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LIQUID METAL FAST BREEDER REACTOR PROGRAM

MASTER

STEAM GENERATOR MATERIALS ENGINEERING

STRESS CORROSION STUDIES FOR THE CLINCH RIVER BREEDER REACTOR STEAM GENERATOR

M. E. INDIG

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U.S. ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION
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GENERAL ELECTRIC

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STRESS CORROSION STUDIES FOR THE CLINCH RIVER BREEDER REACTOR STEAM GENERATOR

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GENERAL ELECTRIC

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ABSTRACT

The steam generator of the Clinch River Breeder Reactor (CRBRP) is to be constructed with 2-1/4Cr-1Mo steel. The alternate material of construction is Incoloy-800. One of the major concerns is the possibility that caustic contamination may occur on the aqueous and steam sides of the steam generator. Under specific environmental and mechanical conditions, caustic solutions are known to cause stress corrosion cracking ferritic austenitic alloys. For these reasons the susceptibility of 2-1/4Cr-1Mo and Incoloy-800 to caustic cracking in badly faulted high temperature aqueous and superheated steam environments was determined. Except for a few experiments at 450°F that were required to understand the mechanism of caustic cracking, all of the experiments were conducted in aqueous solutions at 316°C (600°F) and in superheated steam at 482°C (900°F). These temperatures are the approximate operating temperatures of the evaporator and superheater sections of the CRBRP.

It was found that 2-1/4Cr-1Mo was extremely resistant to caustic cracking in all metallurgical conditions tested and over a range of caustic concentrations (up to 10%) and oxidizing potentials. In the superheated steam tests, steam with NaOH (10 ppm) was used. While no stress corrosion cracking was detected at 316 and 482°C (600 and 900°F), the rate of general corrosion of 2-1/4Cr-1Mo steel was significant in the caustic environment. At 316°C (600°F) in 10% NaOH, major differences in corrosion rates among heats and metallurgical conditions were observed. At 482°C (900°F), all samples corroded excessively (0.05 to 0.1 mil/h). Development and examination of the anodic polarization curves at 316°C (600°F) (electrochemical studies) gave indications of the resistance of 2-1/4Cr-1Mo to caustic stress corrosion. At 232°C (450°F), however, the mechanistic studies showed that the alloy could be readily cracked.

Unlike 2-1/4Cr-1Mo, Incoloy-800 could be cracked at 316°C (600°F). In 5% NaOH solutions, cracking was intergranular. In 10% NaOH solutions, the cracking was transgranular. The susceptibility of the cracking was dependent on the metallurgical condition. The cold-worked and the Grade 1 conditions exhibited the highest resistance to caustic cracking followed by the Grade 2 condition. Limited studies have also indicated that slight changes in system oxidizing potentials can have a major effect on the stress corrosion resistance of Incoloy-800 at 316°C (600°F). At 482°C (900°F) in superheated steam, Incoloy-800 was found to be immune to caustic cracking. The general corrosion rate for this alloy in superheated steam, faulted with caustic, was at least an order of magnitude lower than 2-1/4Cr-1Mo steel.

ACKNOWLEDGMENTS

The author wishes to acknowledge the expertise of Messrs. J. E. Weber and A. N. Bornstein for performing the experiments described in this report.

1. INTRODUCTION

The steam generator of the Clinch River Breeder Reactor Plant (CRBRP) will be constructed of 2-1/4Cr-1Mo steel. The alternate material of construction is Incoloy-800. Figure 1 shows a schematic of the steam generator circuit. In operation, liquid sodium on the shell side of the evaporator and superheater units will heat water and steam within the tubes. The water-side temperature in the evaporator units will be about 316°C (600°F). The steam-side temperature in the superheater will be about 482°C (900°F).

Because of the history of steam generator failures[1,2] caused by aqueous stress corrosion, studies were initiated to determine environmental-materials interactions that might possibly occur during operation of the water and steam sides of the CRBR steam generator circuit. The major consideration in these studies was caustic stress corrosion. Caustic could accumulate within the steam generator tubes from contamination from the liquid sodium shell side or as a result of caustic in-leakage through the feedwater system. The feed-water system will contain condensate polishers, ion exchangers, which can, under operating conditions, leak a small amount of caustic into the steam generator circuit. Because of the natural operating characteristics of the steam generator circuit, small amounts of caustic in-leakage may concentrate during operation to several percent locally within the evaporator section. The evaporator concentrating mechanism has been discussed previously by Dutina, et al.[3] Caustic contamination within the superheater tubes can occur by direct contamination from the liquid sodium side or by dissolution of caustic in the steam phase and subsequent carryover.

Since the stress corrosion studies were concerned with steam generator operation, most of the experiments were conducted at 316°C and 482°C (600°F and 900°F). A few experiments were conducted at 232°C (450°F), strictly as an aid to understanding the mechanism of caustic cracking.

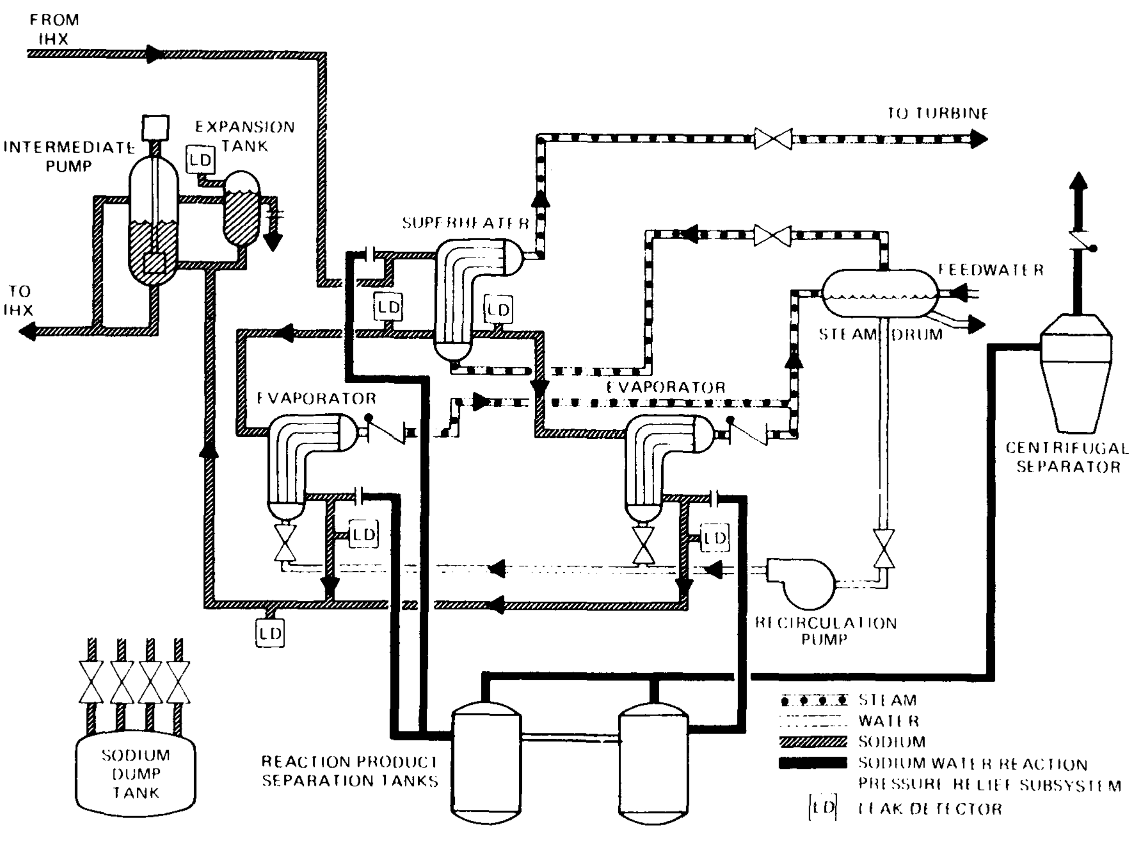


Figure 1. Schematic of the CRBR Steam Generator Circuit

Caustic cracking experiments with 33% NaOH solution at 118°C and one atmosphere were conducted by H. S. Isaacs at ORNL. These studies were concerned with the possible formation of caustic solutions on the sodium side as a result of cleaning operations during or following maintenance, and are a part of a joint GE/ORNL stress corrosion program.[4] Because the Isaacs studies have not been formally reported by ORNL, his major findings will be presented here.

Isaacs found the susceptibility of 2-1/4Cr-1Mo to intergranular stress corrosion cracking to be dependent on the metallurgical condition, the oxidizing potential and alloy carbon content. In constant strain rate testing at controlled anodic potentials, Isaacs found that the cold-worked state had the highest resistance to stress corrosion, followed by the quenched and tempered state, with the annealed alloy having the least resistance to caustic cracking. All of his samples were susceptible to stress corrosion, but it was a matter of severity. At cathodic protection potentials $\leqslant -1.3$V (S.C.E.),* no stress corrosion occurred. The potential range of highest susceptibility was –0.7 to –0.11V (S.C.E.).

Isaacs also performed constant load tests in the 33% caustic solution. He indicates that for each increase of 10 ksi in stress, the cracking time decreases by a factor of five.

Isaacs studied two different heats of 2-1/4Cr-1Mo: an experimental heat which contained 0.08% carbon and a commercial heat which contained 0.135% carbon. Although both heats cracked, the results indicated that the higher carbon containing alloy was far more resistant to caustic cracking than the lower carbon alloy. The alloys were studied under potential control in the quenched and tempered and annealed conditions.

Caustic cracking of a related alloy 3Cr-0.5Mo was studied by Dahl, et al.,[5] in 20% NaOH at 225°C (437°F). These workers stressed tensile samples to the yield strength at controlled electrochemical potentials. Cracking was found over a range of cathodic and anodic potentials from the rest potential. Polarizing samples anodically, 0.3V or greater from the rest potential, resulted in high rates of general dissolution rather than stress corrosion.

A few stress corrosion experiments were performed with 2-1/4Cr-1Mo u-bends in 50% NaOH solution at 316°C (600°F) by McIlree and Michels.[6] They found stress corrosion occurred if the samples were in an abnormal metallurgical condition, air quenched from 871°C (1600°F). If these samples were subsequently tempered at 649°C (1200°F), stress corrosion no longer occurred. However, in the 50% caustic solution high general rates of corrosion were observed.

Because the alternate alloy of the steam generator is Incoloy-800, it is worthwhile to review the available information concerning caustic cracking of Incoloy-800 and other austenitic alloys. An extensive review of stress corrosion and general corrosion of Fe-Ni-Cr alloys was presented by Subrahmanyam and Staehle[7] in 1969. They report that the susceptibility of austenitic alloys to caustic cracking decreases as the total nickel and chromium content is raised. Nickel appeared to be the most effective alloying element in increasing resistance to caustic cracking.

More recent studies of the caustic cracking of various austenitic alloys were conducted by Wilson and Aspden,[8] Cels,[9] McIlree and Michels,[6] Theus,[10] and Berge, et al.[11] With the exception of Berge, et al.,[11] all of these workers concur that over the temperature range of 289°C-316°C (550°F-600°F), Inconel-600 is more resistant to caustic cracking than Incoloy-800 in de-oxygenated caustic solutions. In tests at 350°C (662°F) Berge, et al.,[11] reports that Incoloy-800 was significantly more resistant to caustic cracking than Inconel-600. Perhaps this difference may be due to the higher test temperature and the fact that Berge tested only a single metallurgical condition of Incoloy-800, namely, the Grade 1 condition [annealed at 980°C (1796°F)].

Heat treatments at temperatures >538°C (1000°F) have also been a source of controversy. These heat treatments are used for stress relief of various components and simultaneously produce chromium carbide precipitation (sensitization) at the grain boundaries. Reference 8 reports that caustic cracking increased for Incoloy-800, but was unchanged for Inconel-600 as a result of the stress relief treatment. References 6, 9, and 10 report that stress relief treatments are effective in reducing the susceptibility of Inconel-600 and Incoloy-800 to stress corrosion cracking in deaerated caustic solutions at elevated temperatures. In our own[12] previously reported studies, we found that cold-work essentially eliminated caustic cracking of Incoloy-800, whereas Reference 8 found cold-work to produce an

*Standard calomel electrode.

accelerating effect. Since the present study was specifically aimed at determining the behavior of materials for the CRBRP, there was no detailed attempt to sort out these differences.

A complete description of the experimental procedures and results for the LMFBR caustic stress corrosion program were presented in August 1974.[12] The present report is the continuation of these studies to a logical conclusion. Where necessary, some of the information presented in Reference 12 will be repeated and in other cases the information will be cited.

The major findings previously presented[12] for 2-1/4Cr-1Mo and Incoloy-800 were:

1. At 316°C (600°F), 2-1/4Cr-1Mo steel was found to be completely resistant to caustic stress corrosion in 3% and 5% NaOH aqueous solutions for all tested metallurgical conditions.

2. At 482°C (900°F), with ≤10 ppm NaOH dissolved in superheated steam, 2-1/4Cr-1Mo steel was found to be immune to caustic cracking.

3. At 316°C (600°F), Incoloy-800 was found to be susceptible to intergranular stress corrosion in 3% and 5% NaOH solutions.

4. The susceptibility of Incoloy-800 to caustic cracking in aqueous solutions at 316°C (600°F) was found to be dependent on the metallurgical condition and the applied stress. Of those metallurgical conditions studied the most susceptible was the mill-annealed, followed in order by the sensitized, Grade 2 (solution-annealed) and cold-worked condition. The cold-worked condition exhibited immunity to caustic cracking.

The main emphasis in the present studies was on caustic cracking of 2-1/4Cr-1Mo welded materials in both high-temperature aqueous and superheated steam environments, determining stress corrosion behavior in 10% NaOH solutions, determining the effect of oxidizing potential on stress corrosion, and completing the planned superheat stress corrosion experiments.

2. EXPERIMENTAL PROCEDURES

2.1 MATERIALS AND SAMPLE CONFIGURATIONS

The composition of the 2-1/4Cr-1Mo and Incoloy-800 alloys used in the experimental studies are given in Table 1. The metallurgical treatments used for these alloys are given in Table 2.

The stress corrosion tests in high-temperature aqueous environments were conducted with dog-bone tensile samples shown in Figure 2. Pressurized tubes, Figure 3, were used as samples in the superheated steam tests. Three types of welded samples of 2-1/4Cr-1Mo steel were tested. Under the joint ORNL/GE stress corrosion program, ORNL manufactured two types of weldments.

For high-temperature aqueous testing, ORNL manufactured linear simulated tube-to-tubesheet weldments. The weldments were made from 1-inch plate and 0.5-inch o.d. tubing with a wall thickness of 0.188 inch. The tubing was split axially and flattened. Both the plate and the tubing were annealed and then welded with an automatic tungsten-arc welder. 2-1/4Cr-1Mo filler material was used in the welding rather than the autogeneous welding that will be used for the CRBR tube-to-tubesheet welds. It is believed that the use of weld filler material could not have significantly affected the properties of the weldment, because the chemical composition of the filler was similar to the plate and tube materials, and because there were no unusual microstructural features in the weld and heat-affected zones.

After welding, the weldments were machined into dog-bone tensile samples, Figure 4, and given a post-weld heat treatment of 732°C (1350°F) for one hour. In final form, as shown in Figure 4, the tensile samples had one end from the 1-inch plate (simulated tubesheet) and the other end from the split and flattened tubing (simulated tube portion). At the center of the gauge section was the weld which joined the two.

Table 1
ALLOY COMPOSITIONS

1. **2-1/4Cr-1Mo**

Product Form	Application	C	Mn	Fe	P	S	Si	Ni	Cr	Cu	Mo
Bar	600°F tests	0.12	0.47	+	0.017	0.025	0.39	0.12	2.25	0.14	0.97
Tubing	900°F tests	0.10	0.46	+	0.011	0.013	0.34	–	2.31	0.08	–
Plate	600°F simulated tubesheet	0.11	0.55	+	0.011	0.012	0.29	–	2.13	–	0.96
Filler Rod	600°F, weld for above	0.10	0.74	+	0.017	0.017	0.14	–	2.62		0.96
Split Tubing	600°F, simulated tube	0.11	0.48	+	0.015	0.015	0.21	–	2.22	--	0.96

2. **Incoloy-800**

Product Form	Application	C	Mn	Fe	S	Si	Ni	Cr	Cu	Ti
Bar	600°F tests	0.04	0.81	43.5	0.007	0.25	35.5	20.5	–	0.43
Tubing	900°F tests	0.03	0.86	44.6	0.007	0.25	31.2	22.0	0.34	–

Table 2
METALLURGICAL TREATMENTS

Alloy		Treatment
2-1/4Cr-1Mo	1.	Annealed – 1695°F for 20 minutes, furnace cool to 1350°F and hold for 45 minutes; air cool
	2.	Normalized and tempered – 1695°F for 30 minutes, air cool, temper at 1250°F for 1 hour, air cool
	3.	Cold-worked – annealed, cold-rolled 25%
	4.	Cold-worked – normalized and tempered, cold-rolled 25%
	5.	Welded tensile samples and weld tubes. After welding, given post-weld heat treatment, 1350°F for 1 hour
Incoloy-800	1.	Annealed (Grade 2) – 15 minutes at 2100°F, water quench
	2.	Cold-worked – annealed, cold-rolled 25%
	3.	Annealed (Grade 1) – 1700°F for 1 hour, water quench

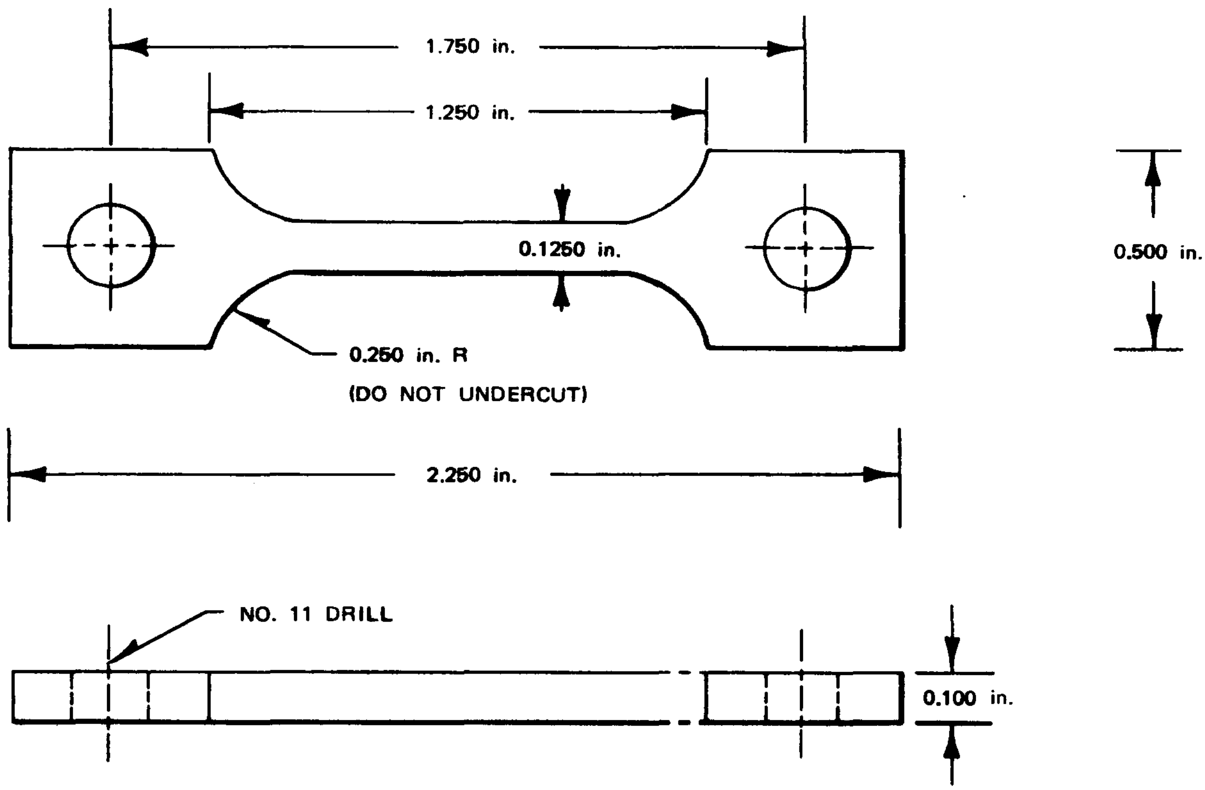


Figure 2. Corrosion Tensile Sample

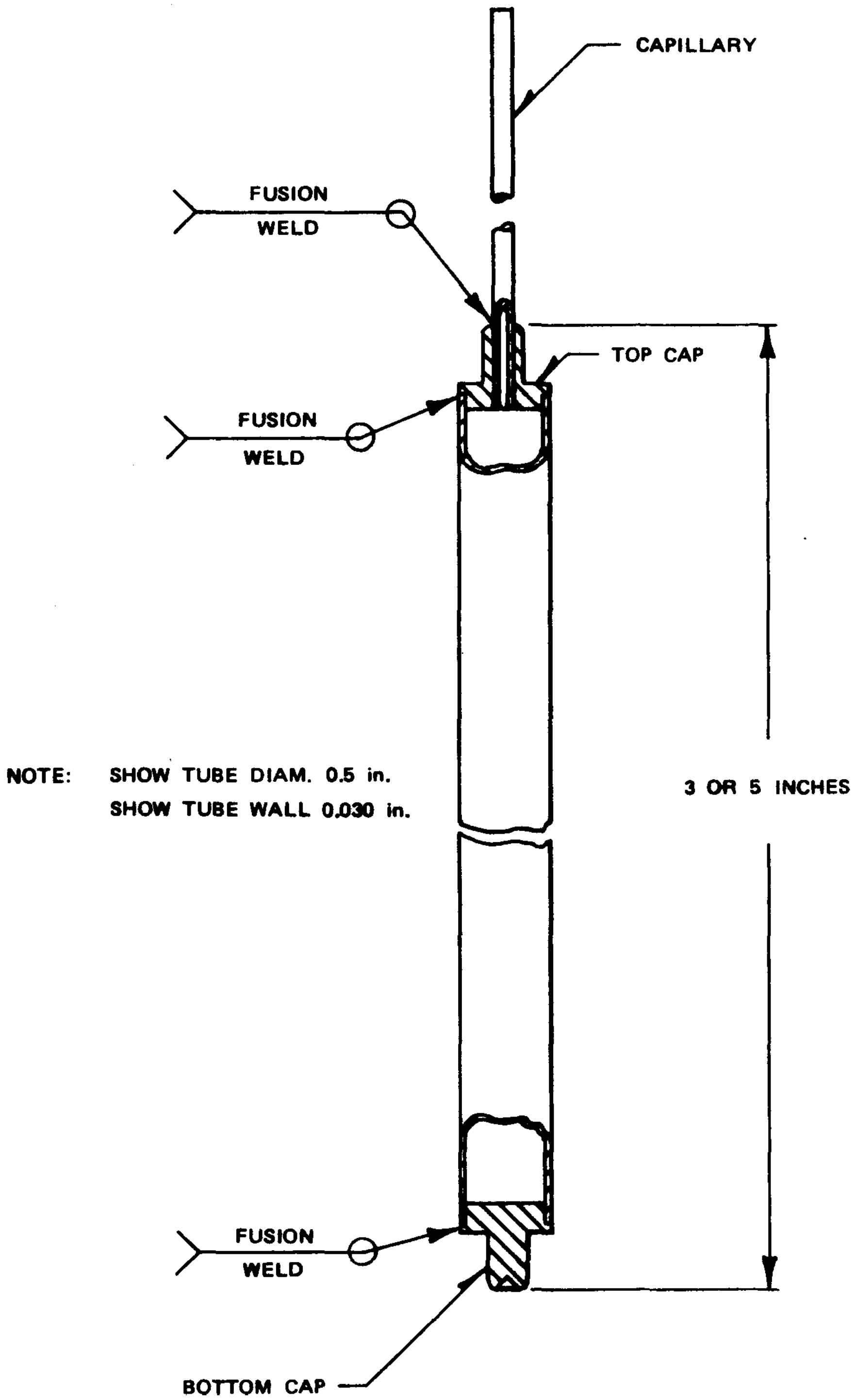


Figure 3. Pressurized Tube Sample

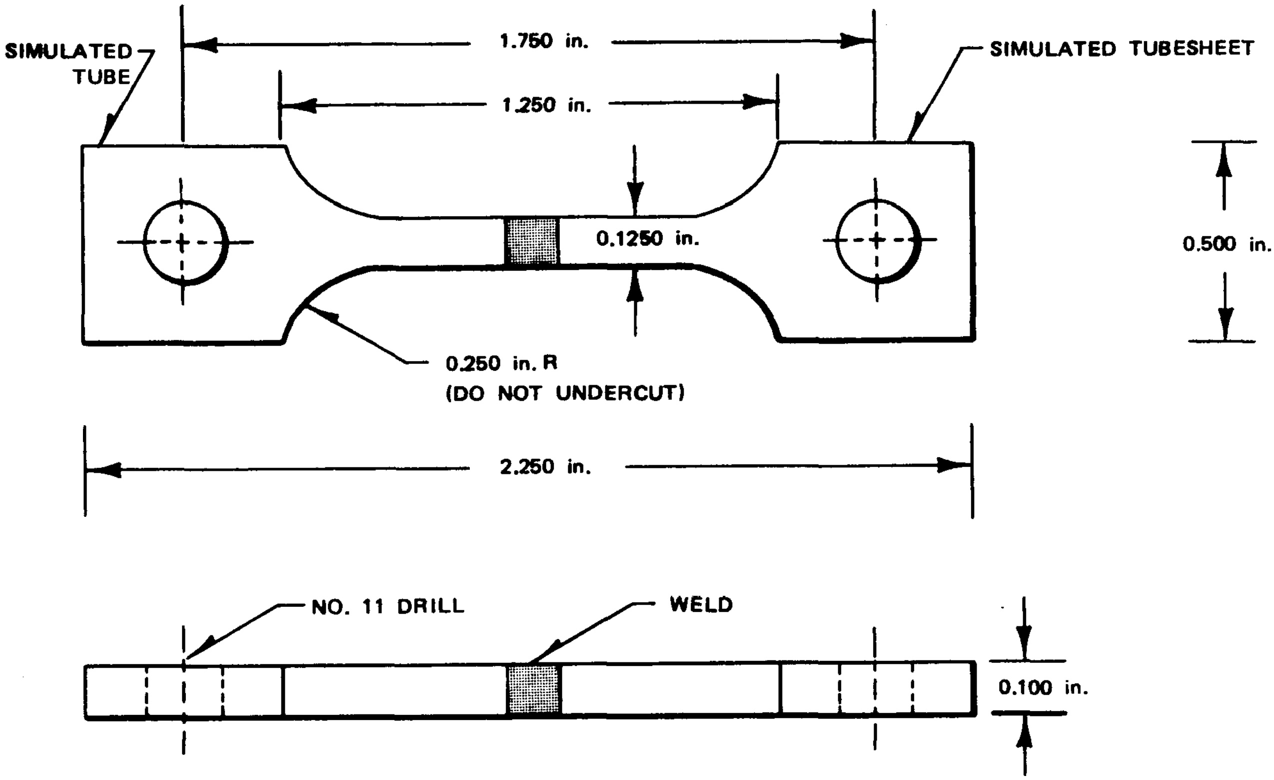


Figure 4. Tube-To-Tubesheet Weld Sample

For the superheat stress corrosion studies, two types of weld samples were used. The samples supplied by ORNL were prepared by welding two sections of tubing by means of an orbital weld to form a single length. The second type of sample was prepared at the General Electric Company and consisted of an all-weld metal tube. The weld metal tubes were produced by overlaying weld metal onto a pipe of 2-1/4Cr-1Mo steel. The process developed by Licina[13] utilized a multi-pass tungsten inert gas welding process with 2-1/4Cr-1Mo filler metal deposited on a 1/4-inch Schedule-80 pipe. After the overlaying, the inside pipe was removed by machining and the outside diameter was machined to produce the required wall thickness. The all-weld tube was then cut into the proper lengths and stress relieved at 732°C (1350°F) for one hour.

2.2 HIGH TEMPERATURE AQUEOUS TESTING

The stress corrosion tests at 316°C (600°F) were conducted by either constant load or constant extension rate techniques. Schematics of the constant load and constant extension rate facilities are shown in Figures 5 and 6. A full description of these facilities was previously given.[12]

In the earlier experiments conducted in 3% NaOH solutions, the constant load facility was part of a refreshed system which allowed for continuous change of electrolyte. However, the present constant load experiments in 10% NaOH were conducted in a static 2-gallon Inconel-600 autoclave. The change to a static system was necessary because leaks developed during hydrostatic operation of autoclave in 10% NaOH at 316°C (600°F). Because the electrolyte was not changed, sampling and chemical analyses were performed during shutdown. The analyses of the electrolyte showed that no significant change in caustic concentration had occurred. The experiments conducted in the constant extension rate facility were also performed in 10% NaOH. In this case, a nickel-lined stainless steel autoclave was used. In addition to those experiments performed by exposing samples at the natural corrosion potential of the system, a series of samples were also strained under electrochemical (potential) control. For these experiments, the constant extension rate facility was modified to a straining electrode facility.

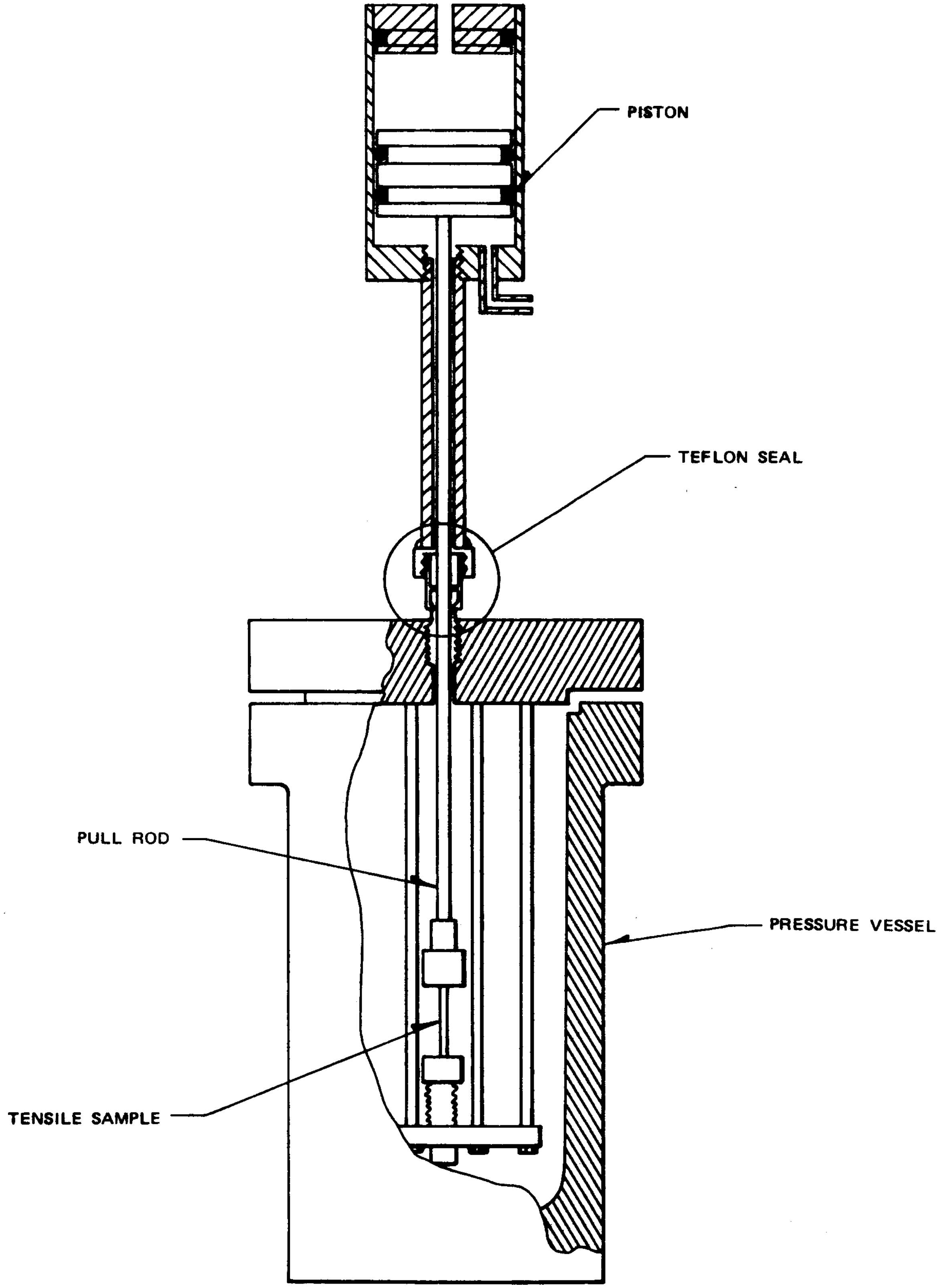


Figure 5. Stressing Arrangement for Constant Load Facility

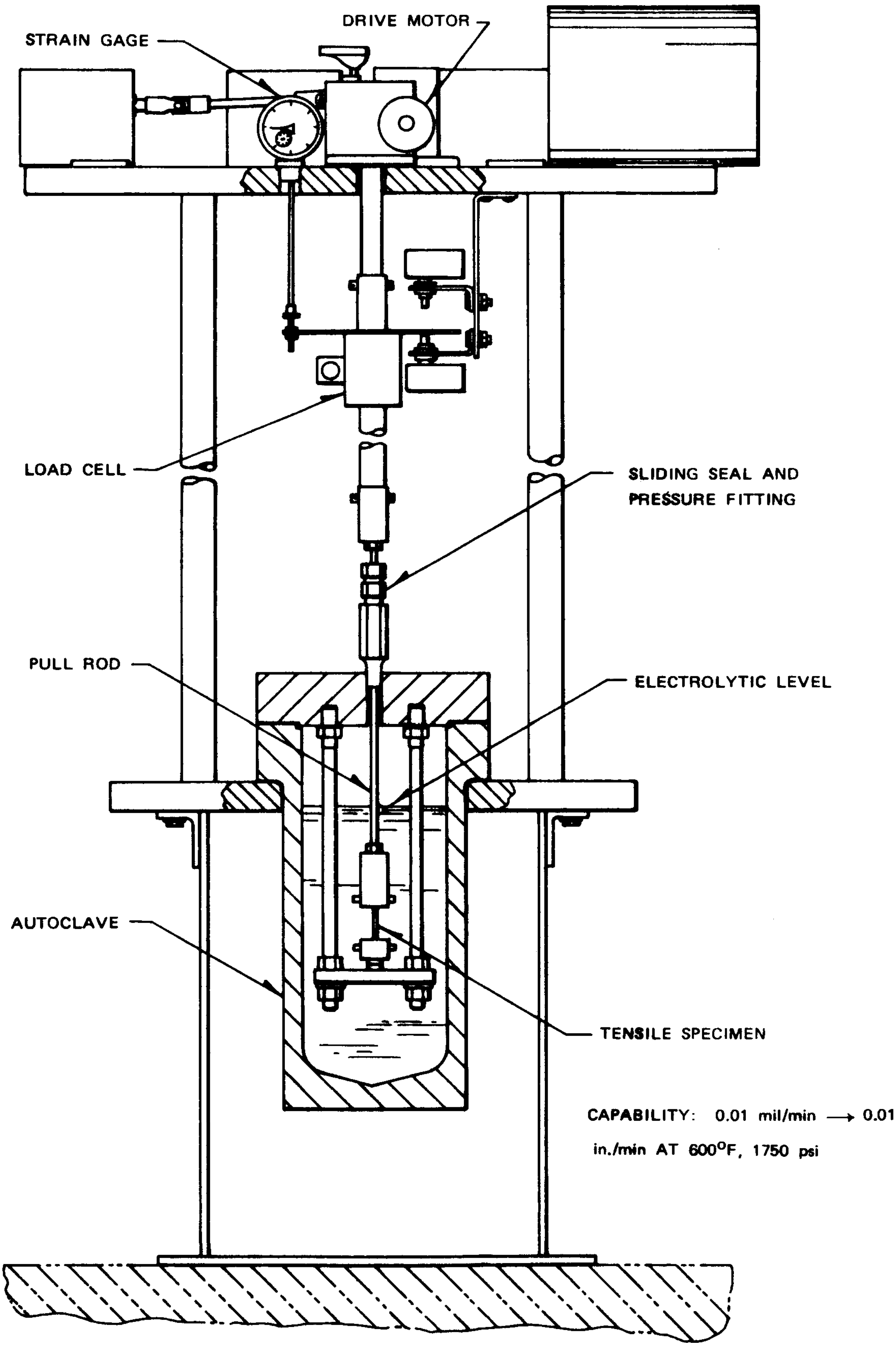


Figure 6. Constant Extension Rate Facility

2.3 HIGH TEMPERATURE ELECTROCHEMICAL STUDIES

In preparation for straining electrode experiments to be performed in the constant extension rate facility, high temperature anodic polarization experiments were conducted. Degassed 1, 5, and 10% NaOH solutions were used at 316°C (600°F) as the electrolyte. Cylindrical samples that had a diameter of 0.250 inch and a length of 0.750 inch were used as electrodes. The electrodes were center tapped at one end to accept a 6/32 threaded stainless steel rod which was used as the conductor. The conductor was coated with an 0.005-inch layer of Teflon which provided electrical insulation from the electrolyte and the sample. The conductor was passed out of the autoclave through an electrically insulated Conax fitting. A platinum electrode of the same dimensions and design as the working electrodes was used as the reference electrode. The autoclave was grounded and used as the counter electrode. The anodic polarization curves were determined potentiostatically using a Wenking model 68T53 potentiostat. In the active region, 10-millivolt potential steps were used. In the passive and transpassive region, 50- or 100-millivolt steps were used. The polarization curves were determined in the region from the rest potential to oxygen evolution.

2.3.1 Straining Electrode Experiments

After determining the shape of the anodic polarization curves, various potential regions could be identified where there was the possibility that stress corrosion might occur. Straining electrode experiments were then conducted in 5 and 10 percent caustic at these predetermined potentials. The experiments were conducted in the constant extension rate facility with a few system modifications. The "straining electrodes" were tensile samples as shown in Figure 2. However, it was necessary to electrically insulate the sample from the autoclave and the retaining fixtures so that the required anodic potentials could be applied. Pre-oxidized Zr-2.5Nb pins, which are electrically insulating, were used in place of the usual Inconel X-750 pins to couple the tensile sample to the upper and lower clevices in the autoclave. The tab sections of the tensile specimens were lined with strips of Teflon to further insulate the sample from the clevices. A stainless steel wire with a Teflon covering was connected to the specimen and the wire was passed out of the autoclave through an insulated Conax fitting. The potential of the tensile sample was controlled by connecting the specimen wire and the lead from the reference electrode to the potentiostat and using the autoclave as the counter electrode. The design of the reference electrode is shown in Figure 7. Experiments were conducted by heating the autoclave to 316°C (600°F), adjusting the sample strain rate to about 10^{-5}/min (extension rate of 0.001 in./h) and potentiostatically controlling the potential between the sample and reference electrodes. During the experiment the anodic current was monitored and the load-deformation curve was recorded.

2.3.2 Superheat Stress Corrosion Studies

Several experimental arrangements were used to test pressurized tubes of 2-1/4Cr-1Mo steel and Incoloy-800 in superheated steam at 482°C (900°F) 1750 psi.[12]

A schematic of the present system is shown in Figure 8. In operation, pure water was pumped from the feedtank to the boiler located just below the autoclave. The water flashed to steam at about 400°C (752°F) and passed into the autoclave. In the autoclave the steam was further heated to 482°C (900°F) and contacted a nickel tray loaded with NaOH. Some of the caustic dissolved within the steam and the mixture then contacted 15 pressurized tubes in the autoclave. The steam with dissolved NaOH then passed out of the autoclave, and was condensed, depressurized and dumped or sampled. The system pressure was maintained at 1750 psi by the method described previously for the refreshed aqueous system.[12] The sample tubes were stressed separately by pressurizing to the desired level with an external pump and manifold system. Each tube (Figure 3) was connected via the top capillary to a pressure gage. Each capillary was passed out of the autoclave through a multi-hole Conax sealing gland where it connected to the gage and pressurizing system. The equivalent stress (Von Mises) on each tube was calculated by:

$$\sigma = \frac{0.866\ \Delta P r}{t}$$

where

σ = effective tensile stress

ΔP = the difference between the internal tube pressure and external system pressure (1750 psi)

r = mean tube radius

t = thickness of tube wall

The tube failure was determined by a drop-off in the internal tube pressure.

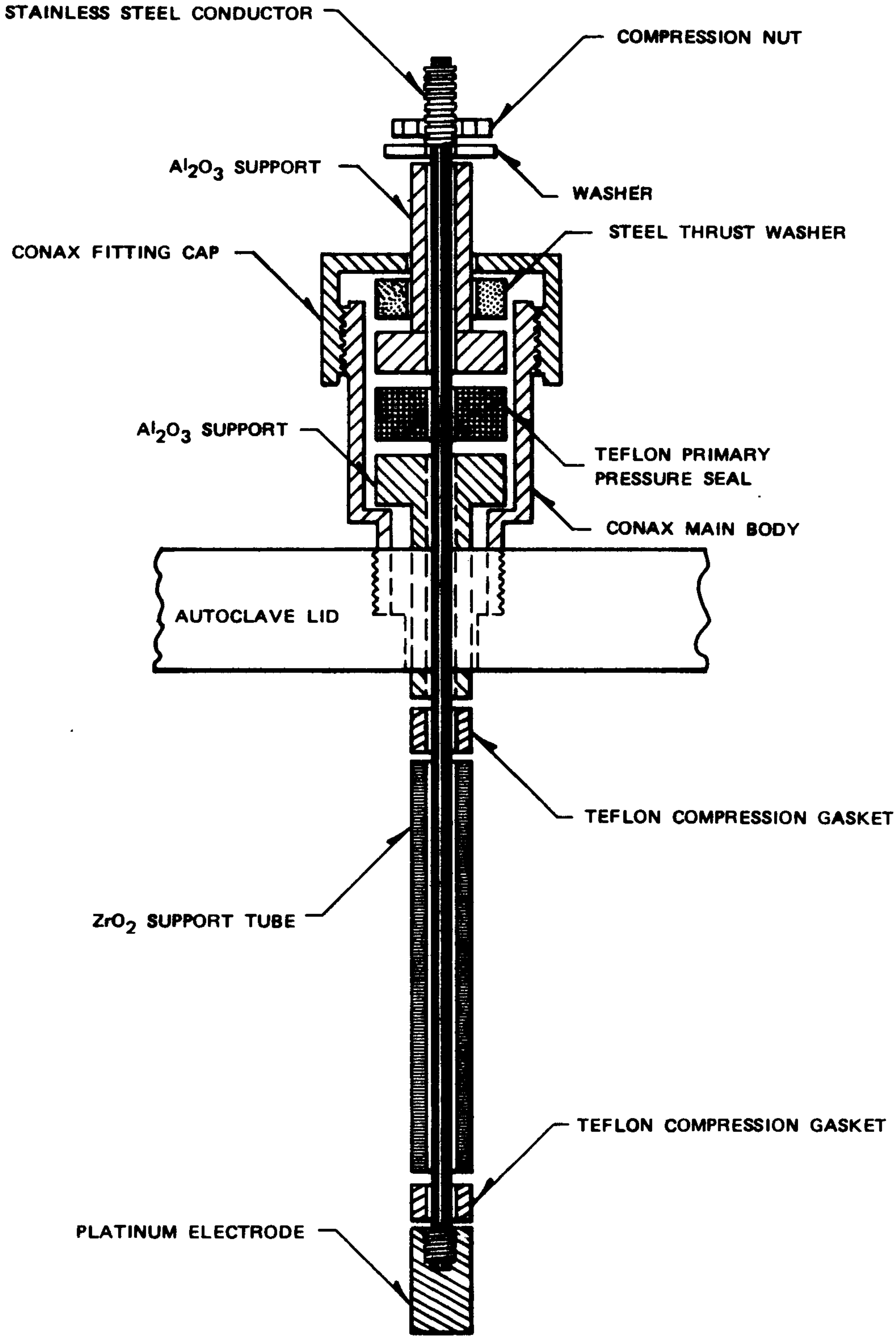


Figure 7. Schematic of Platinum Reference Electrode

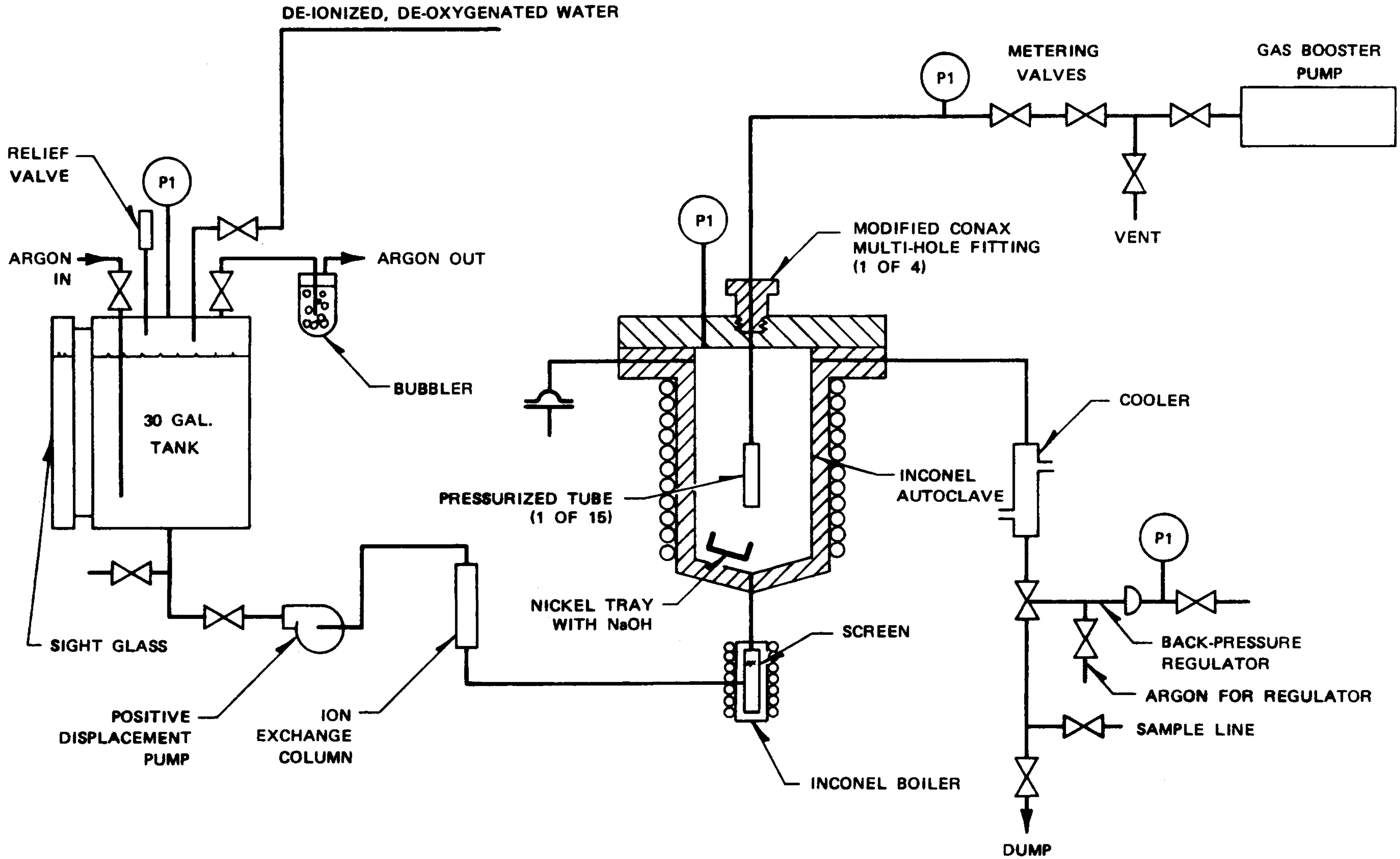


Figure 8. Superheat Stress Corrosion Facility

In addition to the experiments completed in the caustic-superheated steam environments, a single experiment was conducted in argon with a few pressurized tubes. The purpose of this experiment was to determine the stress rupture life of 2-1/4Cr-1Mo steel in the normalized and tempered, and annealed conditions in the absence of a corroding environment.

2.4 RESULTS

2.4.1 High Temperature Aqueous Testing

The results of constant load studies in 10% NaOH at 316°C (600°F) are given in Table 3. No evidence of stress corrosion was detected for any of the 2-1/4Cr-1Mo steel samples (Table 3) or for two Incoloy-800 samples after exposure. However, significant differences in the general corrosion rates were observed for the different heats of 2-1/4Cr-1Mo. The highest corrosion rates were noted for the simulated tube-to-tubesheet samples fabricated from the weldments supplied from ORNL. These samples corroded at such high rates that the gage sections thinned significantly. Since the load was constant, the stress on the thinned gage section rose to the ultimate tensile strength. As indicated on Table 3, Samples 1219 and 1212 failed mechanically for this reason. An example of the general corrosion attack for the welded samples is shown in Figures 9a and 9b. The corroded sample was Sample 1222 and the companion sample was unexposed. Because of the ever-increasing stress on the corroding gage section, Sample 1222 was on the verge of ductile failure as noted by the necked region. In all cases, regions within a single welded sample exhibited different corrosion rates. The simulated tube and tubesheet portions had poorer corrosion resistance than the welded region. The weld fusion zone was sharply defined by a thin line of the thick oxide on either side of the weld. The heat-affected zones appear to have the smallest remaining cross section and thus probably suffered the highest corrosion rate. Table 4 lists some of the dimensional changes on typical 2-1/4Cr-1Mo and Incoloy-800 samples after exposure to 10% NaOH under stress. The annealed electro-slag remelt alloy appeared to have the greatest corrosion resistance. Thinning of these samples did not occur and a thin black oxide formed on the surface. Samples fabricated from the air-melted 2-1/4Cr-1Mo steel heat showed slightly poorer corrosion resistance than the electro-slag remelt samples. Metallurgical condition may have an effect on the general corrosion rates. For example, the normalized and tempered samples had higher corrosion rates than did the annealed samples within the same heat.

The constant extension rate experiments in the present phase were conducted mainly in 10% NaOH solutions at 316°C (600°F). A summary of the results for 2-1/4Cr-1Mo samples tested in a variety of metallurgical conditions are given in Table 5. For comparison, a few of the results previously obtained in 5% NaOH at 316°C (600°F) are also given. In 5% NaOH, no cases of stress corrosion had been reported.[12] However, in 10% NaOH, a single case of marginal stress corrosion was produced. The cracks, shown in Figure 10, propagated to a maximum length of about 75μm before blunting. For comparison, Figure 10 also shows the fingers of oxide extending into the metal matrix that were found in samples of 2-1/4Cr-1Mo strained to failure in 5% NaOH.

The simulated tube-to-tubesheet weld samples also failed mechanically. The failures were always away from the weld as the weld region was mechanically stronger (similar to quenched and tempered material) than the annealed tube or tubesheet regions. In 10% NaOH, as observed in the constant load experiments, regions of the welded samples exhibited extremely high corrosion rates. Thus the gage sections were considerably reduced by corrosion as well as strain.

A few constant extension rate tests were performed at 232°C (450°F) in 5 and 10% NaOH. Although 232°C (450°F) is not prototypical of the CRBRP evaporator operation, this temperature was chosen to determine whether the materials and test conditions used in the present experimental program would result in caustic cracking at the lower temperature. As predicted, caustic cracking, both intergranular and transgranular, occurred for the annealed and welded samples. Figures 11a and 11b show some of the cracks in a welded sample at some distance from the weld. The weld region appeared more resistant to cracking and showed some rather minor cracks.

The results for Incoloy-800 obtained using the constant extension rate facility are given in Table 6. Data are presented for Grade 2, Grade 1, and cold-worked conditions. The Grade 1 condition was tested because this metallurgical condition, although not coded for use in the United States, is the steam generator material choice for Super Phoenix in France.

Table 3
SUMMARY OF THE FINAL CONSTANT LOAD EXPERIMENT, 316°C (600°F), 10% NaOH

Metallurgical Condition	Applied Stress MPa	(Ksi)	Exposure Time Under Stress (h)	Results
Welded and Stress Relieved	379.2	(55)	948[d]	No SCC[c]
	379.2	(55)	836	↓
	413.7	(60)	861[d]	↓
	413.7	(60)	298	↓
Temper Embrittled[a]	448.1	(65)	1347	↓
	448.1	(65)	1626	↓
Annealed	241.3	(35)	2033	↓
	241.3	(35)	2033	↓
	344.7	(50)	1822	↓
	344.7	(50)	1324	↓
ESR,[b] Annealed	344.7	(50)	1115	↓
	344.7	(50)	1115	↓
	344.7	(50)	1895	↓
	344.7	(50)	1895	↓
Normalized and Tempered	448.1	(65)	1324	↓
	448.1	(65)	1324	↓
Incoloy-800, Grade 2	344.7	(50)	1738	↓
	344.7	(50)	1738	↓

a. 1000 hours at 955°F
b. Electro-slag remelt
c. Stress corrosion cracking
d. Sample fractured due to severe general attack and mechanical overload.

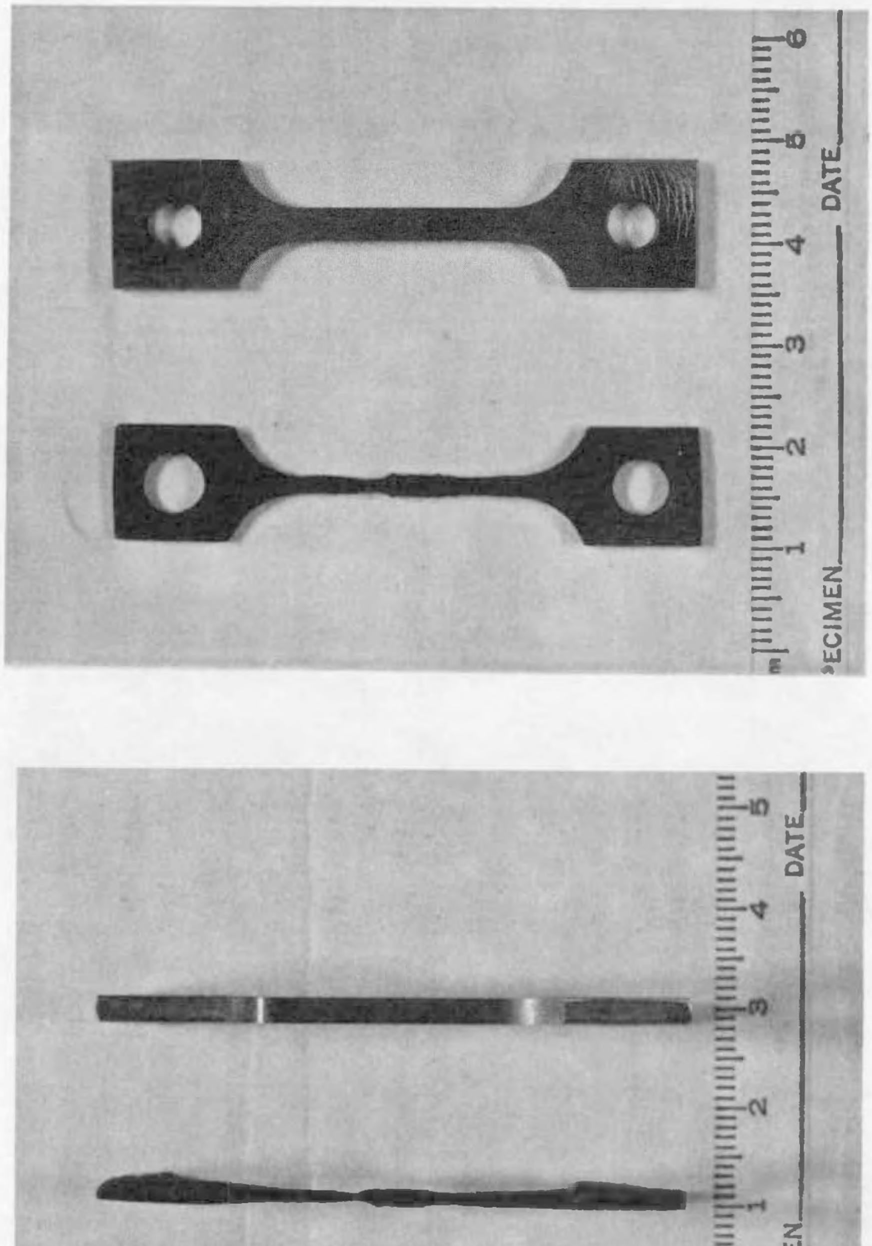


Figure 9. Weld Sample Before and After Exposure to 10% NaOH, 316°C (600°F)

Table 4
TYPICAL DIMENSIONAL CHANGES FOR SAMPLES EXPOSED TO 10% NaOH, 316°C (600°F)

Sample No.	Metallurgical[a] Condition	Exposure (h)	Sample Region	Sample Cross Section (in.)	
				Before Exposure	After Exposure
1222	Welded and stress relieved	836	Base	0.099 x 0.120	0.059 x 0.078
			HAZ[b]		0.045 x 0.067
			Fusion line		0.069 x 0.092
			Weld		0.068 x 0.089
			Fusion line		0.074 x 0.096
			HAZ		0.028 x 0.048[c]
			Base		0.045 x 0.062
1214	Welded and stress relieved	298	Base	0.100 x 0.120	0.078 x 0.099
			HAZ		0.073 x 0.093
			Fusion line		0.099 x 0.122
			Weld		0.102 x 0.118
			Fusion line		0.104 x 0.125
			HAZ		0.073 x 0.094
			Base		0.078 x 0.098
1263	ESR,[d] annealed	1895	Average gage	0.097 x 0.122	0.096 x 0.120
1264	ESR, annealed	1895	Average gage	0.100 x 0.123	0.099 x 0.123
1021	Annealed	2033		0.097 x 0.120	0.090 x 0.114
1042	Normalized and tempered	1324		0.099 x 0.121	0.095 x 0.119
128	Incoloy-800, Grade 2	1738		0.098 x 0.124	0.092 x 0.0

a. With the exception of the heat manufactured by the ESR process, all 2-1/4Cr-1Mo samples were from air-melted heats.
b. Heat affected zone.
c. Sample neck.
d. Electro-slag remelt.

Table 5
CONSTANT EXTENSION RATE TESTING FOR 2-1/4Cr-1Mo AT 316°C (600°F)

Metallurgical Treatment	Environment	Extension Rate (in./h)	Tensile Strength Mpa	Tensile Strength (ksi)	Elongation (%)	Reduction in Area (%)	Observation
Annealed	Pure water	0.004	491.2	(71.3)	22	53	No SCC[a]
	5% NaOH	0.004	473.3	(68.7)	16	25	
	5% NaOH	0.001	490.6	(71.2)	18	31	
	5% NaOH+O_2	0.001	468.5	(68.0)	23	41	No SCC[b]
	10% NaOH	0.001	461.6	(67.0)	13	26	Minor cracks 75μm depth
	10% NaOH	0.001	527.0	(76.5)	14	25	No SCC
Annealed and notched	5% NaOH	0.001	479.5	(69.6)	–	–	
Normalized and tempered	Pure water	0.001	601.5	(87.3)	18	50	
	5% NaOH	0.001	553.9	(80.4)	14	50	
	10% NaOH	0.001	655.9	(95.2)	12	28	
Cold-worked 25%	Air	3.0	635.9	(92.3)	–	39.1	
	10% NaOH	0.001	654.5	(95.0)	4.6	12.7[c]	d
Welded and stress relieved	Pure water	0.001	527.0	(76.5)	15.7	64.7	
	5% NaOH	0.001	516.1	(74.9)	14.9	60.6	
	10% NaOH	0.001	437.5	(63.5)	e	56.4	c
	10% NaOH	0.034	488.5	(70.9)	161.9	49.4	

a. Stress corrosion cracking.
b. Stress corrosion cracking of 17 Ph stainless steel retaining pins.
c. Metal cross section reduced by general corrosion as well as strain.
d. Severe general corrosion.
e. Severe general corrosion, gage marks obliterated.

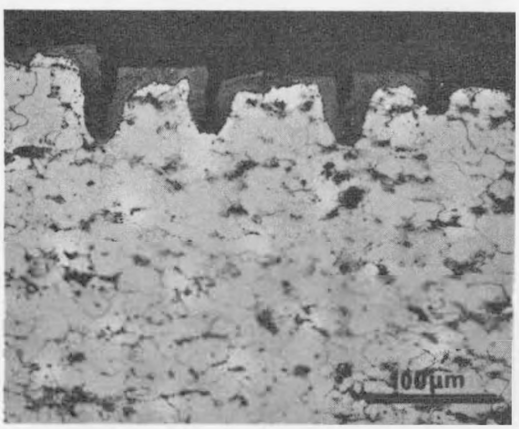


Figure 10a. Annealed 2¼ Cr - 1 Mo Strained at 10^{-5}/min 5% NaOH, 316°C (600°F)

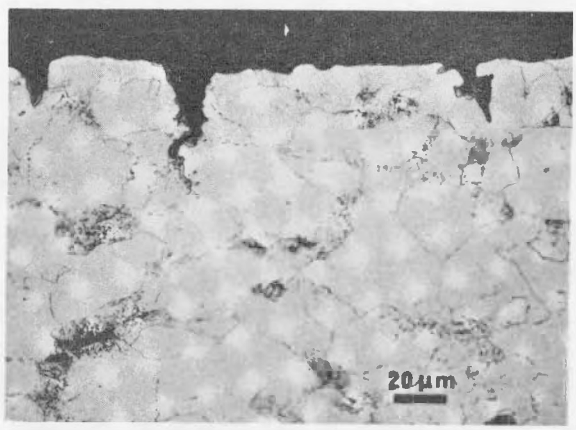
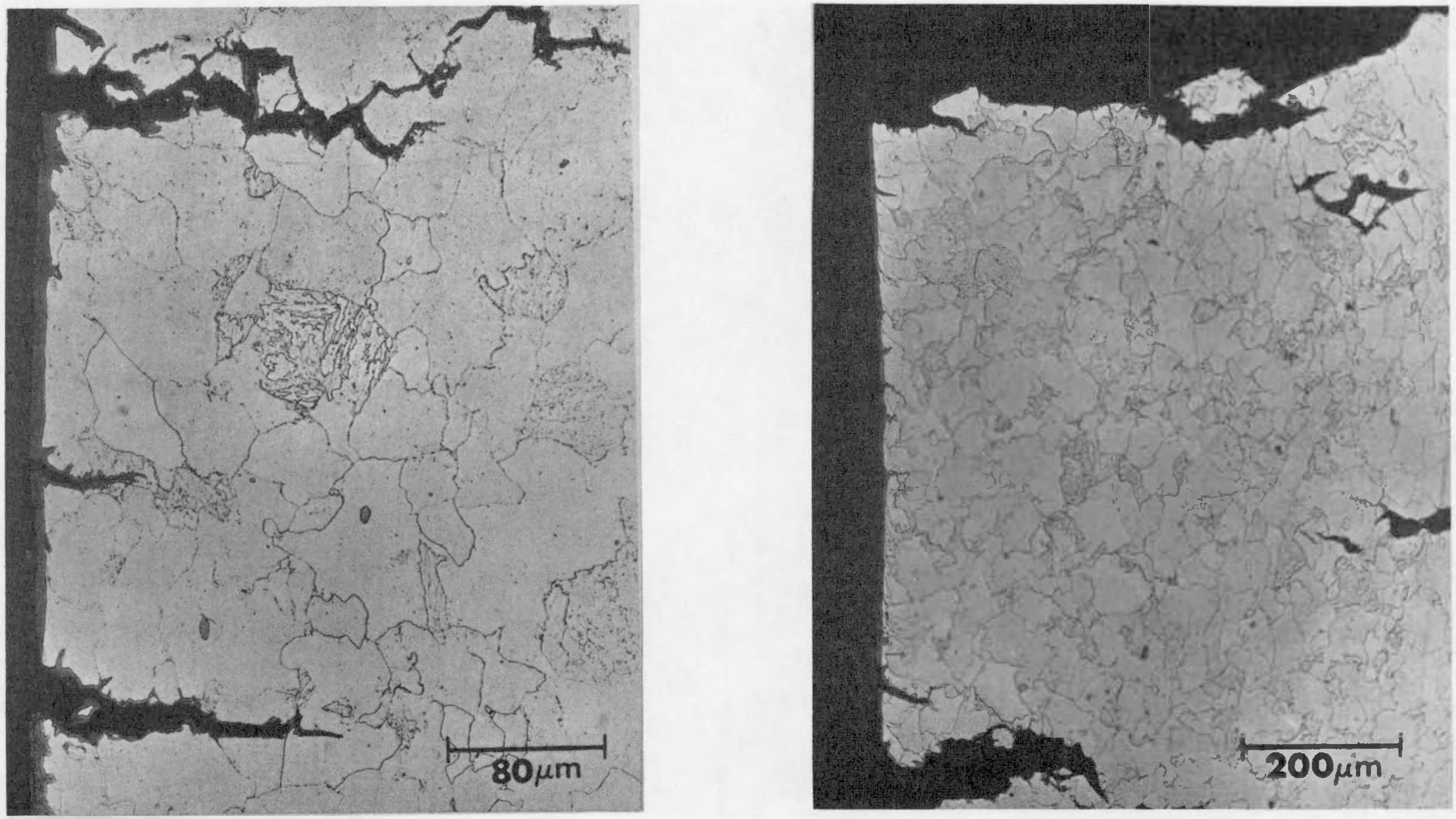


Figure 10b. Marginal SCC on 2¼ Cr - 1 Mo in 10% NaOH, 316°C (600°F), Strained at 10^{-5}/min



a b

Figure 11. Stress Cracks in 2-1/4Cr-1Mo Sample , 10% NaOH, 232°C (450°F)

Table 6
CONSTANT EXTENSION RATE TESTING, 316°C (600°F) – INCOLOY-800

Condition	Environment	Extension Rate (in./h)	Tensile Strength Mpa	Tensile Strength (ksi)	Elongation (%)	Reduction in Area (%)	Observation
Annealed, Grade 2	Calibration in water	0.001	457.5	(66.4)	61	54	Ductile failure
↓	5% NaOH	0.001	301.8	(43.8)	38	15	Intergranular SCC
↓	5% NaOH	0.072	435.4	(63.2)	57.3	57	Surface cracks, ductile rupture
↓	10% NaOH	0.001	320.4	(46.5)	26.9	16	Transgranular SCC
Annealed, Grade 1	10% NaOH	0.001	505.7	(73.4)	44.7	38.2	No failure; test stopped before sample failure
Cold-worked 25%	Calibration in air	3.0	655.2	(95.1)	6.9	32.0	Ductile failure
↓	5% NaOH	0.001	744.1	(108)	6	34.0	Ductile failure, minor SCC at neck
↓	10% NaOH	0.001	673.8	(97.8)	6.7	18.4	Mostly ductile failure, minor SCC at neck

The cold-worked Incoloy-800 exhibited excellent resistance to stress corrosion as no cracking occurred in the 5% caustic solution. In 10% NaOH, a slight amount of cracking occurred. This minor cracking occurred at the neck (onset of plastic instability) prior to mechanical failure. The Grade 2 condition failed intergranularly in 5% NaOH[12] and transgranularly in 10% NaOH (Figure 12). A single test was run with the Grade 1 condition in 10% NaOH. No cracking could be found in this sample although considerable plastic strain had occurred (see Figure 26).

2.4.2 Superheat Stress Corrosion Studies

The tests run in superheated steam with dissolved caustic were short term. The maximum run time was 144 hours. Sampling of the downstream condensate from run to run indicated that the amount of NaOH dissolved within the steam was 5 to 10 ppm. However, measurements of the internal system surfaces, (the autoclave, the o.d. of the tubes) with moistened pH paper following each run, gave a pH of 11. The high post-test pH, about an order of magnitude greater in caustic concentration than measured from the downstream condensate, probably results from the dropout of solid NaOH on surfaces as the system was cooled and depressurized.

The two main factors limiting run times were the general corrosion rate of 2-1/4Cr-1Mo steel and stress rupture. Stress rupture lives of tubes were determined to be 2 to 4 hours when stressed at 310 and 344.7 Mpa (45 and 50 ksi) in pure argon. Annealed tubes failed at 310 Mpa (45 ksi), and normalized and tempered tubes failed at 344.7 Mpa (50 ksi). Exposure of 2-1/4Cr-1Mo to the caustic-steam environment resulted in accelerated general corrosion and tube thinning. The general corrosion rate of 2-1/4Cr-1Mo with 5 to 10 ppm dissolved caustic was in the range of 0.05 to 0.1 mil/h. For Incoloy-800, the corrosion rate was 1/10 to 1/15 that of 2-1/4Cr-1Mo.

No cases of stress corrosion of 2-1/4Cr-1Mo or Incoloy-800 occurred in the present series of superheat experiments. In an earlier experiment[12] a single case of stress corrosion did occur for Incoloy-800. However, the sample was furnace sensitized, stressed 352 MPa (51 ksi) and was exposed to a severe environment of steam with molten caustic.

The general corrosion rate of 2-1/4Cr-1Mo resulted in significant wall thinning, which often increased the stress above the short-term stress rupture values. As a result, mechanical failure occurred. Tables 7, 8, and 9 summarize single Inconel-600 stress corrosion failure, Table 7, reproduced results reported previously.[12]

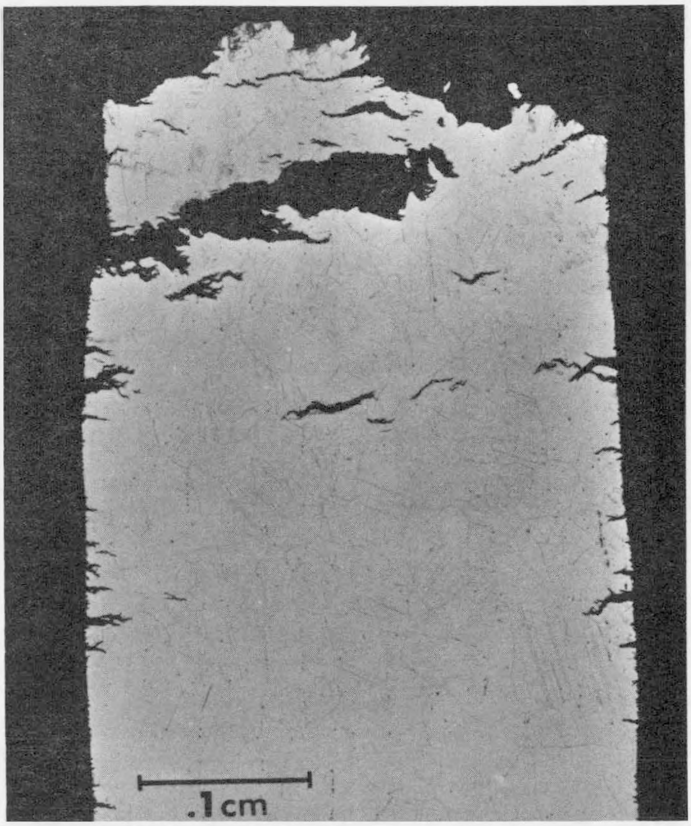


Figure 12. Transgranular Crack, Inconel-800, 316°C (600°F), 10% NaOH

Table 7
SUMMARY OF CAUSTIC-SUPERHEAT, STRESS CORROSION RUN 506, 482°C (900°F), 1750° psi, 28 HOURS

Alloy	Metallurgical Condition	Stress Mpa	Stress (kpsi)	Result
2-1/4Cr-1Mo	Annealed	172	(25)	No failure
↓	↓	172	(25)	↓
↓	↓	241	(35)	↓
↓	↓	241	(35)	↓
↓	↓	310	(45)	No SCC,[a] stress rupture, 1 h
↓	↓	310	(45)	No SCC,[a] stress rupture, 2 h
↓	Normalized and tempered	276	(40)	No failure
↓	↓	276	(40)	No failure
↓	↓	345	(50)	Leaked during stressing
↓	↓	345	(50)	No SCC, stress rupture, 2.5 h
Incoloy-800	Grade 2	276	(40)	No failure
↓	↓	276	(40)	↓
↓	↓	276	(40)	↓
↓	Furnace sensitized	276	(40)	↓
Inconel-600[b]	Mill annealed	207	(30)	SCC, 6 hours

a. Stress corrosion cracking.
b. Indicator tube.

Table 8
SUMMARY OF CAUSTIC-SUPERHEAT STRESS CORROSION RUN 507, 482°C (900°F), 1750 psi, 144 HOURS

Alloy	Metallurgical Condition	Stress Mpa	Stress (kpsi)	Result
2-1/4Cr-1Mo	Annealed	172	(25)	No failure
		172	(25)	No SCC,[a] tube leak between 123 and 138 h
		241	(35)	No SCC, stress rupture between 96 and 114 h
		241	(35)	No SCC, tube leak between 96 and 114 h
		269	(39)	No SCC, tube leak between 4 to 13 h
		276	(40)	No SCC, stress rupture between 4 to 13 h
	Normalized and tempered	241	(35)	No SCC, stress rupture between 96 to 114 h
		241	(35)	No SCC, stress rupture between 52 to 71 h
		276	(40)	No SCC, stress rupture between 71 and 96 h
		310	(45)	No SCC, stress rupture between 52 and 71 h
	Weld metal	282	(41)	No SCC, stress rupture between 123 and 138 h
		282	(41)	No SCC, stress rupture between 123 and 138 h
Incoloy-800	Grade 2	276	(40)	No failure
	Sensitized	282	(41)	No failure

a. Stress corrosion cracking.
b. Due to corrosion of sample.

Table 9
SUMMARY OF CAUSTIC-SUPERHEAT STRESS CORROSION RUN 508, 482°C (900°F), 12.1 Mpa (1750 ksi), 133 h, 2-1/4Cr-1Mo WELDMENTS*

Sample No.	Stress Mpa	(ksi)	Results
1290	138	(20)	No failure
1291	138	(20)	Mechanical failure, between 99 and 113 h
1292	138	(20)	Mechanical failure, between 99 and 113 h
1293	172	(25)	No failure
1294	172	(25)	No failure
1295	172	(25)	No failure
1296	207	(30)	Mechanical failure, between 49 and 65 h
1297	207	(30)	Mechanical failure, 120 h
1298	207	(30)	No failure
1299	241	(35)	Mechanical failure, 98.5 h
1300	241	(35)	Mechanical failure, 120 h
1301	241	(35)	Mechanical failure, between 73 and 89 h
1302	276	(40)	Mechanical failure, between 15.5 and 18 h
1303	276	(40)	Mechanical failure, between 42 and 43.5 h
1304	276	(40)	Mechanical failure, between 49 and 65 h

*Annealed sections of 2-1/4Cr-1Mo tube joined in an orbital weld, followed by a stress relief at 732°C (1350°F).

Examples of the significant general corrosion of 2-1/4Cr-1Mo, but lack of stress corrosion, are shown for tubes in two metallurgical conditions in Figures 13 and 14. The annealed tube was stressed to 172 Mpa (25 ksi) and the all-weld metal tube was stressed to 276 MPa (40 ksi). After 144 hours of testing, 7 to 12 mils of metal from the annealed tube were lost and a thick surface oxide formed. The all-weld metal tube wall was reduced from 0.030 in. to a range of 0.016 to 0.020 in. Since the all-weld metal sample was stressed to 276 Mpa (40 ksi), a fraction (1-2 mils) of the 10- to 14-mil decrease in tube wall was due to plastic strain.

The all-weld metal tubes were fabricated from weld-deposited filler alloy. However, the tube-to-tubesheet welds in the steam generator of the CRBRP will be autogenous internal orbital bore butt welds. For this reason the final stress corrosion experiment in the caustic superheat environment (Table 9) was conducted with tube sections joined by an orbital butt-weld (welded by ORNL). As has been reported no stress corrosion occurred. Figure 15 is a post-test cross-section of one of these samples, exhibiting the weld and the regions on either side of the weld. Figure 16 shows a typical region away from the weld. Although the oxides were cracked, no sign of localized attack occurred in any sample. The weld region appeared to have a slightly thinner oxide and less metal attack than the regions on either side. However, these corrosion differences were not considered significant when compared to the overall general corrosion attack.

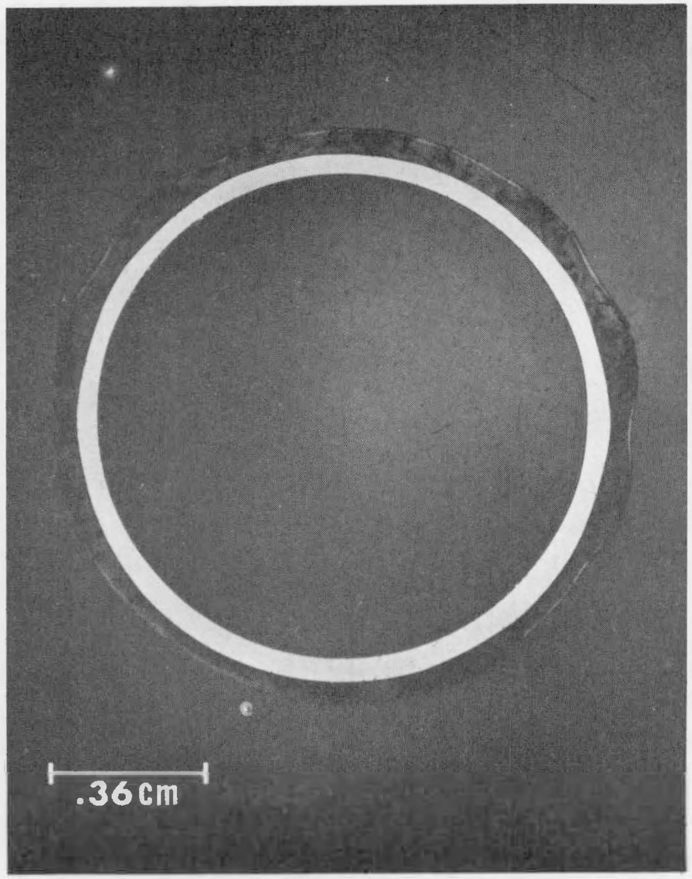


Figure 13. Cross Section of Annealed 2-1/4 Cr–1 Mo Tube from Caustic-Superheat Run Sample 1245

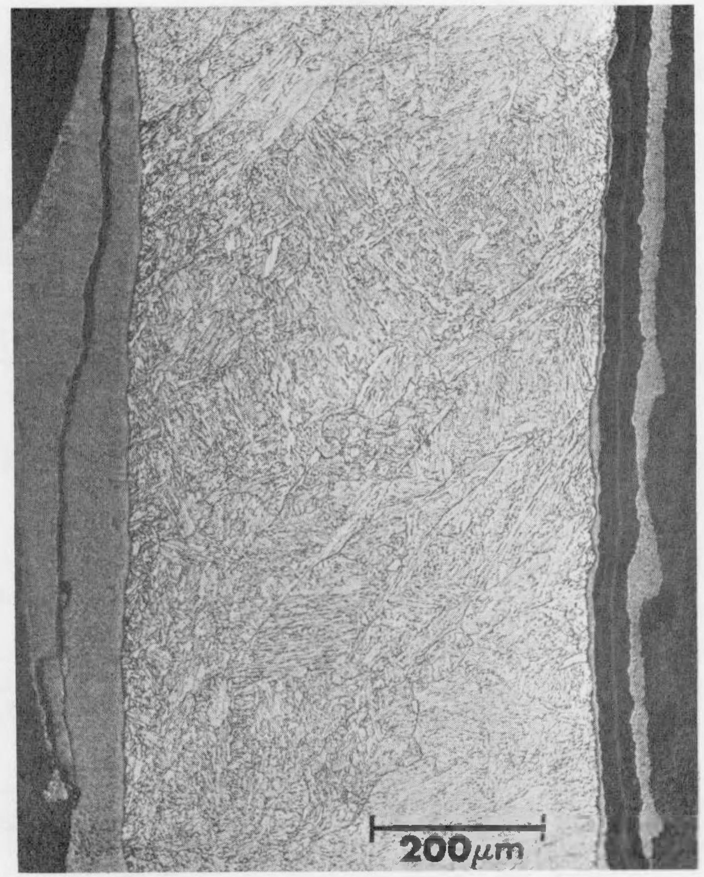


Figure 14. Cross Section of All-Weld Metal 2-1/4 Cr–1 Mo Tube After Caustic- Superheat Run

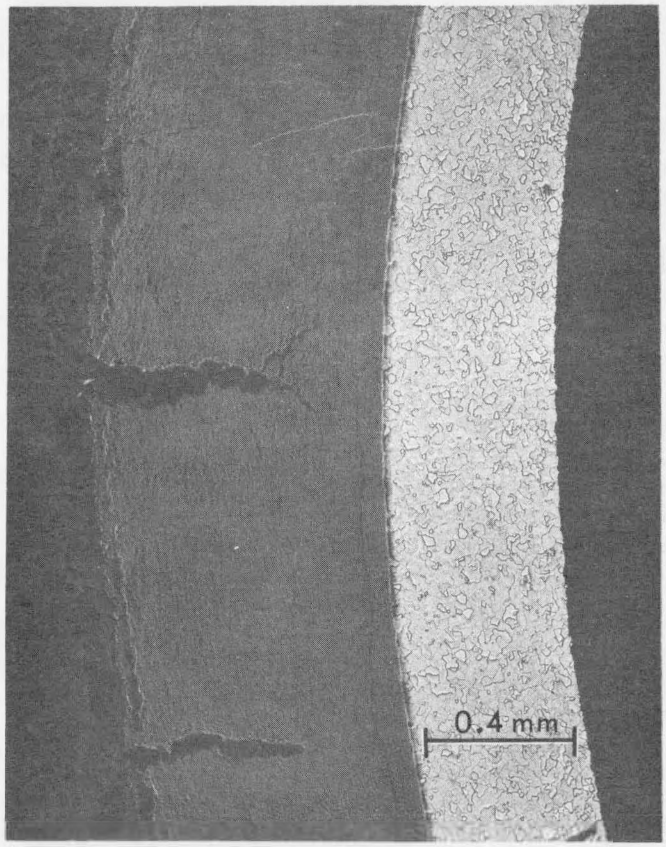


Figure 15. Cross Section of Orbital Tube Weld Sample Away from the Weld After Caustic Superheat Run

Figure 16. Cross Section of Orbital Tube Weld After Caustic Superheat Run

2.5 HIGH TEMPERATURE ANODIC ELECTROCHEMICAL STUDIES

The anodic polarization curves for 2-1/4Cr-1Mo and Incoloy-800 in several metallurgical conditions and in several caustic solutions at 316°C (600°F) are shown in Figures 17 through 22.

The main feature of the 2-1/4Cr-1Mo curves, Figures 17 to 19, is the increasing presence and sharpness of the active region with increasing sodium hydroxide concentration. Sharp transitions between the active and passive region often indicate regions of film instability and susceptibility to stress corrosion. This may account for the marginal stress cracking in 10% NaOH.

The Incoloy-800 curves, Figures 20 to 22, also show an increased active region with increased NaOH concentration. The lack of an active region in 1% NaOH may explain the apparent immunity of the alloy to stress corrosion in the constant load testing at concentration <3%. The Incoloy-800 curves show a secondary passivation region at high potentials. The most probable reaction at these high potentials is the oxidation of chromium in the oxide film from the +3 to the +6 state, according to reaction $Cr(OH)_3 + 5\,OH^- \rightarrow CrO_4^= + 4H_2O + 3e^-$. The final upturn in current for both materials in all metallurgical conditions is caused by oxygen evolution according to the reaction: $4OH^- \rightarrow O_2 + 2H_2O + 4e^-$.

2.6 STRAINING ELECTRODE EXPERIMENTS

The results of the straining electrode experiments for 2-1/4Cr-1Mo at 316°C (600°F) in 5 and 10% NaOH are summarized in Table 10. For comparison, data on the results (mechanical properties) obtained from experiments without the application of potential, (constant extension rate tests) are also presented for 2-1/4Cr-1Mo in pure water, 5% NaOH and 10% NaOH.

The application of anodic (oxidizing) potentials during straining did not cause any cases of stress corrosion. Metallographic examination indicated that the oxidizing potentials resulted in some increase in oxide formation and minor localized attack. The attack was manifested in the formation of fingers of oxide, which penetrated several grains into the metal before terminating, and a slight lowering of elongation. Figures 23 and 24 are examples of the thick reaction product and minor localized attack. In 10% NaOH, the applied anodic potentials greatly increased the general dissolution which significantly thinned the samples.

Straining electrode experiments were also performed at reducing (cathodic) potentials. The cathodic potentials (negative) were used to determine whether a forced decrease in the general corrosion could result in stress corrosion of 2-1/4Cr-1Mo. In Steam generator operation, reducing potentials in the water side could result from the presence of a significant concentration of hydrazine. As indicated in Table 10, minor cracking occurred. Figure 25 shows the microstructure of a sample strained to failure under cathodic control. The penetrations were slightly deeper, about 0.1 mm (0.004 in.), and somewhat sharper than those formed under anodic potentials. In addition, the oxides formed under cathodic control were reduced in thickness.

Two straining electrode experiments were run with Incoloy-800. In these experiments the Grade 1 and Grade 2 metallurgical conditions were tested at the same potential. The results are given in Table 11 as well as results obtained with no applied potential.

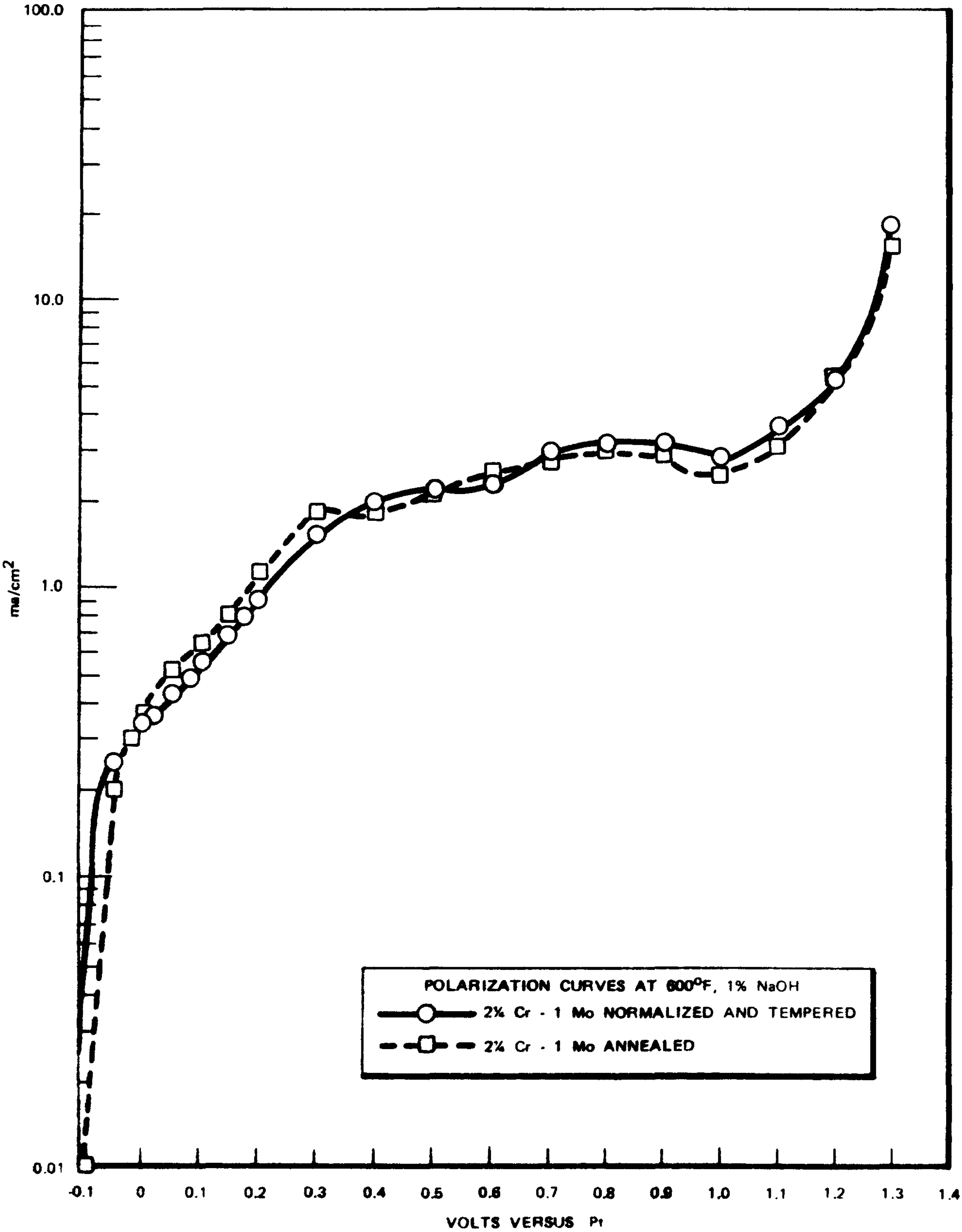


Figure 17. Polarization Curves, 2¼ Cr - 1 Mo, 1% NaOH, 316°C (600°F)

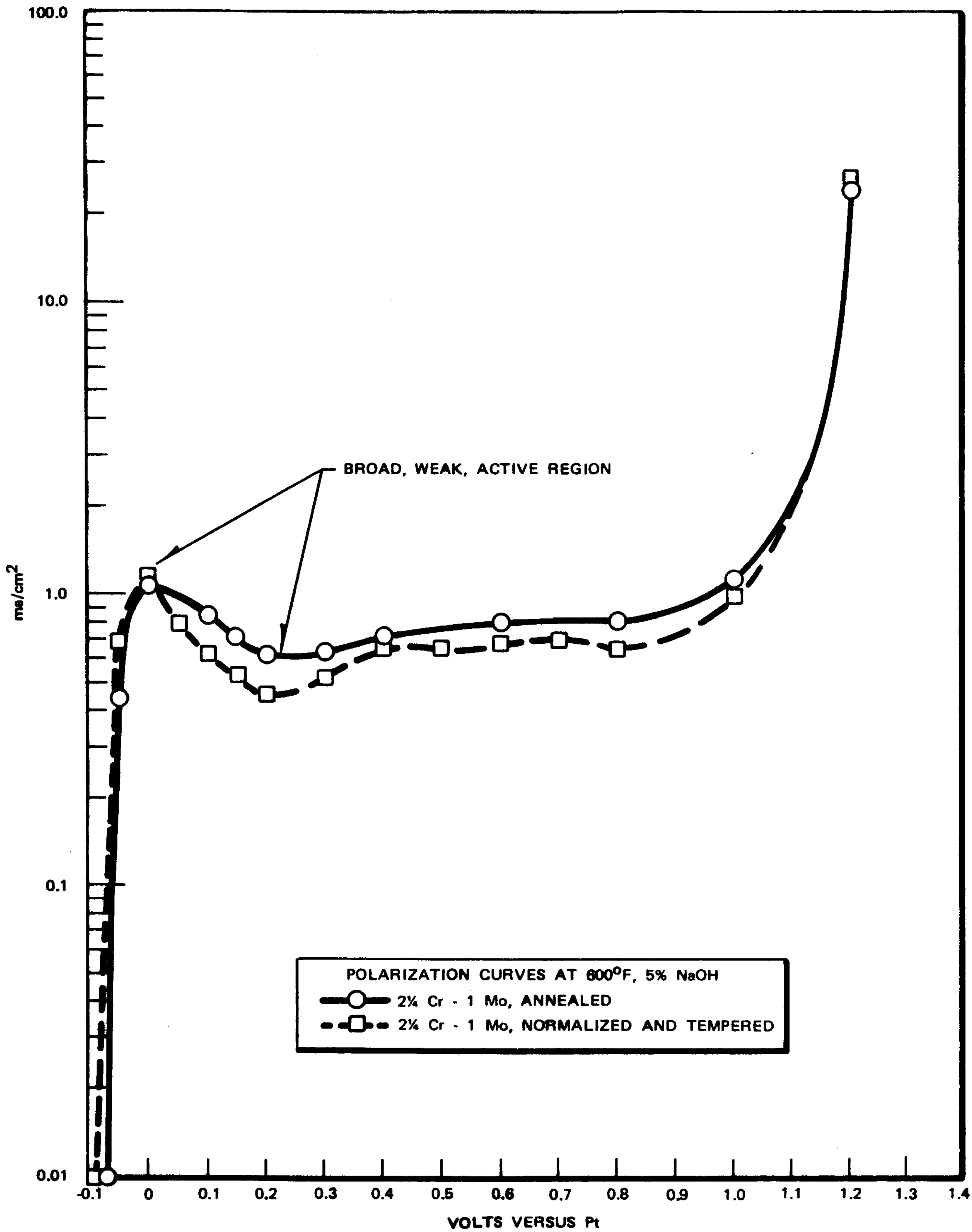


Figure 18. Polarization Curves, 2¼ Cr - 1 Mo, 5% NaOH, 316°C (600°F)

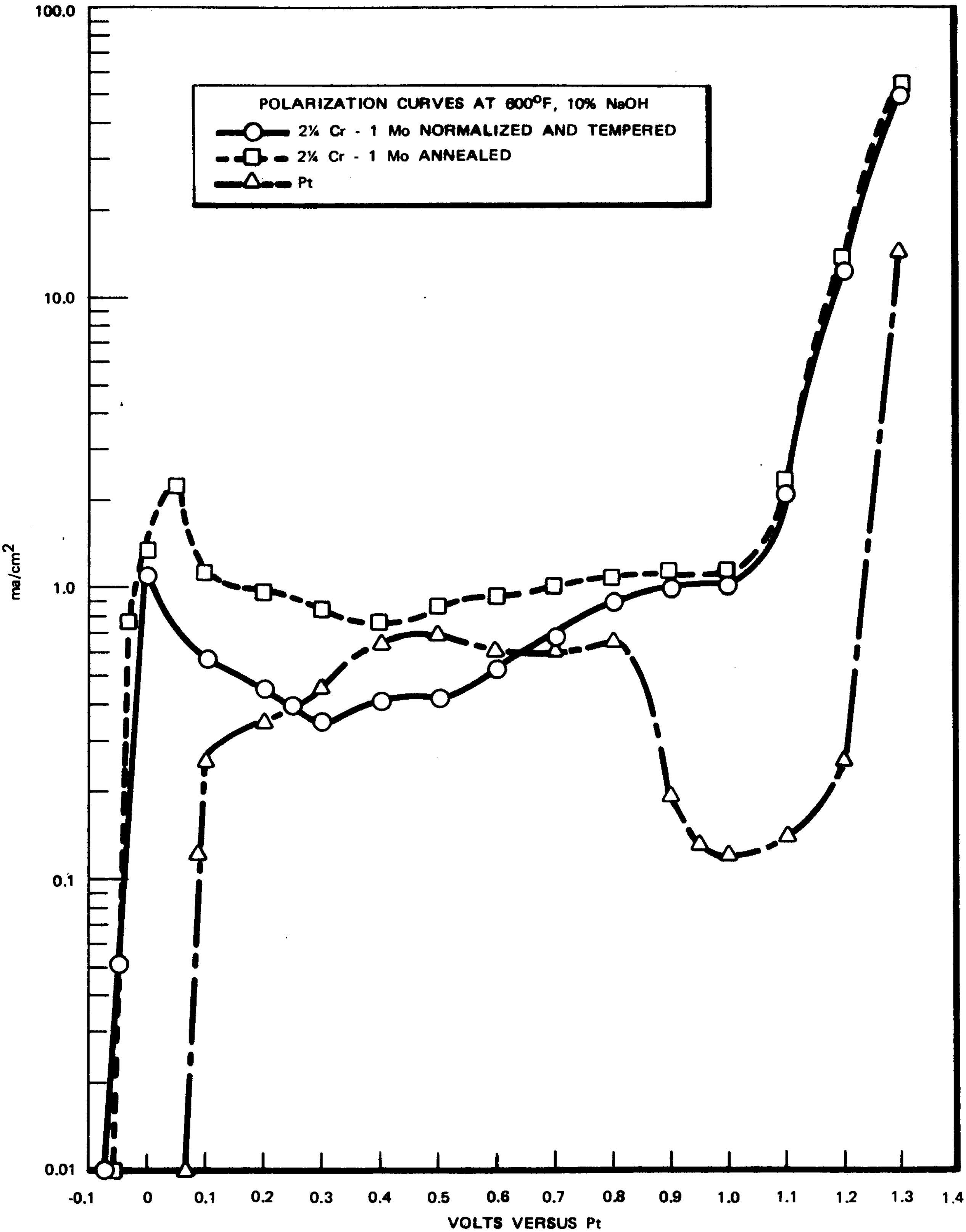


Figure 19. Polarization Curves, 2¼ Cr - 1 Mo, 10% NaOH, 316°C (600°F)

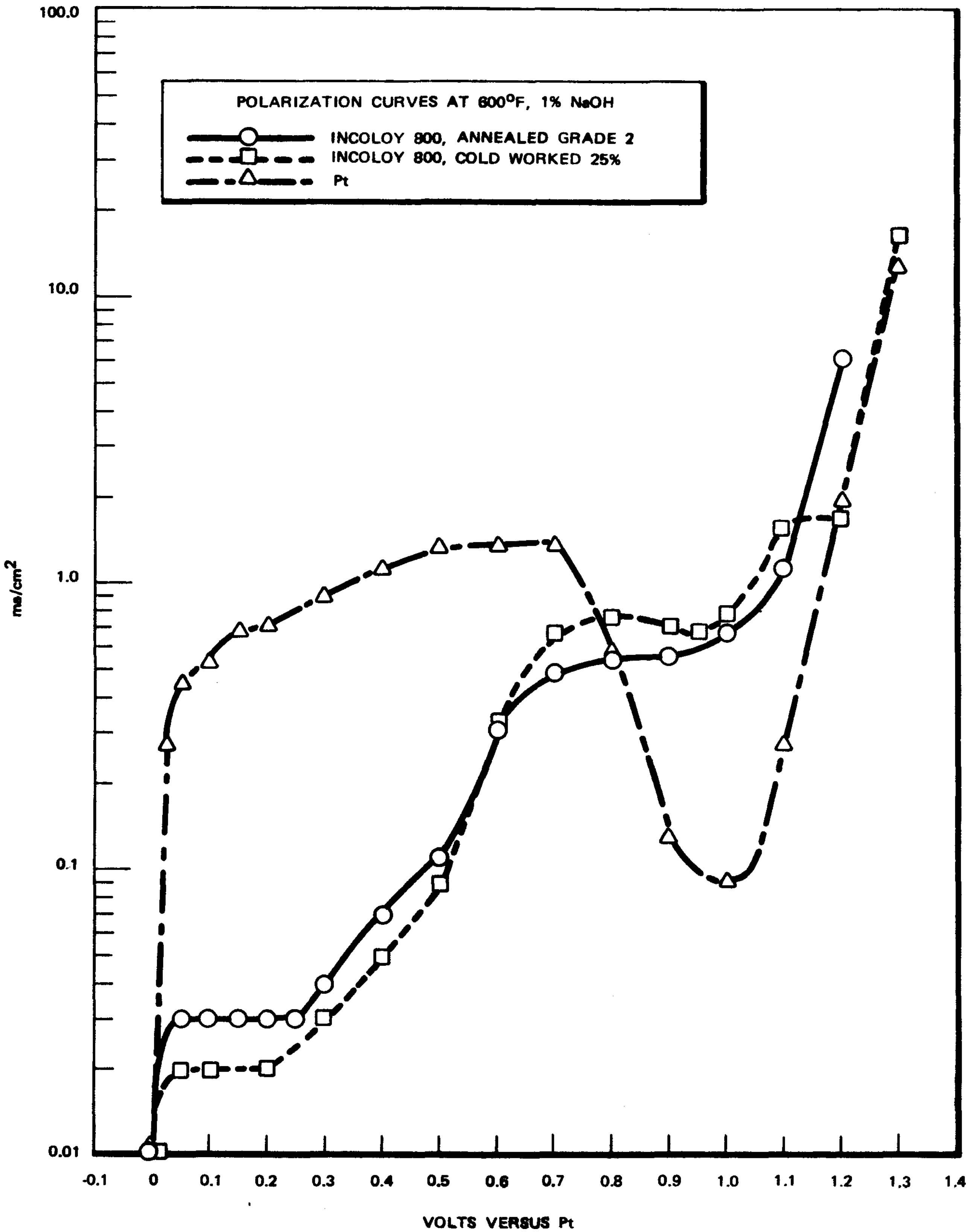


Figure 20. Polarization Curves, Incoloy 800, 1% NaOH, 316°C (600°F)

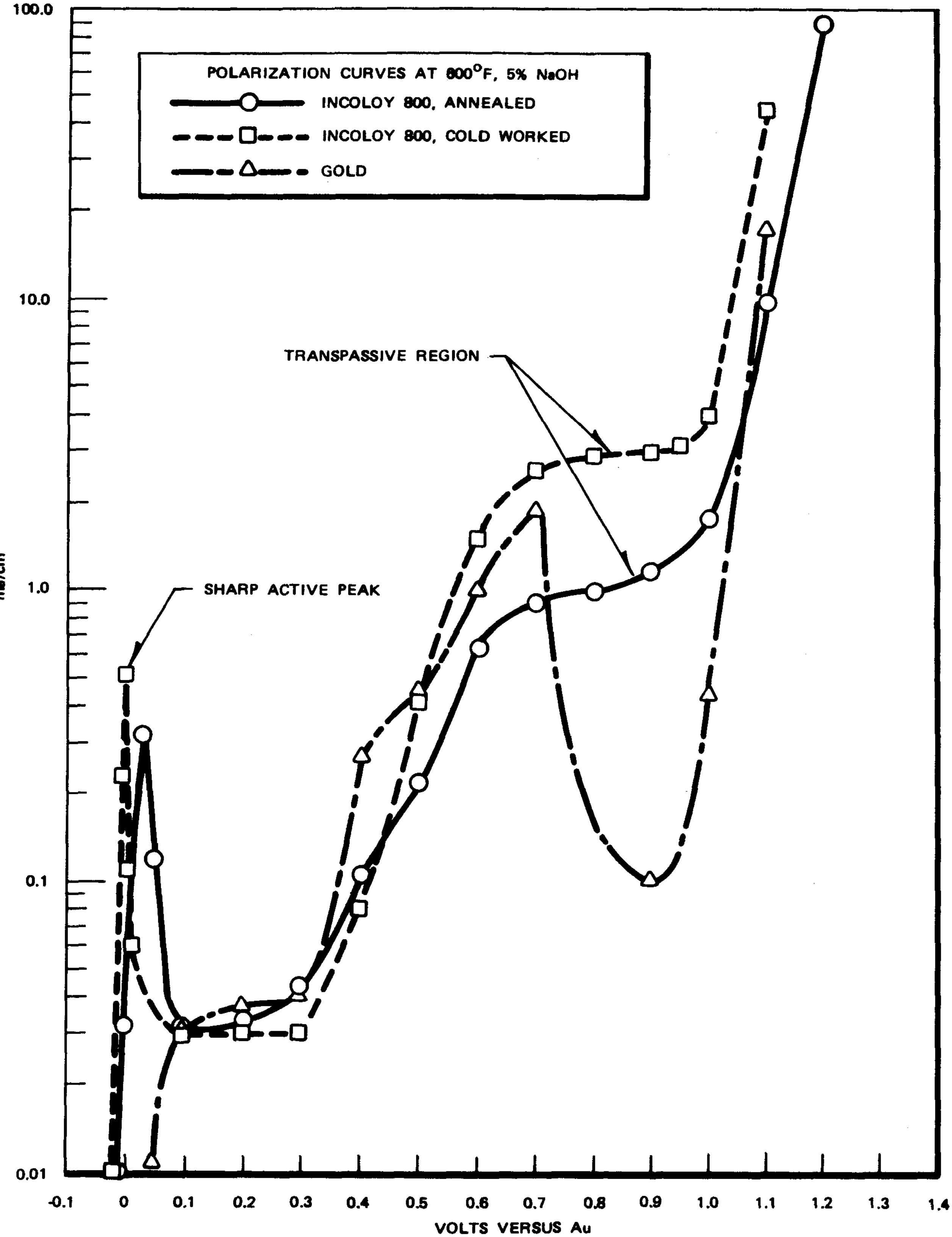


Figure 21. Polarization Curves, Incoloy 800, 5% NaOH, 316°C (600°F)

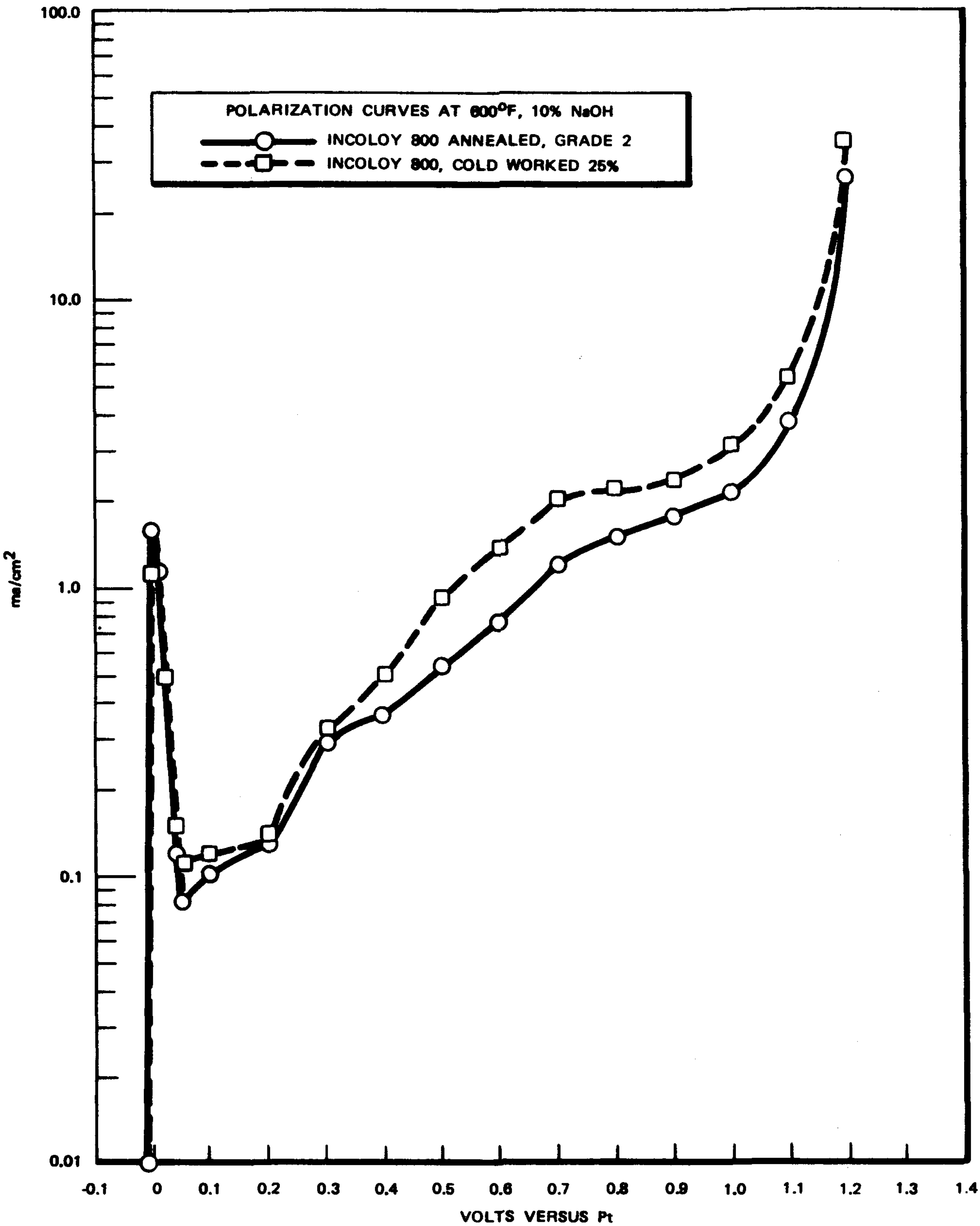


Figure 22. Polarization Curves, Incoloy 800, 10% NaOH, 316°C (600°F)

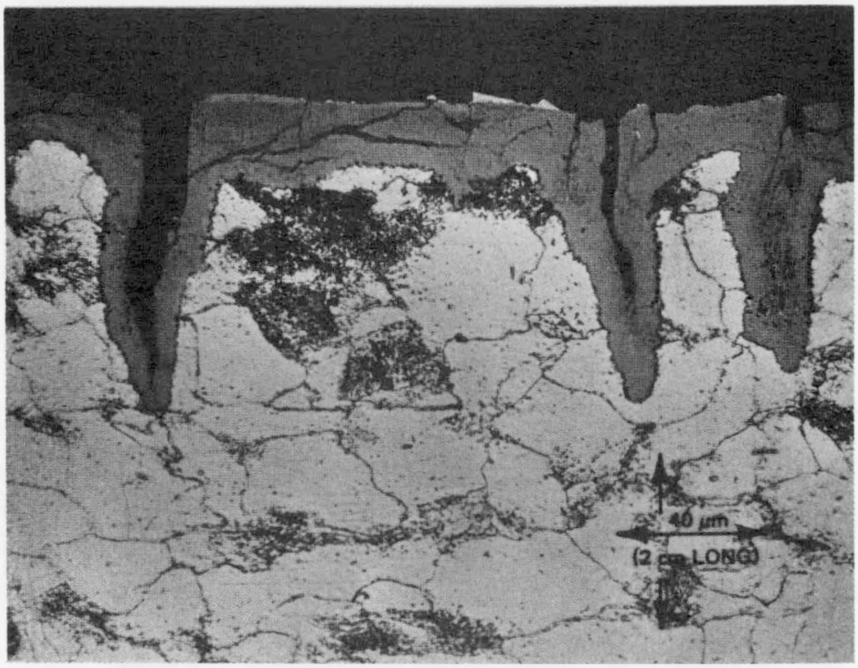


Figure 23. 2-1/4Cr-1Mo Annealed, 5% NaOH, 316°C (600°F), 10^{-5}/Min Strain Rate, 0.100 Volt versus Pt

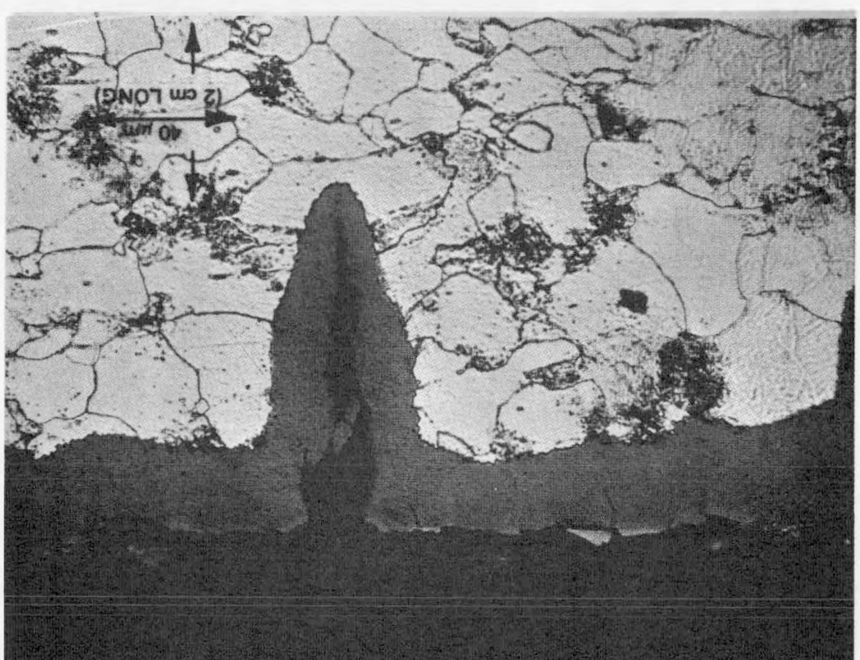


Figure 24. 2-1/4Cr-1Mo Annealed, 5% NaOH, 316°C (600°F), 10^{-5}/Min Strain Rate, 0.150 Volt versus Pt

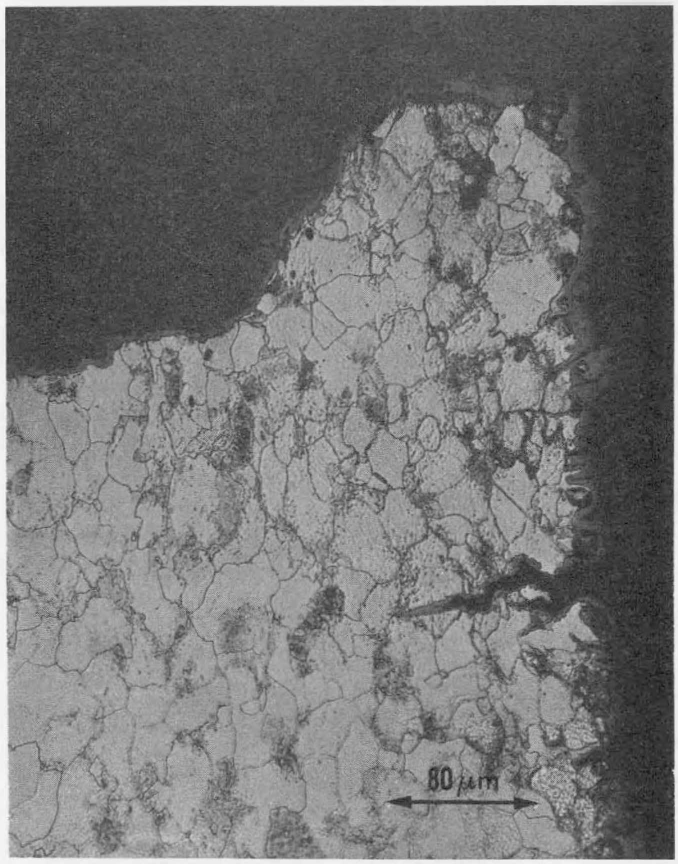


Figure 25. Annealed 2-1/4Cr-1Mo, 5% NaOH, 316°C (600°F), 10^{-5}/min Strain, Cathodic Control

Table 10
SUMMARY OF STRAINING ELECTRODE RESULTS, ANNEALED 2-1/4Cr-1Mo STEEL, 316°C (600°F), 2×10^{-5} STRAIN RATE

Wt. % NaOH	Applied Potential versus Pt (Volts)	Tensile Strength MPa	Tensile Strength (ksi)	Elongation (%)	Reduction in Area (%)	Observation
0	0	491.6	(71.3)	22.0	53	No SCC[a]
5	0	490.9	(71.2)	18.0	31	No SCC
10	0	462.0	(67.0)	13.3	26	Minor cracks, maximum depth ~75 μm
5	0.050	>434.4	(>63)[b]	11.6	27.4	No SCC
5	0.100	510.2	(74.0)	11.4	31.0	No SCC
5	0.150	504.0	(73.1)	12.5	33.0	No SCC
5	0.400	487.5	(70.7)	14.2	39.6	No SCC
5	-0.150	482.6	(70.0)	10.1	10.5	Minor cracks, maximum depth[c] ~100μm
10	0.080	398.5	(57.8)	11.9	74.7[f]	No SCC
10[d]	0.080	440.6	(63.9)	e	72.9[f]	No SCC
10	0.300	471.6	(68.4)	14.2	67.2[f]	No SCC

a. Stress corrosion cracking.
b. Electronic malfunction in load cell, after load of 434.4 MPa (63 ksi); test continued to sample failure.
c. See Figures 23 and 24.
d. Electro-slag remelt (ESR) alloy used.
e. Gage marks not visible due to general corrosion.
f. High apparent reduction in area values due to sample thinning from high corrosion rate rather than strain. Sample thinning also contributed to lower apparent values of the tensile strength.

Table 11
SUMMARY OF STRAINING ELECTRODE EXPERIMENTS FOR INCOLOY-800, 2×10^{-5}/min STRAIN RATE, 316°C (600°F)

Metallurgical Condition	Environment	Applied Potential versus Pt (Volts)	Tensile Strength Mpa	Tensile Strength (ksi)	Elongation (%)	Reduction in Area (%)	Observation
Grade 2	Calibration in pure water	–	457.4	(66.4)	61	54	Ductile failure
Grade 2	5% NaOH[a]	0	301.8	(43.8)	38	15	Intergranular SCC[c]
Grade 2	10% NaOH[a]	0	320.4	(46.5)	27	16	Transgranular SCC[c]
Grade 2	10% NaOH[b]	+0.030	457.5	(66.4)	43	49	Ductile failure
Grade 1	5% NaOH[a]	0	506.4	(73.5)	45	38	No failure[d]
Grade 1	10% NaOH[b]	+0.030	490.6	(71.2)	47	42	Ductile failure
Grade 1	10% NaOH[b]	+0.200	356.9	(51.8)	15.5	11.5	Many cracks initiated along gage section[e]

a. Argon cover gas.
b. 90% A – 10% H_2 cover gas.
c. Stress corrosion cracking.
d. Test stopped prior to mechanical failure (see Figure 26).
e. Test interrupted due to electronic malfunction.

3. DISCUSSION

3.1 2-1/4Cr-1Mo STEEL

In the present studies, 2-1/4Cr-1Mo continued to exhibit excellent resistance to stress corrosion at 316°C and 482°C (600°F and 900°F). In the constant load tests, the increase of caustic concentration from 3 to 10% did not result in any cases of stress corrosion. A single marginal case of caustic cracking was reported earlier[12] in a constant extension rate test in 10% NaOH; see Figure 10. More recent attempts to reproduce even this marginal case were not successful either by the constant extension rate test or with the application of potential by the straining electrode technique.

The electrochemical anodic polarization curves for 2-1/4Cr-1Mo (Figures 17 to 19) showed increasing active-to-passive current transitions with increasing caustic concentration. According to electrochemical theory, over the potential range of transitions, the surface reaction product is not stable and, under strain, the alloy may be susceptible to stress corrosion. However, normally the current between peak of the active region and the steady-state passive current will vary several orders of magnitude. In the cases presently studied, there was no measurable active-to-passive transition in one percent NaOH, and only slight active-to-passive transitions in the 5 and 10 percent NaOH solutions. The lack of sharp transitions as well as the high level of current in the passive region probably contribute to the resistance to stress corrosion in the environments studied. The level of passive current, ~1 mA/cm^2, is an indication of moderately high corrosion rates. High levels of general corrosion may be responsible for the crack blunting observed.

As the test temperature is reduced, the rate of general corrosion is reduced. Thus after a film rupture event, caused by strain, the localized strain-enhanced corrosion may be considerably greater than general corrosion. It is the difference between the strain-enhanced corrosion and the general corrosion rates that allow a sharp crack to propagate. Thus at lower temperatures, 232°C (450°F) in the present tests, or in the tests conducted at ORNL in boiling 33% caustic solutions, stress corrosion occurred.

A reduction of the general corrosion rate was also obtained at 316°C (600°F) by cathodic polarization. A sample pulled to failure while under a reducing potential had a thin surface oxide. Penetrations had formed that appeared to have more of the characteristics of stress cracks than the usual blunt fingers of oxide that would form during strain under anodic or the free corrosion potentials.

With increasing temperature, both the strain-enhanced corrosion and the general corrosion increased but their differences are probably not large enough to produce a sharp crack. Thus at 482°C (900°F), in the superheat experiments, strain was only a slight accelerator and no indication of localized attack was observed in the post-test metallographic examination.

Electrochemical evidence of stress corrosion susceptibility at the lower temperature may be found at transition regions of the anodic polarization curves. Regions just below or just above the active peak in the polarization curve are regions where susceptibility may exist. Bohnenkamp[14] was able to locate the potential range of stress corrosion susceptiblity for carbon steels in caustic solutions just below the active peak.

Significant differences in general corrosion rates were found for different heats of 2-1/4Cr-1Mo steel in caustic solutions at 316°C (600°F). In regions where locally high caustic solutions may be postulated to exist, a particular corrosion-resistant heat and metallurgical condition could extend tube life significantly. In the present experiments, the electro-slag remelt alloy in the annealed condition gave the lowest corrosion rate in caustic, while the welded samples suppled by ORNL gave the highest.

3.2 INCOLOY-800

In contrast to 2-1/4Cr-1Mo steel, Incoloy-800 was found to be susceptible to caustic cracking at 316°C (600°F). Cracking was intergranular in 5% NaOH and transgranular in 10% NaOH.

The anodic polarization curves give some hint to the stress corrosion susceptibility. In 5 and 10% NaOH, Figures 20 to 23, sharp active to passive transitions were observed, where the magnitude of the current varied at least an order of magnitude. At higher potentials transpassive regions are also observed. Thus stress corrosion susceptibility may exist over the potentials of the transitions. Stress corrosion susceptibility in the transpassive region is only of academic interest in the present studies, because the transpassive potentials represent a powerful oxidizing environment and one that would be difficult to obtain in an operating steam generator.

In general, the presence of the transition means that following rupture of a protective oxide in the passive region, a large current transient occurs as the metal re-oxidizes to heal the break. In 1% NaOH the active-passive transition transition was not observed; probably because the alloy is already passive at the natural corrosion potential. Rupture of the passive film as results of strain might not be followed by a large anodic dissolution current transient and the alloy in 1% NaOH would not be susceptible to stress corrosion. Experimentally, Incoloy-800 was not found susceptible to caustic cracking in ≤1% NaOH at 316°C (600°F).[12]

The stress corrosion results in 5 and 10% NaOH in the present studies were obtained in the constant extension rate facility; see Tables 6 and 11. Tests conducted in 10% NaOH in the constant load facility did not result in any stress corrosion failures for Grade 2 Incoloy. The explanation for the lack of failures can be postulated as follows: As can be seen from Table 11, the fracture strength of Grade 2 Incoloy was not very different in 5 and 10% NaOH. As a matter of fact, the value in 10% NaOH was somewhat higher than the value in 5% NaOH. From this fact we would expect the cracking times; at constant load to be about the same in the two environments. Previously, it was found that the cracking time at 344.7 Mpa (50 ksi) in 3% NaOH for Grade 2 Incoloy-800 was about 2200 hours.[12] In the present tests in 10% NaOH, the stress and exposure time for duplicate samples were 344.7 Mpa (50 ksi) and 1738 hours, respectively. It may be that either a longer exposure time or a higher stress was required to initiate cracking.

From an electrochemical view, another explanation concerning the lack of cracking is possible. The original constant load tests in 3% NaOH were conducted in a circulating system. The source of the electrolyte was a low pressure 30-gallon stainless steel tank which was purged continuously with argon. Thus the concentration of dissolved oxygen and hydrogen in the solution that was pumped into the autoclave was very low. We know by chemical analysis of the feedwater that the oxygen content was <5 ppb. The constant load tests in 10% NaOH were conducted in a static autoclave. In the 10% NaOH tests, most of the stressed samples during test were of 2-1/4Cr-1Mo. The general corrosion of 2-1/4Cr-1Mo would generate an increasing concentration of hydrogen. Hydrogen in sufficient concentrations can shift the corrosion potential of Incoloy-800 to lower (more negative) values. At the lower corrosion potential, Incoloy-800 may be immune to caustic cracking. Evidence of this electrochemical effect was obtained in recent constant extension rate and straining electrode experiments. As has been reported, Incoloy-800 cracked transgranularly in 10% NaOH when tested in the constant extension rate facility. The cracking occurred when the electrolyte and the gas space in the autoclave were purged with argon. In recent experiments in 10% NaOH, a 90% argon-10% hydrogen gas mixture was used. At a potential of +0.030 volt versus the platinum electrode, no stress corrosion occurred for either the Grade 2 or Grade 1 condition. Apparently the hydrogen in the cover gas lowers the corrosion potential to a region of immunity for both heat-treated conditions. We can compensate the environmental effect by raising the potential with a potentiostat and in the last straining electrode experiment, the potential was increased to +0.200 versus the platinum electrode. Incoloy-800, in the most crack-resistant heat treatment (the Grade 1 condition), was used. This experiment was terminated before failure due to an electronic malfunction. However, examination of the sample by optical microscopy showed numerous stress corrosion cracks had nucleated, and began to propagate. Thus for Incoloy-800, unlike 2-1/4Cr-1Mo, at 316°C (600°F) in caustic solutions, there appears to be a strong electrochemical potential dependency on stress corrosion.

The metallurgical condition of Incoloy-800 appears to be a major factor in the susceptibility of the alloy to caustic cracking. It had been previously shown that heat treating the mill-annealed alloy to produce the Grade 2 condition or cold-working resulted in a significant increase in stress corrosion resistance.[12] In the present studies it was found that the alloy heat, treated to produce the Grade 1 condition, was far more resistant to caustic cracking than the alloy in the Grade 2 condition. A single constant extension rate test was conducted with Incoloy-800 in the Grade 1 condition. The test was terminated at the onset of plastic instability (before mechanical failure). Only minor cracks were detected in the neck, although the alloy had been stressed to its ultimate strength. Figure 26 shows the appearance of the Grade 1 sample after test, compared to a similar untested sample. An argon overpressure and a 5% NaOH solution was used in this experiment. Several experiments were also run under potential control; see Table 11. In the straining electrode experiment described above, we found that cracks could be initiated on the Grade 1 condition. However, in this case, a stress >352 MPa (51 ksi), in addition to the high potential, was required for crack initiation. In comparison, the Grade 2 condition had failed completely in 10% NaOH at 317 MPa (46 ksi).

One of the most puzzling aspects of the studies with Incoloy-800 is the variation of stress corrosion behavior with metallurgical treatment. Although reasons may be postulated that concern grain size effects, types of grain boundaries or the presence or absence of solute segregation, the fundamental studies required to separate these variables have not been performed. A major effort would be required before fundamental understanding and predictable behavior could be achieved. At the present, we are forced to rely on empirical studies to develop any sort of material predictability criteria.

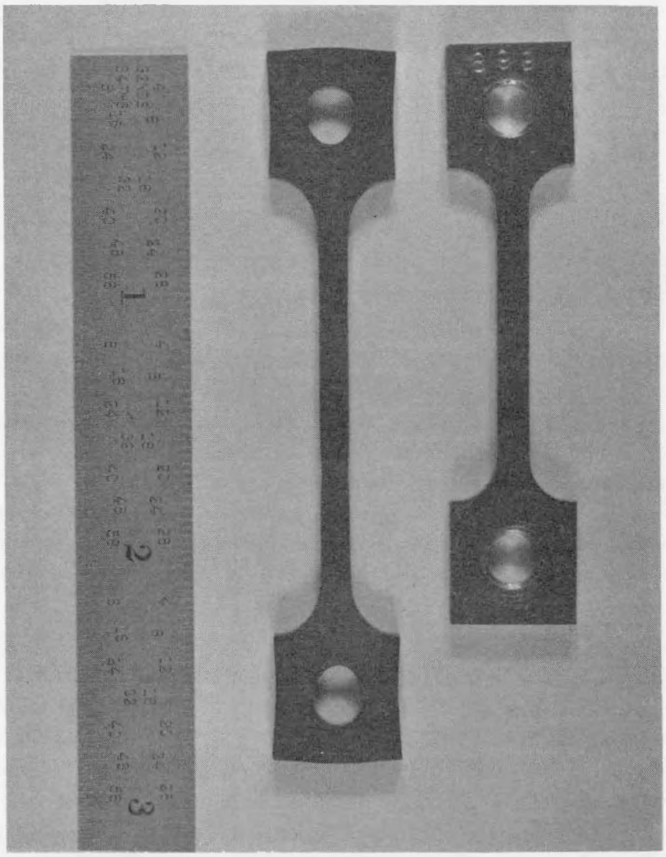


Figure 26. Incoloy-800, Grade 1, Before and After Constant Extension Rate Testing, 316°C (600°F), 5% NaOH, 10^{-5}/min Strain Rate

4. CONCLUSIONS

1. 2-1/4Cr-1Mo steel has continued to exhibit excellent resistance to caustic cracking at simulated evaporator temperatures, 316°C (600°F) and simulated superheater temperatures 532°C (900°F). Stressed samples were exposed to a maximum NaOH concentration of 10% at 316°C (600°F) and 10 ppm in steam at 532°C (900°F).

2. Weld metal and welded samples of 2-1/4Cr-1Mo exhibited immunity to caustic cracking under the above conditions.

3. At lower temperatures, 232°C (450°F), 2-1/4Cr-1Mo is susceptible to caustic cracking. As the temperature is increased, the rate of general corrosion increases, but stress corrosion susceptibility decreases. It is postulated that the increased rate of general corrosion causes crack blunting which stifles caustic cracking of 2-1/4Cr-1Mo steel.

4. Significant differences of corrosion rates for 2-1/4Cr-1Mo in caustic solutions at 316°C (600°F) were measured. The most corrosion resistant heat of 2-1/4Cr-1Mo was produced by the electro-slag remelt process.

5. Anodic polarization curves of 2-1/4Cr-1Mo steel did not show significant active-passive transitions which is an indication of stress corrosion resistance.

6. Incoloy-800 can be cracked intergranularly in 5% NaOH and transgranularly in 10% NaOH at 316°C (600°F). At 532°C (900°F), Incoloy-800 is extremely resistant to caustic cracking.

7. In caustic solutions at 316°C (600°F), the susceptibility of Incoloy-800 to caustic cracking is strongly dependent on the metallurgical condition. In constant extension rate testing, the Grade 1 and cold-worked condition appear to be far more resistant to caustic cracking than the Grade 2 condition.

8. The anodic polarization curves for Incoloy-800 in caustic solutions show significant active-passive and passive-transpassive regions. Stress corrosion at over these potential regions is a possibility.

9. The general corrosion of 2-1/4Cr-1Mo steel in superheated steam containing 10 ppm dissolved caustic is 0.0126 mm/h (0.0005 in./h) to 0.0254 mm/h (0.001 in./h). For Incoloy-800 the corrosion rate is 1/10 to 1/15 of the above values.

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