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**Supercritical Water Oxidation
Data Acquisition Testing**

OSTI

Contract No. DE-FC07-94ID13303

FINAL REPORT

VOLUME I

PHASE I DOE TESTING

November 1996

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**U.S. Department of Energy,
Idaho Operations Office
&
Strategic Environmental Research
and Development Program**

**Stone & Webster Engineering Corporation
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3.0 ENGINEERING AND DESIGN

Process Concept

Through various U.S. government and privately sponsored research and development programs, MODAR demonstrated the ability of its SCWO process to effectively destroy a wide range of organic materials. In these previous programs, MODAR developed the methods to control the deposition of "sticky salts," and minimize corrosion. These earlier developments, which were performed using MODAR's bench scale and pilot scale plants, enabled MODAR to develop a process concept for the treatment of mixed wastes.

At the beginning of the SCWODAT program, a process concept was developed to test alternative configurations that were expected to achieve the required treatment. The existing pilot plant was modified to include:

- a. Pretreatment of TRIM®SOL prior to its oxidation, to attain neutralization of hydrochloric acid formed from the chlorine contained in TRIM®SOL.
- b. Use of a low energy oxidizer nozzle to minimize turbulence, and hence salt deposition, in the oxidizer.
- c. Quenching the overhead effluent to prevent salt deposits from obstructing the oxidizer effluent line.
- d. Addition of a neutralizing agent in the overhead effluent quench to control effluent pH.
- e. Use of a liner to protect the alloy pressure vessel from the process environment.
- f. Removal, from the pilot plant, of a heat exchanger (feed versus effluent) which had experienced corrosion failure during a previous program. The capacity of the air/water heater was increased to compensate for the loss of regenerative heat exchange.

FIGURE 1
MODAR PILOT PLANT
SYSTEM CONFIGURATION FOR SCWODAT TRIMSOL/NAVY CAMPAIGN

4.0 TESTING SUMMARY

The following sections describe the objectives and approach for the Phase I SCWODAT program activities.

4.1 OBJECTIVE: DOE TESTING

Eight test runs were performed, seven with TRIM®SOL (944-950), for the DOE portion of the SCWODAT program to validate organic destruction and evaluate system performance in controlling solids generated in the oxidizer. The testing focused on the evaluation of operating conditions and system hardware to identify any constraints or limitations as well as to optimize process performance.

4.2 APPROACH

Based on previous MODAR SCWO testing, the ability to process wastes containing acid precursors was dependent on being able to neutralize the acids formed and successful removal of the salt formed. The neutralization of the acids and control of solids deposition had previously been controlled by the same process device, the oxidizer inlet feed nozzle. This nozzle provided the proper mixing of organic feed material and the SCW/Air mixture. The characteristic nozzle velocities affect both neutralization and salt flow in the oxidizer.

For the SCWODAT program, more flexibility was given to the MODAR process with two separate sub-systems, the reformer and the quench system. The reformer heated the TRIM®SOL feed while mixing it with caustic. Chlorine was broken away from the TRIM®SOL and was neutralized in-situ by sodium hydroxide. The quench system was designed to rapidly cool the overhead effluent exiting the oxidizer to quickly dissolve particulate salt which might plug the small diameter downstream piping.

5.0 ANALYSIS: MODAR SCWO TESTING RESULTS

Following mechanical testing to ensure safe and proper system operation, a series of runs were performed to optimize the surrogate mixed waste treatment. This series of tests is described in Appendix B. The two key runs of the program, Runs 948 and 950, are analyzed in the following sections.

5.1 PROCESS OPTIMIZATION: KEY TRIM®SOL TEST RUNS

The first key test was identified as Run 948. In this test, neutralization of acid was accomplished by adding sodium bicarbonate to the quench water and brine makeup water only. Caustic was not added into the oxidizer.

In the second key run, Run 950, caustic was delivered with the TRIM®SOL feed to provide neutralization in the oxidizer. Neutralization of the overhead aqueous effluent was completed by adding sodium bicarbonate in the quench water.

To simplify the interpretation of the analytical chemistry, demineralized water was used for all aqueous input streams with all streams being once-through flow. The quench stream was a relatively large flow and made up the majority of the volume of the SCWO process effluent flow. Calculation of waste destruction efficiencies was skewed by the use of high quench water flow in combination with the analytical detection limits for analysis of waste residuals. The resultant destruction efficiencies calculated with high quench water flows were therefore, skewed to a lower value than could be demonstrated if SCWO process effluent water had been reused.

Energy Laboratories, Inc. of Casper, Wyoming analyzed the TRIM®SOL waste feed, the liquid effluent, and the solid process effluent for Run 948 and Run 949. INEL's laboratory analyzed the Run 950 samples for most of the inorganic species of interest in this program, while Alpha Analytical Laboratories, of Westborough, MA performed additional inorganic analyses. Because neither of the two laboratories performed organic analyses for Run 950 and the operating conditions for Run 950 were nearly identical to Run 949, the organic results for Run 949 were tabulated as representative of Run 950. Gas analysis was done using on-line analyzers.

In all calculations of mass balances and destruction efficiency, analytical detection limits have been used when the analytical laboratory reported "Not Detected."

5.2 ANALYSIS OF OPTIMIZED RUNS

Of the eight runs performed for the DOE portion of the SCWODAT program, six were associated with testing to identify the effectiveness of new processes and/or determine optimum process conditions. The following analyses compares the results of the two optimized runs, Runs 948 and 950, in the areas of waste destruction, neutralization, and distribution of surrogate metals and inorganics.

5.2.1 FLOW CONDITIONS AND SURROGATE COMPOSITION

Figures 2 and 3 depict "black box" representations of the MODAR SCWO process for Runs 948 and 950 respectively. While the exact composition of TRIM®SOL is proprietary to its manufacturer, Table 1 shows two elemental analyses carried out as part of this program. As shown in this table, TRIM®SOL contains high concentrations of Cl and S which form acids during SCWO treatment.

The metals surrogate concentrations used for this program were established by INEL as a mass ratio to TRIM®SOL. These ratios are shown in Table 2 with all the metals being added as water soluble acetates in demineralized water. Cerium, the highest concentration metal, is the surrogate for plutonium. It was chosen by DOE on the basis of its similar migration through soil. However, it is not known how its disposition might differ from plutonium in a SCWO system.

Compressed air was the oxidant used in the SCWODAT program. Supercritical water helped initiate the oxidation and provided the reaction medium. High pressure purge air was used in the annulus between the pressure vessel I.D. and the liner O.D. to maintain a slightly higher pressure outside the liner than inside. This kept corrosive materials away from the Alloy 625 oxidizer vessel.

Quench water contained NaHCO_3 as shown in the "black box" figures. Sodium bicarbonate was delivered with the brine make-up water only when NaOH was not used in the upper part of the oxidizer (Run 948). Table 3 summarizes the overall TRIM®SOL test conditions for optimized Runs 948 and 950.

5.2.2 WASTE DESTRUCTION

At least 99.97 percent organic carbon destruction efficiency was achieved in both Runs 948 and 950 (Table 4). TRIM®SOL alone provided the fuel value to maintain the oxidation temperature of 600° to 620°C. Aqueous effluent TOC was at or below the analytical detection limit of 2 mg/L (Table 5). Table 6 summarizes the data on the inorganics in solution found in both the overhead and brine effluents for Runs 948 and 950. Table 7 provides data on the solids analyses for both the overhead and brine effluents for both of the optimized Runs 948 and 950.

TRIM®SOL proved to be one of the more refractory organic feeds encountered by MODAR. The propylene glycol ether and propylene glycol constituents of TRIM®SOL may account for its resistance to oxidation. The addition of sodium hydroxide to the oxidizer in Run 949/950 slightly inhibited the oxidation of TRIM®SOL. This was observable, however, only at the parts per

billion concentration level for several non-chlorinated species and at 0.05 mg/L for total organic halogen, TOX.

Table 8 presents the averaged, steady state effluent gas quality. Excellent results were achieved with residual carbon monoxide in the range of 4 to 6 ppmv and NO_x less than 0.5 ppmv.

5.2.3 NEUTRALIZATION

As noted in Table 1, TRIM®SOL contained substantial concentrations of both chlorine and sulfur which generate strong acids upon oxidation. Although TRIM®SOL does contain the cations Na and K, they were not present in sufficient concentration to completely self neutralize the acids associated with Cl and SO₄.

MODAR intended to reform TRIM®SOL prior to its oxidation in the SCW oxidizer utilizing a newly patented process of heating the TRIM®SOL at elevated temperature and pressure in the presence of caustic and the absence of oxygen. The objective was to chemically split off TRIM®SOL's Cl and S and approach complete neutralization with NaOH. A series of relatively short duration runs were conducted using this approach. It was determined in late July 1995 that more of an optimization effort would be required than the project schedule would allow. Therefore, SCWODAT program personnel shifted to the two alternatives noted above: neutralization in the quench (Run 948) and neutralization in the oxidizer followed by neutralization in the quench as necessary (Runs 949 and 950). This alternative approach to the neutralization of acids formed during the oxidation of TRIM®SOL was first implemented during the SCWODAT program.

In all the tests, aqueous pH values were measured as follows:

Overhead Effluent

- Measured continuously, on-line with an electrode that was calibrated every 8 hours.
- Measured every hour on grab samples with a minimum of two ranges of pH paper.
- Measured by Energy Laboratories on test composites.

Brine Effluent

- Measured every hour on grab samples with a minimum of two ranges of pH paper.
- Measured by Energy Laboratories on test composites.

The extent of acid neutralization was indicated by the pH of the overhead effluent and brine

streams exiting the SCWO process. If no neutralization had been achieved, the overhead effluent pH would have been approximately 1.5. Percent neutralization efficiency as a function of the logarithmic pH scale is approximately as follows:

<u>Effluent pH</u>	<u>Acid Neutralization Efficiency (%)</u>
1.5	0
2.5	90
3.5	99
4.5	99.9
5.5	99.99
6.5	99.999

In Run 948, complete acid neutralization was achieved in both the overhead effluent and the brine. The pHs attained were 6.8 and 7.6 respectively (Table 4), with the quench water containing 0.57 wt % NaHCO_3 and the brine makeup containing 2.4 wt % NaHCO_3 .

In Run 950, caustic was metered in with the TRIM[®]SOL feed to provide in-oxidizer neutralization. Seventy-five percent neutralization was achieved in the oxidizer and quench neutralization yielded a final overhead effluent pH of 5.5 (Table 4). The brine effluent pH was 6.5.

5.2.4 DISTRIBUTION OF SURROGATE METALS AND INORGANICS

The surrogate metals which were added to the process influent were: Ce, Pb, Zn, Fe, and Ca. In Run 948, the actual feed concentrations were approximately 16% above the target concentrations. In Run 950, they were 6% below the targets. All metals were added as reagent grade acetates. Supercritical water oxidation destroyed the acetate portion of the metals feed.

Tables 9 and 10 present the detailed information on the distributions of the inorganic elements and sulfate (the product of oxidation of sulfur) for Runs 948 and 950. The fifth column lists the mass of the individual species delivered to the process. These were calculated from volumes pumped, fluid specific gravities, and constituent concentrations. The last column is the mass balance closure: element recovered by sampling and chemical analysis divided by mass of the element fed. In Run 948 all were within acceptable limits of closure (except Fe - see the table's footnote). This column, therefore, validates the sampling and chemical analysis techniques and methods.

The mass balances noted above for the elements and anions listed were calculated using the procedure described here. As an example, consider the element cerium, Ce.

Input Mass of Ce

$$\begin{aligned} \text{grams Ce} = & \text{Aqueous feed flow}^a \text{ (mL/min)} \times \\ & \text{Ce concentration}^b \text{ (g/L)} \times \\ & \text{Run time(min)} \times \\ & 1\text{L}/1000\text{mL} \end{aligned}$$

Output Mass of Ce

$$\begin{aligned} \text{grams Ce} = & \text{Overhead effluent flow}^a \text{ (mL/min)} \times \\ & \text{Ce concentration}^c \text{ (g/L)} \times \\ & \text{Run time(min)} \times \\ & 1\text{L}/1000\text{mL} \\ & + \text{Brine Flow}^a \text{ (mL/min)} \times \\ & \text{Ce concentration}^c \text{ (g/L)} \times \\ & \text{Run time(min)} \times \\ & 1\text{L}/1000\text{mL} \\ & + \text{Brine Drain}^d \text{ (L)} \times \\ & \text{Ce concentration}^c \text{ (g/L)} \\ & + \text{Sum of Various Separate Rinses}^e \text{ (L)} \times \\ & [\text{Ce concentration}^c \text{ (g/L)} + \text{Suspended Solids}^e \text{ (g/L)} \times \text{Ce concentration}^c \text{ (g/g solids)}] \end{aligned}$$

- Notes: a Average flow rate during test
b Average of Energy Labs or INEL Ce analysis of the feed solution and the calculated value from the "as formulated" in the MODAR laboratory
c Energy Labs or INEL analysis
d Drained from the bottom of the oxidizer after the test run
e At the conclusion of each test various drains and rinses were performed. These were sampled, collected, measured, and analyzed separately.

In Run 950, the balance closures for K, Cl, Zn, Fe, and Ca were acceptable. Deficiencies for Pb, and particularly Ce, should be noted. After calculating a similar cerium mass balance deficiency

in Run 949, MODAR spiked several samples with known amounts of cerium sulfate, cerium oxide, and cerium carbonate. The analytical results on these known addition samples pointed toward problematic analyses of cerium oxide. Both Energy Laboratories and INEL's laboratory noted this difficulty.

In Tables 9 and 10 all the element distributions were based on normalizing the analytically recovered quantities to 100 percent. The location or locations of the missing mass of Pb and Ce in Run 950 could not be determined.

Table 4 best summarizes the partitioning of the metals. When NaOH was not present in the oxidizer, Run 948, approximately 60 percent of the surrogate metals went overhead. When NaOH neutralization was conducted in the oxidizer, only about 30 percent went overhead. This was most likely due to the lower solubility of the metal compounds formed under lower acid conditions.

In neither processing mode was there a clean split of the surrogate metals between the overhead effluent and the brine. The Fe result in Run 948 was an anomaly caused by the presence of a large number of iron containing corrosion coupons in the oxidizer. These coupons were added with the permission of DOE/INEL at the request of MIT which was conducting SCWO materials of construction studies.

Supercritical water oxidation of TRIM[®]SOL precipitated "sticky salts" whether or not a neutralizing agent was added to the oxidizer influent. TRIM[®]SOL, as previously noted, contains Na, K, Cl, and S which generate sticky chloride and sulfate salts. Due to the large quantities of carbon dioxide present, carbonates were also formed if excess cation was present.

At approximately the 40 and 80 hour marks of Run 950, the TRIM[®]SOL, surrogate metals, and caustic feed flows were interrupted to rinse the salts out of the oxidizer. This was accomplished by raising the cool brine level and then draining it out the brine letdown train. This procedure was not used at the end of the test. Table 10 indicates that rinsing may have decreased the accumulation of cerium (the surrogate for plutonium) in the oxidizer. However, it is important to recall the poor cerium mass balance closure in Run 950. No rinsing was conducted in Run 948.

FIGURE 2
Steady State Flows
Run 948

Note: 1) All flows are kg/h
2) To simplify the interpretation of the chemical analyses, all water used was deionized to 1 micro S/cm and was used "once-through" the process.

FIGURE 3
Steady State Flows
Run 950

Note: 1) All flows are kg/h
2) To simplify the interpretation of the chemical analyses, all water used was deionized to 1 micro S/cm and was used "once-through" the process.

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TABLE 1
TRIM®SOL ANALYSES
ALL VALUES ARE WEIGHT %

MODAR SAMPLE NO.	944-1	944-2
ENERGY LABS NO.	C95-35363	C95-35364
C	66	66
H	10.7	10.9
N	0.21	0.21
S	1.3	1.04
Cl (Energy Labs TX Method 9076)	12-12.1	10.7
Cl (TOX Method 9020B)	12 - 13	Not Analyzed
Cl (Commercial Lab) ¹	11.1	11.8
Na	0.52	0.51
K	0.20	0.20
F	2.9×10^{-5}	2.7×10^{-5}
Si	0.0046	0.0059
O (by difference)	10	10

¹ Subcontracted to Energy Laboratories

TABLE 2
TARGET SURROGATE METALS
RATIO TO TRIM®SOL

Metal	mg Metal/kg of TRIM®SOL ¹	Added As ²
Ca	300	Ca(C ₂ H ₃ O ₂) ₂ · H ₂ O
Fe	100	Fe(C ₂ H ₃ O ₂) ₂
Pb	1676	Pb(C ₂ H ₃ O ₂) ₂ · 3H ₂ O
Zn	1367	Zn(C ₂ H ₃ O ₂) ₂ · 2H ₂ O
Ce	3000	Ce(C ₂ H ₃ O ₂) ₃ · 1.5 H ₂ O

¹ As specified in letter of C. Shapiro of INEL to Stone & Webster dated January 20, 1995.

² These are acetates.

TABLE 3

TRIM®SOL TEST CONDITIONS

MODAR RUN NO.		948	950
TRIM®SOL Processing Rate	kg/h	3.7	3.8
Stoichiometric Air	% Excess	53	57
TRIM®SOL Neutralization		In quench only	In-oxidizer and quench
Neutralizing Agent			
In-oxidizer		None	NaOH
Quench		NaHCO ₃	NaHCO ₃
In-oxidizer Concentrations	mg/kg H ₂ O		
Cl		5600	4700
S		540	470
K		93	80
Surrogate Metals Concentrations	mg/kg TRIM®SOL		
Ca		360	290
Fe		100	90
Pb		1950	1560
Zn		1710	1290
Ce		3550	2870
Oxidizer Liner		Metallic Ti	Ceramic TiO ₂ Coating on Ti
Operating Pressure	bar	229	229
Maximum Operating Temperature	°C	600°	619°
Steady State Feed Duration	Hours	47	94

TABLE 4
PHASE I TESTING
OVERALL RESULTS

MODAR RUN NO.		948	950
Total Feed Time	Hours	47	94
Acid Formation Rate	kg HCl/h	0.44	0.46
In-Reactor Neutralization Attained		None Attempted	75%
Salt Generated in Oxidizer	kg	3.5	68.3
Overhead Effluent pH		6.8	5.5
Brine pH		7.6	6.5
Carbon Destruction Efficiency	%	99.97	> 99.97
Partitioning of Surrogate Metals ¹	<u>% Into Overhead Aqueous Effluent</u> <u>% Precipitated</u>		
Ce		56/44	38/62
Pb		73/27	18/82
Zn		48/52	28/72
Fe		7/92	21/79
Ca		57/43	45/55
Material Performance			
Oxidizer Liner		Some Pitting	Some Coating Delamination
All Other Piping and Heat Exchangers		Excellent, Unaffected	Excellent, Unaffected

¹ Based on quantity analytically recovered.

TABLE 5
PHASE I TESTING
AQUEOUS EFFLUENT QUALITY
ORGANIC ANALYSES

MODAR RUN NO.		948		949 (950)	
In-Oxidizer Neutralization		None		With NaOH	
		Overhead	Brine	Overhead	Brine
TOC	mg/L	2	<2	<2	<2
TOX	mg Cl/L	<0.01	<0.01	¹	<0.01
TX ²	mg Cl/L	1200	1500	280	1100
VOC					
57 Compounds		ND ³	ND ³	ND ³	⁴
Acetone	μg/L	10	17	18	40
Benzene	μg/L	ND	ND	ND	1.6
Bromoform	μg/L	2.3	ND	ND	ND
Naphthalene	μg/L	ND	ND	ND	1
Semi-VOC					
64 Compounds		ND ⁵	ND ⁵	ND ⁵	ND ⁵

¹ Two analyses <0.01, one analysis 0.05.

² TX is total halide which includes inorganic Cl

³ Not detected at 1 - 5 μg/L

⁴ 57 compounds not detected at 1-5 μg/L

⁵ Not detected at 10-50 μg/L

TABLE 6
PHASE I TESTING
AQUEOUS EFFLUENT QUALITY
INORGANICS IN SOLUTION

MODAR RUN NO.	948		950	
In-Oxidizer Neutralization	None		With NaOH	
	Overhead	Brine	Overhead	Brine
Na	1,200	3,400	270	2,100
K	10	76	4	110
Cl	1,200	1,500	240	2,300
SO ₄	150	730	80	640
Ce	2.5	<0.05	0	0.06
Pb	7.3	0.15	0.46	0.58
Zn	8.0	17	2.4	16.30
Fe	0.24	<0.05	<0.04	<0.04
Ca	1.4	1.6	1	4
Ni	<0.05	1.6	<0.04	0.06
Mo	<0.10	<0.10	<0.04	0.05
Ti	<0.01	<0.01	<0.04	<0.04
Cr	0.08	0.07	<0.04	<0.04
pH	6.8	7.6	5.5	6.5
TDS	3,200	9,200	750	6,000
TSS	37	120	<5	72

Note: All values mg/L except pH.

TABLE 7
PHASE I TESTING
AQUEOUS EFFLUENT QUALITY
SOLIDS ANALYSES

MODAR RUN NO.	948		950	
In-Oxidizer Neutralization	None		With NaOH	
	Overhead	Brine	Overhead	Brine
TSS	37	120	<5	72
Na	23,000	6,200	4,500	13,000
K	2600	830	0	11,000
Ce	300,000	67,000	453,000	409,000
Pb	240,000	152,000	4,600	170,000
Zn	12,000	294,000	16,000	12,000
Fe	14,000	13,000	27,000	14,000
Ca	15,000	6,000	63,000	9,900
Ni	1,300	22,000	15,000	2,700
Mo	4,700	830	0	1,500
Ti	260	560	15,000	1,100
Cr	1,300	420	13,000	900

Note: All values mg/kg of dry solids except TSS which is mg/L.

TABLE 8
PHASE I TESTING
EFFLUENT GAS QUALITY ¹

MODAR RUN NO.		948	950
In-Oxidizer Neutralization		None	With NaOH
N ₂	Vol %	81	81
O ₂	Vol %	13	13
CO ₂	Vol %	5.7	5.2
CO	ppmv	4	6
N ₂ O	Vol %	<0.01	<0.010
NO _x	ppmv	<1.0	<1.0

¹ Includes purge air which may not participate in the chemical oxidation.

TABLE 9
RUN 948 DISTRIBUTION OF ELEMENTS
UNNEUTRALIZED TRIM®SOL (IN THE OXIDIZER)

Element	Percent of Recovered				Element Recovered Element Fed %
	Overhead	Brine	In-Oxidizer	Total Mass Fed (g)	
Na	80	19	1	19,500	110
K	48	30	22	346	89
Cl	90	10	0	20,700	88
SO ₄ ¹	55	23	22	6,065	64
Ce	56	4	40	647	80
Pb	73	11	16	361	97
Zn	48	36	16	296	86
Fe	7	2	90	22	930 ²
Ca	57	8	35	65	88

¹ TRIM®SOL contains 1.2 wt% S present as a petroleum sulfonate. The reaction product of SCWO is sulfate.

² Forty-seven corrosion coupons, most containing iron, were mouned in the oxidizer vessel.

TABLE 10
RUN 950 DISTRIBUTION OF ELEMENTS
NEUTRALIZED TRIM®SOL (IN THE OXIDIZER)

Percent of Recovered					
Element	Overhead	Brine	In-Oxidizer	Total Mass Fed (g)	Element Recovered Element Fed %
Na				64,800	NA
K	21	76	4	694	109
Cl	27	65	9	40,400	75
SO ₄ ¹				12,200	NA
Ce	33	67	0	1,010	30
Pb	11	76	13	550	45
Zn	25	45	30	453	76
Fe	20	34	46	32	97
Ca	48	37	15	102	119

¹ TRIM®SOL contains 1.2 wt% S present as a petroleum sulfonate. The reaction product of SCWO is sulfate.

5.3 COMPONENT PERFORMANCE

The following sections provide detailed descriptions of the performance of various components throughout the SCWODAT program.

5.3.1 LINER PERFORMANCE

The following sub-sections provide a detailed account of the liner performance for the SCWODAT program. A history of each of the liners used during the testing can be found in Appendix A.

5.3.1.1 PERFORATION OF LINER NO. 1 IN RUN 949

Liner No. 1, fabricated primarily from titanium Grade 12 was used in the MODAR SCWO pilot plant between the Summer of 1993 and Summer of 1995. It was exposed to a variety of environments for a total of approximately 1,000 operating hours.

In SCWODAT Runs 946-949, TRIM[®]SOL was used, with the surrogate metals Ce, Pb, Zn, Fe, and Ca in the form of acetates and with and without in-situ neutralization. The form of the metals in the actual waste to be treated in the future is unknown. Prior to Run 949, Liner No. 1 had not shown signs of severe degradation except for small titanium Grade 2 sections above the brine level. The Grade 12 base metal and welds performed remarkably well. Previous damage can be described as occasional shallow pits, primarily in the base metal.

In Run 949, Liner No. 1 suffered severe corrosion which occurred at numerous locations on the I.D. surface of the liner above the brine level. The corrosion resulted in multiple perforations over a 3-ft high section, starting approximately 1½ ft below the quench port level. A severe attack was also observed on the outside surface of the nozzle purge shell below the flange; at the time the shell was made from titanium Grade 2.

At each severely attacked location of the liner, large dark nodules formed; these protruded above rather uniform, seemingly dense, lighter colored salt deposits.

An extremely strong odor normally associated with hydrogen sulfide emanated from the liner and lingered for hours. A subsequent examination clearly demonstrated that the odor was associated with the nodules. A piece separated from one of the nodules was placed in a scanning electron microscope chamber, and the chamber could not be evacuated. The copper-alloy holder was discolored around the sample within a matter of minutes. Apparently, the piece still retained

hydrogen sulfide, a week after removal from the oxidizer vessel.

As a part of an investigation to determine the cause of the severe attack in Run 949, the following examinations of selected samples were performed:

- I. Scanning electron microscopy (SEM)
- ii. Energy dispersive spectroscopy (EDS)
- iii. Wave-length dispersive spectroscopy (WDS)

The objectives of the examinations were to obtain information which could help to determine the most likely mechanism of the severe corrosion and identify the most likely contributor to acceleration of corrosion attack in Run 949.

Four samples:

- Sample (1) char-like material from the I.D. side of the liner over a perforation including the nodule
- Sample (2) deposit from an unattacked area
- Sample (3) titanium sample including an attacked area cut from the liner wall
- Sample (4) char-like material from perforation sites collected near O.D.

were examined in a JEOL Superprobe 733, with the participation of SCWODAT program personnel, at the Geller MicroAnalytical Laboratory in Topsfield, MA, where the examinations (SEM, EDS, and WDS) were performed. In examining the deposits/corrosion products, the intent was to characterize the local chemistry of the surfaces which had been in contact with the liner surface. The findings are summarized in Table 5.3.1.

In these examinations, the predominant elements present in the samples were as follows (listed in the order of relative intensity of the peaks on the spectra):

- Sample (1) Cl, Na, Ti
- Sample (2) Cl, Ti, Na, S
- Sample (3) Ti, Cl
- Sample (4) Cl, Na, Ti

Oxygen was detected only in samples (2) and (3). Sample (2) apparently contained only small amounts of oxygen based on an observation of a barely detectable oxygen peak at local spots. No oxygen was detected in samples (1) and (4).

Other elements detected in the samples were as follows:

Sample (1)	Zn, S, Pb, Ce
Sample (2)	Ce, Mo, K, Na
Sample (3)	Ca, K, S, Pb, Ni, Fe, Zn, Ce
Sample (4)	Pb, K, Fe, Ni

Five elements representing the surrogate metals are in bold to show their distribution between the samples. Iron could also have come from the liner base metal.

In addition, two samples removed from the liner, one representing deposit/corrosion product at a perforation and the other representing liner material and containing deposits away from a perforation, as well as one titanium U-bend specimen exposed to the supercritical zone environments in Phase I of the SCWODAT program, were examined at INEL.

The results of examinations of these three samples will be reported elsewhere. Preliminary reports from INEL indicated that, among other metals detected, cerium was present in a number of examined spots.

Discussion of the Laboratory Examination Results

The corrosion product/deposit from a perforated area, i.e. sample (1), as well as the deposit from an unattacked area, i.e. sample (2), contained primarily chlorine, sodium, and titanium, at least in the layer near the interface with the liner. There was no evidence of oxides in samples (1) and (4) based on the surface examinations capable of detecting oxygen. Thus, it would appear that the corrosion product and near-interface layer of the deposits were rich in sodium chloride and at least one of the titanium chlorides. Since no X-ray diffraction was done on samples (1) and (4), it is far from clear in what form Ti was present in the deposits.

A fairly high concentration of sulfur was detected only in the deposit at an unattacked area. Only small amounts of sulfur were present at the perforation where the examined samples were taken. The hydrogen sulfide odor suggests that locally, under the deposits, there were reducing conditions.

A significant amount of metals added to the feed were found in the deposits, corrosion product, and on the surface of the titanium Grade 12 sample. The following metals were detected in the examinations:

Ti, Na, Zn, Pb, Ce, Fe, Mo, K, Ni, and Ca.

Some of the detected metals were a part of the titanium Grade 12 chemistry; others, i.e. Zn, Pb, Ce, Fe, and Ca apparently came from the feed where they were introduced as surrogate metals. Ni could have come from the high-nickel alloys in the feed system parts, the liner base metal, and/or corrosion specimens. Na and K apparently came from the waste feed and from the neutralizing agent.

The severe attack of the titanium liner can be attributed to a special case of underdeposit, or crevice corrosion which resulted in the formation of large and deep "pits". Crevice attack is known to occur in chloride and sulfate solutions and is enhanced by cathodic depolarizers such as dissolved oxidizing species, including Fe^{+3} , Ni^{+2} , Ti^{+4} , Ce^{+4} , and H^{+} ions. (R.W. Schulz, "Understanding and Preventing Crevice Corrosion of Titanium Alloys-Part I", Materials Performance, V.31, No.10, pp. 57-62, 1992.)

Some other cations, such as Zn^{+2} and Ca^{+2} can aggravate localized corrosion and result in a special form of localized corrosion resembling crevice corrosion, except that initiation may occur in the absence of normal crevices.

Susceptibility of titanium to underdeposit corrosion was apparently enhanced by the presence of some of the metals near the areas at the interface between the titanium surface and deposits where highly reducing conditions could have been created leading to the severe attack and perforations observed in Run 949.

TABLE 5.3.1

Summary of Results From Examinations at Geller Laboratories

Sample I.D.	Sample Description	Elements Detected	Comments
1	Deposit/corrosion product over a "pit"	Prevalent: Cl, Na, Ti Spots containing Zn, S, Pb, and Ce	No oxygen. Apparently only chloride salts of Na, Ti, Pb, and Ce except for spots containing Zn and S where ZnS was probably present. Peaks of Zn and Ce where present are quite pronounced. The sample still contained a fair amount of what appeared to be H ₂ S as evidenced by 1) intensive gassing out in the SEM chamber during an attempt to evacuate it and 2) rapid brightening of a bronze disk around the sample when the latter was placed on the disk
2	Deposit from unattacked area	Prevalent: Cl, Ti, Na, S. Mo was positively identified in one of the four areas examined. Spots containing Ce. K and Ni show as very low intensity peaks in some of the spectra.	Mo peak overlaps with S A barely detectable oxygen peak at local spots
3	Ti 12 including an attacked area	Apart from Ti, Cl was detected at virtually all examined spots. The following elements were detected at least at 3 of the 7 examined spots: Ca, K, and O. Other elements detected at some of the analyzed spots: S, Pb, Ni, Fe, Zn, and Ce	In one case, Pb and S were confirmed by the wave dispersive spectroscopy while in other cases sulfur and possibly coincident Mo were detected; all three elements overlap in energy dispersive spectra. Where Pb was present, mapping indicated a correlation between Pb and Cl incidence.
4	Black char-like material collected from various perforation sites near the O.D. surface of the liner	Prevalent: Cl, Na, Ti. A strong Pb peak in a spectrum taken from one of numerous scattered "specks". K shows in all 3 spectra taken with a pronounced peak in one of them. Fe and Ni show locally as very low intensity peaks in a spectrum taken from one of the yellowish spots.	No oxygen. No S or Mo which normally overlap with Pb in an EDS spectrum.

5.3.1.2 POST-TEST VISUAL EXAMINATIONS OF THE COATED LINER NO. 2

A multilayer graded coating was applied by thermal spray onto the internal diameter of titanium Liner No.2. Liner No. 2 was used in Run 950, removed after the run, and visually inspected. The cumulative exposure of Liner No. 2 to high temperatures was 129 hours. Visual examinations of the liner inside surfaces after the run were performed independently by Zatorski Coatings and by Stone & Webster. The examinations determined that parts of the coating had detached and/or had shown cracking. The coating failures occurred primarily in the same areas that presented problems during the application of the coating, i.e. in the lower half of the liner over a circumferential band approximately mid-way in the cylindrical section. There was lifting of the coating in smaller sections in other areas, again primarily in the lower half of the liner. In the upper half of the liner, coating detached in two areas: one area at the edge, i.e. near the lower face of the liner upper half and one area near the quench port.

Observations of coating failures on the inside surfaces of the lower and upper halves of the liner are described below by the areas starting from the bottom of the liner upwards. Possible causes are discussed for each of these areas.

Lower half of the Liner No. 2:

- Observation - Some minor lifting of the coating over an arc of less than 30 degrees along the circumferential weld at the joint of the conical section to the cylindrical section.

Possible Causes - Stress in the coating from deposition on irregular surfaces of the weld or at sharp local geometry changes. Possible use of steel brushes in the finishing of the weld and resulting iron embedment in the weld was also suggested as a plausible cause.

- Observation - Gross lifting of the coating around the circumference within 10 to 30 mm wide bands. These bands extended from less than 30 degrees to over 180 degrees around the circumference. The axial length of the affected area was over 300 mm. In this area, some of the coating flaked off completely.

Possible Causes - Continued peeling of the substrate in the same manner as occurred during the grit blast operation. Another plausible cause could be overheating of the coating during deposition. This second cause is unlikely since the temperature during deposition on the lower half was monitored in the same fashion as in the upper half of the liner and the temperatures were the same within 10°C.

- Observation - Minor lifting of the coating along the top edge in more than one area. Each of these areas extended over an arc of less than 15 degrees.

Possible Cause - Thermal stresses from differential thermal expansion at an edge. This can be solved by wrapping the coating around the edge or beveling the edge. The edge can also be rounded.

Upper part of the Liner No. 2:

- Observation - Minor lifting at the bottom edge along an arc less than 15 degrees along the circumference.

Possible Cause - Stress from differential thermal expansion at an edge. This can be solved by wrapping the coating around the edge or beveling the edge. The edge can also be rounded.

- Observation - Lifting in the area below the quench port in a patch approximately 50 mm by 70 mm.

Possible Causes - Peeling of the substrate or localized overheating of the coating during deposition. Overheating could be associated with the placement of the cooling jets on the arc-plasma gun assembly. Potential for overheating can be mitigated by the placement of additional cooling jets on the gun assembly.

The possible root causes of the substrate lifting were (1) defects in the titanium sheet, e.g. alpha-casing or severe hydriding, (2) embedded ferrous material transferred onto the titanium surface during rolling, forming, or finishing operations, or (3) embedded foreign materials introduced during the surface roughening by grit blasting prior to coating. Stress corrosion cracking due to propanol used during cleaning was also suggested as a possibility. Also, the liner was annealed prior to coating, and the remaining residual stresses from forming and welding may have been too low to cause the stress corrosion cracking. Although titanium has been reported to be susceptible to stress corrosion cracking when exposed to ethanol or methanol, Grades 2, 7, and 12 are generally immune to stress corrosion cracking except for a few environments including anhydrous methanol solutions containing halides.

The condition of the substrate and its possible effect on the performance of the liner coating have not been investigated. Such an investigation requiring detailed metallurgical laboratory examinations would help establish the root cause of the coating failures and help eliminate the problem in future applications.

The coating failures could also have been attributed to the liner fabrication process. The fabrication history including forming and finishing was not fully known. The weld shop could have used ferrous rollers to roll the sheets. The cleanliness of the rolls was not known. The other possibility, of embedding foreign material during the grit blasting is unlikely since the cleanliness and composition of the grit was known and both halves were prepared at the same time using the same blast setup and operator.

The lifting of the coating during service can be also indicative of coating or substrate overheating during the coating application. The temperature during coating application was monitored using an IR technique which measured the back side temperature of the substrate. This temperature measurement method would not detect small fluctuations on the coating side. The possible causes of overheating are localized temperature fluctuations due to (1) variations in the spray distance, (2) cooling jet fluctuations or (3) gun parameter changes.

As to the first possibility, gun-to-substrate spray distance variations were determined by the mechanical setup. No changes in the spray distance were noted based on visual observations during coating application. In future applications, in-process recording of the spray distance is recommended. The second possibility, cooling jet fluctuations, can be detected by recording the flow or pressure during coating application. This is recommended in future thermal spray applications. The third possibility, gun parameter changes, were unlikely since the spray parameters were in closed-loop control, and the system detects and records any parameter changes.

While the coating failed in a number of areas, a significant portion of the coating, particularly in the upper half appeared to have remained intact. SCWO environment exposure tests of the coating should be continued once the root cause of substrate flaking is determined. Measures to be taken to avoid problems associated with geometry (sharp edges, irregular surfaces etc.) should be coordinated with the design and fabrication activities.

5.3.1.3 LINER NO. 1 AFTER REPAIRS

Liner No. 1 suffered severe corrosion during Run 949. The decision was made to repair Liner No. 1 to support the Navy waste testing portion of the SCWODAT program. Prior to the Navy waste testing the part of Liner No. 1 which contained perforations was cut off approximately 2 in. above the conical bottom section. A cylindrical replacement piece was fabricated from new titanium Grade 12 sheet, rolled and seam-welded sections and welded to the salvaged bottom part. This bottom part had been in service since the first titanium Grade 2 liner was installed in the Summer of 1993 and performed well.

The refurbished Liner No. 1 was used in all the runs of the Phase II Navy waste testing (Runs 951- 955B). The refurbished Liner No. 1 was inspected visually in December 1995 upon completion of the Phase II Navy waste testing. All deposits had been removed from the liner prior to the inspection, except for some remaining sticky solid deposits at the bottom of the liner. These solid deposits formed, according to MODAR, primarily during the Navy composite waste test. In individual waste runs, predominantly powdery, much less sticky, relatively light deposits were reported.

On the inside surface of the refurbished Liner No. 1, there was a fairly thin scale-like deposit ranging in color from light pink to cream. In the areas where this scale was missing, there was no apparent corrosion below mark 29" (distance from the top of the liner), very little corrosion between mark 19" and mark 29", and pronounced pitting between mark 9" and mark 19". Above mark 9", there was no pitting and most scale was intact. Over the 10-in. high area between mark 9" and mark 19", there were areas of a fairly extensive "general" corrosion. The corrosion could be described as clusters of multiple overlapping pits as well as a number of isolated wide open pits. The depth of attack in most cases was close to or under 1/64 inch, but some were as deep as 1/32 inch. Corrosion affected both titanium base metal and in the seam weld; the severity of attack in the weld metal and in the base metal were comparable.

Corrosion to refurbished Liner No. 1 could have occurred primarily in Run 952 when so-called "non-chlorinated" solvents were treated and the resulting oxidizer pH was very low before corrective actions were taken to raise the oxidizer pH.

5.3.2 DECEMBER 1995 INSPECTION OF OTHER PILOT PLANT COMPONENTS

A visual inspection of selected critical components of the pilot plant was performed upon completion of the SCWODAT program. The objective of the inspection was to characterize performance of the pilot plant components by visual examinations.

The components were examined with the naked eye, with the aid of magnifying glasses (3X, 5X, and 8X), and, when required, with a borescope. The following components/areas were examined:

inside surfaces of the oxidizer pressure vessel

inside surfaces of the filter arms

inside and outside surfaces of the uncoated, refurbished Liner No. 1

quench mouth

quench purge shell

quenched effluent line inlet end

quenched effluent line outlet end and quench cooler inlet end

nozzle purge shell and end plate

feed nozzle and end face of the nozzle core tube

A summary of essential observations made in the course of this inspection follows:

Oxidizer Pressure Vessel and Filter Arms

The inside diameter surfaces of the oxidizer pressure vessel and filter arms were examined visually where accessible and with a borescope. The oxidizer vessel was examined prior to and after rinsing. Even prior to rinsing, the vessel inside surfaces were generally clean, except for deposits at the very bottom of the vessel. Similar deposits were observed at the bottom of the refurbished Liner No. 1. In the top section of the oxidizer, i.e. in the flange area, a few white streaks formed on the inside surface. Staining was observed on the oxidizer vessel inside surface under the filter arm openings, apparently due to a flow of a particulate-laden fluid from the bottom of the filter arms. Similar staining was observed on the lower part of both filter arms between 3 and 9 o'clock, i.e. up to what appeared to be a waterline. Above the waterline, there was a thin reddish deposit. At the very bottom of the filter arms, there was accumulation of light grey, fairly fine particulates around the 6 o'clock position.

All observations of pitting on the inside surfaces of the oxidizer were compared to the detailed notes taken in previous inspections of the vessel and filter arms. No additional pitting, noticeable growth of previously formed pits, or any other type of corrosion attack was detected. That is, all pitted areas appeared to be unchanged since the inspections performed prior to the SCWODAT program.

The weld joining the vessel "shell" to the top flange did not show any signs of degradation. This weld was made during the 1995 repairs of the vessel, just before the start of the SCWODAT program and thus, was exposed only to the environments which existed between the vessel and liner during the SCWODAT program.

Thus, during the SCWODAT program the environment behind the liner was apparently benign, and no additional degradation of the vessel including the filter arms occurred.

Quench Fitting

At the time of the inspection, the quench fitting opening was partially obstructed with a powdery substance which was readily removed. The inside diameter surface was difficult to examine through the opening but a small area which could be examined appeared to be in good condition, i.e. it did not show any signs of localized corrosion or erosion. The end face of the quench mouth retained original machining marks. A more detailed evaluation of the inside diameter surface would require sectioning of the tube to expose the I.D. surface.

Quench Purge Shell

A few scattered pits developed on the machined flange surface. Other surfaces accessible for visual inspection did not show any evidence of corrosion.

Quenched Effluent Line

Only the quench line inlet and outlet ends were examined. The inlet end was partially obstructed with a yellowish powdery substance which was readily removed with a toothbrush. The end faces and the inside diameter surfaces accessible for visual examination appeared intact.

Quench Cooler Inlet

The quench cooler inlet did not show any signs of plugging. The inside diameter surface was covered by a thin uniform layer of pink deposit. There was no evidence of localized or general corrosion.

None of the components from the quench mouth, downstream to and including the cooler, required any repairs and/or replacements throughout the entire program from Run 943 to Run 955B.

Nozzle Purge Shell and End Plate

The original component fabricated from titanium Grade 2 was in service in Runs 943 through Run 949. In Run 949, it suffered a severe corrosion attack. The replacement component fabricated from titanium Grade 12 was used in runs 950 through 955B.

An inspection of the component upon completion of the Navy Wastes Testing showed a pronounced non-uniform corrosion on the outside diameter surface of the shell and the bottom of the end plate, or flange. Severity of corrosion in the base metal and in the longitudinal seam weld metal was comparable. The depth of attack was up to 0.08 inch.

Based on a cursory inspection of the replacement purge shell and end plate by MODAR personnel after Run 950, some of the corrosion occurred during this run. Additional corrosion occurred most likely in the Run 952 when so-called "non-chlorinated" solvents were treated and the resulting oxidizer pH was very low before corrective actions were taken to raise the pH.

Feed Nozzle and End Face of the Nozzle Core Tube

The feed nozzle was in service from Run 945 through run 955B. Only the outside diameter surface of the feed nozzle was examined. In its lower portion, which had been protruding into the oxidizer, there were areas which can be described as "locally uniform" corrosion. A few shallow pits had developed on the conical surface near the bottom of the feed nozzle.

The feed nozzle core tube was in service throughout the entire program, i.e. Runs 943 through 955B. Only its end face could be examined; it did not show any pronounced degradation.

5.3.3 REFORMER NOZZLE

A reformer inlet nozzle, which was fabricated for the SCWODAT program from a previously used MODAR nozzle referred to as nozzle N-40, was essentially the only part of the reformer which failed during its service, limited in this program to Run 944. In order to put this failure in perspective, a history of nozzle N-40 has been provided.

A number of nozzles in the pilot plant oxidizer vessel including Alloy 625 nozzle N-40, located in the brine section, were removed after Run 924 (A previous DOE Program) in May 1993 and replaced with Alloy C-276 nozzles. Subsequently, MODAR performed Runs 925 through 927 (pH down to 1.7) without a liner, i.e. nozzle N-40 was not shielded from a range of aggressive environments in the oxidizer at that time. In Run 928, started on July 13, 1993, a titanium liner was installed for the first time.

Early in the SCWODAT program, a decision was made to replace all the oxidizer vessel nozzles prior to the start of the any SCWODAT program testing. This decision was based on a borescopic examination of accessible nozzles when pits and linear indications were detected in a number of the oxidizer nozzles. Upon review of the borescopic examination findings and evaluation of the history of nozzle N-40, the decision was made to reuse nozzle N-40 in the SCWODAT program

as the reformer inlet nozzle.

Nozzle N-40 was thoroughly cleaned, machined for weld preparations, and installed. The reformer assembly was annealed with proper precautions and subsequently used in Run 944 with a TRIM®SOL and NaOH feed.

A leak in the reformer inlet fitting was detected during Run 944. Upon shutting down the reformer, the fitting was tightened using wrenches with extension bars; which may have damaged the nozzle from over-torque. Later in Run 944, a leak was detected in the reformer fitting. Subsequent examinations by SCWODAT program personnel assisted by INEL revealed multiple, predominantly axial cracks varying in length from 1/8 inch to almost 1 inch at different locations around the fitting. It was concluded that these cracks had developed by a stress corrosion cracking mechanism. The evaluation was limited to visual examinations in a stereomicroscope and metallographic examinations. No cracks were opened up for fractographic and surface chemical analyses. Thus, one can only speculate when stress corrosion cracking actually initiated and whether both crack initiation and propagation occurred during the brief service in the reformer or initial cracks formed in nozzle N-40 possibly well before the start of the SCWODAT program and then propagated through the wall when exposed to the reformer environment. It cannot be ruled out however, that it was a case of rapid caustic stress corrosion cracking in the high pH environment of the reformer inlet. Stress field induced during over-torquing may have contributed to the rapid crack propagation.

APPENDIX A

A.1.0 FABRICATION

The design and fabrication for the TRIM®SOL testing focused on these key process components: the oxidizer, the oxidizer liner, the reformer, and the quench system. A detailed description of each follows in the text below.

A.1.1 OXIDIZER VESSEL

Prior to July 1993, the oxidizer vessel internal surfaces were directly exposed to the aggressive SCWO environments for approximately 1500 hours. In July 1993, MODAR installed a titanium liner inside the oxidizer vessel to protect a portion of the vessel and extend its life. In early 1994, prior to the SCWODAT program, INEL and MODAR conducted a testing program evaluating the performance of developmental ceramic coatings (Garcia, K.M. and Mizia, R., "Corrosion Investigation of Multilayered Ceramics and Experimental Nickel Alloys in SCWO Process Environments," Idaho National Engineering Laboratory Publication INEL-95/0017, February 1995). In this program, dozens of samples were exposed to very aggressive, sub and supercritical environments. The upper part of the vessel was protected from direct exposure to these environments by a stack of ceramic coated rings.

Prior to the SCWODAT program testing, it was determined that to ensure safety and integrity of the oxidizer vessel, it was necessary to perform a non-destructive examination. Section 2 of Appendix A provides a detailed description and discussion of the non-destructive examination methods used, the findings, the repair, and the steps taken to maintain the oxidizer as an ASME code approved pressure vessel.

A.1.2 LINER FABRICATION

A liner was placed inside the oxidizer pressure vessel to maintain isolation between the corrosive oxidizing environment and the pressure containing wall. The liner was designed to be replaceable, when necessary, for a small fraction of the pressure vessel cost. Three liners were used in the SCWODAT program:

- **Liner No. 1** - All metallic, titanium Grade 12 used with TRIM®SOL, heavy metals, and NaOH.
- **Liner No. 2** - TiO₂ ceramic coating on titanium Grade 12 used with TRIM®SOL, heavy

metals, and NaOH.

- **Refurbished Liner No. 1** - All metallic new titanium Grade 12 used for nine individual Navy wastes and composite Navy waste tests.

Note: Liner No. 1 and Refurbished Liner No. 1 have a common, reused titanium Grade 2 portion in the lower "boot" section.

A.1.2.1 HISTORY OF LINER NO. 1

During the SCWODAT program, three SCWO oxidizer liners were evaluated to determine the proper configuration and materials for future liners. Liner No. 1 was fabricated in the fall of 1993 from a new upper cylindrical section and a lower section salvaged from an earlier liner used during the latter stages of the 1993 DOE program. The new upper section was fabricated from Grade 12 titanium sheet which was rolled and welded to form a 9.5-inch diameter cylindrical shell. The salvaged titanium Grade 2 lower section consisted of a 2-inch long cylindrical section with a diameter matching the upper liner, a conical section, and a bottom section. No postweld heat treatment was performed after fabrication.

The liner was first used for MODAR Runs 934 through 936 where it was exposed to a typical range of oxidizer temperature-pressure conditions, feeds containing various chlorinated and sulfonated organics (with in-situ neutralization), and dissolved salts.

This liner was subsequently utilized in the 1994 INEL corrosion program. In these test runs, the I.D. surfaces of the upper, hot section were shielded by ceramic-coated rings while the lower unprotected section was exposed to an environment formed after neutralizing and quenching had occurred within the lower part of the ceramic-ring stack. The feed material for the INEL corrosion program was also TRIM[®]SOL cutting fluid. The oxidizer operated with no in-situ neutralization performed in the reaction zone.

Liner No. 1 was again utilized in the 1995 SCWODAT program for Runs 943 through 949. Modifications to Liner No. 1 prior to the start of the SCWODAT program testing included a welded extension to the upper titanium Grade 12 cylindrical section. A removable top hat/nozzle purge shell and a welded quench mouth adapter, both fabricated from titanium, were added.

During Run 949, Liner No. 1 suffered major corrosion attack resulting in perforations. After the run, the liner was removed for repairs. Samples of the attacked metal and solid deposits were analyzed at Geller Microanalytical Laboratory. A sample removed from one of the perforations was also sent to INEL for analysis. See Subsection 5.3.1 for more details. A titania-coated liner,

identified here as Liner No. 2, was installed for Run 950.

A.1.2.2 LINER NO. 2 (liner with a graded ceramic coating)

Titanium alloys are usually considered to have a limited applicability at temperatures in excess of 400°C because of accelerated oxidation as well as enhanced susceptibility to hydriding and nitriding. Also, titanium is susceptible to pitting and crevice attack in some of the environments encountered in the SCW oxidizer. Protection of titanium surfaces by titania-based ceramic coatings appears to be a viable means of mitigating the above problems and potentially enhancing the service life of the liner (Garcia, K.M. and Mizia, R., "Corrosion Investigation of Multilayered Ceramics and Experimental Nickel Alloys in SCWO Process Environments," Idaho National Engineering Laboratory Publication INEL-95/0017, February 1995). Gradient-composition coatings also known as graded coatings are logical candidates for applications where ceramic-coated components are exposed to significant temperature changes. Properly designed graded coatings are known to minimize thermal expansion incompatibility effects.

Liner No. 2 was designed by MODAR as a two-part titanium liner consisting of an upper-half and a lower-half. This two part liner design was selected to test the concept of a liner with a replaceable bottom half. Liner No. 2 used in the SCWODAT program was coated by the Zatorski Coating Co. of East Hampton, CT under contract to INEL.

The two-part titanium Liner No. 2 upper half and lower half were supplied by MODAR for coating of the inside diameter surfaces. The areas for coating were the straight cylindrical sections, the joint area, and the quench mouth adapter.

Problems were encountered during the surface preparation prior to coating the internal diameter surface of the liner. The most significant of these problems involved cracking on the inside diameter surface of the liner. During the grit blast operation, some areas of the titanium liner surface started to show cracking and peeling. These surface defects were in the lower half of the liner approximately mid-way in the cylindrical section. The upper half of the liner showed none of these problems.

The peeled titanium was less than 0.005 inches (0.127 mm) thick. The crack pattern could be described as a network of cracks similar to those in dry mud. The visible cracks were readily removed to apparently sound metal using the stone. Upon re-blasting the areas, there was a minimum of additional cracking. No further removal was attempted.

The coating was applied using a Metco 3MB plasma gun connected to a PlasmaTechnic control

console utilizing closed-loop control on gas flows and power. Additional cooling jets and gun cooling were employed to cool the equipment and the part.

On the liner lower half, there was some lifting of the substrate during the coating application of the bond coat, but after inspection, it was decided to proceed with coating rather than strip the entire coating and reapply. This lifting appeared as coated, raised bumps in a circumferential band area mid-way in the cylindrical section. The two areas where it was observed were approximately 1 inch (25 mm) long and 0.100 inches (2.5 mm) wide and in the same general area as the previously observed cracking. No further incidents occurred during coating the lower half of the liner. There were no problems in coating the upper half of the liner.

A.1.2.3 REFURBISHED LINER NO. 1

After Run 949, the titanium Grade 12 cylindrical section of liner No. 1, which had suffered severe corrosion, was cut from the bottom section. To facilitate reassembly, the separation line was selected 2 1/4 in. above the transition to the titanium Grade 2 conical section. Two titanium Grade 12 cylinders were formed and reattached to the original bottom section. The quench mouth adapter, titanium Grade 12 dimple for a thermocouple, and bolted flange ring were attached to the upper part of the cylinder.

Refurbished Liner No. 1 was reinstalled for the Navy waste testing (Runs 951 through 955 B). Table A.1.2 defines the exposure hours for Liner No. 1 prior to and after the repair.

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TABLE A.1.2

LINER No. 1 EXPOSURE SUMMARY

RUN	HOT HOURS	FEED HOURS	NOTES
934-936	183.8	84.5	MODAR in-house waste runs and feed nozzle testing. Various chlorinated organics, sulfonated organics, solution containing NaCl and Na ₂ SO ₄ .
937-942	341.7	238.0	1994 INEL corrosion program. The liner was shielded by ceramic-coated test rings. Feeds contained TRIM®SOL (unneutralized) and metal surrogates.
943-949	476.5	248.0	Phase I SCWODAT program utilizing TRIM®SOL feed (neutralized and unneutralized; reformed and non-reformed) with heavy metal surrogates. Post Run 947 observations showed that the TE-4016 dimple made of Ti, Grade 2 failed. Replaced with Ti, Grade 12 dimple for subsequent runs. Liner No. 1 was perforated at numerous locations in Run 949. Liner No. 2 with a graded coating including a titania topcoat was installed for Run 950. Liner No. 1 was repaired and reinstalled starting with Run 951.
951-955B	265.2	188.1	Phase II Navy waste testing
TOTAL	1267.2	758.6	Since liner has undergone a number of repairs, total hours for the various parts of the liner vary.

A.1.3 REFORMER DESIGN AND FABRICATION

Previous MODAR bench scale experimentation demonstrated that complete neutralization of certain chlorinated organic compounds could be achieved after short exposure to near critical temperature conditions in the presence of NaOH. This exposure was accomplished prior to the introduction of the TRIM®SOL waste to the SCWO oxidizer. This technique, referred to as reforming, is described in detail in U.S. Patent No. 5,492,634 dated February 20, 1996. To facilitate improved in-situ neutralization, SCWODAT program personnel designed, fabricated, and integrated into the existing pilot plant system a TRIM®SOL reforming unit.

The operating parameters and selection of materials were based on the data collected from the bench scale experiments. The proper pipe diameter and length were selected.

Heating requirements were met by applying radiant energy to the surface of the piping and by introducing a small flow of SCW into the fluids to be reformed. The reformer plumbing design package was reviewed by Stone & Webster engineers prior to fabrication. The package was designed in accordance with ANSI/ASME B31.3 Code.

A completely welded fabrication was selected to minimize potential problems associated with the environment at the temperatures and pressures in the reformer. All welds were annealed to minimize residual stresses. Welded joints were also used in the tubing run carrying the reformed fluid from the reformer to the oxidizer. These joints were annealed in place utilizing techniques and equipment developed by SCWODAT program personnel.

Temperature and pressure sensing instruments were wired directly to the pilot plant process control system to allow remote monitoring of reformer process variables. These instruments were embedded in the overall process control configuration to allow for monitoring and safe operation.

The integrated reformer package was subjected to a Hazards and Operability review performed by SCWODAT program personnel as part of the overall pilot plant review prior to testing and operation.

A.1.4 QUENCH SYSTEM DESIGN AND FABRICATION

The MODAR pilot scale quench system was designed to rapidly reduce the oxidizer overhead effluent temperature from 600° C to 300° C and neutralize the effluent to maintain a pH greater than 5. The quenched effluent design temperature was chosen to:

1. Solubilize the small quantity of entrained sticky salt exiting the oxidizer to avoid plugging of the downstream components.
2. Use corrosion-resistant titanium alloys in pressurized process components at temperatures where the ASME Section VIII Code provides allowable stress values.

Prior to the SCWODAT program, Liner No. 1 was modified to accept a MODAR designed fitting or "quench mouth" in which the actual direct contact quenching would occur. Later, the same quench mouth design was used with the titania-coated Liner No. 2 in Run 950 as well as in the uncoated refurbished Liner No.1.

An existing high pressure pump which had previously been used in the pilot plant, was determined to be of adequate capacity for the delivery of the quench water to the fitting. The suction of this pump was modified to accept a small flow of neutralizing agent. A low pressure metering system was designed and fabricated to deliver the neutralizing agent to the quench pump suction in a precise fashion. This configuration provided additional overhead effluent neutralization capabilities and, hence, improved effluent pH control. A new high pressure SCW pump was specified, purchased, and installed.

Final overhead effluent temperature reduction to 45° C was required to achieve optimal liquid/gas phase separation prior to pressure letdown. A new heat exchanger was designed and fabricated to perform this cooling.

An open gravity drain cooling water system was chosen to avoid the need to design a pressurized cooling jacket. A Type 316 stainless steel removable top drum was designed and fabricated to house the heat exchanger. The drum had a cooling water inlet fitting at the lower wall section of the drum and an upper cooling water outlet fitting. Instrumentation for the cooling water system included a flow meter, flow control valve, and numerous thermocouples.

The heat exchanger was positioned on one of the existing pilot plant skids. The high pressure plumbing from the quench fitting to the inlet of the heat exchanger was fabricated from the same pipe as used for the heat exchanger. It utilized end adapters which were fabricated from bar stock and were similar to those used in the heat exchanger. This plumbing was also annealed to minimize residual tensile stresses.

Pressure and temperature sensing instrumentation for the entire quench system was wired directly to the process control system to allow for remote monitoring of its performance. Emergency shut-

down routines were integrated into the process control configuration to maintain safe operation.

A.2.0 OXIDIZER VESSEL INSPECTION AND REPAIRS

Prior to the aggressive environment tests of the 1994 program mentioned in the text of this report, the Alloy 625 oxidizer vessel had operated for approximately 1500 hours with no protective inner liner.

In June of 1994, prior to commencement of the SCWODAT program testing phase, the MODAR oxidizer vessel was subjected to an in-house nondestructive examination (NDE) program developed and implemented by SCWODAT program personnel. The NDE scope was limited by accessibility with a special emphasis placed on the oxidizer vessel nozzles. The techniques utilized included:

- Visual inspection
- Liquid penetrant inspection
- Ultrasonic straight beam inspection
- Ultrasonic shear-wave inspection
- Borescopic inspection

This examination revealed numerous corrosion pits and in some cases, crack-like indications on the inside diameter surfaces of the nozzles. Based on the findings, a decision was made to replace twenty-nine small diameter, welded nozzles (most were thermowells) to assure the mechanical integrity of the oxidizer vessel. SCWODAT personnel developed the formal repair plan, which was approved by the local ASME/National Board inspector. The repair plan required stringent post-repair cleaning and annealing of the complete oxidizer vessel. The repairs were performed by ACME Industrial Equipment Inc. of Boston.

The completed vessel and top flange assembly were annealed by METLAB Inc. of Philadelphia, and returned to ACME Industrial Equipment for final hydrostatic pressure testing and code stamping. During a preliminary hydrostatic pressure test, a leak was detected below the top flange of the oxidizer vessel between two closely spaced circumferential welds. The finding of the leak precipitated another, more detailed NDE program as described in this appendix. Liquid penetrant examinations, performed by Stone & Webster at ACME, revealed a tight axially-oriented through-wall crack in the vessel shell. Liquid penetrant examination of this area in 1994 was hindered by accessibility on the outside diameter surface and condition of the inside diameter surface at the time. Moreover, the crack may have propagated through the wall, quite likely from a previously formed part-through crack, during the heat treatment at METLAB Inc. and thus would not be

detectable on the outside diameter surface during the 1994 NDE even if that area had been accessible at the time. Accessibility problems precluded detailed ultrasonic examinations which could possibly have detected an axial crack at that location during the 1994 NDE inspection. The crack was detected ultrasonically with great difficulty during the January 1995 inspection even when accessibility was not an issue and the location was known.

A.2.1 JANUARY 1995-FEBRUARY 1995 NONDESTRUCTIVE EXAMINATIONS OF OXIDIZER VESSEL

These nondestructive examinations were prompted by a leak detected during a January 1995 hydrostatic test performed at the ACME Industrial Equipment plant following replacement of all the nozzles and heat treatment of the oxidizer vessel at METLAB Inc. (see Subsection A.2.0). The objective of the examinations was to assess the condition of the oxidizer vessel using a wider range of inspection methods than the June 1994 inspection while taking advantage of the complete accessibility to the outside surfaces of the vessel. This inspection was to verify whether any other cracks still existed in the vessel and establish a basis for a repair plan.

The NDE included:

- visual examinations with the naked eye and with a magnifying glass at magnifications of 3X and 5X
- borescopic examinations
- liquid penetrant examination (LP)
- radiographic examination (RT)
- ultrasonic shear-wave examination (UT)
- straight-beam ultrasonic examination
- alloy analysis

The UT and LP examinations, and the alloy analysis, were performed by a Stone & Webster Level III NDE inspector; the RT examinations were performed by Baker Testing Services, Inc. of Rockland, MA, and the RT results were evaluated by Stone & Webster; borescopic and visual examinations were performed by SCWODAT program personnel.

The visible LP examinations were performed with the Sherwin Dubl-Chek penetrant materials. In the UT examinations, 8x9 mm, 45-degree angle, 2 and 4 MHZ transducers were used for scanning from the O.D. surface. A limited UT examination from the I.D. surface was done with a 1/4-in., 2 1/4-MHZ transducer. A 1/16-in. notch in a calibration block with a prototypical geometry/material was used to calibrate the UT response.

The RT examinations were performed in accordance with the procedural requirements of the ASME Boiler and Pressure Vessel Code, Section V, Article 2, with the following exceptions:

- geometric un-sharpness of ≤ 0.020 in. and
- Kodak "M" film or its equivalent

were specified to improve the resolution for the purposes of the vessel condition assessment.

In 1992, the top portion of the oxidizer vessel had been modified. As part of these modifications, a new girth weld was fabricated to join a remaining short stub to a cross piece carrying the horizontal filter arms nozzles.

The key findings were:

- An axial through-wall crack was detected in the short stub between two closely spaced welds. The crack was found at the location where a leak occurred during the preliminary hydrotest. The crack was detected visually (with a magnifying glass), by LP, by RT, and by UT when scanning from the I.D. side. On both O.D. and I.D. surfaces, it ran from one girth weld to the other. Its length was 2 in. on the I.D. surface and ~5/16 in. on the O.D. surface. The crack was located 1 1/4 in. from the nearest toe of the seam weld, i.e. it was not associated with the seam weld in the stub. The crack had developed in a plane perpendicular to the maximum expected residual welding stresses associated with one of the girth welds.
- Intermittent lack-of-fusion circumferential indications were detected by the RT examination in one of the girth welds. There were approximately a dozen aligned (i.e. at the same axial position or the same distance from the vessel flange) indications with lengths between 1/4 and 3 in. These indications were ~1/2 in. from the center of the weld root toward the adjacent cross piece. They were subsurface (i.e. not connected to either I.D. or O.D. surfaces) indications, apparently from the fabrication associated with the modifications of the vessel made in 1992. All the circumferential indications appeared to be in one weld bead where a lack of fusion might have occurred as the weld bead was deposited during welding.

- A crack-like indication was detected at the I.D. surface in the longitudinal seam weld of the original cylindrical portion of the vessel. This indication was found first by borescopic examination and then by UT. RT performed in this area did not show any indications at this location. Based on the UT examination, this I.D.-connected indication was $\frac{1}{2}$ in. long. The length as measured with a tape and read through the borescope was $\frac{5}{16}$ in. This indication was located at the toe of the root weld which was closer to the nozzles. The distance from the indication to the flange top was 33 in. This indication proved to be superficial as it was readily removed by an abrasive paper.
- A $\frac{1}{16}$ in. deep crack-like indication was detected by UT in the same general area at the O.D. surface of the vessel, apparently at the longitudinal seam weld. It was located under the fillet weld which joins the upper support gusset to the reactor body. The axially-oriented indication was traced over a 3 in. long section (33 to 36 in. from the flange top). An adjacent support bracket was removed to provide an access for RT in this area. The area was polished after the removal of the bracket and reinspected by UT, LP, and RT; the originally reported indication was not detected by any of these methods as it was apparently removed in the process of providing access for the examinations.
- In the support gusset located under one of the filter arms, a $1\frac{1}{4}$ in. long crack was visually detected in a fillet between the support lug and upper gusset. The crack was located in a plane transverse to the vessel axis, i.e. perpendicular to the seam weld. The crack length based on the LP indication was also $1\frac{1}{4}$ in. According to the UT, there was a planar indication at the O.D. surface of the vessel which suggested that the crack in the support could have grown into the wall of the vessel by $\sim\frac{1}{16}$ in. Based on a subsequent LP examination, this indication was eliminated when an adjacent support bracket was removed to provide an access for RT in this area. This RT did not detect any indications.
- An $\frac{1}{8}$ -in. long indication was detected by LP on the O.D. surface after the removal of the support bracket; this indication was located $38\frac{1}{4}$ in. from the top of the vessel flange and $\frac{1}{4}$ in. above the top toe of the longitudinal seam weld. Based on the UT shear wave examination, this planar indication was very shallow and its depth was likely to be well below $\frac{1}{32}$ in.
- Scattered pits were present on the I.D. surfaces in virtually all individual parts of the vessel. Typically, their depth was in the range between 0.005 and 0.030 in. In the upper part of the vessel, a few pits, including some pits in the Alloy 625

overlay were as deep as 0.050 in. In a number of areas, pits were aligned and interconnected. An area 1 1/2 in. by 3/4 in. on the I.D. surface of a filter arm, 17 in. from the end face of the weld neck flange at the 10 o'clock position, was attacked to a depth of up to 0.040 in.

- The alloy analysis using a Texas Nuclear semi-quantitative analyzer confirmed specified materials for all tested components of the vessel, including but not limited to the main cylinder, 2-in. stub, frustum, lower cylinder, cross piece, filter arms, longitudinal seam welds, and weld necks; head flange and nozzle tubes.
- Wall thickness of the vessel exceeded the minimum design wall, except at the machined bands in the vessel where it was found to be slightly less than the calculated minimum wall for the design conditions.

A.2.2 SPRING 1995 OXIDIZER VESSEL REPAIRS

The oxidizer vessel NDE program identified three areas which required repair:

- Through-wall crack in the upper part of the vessel shell
- Crack in a fillet weld joining a support lug to the body of the vessel
- Wall thickness deficiency in vessel shell at machined bands.

In March 1995, MODAR issued a formal repair plan that was approved by the local ASME/National Board inspector. ACME Industrial Equipment performed the required repairs.

The repair of the through-wall crack required removal of a 2-in long section in the upper part of the vessel shell to excise the cracked area. The removed "ring", which contained the crack, was saved for future study to determine the mode of failure. However, such a study has not yet been performed.

The upper part of the vessel known as the "top flange" was originally fabricated from Alloy 800H with Alloy 625 overlay on all surfaces which could potentially be exposed to the process fluid. It was machined back to the base 800H alloy to remove the initial overlay affected by pitting, overlaid with fresh Alloy 625 weld deposit, and machined. Careful attention was given to dimensional tolerances to ensure that the "finish machining" met the specifications of the flange manufacturer.

A 0.5 in. long and 0.1 in. deep band was machined out at the inside diameter surface at the top

of the lower part of the vessel section and filled with Alloy 625 weld material. The inside diameter surface at that location was then machined, over the 0.5 in. length, back to its original 9.9 in. diameter. Weld preparations were made at the end of the refurbished flange and at the end of the lower vessel section; the flange and the vessel were then aligned and reattached by welding. Tight angular tolerances were met so that the original orientation of both pieces was maintained.

The NDE inspection showed that the crack in the fillet weld connecting the vessel support bracket to the outer vessel shell extended approximately 1/32 in. into the vessel wall. The area in which the crack was observed was ground to remove the crack; after verifying the crack removal with liquid penetrant inspection, the area was refilled with Alloy 625 weld metal. The repaired surface was then polished and reinspected. No relevant indications were detected. The mounting lug was inspected, deemed free of defects and rewelded in its original position to the vessel shell.

The machined "bands" around the vessel shell were made in 1992 to allow the centering of the vessel in a lathe for a previous modification to the vessel. The January 1995 NDE program showed that the vessel wall thickness at these bands was somewhat less than required for the design conditions per ASME Sec. VIII, Div.1. This deficiency was rectified by grinding the edges of the grooves to eliminate potential stress raisers and filling the grooves with Alloy 625 weld metal. The repair welds were ground flush to the existing surface of the vessel shell and inspected; no relevant indications were found.

The inside surfaces of the repaired vessel were treated with controlled shot peening to impart compressive residual stresses on the surfaces which could potentially be exposed to the process fluid. This technique was chosen to mitigate concerns of stress corrosion cracking in the weld-repaired areas. The shot peening was performed by Metal Improvement Co., Inc. of Windsor, CT.

The refurbished vessel was returned to ACME Industrial for final inspection, hydrostatic testing, and code stamping. The unit was delivered to MODAR on May 11, 1995 for installation.

APPENDIX B

B.1.0 MATERIALS TESTING

Eleven corrosion specimens were exposed to the SCW environment at elevations above the feed nozzle injection level, i.e. at temperatures near 600°C. The specimens were suspended from the liner top flange on a tree placed 180 degrees from the quench mouth and within 3 in. from the axis of the nozzle purge shell. Exposures of the samples significantly varied, i.e. some specimens were inserted later in the program and some were removed prior to its completion.

Three groups of materials were tested:

- Titanium Various Grades
- Nickel-based alloys such as Alloy 625 and Alloy 686
- Noble wires such as Ir and Pt-10%Ir

A list of the specimens, their form, dimensions, run numbers in which they were exposed, and exposures expressed in cumulative hot hours and cumulative feed hours are summarized in Tables B.1 through B.4. Each specimen was weighed before testing and after cleaning. Prior and subsequent to cleaning, all the specimens were examined in a stereomicroscope. Mass losses and observations prior to and subsequent to cleaning are presented in Tables B.1 through B.4. A discussion of each group of specimens follows.

Titanium Specimens

Some of the titanium specimen grades, identifications, and specimen types were as follows:

- Titanium Grade 2: Ti-2w-1, U-bend with a weld
- Titanium Grade 2: Ti-2w-4, U-bend with a weld
- Titanium Grade 12: Ti-12w-1, U-bend with a weld
- Titanium Grade 12: Ti-12w-5, U-bend with a weld

The flat coupon and U-bend specimens were fabricated by Metal Samples of Munford, Alabama. All U-bend test specimens contained a weld located across a specimen in the middle of the bend. The flat coupon contained a weld along the specimen length. The composite specimen was fabricated by Harwood Engineering of Walpole, MA using their proprietary technology. In the composite tube specimen, high compressive stresses were locked in on the inside diameter surface of the Grade 2 tube.

The criteria for selection of the materials were as follows. Titanium Grade 2 and Grade 12 were used by MODAR in the pilot plant components at the reaction zone temperatures since 1993 but only limited test data had been available. Titanium grades for the composite tube were selected from available materials/sizes rather than based on anticipated needs for the reaction zone applications.

An examination of the titanium specimens in a stereomicroscope prior to cleaning revealed up to four readily detectable layers of oxides/corrosion products:

- an apparently adherent black layer at the bottom i.e. at the base metal
- another black layer which had partially spalled off
- a yellow layer which had an the appearance of baked powder
- a brownish layer which had detached at many locations and was flaking off

No examination of the chemistry or crystal structure of the four individual layers observed on the surface of the specimens prior to cleaning was performed.

Around the holes in the U-bend specimens, where tight crevices existed under the washers during testing, a uniform apparently adherent black film formed. There were no signs of crevice corrosion in any of the titanium U-bends, in spite of the fact that two out of seven titanium specimens were in the Run 949 in which the liner suffered a severe underdeposit corrosion.

Pre-test weighing was done by MODAR. Post-test cleaning and weighing of the specimens was performed by CLI International, of Houston, TX. Prior to post-test cleaning, the specimens were cleaned first by brushing and then by chemical cleaning. After the chemical cleaning, glass bead blasting was used for the titanium specimens after it was determined that chemical cleaning would not remove what was described as a remaining "dark orange to black" film. Moreover, the remaining film could not be completely removed even by glass bead blasting.

A post-cleaning examination of the specimens at magnifications of 50X and 100X revealed that the "remaining film" actually consisted, in most cases, of a black layer at the bottom and dark orange top layer. An average combined thickness of the film was estimated for each titanium specimen from measurements in a light optical microscope. The specimens were secured on the microscope stage, and a number of areas at the edges of the film were selected where one could focus on the top surface of the film and then move the stage vertically until the titanium base metal surface was in focus. The stage vertical movement was measured within ± 0.001 mm. Estimated average thickness value of the combined film was as follows:

Titanium Grade 2 and Grade 12 specimens - 0.15 mm

Surface areas still covered by the film were estimated for each specimen so that a correction could be made in the reported mass losses. Since the chemistry of the film layer had not been determined, a density of 3 g/cm³ was used as representative for a range of titanium compounds. The mass loss determined from weighing and corrected for the remaining film was likely to be conservative, i.e. overestimated since some titanium base metal was probably lost during glass bead blasting.

The U-bend area in the five titanium U-bend specimens was examined in a stereomicroscope before and after cleaning. No cracks were detected in any of the titanium U-bend specimens.

In calculating the metal loss rate, the entire area of the specimens was used, including the areas shielded by the washers. The metal loss rates are given in Table 2 based on post-cleaning specimen mass values with and without a correction for the remaining film. Also, these rates were based on the feed hours rather than total hot hours. Using the total hot hours would reduce the rates by about 30 percent. The actual rates may have been varying with time and most likely from one run to another. Nevertheless, the averaged metal loss rates provide a useful measure of performance in the absence of pronounced localized corrosion.

For the titanium alloys tested, the metal loss rate varied typically between 2.5 and 3.5 mm/year except for the composite specimen where the calculated metal loss rate was near 1 mm/year.

While the calculated metal loss rates were conservative, they imply uniform oxidation/corrosion, which are fairly predictable degradation mechanisms. It was not clear why the titanium samples such as Ti-2w-1 and Ti-12w-1 survived Run 949 without any of the pronounced localized corrosion which attacked Liner No. 1 and the nozzle purge shell. Perhaps, a comparison with the Liner No. 1 was not fair since the liner was primarily affected by corrosion below the level of the feed injection point where the local conditions may have differed. The nozzle purge shell, on the other hand, must have been exposed to the same environmental conditions as the samples since they were located close to the nozzle purge shell. One possibility was that the fabrication history of the specimens compared to the nozzle purge shell differed enough to account for the differences in performance. While specific differences in the fabrication histories which could be instrumental in the poor performance of the nozzle purge shell cannot be reliably determined at this time, close fabrication controls of titanium components cannot be overemphasized.

At the SCW conditions, some other changes, e.g. hydriding and nitriding, could have taken place in the titanium specimens. No examinations to verify whether any of these degradation mechanisms occurred in the specimens have been done to date.

Nickel-Based Alloys

Two nickel-based alloy specimens, both in the U-bend form, were tested:

- Alloy 625
- Alloy 686

Alloy 625 was the material of the pressure vessel and SCW tube. Its average to poor performance when directly exposed to aggressive SCW oxidizer environments was known based on previous tests and the history of component degradation. The Alloy 625 specimen was used in these tests as a "reference" material.

The Alloy 625 specimen was inserted prior to Run 945 and was removed after Run 950; it had seen about 350 cumulative feed hours in Runs 945 through 950 and had suffered a heavy general corrosion. There was no evidence of cracking in the U-bend area or anywhere else in the specimen. No pronounced crevice corrosion had developed in the crevices under the washers.

The corrosion rate calculated from the Alloy 625 specimen metal loss in these tests, while fairly high (~4 mm/year), was not much higher than the calculated metal loss for some of the titanium specimens. One significant difference is that the surface of the Alloy 625 specimen was very rough, i.e. its metal loss was far less uniform than in the titanium specimens. This was probably due to the different governing mechanisms of metal loss in the Alloy 625 specimen versus the titanium specimens. While metal loss in the Alloy 625 specimen occurred primarily by "general" corrosion which, in the case of high-nickel alloys, often develops by formation of numerous overlapping wide-open pits, the metal loss in the titanium alloys apparently occurred primarily by oxidation.

Alloy 686 was a new high-nickel alloy which was developed as a material with superior corrosion resistance in a range of highly aggressive reducing and oxidizing environments. In fact, one of the pitting resistance equivalents, PRE, defined as

$$PRE = \%Cr + 1.5(\%Mo + \%W + \%Nb)$$

was quite high, about 51, which significantly exceeded PRE for Alloys 625 (PRE=40), C-22(PRE=46), and C-276 (PRE=45) and would suggest a rather high pitting resistance. Also, its critical crevice temperature as determined in a 6 percent ferric chloride solution, was much higher than for Alloys 625, C-22, and C-276.

The Alloy 686 specimen was inserted prior to Run 945. A visual examination of the specimen

after Run 948 showed that it had undergone a severe corrosion attack. After Run 949, a major part of the U-bend was missing. Only a severely corroded portion of each leg of the specimen had survived; the rest of the specimen was apparently dissolved.

Noble Wires

Two noble wires were tested in Runs 945 through Run 955B:

iridium
platinum - 10 percent iridium

There were no apparent signs of corrosion on either of the wire specimens. The reported mass of the specimens was as follows:

<u>Specimen</u>	<u>Mass before Testing, g</u>	<u>Mass after Cleaning, g</u>
Ir wire	0.2725	0.2728
Pt-10%Ir wire	0.2396	0.2397

Thus, there was no loss of metal during the 535-hour exposure (feed hours) in the SCWODAT program in either of the noble wire specimens. In fact, formally one could conclude there was a slight mass gain provided repeatability and accuracy of weighing in two different laboratories was better than 0.0001 g.

TABLE B.1

TITANIUM CORROSION SPECIMENS - BASIC INFORMATION

#	Specimen I.D.	Material	Form	Run No	Cumulative Hot Hours	Cumulative Feed Hours	Dimensions mm
1	Ti-2w-1	Ti Gr.2	U-bend	945-950	507.5	347.25	127x18.9x1.52; hole-9.5
2	Ti-2w-4	Ti Gr.2	U-bend	951-955B	265.2	188.1	127x18.9x1.52; hole-9.9
3							
4							
5	Ti-12w-1	Ti Gr.12	U-bend	945-950	507.5	347.25	127x18.97x3.02; hole-9.9
6	Ti-12w-5	Ti Gr.12	U-bend	951-955B	265.2	188.1	127x18.97x3.02; hole-9.5
7	Composite Tube		Tube within a tube ¹⁾	951-955B	265.2	188.1	20.64 O.D.; 13.7 interface dia.; 9.4 I.D.; l=73

1) Interference fit between the tubes obtained by a proprietary Harwood Engineering process; no evidence of corrosion at the interface.

TABLE B.2

TITANIUM CORROSION SPECIMENS - MASS CHANGES AND METAL LOSS RATES

#	Specimen I.D.	Cumulative Feed Hours	Original Mass, g	Post-Cleaning Mass, g	Mass Change, g	Area, cm ²	Ave. Film Thickness, mm	Area Fraction of the Film	Corrected Mass Change, g ¹⁾	Metal Loss Rate ^{2),3),5)} , mm/year	Metal Loss Rate ^{2),4),5)} , mm/year
1	Ti-2w-1	347.25	15.6055	13.2449	-2.3606	50.51	0.15	0.15	-2.7016	2.61	2.99
2	Ti-2w-4	188.1	15.9770	15.8303	-0.1467	50.31	0.15	0.55	-1.3918	0.3	2.86
3											
4											
5	Ti-12w-1	347.25	30.3435	28.3333	-2.0102	55.80	0.15	0.60	-3.5168	2.05	3.59
6	Ti-12w-5	188.1	30.5523	31.1167	+0.5644	55.97	0.15	0.95	-1.8282	Mass gain	3.43
7	Composite Tube	188.1	92.28	91.7649	-0.5151	74.191	0.10	0.95	2.0274	0.7	1.1

1) The mass change was corrected for the remaining film not removed during cleaning, assuming film density of 3 g/cm³, average film thickness, and estimated area fraction of the film.

2) Density of 4.51 g/cm³ was used in this Table for grades 2 and 4.43 was used for grade 12.

3) Based on metal losses without a correction for remaining film.

4) Based on metal losses with a correction for remaining film;

5) Rates based on total hot hours would have been about 30 % lower.

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TABLE B.3

NICKEL-ALLOY AND NOBLE WIRE CORROSION SPECIMENS - BASIC INFORMATION

#	Specimen I.D.	Material	Form	Run #s	Cumulative Hot Hours	Cumulative Feed Hours	Dimensions mm	Notes
1	625	Alloy 625	U-bend	945-950	507.5	347.25	127x18.92x1.549; hole-9.9	
2	686	Alloy 686	U-bend	945-949	394	251.25	127x18.92x1.5; hole-9.9	The specimen disintegrated in Run 949
3	Ir	Iridium	Wire	945-955B	772.7	535.4	0.508 dia; 60.45 long	One of the two specimens exposed to both Phase I and Phase II testing
4	Pt-10Ir	Platinum-10 percent Iridium	Wire	945-955B	772.7	535.4	0.508 dia; 54.61 long	One of the two specimens exposed to both Phase I and Phase II testing

TABLE B.4

NICKEL-ALLOY AND NOBLE WIRE CORROSION SPECIMENS - MASS CHANGES

#	Spec. I.D.	Cumulative Feed Hours	Original Mass, g	Post- Cleaning Mass, g	Mass Change, g	Percent Mass Change, %	Area, cm ²	Density, g/cm ³	Corrosion Rate, mm/year
1	625	347.25	28.8442	22.0935	-6.7507	-23.4	53.061	8.44	3.8 ²⁾
2	686	251.25	28.8338	N/A ¹⁾	N/A	N/A	N/A	N/A	N/A
3	Ir	535.4	0.2725	0.2728	+0.0003	+0.11	N/A	N/A	Mass gain
4	Pt-10Ir	535.4	0.2396	0.2397	+0.0001	+0.04	N/A	N/A	Mass gain

Notes:

1) The specimen disintegrated in Run 949. Most of the specimen including the bend area was missing after Run 949. The only material remaining were parts of the U-bend legs retrieved after the test.

2) Based on the cumulative feed hours; if corrosion rate during hot hours without feed were assumed comparable to the rate during the feed period, the corrosion rate would be 30 percent lower.

B.2.0 MECHANICAL TESTING

Run 943

Dates: 5/23/95-5/26/95 and 5/30/95-5/31/95

Duration:

Hot Hours- 36 hours 51 minutes

Feed Hours- 6 hours 50 minutes

Waste Feed Flow: 275 gpd (IPA only. No TRIM®SOL was processed during this run.)

In Run 943 various components of the pilot system were tested, the first of which was the high pressure air compressor. During this segment of the run the control of the motor was successfully tested during synchronous (compressor motor switches on and off depending on demand) and asynchronous (compressor motor runs continuously) operation.

The quench system was successful in lowering the temperature of the overhead effluent. The quench system was also designed to inject a bicarbonate solution to aid in the neutralization of the overhead effluent. This portion of the testing proved inconclusive as very small concentrations of acid and bicarbonate were used. It was therefore decided to use higher concentrations of each in Run 944.

The supercritical water/air superheater, which had been redesigned for this program, was also tested in this run. The heater's SCW output achieved only 65 % of the planned SCW flow.

Run 944

Dates: 6/12/95-6/16/95

Duration:

Hot Hours- 65 hours 35 minutes

Feed Hours- 9 hours 45 minutes

Waste Feed Flow: 200 gpd

Run 944 involved completing the mechanical testing of the modifications to the MODAR pilot plant. The first test was of the supercritical water heater which was reconfigured after Run 943 to group the electric heater panel controllers in a more effective manner. This proved to be successful for producing approximately 85 % of the SCW needs which was determined to be adequate to support the SCWODAT program requirements.

The reformer was designed to begin to neutralize the TRIM®SOL feed prior to entering to the

oxidizer, and was tested to assure that the desired design temperatures could be achieved. The second test was the neutralization capability of the reformer. This was determined by sequential testing with and without reforming. Without reforming the neutralization efficiency varied between 60%-68% and with reforming it was greater than 97%.

The final test of this run was to test the quench system using higher bicarbonate concentrations. The goal was to obtain an effluent pH greater than 5.0 for two hours. A pH of 5.5 was measured after the first hour, but a mechanical failure at the reformer inlet required a system shutdown and terminated Run 944.

B.2.1 PROCESS TESTING

Run 945

Dates: 6/26/95-6/29/95

Duration:

Hot Hours- 68 hours 30 minutes

Feed Hours- 33 hours 20 minutes

Waste Feed Flow: 366 gpd

Run 945 was the first run of the optimization phase of the TRIM[®]SOL testing portion of the SCWODAT program. The major goals of this run were to obtain good organic destruction and neutralization of TRIM[®]SOL, determine salt deposition patterns and to continue the assessment of the liner system performance. The run plan called for the TRIM[®]SOL feed to be progressively increased from 1/3 to 2/3 to full material balance flows. The final portion of the run was to process TRIM[®]SOL and the surrogate metals solution for approximately 8 hours. However, due to various system difficulties, full design flows could not be achieved. The reformer pressure differential increased an average of 8 psi per hour, indicating an obstruction. Throughout this run the quench system worked successfully.

During post-run inspection a black char substance was found on the inlet to the reformer. It was believed that this was the cause of the increase in the pressure differential of the reformer. The destruction efficiencies were also lower than anticipated for this run.

Run 946

Dates: 7/11/95-7/14/95

Duration:

Hot Hours- 44 hours 21 minutes

Feed Hours- 12 hours 2 minutes

Waste Feed Flow: 365 gpd

During the post run examination of Run 945, oxidizer vessel interior markings indicated liquid flowing down the vessel from the vicinity of the quench mouth. It was thought that this liquid pattern could have resulted from shutdown, condensation during operation, or a portion of the quench fluid flowing back into the vessel. To determine if back flow of quench fluid contributed to the less than expected oxidation results achieved, a quench spill back tracer test was performed. It involved oxidizing IPA with the quench neutralization system running. The brine was analyzed every 15 minutes for the presence of a sodium trace that was used. This test indicated that there was very little, if any, spill back from the quench system.

During a segment of this run, an attempt was made to oxidize TRIM®SOL without the use of the reformer to determine if the reformer was contributing to the less than expected oxidation levels of previous runs. Oxidation levels were, however, still below acceptable levels.

The next segment of this run involved ramping up the reformer temperature during operation in an attempt to determine the effect of temperature on charring in the reformer. At 1/3 of the full TRIM®SOL and caustic flows, the system became plugged and it was decided to terminate this run.

Run 947

Dates: 7/24/95-7/28/95

Duration:

Hot Hours- 97 hours 5 minutes

Feed Hours- 49 hours 34 minutes

Waste Feed Flow: 132 gpd

Various equipment changes were made between Run 946 and Run 947. The reformer was by-passed and the feed nozzle was modified to determine the affect on destruction efficiency. The major goals of this run were to achieve good overall organic destruction efficiency and to narrow down the possibilities for the less than expected oxidation results of Runs 945 and 946. To determine whether the caustic being used to neutralize the flows was having an adverse effect

on destruction efficiencies, TRIM®SOL was introduced to the system at 1/3 flow un-neutralized for a period of two hours. This segment produced a destruction efficiency of 99.99% and good brine quality. To achieve good oxidation and brine quality, provisions were made to increase SCW flow and temperatures and/or introduce ethanol as an auxiliary fuel. During this run acceptable destruction efficiencies and brine quality were only obtained for 1/3 TRIM®SOL flow.

The last segment of this run was to perform a salt deposition and heavy metals test which consisted of running a metals solution at 1/3 TRIM®SOL flow with the same SCW flow and temperature that yielded good destruction efficiency and brine quality. This was done to determine the deposition of salt in the vessel and the fate of any metals added to the system. This segment lasted for approximately 8 hours during which time the destruction efficiency and brine quality were at desired levels.

Important Note:

In Runs 947, 948, 949, and 950 the mass flow of the water carrying the surrogate metals into the oxidizer was decreased. This water volume was used in calculating the Waste Feed Flow rating of the pilot plant. Because of the decreased water flow of this feed stream, the 50 to 130 gpd ratings of Runs 947-950 cannot be strictly compared to the nominal 500 gpd capacity of the pilot plant. Most importantly, the target mass flow rates of both TRIM®SOL and the surrogate metals were achieved in Runs 948, 949, and 950.

Run 948

Dates: 8/8/95-8/11/95

Duration:

Hot Hours- 90 hours 0 minutes

Feed Hours- 66 hours 12 minutes

Waste Feed Flow: 83.5 gpd (SEE NOTE ABOVE)

In Run 947, good destruction efficiencies and brine quality were observed when running un-neutralized at 1/3 flows. A major goal of Run 948 was to duplicate these results at full flows. To achieve good destruction efficiencies and brine quality at full TRIM®SOL flow, the SCW flow and temperature were increased from the original set points. The second goal of this run was to process surrogate metals for approximately 48 hours. During this segment the brine did not contain any visible quantities of black particulate as seen in earlier runs.

Run 949

Dates: 8/21/95-8/28/95

Duration:

Hot Hours- 94 hours 26 minutes

Feed Hours- 85 hours 25 minutes

Waste Feed Flow: 50.2 gpd (SEE NOTE ABOVE)

After achieving good organic destruction in Run 948 while running un-neutralized, the goal of Run 949 was to achieve the same results while running neutralized at full flows. To achieve this the pilot plant was first operated at full TRIM®SOL flows un-neutralized. Once acceptable operating conditions were met, caustic was introduced to the system and slowly increased. By increasing the SCW flow and temperature the system was successful at processing TRIM®SOL at full flows with neutralization. The other major segment of this run was to run the surrogate metals solution for longer than 48 hours. This segment was also completed successfully.

A post run inspection identified extensive corrosion of oxidizer vessel Liner No. 1. Attempts to remove the salt build-up that occurred inside Liner No. 1 were difficult due to the salt's hardness. A description of the extent of corrosion to the liner can be found in Appendix A.

Run 950

Dates: 9/25/95-9/30/95

Duration:

Hot Hours- 128 hours 51 minutes

Feed Hours- 95 hours 56 minutes

Waste Feed Flow: 49.4 gpd (SEE NOTE ABOVE)

The coated Liner No. 2, implemented to reduce corrosion, was installed in the vessel for this run. The goal of Run 950 was to again oxidize TRIM®SOL at full flows with full in-situ neutralization and surrogate metals solution for a period of approximately 100 hours. During the run two vessel rinses were performed to dissolve salts that had accumulated from the operation of the system. This run achieved high organic destruction efficiency at full TRIM®SOL flows, with in-situ neutralization, and the metals surrogate solution for an extended duration.