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PROGRESS REPORT OF ACTIVITIES AND RECOMMENDATIONS IN THE  
INTEGRATED WASTE PACKAGE EXPERIMENTAL PROGRAM

MAY 1988 - APRIL 1990

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INTERMEDIATE MILESTONE REPORT  
CNWRA Task Activity 20-3704-042-005-900

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## 1. INTRODUCTION

The Integrated Waste Package Experimental (IWPE) program was initiated in May 1988. The specific objectives of the program were to:

- o To develop a good understanding of the information currently available on corrosion and on other degradation processes of container materials.
- o To assess the current status of Yucca Mountain Project (YMP) Waste Package Programs.
- o To conduct waste package experiments to scope and study the key parameters affecting long-term material performance.
- o To assess, experimentally, YMP selected waste package materials and designs and provide independent evaluation for reasonable assurance of long-term performance.

This report documents the salient results of the activities carried out up to April of 1990. The report is divided in a chronological order into:

Section A: Report of activities prior to December of 1989

Section B: Report of activities from December of 1989 to April of 1990.

Section C: A summary of the above and recommendations for future activities.

Such chronological division of the report is necessitated by the following considerations:

1. Since the inception of the program until December of 1989, the IWPE program was carried out by two staff members - F. F. Lyle Jr. and H. Manaktala. Two more staff members were added to the Engineered Barriers Systems (EBS) group at the end of this period - N. Sridhar (joined at the end of November 1989) and G. Cragolino (joined at the beginning of January 1990). Even though the current activities fall within the scope of the IWPE program plan, many of the tasks have been brought to sharper focus because of the additional man power.
2. It was felt that the original IWPE Program plan lacked specificity in some of the tasks. The addition of the new staff has necessitated a look anew at the plan and a division of the program into tasks that lends clarity to the program plan. It was also felt that this added specificity in the program plan will enable a better evaluation of progress.

Accordingly, this report summarizes the results of experimental work carried out before the addition of new staff in Section A. The experimental investigations carried out after the arrival of the new staff are reported in Section B. Finally, the recommendations for further action, based on the results of existing activities and the recommendations of a peer review panel,

are documented in Section C. The tasks in this report are numbered in accordance with the original IWPE program plan (December 1988).

A new IWPE Program plan has been drafted and sent to the NRC for approval.

## 2. SECTION A TESTS CONDUCTED AT THE CENTER PRIOR TO DEC. 1989

### 2.1 Task 2.1a Electrochemical characterization

The tests conducted under this task consisted essentially of cyclic, potentiodynamic polarization tests performed under various experimental conditions. The purpose of these tests was two fold: 1. To confirm the results of previous investigators (LLNL and Cortest) and 2. To characterize the electrochemical response of the candidate container alloys under various environmental conditions. The early experimental difficulties that were encountered were mainly due to excessive electrical noise especially at low current densities close to open-circuit potentials. The noise problem was solved by the use of a damping capacitor between the working electrode and ground, as well as the provision of an auxiliary conductive path between the reference electrode and the electrometer interface. In SECTION B, some of the other causes of the noise and remedies used later in the program will be outlined. The electrochemical tests were conducted on AISI 304L stainless steel, AISI 316L stainless steel, Incoloy alloy 825, and, the Center's reference material, Hastelloy alloy C-22. Hastelloy alloy C-22 was included because of its well established resistance to localized corrosion and hence its possible use as a reference material. The heat number and the chemical composition of the alloys are shown in Table 1. The alloys were tested in the as-received condition from the mill. In SECTION B, current information regarding the microstructures and surface conditions of these samples will be presented.

The simulated J-13 water used in the tests described in SECTION A were prepared under the standard procedure described by others (BATTELLE - 1987). During the course of this phase of the program, the chemical composition and stability of the simulated J-13 water was examined (PABALAN - 1989). These investigations led to some changes in the preparation of the simulated J-13 water. These changes were examined in some of the tests described in SECTION A. However, they were consistently adopted in the second part of the program as described in SECTION B.

The results will be described below in terms of the alloys examined.

#### 2.1.1 AISI 304L Stainless Steel

The results from cyclic polarization experiments are summarized in Table 2. Two typical polarization curves obtained in simulated J-13 water are shown in Figures 1 and 2. In Figure 1, the polarization curve observed is typical of pitting/crevice corrosion phenomenon. The current increases above a certain potential called variously as pitting or breakdown potential. In this case, this potential is 512 millivolts with respect to a saturated calomel reference electrode (SCE) and can be considered to be a true pitting potential. More importantly, on reversing the scan after attaining a current density of about  $500 \text{ uA/cm}^2$ , the potential-current curve exhibits a marked hysteresis resulting in the intersection of the reverse scan curve with the forward scan curve at a potential of 140 mV vs. SCE (usually called repassivation potential) which is considerably more negative than the breakdown potential. This hysteresis is indicative of localized corrosion because the current density inside an active pit or crevice is much higher than the passive current density outside and hence will reduce the potential required to maintain the high current density. Visual

TABLE 1  
Heat Numbers and Chemical Compositions of the Candidate  
Container Materials in the IWPE Program

<u>Alloy</u>	<u>Heat No.</u>	<u>Composition (wt.%)</u>							
		Ni	Fe	Cr	Mo	W	Cu	Al	Other
304L	T0954	9.14	Bal.	18.3	-	-	-	-	C - 0.022
316L	P80746	10.04	Bal.	16.4	2.1	-	0.3	-	C - 0.01
IN - 825	HH4371FC	41.1	30.4	22.1	3.2	-	1.8	-	C - 0.01 Ti - 0.82
HA-C-22	8-3175	Bal.	3.8	21.4	13.6	3.0	-	-	C - 0.004
CDA - 102	6681	-	-	-	-	-	99.95	-	-
CDA - 613	M5459	-	2.5	-	-	-	90.54	6.65	-
CDA - 715	7037/6132a	29.6	0.5	-	-	-	69.1	-	C - 0.13

- (1) - Incoloy is a registered trademark of Inco Alloys International  
(2) - Hastelloy is a registered trademark of Haynes International Inc.

TABLE 2  
Electrochemical Test Data -- Type 304L Stainless Steel  
(See Notes 1-5)

Environment	Solution Deaerated?	Initial Potential (mV vs SCE)	Corrosion	Pitting	Repassivation	Epit - Erp (mV)	Solution pH		pHi - pHf
			Potential Ecorr (mV vs SCE)	Potential (Epit) (mV vs SCE)	Potential (Erp) (mV vs SCE)		Initial	Final	
Simulated J-13 Water	Yes	-427	-427	512	140	372	6.88	9.14	2.26
Simulated J-13 Water	Yes	-652	-478	451	107	344	6.83	9.10	2.27
Simulated J-13 Water	Yes	-715	-515	514	128	386	7.06	7.55	0.49
Simulated J-13 Water	Yes	-942	-742	476	99	377	6.97	9.22	2.25
Simulated J-13 Water	No	-140	-140	809(NP)	768	41	7.18	9.12	1.94
				552 ± 146 (488 ± 30)*	248 ± 291 (118 ± 19)*	304 ± 148 (370 ± 18)*	6.98 ±0.14	8.83 ±0.71	1.84 ± 0.77 (2.18 ± 0.16)*
5 Sim. J-13 Water (Scan Rate: 1.0 mV/sec; Temp: 90°C)	No	-208	-208	417	221	196	6.91	8.11	1.20
Sim. J-13 Water + Crevice (Initial pH adjusted with CO2)	No	-228	-228	837(NP)	824	13	6.92	8.65	1.73
Sim. J-13 Water + 1,000 ppm Cl-	Yes	-693	-693	-48	-129	81	7.17	8.97	1.80
Sim. J-13 Water 1,000 ppm Cl- (Initial pH adjusted with CO2)	No	-265	-265	152	-21	173	6.86	8.59	1.73

**Notes:**

- (1) Initial pH adjusted with 0.1 N HCl, unless otherwise indicated
- (2) Potential held at Ecorr for 60 minutes prior to scan
- (3) Scan rate = 0.17 mV/sec; Temp. = 95°C, unless otherwise indicated
- (4) Electrode partially immersed in solution
- (5) Current threshold = 5,500 μA

(NP) - No pitting

\* Based on four values (extreme value eliminated)

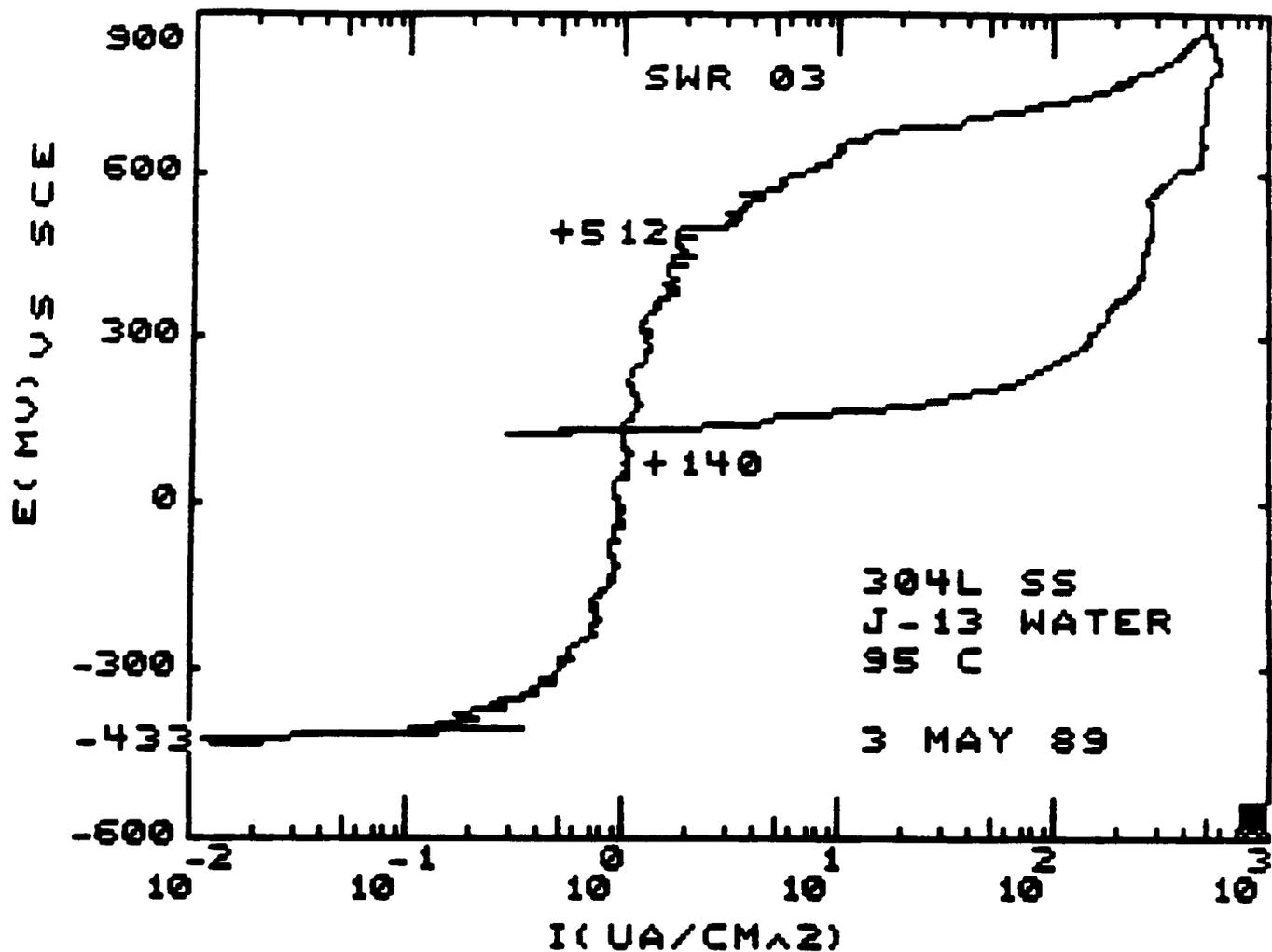


Figure 1. Potentiodynamic Polarization Curve in Simulated J-13 Water on AISI 304L Stainless Steel. Scan Rate - 0.17 mV/sec. Solution was Deaerated

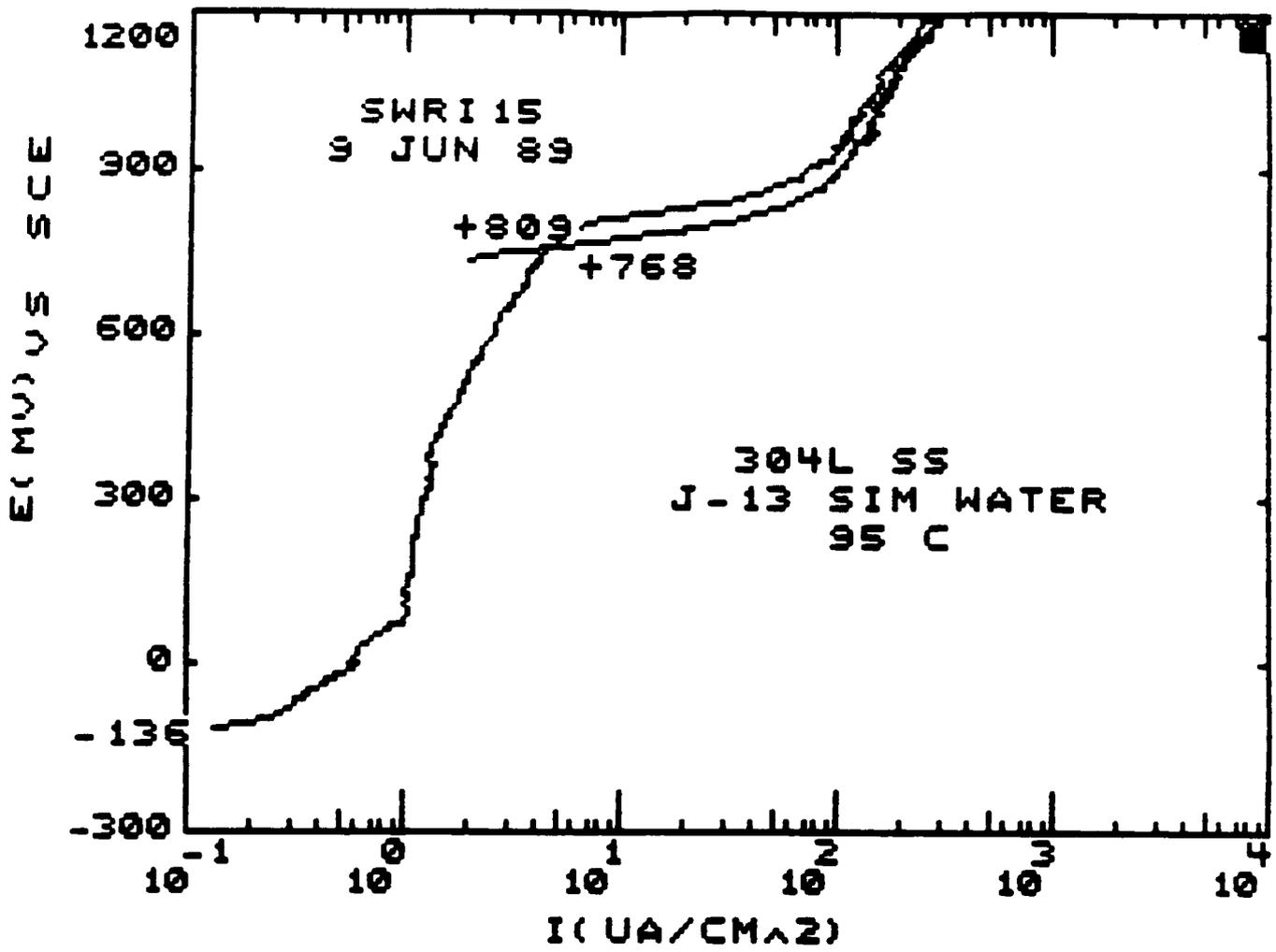


Figure 2. Potentiodynamic Polarization Curve in Simulated J-13 Water on AISI 304L Stainless Steel. Scan Rate = 0.17 mV/sec. Solution was not Deaerated

examination of the sample indicated considerable pitting. In contrast, the curve in Figure 2, indicates a breakdown potential of 809 mV vs. SCE and no significant hysteresis in the reverse scan curve was observed with the intersection of forward and reverse scans occurring at a potential of 768 mV vs. SCE. Examination of the sample at a magnification of about 40X indicated no localized corrosion. The breakdown potential in this case is due to water oxidation resulting in oxygen evolution rather than pitting.

It can be seen from Table 2 that most of the 304L samples that were tested in deaerated solution exhibited pitting. The sample that was not deaerated (i.e. left to equilibrate with atmospheric oxygen pressure) did not exhibit pitting. However, it is not possible to conclude that dissolved oxygen exerted a beneficial effect for the following reasons: 1) As shown in Table 2, another test performed during the same period with a faster scan rate showed pitting even though the solution was not deaerated. Generally faster scan rates result in higher pitting potentials and hence the pitting in this case can not be attributed to scan rate differences, and 2) As described in SECTION B, tests performed subsequently did not show pitting in spite of deaeration.

Most of the tests were conducted in solutions where the pH was adjusted with 0.1N HCl in accordance with the Battelle procedure. In one case, the pH was adjusted by sparging a small amount of CO<sub>2</sub>. No pitting was observed in this case despite the fact that there was an intentional crevice created on the specimen. Generally, localized corrosion is more severe at a crevice than an open surface. As expected, addition of HCl has been shown to result in a higher chloride level (PABALAN - 1989).

Another important factor in localized corrosion exhibited by results in Table 2 is chloride content. The solutions containing 1000 ppm chloride exhibited lower breakdown potential, lower repassivation potential, and pitting irrespective of whether the pH was adjusted with HCl or CO<sub>2</sub>.

The results of CO<sub>2</sub> adjusted simulated J-13 water are in accordance with some of the data reported by LLNL in natural J-13 water (McCRIGHT - 1987). A cautionary note is in order at this time, however, since not all LLNL data are consistent. For example, in an earlier report by McCright et al (McCRIGHT - 1983), the reported protection potentials in natural J-13 water of 304L stainless steel are quite low (200 mV vs. SCE) which is an indication of pitting.

2.1.2 AISI 316L Stainless Steel

The results of tests on AISI 316L are shown in Table 3. A representative polarization curve in simulated J-13 solution is shown in Figure 3. All samples, irrespective of experimental parameters, exhibited pitting. Both the breakdown and repassivation potentials were lower than those of AISI 304L stainless steel on an average. This result is very surprising because based on extensive literature data available on a wide variety of chloride containing environments (SEDRIKS - 1979), the higher Molybdenum-containing 316L stainless steel is expected to be more resistant to localized corrosion than 304L stainless steel. These results are also not in agreement with those reported by LLNL in one of their reports (McCRIGHT - 1983) which showed that neither alloy exhibited pitting in simulated J-13 water.

TABLE 3  
Electrochemical Test Data -- Type 316L Stainless Steel  
(See Notes 1-5)

Environment	Solution Deaerated?	Initial Potential (mV vs SCE)	Corrosion	Pitting	Repassivation		Solution pH		pHi - pHf
			Potential Ecorr (mV vs SCE)	Potential (Epit) (mV vs SCE)	Potential (Erp) (mV vs SCE)	Epit - Erp (mV)	Initial	Final	
Simulated J-13 Water	No	-652	-402	417	129	288	7.18	8.33	1.15
Simulated J-13 Water	Yes	-730	-730	464	131	333	7.03	9.53	2.50
Simulated J-13 Water	Yes	-920	-720	511	110	401	7.13	8.90	1.77
Simulated J-13 Water	No	-212	-212	497	229	268	7.02	8.63	1.61
				472 ± 42	150 ± 54	322 ± 59	7.09 ±0.08	8.85 ±0.51	1.76 ± 0.56
6 Sim. J-13 Water (Scan Rate: 1.0 mV/sec; Temp: 90°C)	No	-162	-162	423	267	156	6.89	7.19	0.30
Sim. J-13 Water + 1,000 ppm Cl-	Yes	-968	-718	21	-58	79	6.88	9.11	2.23

**Notes:**

- (1) Initial pH adjusted with 0.1 N HCl
- (2) Potential held at Ecorr for 60 minutes prior to scan
- (3) Scan rate = 0.17 mV/sec; Temp. = 95°C
- (4) Electrode partially immersed in solution
- (5) Current threshold = 5,500 μA

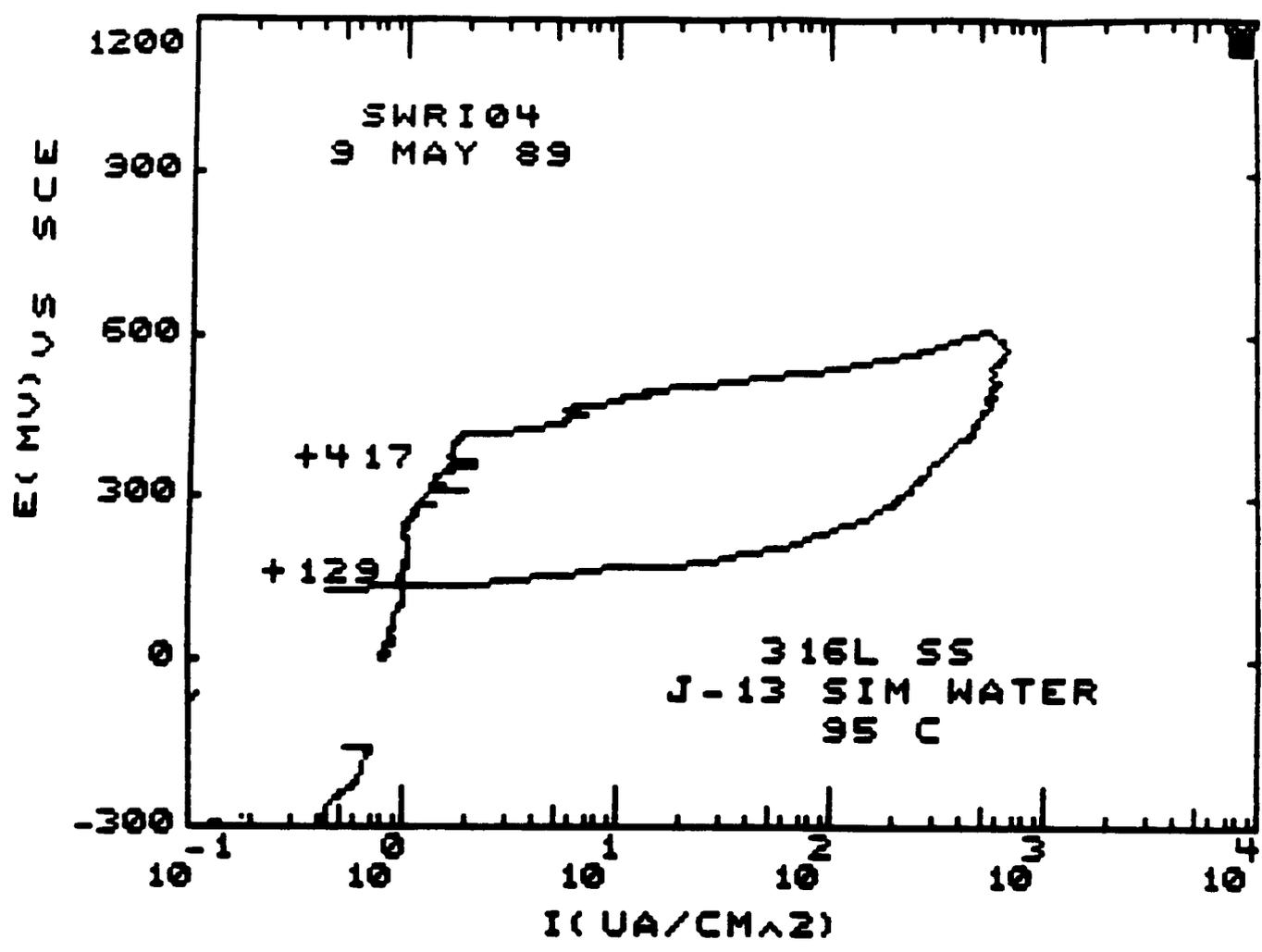


Figure 3. Potentiodynamic Polarization Curve in Simulated J-13 Water on AISI 316L Stainless Steel. Scan Rate - 0.17 mV/sec. Solution was Deaerated.

### 2.1.3 Incoloy alloy 825

The results for Incoloy Alloy 825 are summarized in Table 4. A representative polarization curve in simulated J-13 water is shown in Figure 4. No localized corrosion was observed in any of the tests in simulated J-13 water involving this material. However, addition of 1000 ppm chloride resulted in considerable pitting as evidenced by large hysteresis and lower repassivation potentials. A representative curve for the 1000 ppm chloride solution is shown in Figure 5. This is in agreement with results reported by LLNL (McCRIGHT - 1983, - 1987).

### 2.1.4 Hastelloy alloy C-22

A limited number of tests was conducted on this alloy. The results of these tests are shown in Table 5 and Figure 6. This material was chosen as the CNWRA reference material to compare the performance of the candidate container materials because of its well established resistance to localized corrosion (HIBNER - 1986, RENNER - 1986). Surprisingly however, the tests in simulated J-13 water indicated pitting, both by visual observation and by the hysteresis of the polarization curve. This is an area that needs further verification, especially in light of the fact that DOE/LLNL is considering this alloy as a possible alternate container material. Hastelloy alloy C-22 is expected to be superior in pitting resistance to the other alloys based on literature data (HIBNER - 1986, RENNER - 1986) and experience in a variety of industrial applications. Since the results reported above were only from the simulated J-13 water, the possibility of unusual behavior in low-chloride environments exists, not only for alloy C-22 but also for other nickel-base alloys containing high amounts of alloying elements.

## 2.2 *Task 2.1b Preparation and analysis of simulated J-13 well water*

In the initial part of the experimental program simulated J-13 well water was selected as an adequate electrolytic medium for conducting electrochemical tests. It is known that saturated zone water extracted from the well J-13 located in the Topopah Springs Tuff has been used as the reference composition for the groundwater at the proposed Yucca Mountain repository site (GLASS - 1984). As shown in Table 6, it is a neutral pH water in which the prevailing ionic species are  $\text{HCO}_3^-$  and  $\text{Na}^+$ . Other anions, such as  $\text{Cl}^-$ ,  $\text{F}^-$ ,  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  are present at lower concentrations. It should be noted that the silicon content of the water is relatively high. Waters from other wells in the vicinity of Yucca Mountain have similar chemical composition, but differences in pH and ion concentration ratios are considered to be significant (MURPHY - 1989a).

Simulated J-13 well water was prepared following the procedure developed by Battelle and adopted by Cortest Columbus, Inc. (BATTELLE - 1987, BEAVERS - 1988). Nevertheless, two aspects of the preparation procedure were a matter of concern. The first aspect refers to the preparation of the stock solution which contains  $\text{CaSO}_4$ ,  $\text{Ca}(\text{NO}_3)_2$ ,  $\text{KCl}$  and  $\text{MgCl}_2$ . In the laboratory procedure filtration is recommended if any solid remain undissolved after stirring during solution preparation. However, the composition of the resulting solution may differ from that given in Table 6 and may be variable depending upon the amount of undissolved solids. The second aspect is related to the effect of the pH adjustment with 0.1 N HCl or 0.1 N NaOH solutions to obtain the pH of  $7.0 \pm 0.2$  at room temperature reported for J-13 well water. It was speculated that if such

TABLE 4  
Electrochemical Test Data -- Incoloy 825  
(See Notes 1-5)

Environment	Solution Deaerated?	Initial Potential (mV vs SCE)	Corrosion Potential Ecorr (mV vs SCE)	Pitting Potential (Epit) (mV vs SCE)	Repassivation		Solution pH		
					Potential (Erp) (mV vs SCE)	Epit - Erp (mV)	Initial	Final	pHi - pHf
Simulated J-13 Water (Initial pH adjusted with 0.1 N HCl)	No	-180	-180	833(NP)	833	0	7.04	8.42	1.38
Simulated J-13 Water	No	-229	-229	756(NP)	704	48	7.06	9.31	1.84
Simulated J-13 Water + Crevice	No	-231	-231	790(NP)	790	0	6.93	8.60	1.67
Simulated J-13 Water + 1,000 ppm Cl-	No	-257	-257	512	120	392	7.15	8.90	1.75
Sim. J-13 Water + 1,000 ppm Cl- + Crevice	No	-261	-261	484	168	316	6.92	8.46	1.54

**Notes:**

- (1) Initial pH adjusted with CO<sub>2</sub>, unless otherwise indicated
  - (2) Potential held at Ecorr for 60 minutes prior to scan
  - (3) Scan rate = 0.17 mV/sec; Temp. = 95C°
  - (4) Electrode partially immersed in solution
  - (5) Current threshold = 5,500 μA
- (NP) - No pitting

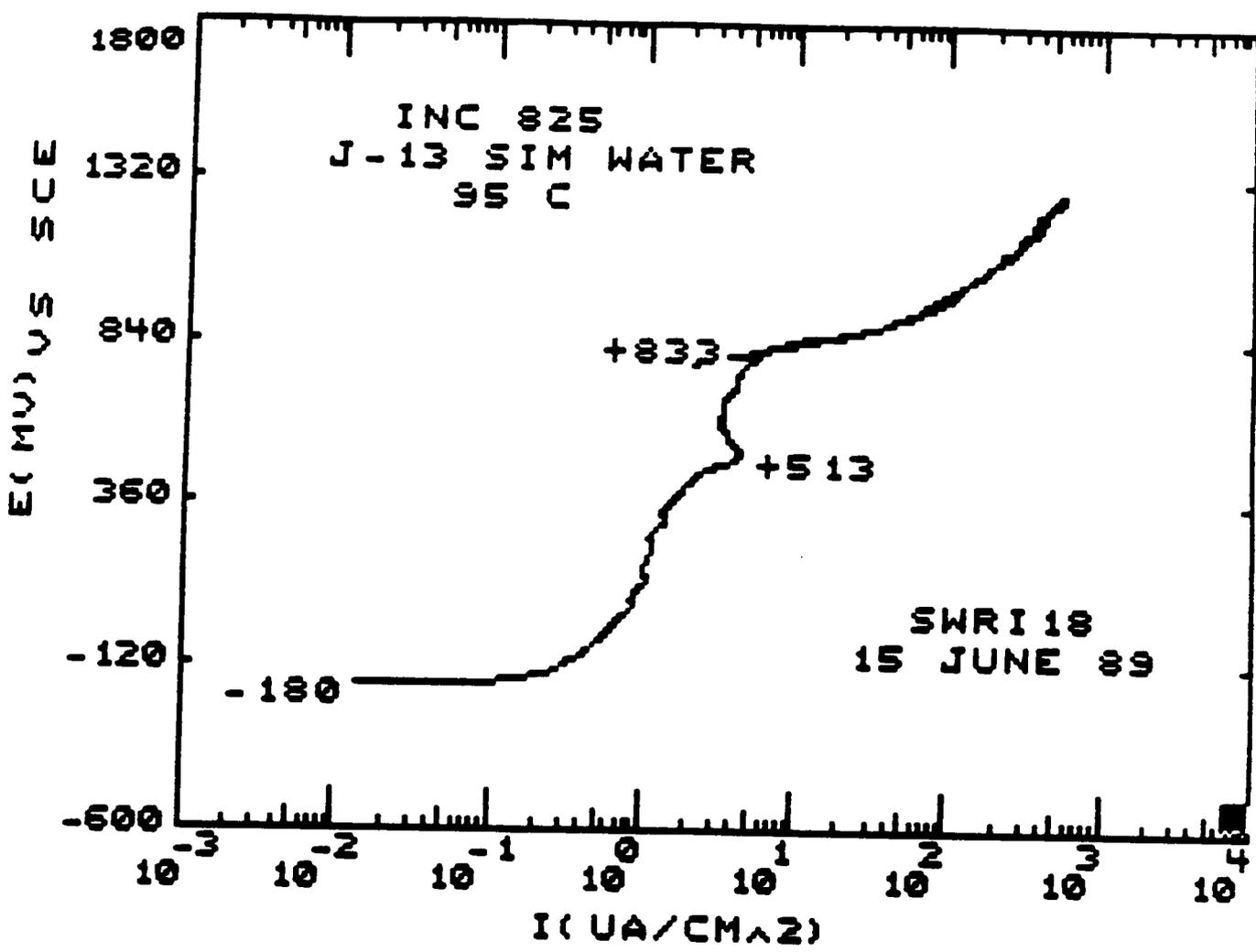


Figure 4. Potentiodynamic Polarization curve in Simulated J-13 Water on Incoloy Alloy 825. Solution was Deaerated. Scan Rate = 0.17 mV/sec.

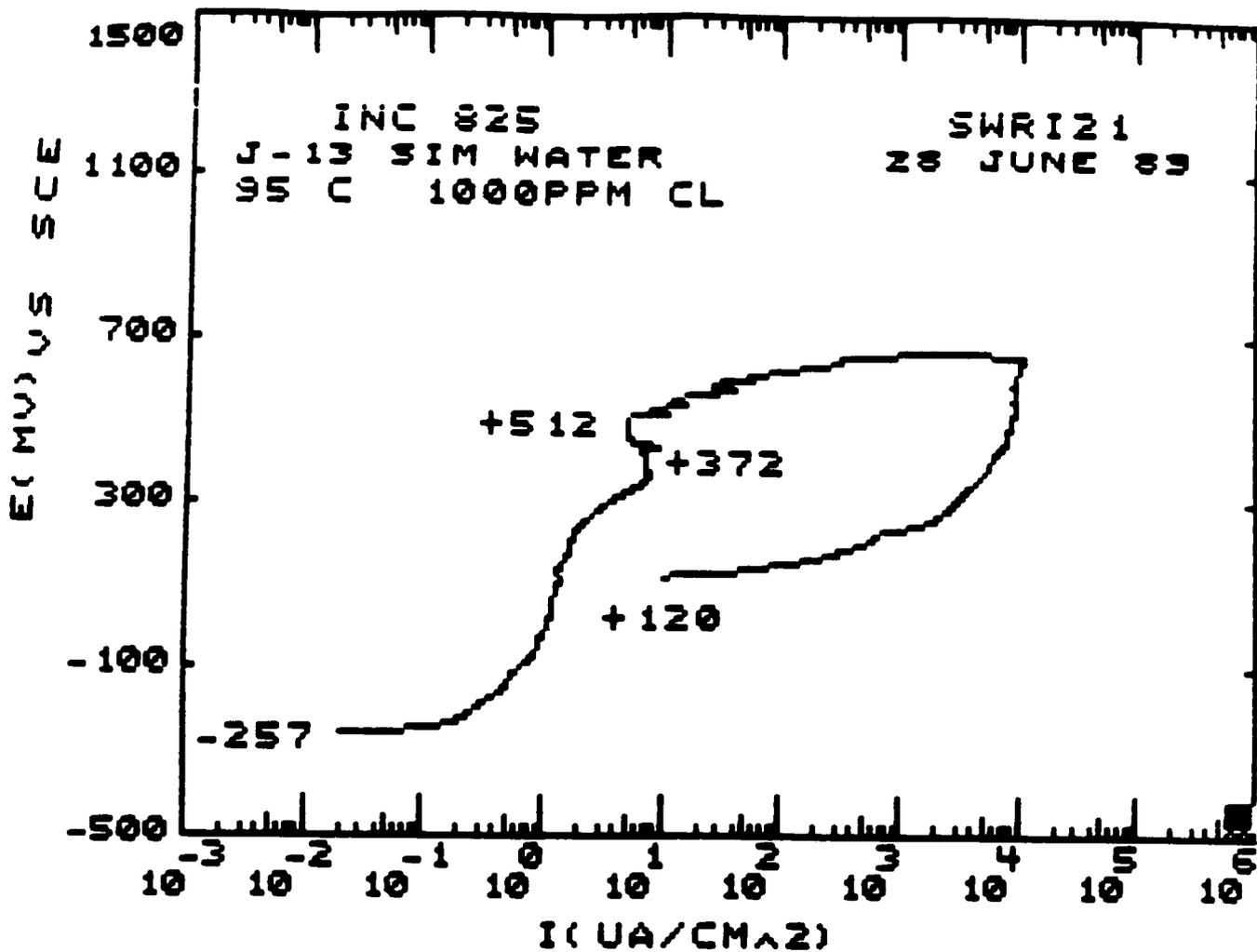


Figure 5. Potentiodynamic Polarization Curve in Simulated J-13 Water Augmented in Chloride to 1000 ppm. Incoloy Alloy 825. Scan Rate = 0.17 mV/sec.

TABLE 5  
Electrochemical Test Data -- Hastelloy alloy C-22

Environment	Solution Deaerated?	Initial Potential (mV vs SCE)	Corrosion	Pitting	Repassivation		Solution pH		pHi - pHf
			Potential Ecorr (mV vs SCE)	Potential (Epit) (mV vs SCE)	Potential (Erp) (mV vs SCE)	Epit - Erp (mV)	Initial	Final	
Simulated J-13 Water (Initial pH adjusted with HCl)	Yes	-914	-664	620	496	224	7.18	9.2	2.0
Simulated J-13 Water (Initial pH adjusted with CO <sub>2</sub> )	No	-198	-198	769	580	189	7.07	8.18	1.1
Simulated J-13 Water (Initial pH adjusted with CO <sub>2</sub> )	No	-191	-191	761	513	248	7.09	8.65	1.6

15

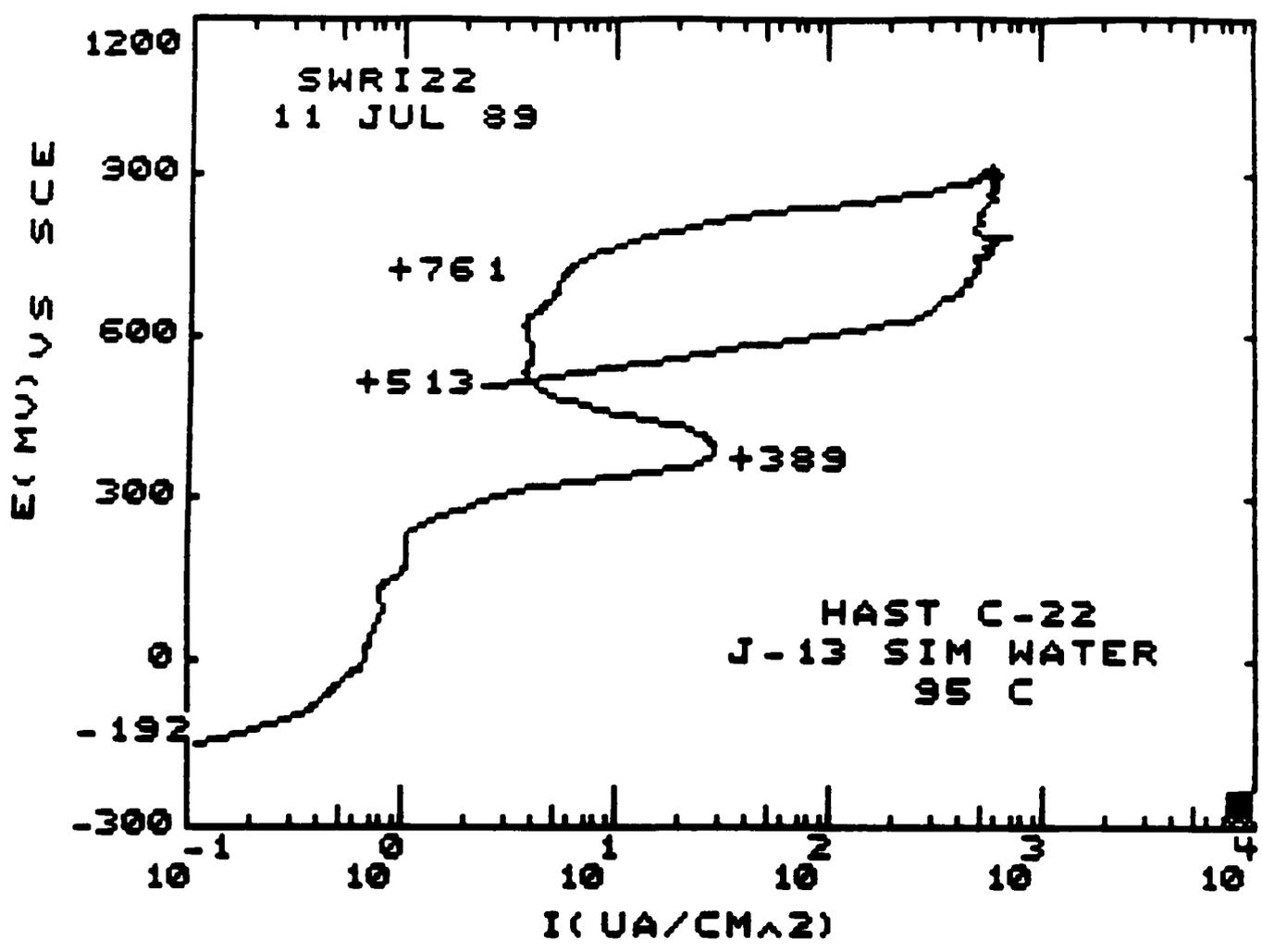


Figure 6. Potentiodynamic Polarization in Simulated J-13 Water on Hastelloy Alloy C-22. Scan Rate = 0.17 mV/sec.

TABLE 6  
Chemical Compositions of Actual and Simulated  
J-13 Well Water Solutions\*

Species	Actual J-13 Well Water (ppm)	Simulated J-13 Well Water (ppm)
<u>Cations</u>		
Na+	45.0	46.0
K+	5.30	5.50
Mg <sup>++</sup>	1.76	1.70
Ca <sup>++</sup>	11.5	12.0
Subtotal	63.56	65.2
<u>Anions</u>		
F-	2.10	1.70
Cl-	6.40	6.40
HCO <sub>3</sub> <sup>-</sup>	143	121
NO <sub>3</sub> <sup>-</sup>	10.1	12.4
SO <sub>4</sub> --	18.1	19.2
Subtotal	179.7	160.7
<u>Other</u>		
SiO <sub>2</sub>	64.2	64.2
Tot. Dis. Solids	307.5	290.1
pH	6.9	7.0 ± 0.2

\*From Cortest Columbus Quality Assurance Document QA003, revision D, based based on Nureg/CR-4955 BMI-2155, November 1987, Battelle Columbus Laboratories, Quality Assurance Procedure WF-PP-34, Revision 0.

an adjustment was necessary, the concentration of  $Cl^-$  or  $Na^+$  ions in the resulting solution may differ significantly from that given in Table 6.

Studies were conducted on simulated J-13 well water to test its stability as a function of time and to identify possible sources of error or uncertainties in the preparation procedure, as those noted above (PABALAN - 1989). Initial calculations were done to determine if dissolution of the masses of reagents in the volumes of water given in the technical operating procedure (TOP) issued by Battelle resulted in solute concentrations that correspond with those reported for J-13 well water. The expected values were confirmed with the exception of  $F^-$  and  $K^+$ . The TOP indicated the use of an anhydrous reagent (KF) to supply the total amount of  $F^-$  and part of the required amount of  $K^+$ . However, since  $KF \cdot 2H_2O$  was used because reagent grade KF was not commercially available, the  $F^-$  and  $K^+$  concentrations were 3.96 and 1.17 mg/l instead of the values shown in Table 6.

Various samples of simulated J-13 well water and reference solutions containing NaCl, KCl,  $KNO_3$  and  $Na_2SO_4$  were prepared. Chemical analyses of the samples were performed using inductively coupled plasma emission spectroscopy for the cations and ion chromatography for the anions, with the exception of  $HCO_3^-$  which was analyzed by a titration method. In addition, the pH and  $Cl^-$  concentrations were measured using pH and ions selective electrodes respectively. Measurements were conducted after solution preparation and also five days later.

Despite some scatter in the data, accurate measurements of anion concentrations were obtained for all the solutions prepared. For  $HCO_3^-$  the results were not precise and were up to about 20% lower than the expected values for the simulated J-13 well water samples. These differences may be due to the nature of the titration method used. On the other hand, concentrations of  $HCO_3^-$  anion above 18 mg/l were measured in the reference solutions in which no  $HCO_3^-$  was added, presumably due to absorption of  $CO_2$  from the atmosphere.

Measurements of cation concentrations were not so precise as in the case of the anions and the values exhibited larger deviations, except for  $Ca^{+2}$ . Nevertheless, a reasonable agreement with the expected values was attained. No indication was found that the ionic concentration of the samples changed over a period of 5 days. However, a noticeable change in concentration was detected in the case of Si. An increase of about 30% in the Si concentration was measured after 5 days, probably associated with a continued dissolution of the solid silica phase. As shown in Table 7, the pH of the simulated J-13 water was found to be 8.2. In two samples the pH was adjusted to 7.0 using 0.121 N HCl. In these samples pH increases slowly with time, as shown in Table 7, presumably due to exsolution of  $CO_2$  to the atmosphere.

It was concluded that silica (added as  $SiO_2 \cdot xH_2O$ ), besides the undetermined amount of water which affects the exact amount of  $SiO_2$  weighed, does not dissolve completely. Computations for 25 C using the EQ-3 program indicated that the simulated J-13 water is supersaturated with respect to several polymorphs of silica (MURPHY - 1989b). Also, calcite precipitation was found to be possible. The use of HCl to adjust the pH to 7.0 seems to be unnecessary. It only increases the  $Cl^-$  concentration and gives values higher than those measured in J-13 well water. As an example, the change of pH is plotted in Figure 7 as a function of the chloride concentration calculated from the volume and concentration of the HCl solution used in a typical preparation of neutral pH,

TABLE 7  
 pH and Cl<sup>-</sup> Concentrations of Simulated J-13 Waters Measured in the Center  
 Geochemistry Laboratory Using pH and Ion Selective Electrodes

Date	Samples			
	1*	2*	3*	4*
	pH Value			
7/21	8.17	8.17	7.00	7.00
7/24	8.19	8.26	7.14	7.51
7/26	8.06	8.16	7.18	7.68
7/28	8.02	8.16	7.25	7.81
7/31	7.96	8.16	7.33	
8/2	7.97	8.16	7.43	8.05
8/3	8.10		7.87	
	Cl <sup>-</sup> Concentration <sup>@</sup>			
8/3	7.46 (6.38)	6.75 (6.38)	20.6 (20.1)	20.6 (20.1)

\*Simulated J-13 solution was prepared without adjusting the pH. Half the solution was stored in a polyethylene bottle (Sample 1), and the other was stored in a glass bottle (Sample 2).

#Initial pH of the solution was adjusted to 7.0. Sample 3 was stored in a polyethylene bottle and Sample 4 in a glass bottle.

@Values in parentheses are calculated values for samples without and with pH adjustment.

simulated J-13 well water. The Cl<sup>-</sup> concentration for pH 7 is very close to that measured in a separate experiment, as shown in Table 7, and reveals also good agreement with the value calculated using the EQ-3 program (MURPHY - 1989b), which is 19.8 mg/kg H<sub>2</sub>O (ppm). The calculated CO<sub>2</sub> fugacity is 10<sup>-2</sup> bar, indicating a strong tendency for CO<sub>2</sub> exsolution to the atmosphere, since the atmospheric CO<sub>2</sub> fugacity is 10<sup>-3.5</sup> bar (MURPHY - 1989b). This is precisely the behavior observed even in a relatively closed container as noted in the evolution of pH shown in Table 7.

**2.3 Peer review of IWPE program plan of 1988**

A peer review group consisting of Dr. M. A. Streicher, Dr. S. Yukawa, and Mr. O. Siebert reviewed the IWPE program plan of December 1988 and provided comments on the approach taken in the plan and recommendations for future considerations. During the peer review meeting, many of the results documented above were presented. A detailed summary of the peer reviewers' comments and recommendations are provided in a letter report (LATZ - 1990). The reviewers essentially made the following recommendations:

1. Conduct long-term studies in not only liquid phase, but also in vapor phase.
2. Consider galvanic corrosion between container material and borehole liner.
3. Continue hydrogen absorption and embrittlement studies.
4. Conduct studies to verify presence of microbiologically induced corrosion under repository conditions.
5. Examine internal corrosion of container materials from waste form.
6. Conduct long-term metallurgical stability tests with and without radiation at temperatures higher than anticipated repository temperatures.
7. Consider heat-to-heat variation or characterize the specific heats examined thoroughly.
8. Conduct a workshop on accelerated test techniques vs. life prediction.

As mentioned in Section C, these peer review comments were taken into consideration in formulating a more specific IWPE program plan.

**2.4 Summary**

A clear trend in the results from this stage of the IWPE is the effect of chloride on pitting in all the Cr-containing alloys. All alloys showed pitting in the simulated J-13 solution containing 1000 ppm chloride. The considerable scatter observed in the pitting results of 304L stainless steel is a matter for further investigation which is being carried out currently. Part of the scatter can be accounted for by the stochastic nature of localized corrosion. Other factors can be variations in solution preparation procedure. The solutions where pH was adjusted by the addition of HCl resulted in higher chloride content

### Chloride Concentration Range for Simulated J-13 Water Produced by Battelle Procedure

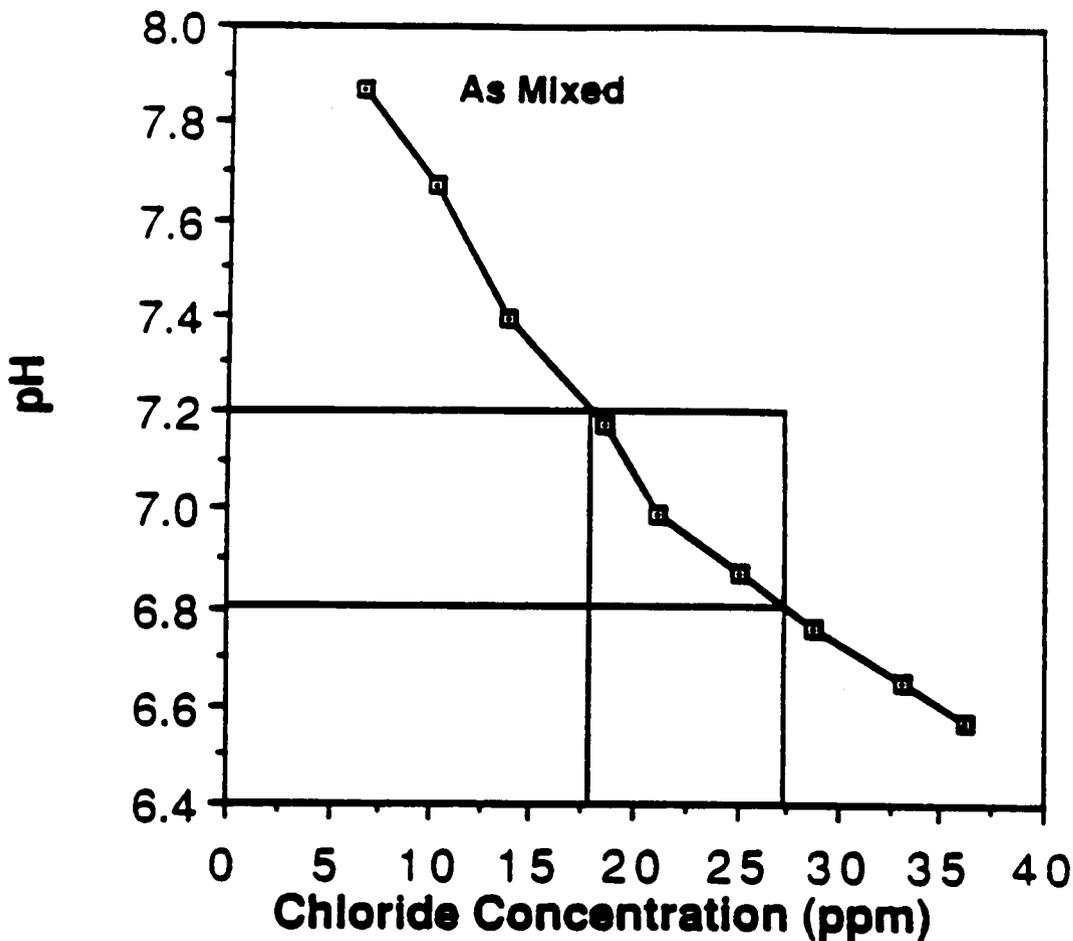


Figure 7. Effect of Addition of HCl to adjust pH on Chloride content of the Simulated J-13 Water.

to as much as 20 ppm compared to the normal chloride level in simulated J-13 water of 6 ppm. This can explain the higher incidence of pitting in these solutions compared to those where pH was adjusted with CO<sub>2</sub> or acetic acid. The initial pH was lower than the final pH in most of the experiments and this can be explained by the bicarbonate concentration attaining equilibrium with atmospheric CO<sub>2</sub>.

The unexpected results are the greater incidence of pitting in alloys C-22 and 316L stainless steel. Both these alloys are expected to perform better than 304L stainless steel in chloride solutions. The question that must be addressed is whether polarization to high potentials in low-chloride solutions result in an as-yet unclear localized corrosion phenomenon and, if so, what implication this has on the considerations for the selection of container materials.

3. SECTION B TESTS CONDUCTED FROM DECEMBER 1989 TO APRIL 1990

3.1 Task 1. Review of the experimental work on corrosion of candidate alloys for the tuff repository

An extensive review of the literature covering the influence of environmental variables on the corrosion behavior of candidate container materials for the proposed tuff repository at Yucca Mountain has been completed recently by Cortest Columbus, Inc. (BEAVERS, 1990). The review contains updated information on the more common forms of localized corrosion and stress corrosion cracking for the austenitic Fe-Cr-Ni alloys (AISI 304L and 316L stainless steels and Incoloy alloy 825) and the Cu-based alloys (CDA 102 [pure Cu], CDA 613 [Al-8Al] and CDA 513 [Cu-30Ni]). The effects of decay heat and radiation on corrosion are included, as well as a brief discussion on the possible impact of microbiologically induced corrosion on the performance of the container alloys. However, it would be highly desirable to have a critical assessment of other possible metal/environment failures modes, even though some of them may not be expected according to our current experience or knowledge. It should be emphasized that an adequate and complete characterization of the tuff repository environment, and in particular its evolution with time taking into consideration the combined effects of radiation and heat, does not exist. An appropriate description, in terms of water chemistry, pH, Eh, trapped and dissolved gases among other variables, is not yet available despite the significant effort devoted during the last years for this purpose (MURPHY - 1989b).

Most of the corrosion studies reviewed by Beavers and Thompson have been carried out using J-13 well water, solutions concentrated by evaporation from J-13 well water, or solutions based on J-13 water containing increasing concentrations of aggressive species (e.g. 100X in Cl- concentration). It should be emphasized that abnormal conditions, although to be identified, are of paramount importance in terms of degradation mechanisms. In addition, a sustained effort is required to advance the understanding of several corrosion processes that are not yet well defined from a purely phenomenological point of view, such as thermally induced galvanic corrosion, some forms of radiation induced corrosion which may be produced as a consequence of modifications in the protective properties of passive films, localized corrosion associated with the sudden transformation of water droplets in steam, etc. The impact of conditions that may be existent only under an unusual set of circumstances must be evaluated in relation to those forms of corrosion. Nevertheless, laboratory studies conducted under a well defined set of environmental conditions are essential to establish an appropriate framework for further correlations, especially when synergistic effects arising from radiation, heat transfer effects, etc., may be present. It is apparent that the purpose of Cortest in the preparation of the review was to explore some of these issues in order to focus their experimental program. In this regard such objective was achieved and the more important conclusions are summarized below.

As expected, the Fe-Cr-Ni alloys were found to be highly resistant to general corrosion under anticipated repository conditions. However, the austenitic stainless steels (AISI 304L and 316L) were considered to be susceptible to localized corrosion in the form of pitting and/or crevice corrosion. Although no pitting corrosion was detected in electrochemical experiments conducted in J-13 well water at 50-100° C, and only a slight tendency to crevice corrosion was observed in 1 year exposure to the same

environment, by no means can it be assured that alterations in the aggressive anion concentration or in the oxidizing conditions prevailing in the repository as a consequence of radiolysis may not have a detrimental effect. In addition, transgranular stress corrosion cracking (TGSCC) was identified as the most serious degradation mode for the stainless steels. In the report it is emphasized that AISI 304L stainless steel in the solution annealed condition exhibited TGSCC when tested in a mixture of air and water vapor at 90 C in the presence of a radiation field ( $3 \times 10^5$  rad/h). On the basis of this observation and additional considerations regarding possible alterations in the microstructure or the occurrence of welding related problems, Beavers and Thompson concluded that the austenitic stainless steels should be eliminated from consideration as container materials. From the results reviewed, it appears that Incoloy alloy 825 would be more resistant to TGSCC as a result of its higher nickel content and to localized corrosion as a consequence of its higher molybdenum content.

To date Cortest Columbus, Inc. has published five progress reports on environmental effects on the corrosion of container materials. The experimental work consisting of Cyclic Potentiodynamic Polarization (CPP) has been completed for Task 2 of the program. The purpose of this task was to examine the effects of environmental and metallurgical variables on the electrochemical behavior of candidate container materials. The approach was based on the use of potentiodynamic polarization curves with a forward potential scanning from a cathodic potential towards anodic potentials, followed by a reverse scanning when the current density reached  $1 \times 10^{-3}$  A/cm<sup>2</sup>. Using this method the pitting potential and the repassivation potential, as well the corrosion current, the passivation current (maximum current) and the passive current were determined. Apparently, the corrosion potential was measured initially, before the potential scan and after the specimen was exposed to the solution overnight. A second aspect of their approach is that they use a statistical experimental matrix for the evaluation of the effect of many environmental variables including pH and temperature.

Four of the six materials initially selected by DOE as candidate materials were tested by Cortest. They are: AISI 304L SS, Incoloy Alloy 825, CDA 102 (Copper) and CDA 715 (Cu-30Ni).

In the Appendix of the First Semi-Annual Report of Cortest (BEAVERS - 1988) the laboratory procedure adopted for running polarization curves is described as well as the procedure used for the preparation of a simulated tuff groundwater with a chemical composition similar to that of J-13 well water. It is worthwhile to note that the composition of J-13 well water reported by various authors varies according to different sources. Only recently the range of concentrations apparently found by different authors for all the species of interest has been reported (GLASSLEY, 1990). Although the variations are not very significant it is convenient to recognize that the range of concentrations measured makes unjustifiable efforts to prepare simulated J-13 well water according to the values reported by a given author. The main effort should be directed to identify the role of the different anionic species in the acceleration or inhibition of localized corrosion and to evaluate whether the different cations exert a distinctive influence.

The approach adopted by Cortest for the statistically designed experiment depends heavily on the criteria used in the selection of the independent

variables of interest and the dependent variables. Fifteen variables were chosen by selecting the concentration of thirteen different species in addition to pH and temperature. Nine of these species are present in J-13 well water, three species ( $\text{NO}_2^-$ ,  $\text{H}_2\text{O}_2$  and oxalic acid) are considered to be formed by radiolysis and the remaining  $\text{O}_2$  is present in the unsaturated zone from air and also formed by radiolysis of water. It should be noted that several problems arise from this particular selection of species and concentration values studied. They are as follows:

1. The concentration of  $\text{HCO}_3^-$  is dependent on pH. This means, for example, that for an initial concentration of  $\text{HCO}_3^-$  equal to 2000 mg/l or 32 mmoles/l the actual concentration will be significantly lower at pH 5 than at pH 10, since at the lowest pH  $\text{HCO}_3^-$  has been mostly transformed in  $\text{CO}_2$ , which has evolved from the solution. Therefore the effect of  $\text{HCO}_3^-$  concentration on the dependent parameters can not be assessed independently of the effect of pH.
2. The concentrations of Si and Al are dependent of the concentration of  $\text{F}^-$  which acts as a complexing agent. In the case of Al, which is added to the solution as a cation [presumably in the form of a salt like  $\text{Al}_2(\text{SO}_4)_3$ ], the stable complex is  $\text{AlF}_6^{3-}$ . The formation of this complex reduces the concentration of  $\text{Al}^{3+}$  well below the initial concentration, mainly when the  $\text{F}^-$  concentration is 200 mg/l, equivalent to 10.5 mmoles/l, and represents a concentration that is more than 10 times higher than the highest  $\text{Al}^{3+}$  concentration used in the test matrix [20 mg/l or 0.74 mmoles/l]. Si is added in the form of  $\text{SiO}_2 \cdot x\text{H}_2\text{O}$ , but it can be easily converted to  $\text{SiF}_6^{2-}$ . This is particularly true at the lowest concentration included in the test matrix, which is 0.035 mmoles/l. Even at the highest initial concentration, 3.5 mmoles/l, the concentration of non-complexed Si is significantly reduced, making invalid the adoption of the initial concentration as representative of the particular environment. The slow solubility of silicic acid (PABALAN - 1989) may also introduce errors in the actual vs. assumed concentration of Si.
- 3) Several species have been included in the test matrix as a result of radiolysis. They are  $\text{NO}_2^-$ ,  $\text{H}_2\text{O}_2$ ,  $\text{H}_2\text{CO}_4$  (oxalic acid) and also  $\text{O}_2$ , although it is pointed out that  $\text{O}_2$  is also included as a consequence of the aerobic nature of the repository. The reasons for the inclusion of oxalic acid in favor of other organic species is not clear. Although it can be argued that in the repository the presence of organic compounds can be expected, by no means can it be assumed that oxalic acid is the prevailing species. Acetic acid is stable up to  $300^\circ\text{C}$ , while oxalic decomposes above 150 to  $170^\circ\text{C}$ . The additional fact that oxalic acid is a good complexing agent for iron may complicate even further the interpretation of the results. Regarding the other species, it should be noted that due to the nature of the experimental method adopted, which is the measurement of anodic polarization curves under potentiostatic control, there is interference between the reducible/oxidizable species in the environment and the true anodic behavior of the material. The ideal situation is to remove all the electrochemically active species that may participate in charge transfer reactions at the metal surface (i.e. species such as  $\text{O}_2$ ,  $\text{H}_2\text{O}_2$ , etc) and study precisely the anodic behavior

of such species by applying controlled potentials. The role of the radiolytically generated species should be studied under open circuit conditions to interpret their effect on the redox potential of the environment and the corrosion potential of the metal. The role of anions that can act both as reducible species and as inhibitors (i.e.  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ , etc) can be studied, however, using potentiodynamic/potentiostatic methods once their effect under open circuit conditions is well established.

From the statistical analyses of the data, presented in the form of bar charts, the magnitude of the beneficial or detrimental effect of the environmental variables on pitting and repassivation potentials can be assessed. It was found that, for AISI 304L stainless steel, chloride promotes a significant decrease of pitting and repassivation potentials, whereas nitrate increases the value of both parameters. No other variable was found to have an effect on the repassivation potential. The pitting potential increases with pH and  $\text{HCO}_3^-$  concentration and decreases with temperature. However, as noted above, pH and  $\text{HCO}_3^-$  concentration are not independent variables. Nevertheless, all these observations are in qualitative agreement with the expected behavior of AISI 304 SS on the basis of experimental results in less complex environments (SMIALOWSKA - 1986, SEDRIKS - 1979). For Incoloy alloy 825 the results are not so straight forward, since no anion including chloride was found to have a detrimental effect on the pitting potential. In contrast,  $\text{F}^-$  exhibited a beneficial effect by increasing that potential. The lack of detrimental effect of chloride on pitting is in direct contrast with the observations of LLNL and CNWRA (see Table 4). Both  $\text{Mg}^{2+}$  and  $\text{H}_2\text{O}_2$  decrease the pitting and the repassivation potential. The repassivation potential also decreases with chloride concentration and pH. This effect of pH is not characteristic of austenitic Fe-Cr-Ni alloys, particularly in the pH range of 5 to 10. On the other hand, only  $\text{NO}_3^-$  and oxalic acid promote an increase in the repassivation potential.

Despite the above mentioned criticisms, the approach used by Beavers and Thompson is an important step towards defining the quantitative effects of relevant environmental variables on localized corrosion. By conducting studies in solutions containing anionic and cationic species found in J-13 well water, but covering a wide range of concentrations, they were able to identify regions of the environmental space where additional research is needed. Their results also emphasize the need to identify interactive effects between various environmental variables. A separate report on the analysis of experimental results in the literature (including LLNL and CORTEST) will be issued in the near future.

**3.2 Task 2.1a Electrochemical characterization**

**3.2.1 Further Tests on 304L Stainless Steel**

These tests were similar to those reported previously. However, the simulated J-13 solution was prepared with  $\text{CO}_2$  instead of HCl to adjust the pH. Silicic acid was not added following the findings of Pabalan (PABALAN - 1989). Additionally, high-purity water with (17-18 Mohm-cm) resistivity was used instead of deionized water of 200 Kohm-cm resistivity for preparing the solutions. To prevent crevice corrosion at the sample-holder crevice, the samples were passivated in nitric acid for about 20 hours, mounted in the

holder, and the exposed surfaces polished to 600 - grit finish. The results are summarized in Table 8. A representative polarization curve is shown in Figure 8. It can be seen that the results are quite reproducible. No pitting was observed in spite of the fact that the solutions were thoroughly deaerated. This suggests that the addition of HCl to adjust pH results in a chloride concentration sufficient to cause pitting in this test. Further systematic studies on the effect of chloride at the 20 ppm level are recommended.

3.2.2 Optimization of The Experimental System

The initial effort of this program was spent in examining the origin of the noise in the electrochemical measurements observed before. The noise was found even in a highly conductive medium such as 1.0 N sulfuric acid used in the ASTM G-5 test. Although the noise was overcome in the previous experiments by placing a damping capacitor between the working electrode and ground, it was felt that this was not a good solution especially if rapid changes in electrochemical behavior were to be observed. It was found that part of the noise was due to a bad capacitor in the electrometer interface associated with the EG&G Model 273 potentiostat. After this problem was corrected, it was found that noise was reduced considerably, especially in more conductive solutions. ASTM G-5 test was conducted on 430 stainless steel and the standard curve was reproduced quite accurately. In the case of low-conductivity solutions, noise was still present at low current densities. An additional consideration was the configuration of the reference electrode salt bridge supplied by EG&G. It was felt that since this salt bridge was short in length, the temperature of the reference electrode was somewhere in between ambient temperature and the solution temperature. This led to unknown thermal junction potentials. To have a reproducible system with reproducible thermal junction potentials, a long salt bridge was introduced whereby the reference electrode was kept at ambient temperature in a separate container. Introduction of the long bridge meant increasing noise in low-conductivity solutions and hence this was compensated by increasing the chloride concentration of the salt bridge solution to 0.5N. The VYCOR tip at the end of salt bridge immersed in the test solution slows down the interdiffusion between the test solution and bridge solution sufficiently to ensure that no significant contamination occurs during the test period. Other modifications to the system included addition of a condenser with a gas trap to prevent evaporative losses and intrusion of air. Standard tests such as ASTM G-5 and G-61 tests have been conducted and have been found to yield polarization curves within the range exhibited in these standards. Tests are underway on various candidate container alloys using this system.

3.2.3 Technical Operating procedures (TOPs)

Based on the experimental work done thus far, the next task was to issue the TOPs to meet the Center's Q.A. requirements. The TOPs have been written, approved, and put in place for electrochemical specimen preparation (CNWRA TOP-003), conducting and verifying potentiodynamic polarization curves (CNWRA TOP-009), conducting and verifying cyclic polarization curves (CNWRA TOP-008), and preparing simulated J-13 water and its modifications (CNWRA TOP-010). As the experimental program progresses, other TOPs will be written where necessary. In addition to special TOPs, tests are being carried out in accordance with standard ASTM practices. The results of these experimental programs are being

TABLE 8  
Electrochemical Test Data -- 304L Stainless Steel in Deaerated, Simulated J-13 Water\*

Initial Potential (mV vs SCE)	Corrosion Potential Error (mV vs SCE)	Pitting Potential (Epit) (mV vs SCE)	Repassivation Potential (Erp) (mV vs SCE)	Epit - Erp (mV)	Solution pH		pHi - pHf
					Initial	Final	
-603	-604	746(NP)	722	24	6.92	8.71	1.8
-683	-683	783(NP)	755	28	6.99	8.30	1.3
-413	-412	773(NP)	757	16	7.02	8.23	1.2
-420	-420	793(NP)	765	28	6.98	8.20	1.2
-308	-308	799(NP)	791	8	6.95	8.22	1.3
-708	-708	754(NP)	736	18	7.06	8.73	1.7
-611	-611	779(NP)	761	18	7.10	9.65	2.6
-614	-614	775(NP)	745	30	6.93	9.70	2.8

**Notes:**

\*Initial pH adjusted with CO<sub>2</sub> and no SiO<sub>2</sub> · x H<sub>2</sub>O was added.

(NP) No pitting

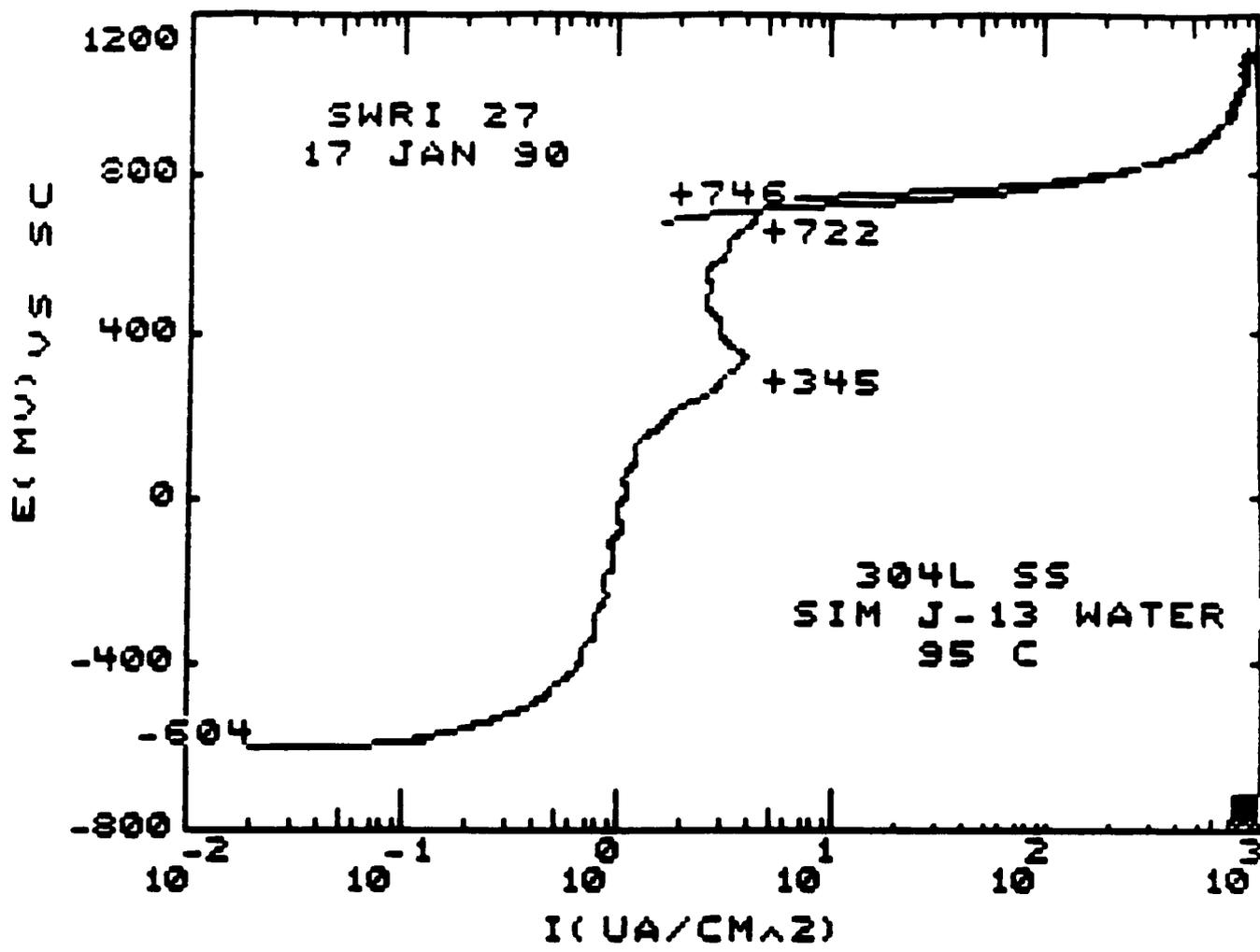


Figure 8. Potentiodynamic Polarization Curve in Simulated J-13 Water Prepared According to New CNWRA Procedure. pH was adjusted by CO<sub>2</sub> and Silicic acid was not added. Scan Rate = 0.17 mV/sec.

recorded in Scientific Notebooks in accordance with CQAM Section 17. The TOPs issued to date are included as Appendix A.

### 3.3 Task 2.4 Material characterization and stability

As a requirement for most of the studies in the IWPE program, it is essential that the initial condition of the candidate container materials be characterized fully. This characterization will result in a better understanding of differences in corrosion data between various laboratories, ensure that testing is performed on sound materials, and enable quantification of any microstructural changes due to long-time exposure to temperatures in the range of 200 - 300° C. The material characterization program consists of optical metallography, SEM-EDX analysis of various microstructural features, and corrosion studies in standard solutions designed to test the intergranular corrosion susceptibility.

#### 3.3.1 Optical Metallography

The candidate container materials are in the form of 0.5 in. (12.5mm) thick plates. The list of materials received along with their heat numbers and chemical compositions is shown in Table 1. Samples for metallographic studies were cut from these plates such that cross-sections parallel and perpendicular to the rolling direction were both examined. The results to-date from the metallographic examination are reported below.

**3.3.2 Incoloy Alloy 825:** The microstructures at two magnifications are shown in Figures 9a and 9b. The 500X micrograph indicates that the grain boundaries are free of precipitates (at least at this magnification). The cuboidal precipitate appears orange in color and is most probably a titanium nitride. Titanium is added in this alloy to stabilize the alloy against grain boundary carbide precipitation. The low-magnification micrograph shows that there is great variation in grain size in this plate with large grains being surrounded by small grains. The cause of the dual grain size distribution is not clear. It can be due to too short a time at annealing temperature which resulted in insufficient grain growth or it can be due to inhomogeneities in prior hot work. Further investigation is necessary to ascertain whether this microstructure is untypical and whether further annealing can eliminate this problem.

It is felt that since the grain boundaries are clean, localized corrosion behavior is most probably independent of grain size. Hence, localized corrosion studies are proceeding with this material. However, there is a potential concern for stress corrosion cracking and thermal stability studies because these phenomena may be affected significantly by differences in grain size. Hence further studies will be conducted to resolve this issue.

**3.3.3. 304L Stainless Steel:** The microstructures are shown in Figures 10a and 10b. The grain boundaries appear to be free of precipitation. The dark, elongated particles within the grains are most probably sulfide inclusions. This will be verified by SEM-EDX analysis.

**3.3.4 316L Stainless Steel:** The microstructure was found to be similar to that of 304L Stainless Steel. The grain boundaries appeared to be free of precipitates. As in the case of the 304L Stainless Steel, sulfide inclusions were seen as elongated particles.

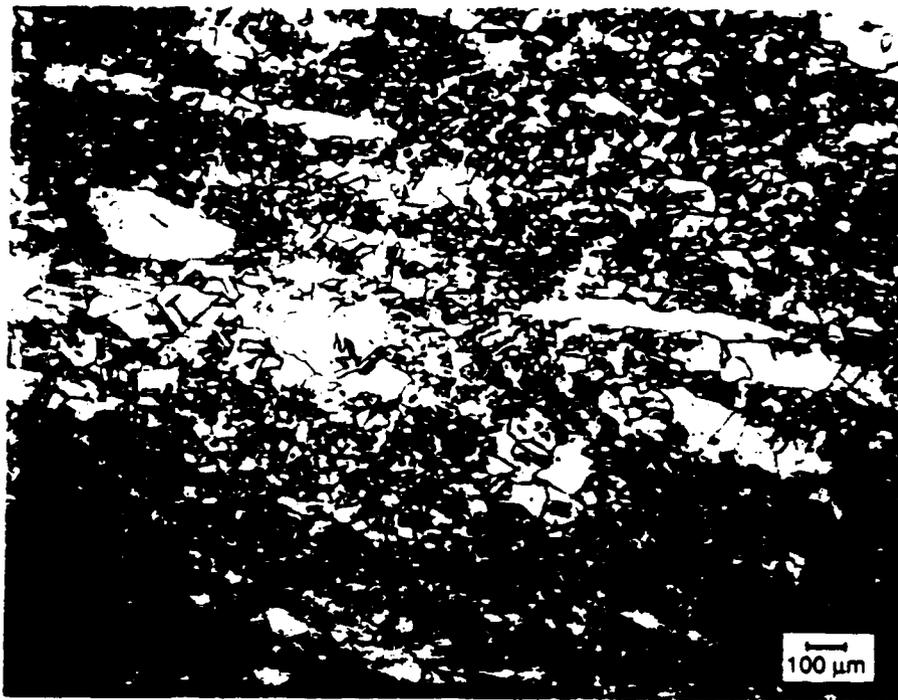


Figure 9a. Microstructure of Incoloy Alloy 825, 0.5 in. Plate. Transverse Cross-section. 50X Magnification.

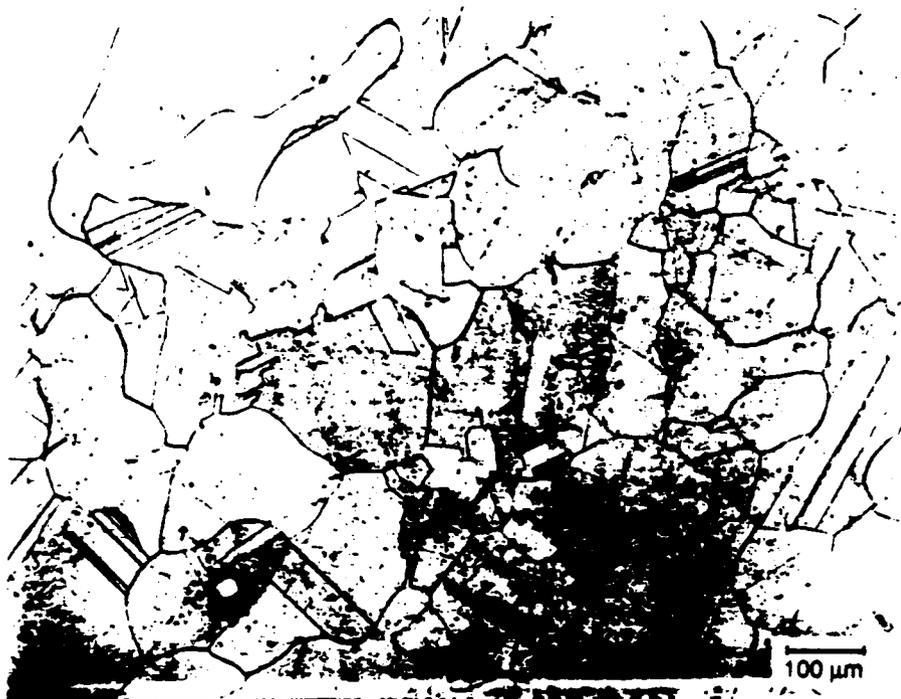


Figure 9b. Microstructure of Incoloy Alloy 825, 0.5 in. Plate. Transverse Cross-section. 500X Magnification.



Figure 10a. Microstructure of 304L Stainless Steel.  
Transverse Cross-Section. 100X Magnification.



Figure 10b. Microstructure of 304L Stainless Steel.  
Transverse Cross-section. 200X Magnification.

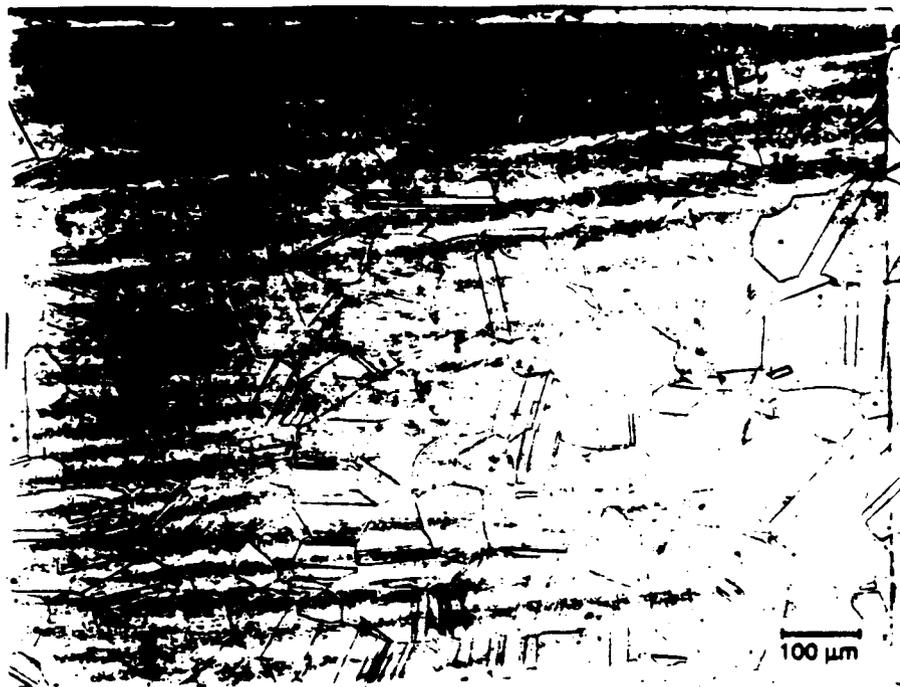


Figure 11. Microstructure of Hastelloy Alloy C-22.  
100X Magnification.



Figure 12. Microstructure of OFH copper (CDA-102). Longitudinal  
Cross-section. 50X Magnification.

3.3.5 *Hastelloy Alloy C-22*: The microstructure is shown in Figure 11. As in the other austenitic materials, the grain boundaries appear to be free of precipitates. There are a few dark particles in the form of bands and these are believed to originate from the solidification stage.

3.3.6 *CDA-102 (OFH Copper)*: The microstructure is shown in Figure 12. The relatively equi-axed grains are typical of this material. The inclusion content is relatively low.

3.3.7 *CDA 613 (Cu-Al Alloy)*: The microstructure is shown in Figures 13a and 13b. It is uncertain at this time whether this is a typical microstructure for this alloy and whether some of the features of the microstructure shown are metallographic artifacts. The tentative conclusion from the micrographs is that the material is in the as-hot worked condition and that the precipitates (dark particles) are probably Cu-Fe intermetallics. This was confirmed by performing SEM-EDX analysis of an etched cross-section. Spot analysis indicated that the black particles were rich in iron and copper and low in aluminum.

A survey of metallographic information for all the alloys under study is also being conducted to identify typical microstructures and possible deviations related to thermo-mechanical treatments.

### 3.3.8 SEM-EDX Analysis

SEM-EDX analysis was performed specifically to identify compositional differences between the bulk and surface of materials. This is especially of importance to the chromium containing alloys that are in the annealed condition. Hence SEM-EDX analysis was conducted only on these materials. Analyses were performed on the mill-surface (as-descaled surface) and the mid-section of the plates. The results are shown in Table 9. It can be seen that there is a significant depletion of chromium at the surface of both Hastelloy Alloy C-22 and Incoloy Alloy 825. The mid-section analysis, which should reflect the expected composition of the material, matches the certified chemical composition of the alloy (Table 1), thus verifying the accuracy of the SEM-EDX analysis for chromium. It must be noted that the SEM analysis for heavy elements such as tungsten can differ from other spectroscopic analyses. Table 9 also shows that there is no significant chromium depletion for the two stainless steels.

In laboratory tests, the surface layer is machined off and hence chromium depletion is generally not of concern. The surface composition is of importance in the actual field performance of the container material where the surface is not machined. The origin of the depletion is speculative at this time. It is hypothesized that chromium depletion occurs during the annealing stage when the surface chromium is converted to an oxide which then is removed by descaling operation (also called pickling operation) in the mill.

### 3.4 *Task 2.5 Hydrogen absorption and embrittlement*

A potential failure mode of metallic containers that has received scant attention is hydrogen induced cracking or hydrogen embrittlement. It was felt that hydrogen can be generated and absorbed into the metal by: 1. Galvanic coupling of the more noble container material with the less noble bore-hole liner (conceived to be made of carbon steel) and 2. Radiolytically generated hydrogen atoms. Once absorbed, embrittlement can occur by a suitable



Figure 13a. Microstructure of CDA-613 (Aluminum Bronze).  
Transverse Cross-section. 500X Magnification.



Figure 13b. Microstructure of CDA-613. Longitidine  
Cross-section. 500X Magnification.

TABLE 9  
Surface and Bulk Analyses of Chromium Containing Alloys by SEM-EDX

Alloy	Element Analyzed	Weight Percent	
		Mill Surface	Bulk
304L	Fe	68.7	69.2
	Ni	8.9	8.9
	Cr	18.99	18.59
	Si	1.2	1.5
	Al	0.4	0.2
	Mn	1.6	1.4
	Cu	0.3	0.3
316L	Fe	68.5	68.5
	Ni	9.4	9.4
	Cr	16.9	16.9
	Si	0.9	0.9
	Al	0.3	0.3
	Mn	2.0	2.0
	Cu	0.3	0.3
	Mo	1.7	1.7
IN-825	Fe	43.5	29.0
	Ni	35.3	42.0
	Cr	15.8	22.7
	Si	0.9	0.5
	Al	0.5	0.2
	Ti	0.4	0.9
	Cu	1.6	1.5
	Mo	2.1	3.2
HA - C-22	Fe	4.0	4.2
	Ni	62.1	57.7
	Cr	13.6	21.4
	Al	1.5	0.7
	Mo	13.0	11.3
	W	4.6	4.2

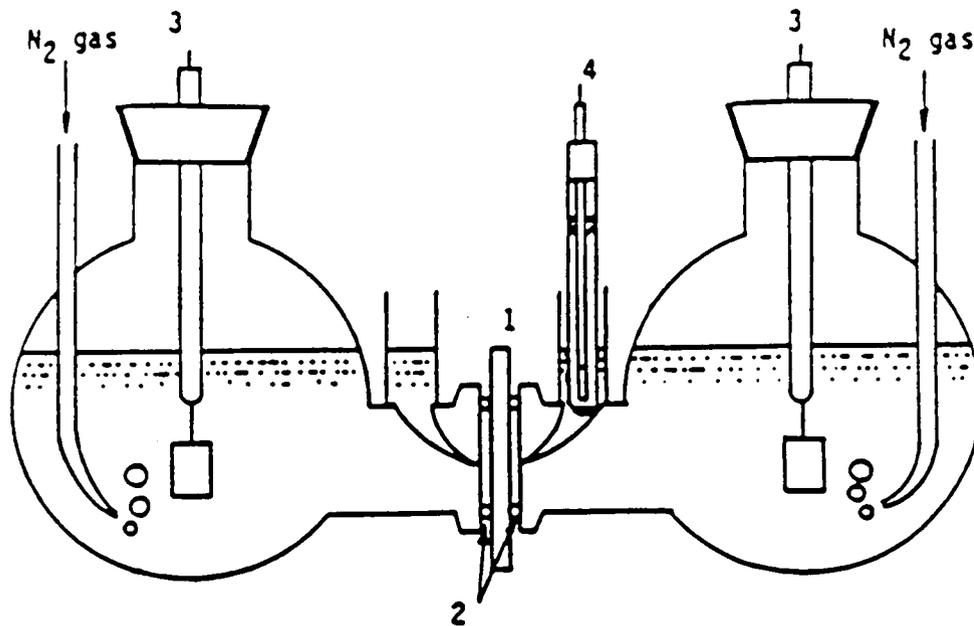
combination of hydrogen concentration, container phase transformation (via thermal exposure over long time periods), temperature, and stresses. While this mode of failure is not considered to be of major importance, it was thought that a test methodology to measure hydrogen absorption under the repository conditions needs to be established. A further need is to establish if embrittlement is indeed possible once hydrogen is absorbed. The task of developing test techniques to measure hydrogen absorption under repository thermal and radiation conditions was sub-contracted to Prof. Bryan Wilde's group at the Fontana Corrosion Center of The Ohio State University. The results generated thus far have been issued as an intermediate report to the Center. A summary of the accomplishments thus far are given in this section.

The method adopted to measure absorption and permeation of hydrogen is the electrochemical permeation technique. The technique was developed originally by Devanathan and Stachurski (DEVANATHAN - 1962) and has been used quite widely to measure hydrogen transport in metals. One of the goals of this program was to develop the technique to measure hydrogen transport at elevated temperatures up to 95 C and at temperatures above with higher than ambient pressures. Another goal was to measure hydrogen transport in copper based alloys where such measurements have not been made extensively. A third goal was to carry out these measurements under conditions of applied mechanical strain. The details of the technique will not be given here. It consists essentially of generating hydrogen electrolytically (charging) on one side (cathodic side) of the sample which is in the form of a membrane and detecting the hydrogen diffusing through by electrolytic oxidation on the other side (anodic side) of the membrane. A schematic of the apparatus used at the Fontana Center is shown in Figure 14. A certain time after the hydrogen charging is started, an increase in oxidation current is detected in the anodic side and the transient is recorded till a steady state current corresponding to a steady state permeation rate is reached. A number of parameters can be obtained from this transient, chief of which can be diffusivity, solubility and discharge mechanisms. Details of how this can be obtained can be referred to in other papers (ATRENS - 1980). Diffusivity of hydrogen at 95 C has been calculated from the Fontana Center's data to be:

- Hastelloy alloy C-22:  $D = 4.5 \times 10^{-10} \text{ cm}^2/\text{sec}$
- Incoloy alloy 825 :  $D = 8.6 \times 10^{-11} \text{ cm}^2/\text{sec}$
- 316L stainless :  $D = 1.3 \times 10^{-10} \text{ cm}^2/\text{sec}$

The diffusivity for alloy C-22 agrees quite well with the diffusivity measured by Mezzanotte et al. (MEZZANOTTE - 1980) at 90 deg. C on Hastelloy alloy C-276 an alloy which is close in composition to alloy C-22. The diffusivity measured for 316L stainless steel agrees well with that measured by Ohnaka and Furutani (OHNAKA - 1990) on 304L stainless steel at 95 C.

Permeation measurements in Cu alloys are difficult because of the low solubility and diffusivity of hydrogen in these alloys. These measurements are in progress. A further question is the potential embrittlement due to hydrogen absorption. The relatively high repository temperature may lessen the tendency to embrittle. Further, it has been shown that embrittlement in the Ni-base alloys is a critical function of phase transformation such as long-range ordering (SRIDHAR - 1981). Hence, preliminary investigation of embrittlement



- |                           |                                |
|---------------------------|--------------------------------|
| 1. Membrane specimen      | 2. Rubber O-ring               |
| 3. Pt auxiliary electrode | 4. Calomel reference electrode |

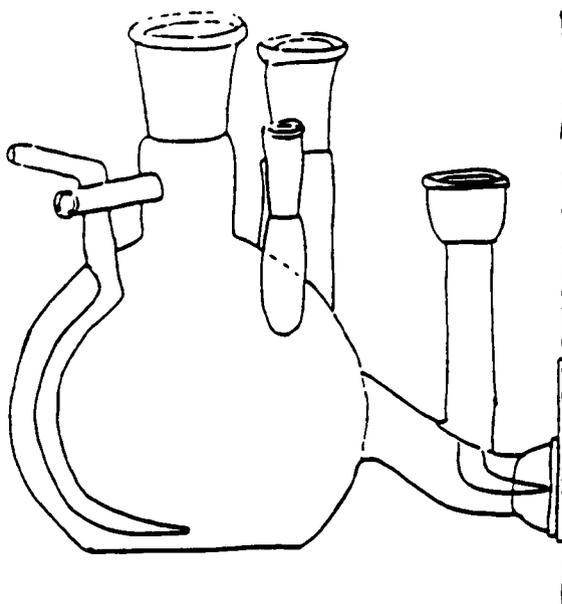


Figure 14. Schematic Diagram of the Glass Cells Used for the High Temperature Hydrogen Permeation Measurements.

are being carried out to study the extent of this effect at repository temperatures.

If the embrittlement studies and literature survey warrant further measurement of hydrogen absorption under radiolysis conditions, it is the intent of the IWPE to carry out these studies at the Southwest Research Institute hot-cell facilities.

#### 4. SECTION C SUMMARY AND RECOMMENDATIONS

##### 4.1 *Summary of investigations to-date*

The foregoing sections described the results of experimental program to-date and a critical review of relevant experimental programs performed by other laboratories. The main thrust of the scoping experimental investigation in all these programs has been localized corrosion studies, which has consisted mostly of studies of pitting corrosion by controlled potential (potentiostatic and potentiodynamic) techniques.

The experimental studies by controlled potential techniques in simulated J-13 water have indicated that the method of preparation of simulated J-13 water has a great bearing on the observed behavior, at least in the case of the austenitic stainless steels. Thus if pH were adjusted by HCl, the AISI 304L stainless steel samples tested in these solutions exhibited pitting, possibly due to an increase in chloride concentration (from about 6 ppm to 20 ppm). Other experimental variables such as the starting potential, scan rate, and presence of crevices also seem to play a role, albeit a lesser role. Finally, there is the inherent stochastic nature of the pitting process itself causing variability in the measured parameters. It must be emphasized that this inherent variability and sensitivity to small changes in test parameters is especially acute when the material is marginally resistant to pitting. If a specific alloy is highly resistant to a solution (Eg. Incoloy alloy 825 in simulated J-13 water), then the measured "breakdown" potential is unrelated to pitting. The measured potential is that of oxygen evolution reaction which is quite reproducible. By the same token, if an environment is very aggressive to a specific alloy, then pitting initiates relatively rapidly and the measured "true breakdown" potential becomes quite reproducible. Hence, reproducibility at either of these extreme points can be quite misleading. It is imperative that the variability of the pitting parameters be measured by replicate testing in several environmental compositions.

An especially interesting and rather puzzling observation in the results generated by the Center is the pitting found in Hastelloy alloy C-22 and AISI 316L stainless steel in low-chloride, simulated J-13 water. The latter is puzzling because, AISI 316L stainless steel with 2.5% molybdenum is expected to be more resistant to pitting than AISI 304L stainless steel with no molybdenum. Data presented in Tables 2 and 3, however, indicate that 316L showed pitting more consistently than 304L stainless steel. The behavior of Hastelloy alloy C-22 is puzzling because it has been shown to be one of the most pitting resistant alloys. These observations may be just experimental artifacts. Alternatively, there can be some unanticipated phenomena associated with the relatively low chloride levels in these solutions. Prior research on these alloys has been carried out at relatively high chloride concentrations (1000 ppm and beyond). This needs to be resolved by further experimentation.

The microstructures of the alloys have been examined in a rather cursory manner. The microstructures of the austenitic stainless steels (AISI 304L and 316L) and the Ni-base alloys appear to be of acceptable quality i.e. free of precipitates in the grain-boundaries. Incoloy alloy 825 showed considerable variability in grain size. This may have an impact on stress corrosion cracking results, especially when comparing results with those of other laboratories. The microstructure of CDA-613 (Cu-Al alloy) exhibited a large number of black

particles which, upon SEM analysis, were indicated to be iron rich intermetallic precipitates. It is not known at this time whether this microstructure is typical of this material. More significantly, surface chromium depletion was detected in both the Ni-base alloys, alloy 825 and C-22. The effects of this chromium depletion will not be felt in laboratory tests where the surface layers are machined off, but in field service performance. Hence, laboratory tests of localized phenomena must include some testing of surface effects.

Experimental techniques to measure the amounts and rates of hydrogen absorption at 95 C have been developed. The initial analysis of the experimental results indicates that the hydrogen diffusivity measured in the different Ni-Fe-Cr-Mo alloys agree with literature values. These experimental techniques have to be extended to include the copper based alloys. More importantly, studies have to be carried out to characterize the embrittlement susceptibility of these materials once they absorb hydrogen. These tests will be performed during the course of this year.

A review of the results from other investigations, notably those of Cortest Columbus has raised the most important question of what environmental species in the geologic setting are of significance from the point of view of material degradation. The investigations of Cortest, while forming an important first step, need to be carried forward much further. Specifically, the functionality of the dependence of pitting on chloride content needs to be established. Secondly, the interactions between environmental parameters need to be established.

Most of the investigations at CNWRA thus far have focused on the chromium containing alloys. Future experiments will include the copper-based alloys, as indicated in the new IWPE program plan mentioned in the next section.

4.2 *Recommendations for further investigations in IWPE*

The questions and concerns raised by the investigations up to April 1990 and the comments from the peer reviewers have necessitated a fresh and more systematic look at the research program. Furthermore, it was felt that the IWPE plan written in 1988 required greater specificity in terms of tasks and approaches.

A review of research conducted thus far has indicated that the following important degradation phenomena have not been considered in any detail:

1. Crevice corrosion: In many practical systems, corrosion under crevices between surfaces in contact occurs before pitting. In the Cortest Columbus program, crevice corrosion was not considered as a degradation mode for testing. In the DOE/LLNL program crevice corrosion was considered to be a fall-out of potentiodynamic pitting tests. However, some crevice tests were conducted with PTFE surface bolted against the test material surface (McCRIGHT - 1987) and some crevice attack was noted on both 304L and 316L stainless steel in 10,000 hour tests in natural J-13 water at 90°C. The questions that remain are: 1. Is 10,000 hours of testing adequate to conclude that off this degradation mode as unimportant? and 2. Is a crevice created between PTFE and metal equivalent to that created between tuff rock and metal? The creep of PTFE at 90°C will be expected to be

considerably greater than that of tuff. It is the recommendation of the CNWRA staff that more systematic studies of crevice corrosion be performed, in terms of maintaining specific crevice geometries and specific combinations of mating surfaces (for example a metal surface mating against polished tuff surface)

- 2. Corrosion under heat-transfer conditions: The corrosion of a container will take place under conditions of heat transfer from the inside. Heat transfer conditions can result in greater corrosion than isothermal conditions because of wall temperature effects and because of the convective action created by heat transfer processes. The DOE/LLNL program has not reported any results of corrosion or stress corrosion cracking performed under heat transfer conditions. Cortest Columbus performed some corrosion tests under heat transfer conditions, but only in terms of deciphering thermo-galvanic effects. It is recommended that corrosion under conditions of heat flux from one side of the sample be conducted.
  
- 3. Corrosion under wet/dry conditions: It has been shown that the heat flux from the containers in an unsaturated zone will result in dry conditions for at least the first 300 years (DOE - 1988). These calculations are sensitive to the assumed age of the waste and hence cooler conditions may be expected as the date of disposal is postponed. Secondly, inhomogeneities in the temperature can be expected to occur in the waste field. Finally, episodic events of water intrusion should be considered. In such cases, a repeated sequence of drying and rewetting is a possibility. Another example of a drying-rewetting scene may be the top of a vertical container where condensed droplets from the ceiling of the bore-hole may be envisioned to drop on to a hot container. While the purpose of the CNWRA IWPE is not to develop extensive data along these lines, the need is clear to verify the severity of corrosion under heat transfer conditions.
  
- 4. Microbiologically induced corrosion (MIC): MIC has been shown to be important in accelerating corrosion in many natural water systems such as well, river, and sea waters (DEXTER - 1985). While at first thought, it seems improbable that microbial colonies would survive the thermal and radiation conditions in the repository, several scenarios have suggested that MIC can be a factor: 1. Recent findings of microbial activities in Three Mile Island Plant cooling water systems have indicated that microbial colonies can survive the radiation conditions and 2. Microbial colonies can be dormant during the high temperature conditions prevailing at the initial 300 years and then become active as the repository cools down. It is recommended, as a first step, that a full cognizance of existing literature in this area as well as results of research activities at other laboratories such as NIST be taken by the CNWRA staff.
  
- 5. Long-term stability of container and waste package materials: The thermal stability of AISI 304 and 304L stainless steels has been examined in terms of their low temperature sensitization quite extensively by LLNL and others (FOX - 1983). However, far less information is available regarding long-term, low-temperature stability of other candidate container materials. For example, if DOE

selects other candidate materials such as Hastelloy alloy C-22 or Hastelloy alloy C-276, low temperature stability towards long-range ordering reactions need to be examined. In these types of alloys, carbide precipitation is not as important as in the case of AISI 304 or 304L stainless steels. In the case of the copper based alloys, long term exposure to low temperatures may lead to segregations or second phase precipitation and result in dealloying or other forms of localized corrosion upon exposure to repository environment. Hence, it is recommended that studies of alloys other than the stainless steels be undertaken as part of the long-range strategy of the CNWRA experimental program.

- 6. Stress corrosion cracking(SCC): SCC is considered to be one of the most detrimental modes of failure for the majority of the candidate container alloys selected by DOE. Whereas the austenitic alloys seem to be resistant to transgranular stress corrosion cracking (TGSCC) in J-13 water, even in the presence of different additions (eg. CO<sub>2</sub>, H<sub>2</sub>O<sub>2</sub> and NaCl) when tested using slow strain rate tests, there is some concern about the capability of this technique to reveal this type of environmental cracking where long initiation time may be involved. The subject should be studied in depth taking into consideration environmental variations in terms of Cl<sup>-</sup>/SO<sub>4</sub><sup>2-</sup> concentration ratio, pH, temperature, potential, etc. This activity is being coordinated with Cortest Columbus. In the case of the Copper-based alloys the presence of Nitrogen-containing compounds in the repository environment is a matter of concern because it is known that such species are detrimental for pure Copper and brasses. Specific conditions which promote cracking will be studied, with the additional purpose of assessing experimental techniques for predicting long term behavior. A detailed discussion on the subject is presented in the IWPE plan.
- 7. Other degradation modes: Hydrogen absorption and embrittlement is already being considered in the current IWPE program. The possibility of hydrogen absorption under repository environmental conditions still needs to be established and awaits the development of suitable techniques in the present program.

While all the current research activities have been concentrated on degradation of the outside wall of the container material from the unsaturated environment of the Yucca Mountain site, the possibility of internal corrosion can not be ignored. The internal corrosion can occur, for example from moisture carried in by the stored spent fuel and from leakage in the spent fuel cladding which may contain moisture. This may create a pressurized atmosphere of aqueous solution containing several dissolved species. It is premature to carry out any experimental program addressing this aspect. However, it is recommended that a research activity be started to explore the possible internal environments that can exist. The NRC staff assistance in this area is considered to be especially valuable.

The future program should also consider other alternative designs that may proposed by DOE. For example, a steel clad with a corrosion resistant alloy has been proposed as an alternate design (CLARKE -

1990). The current budget and man power of the CNWRA will not permit a detailed examination of these alternate concepts proposed by DOE, but the future IWPE program should allow room to direct the program in these directions if warranted.

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APPENDIX A

CENTER FOR NUCLEAR WASTE  
REGULATORY ANALYSES

Proc. TOP-003-01

Revision 0

TECHNICAL OPERATING PROCEDURE

Page 1 of 4

Title PROCEDURE FOR PREPARING ELECTROCHEMICAL/CORROSION TEST SPECIMENS

EFFECTIVITY AND APPROVAL

Revision 0 of this procedure became effective on 1/26/89. This procedure consists of the pages and changes listed below.

<u>Page No.</u>	<u>Change</u>	<u>Date Effective</u>
1 through 4	-	26 January 1989

**UNCONTROLLED**

Supersedes Procedure No. None

Approvals

Written By Herh K. Manaktala <i>Herh K. Manaktala</i>	Date 1/20/89	Technical Review <i>[Signature]</i>	Date 1/26/89
Quality Assurance <i>[Signature]</i>	Date 1/26/89	Cognizant Director <i>Allen R. Whiting</i>	Date 1/26/89

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PROCEDURE FOR PREPARING ELECTROCHEMICAL/CORROSION TEST SPECIMENS

1. PURPOSE

The purpose of this procedure is to describe the requirements for preparing test specimens for evaluating the electrochemical behavior of metallic materials for HLW canisters.

2. SCOPE AND APPLICATION

This procedure describes the equipment to be utilized for specimen preparation, and specimen storage, record keeping and identification, and sample archive requirements.

2.1 APPLICABLE DOCUMENTS

The following documents form a part of this procedure, as applicable:

- (1) CNWRA Technical Operating Procedure Manual
- (2) CNWRA Quality Assurance Program Manual

3. RESPONSIBILITY

- (1) The cognizant engineer of the project shall be responsible for the implementation and control of this procedure.
- (2) The specimen fabricator shall be responsible for implementing the requirements of this procedure.

4. EQUIPMENT

- ( 1) Band Saw
- ( 2) Milling Machine
- ( 3) Lathe
- ( 4) Threading taps

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- ( 5) Shaper
- ( 6) Grinder
- ( 7) Measuring tools (calipers, micrometers, etc)
- ( 8) Surface roughness measuring equipment
- ( 9) Bench/tool-makers microscope
- (10) Other, as approved prior to specimen fabrication
- (11) NDT equipment, as necessary

5. PROCEDURE

- (1) The test specimens shall be prepared using standard machine shop techniques and practices.
- (2) The specimens shall be of shape and size, and shall meet the dimensional tolerance, surface finish, chamfer, and other requirements as stated in the work order and/or drawings/sketches accompanying the work order.
- (3) No procedures or tools(s) that can alter the surface/bulk microstructure or corrosion properties of the fabricated specimens shall be used, e.g. flame/gas cutting torch, laser beam, cutting/grinding without adequate cooling, chemical etchants/acids, etc.
- (4) The specimen fabricator shall return the test samples in plastic containers/bags with proper identification and specimen material traceability records. Specimens fabricated from different materials, or different heat/lot of the same material shall be properly identified and stored in separate containers/bags.

6. IDENTIFICATION AND STORAGE (AT CNWRA LAB)

- (1) The fabricated test samples shall be stored in sealable plastic containers/bags. Proper identification records of

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material (alloy), traceability of chemical composition and wrought material fabrication records, heat/lot number, date of specimen fabrication, and number of archive specimens to be retained are to be kept with the test specimens.

- (2) The containers/bags containing specimens shall be stored in a dessicator, prior to use, to reduce the interaction of atmospheric moisture with the specimens.

<b>CENTER FOR NUCLEAR WASTE REGULATORY ANALYSES</b>  <b>TECHNICAL OPERATING PROCEDURE</b>	Proc. <u>TOP-008</u> Revision <u>0</u> Page <u>1</u> of <u>8</u>
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Title      PROCEDURE FOR CONDUCTING AND VERIFYING CYCLIC POLARIZATION TESTS

**EFFECTIVITY AND APPROVAL**

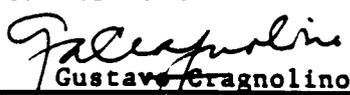
Revision 0 of this procedure became effective on 4-20-90. This procedure consists of the pages and changes listed below.

<u>Page No.</u>	<u>Change</u>	<u>Date Effective</u>
ALL	-	4-20-90

**UNCONTROLLED**

Supersedes Procedure No.

**Approvals**

Written By  Narasi Sridhar	Date 4/20/90	Technical Review  Gustavo Cragnolino	Date 4/20/90
Quality Assurance  Robert D. Brient	Date 4/20/90	Cognizant Director  Allen R. Whiting	Date 4/20/90

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TECHNICAL OPERATING PROCEDURE

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TOP-008

PROCEDURE FOR CONDUCTING AND VERIFYING CYCLIC POLARIZATION TESTS

1. PURPOSE

The purpose of the document is to describe procedures for conducting cyclic polarization tests to evaluate the susceptibility of metallic alloys to localized corrosion (pitting and crevice corrosion) in aqueous environments. This procedure establishes controls required by CQAM Section 3, "Scientific Investigations and Analysis Control."

2. SCOPE

This document describes two types of tests:

- 1. Verification test: This is performed as prescribed in ASTM G-61 on a 304L stainless steel sample in a solution of 3.56% Sodium Chloride. The resulting current-voltage curve is compared to the band of curves given in the ASTM standard. The purpose of this test is to ensure that the electrochemical system, including potentiostat, data acquisition system, and the cell are functioning properly. Hence, this is more than an electronic calibration of the individual instruments such as potentiostat.
- 2. Data Collection tests: This pertains to all other tests performed to collect data on the electrochemical polarization behavior of a given material in a given electrolyte at any temperature.

3. Applicable Documents

- (1) ASTM Designation G5 - "Standard Practice for Standard Reference Method for Making Potentiostatic and Potentiodynamic Anodic Polarization Measurements"
- (2) ASTM Designation G15 - "Standard Definitions of Terms Relating to Corrosion and Corrosion Testing"
- (3) ASTM Designation G3 - "Standard Practice for Conventions Applicable to Electrochemical Measurements in Corrosion Test"

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**TECHNICAL OPERATING PROCEDURE**

- (4) ASTM Designation G61 - "Standard Practice for Conducting Cyclic Polarization Measurements for Localized Corrosion"
- (5) CNWRA Technical Operating Procedure 003-01 - (latest revision) for preparing electrochemical/corrosion test specimens.

4. RESPONSIBILITY

- 4.1 The cognizant Element Manager shall be responsible for the development and maintenance of this procedure.
- 4.2 The cognizant Principal Investigator shall be responsible for the implementation of this procedure.
- 4.3 Personnel performing tests described in this procedure are responsible for complying with its requirements.

5. APPARATUS

5.1 Test Cell

A polarization test cell such as described in ASTM G5 or ASTM G61 is required. Other polarization cell designs may be equally suitable, provided the cell has a capacity of approximately 1 liter and has suitable ports to permit the introduction of working electrode (test sample), counter electrode, a salt bridge (Luggin probe with PARC-Vycor tip, or equivalent), gas inlet and gas outlet through a water trap, and a thermometer (or other temperature sensing device such as a thermister or thermocouple). The tip of the salt bridge shall be movable so that it can be brought in close proximity to the working electrode. A suitable heating device, such as a mantle heater or a constant temperature bath, is also required.

5.2 Working Electrodes

**Verification Test:**

For verification tests, a sample of AISI 304L supplied by ASTM shall be used. These are flat samples made from a single heat of the material.

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**Data Collection Tests:**

For conducting cyclic polarization tests on samples other than the ASTM sample, samples shall be machined according to the practice described in CNWRA TOP-003-01. If a sample of sufficient thickness is not available, a flat sample prepared as described in ASTM G-61 may be used. The type of sample used shall be noted in reporting the results. Samples may be polished to any finish desired. Usually, they are polished to a 600-grit finish with silicon carbide paper.

**5.3 Working Electrode Electrical connection**

To make electrical connection to the sample, cylindrical specimens shall be mounted on a suitable holder as described in ASTM G5. Flat samples shall be mounted in a suitable holder as described in ASTM G61. In cases where mounting in such holders is not suitable due to concerns with crevice corrosion in the mounted interface, alternate electrical connections may be made provided galvanic contact with the electrical connector is avoided. Such methods may involve spot welding a wire of the same material to the tip of the sample and ensuring that the spot welded area is not immersed in the solution.

**5.4 Counter Electrode**

Counter electrodes normally will be made of platinum, the surface of which may be platinized to increase the surface area. The detailed procedure for platinizing the platinum electrode is given in ASTM G-5, and is essentially an electrolytic deposition of platinum from a platinic chloride solution. High-density graphite rods may also be used as counter electrodes. The total surface area of the counter electrode that is immersed in the test solution shall be at least twice that of the immersed surface area of the working electrode.

**5.5 Reference Electrode**

A Saturated Calomel Reference Electrode (SCE) shall be used in the verification test as described in ASTM G5. Reference electrodes shall have a controlled leakage rate on the order of 3 to 8 micro liter/hr.

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Normal precautions shall be taken to maintain the reference electrodes in good condition. They shall be stored with the tips immersed in a saturated KCl solution when they are not in use. Potentials of the reference electrodes shall be checked against an unused electrode before and after each test to ensure that they remain accurate. For such measurements, a high impedance voltmeter/electrometer is essential. An example of such an electrometer is Keithley Model 602 electrometer (a detailed procedure for measuring the potential difference using this instrument is given at the back of the instrument box). Reference electrode potentials shall not differ from each other by more than 5 millivolts.

In potentiodynamic tests conducted in systems other than that described in ASTM G61 test, the reference electrode may be chosen to match the test needs. For example, Silver/Silver Chloride electrode may be chosen for tests involving temperatures higher than about 70 deg. C.

**5.6 Reagents**

The 3.56% (by wt.) NaCl solution used in the ASTM G61 test is prepared by dissolving 34.0 grams of reagent grade NaCl in 920 ml of high purity water (17-18 Mohms resistivity). An inert gas such as Argon, or Hydrogen shall be used to deaerate the solution for 1 hour (minimum) prior to test.

Saturated KCl for reference electrode storage is made by dissolving potassium chloride salt in high purity water.

Reagent grade acetone shall be used to degrease the specimen.

20% nitric acid is made from reagent grade, 70% nitric acid diluted with high purity water.

**5.7 Instrumentation**

Potentiostats meeting the general requirements outlined in ASTM G5/G61 shall be used. Voltage scans shall be performed by using a programmable voltage scan generator or by means of a digital computer and appropriate software. Separate instruments or instruments integral to the potentiostat may be used to measure and monitor the test parameters. These instruments shall be calibrated periodically.

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6. EXPERIMENTAL PROCEDURE

6.1 Verification Test:

The verification test shall be conducted in accordance with the detailed procedure given in ASTM G61. The current-vs-potential data shall be acquired and plotted directly on an X-Y recorder or stored on a computer disk for later retrieval and display or printed as a hardcopy.

The verification test shall be conducted periodically on all potentiostats at the beginning and end of a set of potentiodynamic experiments. The frequency of the verification test will be dictated by the number of potentiodynamic experiments that are in progress.

6.2 Data Collection Tests:

The general procedure for conducting a cyclic polarization test consists of increasing the potential in steps or by continuous scanning of the potential and recording the resulting current flow. After a pre-determined maximum in potential or current density is reached, the scan direction is reversed and the scan/stepping performed down to a pre-determined end point. The data is plotted as a graph of logarithm of current density (total current divided by the working electrode area) vs. applied potential.

In all the tests conducted, the pertinent experimental information shall be recorded in Scientific Notebooks. A hardcopy of the plot of current-vs-potential shall be placed in a file that is identified appropriately. If the test was performed under computer control, a printout of the data points shall also be included in the file. All computer files shall be backed-up with a copy and kept in the same file. The test results at the end of a sequence of experiments to be determined by the cognizant Principal Investigator shall be recorded in the Scientific Notebooks and signed by the person conducting the test and countersigned by the cognizant Principal Investigator.

The procedure for conducting these tests follows, in general, the procedure given in ASTM G-61. However, the details of

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variations from this procedure shall be recorded as discussed in the following sections.

6.2.1 Initial Conditions

The starting conditions may depend on the specific purpose of the test. In some cases, the samples may be pre-passivated by immersing them in a 20% (by wt.) HNO<sub>3</sub> solution for 24 hours at room temperature. The sample then is rinsed in high purity water, acetone and then dried before introducing the sample into the test solution. In some cases, pre-passivation is necessary to obviate crevice corrosion at the mounted surface. In this case, the rest of the surfaces may be mechanically polished, cleaned and then put in test solution. The normal starting potential in this test shall be the open-circuit potential. The starting conditions, such as gas purging time before introducing the sample, open-circuit potential, time at open-circuit potential, the starting potential (if different from open-circuit potential), time at starting potential, and any cathodic conditioning given, shall be recorded. The specimen surface preparation shall also be recorded. It is also recommended that the open-circuit potential of the counter electrode be recorded at the start and end of test.

6.2.2 Scanning

The scan rate in a continuous scan test or potential steps and time increments in a stepwise test shall be recorded. Generally, the cyclic polarization tests are scanned in the direction of increasing potential (anodic scan) first followed by a reverse scan. The scan directions shall be recorded on the plot.

6.2.3 Information To Be Recorded

The conventions applicable to electrochemical measurements and the terms used shall follow those given in ASTM G-3.

In addition to the data that can be gathered from the generated curve, the following information shall be recorded for each test:

1. Time ( $t_i$ ) at corrosion (open-circuit) potential

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2. Corrosion potential at the start of the test (before  $t_i$ )
3. Potential of the counter electrode at the start of the test (before  $t_i$ )
4. Conditioning potential (If applicable)
5. Conditioning time (If applicable)
6. Prepassivation treatment (If applicable)
7. Specimen condition (rolled, annealed etc)
8. Temperature at the start of the test
9. pH of the solution at the start of the test
10. Purge gas used (If applicable)
11. Scan rate
12. Temperature at the end of the test
13. pH at the end of the test
14. Visual observation of the sample including the crevice at the mounting surface.

Visual observation of the sample shall be made at the end of the test. The observation shall include presence/absence of pitting, crevice corrosion in the specimen mount area, and any discoloration of the sample. This observation may be made by using a variety of techniques such as stereoscopic examination and microscopic examination. The results of the visual observation shall be recorded along with other pertinent data.

7. RECORDS

The files containing the test data and the Scientific Notebooks shall be controlled as records in-process in accordance with CQAM Section 17. These shall be maintained in project files until completion of the project activities at which time they will be compiled in to a project data package, and processed as QA records as specified by CQAM Section 17.

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Title  
 PROCEDURE FOR CONDUCTING AND VERIFYING POTENTIODYNAMIC POLARIZATION TESTS

EFFECTIVITY AND APPROVAL

Revision 0 of this procedure became effective on 4-20-90. This procedure consists of the pages and changes listed below.

<u>Page No.</u>	<u>Change</u>	<u>Date Effective</u>
ALL	-	4-20-90

**UNCONTROLLED**

~~UNCONTROLLED~~

Supersedes Procedure No. None

Approvals

Written By <i>Narasi Sridhar</i> Narasi Sridhar	Date <u>4/20/90</u>	Technical Review <i>Gustavo Cragnolino</i> Gustavo Cragnolino	Date <u>4/20/90</u>
Quality Assurance ✓ <i>Robert D. Brient</i> Robert D. Brient	Date <u>4/20/90</u>	Cognizant Director <i>Allen R. Whiting</i> Allen R. Whiting	Date <u>4/20/90</u>

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PROCEDURES FOR CONDUCTING AND VERIFYING POTENTIODYNAMIC POLARIZATION TESTS

1. PURPOSE

The purpose of the document is to provide procedures for conducting a potentiodynamic polarization scan and for verifying the accuracy and reproducibility of potentiodynamic measurements. This procedure establishes controls required by CQAM Section 3, "Scientific Investigations and Analysis Control."

2. SCOPE

This document describes two types of tests:

1. Verification test: This is performed as prescribed in ASTM G-5 on 430 stainless steel in a solution of 1.0N sulfuric acid. The resulting current-voltage curve is compared to the band of curves given in the ASTM standard. The purpose of this test is to ensure that the electrochemical system, including potentiostat, data acquisition system, and the cell are functioning properly. Hence, this is more than an electronic calibration of the individual instruments such as potentiostat.

2. Data Collection tests: This pertains to all other tests performed to collect data on the electrochemical polarization behavior of a given material in a given electrolyte at any temperature.

3. Applicable Documents

- (1) ASTM Designation G5 - "Standard Practice for Standard Reference Method for Making Potentiostatic and Potentiodynamic Anodic Polarization Measurements"
- (2) ASTM Designation G15 - "Standard Definitions of Terms Relating to Corrosion and Corrosion Testing"
- (3) ASTM Designation G3 - "Standard Practice for Conventions Applicable to Electrochemical Measurements in Corrosion Test"

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- (4) ASTM Designation G61 - "Standard Practice for Conducting Cyclic Polarization Measurements for Localized Corrosion"
- (5) CNWRA Technical Operating Procedure 003-01 - (latest revision), for preparing electrochemical/corrosion test specimens.

**4. RESPONSIBILITY**

- 4.1 The cognizant Element Manager shall be responsible for the development and maintenance of this procedure.
- 4.2 The cognizant Principal Investigator shall be responsible for the implementation of this procedure.
- 4.3 Personnel performing tests described in this procedure are responsible for complying with its requirements.

**5. APPARATUS**

**5.1 Test Cell**

A polarization test cell such as described in ASTM G5 is required. Other polarization cell designs may be equally suitable provided the cell has a capacity of approximately 1 liter and has suitable ports to permit the introduction of working electrode (test sample), counter electrode, a salt bridge (Luggin probe with PARC-Vycor tip, or equivalent), gas inlet and gas outlet through a water trap, and a thermometer (or other temperature sensing device such as a thermister or thermocouple). The tip of the salt bridge shall be movable so that it can be brought in close proximity to the working electrode. A suitable heating device such as a mantle heater or a constant temperature bath is also required.

**5.2 Working Electrodes**

**Verification Test:**

Standard AISI Type 430 stainless steel samples obtained from ASTM Headquarters shall be used for the verification test. These are cylindrical specimens made from a single heat of metal.

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**Data Collection Tests:**

For conducting potentiodynamic tests on samples other than the ASTM sample, samples shall be machined according to the practice described in CNWRA TOP-003-01. If a sample of sufficient thickness is not available, a flat sample as described in ASTM G-61 may be used. The type of sample used shall be noted in reporting the results. Samples may be polished to any finish desired. Usually, they are polished to a 600-grit finish with silicon carbide paper.

**5.3 Working Electrode Electrical connection**

To make electrical connection to the sample, cylindrical specimens shall be mounted on a suitable holder as described in ASTM G5. Flat samples shall be mounted in a suitable holder as described in ASTM G61. In cases where mounting in such holders is not suitable due to concerns with crevice corrosion in the mounted interface, alternate electrical connections may be made provided galvanic contact with the electrical connector is avoided. Such methods may involve spot welding a wire of the same material to the tip of the sample and ensuring that the spot welded area is not immersed in the solution.

**5.4 Counter Electrode**

Counter electrodes normally will be made of platinum, the surface of which may be platinized to increase the surface area. The detailed procedure for platinizing the platinum electrode is given in ASTM G-5, and is essentially an electrolytic deposition of platinum from a platinic chloride solution. High-density graphite rods may also be used as counter electrodes. The total surface area of the counter electrode that is immersed in the test solution shall be at least twice that of the immersed surface area of the working electrode.

**5.5 Reference Electrode**

A Saturated Calomel Reference Electrode (SCE) shall be used in the verification test as described in ASTM G5. Reference electrodes should have a controlled leakage rate on the order of 3 to 8 micro liter/hr.

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Normal precautions shall be taken to maintain the reference electrodes in good condition. They shall be stored with the tips immersed in a saturated KCl solution when they are not in use. Potentials of the reference electrodes shall be checked against an unused electrode before and after each test to ensure that they remain accurate. For such measurements, a high impedance voltmeter/electrometer is essential. An example of such an electrometer is Keithley Model 602 electrometer (a detailed procedure for measuring the potential difference using this instrument is given at the back of the instrument box). Reference electrode potentials shall not differ from each other by more than 5 millivolts.

In potentiodynamic tests conducted in systems other than that described ASTM G5 test, the reference electrode may be chosen to match the test needs. For example, Silver/Silver Chloride electrode may be chosen for tests involving temperatures higher than about 70 deg. C.

5.6 Reagents

The 1.0N sulfuric acid used as the test solution in the ASTM G5 test shall be prepared with 27.2 mL of reagent grade (98%) sulfuric acid diluted with high purity (17-18 Mohms) water to 1 liter total solution volume. High-purity hydrogen is recommended as the purge gas although high-purity argon is also acceptable.

Saturated KCl for reference electrode storage is made by dissolving potassium chloride salt in nanopure water.

Reagent grade acetone shall be used to degrease the specimen.

20% nitric acid is made from reagent grade, 70% nitric acid by dilution with high purity water.

5.7 Instrumentation

Potentiostats meeting the general requirements outlined in ASTM G5 shall be used. Voltage scans shall be performed by using a programmable voltage scan generator or by means of a digital computer and appropriate software. Separate instruments or instruments integral to the potentiostat may

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be used to measure and monitor the test parameters. The instruments shall be periodically calibrated.

6. EXPERIMENTAL PROCEDURE

6.1 Verification Test:

The verification test shall be conducted in accordance with the detailed procedure given in ASTM G5. The current-vs-potential data shall be acquired and plotted directly on an X-Y recorder, or stored on a computer disk for later retrieval and display or printed as a hardcopy.

The verification test shall be conducted periodically on all potentiostats at the beginning and end of a set of potentiodynamic experiments. The frequency of the verification test will be dictated by the number of potentiodynamic experiments that are in progress.

6.2 Data Collection Tests:

The general procedure for conducting a potentiodynamic polarization test consists of increasing the potential in steps or by continuous scanning of the potential and recording the resulting current flow. The data is plotted as a graph of logarithm of current density (total current divided by the working electrode area) vs. applied potential.

In all the tests conducted, the pertinent experimental information shall be recorded in Scientific Notebooks. A hard copy of the plot of current-vs-potential shall be placed in a file that is identified appropriately. If the test was performed under computer control, a printout of the data points shall also be included in the file. All computer files shall be backed-up with a copy and kept in the same file. The test results at the end of a sequence of experiments to be determined by the Principal Investigator shall be recorded in the Scientific Notebooks and signed by the person conducting the test and countersigned by the cognizant Principal Investigator.

The procedure for conducting these tests follows, in general, the procedure given in ASTM G-5. However, the details of the

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variations from the ASTM procedure shall be recorded as discussed in the following sections.

6.2.1 Initial Conditions

The starting conditions may depend on the specific purpose of the test. In some cases, the samples may be pre-passivated by immersing them in a 20% (by wt.)  $\text{HNO}_3$  solution for 24 hours at room temperature. The sample then is rinsed in high purity water, acetone and then dried before introducing the sample into the test solution. In some cases, pre-passivation is necessary to obviate crevice corrosion at the mounted surface. In this case, the rest of the surfaces may be mechanically polished, cleaned and then put in test solution. The starting conditions such as gas purging time before introducing the sample, open-circuit potential, time at open-circuit potential, the starting potential (if different from open-circuit potential), time at starting potential, and any cathodic conditioning given shall be recorded. The specimen surface preparation shall also be recorded. It is also recommended that the open-circuit potential of the counter electrode be recorded at the start and end of test.

6.2.2 Scanning

The scan rate in a continuous scan test or potential steps and time increments in a stepwise test shall be recorded. Generally, the potentiodynamic curves are scanned in one direction of increasing potential (anodic scan). However, the scan direction must be recorded if performed otherwise.

6.2.3 Information To Be Recorded

The conventions applicable to electrochemical measurements and the terms used shall follow those given in ASTM G-3.

In addition to the data that can be gathered from the generated curve, the following information shall be recorded for each test:

1. Time ( $t_i$ ) at corrosion (open-circuit) potential
2. Corrosion potential at the start of the test (before  $t_i$ )
3. Potential of the counter electrode at the start of the test (before  $t_i$ )

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- 4. Conditioning potential (If applicable)
- 5. Conditioning time (If applicable)
  
- 6. Prepassivation treatment (If applicable)
- 7. Specimen condition (rolled, annealed etc)
- 8. Temperature at the start of the test
- 9. pH of the solution at the start of the test
- 10. Purge gas used (If applicable)
- 11. Scan rate
- 12. Temperature at the end of the test
- 13. pH at the end of the test
- 14. Visual observation of the sample including the crevice at the mounting surface.

7. RECORDS

The files containing the test data and the Scientific Notebooks are controlled as records in-process in accordance with CQAM Section 17. These shall be maintained in project files until completion of the project activities at which time they will be compiled in to a project data package, and processed as QA records as specified by CQAM Section 17.

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Title **TECHNICAL OPERATING PROCEDURE FOR PREPARING SIMULATED J-13 WATER AND ITS MODIFICATIONS**

**EFFECTIVITY AND APPROVAL**

Revision 0 of this procedure became effective on 5-8-90. This procedure consists of the pages and changes listed below.

<u>Page No.</u>	<u>Change</u>	<u>Date Effective</u>
ALL	-	5-8-90

UNCONTROLLED

Supersedes Procedure No. **NONE**

**Approvals**

Written By <i>Narasimhaiah</i>	Date 5/8/90	Technical Review <i>J. C. ...</i>	Date 5/8/90
Quality Assurance <i>Robert D. ...</i>	Date 5/8/90	Cognizant Director <i>Allen R. ...</i>	Date 5/8/90

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**TOP-010  
TECHNICAL OPERATING PROCEDURE FOR PREPARING SIMULATED J-13 WATER  
AND ITS MODIFICATIONS**

1. PURPOSE

The purpose of the document is to describe procedures for preparing aqueous solutions to be used in various corrosion and electrochemical tests on candidate HLW container materials. This procedure establishes controls required by CQAM Section 3, "Scientific Investigations and Analysis Control."

2. SCOPE

This document provides procedures for the preparation of aqueous solutions to be used in conducting corrosion and electrochemical tests on candidate HLW container materials. Specifically, the procedures address the preparation of:

1. An aqueous solution that approximates the reported composition of a water sample obtained from test well J-13 near Yucca Mountain, Nevada. The reported composition of the J-13 well water is shown in Table 1. The solution prepared according to this procedure will be referred to as Simulated J-13 water.
2. Aqueous solutions whose compositions have been modified from the Simulated J-13 water with respect to one or more ionic species. The intents of these modifications may be to identify the quantitative effects of environmental variables on corrosion and conduct corrosion studies under a variety of postulated extreme conditions of the repository environment. The compositions of these modifications may contain fewer ionic species than both the actual J-13 and simulated J-13 waters in order to better identify functional dependencies of corrosion. The solutions prepared under this procedure will be referred to as either Modified Simulated J-13 water or, if the changes are extensive, as Model Solutions.

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3. APPLICABLE DOCUMENTS

The following documents are relevant to the procedures described in this document:

1. ASTM E 288 -(Latest Revision), "Standard Specification for Volumetric Flasks"
2. Federal Specification NNN-P-395 (Latest Revision), "Specification for Volumetric Pipets"

4. RESPONSIBILITY

- 4.1 The cognizant Element Manager shall be responsible for the development and maintenance of this procedure.
- 4.2 The cognizant Principal Investigator shall be responsible for the implementation of this procedure.
- 4.3 Personnel performing tests described in this procedure are responsible for complying with its requirements.

5. EQUIPMENT AND CHEMICALS

5.1. Equipment

1. ASTM E288 Class A volumetric flasks calibrated to contain 1000 ml
2. NNN-P-395 Class A volumetric pipets calibrated to deliver 25 ml, 1ml, or other small quantities
3. Analytical balance accurate to at least  $\pm 0.1$  mg and calibrated periodically.
4. pH meter accurate to at least  $\pm 0.01$  pH unit and appropriate glass electrodes, calibrated before use.
5. Selective Ion analyzer accurate to  $\pm 1\%$  and electrodes, calibrated before use.

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5.2 Chemicals

Solutions shall be prepared using high purity water (about 17-18 Mohms.cm resistivity). The chemicals used for preparing the solutions shall meet the purity specified in American Chemical Society Standards (ACS Grade) where possible. In some chemicals ACS Grade may not be available and a certified grade such as Fisher Certified Grade may be used. The lot number of each chemical used in the preparation of a given batch of solution shall be recorded in the Scientific Notebook. The following chemicals are needed for the preparation of Simulated J-13 water:

- [1] 0.1 N NaOH
- [2] CaSO<sub>4</sub>.2H<sub>2</sub>O
- [3] Ca(NO<sub>3</sub>)<sub>2</sub>. 4H<sub>2</sub>O
- [4] KF. 2H<sub>2</sub>O
- [5] MgCl<sub>2</sub>. 6H<sub>2</sub>O
- [6] NaHCO<sub>3</sub>
- [7] KCl

6. IDENTIFICATION AND DESCRIPTION OF SOLUTIONS

The solutions prepared in accordance with the procedure described in this section shall be identified on the label as shown below:

Sample Label:

```

*****
*
* Preparation Date:                               Expiration:          *
*
* Identification: SN-CNwRA "notebook #-"page #"  *
*
* Description: J-13 Stock Solution A              *
*
*
*****

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The identification of the solution shall be entered in the appropriate Scientific Notebook. The actual concentrations of the components added to the solution shall be entered in the Scientific Notebook. The units for the components in the solutions shall be milligrams/liter of solution for solids and milliliters/liter of solution for liquids. For the liquid components, the concentration (either as weight percent, molarity or normality) or density of the liquid added shall also be entered.

7. PROCEDURE FOR PREPARATION OF SIMULATED J-13 WATER

7.1 Preparation of Stock Solution A

1. Add the following to 900 ml of high purity water at room temperature in a beaker and stir until dissolved:

1.377 g  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$

Then add the following components to the solution and stir until dissolved fully:

0.944 g  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$

0.119 g KCl

0.569 g  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$

Care should be taken to weigh and add  $\text{MgCl}_2$  quickly since it is hygroscopic and can cause inaccuracies in weight measurement.

2. Pour the solution in a 1000 ml volumetric flask and adjust the volume to 1000 ml with high purity water by washing the beaker with the needed water and pouring the wash water into the flask.
3. Stopper flask and label it as described in section 6. Record preparation steps in the Scientific Notebook as described in section 6.

7.2 Preparation of Stock solution B

1. Add the following chemicals to 900 ml of high purity

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water at room temperature in a beaker and stir until dissolved:

6.720 g NaHCO<sub>3</sub>  
0.376 g KF · 2H<sub>2</sub>O

Care should be taken to weigh and add the KF · 2H<sub>2</sub>O quickly since it is hygroscopic and can cause inaccuracies in weight measurements.

2. Pour solution into a 1000 ml volumetric flask and adjust the total volume to 1000 ml with high purity water by washing the beaker with the needed water and pouring the wash water into the flask.
3. Stopper the flask and label it as described in section 6. Record preparation steps in the Scientific Notebook as described in section 6.

**7.3 Preparation of Test Solution**

1. Place 925 ml of high purity water in a volumetric flask and pipet 25.0 ml of Stock Solution A and 25.0 ml of Stock Solution B into the flask.
2. Add high purity water to make up the volume to 1000 ml. Stopper the flask and label it as described in section 6. Record preparation steps in the Scientific Notebook as described in section 6.
3. Measure pH and record it in the Scientific Notebook along with the solution batch number and preparation date as described in section 6.
4. Measure the chloride concentration of the test solution with a selective ion electrode (suitably calibrated) and record the value in the Scientific Notebook.

**7.4. Storage Of Solutions**

The stock solutions shall be used within 15 days of preparation. The test solution shall be used within 5 days of preparation.

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8. PREPARATION OF MODIFIED SOLUTIONS BASED ON SIMULATED J-13 WATER

Modifications to the simulated J-13 water may be made to study the effect of environmental variables on corrosion. The types of modifications that may be made are described below. In all these cases, the solutions shall be identified and documented as described in Section 6.

- 8.1. Increase in the Concentration of Chloride: This increase shall be accomplished by the addition of potassium chloride to Stock Solution A. The total amount of salt added shall be recorded in the Scientific Notebook along with the identification of the solution and preparation date.
- 8.2. Modification of pH: This shall be accomplished by the use of a suitable reagent (buffer, acid or alkali). Specific recommendations of a reagent solution may depend on the needs of the program and may be a compromise between the need to maintain the pH at the desired value and the need to limit other electrochemical changes to the environment. The reagent solution shall be added to the test solution (Step 6.4 above). If a reagent is used to alter the pH, the type and concentration of reagent used, the pH at the start, and the pH at the finish of the test shall be recorded.
- 8.3. Other Modifications to Simulated J-13 Solution: These may involve changes in one or more species such as addition of silicic acid or sodium metasilicate. Silicon is one of the major constituents of the natural J-13 well water (Table 1). Silicon has been introduced via silicic acid in some procedures. Since the silicic acid dissolves slowly, changes in silicon concentration with time may be significant [see footnote 1]. Hence, silicic acid has been omitted in this procedure. However, other silicon compounds such as sodium metasilicate may be added to study the effect of silicon. In these cases the silicon concentration shall be measured as a function of storage time to determine stability of the solution.

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Footnote 1: R. Pabalan, Memorandum, "Test of Technical Operating Procedure for Preparing Simulated and Modified J-13 Well Water," August 10, 1989.