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Effect of Mercury Velocity on Corrosion of Type 316L Stainless Steel in a Thermal Convection Loop

February 2001

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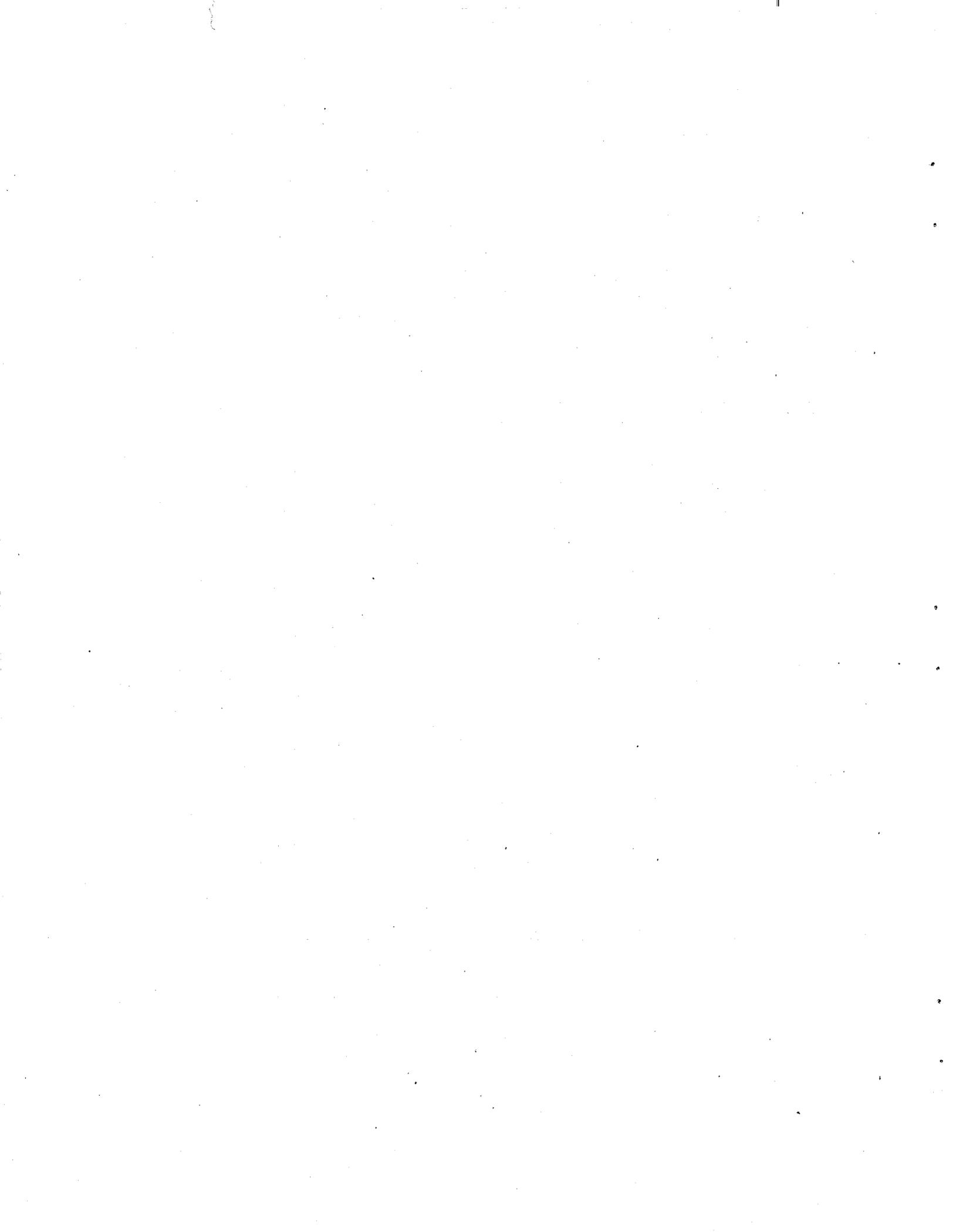
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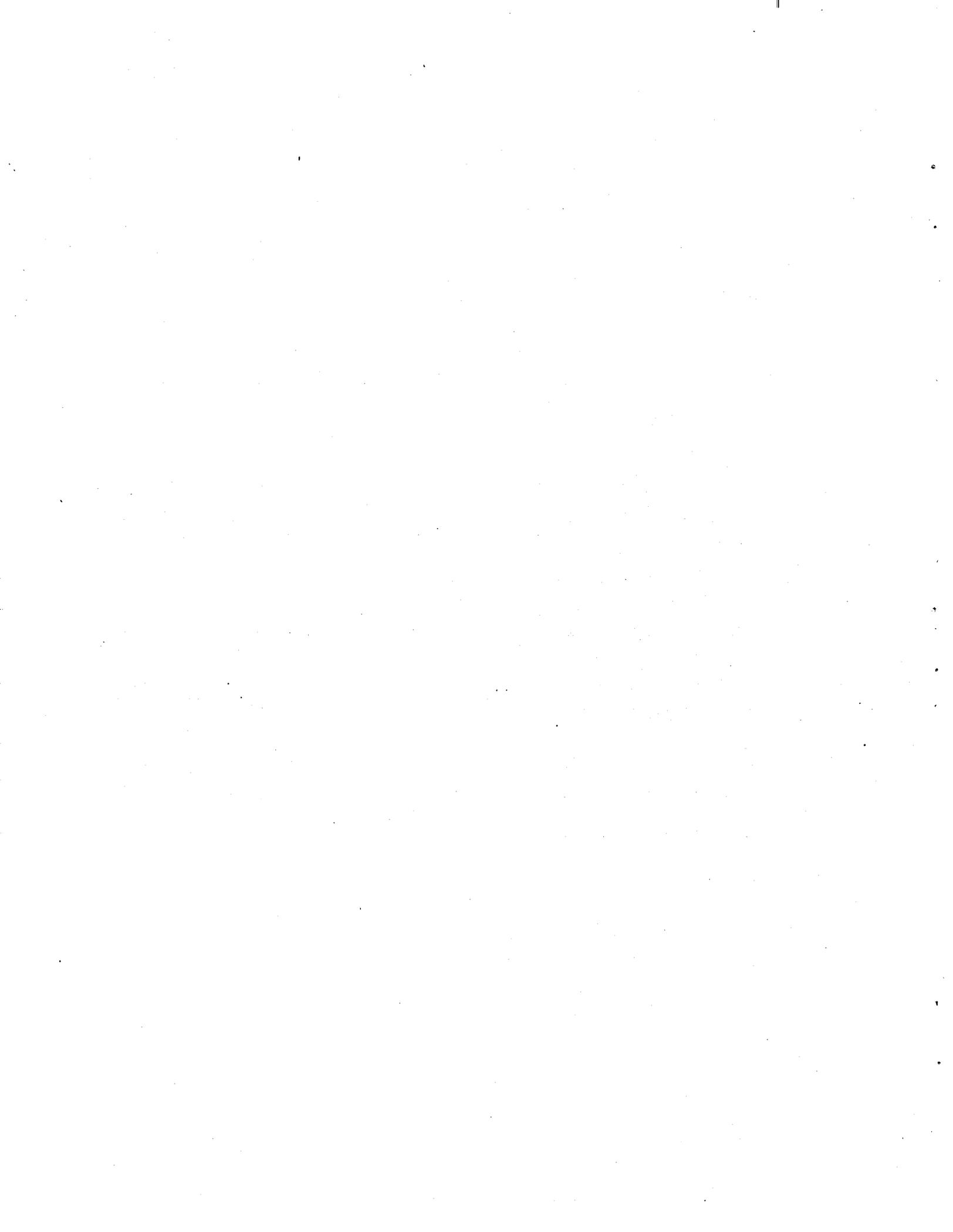
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Spallation Neutron Source

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CONTENTS

	Page
TABLES	v
FIGURES	vii
ABSTRACT	ix
1. INTRODUCTION	1
2. EXPERIMENTAL	3
2.1 LOOP FABRICATION	3
2.2 FILLING WITH MERCURY	7
2.3 LOOP OPERATION	8
3. RESULTS AND DISCUSSION	11
3.1 GENERAL VISUAL ASSESSMENT	11
3.2 WEIGHT CHANGE AND METALLOGRAPHY	12
3.3 NOMINAL 316L COUPONS	12
3.4 GOLD-COATED COUPONS	14
3.5 POLISHED COUPONS	15
3.6 ETCHED COUPONS	16
3.7 COUPONS WITH A SENSITIZING HEAT TREATMENT	17
3.8 ADDITIONAL TESTING OF COUPONS WITH SENSITIZING TREATMENT	19
3.9 TCL SURFACES	21
4. CONCLUSIONS	23
5. ACKNOWLEDGMENTS	25
6. REFERENCES	27



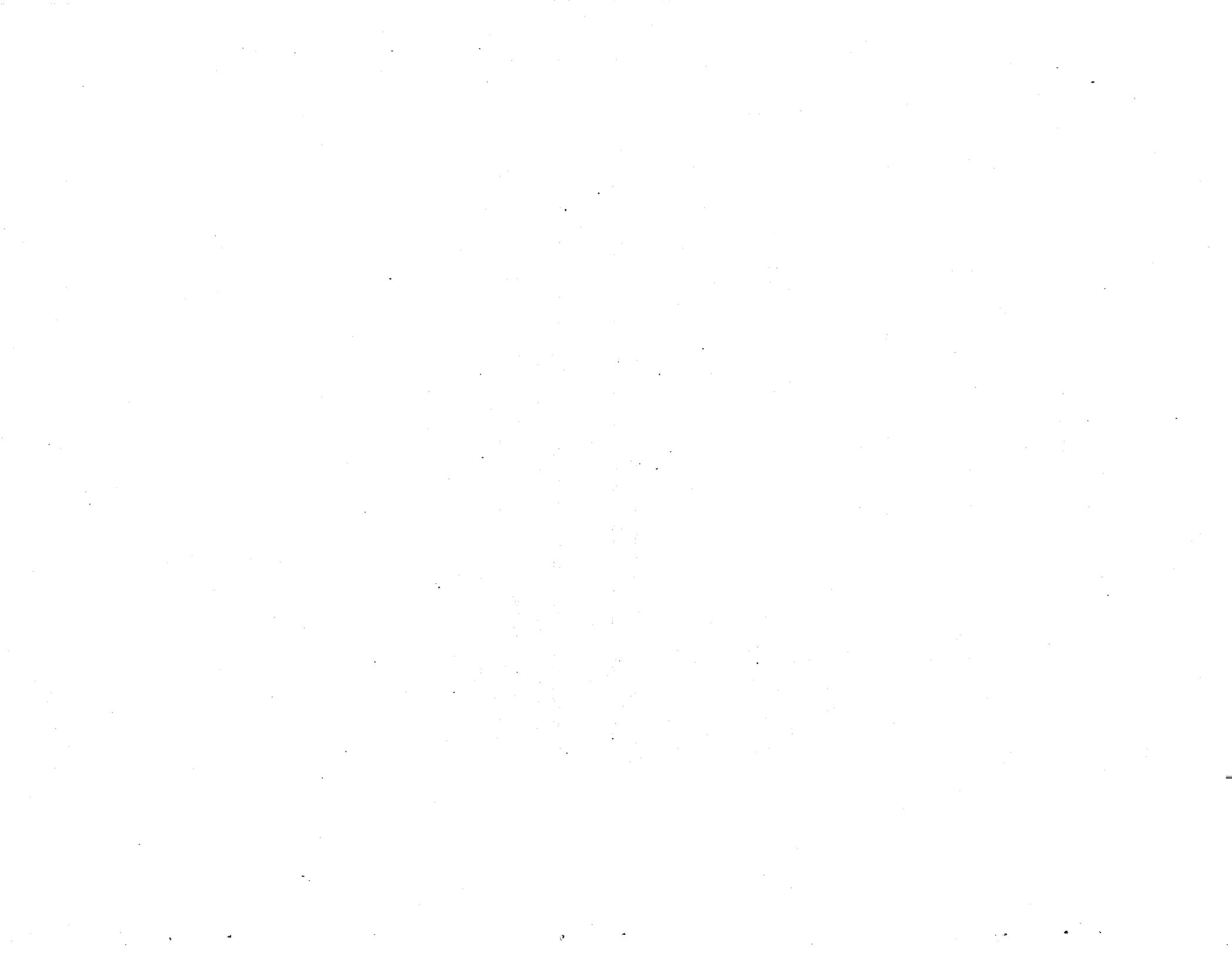
TABLES

Table		Page
1	Composition (weight percent) of 316L loop components and specimens. Values taken from mill certifications	4
2	Nominal temperatures at each "corner" of the thermal convection loops described here along with equivalent data for TCL #1 (a previous 316L TCL). Approximately a $\pm 2^{\circ}\text{C}$ drift over the duration of the experiment was measured at each location	8



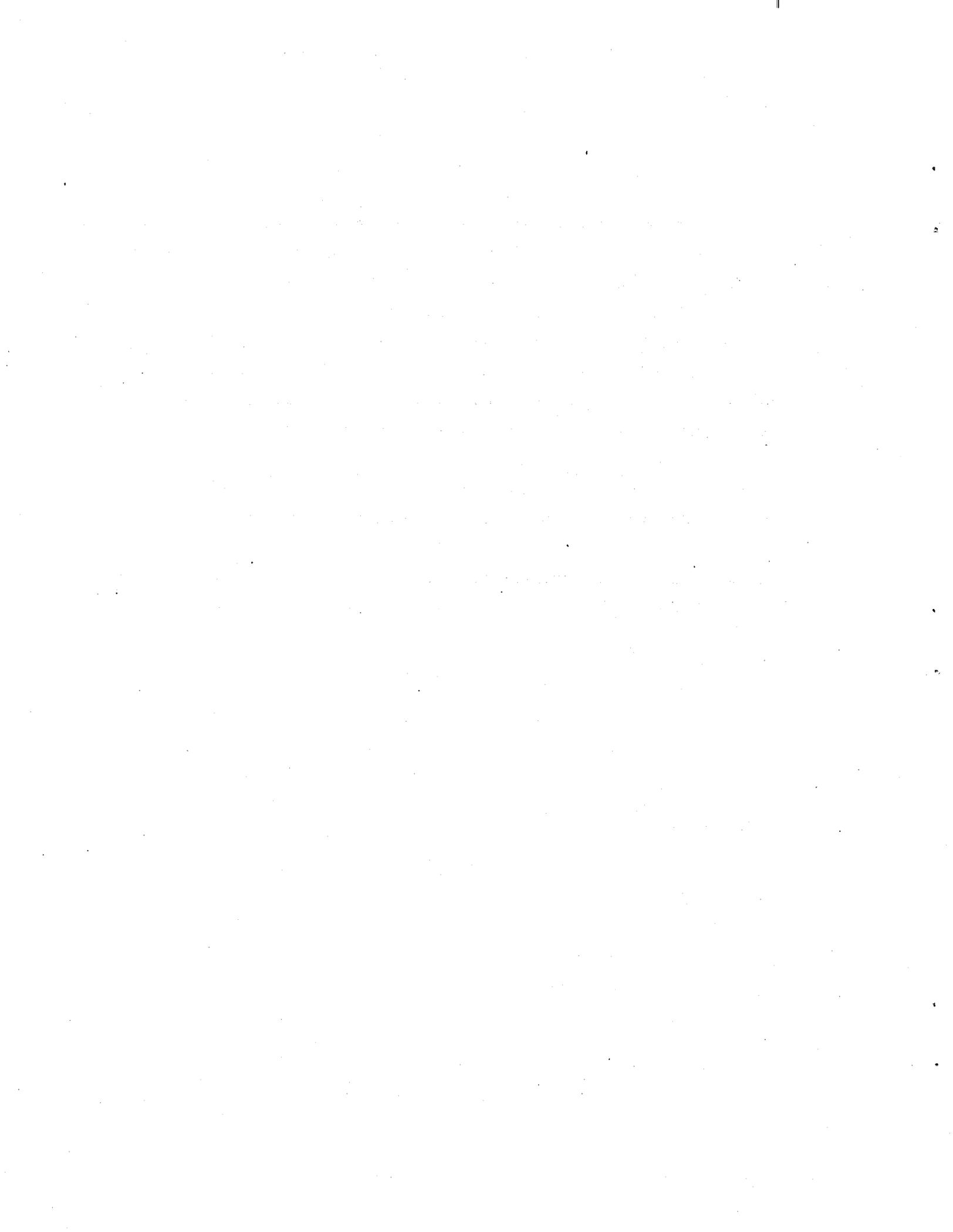
FIGURES

Figure	Page
1 Schematic of the thermal convection loop design used for these experiments. The approximately horizontal sections are about 1 m apart and the vertical sections are about 0.5 m apart	3
2 Detailed design (dimensions in mm) of reduced section in the TCLs	5
3 Small specimen design (dimensions in mm) which was used for most coupons in these TCL experiments	6
4 Post-test appearance of specimens from TCL #8. At left, specimens from the hot leg exhibit some apparent wetting. At right, specimens from the cold leg exhibit little wetting	11
5 As-polished cross-sections from specimen #7 from the cold leg of TCL #7 after 2000 h exposure. Left: appearance of the general surface. Right: appearance of the hole region	17
6 As-polished cross section of sensitized specimen exposed to Hg. (Specimen 7 from TCL #8.) Left: cross-section of hole region. Right: close-up of hole region (view rotated)	18
7 Etched (electrolytic oxalic acid) cross section of sensitized 316L specimen fabricated by EDM process. Adjacent to hole area (at right), ditch structure reveals extensive carbide precipitation several grains deep. Along the specimen profile (general surface, at left), step structure indicates sparse carbide precipitate	19



ABSTRACT

Two 316L thermal convection loops (TCLs) containing several types of 316L specimens circulated mercury continuously for 2000 h at a maximum temperature of 300°C. Each TCL was fitted with a venturi-shaped reduced section near the top of the hot leg for the purpose of locally increasing the Hg velocity. Results suggest that an increase in velocity from about 1.2 m/min (bulk flow) to about 5 m/min (reduced section) had no significant impact on compatibility of 316L with Hg. In addition, various surface treatments such as gold-plating, chemical etching, polishing, and steam cleaning resulted in little or no influence on compatibility of 316L with Hg when compared to nominal mill-annealed/surface-ground material. A sensitizing heat treatment also had little/no effect on compatibility of 316L with Hg for the bulk specimen, although intergranular attack was observed around the specimen holes in each case. It was determined that carburization of the hole area had occurred as a result of the specimen fabrication process potentially rendering the specimens susceptible to corrosion by Hg at these locations. To avoid sensitization-related compatibility issues for SNS components, selection of low carbon grades of stainless steel and control of the fabrication process is recommended.



1. INTRODUCTION

The Spallation Neutron Source (SNS) will generate neutrons via interaction of a 1.0 GeV proton beam with a liquid mercury target. Type 316L/316LN austenitic stainless steel (SS) has been selected as the primary target containment material¹ based on a favorable combination of several factors, including resistance to corrosion by Hg, well characterized behavior in a radiation environment, and the absence of a significant ductile-brittle transition temperature such as that found in irradiated ferritic stainless steels.

The energy deposited in the target by the proton beam (design basis is 2 MW) will be removed by circulating the mercury through standard heat exchangers. Various fluid dynamics computations and simulations of conditions expected in the target predict maximum bulk mercury temperatures on the order of 150°C with nominal temperatures closer to 100-120°C. The mercury temperature at the target inlet is expected to be near ambient temperature.

As a result of the temperature gradient in flowing Hg, one of the potential compatibility problems under investigation is thermal gradient mass transfer. In this form of corrosion, dissolution of the container material by the liquid in relatively high temperature (high solubility) regions is accompanied by deposition of solute in relatively colder regions.² As a result, corrosion of the high temperature region is potentially accelerated over what would be experienced in an isothermal/stagnant system. In addition, in the cold regions, deposition of solute material has been known to cause flow disruptions and can even plug flow paths in liquid metal loops.³ Among the major alloying elements of stainless steels, nickel is expected to have the highest solubility in mercury⁴ at SNS operating temperatures, and therefore this element may be the most susceptible to mass transfer.

At temperatures below about 250°C, pure mercury does not readily wet 316/316L stainless steel. Without chemical wetting (characterized macroscopically by a low contact angle), any potential corrosion process is inhibited. However, mercury can be made to wet 316/316L in air or vacuum by raising the temperature to 225-275°C.⁵ Despite the relatively low expected operating temperatures, chemical wetting of containment surfaces may occur in the SNS target as a result (or combination) of several factors:

1. the presence of thermal hot spots,
2. radiation damage in the presence of Hg, and
3. generation of fresh (oxide-free) surfaces that result from potential cavitation and thermal shock/fatigue loading to which the target containment material will be exposed.

To examine potential "worst case" corrosion, it is desirable to develop wetting in the tests for material compatibility with mercury. Previous 316L/316LN compatibility experiments for the SNS target station^{6,7} utilized thermal convection loops (TCLs) with relatively high peak temperatures (near 300°C) to encourage wetting. In the initial TCL experiment,⁶ coupon wetting and weight loss proved to be a strong function of temperature, with coupons exposed to pure Hg above 250°C exhibiting the development of a porous surface layer substantially depleted of Ni and Cr. Coupons exposed at lower temperatures revealed no interaction with the Hg (no change in weight, appearance, or microstructure). Analysis of the weight loss data as a function of temperature in the TCL indicated that the rate controlling step in the corrosion/dissolution process has a very low activation energy.⁶ In combination with the lack of a gradient of Cr and Ni in the depleted zone, this suggested control by solute diffusion in the saturated liquid boundary layer adjacent to the corroding surface as opposed to solid state diffusion of solute to/across the solid/liquid boundary. This latter observation suggests that corrosion of the 316L target container could be sensitive to Hg velocity. Since mercury velocity in the SNS target is expected to be near 2 m/s, a velocity effect on corrosion could be important. To examine this possibility, the standard TCL design was modified to include a venturi-shaped restricted section to locally increase the Hg velocity by a factor of about five compared to that achieved in previous tests. This document describes the operation of these TCLs and the results obtained.

2. EXPERIMENTAL

2.1 LOOP FABRICATION

A schematic of the TCL design is shown in Fig. 1. Each TCL in this study was fabricated of mill annealed 316L seamless tubing (25.4 mm ID, 1.8 mm wall) with the composition shown in Table 1. The thermocouple wells, which protruded about halfway into the flow channel, were also seamless, mill annealed 316L tubing (6.4 mm OD, 0.7 mm wall). The valves and a few other metallic accessories (connectors, transfer lines, etc) were 316 or 316L stainless steel.

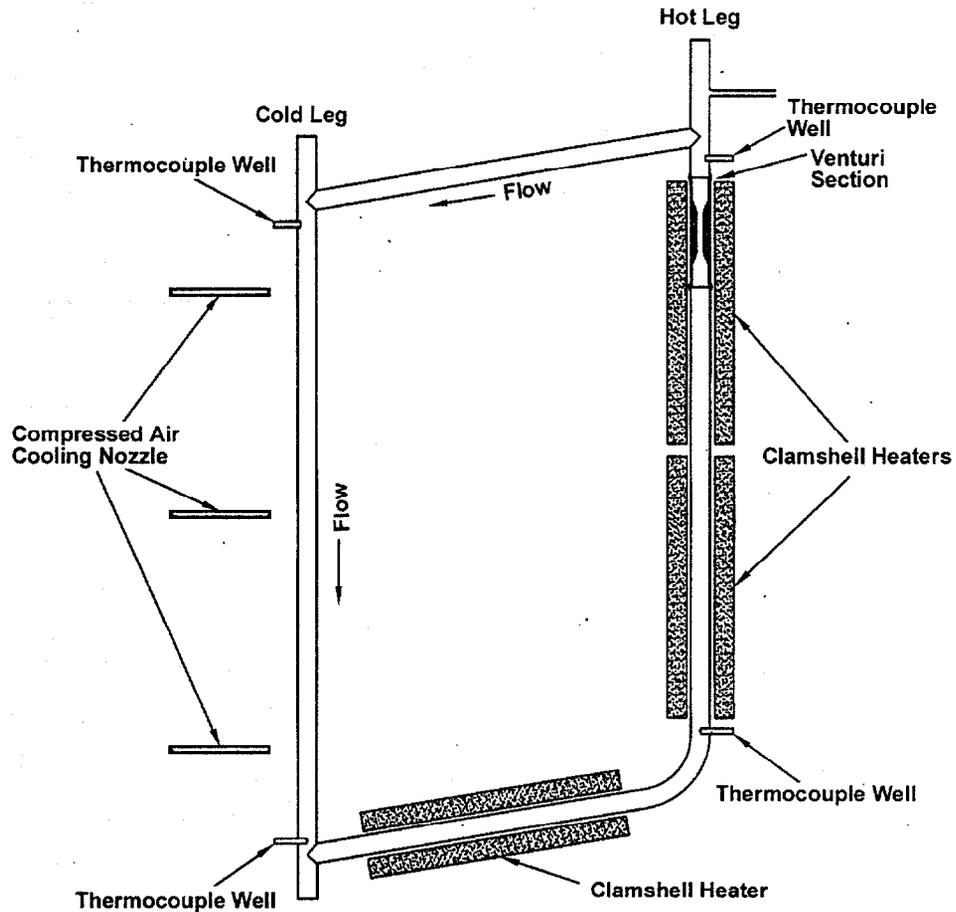


Fig. 1. Schematic of the thermal convection loop design used for these experiments. The approximately horizontal sections are about 1 m apart and the vertical sections are about 0.5 m apart.

**Table 1. Composition (weight percent) of 316L loop components and specimens.
Values taken from mill certifications.**

Element	Small specimens	Tubing	Venturi section	Large specimens
C	0.010	0.03	0.024	0.022
Si	0.35	0.46	0.55	0.48
Mn	1.41	1.30	1.83	1.82
P	0.027	0.039	0.030	0.022
S	0.028	0.005	0.0003	0.002
Cr	16.67	16.27	16.24	16.05
Ni	11.11	12.16	10.19	10.11
Mo	2.28	2.06	2.12	2.08
N	0.079		0.04	0.04

The heated vertical leg of the TCL (typically termed the “hot leg”) was modified to include a venturi-shaped flow path designed to locally increase the Hg flow velocity. The detailed design of the reduced section is shown in Fig. 2. Several different combinations of maximum and minimum diameters, reduced section lengths, and transition profiles were tested using a glass thermal convection loop with water (with about 20% antifreeze) as the working fluid operating with about a 50-60°C temperature gradient. Fluid velocities in the glass loop were confirmed by monitoring the progress of small suspended particles in the water/antifreeze mixture, and the most successful reduced section (generated the highest local velocity without impeding overall loop flow) was implemented in the stainless steel TCLs. Compared to the flow in the bulk of the loop, the velocity increase in the reduced section for this design was a factor of approximately five, and included a significant amount of turbulence at each of the inlet and outlet sections.

Each TCL in this experiment contained a chain of 316L specimens in each of the hot leg and the cold leg (the cooled vertical section). Due to the dimensions of the reduced section in the hot leg, specimens for the hot leg were significantly smaller than those used in previous tests^{6,7} and were fabricated from a different heat of 316L material than that previously used. To permit easy comparison, specimens for the cold leg chain also used the smaller specimen design (even though there was no reduced section that required this decision). Each specimen chain consisted of 28 small coupons and two of the “standard” large size coupons joined together with small pieces of 316 stainless steel wire (about 0.4 mm diameter) via the holes in each end of the specimens. The wire attached to the bottom specimen in each chain was welded to the bottom of the respective vertical sections to keep the chains from floating to the top of the Hg and positioned such that the top and bottom of the chain corresponded approximately to the

thermocouple well positions in each leg. The small specimen dimensions are shown in Fig. 3 and the composition of these is given in Table 1.

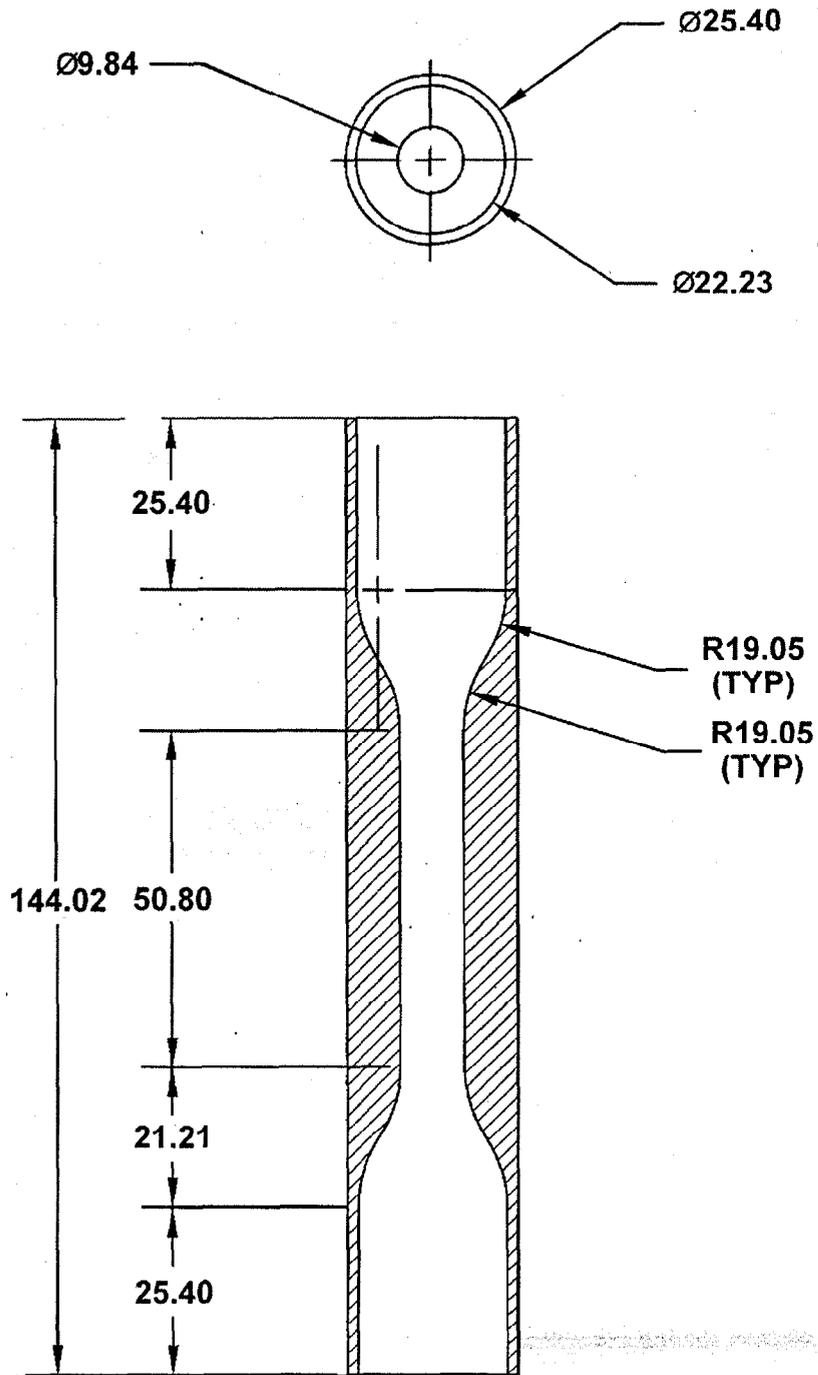


Fig. 2. Detailed design (dimensions in mm) of reduced section in the TCLs.

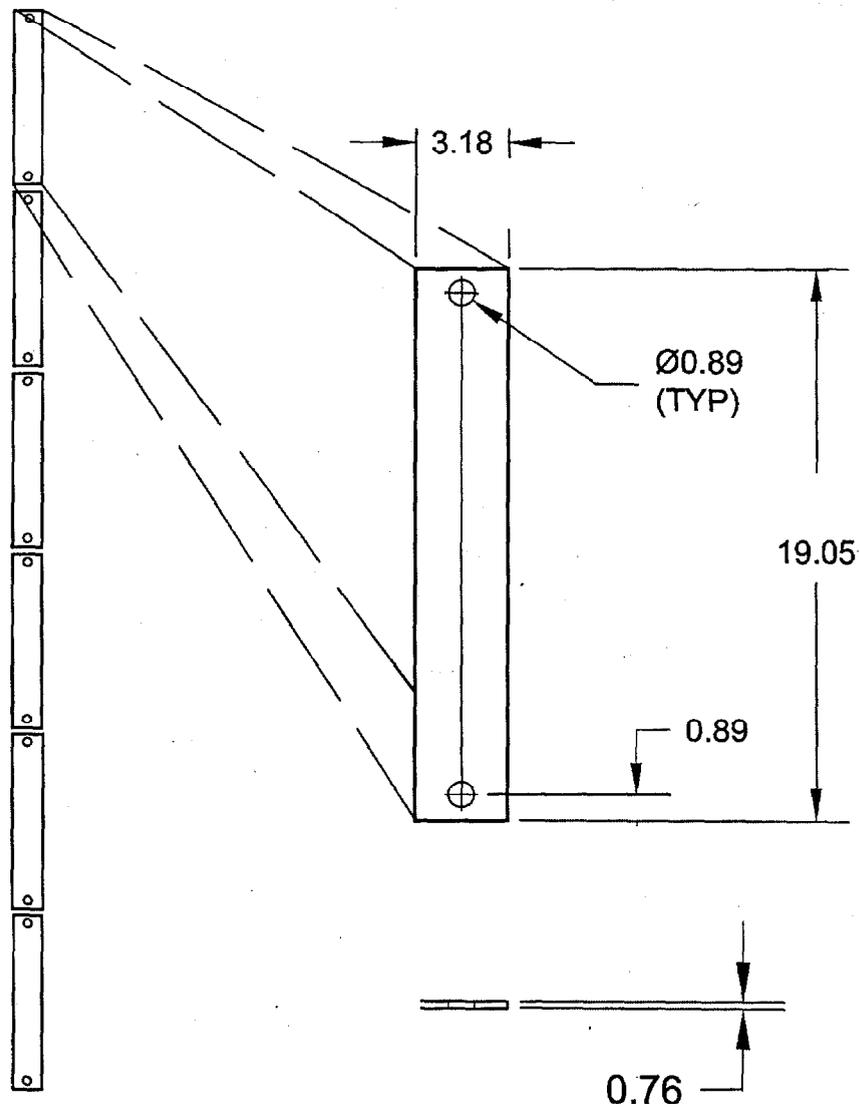


Fig. 3. Small specimen design (dimensions in mm) which was used for most coupons in these TCL experiments.

Most of the specimens on each chain were exposed in the standard mill-annealed/surface-ground condition. However, in order to examine potential sensitivity to wetting, two specimens representing each of the following conditions were exposed at specific locations in each of the hot leg and cold leg:

1. gold coated specimens: both sides of these mill-annealed/surface-ground coupons were sputtered with Ar^+ in a high-vacuum chamber to remove the oxide film, then

sputter coated with gold to a thickness of approximately 0.6 μm in the same chamber without readmitting air.

2. polished specimens: one side of these otherwise mill-annealed/surface-ground specimens was polished through 1200-grit polishing paper.
3. etched specimens: these mill-annealed/surface-ground specimens were immersed in a 40% reagent grade sulfuric acid solution at 75°C for about six minutes; the black “smut” that formed on the specimens was removed by ultrasonic cleaning in acetone.
4. sensitized specimens: these mill-annealed/surface-ground specimens were sealed in glass tubes with a small partial pressure of helium and heated 20 h at 650°C; subsequently, they were lightly pickled to remove the slight surface tarnish.

The specimens in each chain were individually numbered, cleaned ultrasonically in acetone, and weighed (before and after each “treatment”) prior to assembly of the chain. All specimens were handled with gloves and tweezers during the stacking and wiring activities.

Prior to fabrication of the TCLs, the ID of the 316L tubing was mechanically and chemically cleaned to remove fabrication debris and to make the ID surface as smooth and uniform as possible. Mechanical cleaning of the tube ID was accomplished with a 302 SS bristle brush attached to an extended rod and powered by a standard hand drill. Subsequently, tube sections were capped with rubber stoppers and each tube section was filled with a pickling solution (10% nitric acid and 3% hydrofluoric acid in water, ambient) for about 10 minutes at room temperature. Following this treatment, the required cutting and bending of the tubes (tubing filled with a very soft Bi-In-Sn alloy to prevent tube collapse) was performed and the tubing was rinsed with alcohol and air-dried.

Following fabrication, specimen placement, and final assembly, the loops were filled with methanol as a final leak check. One of the TCLs (#7) was operated with no additional “cleaning” steps included in the pre-operational activities, while the other TCL in the experiment (#8) was identical except that a steam treatment (20 minutes of 25 psi steam flowing in one end of loop with condensate collected at the other end) was included in the loop preparation.

2.2 FILLING WITH MERCURY

Each loop was alternately evacuated (internal pressure of a few microns of mercury) and filled with helium several times. Subsequently, the loop was evacuated and filled with mercury from the reservoir at the top (the ullage of which was also evacuated/purged with helium). Approximately one atmosphere of helium was used as a cover gas for the mercury in the loop.

The loop was warmed to near operating temperature and the excess mercury (expanded above fill line at room temperature) was drained off through a side arm of the loop.

Virgin mercury from the same batch as that used for the previous 316L SS loops^{6,7} was used for these experiments. Standard chemical analysis of representative samples indicated the Hg was quite pure, containing only about 85 ppb Ag and 100 ppb Si above detection limits. Immediately prior to use in the loops, the Hg was "filtered" through cheesecloth to remove the small amount of residual debris (oxides) floating on the surface of the Hg.

2.3 LOOP OPERATION

Generally, the heat-up and operation of the TCLs was identical to that reported previously⁶ for 316L SS TCLs. Clamshell-type heaters were placed on the vertical leg (two heaters) and on the near-horizontal lower portion of the loop (one heater) for long term operation. The control temperature of the lower heater was kept somewhat below the temperature of those on the vertical hot leg to help maintain the mercury flow pattern. The vertical section of each cold leg was cooled by compressed air delivered from three roughly equi-spaced copper tubes with outlets placed close to the outer loop surface and an array of small fans providing air movement across the entire cold leg. After a day or so of heater temperature and airflow adjustments, the temperature at each thermocouple well position and the mercury flow rate became quite stable. The temperature at each location varied only by about $\pm 2^\circ\text{C}$ over the entire 2000 h duration of the experiments. (The only interruption was a 2-h loss of electrical power to each loop.) Table 2 compares temperatures at each thermocouple well for these TCLs with the same data for TCL #1.⁶

Table 2. Nominal temperatures at each "corner" of the thermal convection loops described here along with equivalent data for TCL #1 (a previous 316L TCL). Approximately a $\pm 2^\circ\text{C}$ drift over the duration of the experiment was measured at each location.

	TCL #7 ($^\circ\text{C}$)	TCL #8 ($^\circ\text{C}$)	TCL #1 ($^\circ\text{C}$)
Bottom of hot leg	264	263	268
Top of hot leg	304	302	305
Top of cold leg	278	275	280
Bottom of cold leg	234	230	242
Nominal temperature gradient (maximum to minimum)	70	72	63

The overall average flow rate of the mercury inside the loop was determined via a localized "temperature spike" test. In this test, a propane torch was used to heat a small area in the middle of the roughly horizontal section at the top of the loop for about 15 seconds. The time required for the resultant temperature "spike" to reach each thermocouple in sequence around the loop along with the distance between thermocouples was used to estimate the velocity of the mercury. The overall mercury flow rate was found to be approximately constant at 1.2 m/min in each loop (same as for previous experiments). As estimated by the experiments with water in the glass loop, the flow rate in the reduced section was presumed to be about 5 m/min.

3. RESULTS AND DISCUSSION

3.1 GENERAL VISUAL ASSESSMENT

Each TCL was terminated after 2000 h of essentially uninterrupted operation (each loop suffered a 2-h power disruption). Following about an hour of cooling, the mercury was drained from each loop through the valve at the bottom of the cold leg. In each case, the Hg appeared clean and shiny, and only a trace of oxide-like debris was observed on the last few drops of Hg to dribble from the drain.

The wires retaining each specimen chain were cut near the weld joint attaching it to the tube (using a rotary saw to cut the tube and wire-weld) and the chains were carefully lifted from the TCLs. For both loop #7 (no steam treatment) and loop #8 (steam treatment), post-test visual assessment indicated at least localized wetting over significant portions of the specimens in each hot leg. (Specimens from the cold leg in each TCL revealed little or no wetting.) A representative example of this observation appears in Fig. 4, which shows a group of specimens removed from TCL #8. It has been a consistent observation in this research effort that even when wetting of stainless steel surfaces by Hg has occurred (as evidenced by adherent Hg with a low contact angle), extended exposure of the wetted surfaces to air at temperatures below about 250°C causes the Hg film to bead (become spherical droplets with high contact angle and little adherence). Thus, it is likely significant that the degree of apparent wetting observed on the surfaces shown in Fig. 4 was after the specimens were handled in room temperature air for several hours. This suggests that the coupon surfaces in the hot leg were indeed wet by the Hg during the TCL exposure and that, at least based on visual comparison of “wetting” for TCL #7 and #8, the steaming treatment for TCL #8 was not necessarily significant to the wetting process.

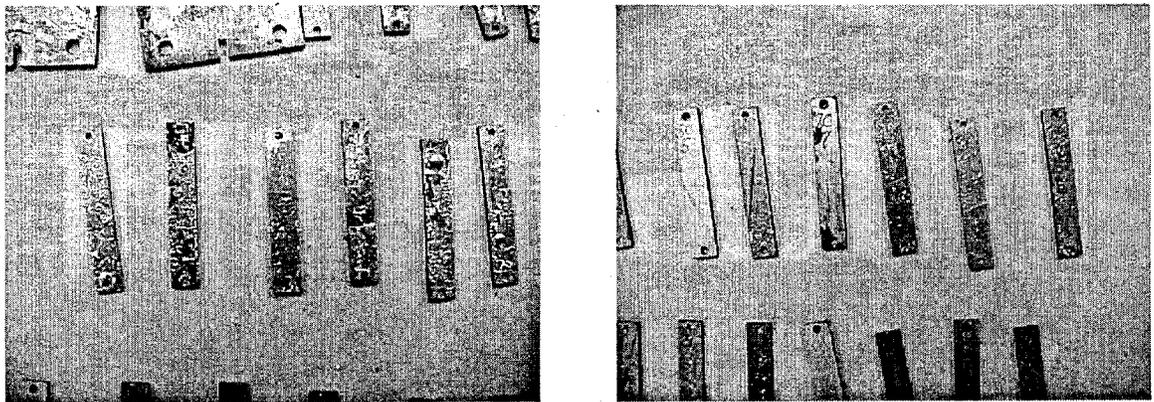


Fig. 4. Post-test appearance of specimens from TCL #8. At left, specimens from the hot leg exhibit some apparent wetting. At right, specimens from the cold leg exhibit little wetting.

3.2 WEIGHT CHANGE AND METALLOGRAPHY

Following initial post-test photography, each coupon was lightly wiped to remove residual Hg, then cleaned ultrasonically in acetone, air dried, and reweighed. Generally speaking, the 316L coupons were quite resistant to Hg at all positions in the TCLs, as evidenced by very small weight changes and metallographic examination indicating no surface roughening or attack. A few minor exceptions were observed, however, and where possible, trends which differentiate coupon behavior as a function of Hg velocity (reduced section or not), pretreatment (e.g., TCL #8 had steam and TCL #7 did not), temperature, or coupon surface condition will be highlighted.

3.3 NOMINAL 316L COUPONS

As for previous experiments, the role of the nominal (mill-annealed, surface-ground) 316L coupons was two-fold: first, to function as near-neighbor "control" specimens for the other coupons with a range of surface/structure variations and, second, to permit comparison with previous coupon data from similar TCL experiments.

In the hot leg of TCL #7, 15 of 20 small nominal specimens (and both larger specimens) revealed a very small weight gain (< 0.2 mg) over the duration of the experiment. Of the other five nominal coupons, three revealed a very small weight loss (< 0.2 mg) and two (both from the bottom of the hot leg) revealed a slightly larger weight loss (up to 0.7 mg). None of the nominal 316L coupons revealed a change in surface roughness or microstructure compared to the virgin (unexposed) coupon condition. Compared with data from the original TCLs,¹ a weight loss of 0.7 mg (adjusted for surface area and assuming linear change with exposure time) corresponds to about 65% of the largest weight loss rate previously observed (and for which a 10-12 μm ferrite layer depleted in Ni and Cr developed). For the conditions in TCLs #7 and #8, however, this rate/extent of weight loss was insufficient to develop any changes in surface roughness, microstructure, or coupon thickness over the duration of the experiment.

Three small specimens fit inside the reduced section at the top of the hot leg in TCL #7, and two of these were nominal 316L coupons. Neither the nominal specimens in the reduced section (Hg velocity near 5 m/min) nor the nominal specimens just below the reduced section (Hg velocity closer to bulk value of 1.2 m/min) exhibited measurable weight change. In addition, there was no difference in appearance between the coupons exposed at these two locations. As a result, at least for the conditions encountered in TCL #7, it would appear that Hg velocity in this range is not a significant factor in the compatibility of 316L with Hg.

In the cold leg of TCL #7, all 20 of the small nominal specimens (and both large coupons) exhibited a small weight gain (typically about 0.6 mg, but one specimen gained 1.1 mg). The source of the weight gain is not obvious, as microstructural examination of these coupons revealed no change in surface roughness or any detectable film/deposit (in cross-section with light microscopy) on the specimens. Most of the specimens exhibiting a small weight gain were observed to have a pale blue/green hue after the exposure (rather than the metallic silver/gray color of the virgin specimens) which suggests a very thin film. Formation of a uniform oxide film of 0.5 μm thickness over the entire surface of the specimen during exposure could account for approximately a 0.4 mg weight gain for the small specimens used in this investigation. After the post-test specimen cleaning, tiny beads of Hg occasionally were found clinging to the rough surfaces in the specimen holes, but these were found to contribute negligible weight changes (and were removed with subsequent cleaning effort). That small weight losses were much more prevalent for TCL #8 compared to TCL #7 (see below) could be related to some aspect of the steam treatment received by specimens in TCL #8. Potentially, the steam-cleaned specimens were rendered slightly more susceptible to wetting or reaction with Hg, but the mechanism of such behavior is not clear.

In the hot leg of TCL #8, only the two large nominal specimens at the top of the loop exhibited a tiny (<0.2 mg) weight gain. Of the 20 nominal small specimens, 16 revealed a weight loss of less than 0.2 mg. Only four lost more weight (0.6-0.8 mg), and these were located in positions with relatively high (297°C) as well as relatively low (264°C) temperatures. Like the specimens with the highest weight loss in the hot leg of TCL #7, the specimens with the highest weight loss in TCL #8 remained largely smooth and free of metallographic changes which could indicate significant interaction with Hg.

The small nominal specimens in the reduced section in the hot leg of TCL #8 revealed essentially no weight change, while those in the bulk flow just below the reduced section were among the highest weight loss specimens. Clearly, the increased velocity in the reduced section was not a factor detrimental to the compatibility of nominal 316L with Hg for the conditions imposed in this loop.

In the cold leg of TCL #8, no weight gains greater than the scatter of the measurement were observed among the nominal specimens, and none exhibited a weight loss greater than 0.2 mg. Metallography of representative coupons revealed no sign of attack as a result of the 2000 h exposure.

3.4 GOLD-COATED COUPONS

Since an air-formed passive film on stainless steel can be a significant barrier to chemical wetting by Hg, a small number of nominal (mill-annealed, surface-ground) specimens were coated (both sides) with gold in an attempt to promote wetting of the stainless steel. In principle, sputtering of the stainless steel surface in a high vacuum chamber with Ar⁺ ions removed the oxide film from the surface of the material. Following sputtering to clean the surface, with the specimen still in the same chamber free from exposure to air, the coupon was rotated to a position in which a thin film of gold could be sputter-coated onto the exposed stainless steel surface. The gold-coated specimens could then be handled in air (removed from the chamber, added to the coupon chain, exposed to Hg) while maintaining the oxide-free nature of the surface beneath the gold. By depositing the gold in this fashion – directly onto an atomically cleaned surface rather than onto an oxide – it was expected that upon exposure, Hg would rapidly amalgamate the Au and place a large area of oxide-free stainless steel surface into direct contact with Hg.

The sputter-coating process to deposit gold was performed for the same length of time for each specimen. Weight change measurements following the cleaning and gold deposition activity indicate the process was very uniform, with the range of weight changes due to gold addition from 1.5 to 1.8 mg for all eight coupons used in this investigation. Using the surface area of the small coupons and the mass of gold added, the average thickness of the gold film was estimated to be approximately 0.6 μm for all the coated specimens. This is approximately twice the gold thickness applied to specimens tested previously.⁷

In the hot leg of each loop, gold-coated specimens were placed in the center of the reduced section (position 4; temperature about 300°C; nominal coupons on either side) and just below the transition to the reduced section (position 8; nominal coupons in positions 6 and 9). In the cold leg of each loop, a gold-coated coupon was placed near the top (position 2, temperature near 275°) and near the bottom (position 27, temperature near 237°C). (For reference, position 1 is at the top of each vertical section.)

In the hot leg of TCL #7, each of the gold-coated coupons lost the same weight as the mass of gold added. This result indicates that the gold was readily amalgamated by the Hg, but no further interaction occurred between these coupons and the Hg. The absence of an interaction was confirmed by cross section metallography indicating no change in surface roughness, no porosity, and no microstructure gradient. Consistent with the indication from the nominal coupons, this result also indicates the velocity difference between position 4 (about 5 m/min) and position 8 (about 1.2 m/min) is not significant in terms of compatibility.

In the cold leg of TCL #7, the gold-coated specimens behaved similarly to those in the hot leg. However, the coupon at the bottom of the cold leg lost 0.2 mg in addition to the mass of gold applied. Coupon metallography confirmed only smooth, porosity-free surfaces for these coupons.

In the hot leg of TCL #8, the gold-coated coupon in the reduced section lost 0.58 mg more than the mass of gold applied, and the gold-coated specimen just below the reduced section lost 0.42 mg more than the mass of gold applied. As stand-alone information, this result suggests that the higher velocity in the reduced section slightly increases dissolution of the stainless steel. However, analysis of the other nearby coupons indicates slightly higher weight losses for nominal specimens located just below the reduced section compared to those in the reduced section. While it could be argued that the gold-coated specimens were more likely to be chemically wetted by the Hg and therefore the mass loss they represent is more significant to a study of compatibility, velocity remains a small factor in any case. In each case, no evidence of surface roughening or porosity development was observed for the gold-coated specimens.

In the cold leg of TCL #8, the gold-coated coupon at the relatively high temperature lost the mass of gold applied and an additional 0.4 mg, while the one at relatively low temperature lost only the weight of gold applied. In both cases, metallographic analysis did not yield any indication of significant interaction with Hg.

3.5 POLISHED COUPONS

The typical surface roughness of the surface-ground coupons used in these experiments is about 0.8 μm (32 microinches). Limited testing in a previous experiment⁷ did not indicate that polishing significantly influences wetting/interaction with Hg in the TCL experiments. However, in order to continue to collect data to address this issue, a limited number of specimens were polished on one side through 1200-grit to approximately a mirror finish and included in this investigation. Polished specimens were placed in position 12 (about 289°C) and position 25 (about 270°C) in each hot leg and at positions 9 (about 265°C) and 21 (about 247°C) in the cold leg of each loop.

In each case, the polished specimens exhibited a weight change identical (within scatter of the measurement) to the nominal specimens on either side of it in the coupon chain. In the case of TCL #7, the result was no weight change in the hot leg and a modest weight gain in the cold leg. For TCL #8, all four polished coupons lost a tiny amount of weight (<0.15 mg) as did the near-neighbor coupons with standard surface finish. Once again, the comparison of polished

and surface-ground specimens indicates that polishing to reduce surface roughness neither significantly enhances nor inhibits wetting/interaction for the conditions examined in these TCLs.

3.6 ETCHED COUPONS

Etching in 40% sulfuric acid at 70°C is an aggressive treatment used for plating baths and related activities to remove the passive film from many stainless steels. After a few seconds exposure to this treatment, typical stainless steel surfaces violently evolve hydrogen from the surface (reduction of the oxide film) and accumulate a dark, lightly adherent smut that is a combination of several iron sulfides and related corrosion products. Although this treatment previously provided only sporadic success in generating apparent wetting/clinging of Hg on stainless steel surfaces,^{5,7} it was utilized here to further gage its utility as a potential aid to wetting in long term Hg exposure tests. Specimens were soaked six minutes in the above solution, then rinsed and ultrasonically cleaned in acetone to remove the smut (leaving a light golden brown tarnish). Subsequent exposure to air re-established a passive film, but perhaps at a slightly reduced Cr-content (and a slightly rougher surface) compared to that present prior to etching. Etched specimens were placed at positions 10 (about 291°C) and 23 (about 274°C) in each hot leg and positions 7 (268°C) and 19 (250°C) in each cold leg.

Post-test examination of the etched specimens indicates some white/gray splotches on/in the tarnish film produced by etching the surface that are not generally present on other coupons with different surface finishes. With only one exception, each etched specimen exhibited a very small weight change essentially identical to that of the nominal specimens on either side in the specimen chain. The exception was the etched coupon near the top (position 7) of the cold leg in TCL #7. The weight loss for the specimen was very large (9.47 mg) – about 12 times that of the next largest weight loss in the entire experiment. On a mass loss per unit area and time basis, this corresponds to a value almost ten times the largest seen in any of these experiments (coupons at the top of TCL #1).⁶ Interestingly, all the other coupons in the cold leg of TCL #7 (except for one near the bottom) gained weight.

Metallographic examination of the etched coupon with a large weight loss revealed a slightly roughened bulk surface (similar to what might result from modest general corrosion) but extensive attack similar to pitting and some grain dropping was observed near the specimen holes. Representative photographs appear in Fig. 5. However, a similar appearance was observed for the other etched specimens (which did not indicate a weight loss). More discussion will be provided in the section on sensitized specimens, but the conclusion here is that the combination of the condition of the material around the holes (slightly carburized) and the

etching procedure (aggressive to carburized material) led to significant attack in the hole area prior to exposure in the TCLs. In the specific case of the specimen at position 7 in the cold leg, a piece (or pieces) of material from the damaged area may have been dislodged during the test contributing to significant weight change. Generally speaking, however, it appears the etching procedure (at least as employed here) is not effective for improving wetting and has no effect on the performance of 316L in the Hg TCL conditions that were used in this test.

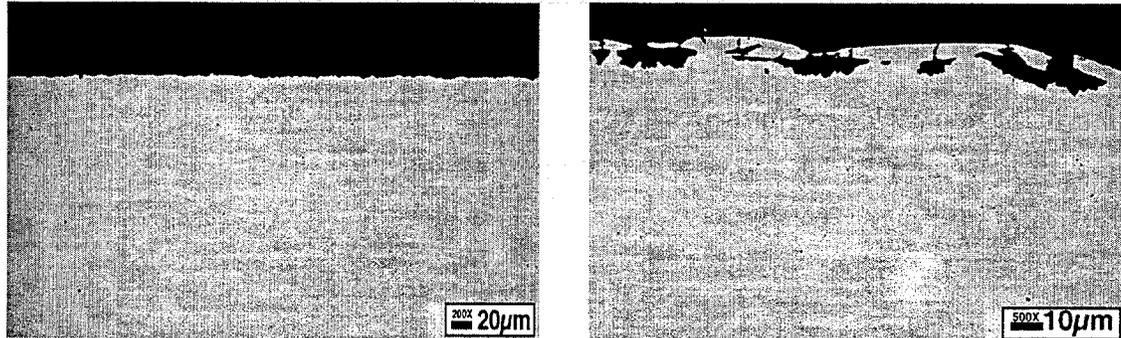


Fig. 5. As-polished cross-sections from specimen #7 from the cold leg of TCL #7 after 2000 h exposure. Left: appearance of the general surface. Right: appearance of the hole region.

3.7 COUPONS WITH A SENSITIZING HEAT TREATMENT

In a solution treated (sometimes called annealed) austenitic stainless steel such as 316/316L, the material has been quenched from a high temperature (about 1100°C) in order to keep alloying elements uniformly distributed and, in particular, retain the carbon content in solution. If such material is reheated into the temperature range of 500-900°C (typically due to welding or stress relief treatments, or during elevated temperature service), precipitates tend to form on grain boundaries in the material. These precipitates are very rich in chromium and tend to significantly deplete the surrounding matrix in chromium. As a result, the regions adjacent to grain boundaries may be sufficiently depleted in Cr that passivity cannot be maintained in a number of environments (leading to intergranular corrosion along these paths). Since previous work⁶ showed that Hg has some affinity for leaching Cr from 316L stainless steel wetted by Hg, the potential for attack on a Cr-rich phase such as chromium carbides was deemed worthy of investigation. (In addition, enhanced wetting of Cr-depleted areas is a possibility.) While “L” grades of stainless steel are generally resistant to the formation of continuous networks of grain boundary precipitate, relatively long heat treatments in the critical temperature range can cause these carbides to form, and a material in this condition is termed sensitized.

To examine potentially sensitized microstructures in Hg, the standard 316L coupons were heat treated for 20 h at 650°C in vacuum (to limit oxidation of the surface). After heat treatment, the specimens were briefly pickled (deionized water with 10% nitric acid with 3% hydrofluoric acid, 2 minutes at ambient) to remove the very light tint resulting from heat treatment in less than a perfect vacuum. (The pickling treatment generated a surface only slightly dull gray compared to the nominal shiny gray surface of the standard specimens.) Heat treated specimens were placed at positions 7 (about 296°C) and 21 (about 276°C) in the hot leg of each loop and at positions 5 (about 272°C) and 17 (about 253°C) in the cold leg of each loop.

The heat treated specimens generally were found to be a dark golden brown after Hg exposure rather than the dull gray of most of the other specimens. In terms of weight change, the heat treated specimens generally behaved very similarly to the nominal near-neighbor specimens in each chain. Two minor exceptions were the heat treated specimens from the cold leg of TCL #8; each of these revealed a modest weight loss (about 0.5 mg – approximately the same as for heat treated specimens in the hot leg of this loop) while the near-neighbor specimens revealed essentially no weight change. However, post-test metallographic examination of all the heat treated coupons exposed to Hg revealed pronounced intergranular attack around the hole areas of each specimen. The remainder of the coupon surfaces exposed to Hg remained relatively smooth and unchanged from the virgin coupon condition. Figure 6 contains representative examples of intergranular penetration at the holes of the heat treated specimens. No other coupon types from this investigation revealed intergranular attack (near the holes or anywhere else). Heat treated specimens not exposed to Hg revealed heavy carbide precipitation near the holes (Fig. 7). Only minor carbide precipitation was observed over most of the heat treated specimens, however, confirming the utility of “L” grade material to resist carbide precipitation.

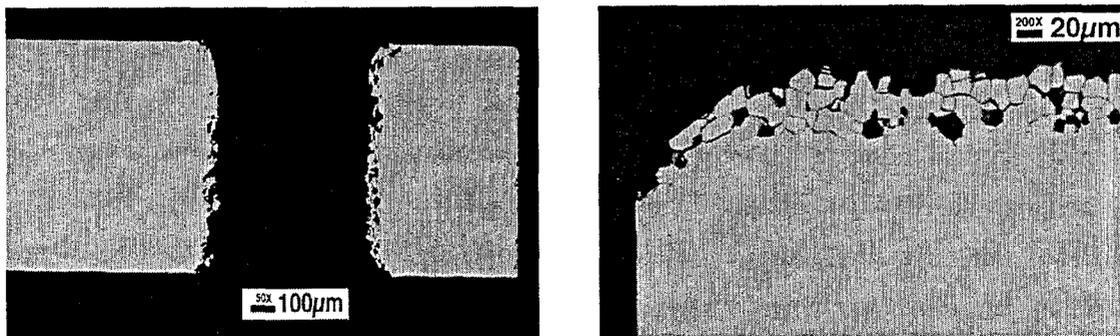


Fig. 6. As-polished cross section of sensitized specimen exposed to Hg. (Specimen 7 from TL #8.) Left: cross-section of hole region. Right: close-up of hole region (view rotated).

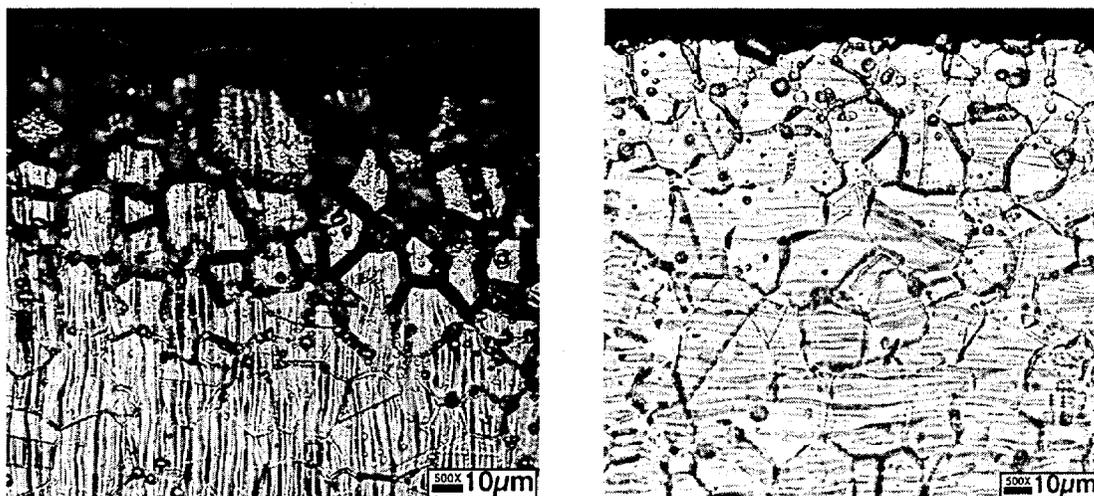


Fig. 7. Etched (electrolytic oxalic acid) cross section of sensitized 316L specimen fabricated by EDM process. Adjacent to hole area (left), ditch structure reveals extensive carbide precipitation several grains deep. Along the specimen profile (general surface, at right), step structure indicates sparse carbide precipitate.

3.8 ADDITIONAL TESTING OF COUPONS WITH SENSITIZING HEAT TREATMENT

At face value, the fact that the entire specimen was heat treated, yet only the material immediately adjacent to the holes exhibited intergranular attack as a result of Hg exposure, suggested that the residual stress field around the holes was a contributing factor. To test that concept, a fixture was built to plastically deform the small flat specimens into a standard “U-bend” configuration for exposure to Hg. The specimens were retained in the U-bend configuration (to maximize plastic plus elastic tensile stresses on the outer surfaces at the apex of the bend) by placing the parallel ends of the “U” into small pieces of type 316L stainless steel tubing of the appropriate inside diameter. Each tube was tack welded to a plate which was then floated (specimen side down) in glassware containing Hg and about an atmosphere of helium.

Specimens in several conditions were exposed to Hg at 300°C for 200 h:

1. as-received (solution treated) specimens in U-bend with no further treatment
2. heat treated (20 h 650°C), then fabricated into U-bend configuration
3. fabricated into U-bend configuration, then heat treated (20 h, 650°C).

None of the U-bend specimens so exposed revealed any significant weight change (none greater than ± 0.05 mg), any discoloration, or any cracking in the bend area. However, each of the specimens that had been heat treated [types (b) and (c) above] again revealed intergranular corrosion/cracking several grains deep around each specimen hole. This result indicated that the

residual stress around the holes was not the principal factor in the observed intergranular attack, as the stress condition at the apex of the bend for each U-bend was much more aggressive than the residual stress field at the hole.

Further examination of these specimens included metallography of all three conditions listed above but for the unexposed (no Hg) condition. No corrosion/cracking was observed – even for the heat treated specimens – indicating that both the sensitization process and exposure to Hg were required to generate the observed intergranular attack around the holes. However, unexposed (to Hg) specimens did not receive the brief pickling treatment to remove the light oxide developed during heat treatment. (There was no need to remove the oxide if the specimens weren't to be exposed in Hg.) Follow-up effort indicated that even very light pickling treatments (deionized water with 10% nitric acid and 3% hydrofluoric acid, ambient, 2 minutes) could at least initiate intergranular corrosion patterns in the specimen hole area similar to those shown in Fig. 6. As a result, it is not clear how much of the observed intergranular attack is due to the pickling treatment compared to the Hg exposure, but in any case the specimens are clearly susceptible to intergranular attack in the hole area following heat treatment in the sensitizing temperature range.

Specimens receiving a “sensitizing” heat treatment in previous Hg testing (the larger size used in the TCLs without a restricted section⁷) were revisited – ie, prepared for metallography such that the cross section through the holes was in the plane of examination, and these did not exhibit corrosion/cracking around the specimen holes (although they received the pickling treatment prior to exposure to Hg). Concern for something physically or chemically unusual about the hole area in the present small specimens then led to an investigation into the fabrication procedure for the sub-size flat coupons.

The shop fabricating the sub-size flat specimens used the electro-discharge machining (EDM) process. It was determined that the raw sheet stock was laser cut into strips that were stacked for cutting the small holes in each specimen. A ram-type graphite electrode which spins and plunges downward as it cuts was used - along with a light hydrocarbon cutting fluid - to make the holes. The outer profile of the specimen, however, was cut with a brass wire electrode and deionized water as the fluid. In concert with the observed pattern of corrosion/cracking around the holes of heat treated specimens, this information suggested that the hole areas of the 316L stainless steel were carburized by the EDM process (graphite rod plus carbonaceous oil) – and thus more susceptible to carbide precipitation during the sensitizing heat treatment - while the edges of the specimen were not (brass wire and water).

Potential carburization of the area around the specimen holes could also explain the pitting/corrosion in this area of the etched specimens before exposure to Hg. A carburized stainless steel would be expected to have much less corrosion resistance to the sulfuric acid etching solution than a nominal low carbon content material, and thus the hole areas were significantly attacked.

To further evaluate potential carburization in the specimen hole area, a few additional tests were performed. Firstly, "sensitized" specimens were solution treated (1 h 1050°C) and it was found that the tendency toward intergranular attack around the holes upon exposure to Hg (and to the pickling treatment) could be eliminated by this process. Secondly, other heats of 316L - including a 316LN heat - were fabricated using the same EDM process used to make the sub-size flat coupons, and carburization as well as corrosion/cracking in the hole following exposure to Hg area was confirmed in each. (This shows that other heats of material are potentially susceptible to the same phenomenon.) Similar to results for other specimens, a brief pickling treatment on specimens receiving a sensitizing heat treatment was found to cause intergranular corrosion around the specimen holes on coupons from these additional heats, so the role of Hg in the observed intergranular attack may be minor. It is perhaps significant that coupons from the 316LN material tended to resist intergranular attack (due to pickling and/or Hg exposure) somewhat via more shallow and less uniform attack across the hole surface area compared to the standard heats of 316L.

In addition, it is potentially noteworthy to recall a series of standard room temperature tensile tests in Hg for type 316 stainless steel performed previously.⁵ Sensitized specimens were included in the test matrix, and the sensitizing treatment produced carbides on essentially 100% of the grain boundaries of the material (it was not an "L" grade alloy). The carbides had little effect, however, on the tensile properties in Hg compared to air, and no intergranular attack was observed for these specimens. The difference in results here suggests that either elevated temperature or extreme carburization or both are required to develop intergranular attack in 316L exposed to Hg.

3.9 TCL SURFACES

At the completion of the experiment, each TCL was destructively analyzed. From a region near each thermocouple well, a small piece of tubing was removed for metallographic analysis to compare with results for coupons. In addition, several cross sections were removed from the venturi component of the loop. In each case, the process side of the tubing (and venturi)

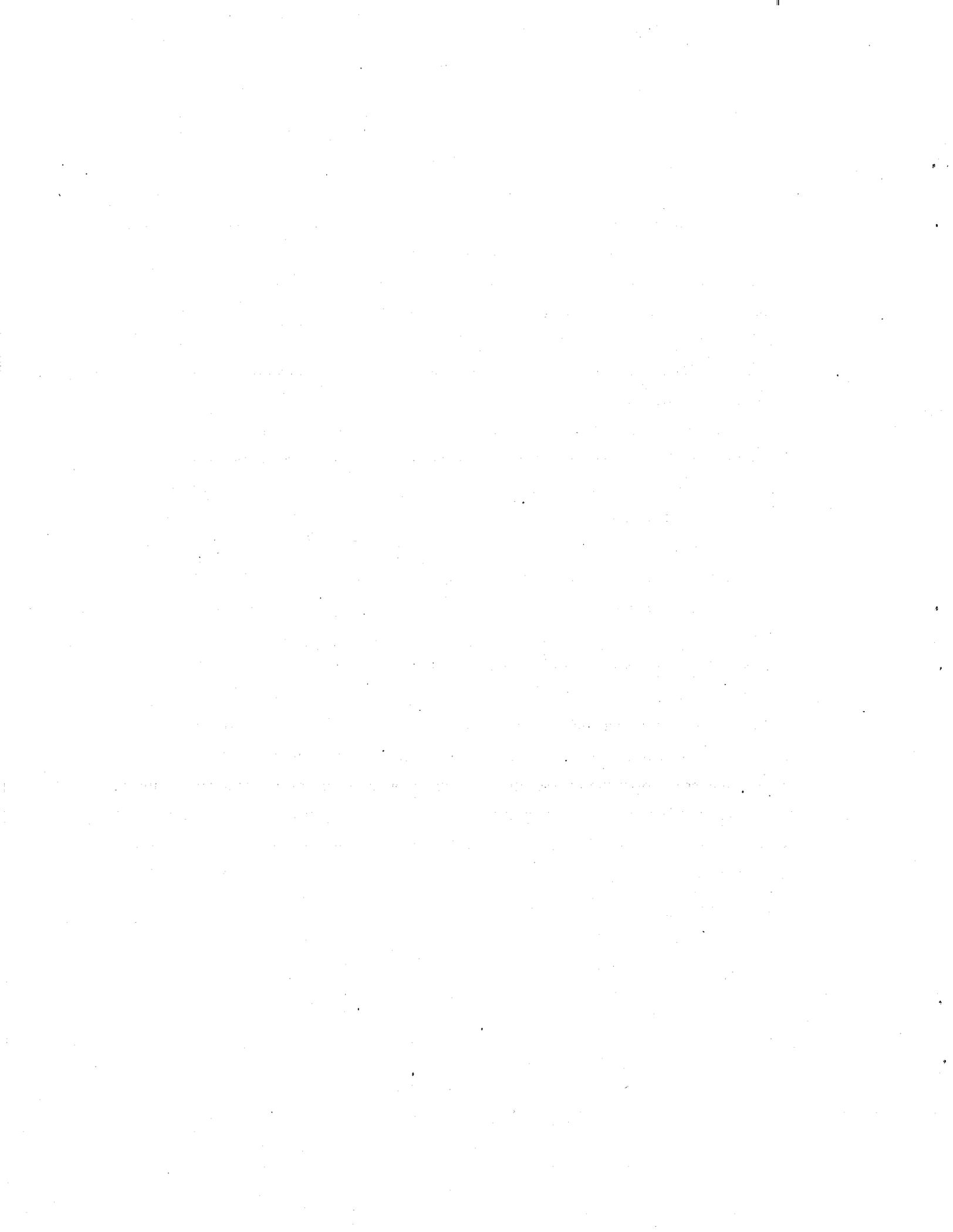
revealed no sign of attack (no increase in surface roughness, porosity, or surface film) compared to the virgin material. In the hot leg, the tube ID surfaces are likely to be somewhat hotter than the bulk Hg as they are directly warmed by the heaters and therefore perhaps prone to a greater extent of reaction/dissolution. In the cold leg, the tubing ID may be slightly colder than the Hg, increasing a driving force for precipitation of any dissolved material. While the absence of attack or deposition at these locations is consistent with results from the loop tubing in previous experiments, it remains somewhat surprising that the heat transfer surfaces of the loop do not experience a greater degree of interaction with Hg than the coupons from similar positions.

4. CONCLUSIONS

To examine the potential effect of Hg velocity on wetting/compatibility, a series of 316L coupons was exposed in thermal convection loops with a reduced section near the top of the hot leg. The reduced section had the effect of locally increasing the Hg velocity from a bulk value of about 1.2 m/min to about 5 m/min (as well as significantly increasing local turbulence). Based on visual appearance, weight change, and metallographic analysis, increasing the Hg velocity to 5 m/min had no significant effect on mill-annealed/surface-ground specimens of 316L or their gold-coated counterparts.

Gold-coating, polishing, and etching were not found to have a significant influence on compatibility of 316L with Hg in these TCLs, independent of whether or not the specimens and loop internals were steam cleaned just prior to loop operation. However, generally speaking, coupons exposed in TCL #8 (steam cleaned) had slightly higher weight losses and/or no weight gain as compared to coupons in equivalent positions of TCL #7 (no steam cleaning), which may suggest some small influence in terms of cleaning and subsequent interaction with Hg.

A sensitizing treatment of 20 h at 650°C did not significantly influence the compatibility of 316L with Hg for the reported conditions, but it did serve to highlight a potential fabrication concern. While the bulk of the sensitized 316L specimens (original flat coupons as well as U-bends) did not suffer any corrosion as a result of the heat treatment, the area around the holes was found to be susceptible to intergranular corrosion/cracking. Subsequent analysis indicated that the EDM process for making the specimen holes (graphite rod and oil) carburized the hole area and rendered it particularly susceptible to carbide formation during the sensitizing treatment. In contrast, the EDM process used to prepare the specimen profile (brass wire and water) did not contaminate the coupons with carbon. This result suggests caution when specifying processes for machining stainless steel components for the SNS and highlights the importance of selection of "L" grades of stainless steel for Hg service.



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6. REFERENCES

1. L. K. Mansur and H. Ullmaier, compiled Proceedings of the International Workshop on Spallation Materials Technology, CONF-9604151, Oak Ridge, TN, April 23-25, 1996.
2. L. F. Epstein, in Liquid Metals Technology – Part I, F. J. Antwerpen, ed. “Static and Dynamic Corrosion and Mass Transfer in Liquid Metal Systems,” Chemical Engineering Progress Symposium Series, 53(20), p.67, 1957.
3. J. R. DiStefano, “A Review of the Compatibility of Containment Materials with Potential Liquid Metal Targets,” ORNL/TM-13056, August 1995.
4. J. R. Weeks, “Liquidus Curves and Corrosion of Fe, Cr, Ni, Co, V, Cb, Ta, Ti, and Zr in 500-750°C Mercury,” Corrosion, 23(4), p.98, 1967.
5. J. R. DiStefano, S. J. Pawel, and E. T. Manneschmidt, “Materials Compatibility Studies for the Spallation Neutron Source,” ORNL/TM-13675, September 1998.
6. S. J. Pawel, J. R. DiStefano, and E. T. Manneschmidt, “Corrosion of Type 316L Stainless Steel in a Mercury Thermal Convection Loop,” ORNL/TM-13754, April 1999.
7. S. J. Pawel, J. R. DiStefano, and E. T. Manneschmidt, “Effect of Surface Condition and Heat Treatment on Corrosion of Type 316L Stainless Steel in a Mercury Thermal Convection Loop,” ORNL/TM-2000/195, July 2000.



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