.04

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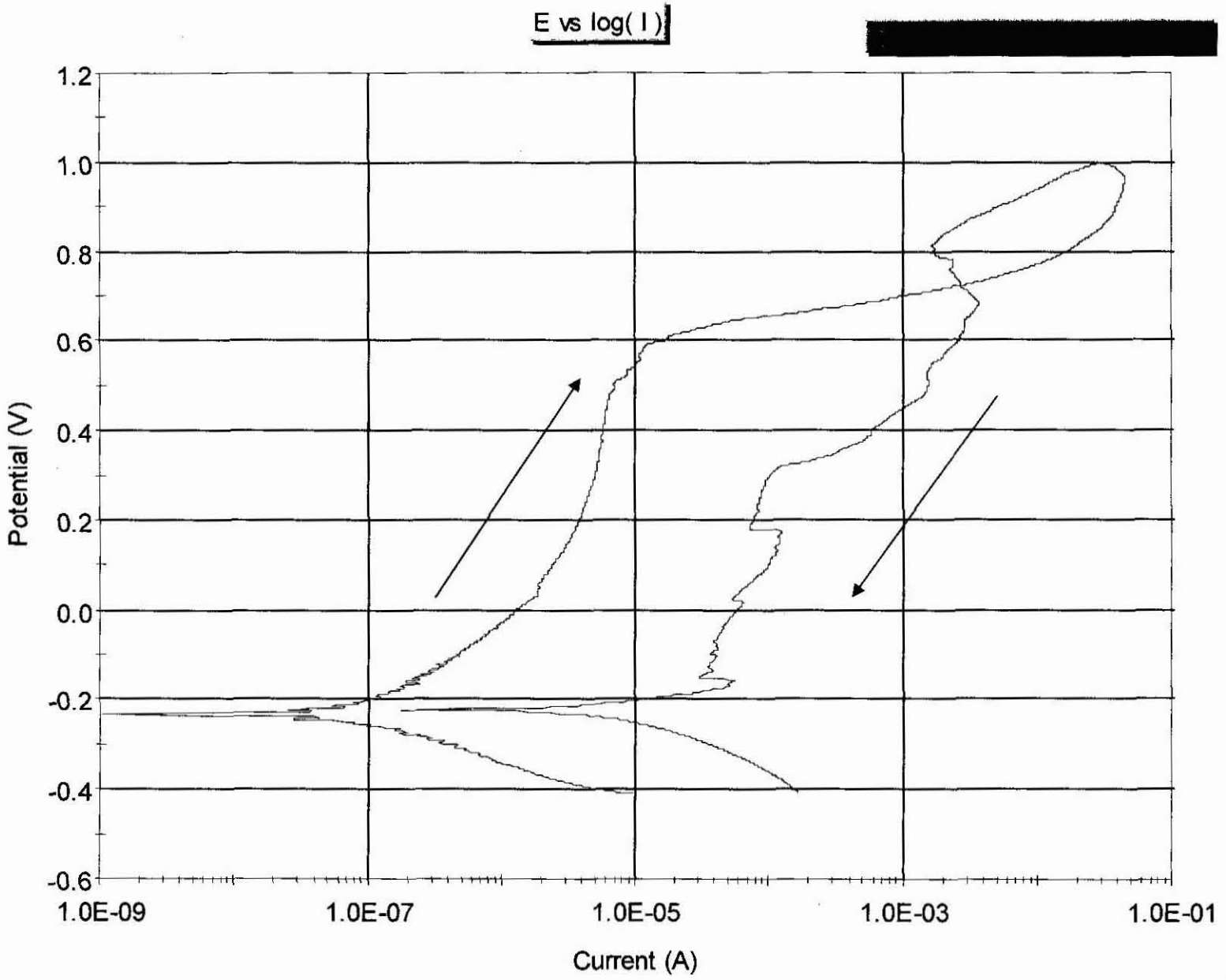
[redacted]

Scan Obtained for AZ-102 Sludge, Reversed at 2.5 mA/cm^2, vs. SCE



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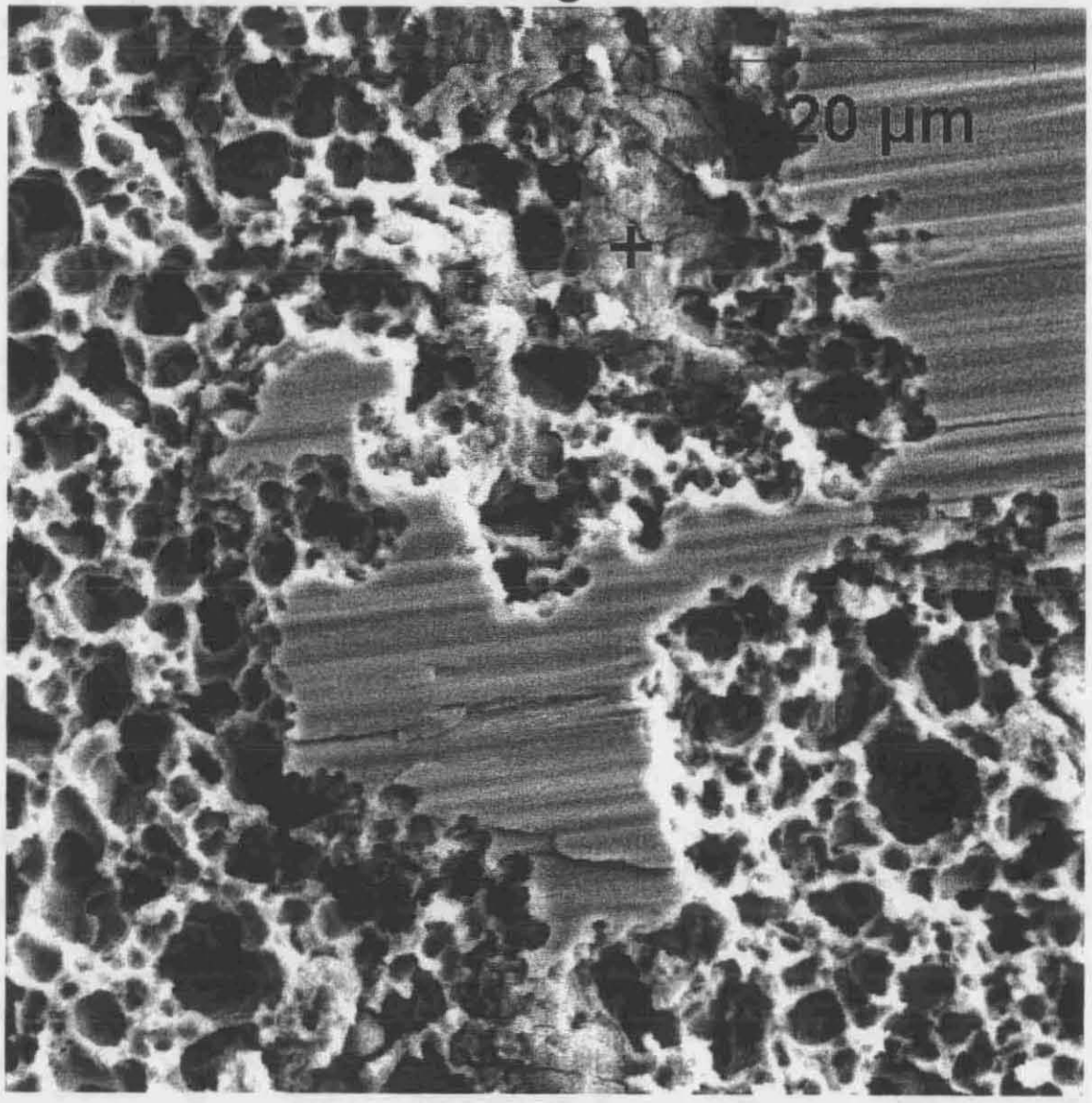
SEM of Coupon Left at OCP 8 Weeks in AZ-102 19R1/19R2 Sludge



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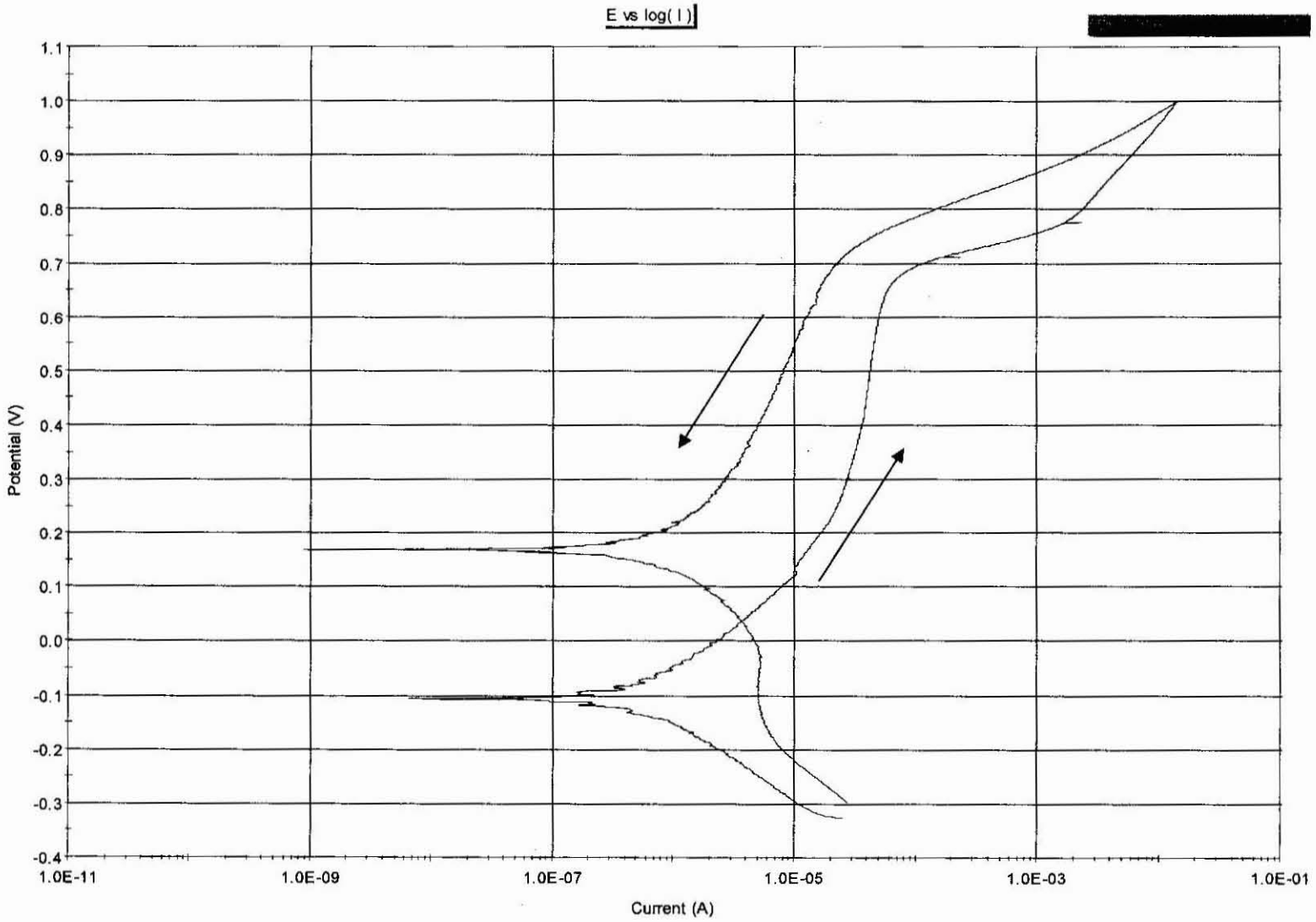
Tank AZ-102 Showed Pitting Propensity, Another Sample, 19R3, was Cored

Segment	% Water	pH	Calculated OH^- (M)	NO_2^- (M)	NO_3^- (M)
19R3	53	11.48	0.003	0.98	0.04

CHG0612-02.35

[redacted]

Scan of AZ-102, 19R3



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CHG0612-02.36

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Conclusions

- SEM and optical microscopy reveal corrosion mechanisms in Hanford Tank Farms steel.
- Whether or not pitting attack occurs against carbon steel in Hanford DSTs is a function of percent moisture as well as [OH], [NO_3], and [NO_2] concentrations
- Underdeposit pitting is exacerbated by low moisture due to limiting mass transfer
- Organics as in SY-102 are suspected to play an important role in electrochemical corrosion passivation
- Many questions on sludge electrochemistry

Ongoing Development Work

- Materials of construction for electrochemical probes must take into account
  - Compatibility of materials (galvanic cells)
  - Aggressive chemical environment
  - Effects of ionizing radiation