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INEL-94/0017

Corrosion Investigation of Multilayered Ceramics and Experimental Nickel Alloys in SCWO Process Environments

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Published February 1995

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MASTER

Prepared for the
U.S. Department of Energy
Assistant Secretary for Environmental Management
Under DOE Idaho Operations Office
Contract DE-AC07-94ID13223

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ABSTRACT

A corrosion investigation was done at MODAR, Inc., using a supercritical water oxidation (SCWO) vessel reactor. Several types of multilayered ceramic rings and experimental nickel alloy coupons were exposed to a chlorinated cutting oil, TrimSol, in the SCWO process. A corrosion casing was designed and mounted in the vessel reactor with precautions to minimize chances of degrading the integrity of the pressure vessel. Fifteen of the ceramic coated rings were stacked vertically in the casing at one time for each test. There was a total of 36 rings. The rings were in groupings of three rings that formed five sections. Each section saw a different SCWO environment, ranging from 650°C to 300°C. The metal coupons were mounted on horizontal threaded holders welded to a vertical rod attached to the casing cover in order to hang down the middle of the casing. The experimental nickel alloys performed better than the baseline nickel alloys. A titania multilayered ceramic system sprayed onto a titanium ring remained intact after 120–180 hours of exposure. This is the longest time any coating system has withstood such an environment without significant loss.

SUMMARY

A goal of the Department of Energy (DOE) is to develop the supercritical water oxidation (SCWO) process for the treatment of some of its mixed waste inventories. In support of the SCWO design process, material systems capable of withstanding the harsh SCWO environment are being investigated. Three corrosion tests were run using the MODAR, Inc., SCWO vessel reactor to treat the chlorinated cutting oil TrimSol combined with surrogates of cerium chloride, zinc chloride, and lead chloride. The goal of the test was to expose the stack of ceramic rings and metal coupons to the five SCWO environments in order to compare their performance. The TrimSol was pumped at 3,400 psi and 40 mL/min. It was mixed with the water and metals stream that had a flow rate of 80 mL/min. This was brought into the reactor and mixed with 350 L/min air and 300 mL/min of water heated up to 400°C. A corrosion casing was designed and mounted in the vessel reactor in a manner that minimized chances of degrading the integrity of the pressure vessel. Fifteen of the 36 ceramic coated rings were stacked vertically in the casing at one time for each test. The rings were metal with multiple layers of ceramic coatings sprayed onto the inside of the rings. Each ring was 3 in. in height and 7 in. in diameter. The rings were cemented together inside of the casing. There were five groupings of three rings. Additionally, metal coupons were mounted on horizontal thread holders welded to a vertical rod attached to the casing cover in order to hang down the middle of the casing. The length of the casing traversed five different temperature zones ranging from 650°C to 300°C. After the reaction zone a quench stream diluted the process effluent from about 8,000 ppm of chloride concentration down to 5,000 ppm chloride concentration. The stream was not neutralized until it entered the cooldown zone near the bottom ring, near the last two coupon holders, just before it exited the casing through an exit pipe at the bottom of the casing. The processed waste stream produced hydrochloric acid, sulfuric acid, and salts during the SCWO reaction. The greatest interest was in the performance of the materials in the high temperature sections, and the transition section from supercritical to subcritical, approximately 400 to 350°C.

The performance of the multilayered ceramics and experimental nickels was evaluated by comparison against the baseline nickel alloys C-22, C-276, Inconel 625, and Inconel 686. Three tests were run. The first test was for 60 hours with five temperature cycles. The second was for 60 hours with just two temperature cycles. The third was for 120 hours with just two temperature cycles. It was anticipated that the temperature cycles would show if the ceramics tended toward delamination during startups or cooldown. For each temperature cycle the casing was allowed to drop to below 300°C. After the first 60-hour test the top three and bottom three rings would be removed and analyzed while three new rings were put into the top and bottom sections for the second 60-hour test. After the second 60-hour test the top and bottom six rings would be removed and replaced, and then the 120-hour test would be run. This plan allows for comparison between rings that saw the same test conditions but with a different number of thermal cycles. At the same time, the metal coupons would be rinsed and measured for weight loss after each test run. The ceramic rings were microsectioned and analyzed to determine what mechanisms of corrosion had affected the coatings. Effluent analysis would indicate how much of the surrogates were retained in the system, providing an indicator of deposition.

The multilayered ceramic rings were designed to avoid delamination by a gradual change in the thermal coefficient of each layer. The high density top layer of the coatings was designed to prevent the absorption of metals or chlorides into the ceramic, though it was assumed that oxygen

would be able to pass through. Perpendicular cracks exist in the ceramic layers so that the layers may expand and contract on the inside diameter of the ring. These cracks are apparent at low temperatures and close at higher temperatures. The results of the test showed that sometimes these cracks became the avenue for corrosive elements to travel down contacting nickel/chrome layers. Once corrosion products formed between the layers spalling or delamination mechanism would begin. Initial results were used to develop a titania coating onto a titanium ring. Though the same cracks were present in the titania coating, the corrosion did not occur between layers and there was no delamination after 120 to 180 hours of exposure.

The baseline metal coupons performed very badly as expected while the experimental nickel alloys performed better in all temperature zones.

ACKNOWLEDGMENTS

The authors wish to thank Gary Fletcher and Del Miley of Lockheed Idaho Technologies Company for their contributions in the metallurgical analysis. The contributions of Ray Zatorski and Janet Lindsey of Engineered Coatings, Inc., and Vladimir Zilberstein of Stone & Webster were critical to the success of the testing. Especially significant were the efforts of all the personnel at MODAR, Inc., whose creativity and cooperation are greatly appreciated.

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Corrosion Investigation of Multilayered Ceramics and Experimental Nickel Alloys in SCWO Process Environments

1. INTRODUCTION

The U.S. Department of Energy (DOE) has accelerated its efforts to convert its mixed waste inventories into disposable materials in the most efficient ways possible. In the past few years supercritical water oxidation (SCWO) has emerged as a technology capable of treating a portion of DOE mixed waste. For further information on the SCWO process, the reader is referred to the bibliography in Appendix A. Extensive testing done in cooperation with the private sector, universities, and other national laboratories has repeatedly shown that the major technical constraint of SCWO is the lack of practical materials of construction capable of withstanding the harsh environments of the SCWO process. A two-fold approach has been taken to overcome this constraint. Reactor designs have attempted to use fluid boundaries to keep the process fluids away from the reactor wall, and tests have been held to identify material systems suitable for the process. Future designs of pilot plants will incorporate the knowledge from both of these approaches.

Some of the different material systems that have been previously investigated[a] beyond the nickel alloys include ceramics, titanium, and the noble metals. The expense of noble metals is not practical as a structural component at a pilot-plant scale, and monolithic ceramics, though inexpensive, can be geometry dependent and too brittle for industrial handling. The approach taken in this work was thermally spraying multiple layers of ceramic onto a metal substrate. This process is widely used in industry, particularly the aerospace industry, for protecting components in harsh environments. A gradual change in thermal expansion properties allows each layer to expand and contract under thermal and pressure stresses without delamination. The multiple layers were sprayed onto the inside surfaces of rings for this experiment because this was considered the most relevant geometry to investigate for the SCWO process.

There are two particular environments of the SCWO process that are the most challenging. The first is the high temperature (650°C) reaction zone where molten salts deposit onto substrates forming severe corrosion cells and the second is the transition temperature zone (400–300°C) where the fluid changes from a supercritical phase to a subcritical phase and forms highly acidic liquids. The test was configured to place the ceramic rings and a variety of metal samples into both of these environments.

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[a] Telephone conversation with Mike Spritzer, General Atomics, July 23, 1993.

2. PURPOSE

The purpose of this work was to fabricate and test a variety of multilayered ceramic coated rings in order to identify the response of the coating-substrate systems to the highly corrosive, high temperature, high pressure environment. The investigation was to determine if different coating-substrate systems reacted differently to the combination of thermal cycles, hoop stress, corrosion, and deposition of salts and metal oxides. It was the intention of the task that a practical, manufacturable material be identified. In addition to ceramic coating-substrate systems, various alloys were tested for comparison during the same tests. Inconel 625, C-22, and C-276 were included to serve as reference points. The composition and microstructure of these developed alloys would give insight into what elements were effective for corrosion resistance in an SCWO environment.

3. TEST PLAN

The tests were run in the MODAR, Inc., pilot-scale SCWO system. The test conditions created an actual operating state within the MODAR reactor. The SCWO environment was created by using TrimSol mixed with water and air heated to produce a reaction at 650°C at 3,400 psi. TrimSol is a chlorinated machine cutting oil produced by Master Chemical Co. It is classified as 20–30% chlorinated alkene polymer combined with alkali petroleum sulfonate, alkyl phenol polyoxyl ethylene, and alkali fatty soap. Analysis shows the compound to consist of chlorine, 120,000 ppm; sodium, 4,990 ppm; sulfur, 9,140 ppm; and potassium, 1,750 ppm.

The following solids were added to simulate an actual DOE waste: 5,400 ppm $CeCl_3$, 2,850 ppm $PbCl_2$, and 2,250 ppm $ZnSO_4$ (later changed to ZnCl). These surrogates were chosen to compare the materials' behavior to a previous test.[b] The TrimSol was pumped at 3,400 psi and 40 mL/min. It was mixed with the water and metals stream that had a flow rate of 80 mL/min. This was brought into the reactor and mixed with 350 L/min air and 300 mL/min of water heated up to 400°C. Three tests were run. The first test was for 60 hours with five temperature cycles. The second was for 60 hours with just two temperature cycles. The third was for 120 hours with just two temperature cycles. It was anticipated that the temperature cycles would show if the ceramics tended toward delamination during startups or cooldown. For each temperature cycle the reaction zone was allowed to drop to below 300°C.

Within the vessel reactor a casing was suspended downward from the nozzle, with an exit pipe at the bottom of the casing. The system configuration is shown in Attachment 1, Figures 1 and 2. A quench stream diluted the process effluent and neutralization occurred just before it exited the casing. Within the casing were 15 stacked rings. The rings were metal with multiple layers of ceramic coatings sprayed onto the inside of the rings. Each ring was 3 in. in height and 7 in. in diameter. The rings were cemented together inside of the casing. A corrosion rack was suspended down the center of the stack of rings and metal coupons were placed on branches of the corrosion rack. The length of the casing traversed five different temperature zones ranging from 650°C to 300°C.

After the first 60-hour test, the top three and bottom three rings (six rings) would be removed and analyzed while three new rings were put into the top and bottom sections for the second 60-hour test. After the second 60-hour test, the top and bottom six rings (twelve rings) would be removed and replaced, and then the 120-hour test would be run. This plan allowed for comparison between rings that saw the same test conditions but with a different number of thermal cycles. At the same time, the metal coupons would be rinsed and measured for weight loss after each test run and then placed back onto the coupon tree. The ceramic rings would then be microsectioned and analyzed to determine what mechanisms of corrosion had affected the coatings. Effluent analysis would indicate how much of the surrogates were retained in the system providing an indication of deposition.

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b. C. Shapiro, K. Garcia, and J. M. Beller, "Treatment of a Simulated Mixed Waste with Supercritical Water Oxidation," *Proceedings of the 2nd International Symposium on Mixed Waste, Baltimore, Maryland, August 17–20, 1993,* pp 10.3.1–10.3.16.

4. TEST SETUP

4.1 Description of Ceramic Ring Arrangement

There was a total of 36 rings. For each test, 15 coated rings, 3 in. high and 7 in. ID were stacked, cemented together, and placed inside a casing. The casing was mounted inside the MODAR SCWO vessel reactor.

The casing was 48 in. long and included five sections of distinct chemical/environmental zones. See Figures 1 and 2. Section 1 includes the top three rings and is defined as in the reaction zone. The temperature decreases through Section 4 where the quench water would be introduced and Section 5 is where the outlet tube mixes the process stream and diluted caustic to produce a neutralized effluent. The quench stream diluted the process effluent from about 8,000 ppm of chloride concentration on an aqueous basis, down to 5,000 ppm chloride concentration. The sulfate-to-chloride concentration was approximately 1:10. As the hot reaction products entered Section 4, they began to condense forming saltwater and acids. These liquids were quenched to a resulting pH of approximately 0.9. Neutralization was carried out in Section 5 and created a brine with a pH of 6 at the bottom 2 in. of the test casing. The stream was not neutralized until just before it exited the casing through an exit pipe at the bottom of the casing. Neutralization was accomplished with sodium hydroxide in the first 60-hour test and with sodium bicarbonate thereafter. Due to the experimental design of stacking the rings, and the ceramic only covering the inside surface and not the edges of the rings, it was assumed that there would be edge attack on each of the rings where the metal substrate could be exposed. Only the middle 1 in. of the ring height would show valid corrosion mechanisms and coating performance. Air and water at 3,400 psi and 400°C were introduced to the vessel reactor through an annulus while the TrimSol and water were brought to 3,400 psi and introduced to the SCWO reactor through a nozzle. The two streams mix, causing the reaction and forming reaction products containing chlorine, sodium, phosphorus, sulfur, calcium, cerium, zinc, and lead. The axial fluid temperature profile was monitored by thermocouples located within thermowells in the center of the casing.

4.2 Description of Metal Arrangement

The casing cover plate carried a vertical rod that spanned the entire length of the ring stack. Short horizontal threaded rods were welded to the vertical rod at each ring position. The rod and holders were made from Inconel 625 without any heat treatment after welding. Several metallic corrosion coupons were mounted onto each threaded rod. Ceramic washers were used as spacers between the coupons. Figure 3 shows this arrangement.

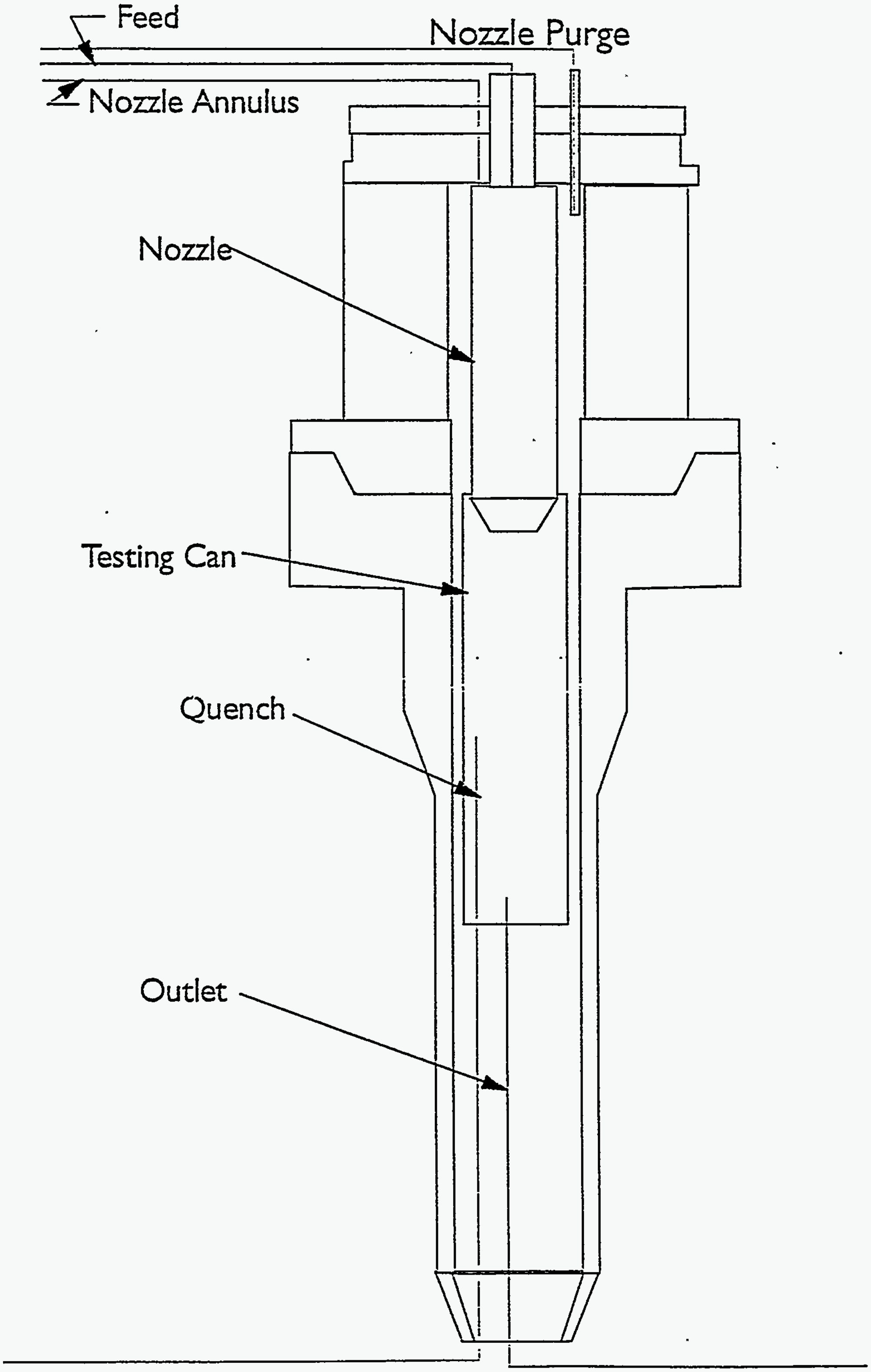

Figure 1. Test setup.

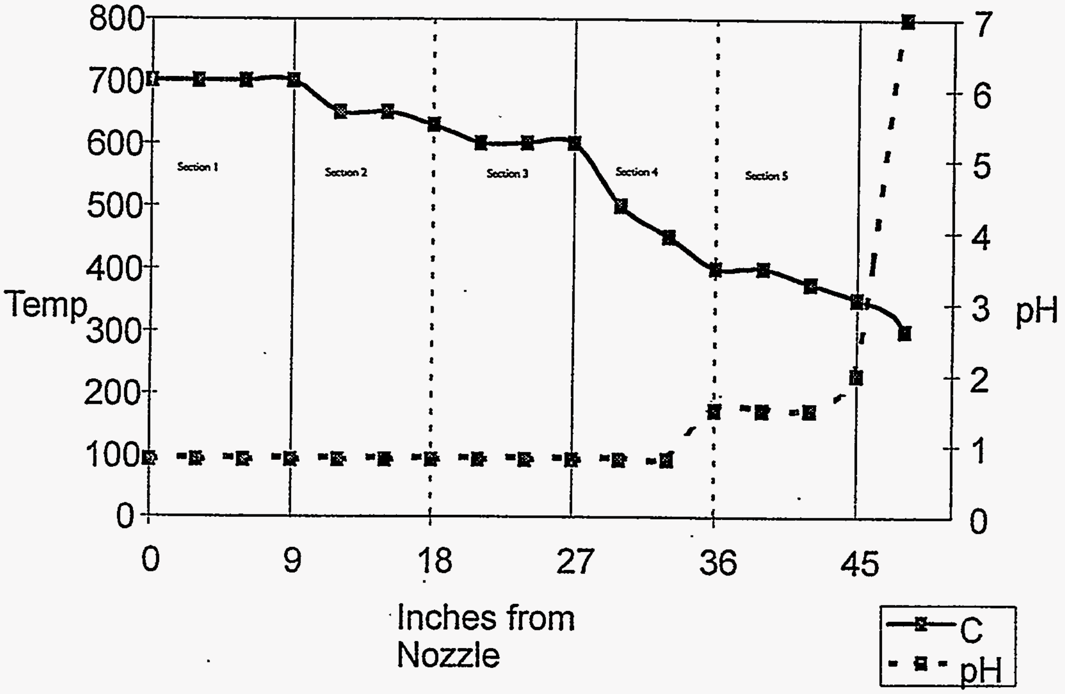

Figure 2. Temperature—pH profile.

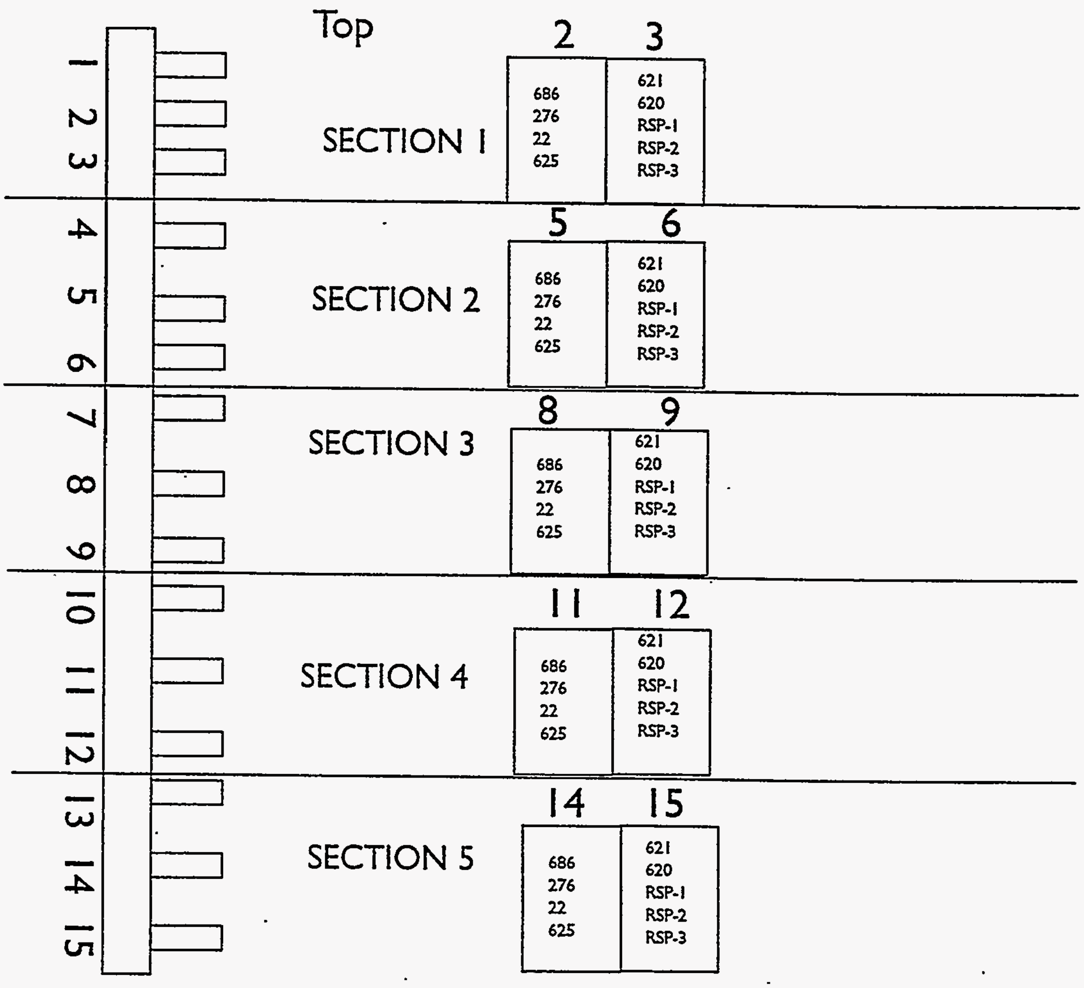

Figure 3. Metal coupon arrangement.

5. COUPON DESCRIPTION

5.1 Plasma Sprayed Multilayered Ceramic Rings

Thermal spraying is a deposition technique where a heat source such as a combustion flame or nontransferred arc plasma is used to heat a feedstock in wire or powder to above the melting point of the material. The small, approximately 0.001 in. (0.02 mm) molten particles are propelled toward the substrate and freeze upon impact at a rate of 10^5 to 10^6 °C/sec. The spray parameters and the rate of material deposited onto the surface is adjusted to maintain the substrate at a desired temperature to obtain certain levels of residual stress. The lower range of these temperatures is from less than 250°F (121°C) to over 1000°F (537°C). Thermal spraying is an industrial technique for coating a range of components from gas turbines for hot corrosion and erosion protection to machine element buildup where heat distortion cannot be tolerated through aluminum and zinc coatings for atmospheric and marine corrosion protection. Spray rates range from 5 lbs/hr (2.2 kg/hr) for ceramics to 40 lbs/hr (18 kg/hr) for metals. Most production coatings are applied with automated systems. The annual value of thermally sprayed coatings in the U.S. is estimated above $1 billion.

The practical lower limit for each layer of coating thickness is 0.003 in. (0.07 mm) for a continuous coating. Most materials can be sprayed to thicknesses in excess of 0.5 in. (13 mm). This line of sight process deposits coatings in layers typically 0.0005 in. (0.013 mm) with each pass of the spray device. Multiple passes of the spray device are made to achieve the desired thickness. There is a porosity associated with the sprayed deposit of between 0.2% and 12% depending on spray parameters and material. In many applications this porosity does not effect service.

The eight different combinations of coatings and rings were defined as A, B, C, C′, D, E, F, and F′. Thirty of the rings used Inconel 625 as the substrate and six used titanium as the substrate. Of the six titanium rings, four were Gr 2 and two were Gr 12 titanium. The thermal spray technique can be adjusted such that the residual stress in the coating is at a minimum at a chosen temperature. The coatings were designed to be at the minimum stress at a midpoint temperature between the high temperature of 650°C and room temperature. See Table 1 for the coating thicknesses. The coatings were designed for a high density top layer. In cases where porosity is of concern, the coating parameters can be adjusted to reduce the porosity to below the level where the pores are interconnected. The porosity and microcracks in the coating allow additional expansion and contraction in the coating system to better match the substrates movement due to stresses. The coating must eventually be evaluated in the service environment to determine the best compromise for the levels of porosity and allowable stress.

The approach to designing a coating system was to select a bond coat similar in thermal properties to the substrate. The bond coat was a nickel/chrome/aluminum combination for 29 of the rings and seven rings received a titanium/alumina/vanadium combination. Of those seven, five had a titanium substrate and two had an Inconel 625 substrate. A common concern is the interlayer adhesive strength of the layers. A graded transition is put between the layers by alternating materials. For example, during the titanium to titania transition, a mixture of titanium and titania is sprayed to increase the intermediate layer's bond strength.

Table 1. Coating/ring descriptions for the 36 rings delivered.

First set—15 rings Layers/average thicknesses

Run number	Ctg./ring spec.	Ring no./mat'l.	NiCrAl bond	NiCrAl/7%YZ	7%YZ	
5(032494)047	A	1*, I-625	0.004 in.	0.007 in.	0.036 in.	
		2-5, I-625	0.004 in.	0.007 in.	0.024 in.	
			NiCrAl bond	NiCrAl/7%YZ	Alumina	7%YZ
5(032494)048	B	6*, I-625	0.004 in.	0.007 in.	0.013 in.	0.016 in.
		7-10, I-625	0.004 in.	0.006 in.	0.007 in.	0.015 in.
			NiCrAl bond	NiCrAl/TiO_2	TiO_2	
5(032594)049	C	16*, I-625	0.004 in.	0.010 in.	0.017 in.	
		11-14, I-625	0.004 in.	0.005 in.	0.015 in.	

Second set—6 rings

Run number	Ctg./ring spec.	Ring no./mat'l.	NiCrAl bond	NiCrAl/7%YZ	7%YZ	
5(040894)058	A	1, I-625	0.006 in.	0.007 in.	0.016 in.	
		2, I-625	0.006 in.	0.008 in.	0.013 in.	
			NiCrAl bond	NiCrAl/7%YZ	Alumina	7%YZ
5(040894)059	B	3, I-625	0.006 in.	0.007 in.	0.004 in.	0.012 in.
		4, I-625	0.006 in.	0.007 in.	0.004 in.	0.015 in.
			NiCrAl bond	NiCrAl/TiO_2	TiO_2	
5(040894)060	C	5, I-625	0.006 in.	0.005 in.	0.016 in.	
		6, I-625	0.006 in.	0.005 in.	0.016 in.	

Third set—7 rings

Run number	Ctg./ring spec.	Ring no./mat'l.	NiCrAl bond	NiCrAl/TiO_2	TiO_2	
5(042594)071	C	1, I-625	0.005 in.	0.005 in.	0.013 in.	
			NiCrAl bond	NiCrAl/TiO_2	TiO_2	7%YZ
5(042594)072	D	4*, I-625	0.004 in.	0.005 in.	0.011 in.	0.007 in.
		2-3, I-625	0.004 in.	0.005 in.	0.011 in.	0.007 in.
			NiCrAl bond	NiCrAl/TiO_2	TiO_2	24%MgZ
5(042594)073	E	7*, I-625	0.005 in.	0.005 in.	0.011 in.	0.006 in.
		5, I-625	0.005 in.	0.005 in.	0.011 in.	0.011 in.
		6, I-625	0.005 in.	0.005 in.	0.011 in.	0.006 in.

Table 1. (continued).
Fourth set—8 rings

Run number	Ctg./ring spec.	Ring no./mat'l.	NiCrAl bond	NiCrAl/TiO_2	TiO_2
5(052794)082	C'	1, Gr 2 Titanium	0.004 in.	0.005 in.	0.013 in.
			Ti-6Al-4V bond	Ti-6Al-4V/TiO_2	TiO_2
5(052794)083	F	2*, Gr 2 Titanium	0.007 in.	0.005 in.	0.015 in.
		3-4, Gr 2 Titanium	0.004 in.	0.005 in.	0.015 in.
		5-6, Gr 12 Titanium	0.004 in.	0.006 in.	0.015 in.
	F'	7-8, I-625	0.004 in.	0.006 in.	0.015 in.

There were two types of zirconia top coats, a zirconia partially stabilized with 7% yttria, and a zirconia partially stabilized with 24% magnesia. See Table 1 for each coating description.

Coating A was the basic design with the nickel/chrome/aluminum bond coat, then a transition coat of nickel/chrome/aluminum/7% partially stabilized yttria/zirconia (7% YZ). The top coat was 7% YZ chosen because previous corrosion tests have shown good performance of zirconia in SCWO environments.[c]

For Coating B an additional alumina interlayer was added beneath the 7% YZ. Coating C used the same bond coat as Coatings A and B but had a transition layer of nickel/chrome/aluminum/titania and a top coat of titania. Coating D was the same as Coating C but with an added top layer of 7% YZ. Coating E was again the same as Coating C but with an added top layer of 24% MgZ.

Coating F was a complete titania/titanium system on a titanium ring. The bond coat was titanium/aluminum/vanadium, the transition coat was titanium/aluminum/vanadium/titania, and the top coat was titania. Coating F' was the same except the substrate was Inconel 625.

5.2 Experimental Nickel Alloys and Baseline Nickel Alloys

The chemistry of the nickel alloys is given in Table 2. The following NiCrMo alloys were chosen for the test program: Inconel 625, Hastelloy C-276, Inconel 686, Hastelloy C-22, and alloys 620 and 621 alloys (experiential alloys developed between the INEL and Haynes International).

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[c] Telephone conversation with Mike Spritzer, General Atomics.

Table 2. Chemistry of the nickel alloys.

Alloy	Heat	Al	C	Cr	Cu	Fe	Mn	Mo	Ni	P	S	Si	Ti	Others
C-276	J018		.003	15.26		5.35	.48	15.39	Balance	.007	.002	.02		Co-1.35; V-.13; W-3.3
C-22	H159		.003	21.20		4.5	.25	13.3	Balance	.006	.003	.38		Co-1.96; V-.14; W-3.0
I-625	J186	.23	.02	21.89		3.34	.05	8.97	61.68	.007	.001	.13	.25	Cb+Ta-3.42
I-686	K065	.22	.01	20.40	.01	1.03	.23	16.42	57.42	.006	.001	.02	.04	Co-.04; Cb-.08; W-4.06
C-22	RSP1		.003	21.20		4.5	.25	13.3	Balance	.006	.003	.38		Co-1.96; V-.14; W-3.0
Flinn	RSP2			25		15		3	Balance					Nio-5.5
Flinn	RSP3			25		15			Balance			2.5		
Mizia	620			25				9.89	Balance					W-3.0
Mizia	621			25				12.51	Balance					W-3.0

6. TEST EVENTS

The goal of Run 937 was to establish the flow rates needed to get the desired temperature profile in the reactor. The temperature at the nozzle was greater than 600°C, the temperature 18 in. below the nozzle was greater than 550°C, 36 in. below the nozzle was approximately 400°C, and 42 in. below the nozzle was approximately 300°C.

Lead sulfate precipitated from the feed mixture in Run 937. An estimated 2% of the lead made it into the feed stream. The zinc sulfate was switched to zinc chloride to alleviate the problem. This run showed flaking, peeling, and separation of ceramic coating from all the rings except those composed of titania. The Type A and B coatings showed severe delamination so all were replaced. Thirteen rings were replaced including three titania rings.

In Run 939/940, the quench water inlet tube was extended up 3 in. with two horizontal streams of water coming out at 180-degree angle. The second 60-hour test was conducted without the five thermal cycles of Run 937/938. See Table 3. This would show if the multiple thermal cycles were the principal difficulty. The performance of the titania coating was better than the zirconia coatings. Further testing focused on several versions of a titania coating system.

In Run 941/942, the 120-hour run had more titania coating rings added and some ZrO_2 coatings were reused to fill the necessary 15 slots. One titania coated on Inconel ring saw a total of 240 hours while three titania on titanium saw a total of 180 hours.

A calendar of the test events is outlined in Table 3. The system was shut down by cutting off all feeds at once. This is called a hot dry shutdown. This allows for deposition to be observed.

Table 3. Calendar of test events during March to June 1994.

Monday	Tuesday	Wed	Thursday	Friday	Saturday	Sunday
03/28	03/29	03/30 Testing starts with IPA	03/31 Testing starts with TrimSol Run 937 Hot dry shut down	04/01 Testing can is pulled	04/02	04/03
04/04 Metal Coupons rinsed and observed	04/05 System shut down	04/06 System brought back on line Run 938	04/07 Hot dry shutdown to observe nozzle then system started again	04/08 System shut down after 26.2 hr of 60-hr test run #938	04/09	04/10
04/11 System start up Run 938	04/12 Hot dry shutdown for cycle #4	04/13 System shut down End of first 60-hr run	04/14 13 rings pulled and replaced	04/15 System shut down	04/16	04/17
04/18	04/19	04/20	04/21	04/22	04/23	04/24
04/25	04/26	04/27	04/28	04/29	04/30	05/01
05/02 Run 939 starts	05/03 Run 939 stops	05/04 System shut down	05/05 System shut down	05/06 System shut down	05/07	05/08
05/09 System shut down	05/10 System shut down	05/11 Run 940 starts	05/12 Run 940	05/13 Run 940 ends. End of 2nd 60-hr run	05/14 8 rings pulled and replaced	05/15
05/16	05/17	05/18	05/19	05/20	05/21	05/22
05/23	05/24	05/25	05/26	05/27	05/28	05/29
05/30 System shut down	05/31 System shut down	06/01 System shut down	06/02 Run 941 begins	06/03 Run 941	06/04 Run 941 ends	06/05
06/06 Run 942 begins	06/07 Run 942	06/08 Run 942	06/09 Run 942	06/10 Run 942	06/11 Run 942 ends	06/12

7. TEST DATA

7.1 Ceramic Rings

The test data are described here in approximate chronological order of the rings that were tested. The successful titania coatings are described last because the decision to go to an all-titania system was only made after the initial 60-hour test results. The ceramic coating was only on the inside of each ring. The substrate was exposed on the top edge of each ring. Edge degradation was expected and was not considered as a failure of the coating. The ring numbering system is derived from the manufacturing numbers (see Table 1 for the composition information).

The following photographs (Figure 4) show the condition of 047-1 (Coating A) and 047-5 (Coating A) after testing. Although both rings have the same coating, they were in two different sections of the test. 047-1 was in Section 1 while 047-5 was in Section 5 during the first 60-hour test. 047-1 had salt deposits and the coating was blistering while 047-5 had already delaminated. The lower temperature section degraded Coating A more than the high temperature zone. Three other rings had similar coatings and were in the first 60-hour test. After the test the rings were described as follows:

- 047-2 Coating A	Blistering, peeling, edge chipping
- 047-3 Coating A	A few blisters, and edge chipping
- 047-4 Coating A	A few blisters, some erosion.

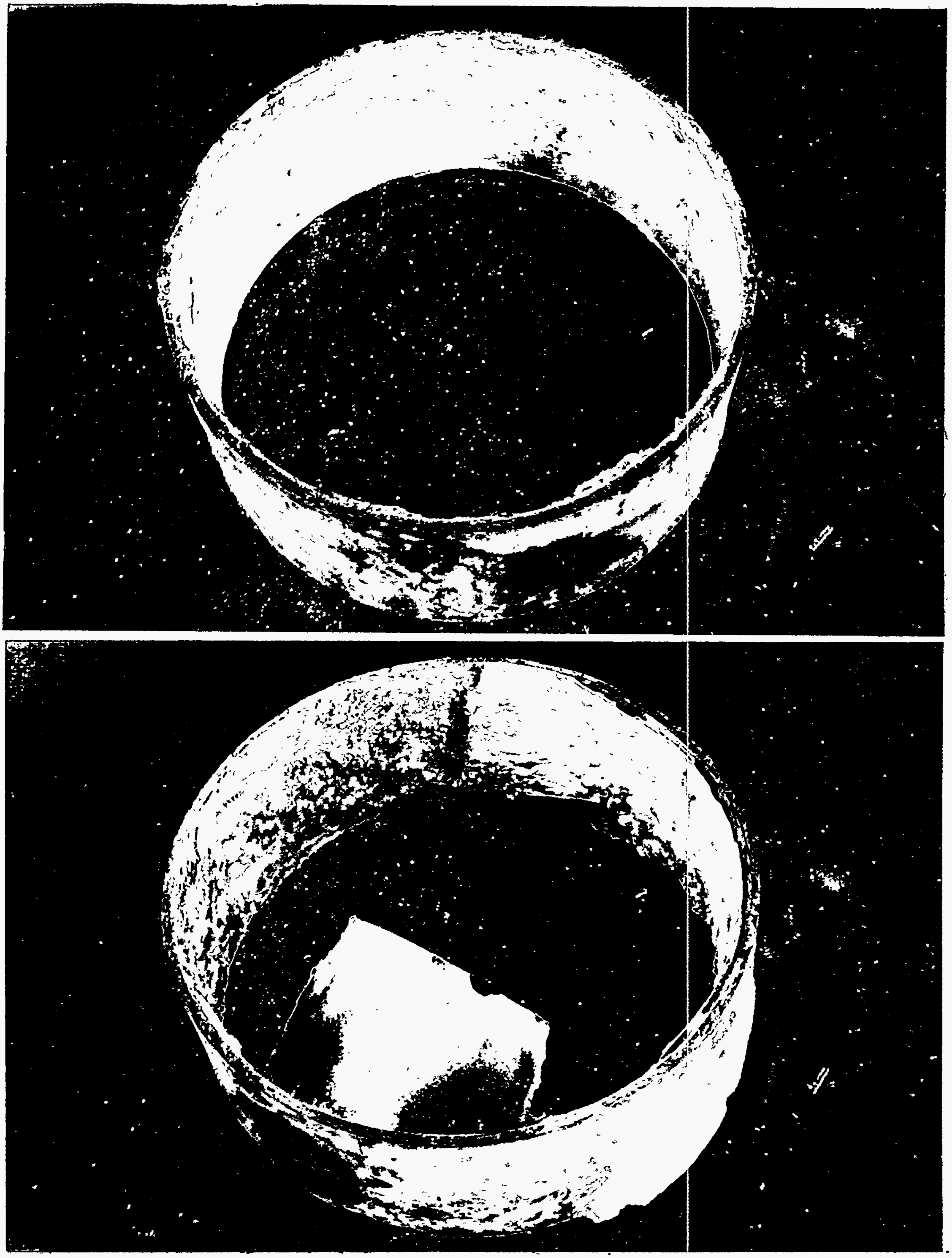


Figure 4. Condition of 047-1 (Coating A) (top) and 047-5 (Coating A) after first SCWO test.

The following photographs (Figure 5) show the condition of 048-6 (Coating B) and 048-10 (Coating B). Coating B was the same as Coating A except an alumina interlayer had been added. 048-6 is from Section 1 and 048-10 is from Section 5 during the first 60-hour test. The temperature range was not as significant to this type of coating as both of these rings delaminated. Three other rings had similar coatings and were in the first 60-hour test. After the test, the rings were described as follows:

- 048-7 B Blistering, peeling, disengagement; delamination at alumina layer
- 048-8 B Blistering, peeling, disengagement
- 048-9 B Cracks, disengagement, and blistering.

Three other rings from the second 60-hour test: 058-1 (Coating A) from Section 1, 058-2 (Coating A) from Section 5, and 059-3 (Coating B) from Section 1 were described as having delaminated.

The ring 059-4 (Coating B) had cracking from an edge attack after 60 hours in Section 5, after an additional 120 hours in Section 2 the coating was gone over 80% of ring.

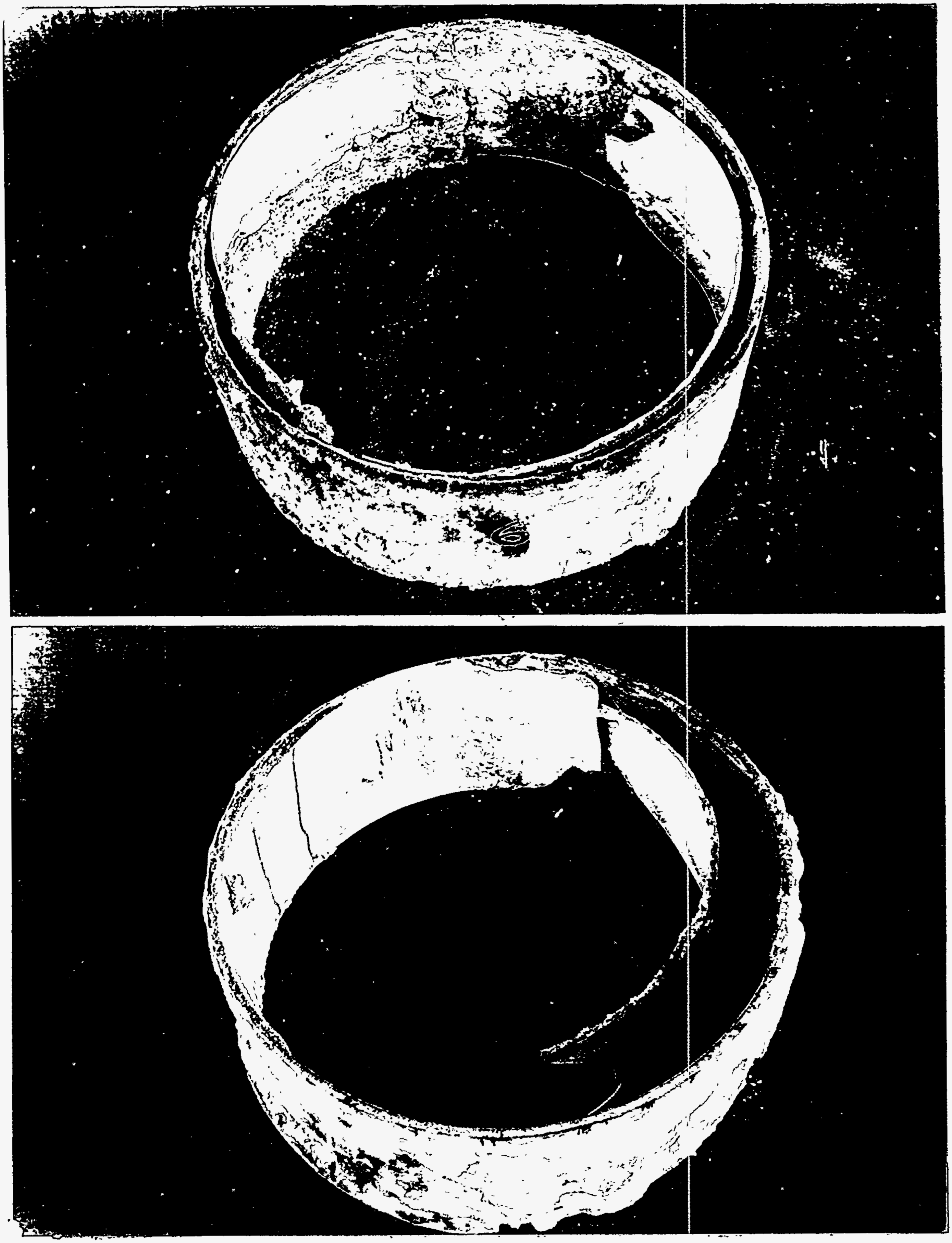


Figure 5. Condition of 048-6 (Coating B) (top) and 048-10 (Coating B) after first SCWO test.

The following photographs (Figure 6) show the condition of 049-11 (Coating C) and 049-16 (Coating C). 049-11 is from Section 1 and 049-16 is from Section 5 during the first 60-hour test. Both of these rings did well after 60 hours. The brine line can be seen in 049-16 as it was the lowest ring in the stack. The top 1 in. of the 049-16 ring shows the edge attack on the coating. The other ring removed after the first 60-hour test was the 049-14 (Coating C) in Section 4 because of edge infiltration causing cracks and corrosion of the base metal.

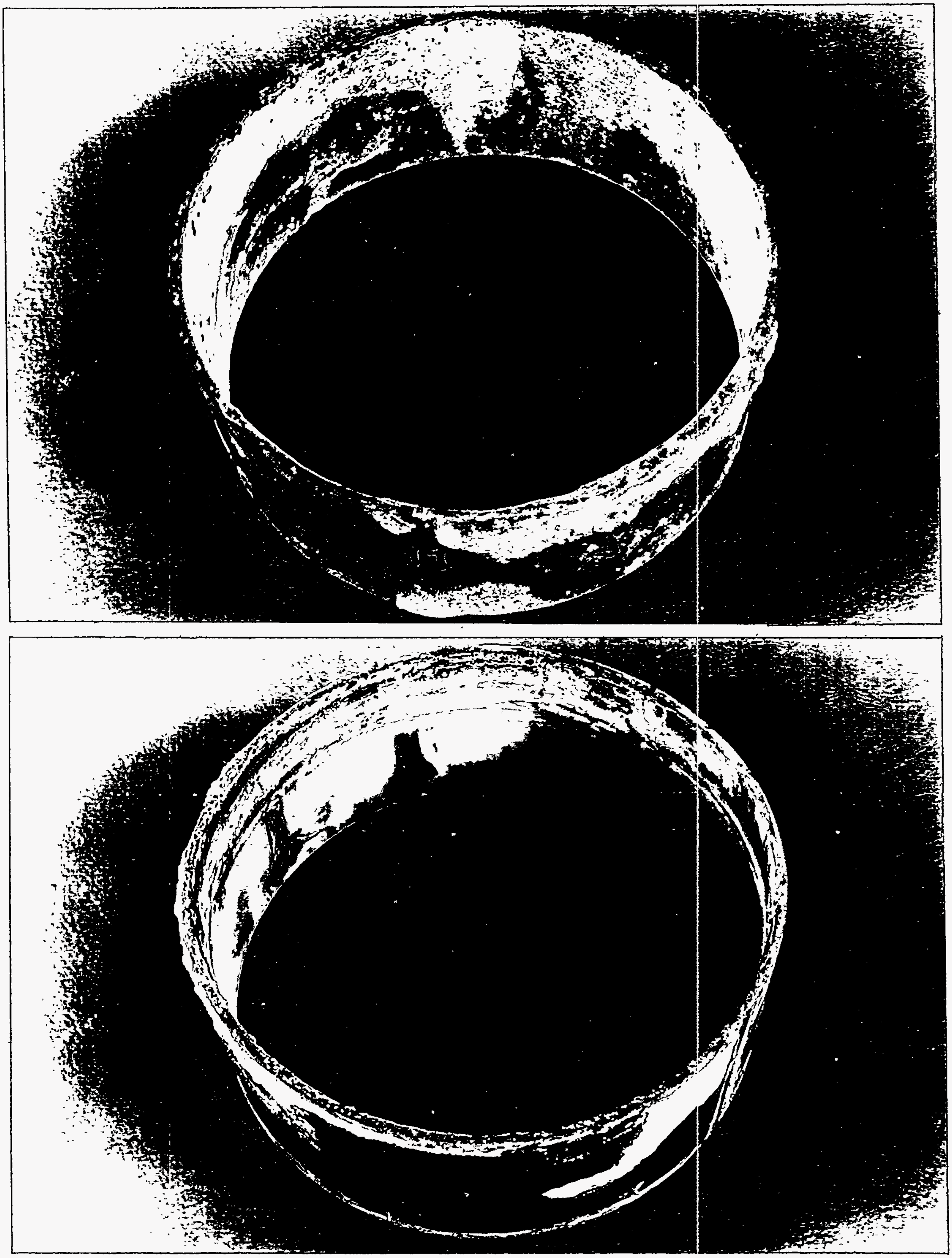


Figure 6. Condition of 049-11 (Coating C) (top) and 049-16 (Coating C) after first SCWO test.

The following photographs (Figure 7) show the condition of 049-12 (Coating C) after 120 hours of testing. The coating had looked intact after the first 60 hours but then had delaminated. The other two rings in the same section (Section 2) were in the reactor for the second 60-hour test. Both 072-3 (Coating D) and 073-5 (Coating E) showed heavy blistering of the zirconia outer layer but the titania layer underneath was still intact. This would correspond to the behavior of 049-12 in the first 60-hour test. Similar rings were described as follows:

- 060-6 C No damage observed
- 072-2 D ZrO_2 gone, significant loss of TiO_2
- 072-4 D Heavy blistering, TiO_2 intact after 60 hours, coating half gone, flaking after 120 hours
- 073-6 E Heavy blistering, TiO_2 intact after 60 hours, coating half gone, flaking after 120 hours
- 073-7 E ZrO_2 gone, TiO_2 intact after 60 hours, cracked, chipped, and flaking after 120 hours.

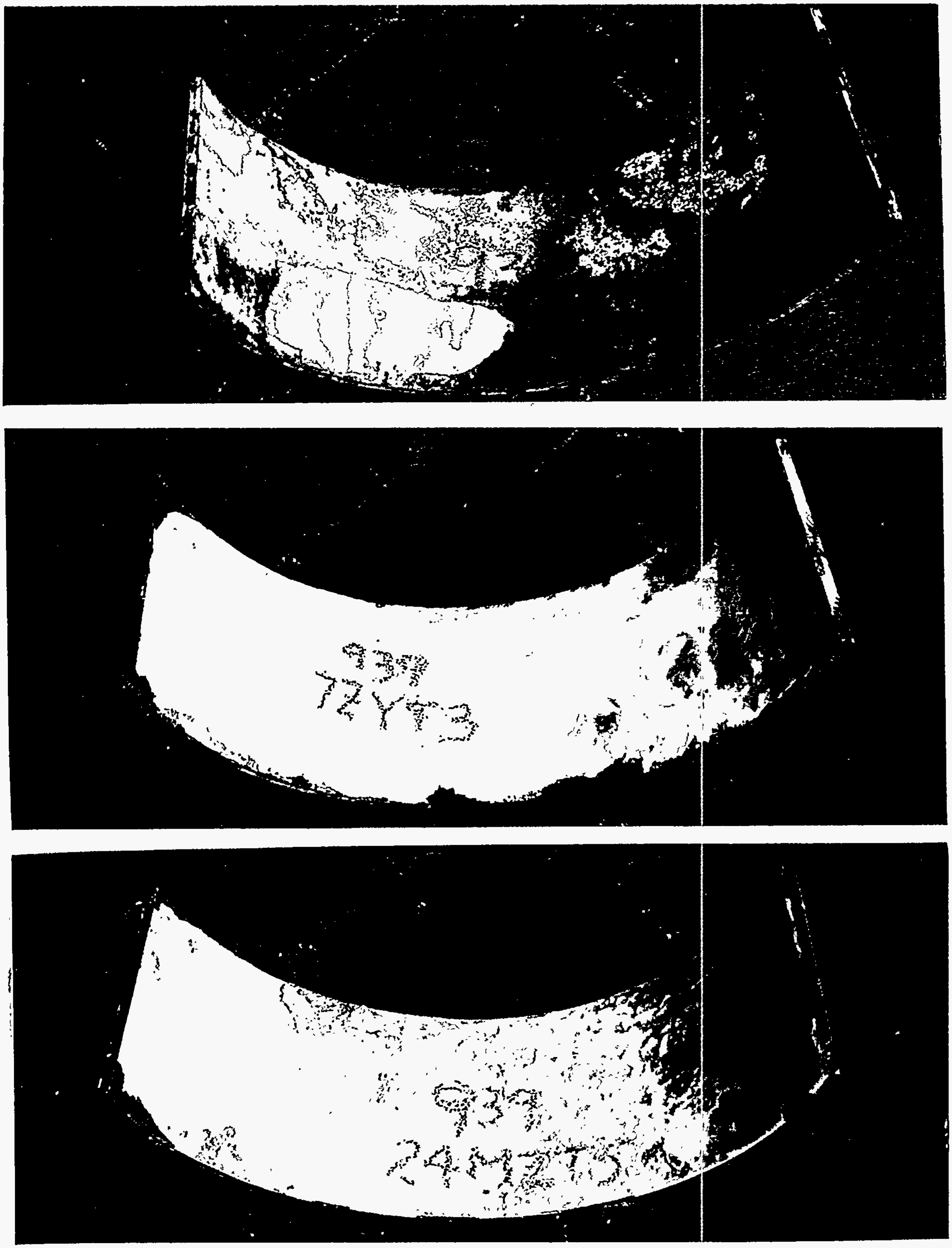


Figure 7. Condition of 049-12 (Coating C) (top), condition of 072-3 (Coating D) (middle), and condition of 073-5 (Coating E) after second SCWO test.

The following photographs (Figures 8 and 9) show the condition of 060-5 (Coating C) from the second 60-hour test. 060-5 was in Section 1. There was some peeling of the titania layer in contrast to how 049-11 (Coating C) had behaved in Section 1 in the first 60-hour test. A similar ring (071-1 Coating C) from Section 4 showed a patch of delamination while 049-13 (Coating C) in Section 3 looked intact after 60 hours. There was no observable degradation after 120 hours, and after a total of 240 hours patches of the substrate were visible. The titania coating had either thinned or small sections had spalled off, when the patches of delamination occurred. Section 3 was considered the least harsh environment present and seem to allow Coating C to survive long enough for either thinning or spalling to occur.

The one Type C coating on a titanium ring looked intact after 120 hours in Section 2 (082-1 coating C′) though one bump was observed.

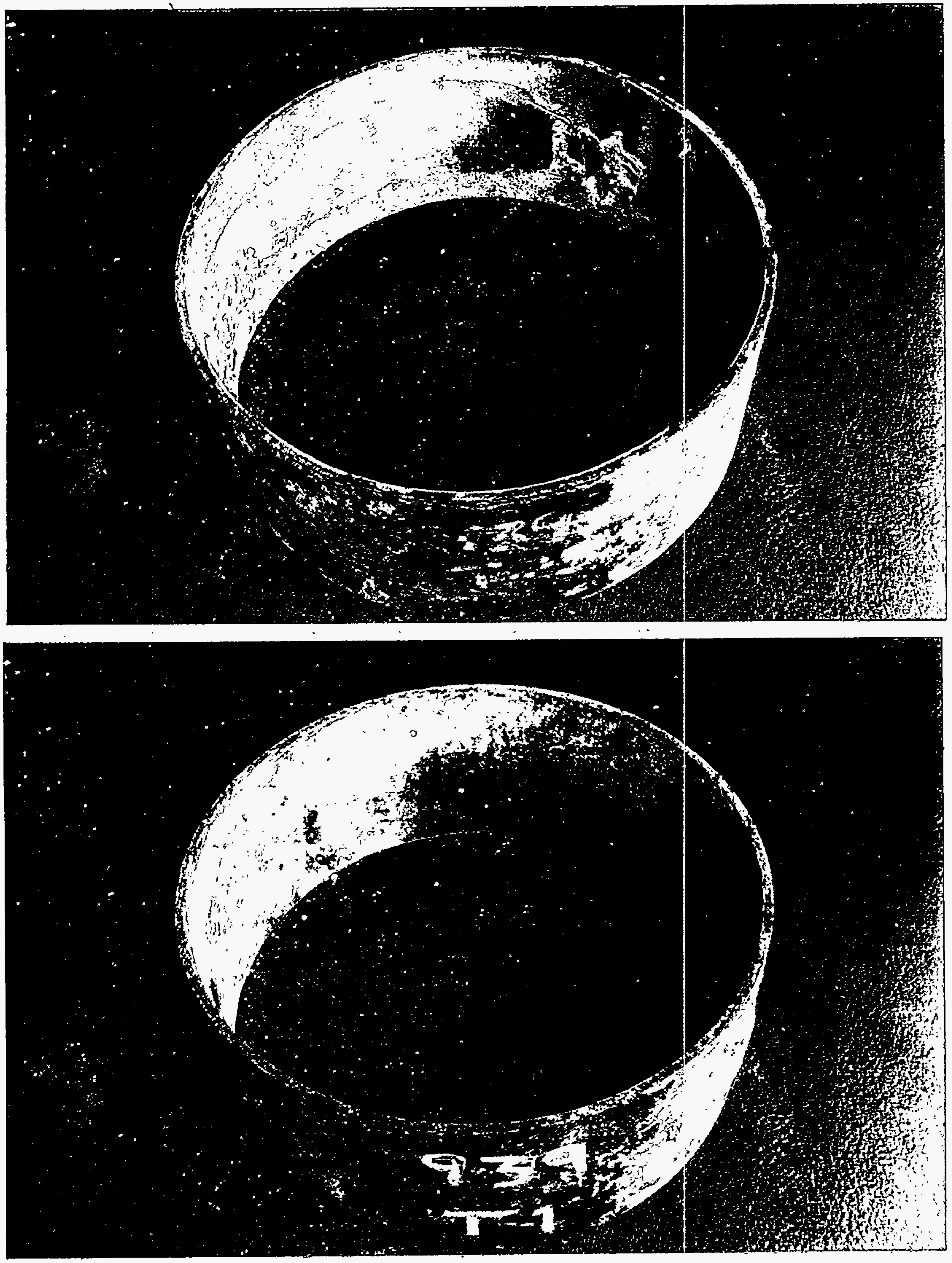


Figure 8. Condition of 060-5 (Coating C) and 071-1 (Coating C).

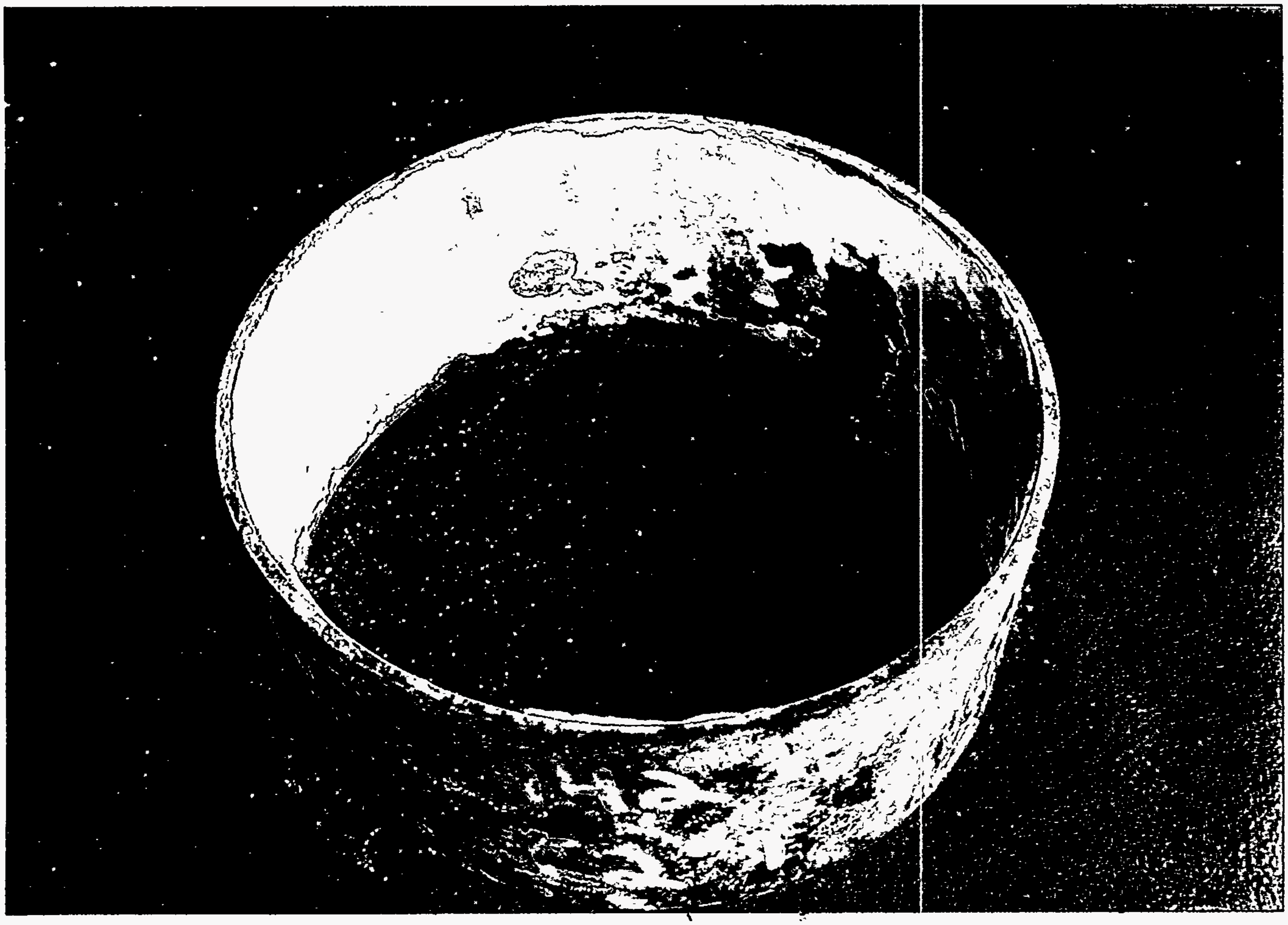


Figure 9. Condition of 082-1 (Coating C). NiCrAl/TiO_2 coating on titanium substrate after 108-hour exposure.

The following photographs (Figures 10-12) show the Type F coatings. 083-4 was in good condition after 120 hours in Section 5 though it is hard to see the coating due to the salt deposition. Both 083-3 in Section 3 and 083-5 in Section 1 were also in good condition after 120 hours while 083-8 in Section 5 shows delamination. The difference between 083-4 and 083-8 was that 083-8 was on an Inconel 625 ring while the others were on a titanium ring. The same results were seen with 083-2 in Section 1 and 083-6 in Section 4, which were on titanium rings and did well, while 083-7 in Section 1 on an Inconel 625 ring was cracked, chipped, and flaking.

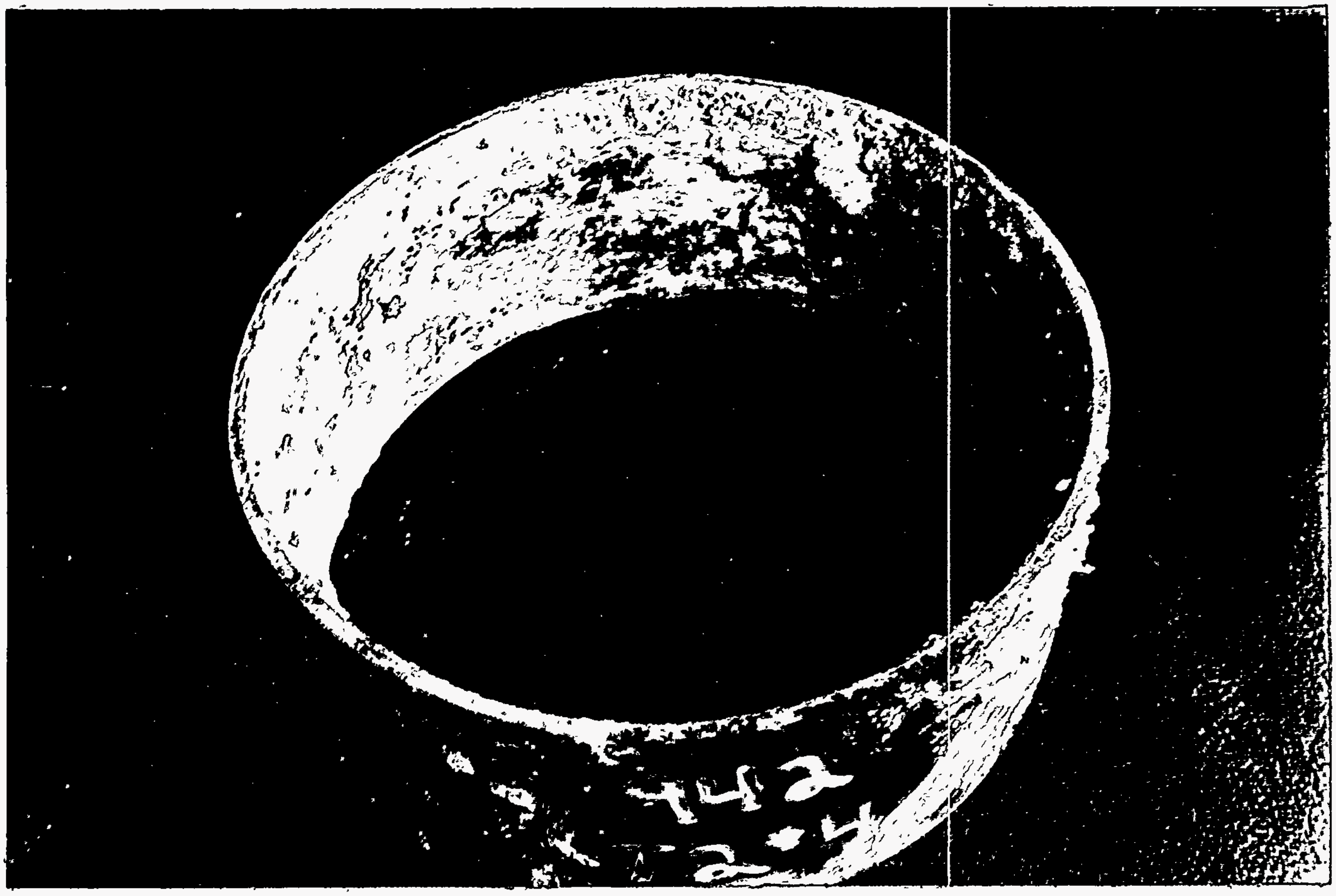


Figure 10. Condition of 083-4 (F Coating). Ti-6Al-4V/TiO_2 coating on titanium substrate intact after 108 hours of exposure in the bottom position of the reactor.

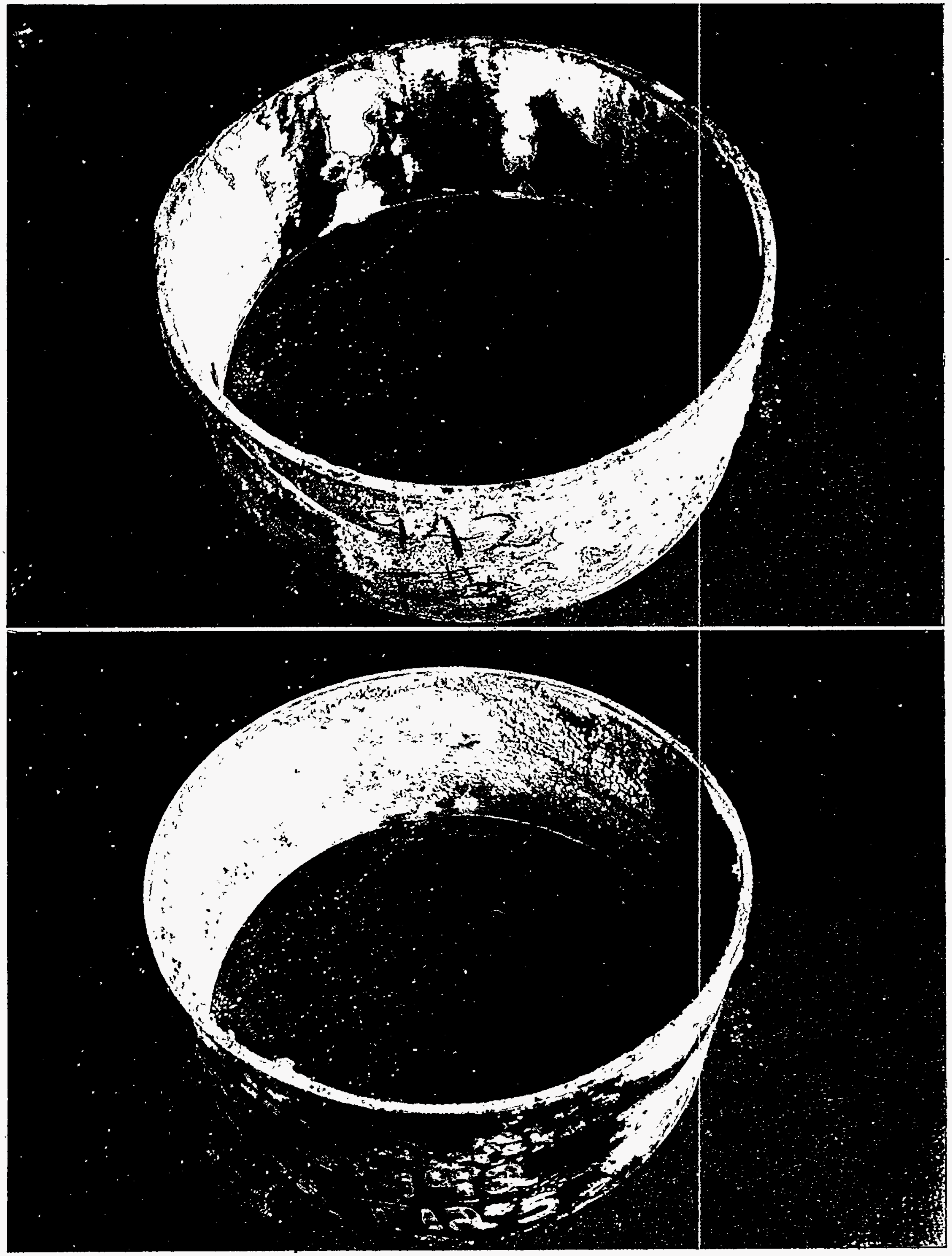


Figure 11. Condition of 083-3 and 083-5. Ti-6Al-4V/TiO_2 coating on titanium substrate intact after 108 hours of exposure.

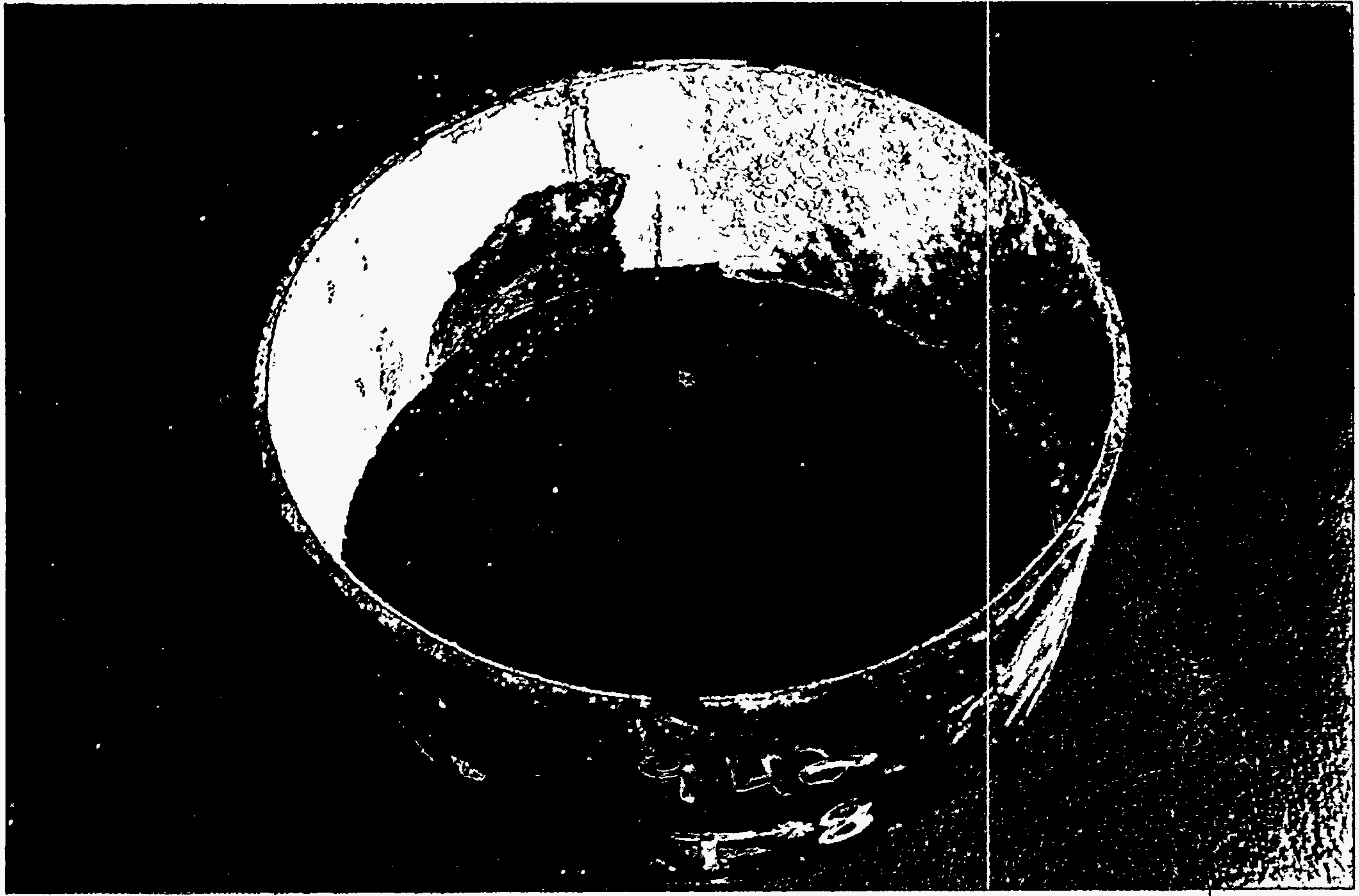
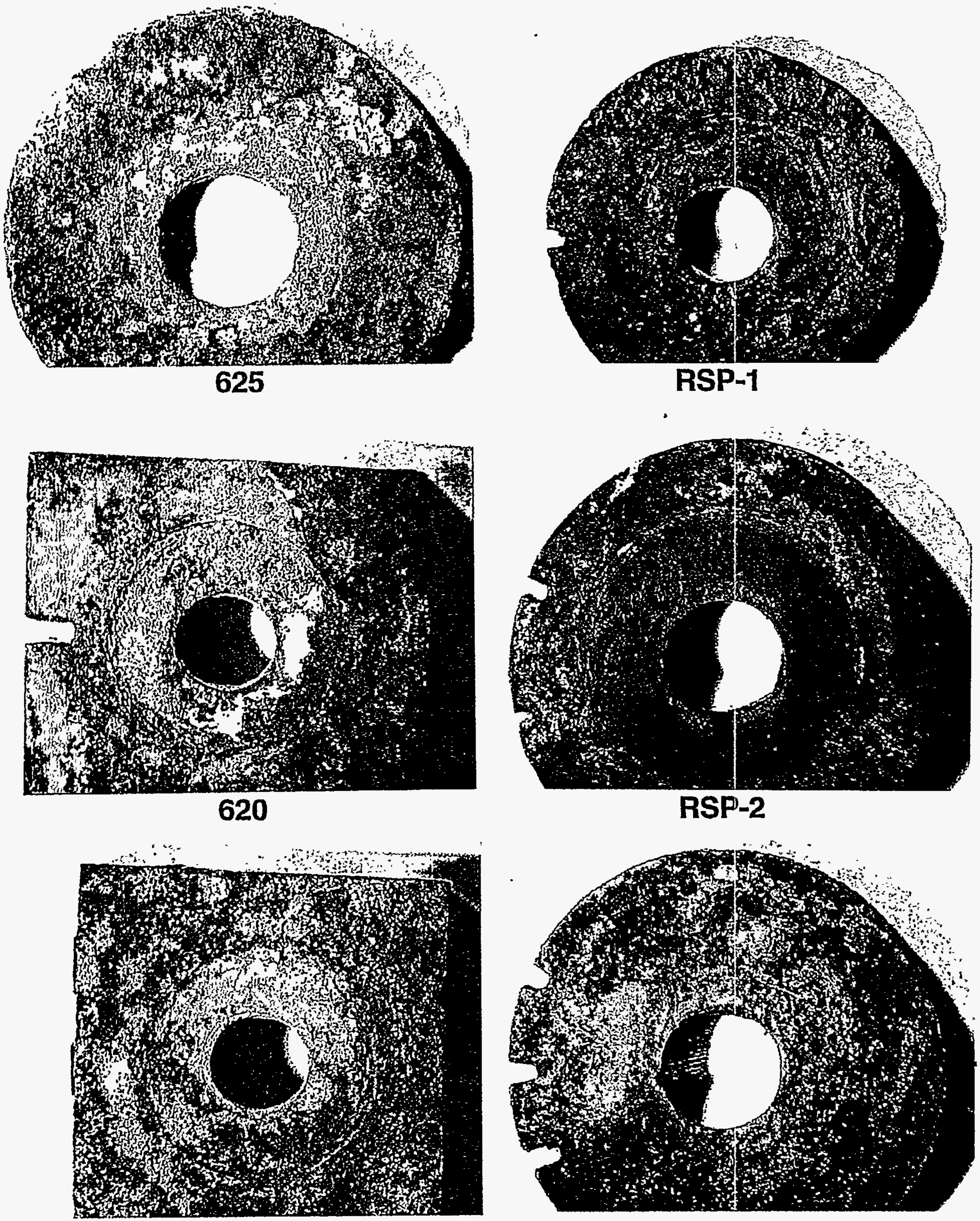


Figure 12. Condition of 083-8. Ti-6Al-4V/TiO_2 coating on IN 625 ring showing lifting and spallation of the coating.

7.2 Experimental Alloys

The following photographs (Figures 13 and 14) show the metal coupons from Section 1 and Section 5. An Inconel 625 coupon is shown in Section 1 for comparison, and a Hastelloy C-22 coupon is shown from Section 5 for comparison. The coupons were weighed after each run after being cleaned in accordance with ASTM procedure. The data are presented in Table 5. Photographs were done with an optical stereomicroscope at 3× to 40× magnification. The results of the photographs showed dissolution and pitting to have been the corrosion mechanisms. Table 4 is a summary of the total mils/year rate of corrosion. All commercial nickel alloy samples suffered severe corrosion with weight losses ranging between 14 and 30% except for the C-276 in Section 1, which had a weight loss of 67% after the first 60 hours of testing. Some coupons were pulled after only a short period of testing due to severe pitting, while all the samples showed signs of pitting and crevice corrosion.

The experimental alloys in Section 5 were below the water line and saw a caustic environment instead of an acid environment.



Section 1

625

RSP-1

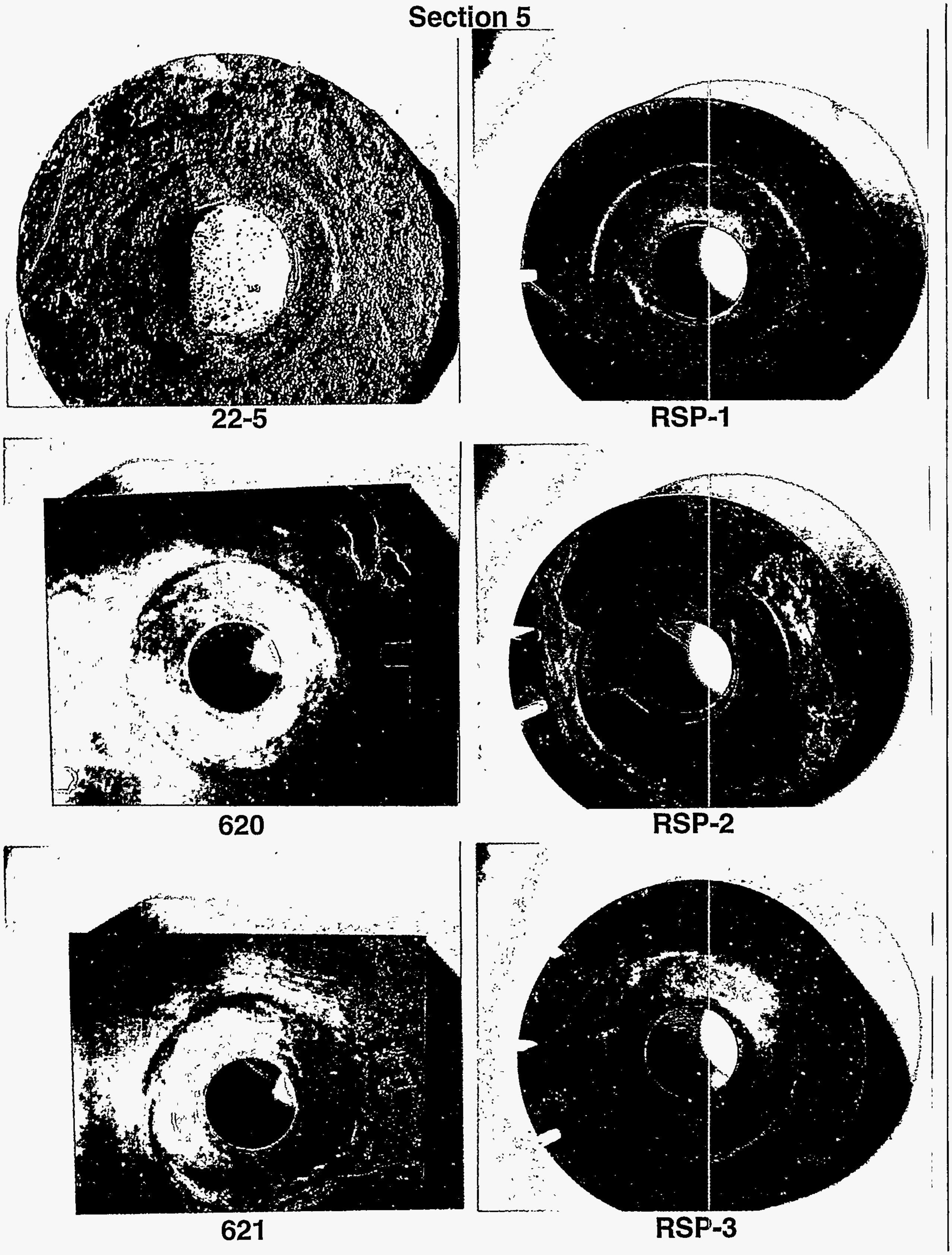
620

RSP-2

621

RSP-3

Figure 13. Metal coupons from Section 1.



Section 5

22-5

RSP-1

620

RSP-2

621

RSP-3

Figure 14. Metal coupons from Section 5.

Table 4. Mils per year corrosion rate of the metal coupons.

	620	621	RSP1	RSP2	RSP3	686	C-276	C-22	I-625
Section 1	266	442	560	173	253	386	4,602	472	369
Section 2	410	327	678	288	231	491	882	498	477
Section 3	175	159	326	177	282	342	647	314	226
Section 4	254	273	323	954	1143	449	732	388	353
Section 5	0.6	0.6	5.3	2.2	14.6	258.3	483.7	270.4	546.6

Table 5. Shows the actual weight change in the metal coupons by section.

	620	621	RSP-1	RSP-2	RSP-3	686	C-276	C-22	I-625
Section 1									
0 hrs			13.155 g	13.466 g	11.848 g		19.444 g	19.266 g	18.518 g
4 hrs	35.6633 g	34.0835g				25.144 g			
60 hrs	35.174 g	33.462 g	12.299 g	13.073 g	11.413 g	23.868 g	6.389 g	18.255 g	17.551 g
% Difference	1%	2%	7%	3%	4%	5%	67%	5%	5%
120 hrs	33.776 g	32.133 g	11.465 g	12.801 g	11.007 g			16.797 g	16.018 g
% Difference	3.97%	3.97%	6.78%	2.08%	3.56%			7.99%	8.73%
240 hrs	32.402 g	28.671 g	10.084 g	12.517 g	10.461 g			13.875 g	14.379 g
% Difference	4.07%	10.77%	12.05%	2.22%	4.96%			17.40%	10.23%
TOTAL	9.14%	15.88%	23.34%	7.05%	11.71%			27.98%	22.35%
Section 2	620	621	RSP-1	RSP-2	RSP-3	686	C-276	C-22	I-625
0 hrs			13.079 g	12.904 g	12.999 g		19.63 g	19.113 g	18.587 g
4 hrs	34.411 g	33.7564 g				25.122 g			
60 hrs	33.081 g	32.987 g	12.064 g	12.536 g	12.264 g	23.582 g	17.295 g	17.659 g	17.458 g
% Difference	4%	2%	8%	3%	6%	6%	12%	8%	6%
120 hrs	31.492 g	31.475 g	11.191 g	12.041 g	11.736 g	21.665 g	12.288 g	15.822 g	16.124 g
% Difference	4.80%	4.58%	7.24%	3.95%	4.31%	8.13%	28.95%	10.40%	7.64%
240 hrs	29.386 g	29.745 g	9.352 g	10.951 g	10.995 g	18.078 g		13.419 g	13.237 g
% Difference	6.69%	5.50%	16.43%	9.05%	6.31%	16.56 g%		15.19%	17.90%
TOTAL	14.60%	11.88%	28.50%	15.13%	15.42%	28.04 %		29.79%	28.78%
Section 3	620	621	RSP-1	RSP-2	RSP-3	686	C-276	C-22	I-625
0 hrs			11.877 g	12.911 g	13.858 g		19.66 g	19.083 g	18.52 g

Table 5. (continued).

	620	621	RSP-1	RSP-2	RSP-3	686	C-276	C-22	I-625
4 hrs	33.7255 g	31.6116 g				25.402 g			
60 hrs	33.281 g	31.265 g	11.523 g	12.703 g	13.162 g	24.147 g	17.918 g	18.31 g	17.895 g
% Difference	1%	1%	3%	2%	5%	5%	9%	4%	3%
120 hrs	32.762 g	30.813 g	11.005 g	12.442 g	12.861 g	22.547 g	14.247 g	17.478 g	17.307 g
% Difference	1.56%	1.45%	4.50%	2.05%	2.29%	6.63%	20.49%	4.54%	3.29%
240 hrs	31.577 g	29.663 g	10.086 g	11.939 g	12.311 g	20.487 g		15.49 g	15.98 g
% Difference	3.62%	3.73%	8.35%	4.04%	4.28%	9.14%		11.37%	7.67%
TOTAL	6.37%	6.16%	15.08%	7.53%	11.16%	19.35%	27.53%	8.41%	6.55%
Section 4	620	621	RSP-1	RSP-2	RSP-3	686	C-276	C-22	I-625
0 hrs			14.014 g	15.2 g	12.685 g		19.258 g	19.01 g	18.556 g
4 hrs	32.7023 g	30.8462 g				25.346 g			
60 hrs	32.334 g	30.516 g	13.646 g	14.731 g	12.232 g	24.525 g	18.3 g	18.72 g	18.222 g
% Difference	1%	1%	3%	3%	4%	3%	5%	2%	2%
120 hrs	31.029 g	29.399 g	12.981 g	13.787 g	10.737 g	23.333 g	17.289 g	17.653 g	17.191 g
% Difference	4.04%	3.66%	4.87%	6.41%	12.22%	4.86%	5.52%	5.70%	5.66%
240 hrs	29.592 g	27.497 g	12.237 g	9.953 g	6.399 g	18.899 g	10.706 g	14.661 g	14.602 g
% Difference	4.63%	6.47%	5.73%	27.81%	40.40%	19.00%	38.08%	16.95%	15.06%
TOTAL	9.51%	10.86%	12.68%	34.52%	49.55%	25.44 %	44.41%	22.88%	21.31%
Section 5	620	621	RSP-1	RSP-2	RSP-3	686	C-276	C-22	I-625
0 hrs			13.644 g	13.623 g	13.887 g		19.363 g	19.057 g	18.666 g
4 hrs	31.93 g	29.284 g				25.172 g			
60 hrs	31.927 g	29.281 g	13.625 g	13.619 g	13.816 g	24.315 g	17.991 g	18.384 g	17.179 g
% Difference	0%	0%	0%	0%	1%	3%	7%	4%	8%
120 hrs	31.923 g	29.275 g	13.618 g	13.614 g	13.807 g	23.322 g		17.746 g	
% Difference	0.01%	0.02%	0.05%	0.04%	0.07%	4.08%		3.47%	
240 hrs	31.923 g	29.276 g	13.615 g	13.611 g	13.807 g	21.467 g		15.971 g	
% Difference	0.00%	0.00%	0.02%	0.02%	0.00%	7.95%		10.00%	
TOTAL	0.02%	0.03%	0.21%	0.09%	0.58%	14.72%		16.19%	

8. DATA ANALYSIS

8.1 Analysis of Performance by Section

The analysis of the ceramic rings and metal coupons was first done by comparing the performance by sections. The chemical environment of each section was described by the pressure, temperature, pH, and presence of particular compounds. Discussions of pH are dependent on assumptions of atmosphere and temperature. When pH is referred to at supercritical conditions, it implies the pH of the corresponding cooled liquid. When HCl is at supercritical conditions it is actually molecular HCl gas and not ionized so the amount of hydrogen ions at the surface of the metal is quite reduced. It is only when the temperature is brought down that the acid forms and dissolves in the water, causing a significant increase in the amount of hydrogen ions present at the surface.

Coating A was the basic design with the nickel/chrome/alumina bond coat, then a transition coat of nickel/chrome/alumina/7% partially stabilized zirconia/yttria (7% YZ). The top coat was 7% YZ chosen because previous corrosion tests have shown good performance of zirconia in SCWO environments.[d] For Coating B an additional alumina interlayer was added beneath the 7% YZ.

Coating C used the same bond coat as Coatings A and B but had a transition layer of nickel/chrome/alumina/titania and a top coat of titania. Coating D was the same as Coating C but with an added top layer of 7% YZ. Coating E was again the same as Coating C but with an added top layer of 24% MgZ.

Coating F was a complete titania/titanium system on a titanium ring. The bond coat was titanium/alumina/vanadium, the transition coat was titanium/alumina/vanadium/titania, and the top coat was titania. Coating F′ was the same except the substrate was Inconel 625.

8.1.1 Section 1 Environment—Temperature 650°C, pH of 0.8

In Section 1 of the corrosion test, the temperature was 650°C and all fluids were in a supercritical phase. The feed included 350 L/min of oxygen, 9,000 ppm of chloride, and 900 ppm of sulfate. Both acids and salts form in this section with the salts depositing onto the ceramic walls and coupon tree.

8.1.1.1 Ceramic Coupon Analysis.

First 60-hour test:	Rings: 047-1 (Coating A), 048-6 (Coating B), 049-11 (Coating C).
Second 60-hour test:	Rings: 060-5 (Coating C), 058-1 (Coating A), 059-3 (Coating B).
120-hour test:	Rings: 083-5 (Coating F), 083-2 (Coating F), 083-7 (Coating F′).

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[d] Telephone conversation with Mike Spritzer, General Atomics.

These nine rings were at the highest temperature of the test. In the first 60-hour test, the two rings with the zirconia top layer (047-1 and 048-6) both showed blistering, peeling, and edge chipping. The ring coated with the titania top coat (049-11) did not show any defects. The two rings with the zirconia top layer (059-3 and 058-1) delaminated in the second 60-hour test. The ring coated with titania (060-5) showed some peeling of the top coat. In the 120-hour test the two rings that were titania sprayed onto titanium (083-2 and 083-5) showed no defects while the one ring that was titania sprayed onto Inconel 625 substrate (083-7) showed cracking, chipping, and spalling. An indepth analysis of Ring 047-1 is presented in Section 8.3.

8.1.1.2 Metal Coupon Analysis.[e]

The experimental nickel alloys of Section 1:

- The 620 coupon had general corrosion over 80% of the exposed surface and crevice corrosion. The depth of attack was up to 8 mils.
- The 621 coupon had general albeit not quite uniform attack virtually over the entire surface.
- RSP1 had severe corrosion up to 12 mils.
- RSP2 had relatively minor crevice corrosion with attack up to 3 mils.
- RSP3 was similar to RSP2 but had attack up to 6 mils.

The baseline nickel alloys of Section 1:

- Alloy 686 was heavily pitted after the first 60-hour test. The pits were up to 8 mils deep.
- Alloy C-276 had severe corrosion after the first 60-hour test with numerous overlapping pits.
- Alloy C-22 also had severe corrosion with overlapping pits with depths up to 20 mils.
- Alloy 625 also had severe corrosion with some crevice attack near the hole of about 45 mils.

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d. Vladimir Zilberstein, *Effect of TrimSol Based SCWO Environment on Materials Tested in the MODAR Pilot Plant Vessel*, Stone and Webster, September 1994.

8.1.2 Section 2 Environment—Temperature 600°C, pH of 0.8

8.1.2.1 Ceramic Coupon Analysis.

First 60-hour test: 047-2 (A), 048-7 (B), 049-12 (C).

Second 60-hour test: 072-2 (D), 073-5 (E), 049-12 (C).

120-hour test: 082-1 (C′), 072-2 (D), 059-4 (B).

In the first 60-hour test the two rings with a zirconia top layer (047-2 and 048-7) showed blistering, peeling, and chipping. Ring 048-7 also had delamination at the boundary between the alumina layer and the zirconia top layer. The titania coated coupon (049-12) showed no defects. In the second 60-hour test the rings coated with a layer of titania and then zirconia (072-2, 073-5) had heavy blistering of the zirconia with the titania intact after 60 hours but after an additional 120 hours the zirconia was gone and there was significant loss of the titania (072-2). The two rings coated with titania were both exposed for 120 hours. 049-12 looked good after 60 hours but was delaminating after 120 hours, while 082-1 still looked good after 120 hours. The difference between these two was that 082-1 was titania sprayed onto a titanium ring though it still had the nickel/chrome/aluminum bond coat. Coupon 059-4 (zirconia top coat) was exposed for 120 hours in Section 2 after being exposed for 60 hours in Section 5. This exposure resulted in heavy delamination.

8.1.2.2 Metal Coupon Analysis.[e]

The experimental nickel alloys of Section 2:

- The 620 coupon had fairly severe corrosion while 621 had pronounced crevice corrosion with attack up to 10 mils.
- RSP1 had severe corrosion attack while RSP2 and RSP3 had an attack of dissolution.

The baseline nickel alloys of Section 2:

- Alloy 686 was severely corroded with pits between 15 to 30 mils.
- Alloy 625 had deep crevice attack up to 16 mils along with severe corrosion.
- Alloy C-22 had severe corrosion similar to Alloy 686.
- Alloy C-276 was removed after 120 hours due to drastic thinning and major corrosion.

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[e] Vladimir Zilberstein, *Effect of TrimSol Based SCWO Environment on Materials Tested in the MODAR Pilot Plant Vessel*, Stone and Webster, September 1994.

8.1.3 Section 3 Environment—Temperature 500°C, pH of 0.8

8.1.3.1 Ceramic Coupon Analysis.

First 60-hour test: 047-3 (A), 048-8 (B), 049-13 (C).

Second 60-hour test: 072-3 (D), 073-6 (E), 049-13 (C).

120-hour test: 083-3 (F), 073-6 (E), 049-13 (C).

This section was considered the most mild environment of the five sections and yet the results of the zirconia coated rings were very similar to Section 2. In the first 60 hour test, 047-3 and 048-8 showed blistering and chipping in the second 60-hour test. 072-3 and 073-6 had heavy blistering of the zirconia with the titania intact after 60 hours but after an additional 120 hours the zirconia was gone and there was significant loss of the titania (073-6). The ring coated with titania on the nickel chrome bond coat (049-13) lasted the length of all three tests (240 hours) although patches of base metal were exposed. The ring coated with titania on a titania bond coat and titania ring (083-3) did very well after 120 hours.

8.1.3.2 Metal Coupon Analysis.[f]

The experimental nickel alloys of Section 3:

- The 620 and 621 coupons had pronounced crevice corrosion with the crevice depth in 620 up to 12 mils near the edge.
- RSP1 also had crevice corrosion up to 10 mils while RSP2 had patchy dissolution up to 6 mils and RSP3 had uniform corrosion attack.

The baseline nickel alloys of Section 3:

- Alloy 686 had deep corrosion attack up to 15 mils.
- Alloy C-22 had severe corrosion attack up to 18 mils.
- Alloy 625 had isolated pits and areas of overlapping pits.
- Alloy C-276 was removed after 120 hours due to major corrosion.

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[f] Vladimir Zilberstein, *Effect of TrimSol Based SCWO Environment on Materials Tested in the MODAR Pilot Plant Vessel*, Stone and Webster, September 1994.

8.1.4 Section 4 Environment—Temperature 400°C, pH of 1.5

8.1.4.1 Ceramic Coupon Analysis.

First 60-hour test: 047-4 (A), 048-9 (B), 049-14 (C).

Second 60-hour test: 072-4 (D), 073-7 (E), 071-1 (C).

120-hour test: 072-4 (D), 073-7 (E), 083-6 (F).

This section had the added variable of the dilution stream coming in and spraying directly onto the rings. One of the zirconia rings (047-4) appeared to do well after the first test while the zirconia with the alumina interlayer showed cracks, blistering and some delamination. The zirconia over the titania layer (072-4 and 073-7) showed heavy blistering of the zirconia after 60 hours. One of the titania coated rings with the nickel/chrome bond (049-14) suffered from edge attack that corroded the base metal of Inconel 625 after only 60 hours, while another similar ring (071-1) did very well except for a patch of delamination that could have been due to the quench water hitting the ring. The titania coated ring with the titania bond on the titania ring (083-6) did well with some possible thinning of the coating.

8.1.4.2 Metal Coupon Analysis.[g]

The experimental nickel alloys of Section 4:

- The 620 metal coupon had severe corrosion with losses up to 16 mils, while the 621 coupon had losses up to 20 mils.
- The RSP1 coupon had losses of 8 mils, RSP2 had losses of 45 mils, and RSP3 was described as having major wastage.

The baseline nickel alloys of Section 4:

- Alloy 686 had deep corrosion attack up to 18 mils.
- Alloy C-22 had severe corrosion.
- Alloy C-276 had major corrosion up to 30 mils.
- Alloy 625 uniform corrosion with an average depth of attack of 12 mils with one pit with 30 mils depth.

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[g] Vladimir Zilberstein, *Effect of TrimSol Based SCWO Environment on Materials Tested in the MODAR pilot Plant Vessel*, Stone and Webster, September 1994.

8.1.5 Section 5 Environment—Temperature 300°C, pH of 1.5

8.1.5.1 Ceramic Coupon Analysis.

First 60-hour test: 047-5 (A), 048-10 (B), 049-16 (C).

Second 60-hour test: 060-6 (C), 058-2 (A), 059-4 (B).

120-hour test: 083-8 (F′), 060-6 (C), 083-4 (F).

This section saw the transition from the supercritical phase and the formation of acids. The water level was apparent by the water line mark on the bottom ring. While the zirconia again showed blistering and delamination (047-5, 048-10, 058-2, and 059-4), the five titania coated rings had a variety of results dependent on their bond coats and ring material. 049-16, 060-6, and 083-4 did well while 083-8 suffered from delamination. The difference is that 083-8 had a titania bond coat on a Inconel 625 ring while the other three rings had bond coats that matched their rings. An in-depth Analysis of coupons 048-10 and 083-4 is presented in Section 8.3.

8.1.5.2 Metal Coupon Analysis.[h]

The liquid level of the brine immersed the experimental nickels. The corrosion rates and descriptions do not reflect the performance in the severe environment of Section 5 but the performance in a brine solution.

The experimental nickel alloys of Section 5:

- The 620 coupon showed no signs of corrosion and 621 had minor attack.
- The RSP1 showed numerous small pits around the outer edge of the sample with crevice corrosion appearing likely to start.
- The RSP2 coupon showed no apparent signs of corrosion except for discoloration, while RSP3 had multiple deep pits and initial stages of crevice corrosion.

The baseline nickel alloys of Section 5:

- Alloy 686 had corrosion with a depth of attack of 3 to 8 mils along with a few deep pits up to 18 mils.
- Alloy C-22 had severe corrosion resulting from overlapping pits with some pits having up to 20 mils depth.

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[h] Vladimir Zilberstein, *Effect of TrimSol Based SCWO Environment on Materials Tested in the MODAR Pilot Plant Vessel*, Stone and Webster, September 1994.

- Alloy 625 was removed after 60 hours due to severe corrosion

- Alloy C-276 was removed after 60 hours due to numerous pits up to 25 mils deep.

8.2 Analysis of Performance by Material

This subsection includes a comparison of performance of each material throughout all five sections:

- Coating A - 047-1, 047-2, 047-3, 047-4, 047-5, 058-1, 058-2
    - Regardless of the section these rings were placed in, or the amount of thermal cycles they received, there was blistering or delamination after 60 hours of operation. The delamination is shown in Figure 25.
- Coating B - 048-6, 048-7, 048-8, 048-9, 048-10, 059-3, 059-4
    - These rings also showed blistering or delamination. The delamination occurred at the alumina layer.
- Coating C - 049-11, 049-12, 049-13, 049-14, 049-16, 060-5, 060-6, 071-1
    - These rings suffered from an edge attack, which given greater than 60 hours would result in delamination. The rings that did not have edge attack showed a thinning of the top coat. Ring 049-13 had sections of the Inconel exposed after 240 hours.
- Coating D - 072-2, 072-3, 072-4
    - These rings showed blistering of the top coat after 60 hours. After 60 hours the titania layer began to wear away.
- Coating E - 073-5, 073-6, 073-7
    - These rings also showed blistering and in some cases the top layer was already gone by the 60-hour run. The titania layer was intact after 60 hours but then began to be worn away.
- Coating C′- 082-1
    - This coating was done on a titanium ring, and remained intact after 120 hours.
- Coating F - 083-2, 083-3, 083-4, 083-5, 083-6
    - These rings performed the best with all five of them looking intact upon visual examination after 120 hours.

- Coating F′- 083-7, 083-8
  - These rings were Inconel 625 and both delaminated at the bond coat substrate interface.

8.3 Analysis of Delamination Mechanisms

8.3.1 Coating 047-1

An overall view of a failed coating (047-1) which shows the major coating spall between the bond layer and the intermediate blended layer is shown in Figure 15. A diagram of the failure mechanism is illustrated in Figure 26. Figures 16 and 17 show areas that were analyzed by the EDS technique. Table 6 documents the results. A description follows:

Areas 1,5,9	This area has the basic chemistry of the ceramic top coat of the Coating A with a slight difference in the yttria concentration.
Area 2,3	These areas are composed of products of the reaction of the surrogate containing supercritical fluid and the ceramic coating. The formation of these surrogate containing second phases has implications as the radionuclides and hazardous elements from a mixed waste stream could be concentrated in a coating that they react with.
Area 6	This area is a nickel sulfide (NiS_2 or Ni_3S_4) reaction product.
Area 7	This area is a mixture of coating elements and waste/surrogate elements.
Area 8	The chemical analysis of this area chemistry only shows the elements present in the metallic bond coat.
Area 10	This area is rich in nickel and chrome, low in aluminum with silicon and iron present.
Area 11	This area appears to be yttria stabilized zirconia
Area 12,13	These areas are complex oxides with small amounts of TrimSol components such as sulfur.
Area 14	This area appears to be a nickel oxide with a small amount of sulfur present.
Area 15	This area shows the bond coat (Ni,Cr,Al) chemistry. (The nominal chemistry of the prealloyed powder is Ni-balance, Cr-19%, Al-6%).

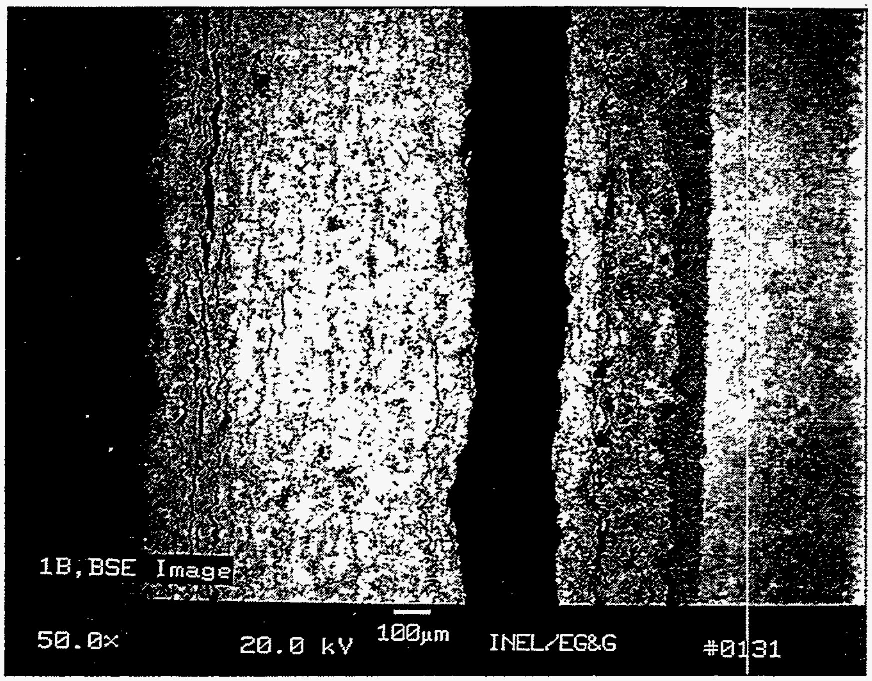


Figure 15. 50× view of 047-1.

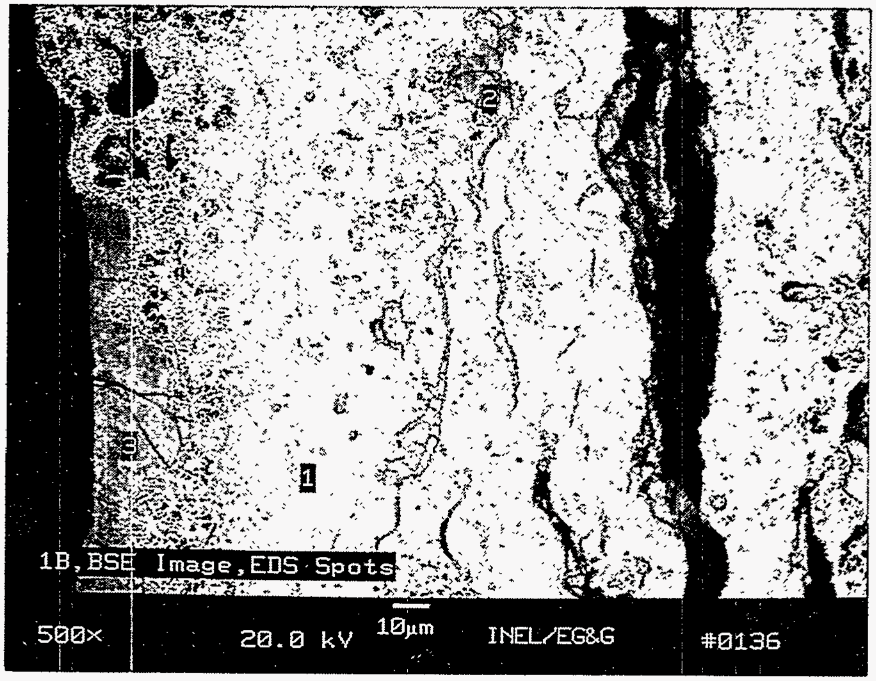


Figure 16. 500× view of 047-1.

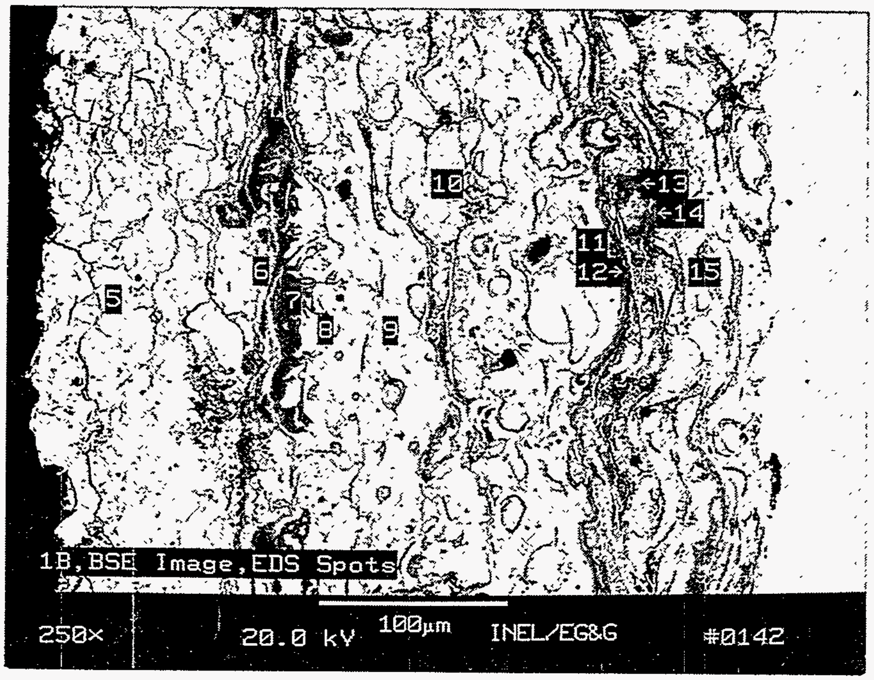


Figure 17. 250× view of 047-1.

Table 6. Results of analysis of 047-1.

```
        06-May-1994 13:43:03         1B-1

    Accelerating voltage                20.0 KeV

    Beam - sample incidence angle     90.0 degrees

    Xray emergence angle              35.0 degrees

    Xray - window incidence angle      0.0 degrees


                     STANDARDLESS EDS ANALYSIS
                   (ZAF CORRECTIONS VIA MAGIC V)


     ELEMENT   WEIGHT    ATOMIC   PRECISION
     & LINE   PERCENT   PERCENT*  2 SIGMA  K-RATIO**

     O  KA     33.10     73.96      1.24    0.0658
     Y  LA      4.32      1.74      0.19    0.0382
     Zr LA     61.38     24.06      0.40    0.5582
     Hf LA      1.20      0.24      0.22    0.0097

     TOTAL    100.00

 ITERATIONS       9

 *NOTE: ATOMIC PERCENT is normalized to 100

 **NOTE: K-RATIO = K-RATIO x R
         where R = reference(standard)/reference(sample)

           NORMALIZATION FACTOR:   1.000
```

Table 6. (continued).

```
        06-May-1994 13:29:56        1B-2

    Accelerating voltage                20.0 KeV

    Beam - sample incidence angle      90.0 degrees

    Xray emergence angle               35.0 degrees

    Xray - window incidence angle       0.0 degrees


                     STANDARDLESS EDS ANALYSIS
                   (ZAF CORRECTIONS VIA MAGIC V)


     ELEMENT   WEIGHT    ATOMIC    PRECISION
     & LINE   PERCENT   PERCENT*  2 SIGMA  K-RATIO**

     O   KA    55.30     79.16      1.04    0.2057
     Na  KA     2.33      2.32      0.15    0.0072
     S   KA    17.25     12.32      0.16    0.1319
     K   KA     3.08      1.81      0.08    0.0253
     Ca  KA     0.77      0.44      0.05    0.0068
     Y   LA     5.06      1.30      0.14    0.0372
     Ce  LA    16.21      2.65      0.25    0.1308

     TOTAL    100.00

  ITERATIONS      16

  *NOTE: ATOMIC PERCENT is normalized to 100

  **NOTE: K-RATIO = K-RATIO x R
          where R = reference(standard)/reference(sample)

            NORMALIZATION FACTOR:   1.000
```

Table 6. (continued).

```
        06-May-1994 13:32:32        1B-3

    Accelerating voltage                20.0 KeV

    Beam - sample incidence angle     90.0 degrees

    Xray emergence angle              35.0 degrees

    Xray - window incidence angle      0.0 degrees


                  STANDARDLESS EDS ANALYSIS
                 (ZAF CORRECTIONS VIA MAGIC V)


     ELEMENT   WEIGHT    ATOMIC   PRECISION
     & LINE    PERCENT   PERCENT*  2 SIGMA  K-RATIO**

     O  KA      54.98     78.63      1.02     0.2175
     Na KA       3.46      3.44      0.18     0.0105
     S  KA      17.02     12.15      0.16     0.1315
     K  KA       2.87      1.68      0.08     0.0238
     Ca KA       0.79      0.45      0.05     0.0070
     Y  LA       2.56      0.66      0.11     0.0184
     Ce LA      18.32      2.99      0.27     0.1485

     TOTAL     100.00

   ITERATIONS      14

   *NOTE: ATOMIC PERCENT is normalized to 100

   **NOTE: K-RATIO = K-RATIO x R
           where R = reference(standard)/reference(sample)


           NORMALIZATION FACTOR:   1.000
```

Table 6. (continued).

```
          06-May-1994 13:45:10        1B-4

    Accelerating voltage                20.0 KeV

    Beam - sample incidence angle      90.0 degrees

    Xray emergence angle               35.0 degrees

    Xray - window incidence angle       0.0 degrees


                      STANDARDLESS EDS ANALYSIS
                    (ZAF CORRECTIONS VIA MAGIC V)


     ELEMENT    WEIGHT     ATOMIC    PRECISION
     & LINE    PERCENT    PERCENT*   2 SIGMA   K-RATIO**

     O  KA      32.04      73.01       1.18     0.0633
     Y  LA       7.59       3.11       0.22     0.0672
     Zr LA      59.06      23.61       0.39     0.5382
     Hf LA       1.31       0.27       0.25     0.0106

     TOTAL     100.00

   ITERATIONS      10

   *NOTE: ATOMIC PERCENT is normalized to 100

   **NOTE: K-RATIO = K-RATIO x R
           where R = reference(standard)/reference(sample)

           NORMALIZATION FACTOR:   1.000
```

Table 6. (continued).

```
        06-May-1994 13:40:02          1B-5


    Accelerating voltage              20.0 KeV

    Beam - sample incidence angle    90.0 degrees

    Xray emergence angle             35.0 degrees

    Xray - window incidence angle     0.0 degrees


                         STANDARDLESS EDS ANALYSIS
                       (ZAF CORRECTIONS VIA MAGIC V)


     ELEMENT    WEIGHT     ATOMIC    PRECISION
     & LINE    PERCENT    PERCENT*  2 SIGMA   K-RATIO**

     O  KA      31.47      72.44       1.23     0.0616
     Y  LA       7.61       3.15       0.22     0.0677
     Zr LA      59.97      24.21       0.40     0.5493
     Hf LA       0.95       0.20       0.21     0.0077

     TOTAL     100.00

 ITERATIONS      10

 *NOTE: ATOMIC PERCENT is normalized to 100

 **NOTE: K-RATIO = K-RATIO x R
         where R = reference(standard)/reference(sample)


           NORMALIZATION FACTOR:   1.000
```

Table 6. (continued).

```
        06-May-1994 13:46:46         1B-6

  Accelerating voltage              20.0 KeV

  Beam - sample incidence angle    90.0 degrees

  Xray emergence angle             35.0 degrees

  Xray - window incidence angle     0.0 degrees


                     STANDARDLESS EDS ANALYSIS
                    (ZAF CORRECTIONS VIA MAGIC V)


   ELEMENT   WEIGHT    ATOMIC    PRECISION
   & LINE   PERCENT   PERCENT*   2 SIGMA   K-RATIO**

   S  KA     39.30     54.21       0.30     0.2904
   Cr KA      0.57      0.48       0.08     0.0054
   Ni KA     60.13     45.30       0.60     0.5730

   TOTAL    100.00

 ITERATIONS      9

 *NOTE: ATOMIC PERCENT is normalized to 100

 **NOTE: K-RATIO = K-RATIO x R
         where R = reference(standard)/reference(sample)

           NORMALIZATION FACTOR:   1.000
```

Table 6. (continued).

```
        06-May-1994 13:50:27        1B-7

    Accelerating voltage              20.0 KeV

    Beam - sample incidence angle    90.0 degrees

    Xray emergence angle             35.0 degrees

    Xray - window incidence angle     0.0 degrees


                  STANDARDLESS EDS ANALYSIS
                 (ZAF CORRECTIONS VIA MAGIC V)


     ELEMENT   WEIGHT    ATOMIC   PRECISION
     & LINE   PERCENT   PERCENT*  2 SIGMA  K-RATIO**

     O  KA     33.66     62.37      1.64     0.1764
     Al KA      2.73      2.99      0.14     0.0116
     Si KA      1.79      1.89      0.10     0.0098
     S  KA      0.75      0.69      0.07     0.0054
     Cl KA      1.77      1.48      0.09     0.0135
     Cr KA     29.66     16.91      0.32     0.2806
     Fe KA      0.60      0.32      0.09     0.0055
     Ni KA     13.18      6.65      0.29     0.1247
     Zn KA     12.24      5.55      0.37     0.1076
     Y  LA      3.01      1.00      0.15     0.0193
     Ce LA      0.62      0.13      0.12     0.0055

     TOTAL    100.01

 ITERATIONS       9

 *NOTE: ATOMIC PERCENT is normalized to 100

 **NOTE: K-RATIO = K-RATIO x R
         where R = reference(standard)/reference(sample)

          NORMALIZATION FACTOR:   1.000
```

Table 6. (continued).

```
        06-May-1994 13:53:39        1B-8

    Accelerating voltage              20.0 KeV

    Beam - sample incidence angle    90.0 degrees

    Xray emergence angle             35.0 degrees

    Xray - window incidence angle     0.0 degrees


                   STANDARDLESS EDS ANALYSIS
                 (ZAF CORRECTIONS VIA MAGIC V)


     ELEMENT    WEIGHT    ATOMIC    PRECISION
     & LINE    PERCENT   PERCENT*  2 SIGMA   K-RATIO**

     O   KA      0.00      0.00      0.00     0.0000
     Al  KA      2.18      4.40      0.15     0.0074
     Si  KA      2.16      4.19      0.13     0.0098
     Cr  KA     20.46     21.48      0.26     0.2128
     Ni  KA     75.21     69.93      0.65     0.7347

     TOTAL     100.01

   ITERATIONS       6

   *NOTE: ATOMIC PERCENT is normalized to 100

   **NOTE: K-RATIO = K-RATIO x R
           where R = reference(standard)/reference(sample)

             NORMALIZATION FACTOR:   1.000
```

Table 6. (continued).

```
        06-May-1994 13:56:00        1B-9


    Accelerating voltage                  20.0 KeV

    Beam - sample incidence angle        90.0 degrees

    Xray emergence angle                 35.0 degrees

    Xray - window incidence angle         0.0 degrees


                     STANDARDLESS EDS ANALYSIS
                   (ZAF CORRECTIONS VIA MAGIC V)


     ELEMENT    WEIGHT     ATOMIC    PRECISION
     & LINE    PERCENT    PERCENT*  2 SIGMA   K-RATIO**

     O  KA      30.08      71.13       1.19     0.0582
     Y  LA       8.38       3.57       0.23     0.0748
     Zr LA      60.47      25.07       0.40     0.5550
     Hf LA       1.07       0.23       0.22     0.0087

     TOTAL     100.00

 ITERATIONS      10

 *NOTE: ATOMIC PERCENT is normalized to 100

 **NOTE: K-RATIO = K-RATIO x R
         where R = reference(standard)/reference(sample)

           NORMALIZATION FACTOR:   1.000
```

Table 6. (continued).

```
        06-May-1994 13:57:45        1B-10


  Accelerating voltage                20.0 KeV

  Beam - sample incidence angle      90.0 degrees

  Xray emergence angle               35.0 degrees

  Xray - window incidence angle       0.0 degrees


                    STANDARDLESS EDS ANALYSIS
                  (ZAF CORRECTIONS VIA MAGIC V)


   ELEMENT   WEIGHT    ATOMIC    PRECISION
   & LINE   PERCENT   PERCENT*  2 SIGMA   K-RATIO**

   O  KA      0.00      0.00      0.00     0.0000
   Al KA      1.01      2.09      0.13     0.0034
   Si KA      1.70      3.36      0.12     0.0077
   Cr KA     19.46     20.82      0.26     0.2034
   Fe KA      0.42      0.42      0.08     0.0047
   Ni KA     77.40     73.31      0.68     0.7576

   TOTAL     99.99

 ITERATIONS      6

 *NOTE: ATOMIC PERCENT is normalized to 100

 **NOTE: K-RATIO = K-RATIO x R
         where R = reference(standard)/reference(sample)


           NORMALIZATION FACTOR:   1.000
```

Table 6. (continued).

```
       06-May-1994 13:59:59        1B-11

   Accelerating voltage                20.0 KeV

   Beam - sample incidence angle     90.0 degrees

   Xray emergence angle              35.0 degrees

   Xray - window incidence angle      0.0 degrees


                          STANDARDLESS EDS ANALYSIS
                         (ZAF CORRECTIONS VIA MAGIC V)


    ELEMENT    WEIGHT     ATOMIC    PRECISION
    & LINE    PERCENT    PERCENT*   2 SIGMA  K-RATIO**

    O  KA      31.84      72.59       1.24     0.0634
    Ni KA       1.23       0.77       0.12     0.0121
    Y  LA       7.62       3.13       0.05     0.0671
    Zr LA      58.25      23.30       0.22     0.5282
    Hf LA       1.05       0.21       0.24     0.0085

    TOTAL      99.99

 ITERATIONS      10

 *NOTE: ATOMIC PERCENT is normalized to 100

 **NOTE: K-RATIO = K-RATIO x R
         where R = reference(standard)/reference(sample)

           NORMALIZATION FACTOR:    1.000
```

Table 6. (continued).

```
        06-May-1994 14:02:54        1B-12


    Accelerating voltage             20.0 KeV

    Beam - sample incidence angle   90.0 degrees

    Xray emergence angle            35.0 degrees

    Xray - window incidence angle    0.0 degrees


                   STANDARDLESS EDS ANALYSIS
                  (ZAF CORRECTIONS VIA MAGIC V)


     ELEMENT   WEIGHT    ATOMIC    PRECISION
     & LINE   PERCENT   PERCENT*  2 SIGMA   K-RATIO**

     O   KA    34.04     60.49      1.36     0.1921
     Al  KA .   7.19      7.58      0.19     0.0312
     Si  KA     1.97      1.99      0.10     0.0104
     S   KA     1.22      1.08      0.07     0.0089
     Cl  KA     0.76      0.61      0.07     0.0058
     Cr  KA    27.34     14.95      0.30     0.2602
     Ni  KA    27.48     13.30      0.40     0.2520

     TOTAL    100.00

 ITERATIONS      9

 *NOTE: ATOMIC PERCENT is normalized to 100

 **NOTE: K-RATIO = K-RATIO x R
         where R = reference(standard)/reference(sample)


           NORMALIZATION FACTOR:   1.000
```

Table 6. (continued).

```
        06-May-1994 14:07:14          1B-13

    Accelerating voltage               20.0 KeV

    Beam - sample incidence angle     90.0 degrees

    Xray emergence angle              35.0 degrees

    Xray - window incidence angle      0.0 degrees


                          STANDARDLESS EDS ANALYSIS
                        (ZAF CORRECTIONS VIA MAGIC V)


     ELEMENT    WEIGHT     ATOMIC    PRECISION
     & LINE    PERCENT    PERCENT*   2 SIGMA   K-RATIO**

     O   KA     24.24      48.30       7.19     0.1282
     Al  KA     10.06      11.89       0.23     0.0430
     Si  KA      2.53       2.88       0.12     0.0129
     S   KA      0.69       0.69       0.07     0.0049
     Cl  KA      0.54       0.49       0.06     0.0041
     Ca  KA      0.24       0.19       0.05     0.0023
     Cr  KA     29.63      18.17       0.32     0.2852
     Ni  KA     32.06      17.41       0.45     0.2968

     TOTAL      99.99

 ITERATIONS       8

 *NOTE: ATOMIC PERCENT is normalized to 100

 **NOTE: K-RATIO = K-RATIO x R
         where R = reference(standard)/reference(sample)


           NORMALIZATION FACTOR:   1.000
```

Table 6. (continued).

```
        06-May-1994 14:09:40        1B-14

  Accelerating voltage                20.0 KeV

  Beam - sample incidence angle      90.0 degrees

  Xray emergence angle               35.0 degrees

  Xray - window incidence angle       0.0 degrees


                    STANDARDLESS EDS ANALYSIS
                  (ZAF CORRECTIONS VIA MAGIC V)


   ELEMENT   WEIGHT    ATOMIC   PRECISION
   & LINE   PERCENT   PERCENT*  2 SIGMA  K-RATIO**

   O  KA     24.67     54.41      1.41    0.1269
   S  KA      0.51      0.56     0.07    0.0034
   Cr KA      0.86      0.58     0.08    0.0090
   Ni KA     73.96     44.45     0.66    0.7108

   TOTAL    100.00

ITERATIONS       9

*NOTE: ATOMIC PERCENT is normalized to 100

**NOTE: K-RATIO = K-RATIO x R
        where R = reference(standard)/reference(sample)

          NORMALIZATION FACTOR:   1.000
```

Table 6. (continued).

```
       06-May-1994 14:11:49         1B-15

   Accelerating voltage               20.0 KeV

   Beam - sample incidence angle     90.0 degrees

   Xray emergence angle              35.0 degrees

   Xray - window incidence angle      0.0 degrees


                     STANDARDLESS EDS ANALYSIS
                    (ZAF CORRECTIONS VIA MAGIC V)


    ELEMENT   WEIGHT    ATOMIC    PRECISION
    & LINE    PERCENT   PERCENT*  2 SIGMA   K-RATIO**

    Al  KA     10.46     19.65      0.26     0.0367
    Si  KA      1.62      2.92      0.12     0.0071
    Cr  KA     13.16     12.83      0.22     0.1364
    Fe  KA      0.30      0.28      0.07     0.0034
    Ni  KA     74.46     64.32      0.65     0.7275

    TOTAL     100.00

 ITERATIONS      6

 *NOTE: ATOMIC PERCENT is normalized to 100

 **NOTE: K-RATIO = K-RATIO x R
         where R = reference(standard)/reference(sample)

          NORMALIZATION FACTOR:   1.000
```

8.3.2 Coating 048-10

An overall view of a failed coating (048-10) is shown in Figure 5. A cross-section of the failed coating shown in Figure 18 shows that there are numerous areas of coating delamination. It appears that the cracking affected all the interfaces between the layers. Figure 19 is a higher magnification view of the failed coating where there is only one crack present between the intermediate blended layer and the bond layer. There is a mixed layer of mixed deposits on the surface which was analyzed and the results tabulated in Table 7. A description follows (see Figures 19-21):

Areas 1–6	These areas are shown in Figure 19 with the EDS analysis given in Table 7. The crystalline deposits have varying compositions that include corrosion products from the nickel-based alloys, the added surrogate materials, and the decomposition products from the destruction of the Trimsol.
Areas 7-8	These areas are the ceramic top coat of yttria-stabilized zirconia.
Area 9	This area is the alumina intermediate ceramic top coat.
Area 10	This area is the alumina intermediate ceramic top coat with a small amount of waste elements.
Area 11	This area is yttria-stabilized zirconia with a small amount of NiCrAl.
Area 12	This area is the NiCrAl bond coat with a large amount of elements from the simulated waste stream (S, Cl) present. Silica is an impurity present in the spray powder and could be an artifact from the preparation prespray surface that uses grinding papers.
Area 13	This area shows the bond layer chemistry (NiCrAl) with spray powder impurities (Fe, Si).
Area 15	This is a mixed oxide particle where the constituent elements were oxidized during the spray process.
Area 14, 16	These areas are the NiCrAl bond coat with the iron and silica being impurities in the plasma spray powder. (The nominal chemistry of the prealloyed powder is Ni-balance, C-19%, Al-6%.)

Observations: The multiple top coatings did not inhibit coating failure.

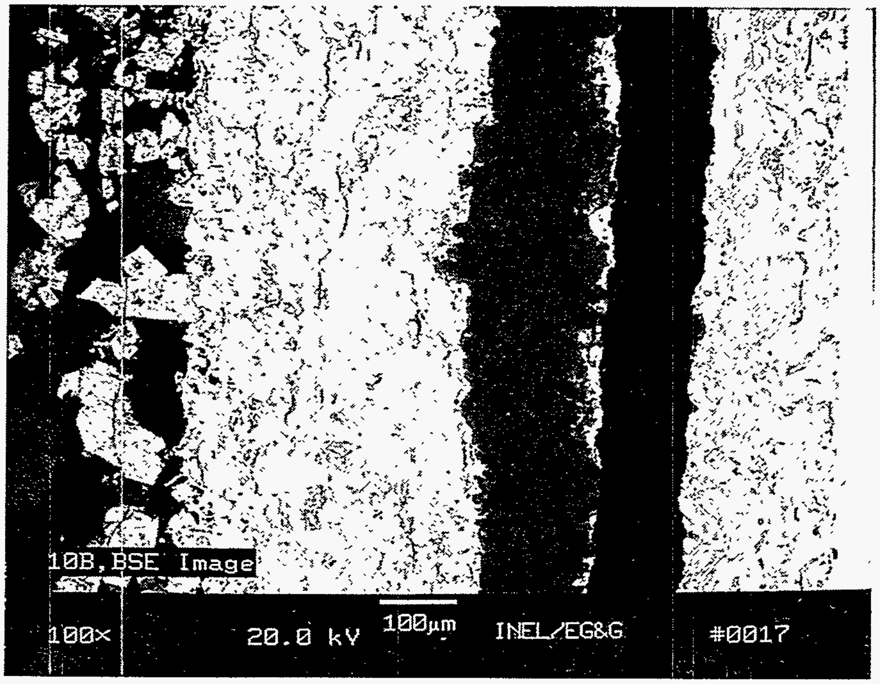


Figure 18. 100× view of 048-10.

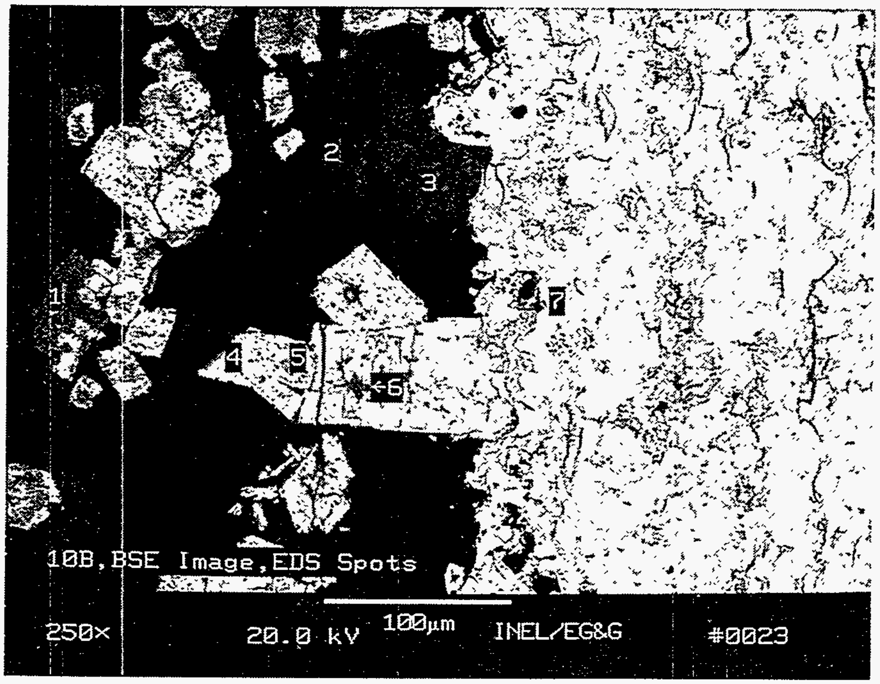


Figure 19. 250× view of 048-10.

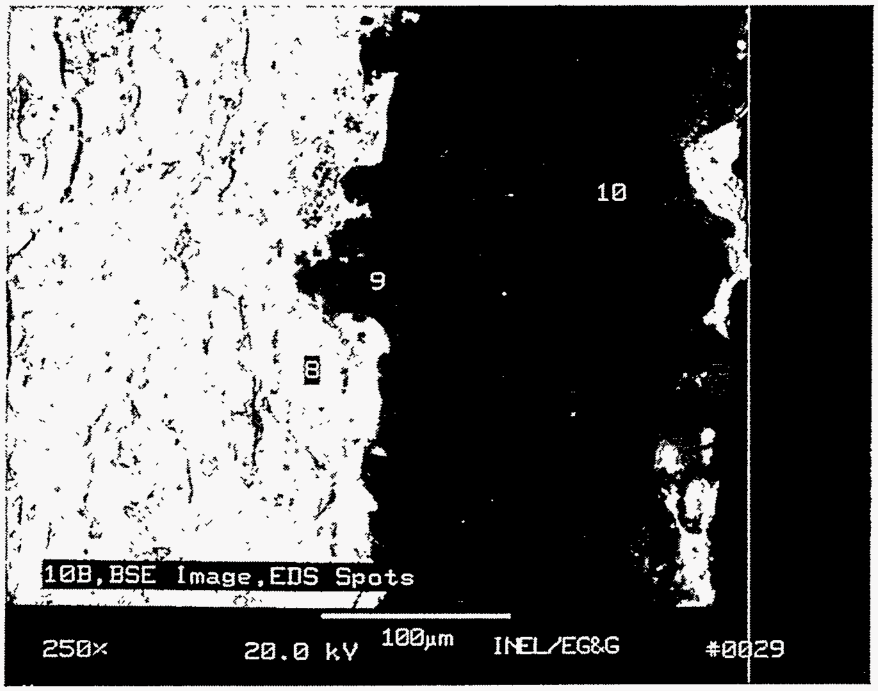


Figure 20. 250× view of 048-10.

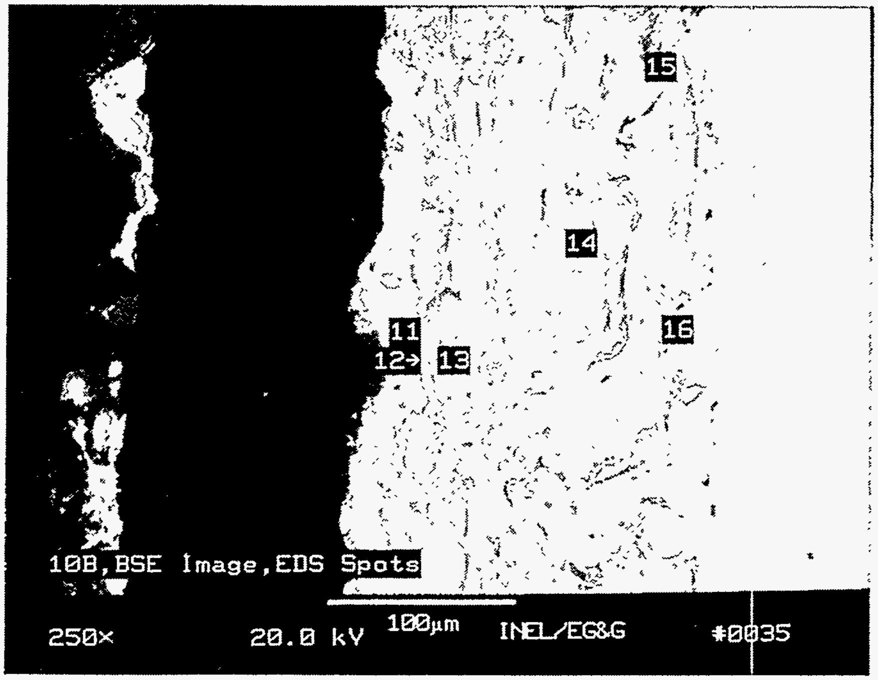


Figure 21. 250× view of 048-10.

Table 7. Results of analysis of 048-10.

```
          10-May-1994 09:25:23        10B-1


    Accelerating voltage               20.0 KeV

    Beam - sample incidence angle     90.0 degrees

    Xray emergence angle              35.0 degrees

    Xray - window incidence angle      0.0 degrees



                         STANDARDLESS EDS ANALYSIS
                       (ZAF CORRECTIONS VIA MAGIC V)



     ELEMENT    WEIGHT     ATOMIC    PRECISION
     & LINE    PERCENT    PERCENT*   2 SIGMA   K-RATIO**

     O   KA     52.29      74.92       1.74     0.2120
     S   KA     20.15      14.41       0.17     0.1575
     Cr  KA      0.27       0.12       0.05     0.0025
     Ni  KA     25.98      10.14       0.32     0.2363
     Zn  KA      1.03       0.36       0.12     0.0086
     Ce  LA      0.28       0.05       0.08     0.0024

     TOTAL     100.00

 ITERATIONS      13

 *NOTE: ATOMIC PERCENT is normalized to 100

 **NOTE: K-RATIO = K-RATIO x R
         where R = reference(standard)/reference(sample)


           NORMALIZATION FACTOR:   1.000
```

Table 7. (continued).

```
        10-May-1994 09:29:40        10B-2


    Accelerating voltage             20.0 KeV

    Beam - sample incidence angle   90.0 degrees

    Xray emergence angle            35.0 degrees

    Xray - window incidence angle    0.0 degrees



                         STANDARDLESS EDS ANALYSIS
                        (ZAF CORRECTIONS VIA MAGIC V)


     ELEMENT    WEIGHT     ATOMIC    PRECISION
     & LINE    PERCENT    PERCENT*   2 SIGMA   K-RATIO**

     O   KA     60.03      73.04       0.91     0.2240
     Na  KA      2.13       1.80       0.11     0.0078
     Al  KA     21.18      15.28       0.18     0.1318
     S   KA     14.46       8.78       0.12     0.1103
     K   KA      2.19       1.09       0.06     0.0179

     TOTAL      99.99

  ITERATIONS     18

  *NOTE: ATOMIC PERCENT is normalized to 100

  **NOTE: K-RATIO = K-RATIO x R
          where R = reference(standard)/reference(sample)


          NORMALIZATION FACTOR:   1.000
```

Table 7. (continued).

```
          10-May-1994 09:33:37        10B-3


    Accelerating voltage                20.0 KeV

    Beam - sample incidence angle      90.0 degrees

    Xray emergence angle               35.0 degrees

    Xray - window incidence angle       0.0 degrees


                        STANDARDLESS EDS ANALYSIS
                      (ZAF CORRECTIONS VIA MAGIC V)


     ELEMENT   WEIGHT    ATOMIC    PRECISION
     & LINE   PERCENT   PERCENT*   2 SIGMA   K-RATIO**

     O   KA    58.25     72.10       1.82     0.2139
     Na  KA     2.05      1.77       0.11     0.0074
     Al  KA    20.13     14.78       0.18     0.1233
     S   KA    15.68      9.68       0.13     0.1199
     K   KA     2.04      1.03       0.06     0.0166
     Cr  KA     0.19      0.07       0.03     0.0017
     Fe  KA     0.24      0.08       0.04     0.0021
     Ni  KA     1.41      0.48       0.08     0.0126

     TOTAL     99.99

   ITERATIONS      17

   *NOTE: ATOMIC PERCENT is normalized to 100

   **NOTE: K-RATIO = K-RATIO x R
           where R = reference(standard)/reference(sample)


           NORMALIZATION FACTOR:    1.000
```

Table 7. (continued).

```
        10-May-1994 09:35:51        10B-4

    Accelerating voltage                 20.0 KeV

    Beam - sample incidence angle       90.0 degrees

    Xray emergence angle                35.0 degrees

    Xray - window incidence angle        0.0 degrees


                     STANDARDLESS EDS ANALYSIS
                   (ZAF CORRECTIONS VIA MAGIC V)


     ELEMENT    WEIGHT     ATOMIC     PRECISION
     & LINE    PERCENT    PERCENT*   2 SIGMA   K-RATIO**

     O   KA     47.18      73.98       0.98     0.1631
     Na  KA      1.75       1.91       0.14     0.0053
     S   KA     20.08      15.71       0.17     0.1540
     K   KA      2.49       1.60       0.08     0.0205
     Ca  KA      3.17       1.99       0.08     0.0280
     Y   LA      2.76       0.78       0.12     0.0197
     Ce  LA     22.57       4.04       0.29     0.1826

     TOTAL     100.00

   ITERATIONS      13

   *NOTE: ATOMIC PERCENT is normalized to 100

   **NOTE: K-RATIO = K-RATIO x R
           where R = reference(standard)/reference(sample)

             NORMALIZATION FACTOR:   1.000
```

Table 7. (continued).

```
        10-May-1994 09:39:03        10B-5

    Accelerating voltage                 20.0 KeV

    Beam - sample incidence angle      90.0 degrees

    Xray emergence angle               35.0 degrees

    Xray - window incidence angle       0.0 degrees


                       STANDARDLESS EDS ANALYSIS
                     (ZAF CORRECTIONS VIA MAGIC V)


     ELEMENT    WEIGHT     ATOMIC    PRECISION
     & LINE    PERCENT    PERCENT*   2 SIGMA   K-RATIO**

     O   KA     40.55      65.06       1.19     0.0959
     Na  KA      2.26       2.52       0.15     0.0074
     S   KA     23.99      19.20       0.20     0.1883
     K   KA      4.11       2.70       0.10     0.0334
     Ca  KA      9.97       6.38       0.14     0.0854
     Ni  KA      0.13       0.06       0.05     0.0011
     Y   LA      5.64       1.63       0.15     0.0433
     Ce  LA     13.37       2.45       0.24     0.1044

     TOTAL     100.02

  ITERATIONS      12

  *NOTE: ATOMIC PERCENT is normalized to 100

  **NOTE: K-RATIO = K-RATIO x R
          where R = reference(standard)/reference(sample)

            NORMALIZATION FACTOR:    1.000
```

Table 7. (continued).

```
        10-May-1994 09:41:10        10B-6

    Accelerating voltage              20.0 KeV

    Beam - sample incidence angle    90.0 degrees

    Xray emergence angle             35.0 degrees

    Xray - window incidence angle     0.0 degrees


                          STANDARDLESS EDS ANALYSIS
                        (ZAF CORRECTIONS VIA MAGIC V)


     ELEMENT   WEIGHT    ATOMIC   PRECISION
     & LINE    PERCENT   PERCENT*  2 SIGMA   K-RATIO**

     O   KA     57.92     75.82     1.20     0.1190
     S   KA     19.98     13.05     0.14     0.1726
     Ca  KA     20.63     10.78     0.15     0.1835
 ?   Sr  LA      1.47      0.35     0.07     0.0115

     TOTAL     100.00

   ITERATIONS      17

   *NOTE: ATOMIC PERCENT is normalized to 100

   **NOTE: K-RATIO = K-RATIO x R
           where R = reference(standard)/reference(sample)

             NORMALIZATION FACTOR:   1.000
```

Table 7. (continued).

```
        10-May-1994 09:44:11        10B-7

    Accelerating voltage               20.0 KeV

    Beam - sample incidence angle     90.0 degrees

    Xray emergence angle              35.0 degrees

    Xray - window incidence angle      0.0 degrees


                    STANDARDLESS EDS ANALYSIS
                  (ZAF CORRECTIONS VIA MAGIC V)


     ELEMENT   WEIGHT    ATOMIC    PRECISION
     & LINE   PERCENT   PERCENT*  2 SIGMA   K-RATIO**

     O  KA     31.09     72.10      1.02     0.0606
     Y  LA      7.71      3.22      0.18     0.0686
     Zr LA     60.16     24.47      0.33     0.5509
     Hf LA      1.04      0.22      0.21     0.0084

     TOTAL    100.00

   ITERATIONS     10

   *NOTE: ATOMIC PERCENT is normalized to 100

   **NOTE: K-RATIO = K-RATIO x R
           where R = reference(standard)/reference(sample)

           NORMALIZATION FACTOR:   1.000
```

Table 7. (continued).

```
        10-May-1994 09:46:16          10B-8


    Accelerating voltage               20.0 KeV

    Beam - sample incidence angle     90.0 degrees

    Xray emergence angle              35.0 degrees

    Xray - window incidence angle      0.0 degrees



                         STANDARDLESS EDS ANALYSIS
                       (ZAF CORRECTIONS VIA MAGIC V)


     ELEMENT   WEIGHT    ATOMIC   PRECISION
     & LINE   PERCENT   PERCENT*  2 SIGMA  K-RATIO**

     O  KA     30.93     71.93     1.03     0.0601
     Y  LA      7.06      2.96     0.18     0.0630
     Zr LA     61.12     24.93     0.34     0.5606
     Hf LA      0.90      0.19     0.19     0.0073

     TOTAL    100.01

  ITERATIONS      10

  *NOTE: ATOMIC PERCENT is normalized to 100

  **NOTE: K-RATIO = K-RATIO x R
          where R = reference(standard)/reference(sample)

           NORMALIZATION FACTOR:   1.000
```

Table 7. (continued).

```
        10-May-1994 09:48:01        10B-9

    Accelerating voltage              20.0 KeV

    Beam - sample incidence angle    90.0 degrees

    Xray emergence angle             35.0 degrees

    Xray - window incidence angle     0.0 degrees


                         STANDARDLESS EDS ANALYSIS
                        (ZAF CORRECTIONS VIA MAGIC V)


     ELEMENT   WEIGHT    ATOMIC   PRECISION
     & LINE   PERCENT   PERCENT*  2 SIGMA  K-RATIO**

     O   KA     50.37     63.12      0.76    0.2150
     Al  KA     49.63     36.88      0.25    0.3494

     TOTAL    100.00

   ITERATIONS     17

   *NOTE: ATOMIC PERCENT is normalized to 100

   **NOTE: K-RATIO = K-RATIO x R
           where R = reference(standard)/reference(sample)

           NORMALIZATION FACTOR:   1.000
```

Table 7. (continued).

```
        10-May-1994 10:02:46        10B-10

    Accelerating voltage                20.0 KeV

    Beam - sample incidence angle      90.0 degrees

    Xray emergence angle               35.0 degrees

    Xray - window incidence angle       0.0 degrees


                        STANDARDLESS EDS ANALYSIS
                      (ZAF CORRECTIONS VIA MAGIC V)


     ELEMENT    WEIGHT     ATOMIC    PRECISION
     & LINE    PERCENT    PERCENT*   2 SIGMA   K-RATIO**

     O   KA     48.12      61.86       1.87     0.1920
     Na  KA      0.45       0.41       0.07     0.0019
     Al  KA     45.24      34.49       0.27     0.3078
     S   KA      3.12       2.00       0.07     0.0208
     K   KA      0.76       0.40       0.04     0.0063
     Cr  KA      0.77       0.31       0.05     0.0068
     Ni  KA      1.53       0.54       0.09     0.0138

     TOTAL      99.99

   ITERATIONS      14

   *NOTE: ATOMIC PERCENT is normalized to 100

   **NOTE: K-RATIO = K-RATIO x R
           where R = reference(standard)/reference(sample)

             NORMALIZATION FACTOR:   1.000
```

Table 7. (continued).

```
          10-May-1994 10:14:31        10B-11


    Accelerating voltage                20.0 KeV

    Beam - sample incidence angle      90.0 degrees

    Xray emergence angle               35.0 degrees

    Xray - window incidence angle       0.0 degrees


                        STANDARDLESS EDS ANALYSIS
                      (ZAF CORRECTIONS VIA MAGIC V)


     ELEMENT   WEIGHT    ATOMIC    PRECISION
     & LINE    PERCENT   PERCENT*  2 SIGMA  K-RATIO**

     O   KA     22.97     61.95      2.48     0.0428
     Al  KA      1.03      1.65      0.07     0.0069
     Cr  KA      0.24      0.20      0.06     0.0022
     Fe  KA      0.24      0.19      0.06     0.0023
     Ni  KA      1.77      1.30      0.12     0.0177
     Y   LA     10.29      5.00      0.13     0.0910
     Zr  LA     62.14     29.39      0.05     0.5665
     Hf  LA      1.32      0.32      0.23     0.0109

     TOTAL     100.00

 ITERATIONS        9

 *NOTE: ATOMIC PERCENT is normalized to 100

 **NOTE: K-RATIO = K-RATIO x R
         where R = reference(standard)/reference(sample)


           NORMALIZATION FACTOR:    1.000
```

Table 7. (continued).

```
        10-May-1994 10:16:46        10B-12


    Accelerating voltage              20.0 KeV

    Beam - sample incidence angle    90.0 degrees

    Xray emergence angle             35.0 degrees

    Xray - window incidence angle     0.0 degrees



                     STANDARDLESS EDS ANALYSIS
                    (ZAF CORRECTIONS VIA MAGIC V)


     ELEMENT   WEIGHT    ATOMIC    PRECISION
     & LINE   PERCENT   PERCENT*  2 SIGMA   K-RATIO**

     O   KA     22.05     44.77      1.21     0.0779
     Al  KA      3.55      4.27      0.13     0.0150
     Si  KA      1.15      1.33      0.07     0.0062
     S   KA      9.14      9.26      0.13     0.0677
     Cl  KA     11.71     10.73      0.14     0.0850
     Cr  KA      9.09      5.68      0.15     0.0865
     Ni  KA     43.30     23.96      0.41     0.4053

     TOTAL      99.99

   ITERATIONS      7

   *NOTE: ATOMIC PERCENT is normalized to 100

   **NOTE: K-RATIO = K-RATIO x R
           where R = reference(standard)/reference(sample)


         NORMALIZATION FACTOR:   1.000
```

Table 7. (continued).

```
          10-May-1994 10:18:25        10B-13

     Accelerating voltage               20.0 KeV

     Beam - sample incidence angle     90.0 degrees

     Xray emergence angle              35.0 degrees

     Xray - window incidence angle      0.0 degrees


                        STANDARDLESS EDS ANALYSIS
                      (ZAF CORRECTIONS VIA MAGIC V)


      ELEMENT    WEIGHT     ATOMIC    PRECISION
      & LINE    PERCENT    PERCENT*   2 SIGMA   K-RATIO**

      Al KA       1.36       2.79       0.12     0.0046
      Si KA       1.63       3.22       0.10     0.0074
      Cr KA      19.61      20.91       0.22     0.2048
      Fe KA       0.41       0.41       0.07     0.0046
      Ni KA      76.98      72.67       0.55     0.7532

      TOTAL      99.99

   ITERATIONS      6

   *NOTE: ATOMIC PERCENT is normalized to 100

   **NOTE: K-RATIO = K-RATIO x R
           where R = reference(standard)/reference(sample)

           NORMALIZATION FACTOR:   1.000
```

Table 7. (continued).

```
        10-May-1994 10:20:14          10B-14


   Accelerating voltage               20.0 KeV

   Beam - sample incidence angle     90.0 degrees

   Xray emergence angle              35.0 degrees

   Xray - window incidence angle      0.0 degrees



                       STANDARDLESS EDS ANALYSIS
                      (ZAF CORRECTIONS VIA MAGIC V)



    ELEMENT    WEIGHT     ATOMIC    PRECISION
    & LINE    PERCENT    PERCENT*   2 SIGMA   K-RATIO**

    Al  KA      8.33      15.87       0.20     0.0294
    Si  KA      1.87       3.41       0.10     0.0084
    Cr  KA     18.33      18.12       0.21     0.1891
    Fe  KA      0.28       0.26       0.06     0.0031
    Ni  KA     71.20      62.34       0.53     0.6934

    TOTAL     100.01

ITERATIONS       6

*NOTE: ATOMIC PERCENT is normalized to 100

**NOTE: K-RATIO = K-RATIO x R
        where R = reference(standard)/reference(sample)


          NORMALIZATION FACTOR:   1.000
```

Table 7. (continued).

```
          10-May-1994 10:22:18        10B-15

    Accelerating voltage                20.0 KeV

    Beam - sample incidence angle      90.0 degrees

    Xray emergence angle               35.0 degrees

    Xray - window incidence angle       0.0 degrees


                   STANDARDLESS EDS ANALYSIS
                 (ZAF CORRECTIONS VIA MAGIC V)


     ELEMENT    WEIGHT     ATOMIC    PRECISION
     & LINE    PERCENT    PERCENT*   2 SIGMA  K-RATIO**

     O   KA      35.72      60.91       1.19     0.2149
     Al  KA      12.94      13.08       0.19     0.0600
     Cl  KA       0.46       0.36       0.04     0.0036
     Cr  KA      33.45      17.55       0.27     0.3149
     Fe  KA       0.32       0.16       0.06     0.0029
     Ni  KA      17.12       7.95       0.27     0.1556

     TOTAL     100.01

   ITERATIONS       9

   *NOTE: ATOMIC PERCENT is normalized to 100

   **NOTE: K-RATIO = K-RATIO x R
           where R = reference(standard)/reference(sample)


           NORMALIZATION FACTOR:    1.000
```

Table 7. (continued).

```
        10-May-1994 10:26:05        10B-16


    Accelerating voltage              20.0 KeV

    Beam - sample incidence angle    90.0 degrees

    Xray emergence angle             35.0 degrees

    Xray - window incidence angle     0.0 degrees



                      STANDARDLESS EDS ANALYSIS
                    (ZAF CORRECTIONS VIA MAGIC V)


     ELEMENT    WEIGHT    ATOMIC    PRECISION
     & LINE    PERCENT   PERCENT*  2 SIGMA   K-RATIO**

     Al KA       7.02     13.60      0.20     0.0245
     Si KA       1.62      3.01      0.10     0.0073
     Cr KA      18.15     18.23      0.22     0.1879
     Fe KA       0.59      0.55      0.08     0.0064
     Ni KA      72.62     64.61      0.56     0.7081

     TOTAL     100.00

 ITERATIONS      6

 *NOTE: ATOMIC PERCENT is normalized to 100

 **NOTE: K-RATIO = K-RATIO x R
         where R = reference(standard)/reference(sample)


           NORMALIZATION FACTOR:   1.000
```

8.3.3 Coating 083-4

An overall view of a successful coating (083-4) is shown in Figure 10. This coating resisted the simulated waste stream with no apparent coating damage visible under light or scanning electron microscopy. The thermally induced cracks will act as a pathway for the corrosive species to penetrate the coating and the key question is whether the coating will then resist spalling from formation of corrosion products if the corrosive environment reacts with the coating at the bottom of the cracks. The coating was scanned for cracks in the SEM and a typical one (crack 3, Figure 22) was analyzed and the chemistry of the areas tabulated in Table 8. The spectra from these cracked areas was distorted in varying amounts due to the fact that some of the emitted electrons from the analysis areas will be absorbed on the walls of the cracks. The electrons from light elements such as aluminum, sodium and oxygen would be preferentially absorbed compared to the electrons from heavier elements such as nickel or zinc. This would result in the spectra for these elements not being fully developed thereby giving a lower concentration value than is really the case. Note that this coupon is label as 942 T2#4 on the photomicrograph.

Area 1 The EDS spectrum for this area shows a high level of titanium with aluminum and oxygen present. This spot was located in the crack which then would distort the spectrum. The values of aluminum and oxygen were probably higher than the values shown in Table 8.

Area 2 Titanium, aluminum, and oxygen are present here along with chlorine. The spectrum was slightly distorted and the amounts of oxygen and aluminum may be higher. Carbon was also detected but the EDS technique cannot quantify this element very well.

Area 3 This area also shows titanium, aluminum, and oxygen with some distortion of the spectra. The aluminum and oxygen values are probably low.

The following analysis is shown on Figure 23 and in Table 9.

Area 4 The analysis area measures the elements present in the surface deposit found on this coupon. There is a large amount of the radionuclide surrogate cerium present with lead and zinc also detected. The nickel,aluminum, and zirconium present are probably corrosion products from the reaction of the test fluid with other coupons.

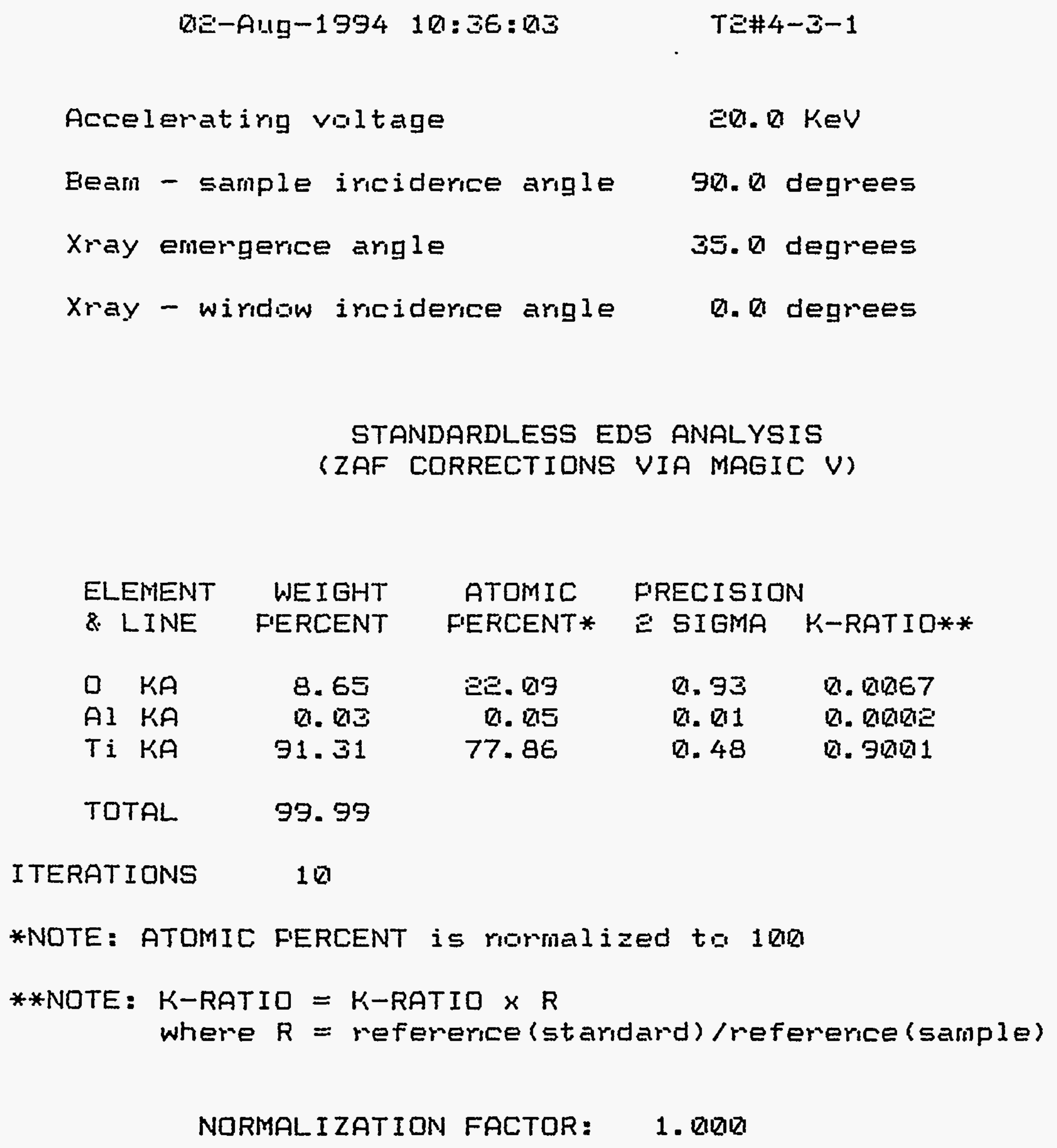
Area 5 The chemical analysis from this area shows titanium and oxygen which form the TiO_2 coating.

Area 6 This area has titanium and aluminum which would be indicative of the Ti-6Al-4V bond layer but no vanadium was detected. A large amount of nitrogen was detected.

Area 7 This area is well into the base metal and shows the expected spectra for titanium. There is also a large amount of nitrogen present.

Figure 22. 1000× view of 083-4.

Table 8. Results of analysis of areas shown in Figure 22.



```
           02-Aug-1994 10:36:03        T2#4-3-1

     Accelerating voltage                20.0 KeV

     Beam - sample incidence angle     90.0 degrees

     Xray emergence angle              35.0 degrees

     Xray - window incidence angle      0.0 degrees


                      STANDARDLESS EDS ANALYSIS
                     (ZAF CORRECTIONS VIA MAGIC V)


      ELEMENT   WEIGHT    ATOMIC   PRECISION
      & LINE   PERCENT   PERCENT*  2 SIGMA  K-RATIO**

      O  KA       8.65     22.09      0.93     0.0067
      Al KA       0.03      0.05      0.01     0.0002
      Ti KA      91.31     77.86      0.48     0.9001

      TOTAL      99.99

   ITERATIONS      10

   *NOTE: ATOMIC PERCENT is normalized to 100

   **NOTE: K-RATIO = K-RATIO x R
           where R = reference(standard)/reference(sample)

            NORMALIZATION FACTOR:   1.000
```

Table 8. (continued).

```
        02-Aug-1994 10:38:50        T2#4-3-2


   Accelerating voltage             20.0 KeV

   Beam - sample incidence angle   90.0 degrees

   Xray emergence angle            35.0 degrees

   Xray - window incidence angle    0.0 degrees


                      STANDARDLESS EDS ANALYSIS
                     (ZAF CORRECTIONS VIA MAGIC V)


    ELEMENT    WEIGHT     ATOMIC    PRECISION
    & LINE    PERCENT    PERCENT*   2 SIGMA   K-RATIO**

    O   KA     24.68      48.50      1.76     0.0241
    Al  KA      2.24       2.61      0.12     0.0122
    Cl  KA      4.04       3.58      0.11     0.0370
    Ti  KA     69.05      45.32      0.49     0.6534

    TOTAL     100.01

 ITERATIONS      10

 *NOTE: ATOMIC PERCENT is normalized to 100

 **NOTE: K-RATIO = K-RATIO x R
         where R = reference(standard)/reference(sample)


          NORMALIZATION FACTOR:   1.000
```

Table 8. (continued).

```
        02-Aug-1994 10:41:02        T2#4-3-3

   Accelerating voltage                20.0 KeV

   Beam - sample incidence angle      90.0 degrees

   Xray emergence angle               35.0 degrees

   Xray - window incidence angle       0.0 degrees


                    STANDARDLESS EDS ANALYSIS
                  (ZAF CORRECTIONS VIA MAGIC V)


    ELEMENT   WEIGHT    ATOMIC   PRECISION
    & LINE   PERCENT   PERCENT*  2 SIGMA  K-RATIO**

    O  KA     22.57     46.25      1.44    0.0208
    Al KA      1.45      1.76      0.07    0.0078
    Ti KA     75.98     51.99      0.43    0.7309

    TOTAL    100.00

 ITERATIONS     11

 *NOTE: ATOMIC PERCENT is normalized to 100

 **NOTE: K-RATIO = K-RATIO x R
         where R = reference(standard)/reference(sample)

            NORMALIZATION FACTOR:   1.000
```

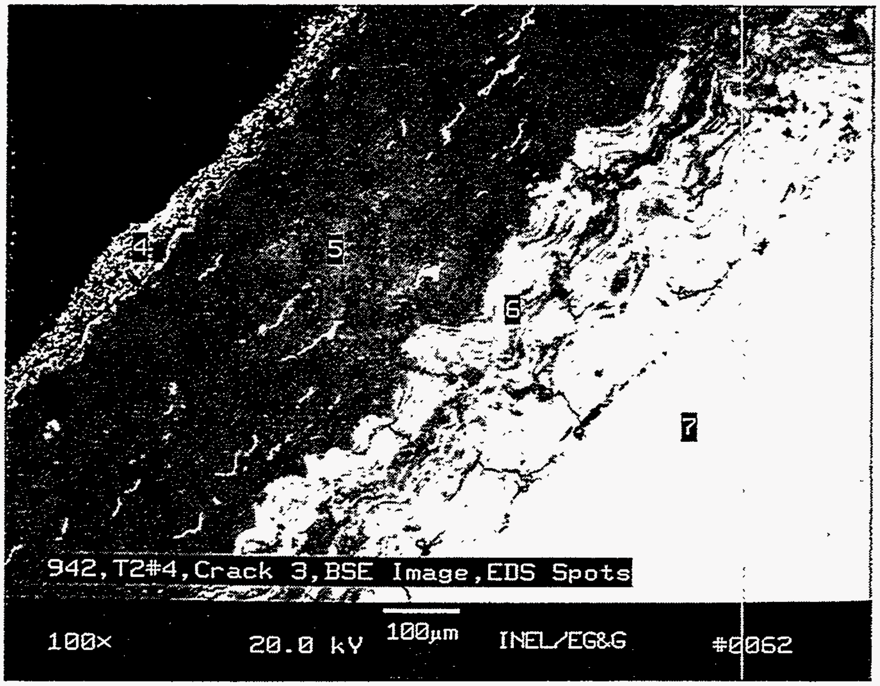
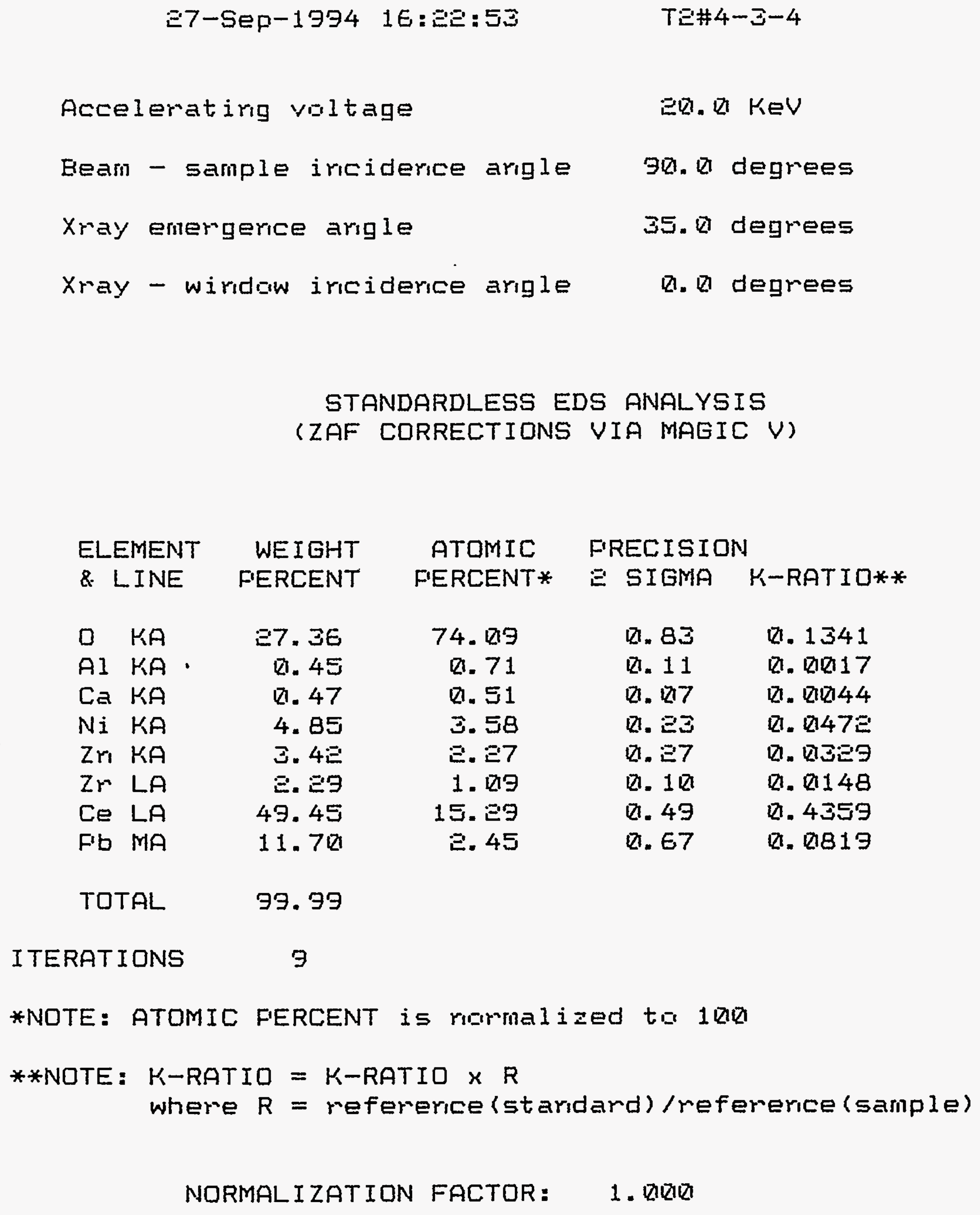


Figure 23. 100× view of 083-4.

Table 9. Results of analysis of areas shown in Figure 23.



```
        27-Sep-1994 16:22:53        T2#4-3-4


   Accelerating voltage               20.0 KeV

   Beam - sample incidence angle     90.0 degrees

   Xray emergence angle              35.0 degrees

   Xray - window incidence angle      0.0 degrees



                       STANDARDLESS EDS ANALYSIS
                     (ZAF CORRECTIONS VIA MAGIC V)


    ELEMENT    WEIGHT     ATOMIC    PRECISION
    & LINE    PERCENT    PERCENT*  2 SIGMA   K-RATIO**

    O   KA     27.36      74.09       0.83     0.1341
    Al  KA      0.45       0.71       0.11     0.0017
    Ca  KA      0.47       0.51       0.07     0.0044
    Ni  KA      4.85       3.58       0.23     0.0472
    Zn  KA      3.42       2.27       0.27     0.0329
    Zr  LA      2.29       1.09       0.10     0.0148
    Ce  LA     49.45      15.29       0.49     0.4359
    Pb  MA     11.70       2.45       0.67     0.0819

    TOTAL      99.99

  ITERATIONS       9

  *NOTE: ATOMIC PERCENT is normalized to 100

  **NOTE: K-RATIO = K-RATIO x R
          where R = reference(standard)/reference(sample)


              NORMALIZATION FACTOR:   1.000
```

Table 9. (continued).

```
        27-Sep-1994 16:25:02        T2#4-3-5

    Accelerating voltage                20.0 KeV

    Beam - sample incidence angle      90.0 degrees

    Xray emergence angle               35.0 degrees

    Xray - window incidence angle       0.0 degrees


                        STANDARDLESS EDS ANALYSIS
                      (ZAF CORRECTIONS VIA MAGIC V)


     ELEMENT    WEIGHT     ATOMIC    PRECISION
     & LINE    PERCENT    PERCENT*  2 SIGMA   K-RATIO**

     O  KA      39.65      66.30      1.95     0.0459
     Ti KA      60.35      33.70      0.32     0.5674

     TOTAL     100.00

  ITERATIONS      10

  *NOTE: ATOMIC PERCENT is normalized to 100

  **NOTE: K-RATIO = K-RATIO x R
          where R = reference(standard)/reference(sample)

              NORMALIZATION FACTOR:    1.000
```

Table 9. (continued).

```
        27-Sep-1994 16:27:27        T2#4-3-6

   Accelerating voltage                20.0 KeV

   Beam - sample incidence angle      90.0 degrees

   Xray emergence angle               35.0 degrees

   Xray - window incidence angle       0.0 degrees


                     STANDARDLESS EDS ANALYSIS
                    (ZAF CORRECTIONS VIA MAGIC V)


    ELEMENT   WEIGHT    ATOMIC   PRECISION
    & LINE   PERCENT   PERCENT*  2 SIGMA   K-RATIO**

    N   KA     21.09     46.66       0.63     0.1319
    O   KA      0.00      0.00       0.00     0.0000
    Al  KA      4.62      5.31       0.10     0.0260
    Ti  KA     73.94     47.83       0.31     0.7091
    Cr  KA      0.34      0.21       0.04     0.0028

    TOTAL      99.99

  ITERATIONS       9

  *NOTE: ATOMIC PERCENT is normalized to 100

  **NOTE: K-RATIO = K-RATIO x R
          where R = reference(standard)/reference(sample)


          NORMALIZATION FACTOR:   1.000
```

Table 9. (continued).

```
        27-Sep-1994 16:29:23        T2#4-3-7

    Accelerating voltage                 20.0 KeV

    Beam - sample incidence angle       90.0 degrees

    Xray emergence angle                35.0 degrees

    Xray - window incidence angle        0.0 degrees


                     STANDARDLESS EDS ANALYSIS
                   (ZAF CORRECTIONS VIA MAGIC V)


     ELEMENT   WEIGHT    ATOMIC   PRECISION
     & LINE   PERCENT   PERCENT*  2 SIGMA  K-RATIO**

     N  KA      7.19     20.94      2.19    0.0484
     Ti KA     92.81     79.06      0.49    0.9170

     TOTAL    100.00

  ITERATIONS      8

  *NOTE: ATOMIC PERCENT is normalized to 100

  **NOTE: K-RATIO = K-RATIO x R
          where R = reference(standard)/reference(sample)

           NORMALIZATION FACTOR:   1.000
```

A second cracked area was analyzed (Figure 24) and the results are shown in Table 10. This crack extends from the cermet layer to the base metal.

Area 1	This area exhibits the approximate chemistry of the Ti-6Al-4V bond coat with an appreciable amount of nitrogen and a small amount of iron present.
Area 2	This chemistry shows evidence of the chemistry of a mixed Ti-6Al-4V/TiO_2 structure with a significant amount of nitrogen present. Iron and a small amount of silicon are also present.
Area 3	This area is basically TiO_2 with aluminum, zinc, lead, and calcium as impurities.
Area 4	This is the Ti-6Al-4V bond coat with a significant nitrogen content.
Area 5	This area is next to Area 4 (bond coat) in the upper reaches of the crack. It looks like the TiO_2 spectrum described earlier with impurities of lead, aluminum, and silicon.
Area 6	This area is farther down the crack near the base metal. It has all elements that would be present in the Ti-6Al-4V/TiO_2 cermet layer with significant impurities such as nitrogen, silicon, zinc, and lead.
Area 7	This area shows a mixed chemistry of the Ti-6Al-4V bond coat and nitrogen.
Area 8, 9	Areas 8 and 9 are on the bond coast base metal interface. It shows a TiO_2 chemistry with the impurities zinc and lead present. The chemistry is not indicative of the bond layer that is Ti-6Al-4V.

Observations: This coating did not delaminate.

Various areas in the coating and the cracks perpendicular to the coating show a large amount of nitrogen pickup.

The heavy metal impurities (zinc, lead) in many cases and the radionuclide surrogate Ce in one case were found in the cracks. These cracks did not propagate and cause coating delamination. These elements were found in the failed areas of the other coatings.

This coating should be tested for a longer time interval to see if the impurities will continue to collect in the cracks and cause failure.

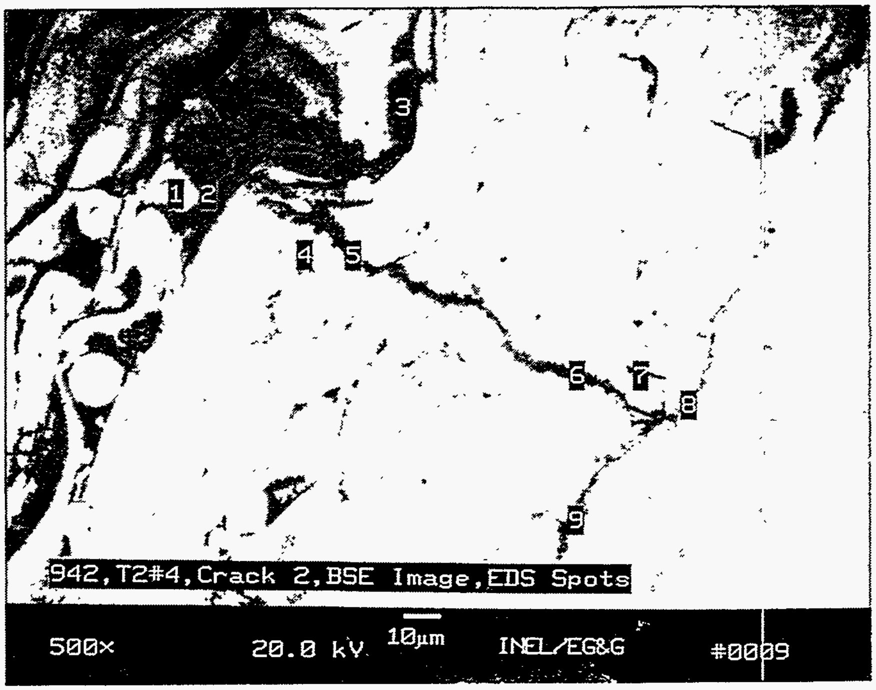


Figure 24. 500x view of 083-4.

Table 10. Results of analysis of areas shown in Figure 24.

```
            02-Aug-1994 10:00:04         T2#4-2-1

      Accelerating voltage               20.0 KeV

      Beam - sample incidence angle     90.0 degrees

      Xray emergence angle              35.0 degrees

      Xray - window incidence angle      0.0 degrees


                         STANDARDLESS EDS ANALYSIS
                       (ZAF CORRECTIONS VIA MAGIC V)


       ELEMENT   WEIGHT    ATOMIC   PRECISION
       & LINE   PERCENT   PERCENT*  2 SIGMA   K-RATIO**

       N  KA      13.63     34.07      1.04     0.0823
       Al KA       5.19      6.74      0.14     0.0289
       Ti KA      78.43     57.34      0.47     0.7604
       V  KA       2.17      1.49      0.20     0.0208
       Fe KA       0.57      0.36      0.08     0.0050

       TOTAL      99.99

    ITERATIONS      8

    *NOTE: ATOMIC PERCENT is normalized to 100

    **NOTE: K-RATIO = K-RATIO x R
            where R = reference(standard)/reference(sample)

               NORMALIZATION FACTOR:   1.000
```

Table 10. (continued).

```
        02-Aug-1994 10:03:50        T2#4-2-2

    Accelerating voltage                20.0 KeV

    Beam - sample incidence angle     90.0 degrees

    Xray emergence angle              35.0 degrees

    Xray - window incidence angle      0.0 degrees


                        STANDARDLESS EDS ANALYSIS
                      (ZAF CORRECTIONS VIA MAGIC V)


     ELEMENT    WEIGHT    ATOMIC    PRECISION
     & LINE    PERCENT   PERCENT*  2 SIGMA   K-RATIO**

     N   KA      8.96     15.89      0.99     0.0604
     O   KA     35.68     55.38      3.56     0.0410
     Al  KA      0.44      0.40      0.06     0.0023
     Si  KA      0.25      0.23      0.05     0.0017
     Ti  KA     51.47     26.68      0.35     0.4804
     V   KA      0.30      0.14      0.13     0.0027
     Fe  KA      2.89      1.29      0.13     0.0249

     TOTAL      99.99

  ITERATIONS     12

  *NOTE: ATOMIC PERCENT is normalized to 100

  **NOTE: K-RATIO = K-RATIO x R
          where R = reference(standard)/reference(sample)

             NORMALIZATION FACTOR:   1.000
```

Table 10. (continued).

```
        02-Aug-1994 10:08:14        T2#4-2-3

   Accelerating voltage              20.0 KeV

   Beam - sample incidence angle    90.0 degrees

   Xray emergence angle             35.0 degrees

   Xray - window incidence angle     0.0 degrees


                         STANDARDLESS EDS ANALYSIS
                       (ZAF CORRECTIONS VIA MAGIC V)


    ELEMENT   WEIGHT    ATOMIC   PRECISION
    & LINE   PERCENT   PERCENT*  2 SIGMA  K-RATIO**

    O  KA     34.75     60.41     1.46    0.0417
    Al KA      5.04      5.19     0.12    0.0269
    Ca KA      0.42      0.29     0.03    0.0047
    Ti KA     57.08     33.15     0.05    0.5328
    Zn KA      2.02      0.86     0.13    0.0179
    Pb MA      0.70      0.09     0.60    0.0059

    TOTAL    100.01

  ITERATIONS      12

  *NOTE: ATOMIC PERCENT is normalized to 100

  **NOTE: K-RATIO = K-RATIO x R
          where R = reference(standard)/reference(sample)

            NORMALIZATION FACTOR:   1.000
```

Table 10. (continued).

```
          02-Aug-1994 10:11:01         T2#4-2-4

     Accelerating voltage              20.0 KeV

     Beam - sample incidence angle    90.0 degrees

     Xray emergence angle             35.0 degrees

     Xray - window incidence angle     0.0 degrees


                          STANDARDLESS EDS ANALYSIS
                        (ZAF CORRECTIONS VIA MAGIC V)


      ELEMENT   WEIGHT    ATOMIC   PRECISION
      & LINE   PERCENT   PERCENT*  2 SIGMA  K-RATIO**

      N   KA    25.59     53.41      0.98    0.1692
      Al  KA     2.67      2.89      0.11    0.0149
      Ti  KA    69.62     42.49      0.44    0.6655
      V   KA     2.11      1.21      0.19    0.0199

      TOTAL     99.99

   ITERATIONS       9

   *NOTE: ATOMIC PERCENT is normalized to 100

   **NOTE: K-RATIO = K-RATIO x R
           where R = reference(standard)/reference(sample)


          NORMALIZATION FACTOR:   1.000
```

Table 10. (continued).

```
          02-Aug-1994 10:13:14        T2#4-2-5

    Accelerating voltage              20.0 KeV

    Beam - sample incidence angle    90.0 degrees

    Xray emergence angle             35.0 degrees

    Xray - window incidence angle     0.0 degrees


                    STANDARDLESS EDS ANALYSIS
                  (ZAF CORRECTIONS VIA MAGIC V)


     ELEMENT   WEIGHT    ATOMIC   PRECISION
     & LINE   PERCENT   PERCENT*  2 SIGMA  K-RATIO**

     O  KA     38.40     64.97       2.35    0.0457
     Al KA      1.33      1.33       0.08    0.0071
     Si KA      0.39      0.37       0.05    0.0026
     Ti KA     58.70     33.17       0.36    0.5487
     Pb MA      1.18      0.15       0.11    0.0102

     TOTAL    100.00

   ITERATIONS     12

   *NOTE: ATOMIC PERCENT is normalized to 100

   **NOTE: K-RATIO = K-RATIO x R
           where R = reference(standard)/reference(sample)

              NORMALIZATION FACTOR:   1.000
```

Table 10. (continued).

```
        02-Aug-1994 10:18:26        T2#4-2-6

     Accelerating voltage              20.0 KeV

     Beam - sample incidence angle    90.0 degrees

     Xray emergence angle             35.0 degrees

     Xray - window incidence angle     0.0 degrees


                     STANDARDLESS EDS ANALYSIS
                   (ZAF CORRECTIONS VIA MAGIC V)


      ELEMENT   WEIGHT    ATOMIC    PRECISION
      & LINE   PERCENT   PERCENT*  2 SIGMA  K-RATIO**

      N  KA      8.22     14.11      0.65    0.0543
      O  KA     39.75     59.73      3.44    0.0481
      Al KA      0.96      0.85      0.08    0.0051
      Si KA      0.42      0.36      0.05    0.0028
      Ti KA     49.03     24.61      0.35    0.4524
      V  KA      0.25      0.12      0.12    0.0023
      Zn KA      0.26      0.10      0.07    0.0023
      Pb MA      1.11      0.13      0.36    0.0095

      TOTAL    100.00

    ITERATIONS      12

    *NOTE: ATOMIC PERCENT is normalized to 100

    **NOTE: K-RATIO = K-RATIO x R
            where R = reference(standard)/reference(sample)

              NORMALIZATION FACTOR:   1.000
```

Table 10. (continued).

```
        02-Aug-1994 10:21:17          T2#4-2-7

   Accelerating voltage                 20.0 KeV

   Beam - sample incidence angle       90.0 degrees

   Xray emergence angle                35.0 degrees

   Xray - window incidence angle        0.0 degrees


                      STANDARDLESS EDS ANALYSIS
                     (ZAF CORRECTIONS VIA MAGIC V)


    ELEMENT    WEIGHT     ATOMIC    PRECISION
    & LINE    PERCENT    PERCENT*   2 SIGMA   K-RATIO**

    N   KA     21.73      48.21       0.94     0.1441
    O   KA      0.00       0.00       0.00     0.0000
    Al  KA      2.13       2.45       0.10     0.0118
    Ti  KA     74.25      48.18       0.44     0.7145
    V   KA      1.89       1.16       0.18     0.0179

    TOTAL     100.00

  ITERATIONS       8

  *NOTE: ATOMIC PERCENT is normalized to 100

  **NOTE: K-RATIO = K-RATIO x R
          where R = reference(standard)/reference(sample)

             NORMALIZATION FACTOR:   1.000
```

Table 10. (continued).

```
      02-Aug-1994 10:24:11          T2#4-2-8

 Accelerating voltage                20.0 KeV

 Beam - sample incidence angle      90.0 degrees

 Xray emergence angle               35.0 degrees

 Xray - window incidence angle       0.0 degrees


                STANDARDLESS EDS ANALYSIS
              (ZAF CORRECTIONS VIA MAGIC V)


  ELEMENT   WEIGHT    ATOMIC   PRECISION
  & LINE   PERCENT   PERCENT*  2 SIGMA  K-RATIO**

  N  KA      4.90      9.23      1.12    0.0326
  O  KA     34.89     57.57      1.95    0.0386
  Al KA      0.90      0.88      0.07    0.0048
  Ti KA     58.22     32.09      0.36    0.5448
  Zn KA      0.32      0.13      0.08    0.0029
  Pb MA      0.76      0.10      0.24    0.0066

  TOTAL     99.99

ITERATIONS    12

*NOTE: ATOMIC PERCENT is normalized to 100

**NOTE: K-RATIO = K-RATIO x R
        where R = reference(standard)/reference(sample)


          NORMALIZATION FACTOR:   1.000
```

Table 10. (continued).

```
      02-Aug-1994 10:27:26        T2#4-2-9

Accelerating voltage                20.0 KeV

Beam - sample incidence angle      90.0 degrees

Xray emergence angle               35.0 degrees

Xray - window incidence angle       0.0 degrees


                 STANDARDLESS EDS ANALYSIS
               (ZAF CORRECTIONS VIA MAGIC V)


 ELEMENT   WEIGHT    ATOMIC   PRECISION
 & LINE   PERCENT   PERCENT*  2 SIGMA  K-RATIO**

 N  KA      3.87      6.78      1.10    0.0260
 O  KA     43.03     65.97      1.92    0.0542
 Al KA      0.86      0.78      0.07    0.0046
 Ti KA     51.40     26.32      0.33    0.4762
 Zn KA      0.14      0.05      0.05    0.0012
 Pb MA      0.70      0.08      0.28    0.0060

 TOTAL    100.00

ITERATIONS      13

*NOTE: ATOMIC PERCENT is normalized to 100

**NOTE: K-RATIO = K-RATIO x R
        where R = reference(standard)/reference(sample)


        NORMALIZATION FACTOR:   1.000
```

9. EFFLUENT ANALYSIS

The effluent analysis of the MODAR corrosion test reveals clues on the behavior of the metals, and chlorides in the system. The complete data analysis is in EDF ID 121217/1032 (Appendix B). The data from the last test run are shown here to make several observations. This test was the 120-hour test.

The feed consisted of the water/metal solution running at 80 cc/min and the TrimSol at 40 cc/min.

The metal solution consisted of 5,400 ppm of $CeCl_3$, 2,200 ppm of $ZnCl_2$, and 2,250 ppm of $PbCl_2$.

The water/metals solution created a total volume of 80 cc/min × (118 hr × 60 min/hr) = 566.4 L.

The TrimSol solution created a total volume of 40 cc/min × (118 hr × 60 min/hr) = 283.2 L.

The chloride content of the feed stream is calculated below:

1. TrimSol (30% $C_{20}H_{37}Cl_5$)
   Carbon 12
   Hydrogen 1
   Chlorine 35.453
   $(C_{20}H_{37}Cl_5) = (12 \times 20) + 37 + (35.453 \times 5) = 454.265$
   Chloride 177.265/454.265 = 0.39
   $0.39 \times .3 = 11.77\%$
   40 cc/min × 118 hr × 60 min/hr = 283,200 mL
   11.77% chloride × 283,200 mL = 33,332.64 g of chlorides

2. $CeCl_3$ $140.12 + (35.453 \times 3) = 246.479$
   Chloride 106.36/246.48 = 0.43
   0.43 × 5,400 ppm = 2,330 ppm
   0.002330 g/mL × 566,400 = 1,319.7 g of chlorides

3. $PbCl_2$ $207.19 + (35.454 \times 2) = 278.1$
   Chloride 70.91/278.1 = 0.255
   0.255 × 2,250 = 573.69 ppm
   0.00057 g/mL × 566,400 = 322.85 g of chlorides

4. $ZnCl_2$ $65.37 + (35.454 \times 2) = 136.278$
   Chloride 70.91/136.278 = 0.52
   0.52 × 2200 ppm = 1144.73 ppm
   0.0011 g/mL × 566,400 = 623.04 g of chlorides

Total Chlorides:
33,332.64 + 1319.7 + 322.85 + 623.04 = 35,598.24 g of chlorides

It is important to note that the metal solution contributed 6.36% of the chloride loading. The metal chlorides are not considered high enough to be of significance.

The total volume of flow into the system was:

TrimSol	283,200 mL
Water/metals	566,400 mL
Purge Lines	1,628,400 mL
Annulus	2,124,000 mL
Total	4,602,000 mL.

The amount of chlorides entering the system was 35,598.24/4,602,000 mL = 0.0077 g/mL = 7,735 ppm of chlorides.

In Section 4 the stream was diluted at 350 cc/min or a total flow of 2,478,000 mL. This lowered the concentration of chlorides to 35,598.24/7,119648 = 5,000 ppm of chlorides.

The liquid effluent had a total flow of 1,250 cc/min × 118 hr × 60 min/hr = 8,850 L.

The lab analysis showed a chloride concentration of 1,800 ppm; 0.0018 × 8,850,000 = 15,930 g of chloride.

The chlorides collected from the various solid samples (see Table 11) was only 0.3792 g 15,930.4/35,598 = 0.4475 or 44.75% mass balance was achieved on the chlorides from the effluent. This does not account for the amount of chlorides recovered from the posttest rinse or that remained settled in the feed tank as part of the surrogates.

Table 11. Solid effluent.

942 Top Rod (70 g)	942 Mid Rod (35 g)	942 Cyclone (16 g)	942 Titanium Liner (568 g)
Sodium 12,000 ppm (0.84 g) Chloride 490 ppm (0.034) Nickel 270 ppm (0.19 g) Cerium 50% (35 g) Lead 3,000 ppm (0.21 g) Zinc 380 ppm (0.027 g)	Sodium 66,000 ppm (2.31 g) Chloride 480 ppm (0.0168 g) Nickel 7,400 ppm (0.26 g) Cerium 36% (12.6 g) Lead 14,000 ppm (0.49 g) Zinc 430 ppm (0.015 g)	Sodium 840 ppm (0.0134 g) Chloride 2,400 ppm (0.038 g) Nickel 27,000 ppm (0.43 g) Cerium 8.4% (1.34 g) Lead 27,000 ppm (0.43 g) Zinc 110,000 ppm (1.76 g)	Sodium 39,000 ppm (22.15 g) Chloride 510 ppm (0.29 g) Nickel 32,000 ppm (18.18 g) Cerium 19% (107.92 g) Lead 24,000 ppm (13.63 g) Zinc 41,000 ppm (23.29 g)

The solids were collected from several locations in the system. (See diagram in Appendix B.) The rod that held the metal coupons became a deposition surface within the casing.

The mass balance for the metals used the following calculations:

1. Cerium calculation
   Cerium 140.12
   Chloride 35.453
   $CeCl_3$ $140.12 + (35.453 \times 3) = 246.479$
   Cerium $140.12/246.479 = 0.5679$
   $0.5679 \times 5,400$ ppm = 3,067 ppm cerium = $(0.003 \times 566,400) = 1,699.2$ g of cerium

2. Zinc calculation
   Zinc 65.37
   Chlorine 35.454
   ZCl_2 $(65.37) + (35.454 \times 2) = 136.28$
   $65.37/136.28 = 0.48$
   $0.48 \times 2,850$ ppm = 1367.1 ppm of zinc = $(0.0014 \times 566,400) = 774.32$ g of zinc

3. Lead calculation
   Lead 207.19
   Chlorine 35.453
   $PbCl_2$ $207.19 + (35.454 \times 2) = 278.1$
   $207.19/278.1 = 0.745$
   $0.745 \times 2,250 = 1676.31$ ppm lead = $(00167 \times 566400) = 945.89$ g of lead

The metals mass balance takes into account the amount of surrogates that settled to the bottom of the tank, and the amount found in the posttest rinses. The feed contained approximately, 1,699 grams of cerium, 774 grams of zinc, and 946 grams of lead.

Lab analysis of the metal feeds indicates that only 4,500 ppm of cerium instead of 5,400 ppm, 1,230 ppm of lead instead of 2,250 ppm, and 1,840 ppm of zinc instead of 2,850 ppm actually went into the system as: feed with the remainder left behind at the bottom of the tank. This results in the total metals in the feed as 1,447 g of cerium instead of 1,699 g, 519 g of lead instead of 946 g and 500 g of zinc instead of 774 g.

The solids effluent from Table 11 gives the following results:

• Cerium	156.86 g
• Zinc	25.09 g
• Lead	14.76 g

The liquid effluent from Table 12 gives the following results:

• Cerium	ND
• Zinc	150.45 g
• Lead	2.56 g

The posttest rinses from Table 13 gives the following results:

• Cerium	450 g
• Zinc	140 g
• Lead	110 g

The total cerium regained was 606.86 g. This is 606.9/1447 = 42%.

The total zinc regained was 315.54 g. This is 315/500 = 63%.

The total lead regained was 127.32 g. This is 127/519 = 24.5%.

The cerium deposits were seen primarily at the top of the rod, then the middle of the rod, and then the titanium liner, with a small amount found in the cyclone and none in the liquid effluent. It would appear that as soon as the surrogates mixed with the oxidant, the cerium begins depositing and probably coated most surfaces inside the casing. The recovery of cerium was 42% with most of that from the posttest rinses. It can be assumed that the remaining cerium is on the ceramic rings. This resistance to rinsing illustrates the importance of controlling deposition on walls versus relying on posttest rinsing to recover deposits. Further investigation is needed of the effect of cerium depositing on the ceramic rings. The SEM analysis shows the cerium showing up on the surface of the ceramic coatings but not being absorbed into the cracks of the coatings. The controlling mechanism for this behavior is not understood.

In the 120-hour run, 1447 g of cerium was fed into the system or approximately 12 g/hr. The amount of cerium that would be captured in the brine of an ongoing system run is not known. A buildup of an actual radionuclide such as plutonium could occur on the scale of several grams per hour. The amount of deposition at the top of the reactor could become an operating constraint.

Deposits of lead were found further downstream than cerium on the titanium liner and in the cyclone. The rinsing process recovered most of the lead while relatively little was found in the top or the middle rod deposits. A brine level in the reactor would most likely increase lead recovery.

The zinc had the highest recovery rate, appearing mostly in the cyclone and rinse processes.

Table 12. Liquid effluent.

Chloride	1,800 ppm
Sulfate	300 ppm
Cerium	ND
Chromium	3.2 ppm
Iron	0.12 ppm
Lead	0.29 ppm
Moly	0.53 ppm
Nickel	5.27 ppm
Potassium	20 ppm
Sodium	2,500 ppm
Zinc	17 ppm

Liquid Effluent:
1,250 cc/min × 118 hours × 60 min/hr = 8,850 liters

Table 13. Posttest rinses.

Vessel/Brine Take Off (17 L)	Rinse #1 (1,517 g)	Rinse #2 (2,988 g)	Rinse Supernatant (215 L)
1 g of cerium	334 g of cerium	63 g of cerium	52 g of cerium
	73 g of lead	36 g of lead	1 g of lead
	15 g of zinc	78 g of zinc	47 g of zinc

10. DISCUSSION

The nickel-based alloys (Hastelloy C-276 and Inconel 625) that have been used in other SCWO test systems do not show adequate corrosion performance in the SCWO environment where TrimSol and surrogates are present as feedstock that results in an oxidizing, chloride containing waste feed. Inconel 686 is the latest corrosion resistant alloy from International Nickel and is advertised as a replacement for Inconel 625 for use in highly oxidizing environments. The results show that Inconel 686 does not offer any improvement over Inconel 625. Hastelloy C-22 is being marketed as a replacement for Hastelloy C-276 for applications such as oxidizing and reducing aqueous media. Hastelloy C-22 was found to offer improved corrosion resistance over Hastelloy C-276 but the corrosion rates would not be acceptable for these conditions. The experimental nickel-based alloys (620 and 621) are based on the Hastelloy C-22 chemistry with increased chromium (25%) with a varying molybdenum content. They have the best corrosion resistance of all the alloys tested but still have rates that will not work for an engineered structure.

Ceramic materials offer attractive corrosion resistant properties but are difficult to fabricate into certain forms. The plasma-sprayed ceramic coating testing was undertaken to see if an overlayed ceramic barrier would provide protection to a metallic substrate and improve its corrosion performance. The coating design was based on the aerospace thermal barrier coating. This coating has been thoroughly characterized for its thermal performance on jet engines due to the formation of fine microcracks throughout the coating.

The coating was applied using the thermal spray process in air. This results in a coating that is less dense than that of a coating sprayed in a vacuum. It will also entrap air during the coating process that will react with the atomized powders to form oxides.

The results from the visual examinations and the light and electron microscopy provide answers to the following question: Does the increased cost and complexity of the coated barrier system offer a measurable increase of corrosion resistance of the liner/reactor system as compared to the best uncoated system? The data indicate that multilayered ceramics can provide protection to substrates that would increase the life of the structural wall. The coating substrate systems did react differently to the combination of a high temperature, high pressure system with a corrosive feedstream.

The results indicate that thermal expansion properties of the coatings were sufficient to withstand the temperature cycles. A ring from each coating was thermally cycled before testing. These rings from the different coating systems were thermally cycled in air from room temperature to over 650°C in less than 5 minute cycles, up to 10 times with no coating cracking or delamination. The coatings did show cracks perpendicular to the surface but this is considered normal because these cracks relieve the thermal stresses during the thermal cyclings. The effect of these cracks on the overall corrosion performance of the ceramic coating system was then evaluated along with corrosion resistance of the coatings. Previous industrial experience has shown the coating systems that were most suited for thermal expansion were the zirconias applied over the nickel/chrome/aluminum bond layer. The results show that these rings suffered from the greatest amount of delamination.

The perpendicular coating cracks will allow the test solution to enter into the coating. When the test was planned the requirements for the top layer of the coating were stated in terms of density. The permeability and density of the coating was thought to be the key to the corrosion resistance of any coating. But the density of the top coating affects the ability of the layer to contract or expand. All ceramic coating system will have perpendicular cracks through the coatings. These cracks open at room temperature and close at higher temperature due to thermal expansion. The cracks would have a different size under the higher temperatures of the test but would not necessarily be completely closed. The cracks are seen in the EDT micrographs. It would appear that the coating delamination observed after the corrosion test was caused by these cracks in the ceramic coatings, allowing the test solution to penetrate through the coating and react with the various layers and the base metal substrate. The nickel/chrome/aluminum layers and the Inconel 625 base metal were the most susceptible to attack.

As the corrosion products formed within the ceramic layers, the volume increase caused an interlayer separation to open and propagate between the ceramic layers, leading ultimately to delamination.

The most important failure mechanism is the reaction of the coating or base metal with the test solution. Based on observation of the data, the mechanisms of thermal expansion or shock are secondary to the generation of corrosion products as the design constraint. The observations used for this conclusion were the behavior of the zirconia coatings. Coating A showed complete delamination in Section 5 and only blistering in Section 1 after 60 hours and five thermal cycles. If thermal expansion was the controlling mechanism, the delamination would have been expected in the ring that was in the higher temperature section.

EDF micrographic analysis showed corrosion products down to the bond coat. The difference between Coatings A and B was the addition of the alumina interlayer. Delamination occurred in Coating B both Section 1 and Section 5 after 60 hours. Figure 18 shows the delamination between the bond coat and the alumina interlayer. Corrosion products were found on the bond coat. There is no crack in the sample to analyze so it is not clear whether the corrosion products could have deposited after the delamination occurred. What can be seen is that some of the bond coat remained with the alumina after the delamination. This is more in keeping with the concept of a volume increase, causing a fissure between the layers. If the coatings had delaminated from thermal expansion all of the bond coat should have remained intact.

In the samples that had an Inconel 625 base substrate or a nickel/chrome/aluminum layer, the metal was attacked with the corresponding generation of corrosion products. This is not surprising based on the poor performance of the bare Inconel 625 samples in this test. An example of this is shown in the comparison of Ring 060-5 (Coating C on Inconel 625) with Ring 083-5 (Coating F on Gr-12 titanium); Ring 060-5 failed while Ring 083-5 did well in the same location. Of the eight rings that had Coating C, only one ring had sufficient coating integrity after 120 hours. This was Ring 049-13 that was located in the least corrosive zone. Of the five rings that had Coating F on a titanium ring, all five of them had an intact top coat after 120 hours. It is felt that the good performance of the F coating was due to the fact that it contains no nickel/ chrome/aluminum layer or Inconel 625 base substrate. In the titania/titanium systems the corrosive species are still present within the cracks but do not attack the titanium. The titania sections have been analyzed for the existence of pitting at the bottom of any cracks but none have been found. See the following diagrams for the ceramic rings (Figures 25-29). This has great significance for the protection of titanium substrates. It is not known how much longer the titania coating will protect the titanium but these data indicate there is a potential for greatly increasing the life of the structure.

Whatever reactor is used to treat mixed waste will become radioactive. Any steps that lengthen the time between changing out components will improve the operating costs of the plant and the volume of waste produced.

It appears that the titania/alumina/vanadium coating system is not as susceptible to corrosion degradation as the nickel/chrome/aluminum coating system. For this reason the titania/titanium coating system is considered superior to the nickel-based system for the SCWO environment. Salt deposition on the any of the ceramics appears not to damage the ceramic, but this needs to be further investigated. The salt may increase the stress on the coating surface that may be removing thin layers of the coating. On some of the zirconia microsections, the salt appeared to be pulling away thin top layers of zirconia. This microspalling may be a mechanism that could degrade the titania. This coating should be subjected to the test environment for longer periods of time to assess any time dependent corrosion degradation.

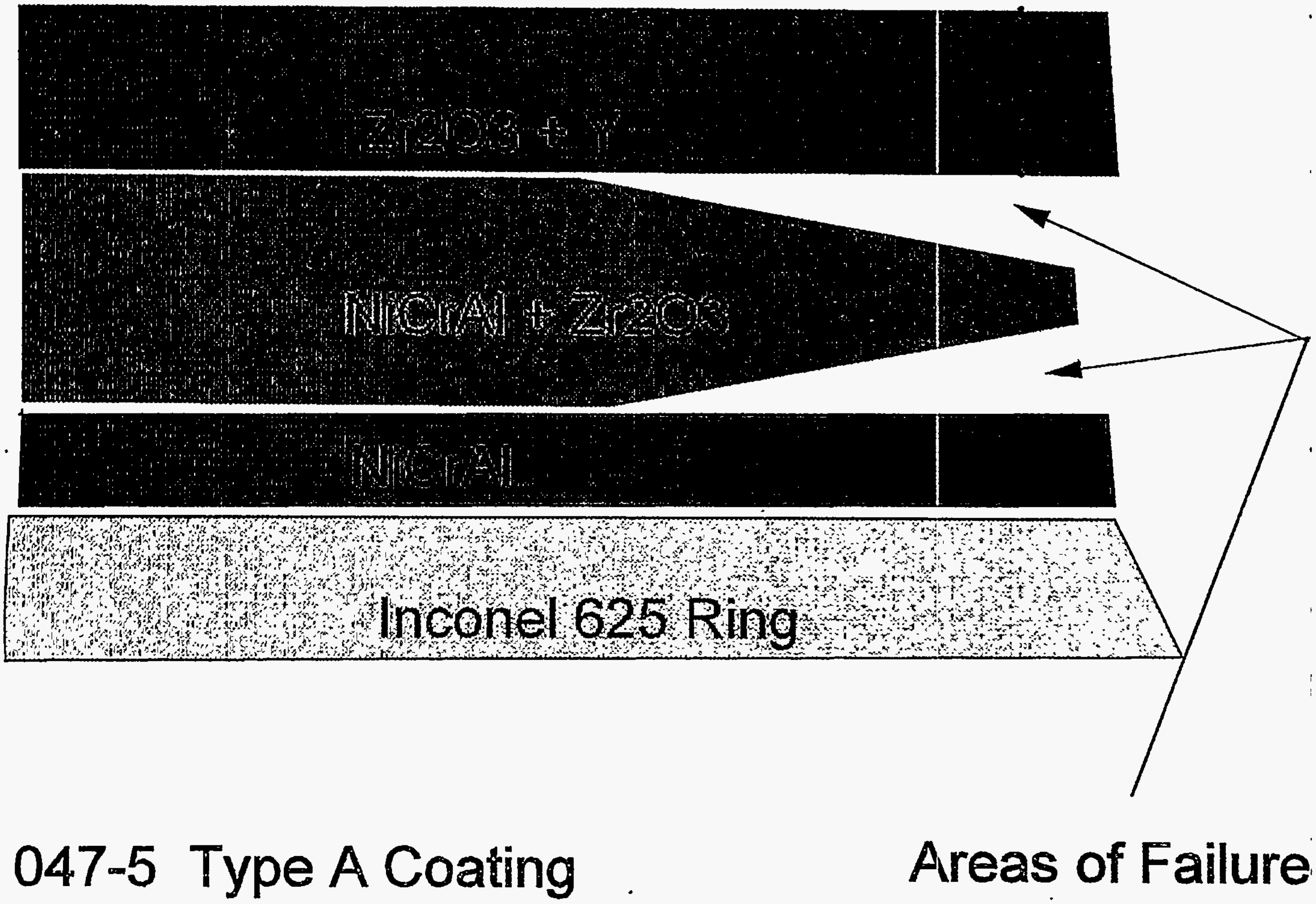
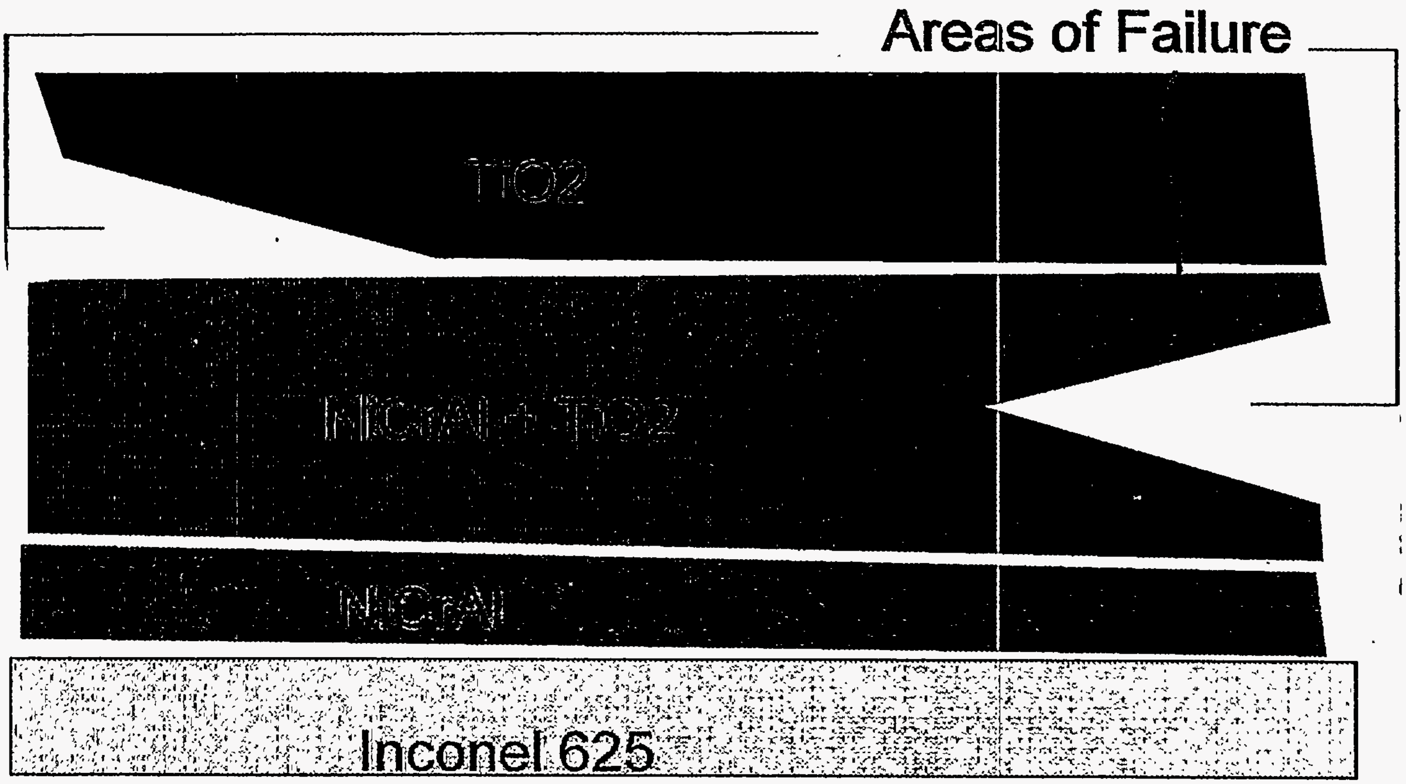


Figure 25. Mechanisms of failure for Ring 047-5, Coating A.



049-16 Type C Ring

Figure 26. Mechanisms of failure for Ring 073-7, Coating C.

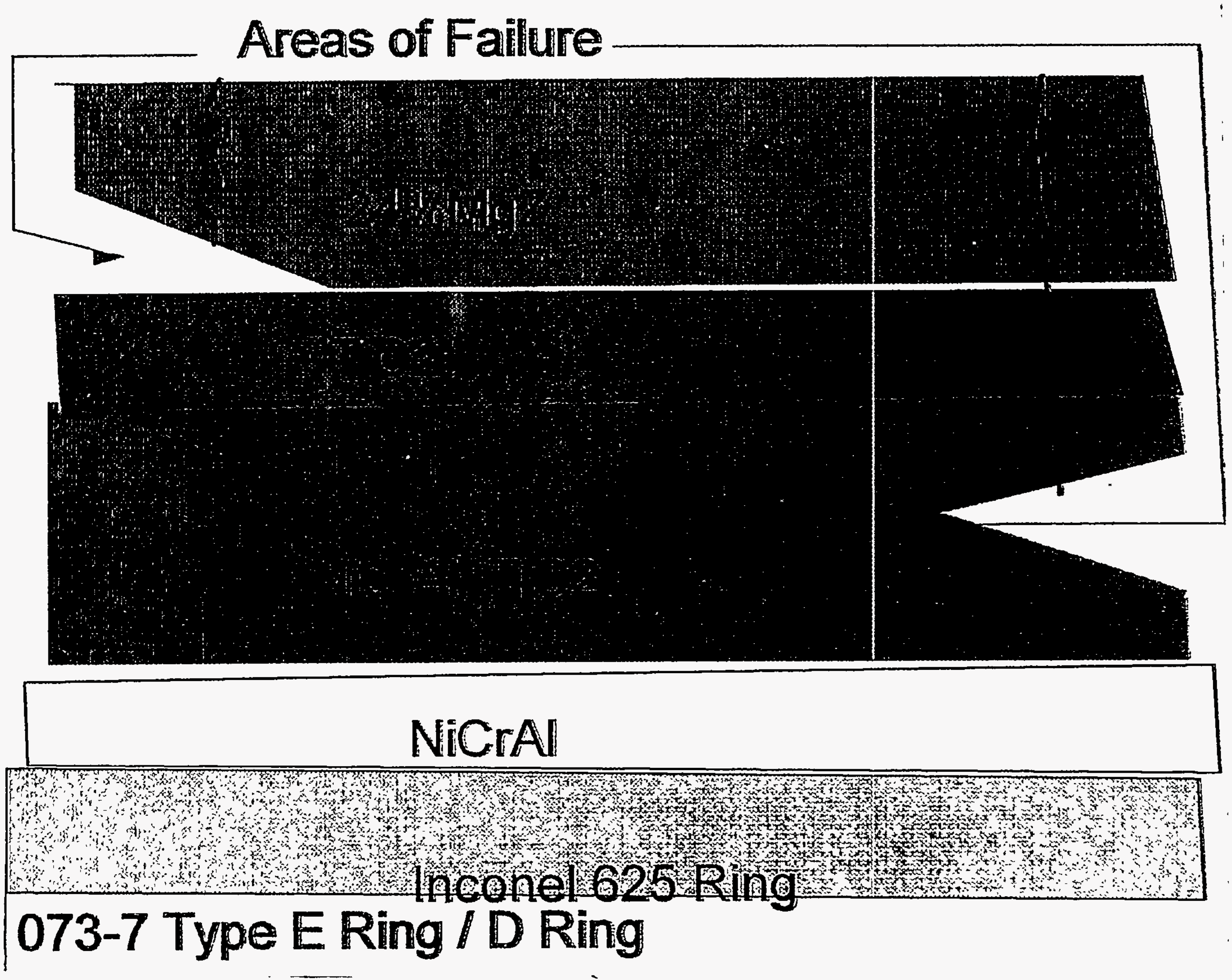


Figure 27. Mechanism of failure for Ring 073-7, Coating E.

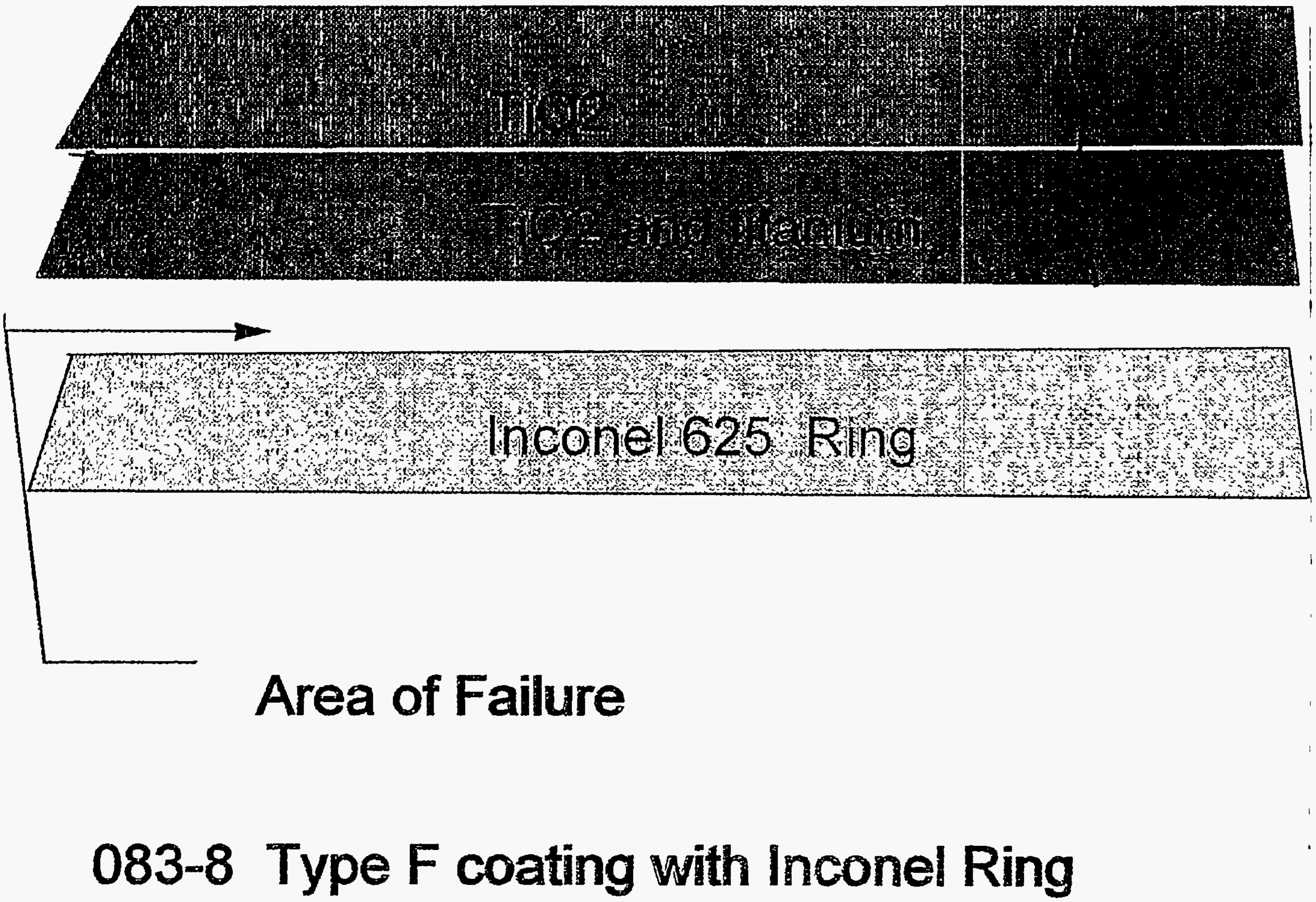


Figure 28. Mechanism of failure for Ring 083-8, Coating F, with Inconel ring.

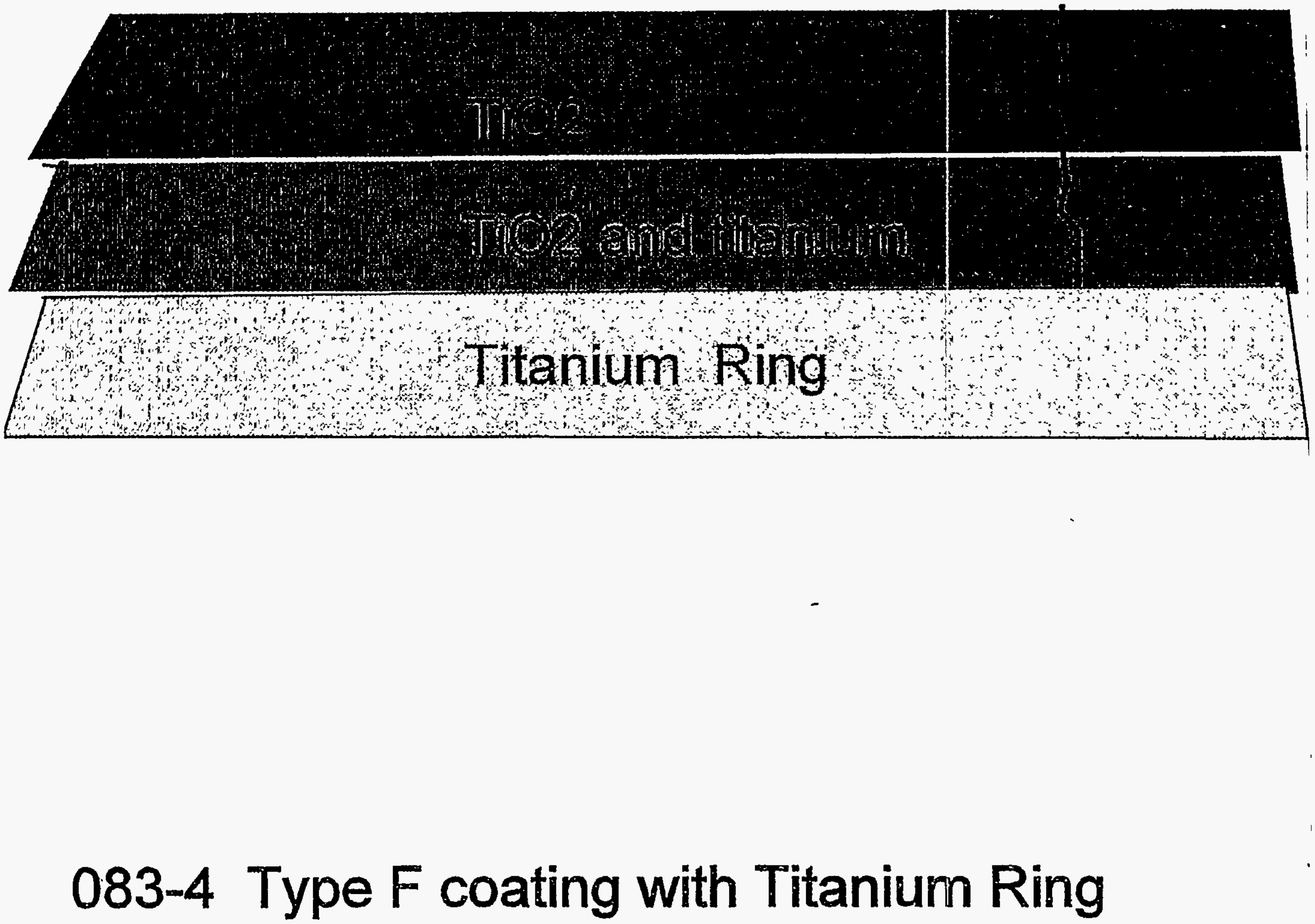


Figure 29. Mechanism of failure for Ring 083-4, Coating F, with titanium ring.

11. CONCLUSIONS

This corrosion test was useful in increasing our understanding of how multilayered ceramics and nickel-based alloys would behave in an SCWO environment. The SCWO environment provides the opportunity for the interaction between the acids, salts, metals, oxygen, and the surface. The mechanisms are not thoroughly understood, only the end net effect can be seen in visual examination, weight loss analysis, and the microscopy. The goal of this testing was to find a system that would increase the life of the structural wall. The following statements can be made from these data:

- The nickel-based alloys (Inconel 625, Hastelloy C-276) commonly used in SCWO environments are severely degraded in the TrimSol containing waste stream.
- The Inconel 686 alloy recommended as a replacement for Inconel 625 in severe corrosion service does not offer any improvement in corrosion resistance in the TrimSol containing waste stream.
- Hastelloy C-22 shows improved corrosion resistance compared to Hastelloy C-276 but the rates would still be too high to be used.
- The experimental nickel showed improved performance over the baseline alloys but still has excessively high rates of corrosion.
- The corrosion rates of the nickel-based alloys decrease with increasing chromium content.
- The coupons in Section 5, the transition zone of the process, were not exposed to the acid environment and, therefore, do not provide any relevant information.
- The plasma-sprayed ceramic coatings show promise as a corrosion control measure.
- The test solution had access to the various coating layers and the metal substrate.
- The nickel-based coating layers and base metal were not resistant to the test solution that caused coating failures.
- The yttria-stabilized zirconia coatings reacted with the coatings forming reaction products that adversely affect coating life.
- None of the multilayered coatings were able to protect the alloy 625 substrate.
- Thermal cycling did not appear to have a dominant effect on the ceramic coatings. The rings withstood the thermal cycling test with no coating delamination.
- The all titania/titanium coating/base metal system was resistant to the test solution. With the initial data produced in this test, the coating system protected the titanium

from the corrosive environment. The titania had very little reaction products within the coating.

- The titania/titanium coating/base metal system will increase the time between the changeout of the reactor. This is important because when treating mixed waste the reactor itself becomes a form of low-level radioactive waste when it is removed from the system.

- There are many parameters that need to be further studied. For example, it is not known if there is a wearing away of the titania on the surface of the coating or if the titania is spalling off locally. The impact of salt and oxide deposition onto the ceramic needs to be understood.

- The radiological and Resource Conservation and Recovery Act (RCRA) implications from the surrogates such as cerium found in the products deposited on the surfaces need to be studied.

12. RECOMMENDATIONS

This corrosion test represents a preliminary effort to identify the direction of material investigations for the SCWO environment.

- Further corrosion testing with the TrimSol solution should be performed to test optimized parameters of coating titania onto titanium metal.

- The program should be repeated with the best performing coatings applied by the vacuum spray process to see if this coating application method is significant. This method should have a higher density with no internal oxides.

- The use of postspray surface thermal treatments (electron beam or laser) should be investigated. These treatments would reduce the residual thermal stresses in the coating.

- Other materials need to be investigated as coating systems such as noble metals.

- Other waste streams (Department of Defense, Department of Energy, and commercial) should be identified for testing with the coated and bare metal samples. Many of these waste streams will not be as aggressive as TrimSol.

- The test results of the nickel alloys indicate that increasing the chromium level decreases the corrosion rate in these solutions. It would be of interest to see if this trend continues as chromium levels increase up to 30%.

- Further investigations are needed into other methods of applying the coating besides the thermal spray method, such as vapor deposition.

- Testing should be extended to welded metal coupons with ceramic coatings.

- It is not known if there is a wearing or wastage of the titania on the surface of the coating or if the titania is spalling off locally. Also, the impact of the salt and oxide deposition onto the ceramic needs to be understood.

- The radiological and RCRA implications of radionuclide deposition must be studied. The location and amount of the surrogate depositions is important to future system design.

Appendix A

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REVISION 10 August 1, 1994

References are listed under the following catagories:

I. SUPERCRITICAL WATER OXIDATION AND REACTIONS IN SUPERCRITICAL WATER
II. SUPERCRITICAL FLUID EXTRACTION
III. MATERIALS & CORROSION
IV. PHYSICAL AND CHEMICAL PROPERTIES
V. DOE MIXED WASTE POLICIES ISSUES OR CHARACTERIZATION
VI. ALTERNATIVE PROCESSES & SCWO COMPARATIVE STUDIES
VII. ENVIRONMENTAL REGULATIONS
VIII. SCWO ITEMS FROM NEWSLETTERS
IX. PRETREATMENT/POSTTREATMENT PROCESSES

Literature is filed in the offices of Ralph Marshall, EROB W2 Room 213, 526-0841 or Charles Barnes, EROB E1 M1, 6-0864. Numbers below refer to the order in which literature is filed. Numbers preceded by "A" refer to abstracts and numbers preceded by "N" to newsletter items.

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Appendix B

Engineering Design File 10121217/1032

Lockheed Idaho Technologies Co
FORM EGG-2631#
(Rev. 01-92)

Project File Number ______
EDF Serial Number ID121217/1032
Funct0ional File Number ______

ENGINEERING DESIGN FILE

Project/Task Supercritical Water Oxidation
Subtask R&D/Corrosion Test

EDF Page 1 of 12

TITLE: Effluent Analysis of MODAR Corrosion Test

SUMMARY

The summary briefly defines the problem or activity to be addressed in the EDF, gives a summary of the activities performed in addressing the problem and states the conclusions, recommendations, or results arrived at from this task.

REVISION 1 OF THIS EDF. REMOVE ORIGINAL VERSION FROM YOUR FILES.

The feed and effluent analysis of the three MODAR tests are used to determine the location and mass balance for the cerium, zinc, and lead surrogates. Conclusions are based on the data from the 120 hour run because the data is more complete for that run.

Distribution (complete package): C.M. Barnes, J.M. Beller, T.R. Charlton, K.M. Garcia, C. Shapiro

Distribution (summary page only): farley Warren MS 3770

Author	Dept.	Reviewed	Date	Approved	Date
K. M. Garcia	4130	C. M. Barnes	1-6-95	J. M. Beller	1/5/95
Karen M Garcia		CM Barnes			

This first run was for 3 hours:
Run 937
Feed:
20 liters of H_20 = 20,000 grams
108 grams of $CeCl_3$, 57 grams of $ZnSO_4$, 45 grams $PbCl_2$
5400 ppm $CeCl_3$, 2850 ppm $ZnSO_4$, 2250 ppm $PbCl_2$ and TrimSol
Water/Metals Solution - 60 cc/min x(3x60 min) = 10.8 liters
1) Cerium calculation
Cerium 140.12
Chloride 35.453
$CeCl_3$ 140.12 + (35.453x3) = 246.479
Cerium 140.12/246.479 = .5679
.5679 x 5400 ppm = 3067 ppm cerium = (.003 x10800) = 33.12 grams of cerium
Lab Analysis: 1800 ppm of cerium in the metals feed
.0018 x 10800 = 19.44 grams of cerium

2) Zinc Calculation
Zinc 65.37
Sulfur 32.064
Oxygen 16
$ZnSO_4$ (4x16) + (32.064) + 65.37 = 161.434
65.37/161.434 = .4049
.4049 x 2850 ppm = 1154 ppm of zinc = (.0011x10800) = 12.46 grams of zinc
Lab Analysis: 830 ppm of zinc
.00083 x 10800 = 8.96 grams of zinc

3) Lead Calculation
Lead 207.19
Chlorine 35.453
$PbCl_2$ 207.19 + (35.454 x2) = 278.1
207.19/278.1 = .745
.745 x 2250 = 1676.31 ppm lead = (00167x10800) = 18.1 grams of lead
Lab Analysis: 33 ppm of lead
3.3×10^{-5} x 10800 = .3564 grams of lead

4) Chlorine Calculation
TrimSol (30% $C_{20}H_{37}Cl_5$)
30 cc/min x (4.6 hrs x 60 min) = 8.28 liters of TrimSol
Carbon 12
Hydrogen 1
Chlorine 35.453
($C_{20}H_{37}Cl_5$) = (12x20) + 37 + (35.453x5) = 454.265
Chlorine 177.265/454.265 = .39
.39 x .3 = 11.77 % (.1177 x 8280) = 968.8 grams of chlorine

$CeCl_3$ 140.12 + (35.453x3) = 246.479
chlorine 106.36/ 246.48 = .43
.43 x 5400 ppm = 2330 ppm = (.00233x 10800) = 25.16 grams of chlorine

$ZnSO_4$ (4x16) + (32.064) + 65.37 = 161.434

$PbCl_2$ 207.19 + (35.454 x2) = 278.1
chlorine 70.91/278.1 = .255
.255 x 2250 = 573.69 ppm (.00057369 x 10800) = 6.2 grams of chlorine

Effluent: 1250 cc/min x (4.6 hrs x 60 min) = 345 liters
Liquid Effluent - Chloride 2600 ppm, Sulfate 170 ppm, Chromium 4.8 ppm, Iron .4ppm, lead .16 ppm, moly 3.4 ppm, nickel 15.8 ppm, potassium 16 ppm, Sodium 2100 ppm, zinc 5.5 ppm
Chloride: (.0026 x 345,000) = 897 grams of chlorine
Zinc ($5.5xE^{-6}$ x 345,000) = 2 grams of zinc
Sodium (.0021 x 345,000) = 724.5 grams of sodium
Lead ($1.6E^{-7}$ x 345,000) = 0.06 grams of lead

Solid : Bottom 1 gram	Solid: Top 2 grams	Solid : 937-11 .063 grams
Sodium 300,000 ppm (.3 grams) Chloride ND Nickel 110,000 ppm (.11 grams) Cerium 3, 700 ppm (.0037 grams) Zinc 8, 200 ppm (.0082 grams) Lead 180 ppm (.00018 grams)	Sodium 9,700 ppm (.0194 grams) Chloride 6,600 ppm (.0132 grams) Nickel 500,000 ppm (1 gram) Cerium 5,800 ppm (.0116 grams) Zinc 4,600 ppm (.0092 grams) Lead 320 ppm (.00064 grams)	Sodium 3500 ppm (.00022 grams) Chloride Unknown Nickel 74000 ppm (.0047 grams) Cerium 300000 ppm (.019 grams) Zinc 5200 ppm (.0003 grams) Lead 1200 ppm (.000076 grams)

Chlorine 897/(969+25+6) = 89.7%

Cerium	.034 grams	.034/19.4 = 0.2 %
Zinc	2.018 grams	2.02/8.96 = 8.3%
Lead	.061 grams	.061/.3564 = 17.1%

Run 937 OBSERVATIONS: A 90% chlorine mass balance is achieved in the liquid effluent. Sodium present in the bottom solids could be from bicarbonate. The cerium does not appear to be coming completely through the reactor while most of the lead remained in the feed tank. The cerium is not soluble but is settling out or depositing on the walls.
Lead Sulfate precipitated from the Run 937 feed mixture leaving an estimated content of the lead in the feed of 30 ppm. This is less than 2 % of the lead added.

This run is for 56.5 hours

Run 938

Feed:
Zinc chloride has been used instead of zinc sulfate to prevent the lead from precipitating out of the feed mixture.
20 liters of $H_2$0 = 20,000 grams
108 grams of $CeCl_3$, 44 grams of $ZnCl_2$, 45 grams $PbCl_2$
5400 ppm $CeCl_3$, 2200 ppm $ZnCl_2$, 2250 ppm $PbCl_2$ and 13 wt% of TrimSol
Water/Metals Solution - 60 cc/min x (56.5 x 60 min) = 203.4 liters
1) Cerium calculation
Cerium 140.12
Chloride 35.453
$CeCl_3$ 140.12 + (35.453x3) = 246.479
Cerium 140.12/246.479 = .5679
.5679 x 5400 ppm = 3067 ppm cerium = (.003067 x203400) = 623.8 grams of cerium

2) Zinc Calculation
Zinc 65.37
Chlorine 35.454
ZCl_2 (65.37) + (35.454 x 2) = 136.28
65.37/136.28 = .48
.48 x 2850 ppm = 1,368 ppm of zinc = (.0014x203400) = 278.25 grams of zinc

3) Lead Calculation
Lead 207.19
Chlorine 35.453
$PbCl_2$ 207.19 + (35.454 x2) = 278.1
207.19/278.1 = .745
.745 x 2250 = 1676.31 ppm lead = (00167x 203400) = 341.0 grams of lead

4) Chloride Calculation (not including surrogates)

30 cc/min x 55.5 hrs x 60 min/hr =99,900 milliliters
11.77% x 99,900 milliliters = 11,688 g of chlorides

Effluent:

938-1 6 grams	938-2 17.8 grams	938-3 4.5 grams
Sodium 2000 ppm (.012 grams) Chloride ND Nickel 48000 ppm (.288 grams) Cerium 98000 ppm (.588 grams) Lead 8200 ppm (.05 grams) Zinc 64000 ppm (.38 grams)	Sodium 54000 ppm (.96 grams) Chloride 3800 ppm (.068 grams) Nickel 74000 ppm (1.317 grams) Cerium 180000 ppm (3.2 grams) Lead 120 ppm (.0021 grams) Zinc 30000 ppm (.53 grams)	Sodium 170000 ppm (.765 grams) Chloride 350 ppm (.0016 grams) Nickel 71000 ppm (.32 grams) Cerium 90000 ppm (.405 grams) Lead 70 ppm (.0003 grams) Zinc 34000 ppm (.15 grams)

Liquid Effluent (1250 cc/min x 56.5 x 60 min) = 4, 237.5 liters
Chloride 2500 ppm, Sulfate 190 ppm, Chromium 2.7 ppm, Iron .3 ppm, lead .4 ppm, moly 2.3 ppm, nickel 3.9 ppm, potassium 53 ppm, sodium 3000 ppm, zinc 9.6 ppm
Chloride : (.0025 x 4237500) = 10,593.75 grams
Zinc: 9.6 E^{-6} x 4237500 = 40.68 + 1.06 = 41.74 grams 41.74/234.7 = 17.8%
Lead 1.695 + .0524 = 1.747 grams 1.747/341.0 = .51%
Cerium 4.193 grams 4.193/623.8 = .67%

Run 939-940

This run is for 59.6 hours

Feed:

Water/Metals Solution - 60 cc/min x (59.6 hrs x 60 min) = 214.56 liters

1) Cerium calculation

Cerium 140.12

Chloride 35.453

$CeCl_3$ 140.12 + (35.453x3) = 246.479

Cerium 140.12/246.479 = .5679

.5679 x 5400 ppm = 3067 ppm cerium = (.003 x214560) = 643.68 grams of cerium

2) Zinc Calculation

Zinc 65.37

Chlorine 35.454

ZCl_2 (65.37) + (35.454 x 2) = 136.28

65.37/136.28 = .48

.48 x 2850 ppm = 1368 ppm of zinc = (.0014x214560) = 293.52 grams of zinc

3) Lead Calculation

Lead 207.19

Chlorine 35.453

$PbCl_2$ 207.19 + (35.454 x2) = 278.1

207.19/278.1 = .745

.745 x 2250 = 1676.31 ppm lead = (00167x 214560) = 358.32 grams of lead

4) Chloride Calculation (not including surrogates)

30 cc/min x 59.6 hr x 60 min/hr = 107280 milliliters

11.77% x 107280 milliliters = 12,552 g of chlorides

Effluent:

940 Hot Zone 20.3 g	940 Quench 23.9 g	940 Cyclone 3.5 g	940 Composite Rinse unknown mass
Sodium 59000 ppm (1.2 grams) Chloride 1900 ppm (.04 grams) Nickel 3000 ppm (.06 grams) Cerium 310,000 ppm (6.29 grams) Lead 18,000 ppm (.37 grams) Zinc 17,000 ppm (.35 grams)	Sodium 76,000 ppm (1.82 grams) Chloride 14,000 ppm (.33 grams) Nickel 39,000 ppm (.93 grams) Cerium 68,000 ppm (1.63 grams) Lead 25,000 ppm (.6 grams) Zinc 19,000 ppm (.45 grams)	Sodium 2,200 ppm (.01 grams) Chloride780 ppm (.002 grams) Nickel 20,000 ppm (.07 grams) Cerium 46,000 ppm (.16 grams) Lead 270,000 ppm (.95 grams) Zinc 12,000 ppm (.042 grams)	Sodium 4,000 ppm Chloride 5200 ppm Nickel 11,000 ppm Cerium 160,000 ppm Lead 10,000 ppm Zinc 6,200 ppm

Run 941-942

This run is for 118 hrs

The feed consisted of the water/metal solution running at 80 cc/min, and the TrimSol at 40 cc/min.

The metal solution consisted of:

5400 ppm of $CeCl_3$, 2200 ppm of $ZnCl_2$, and 2250 ppm of $PbCl_2$.

The water/metals solution created a total volume of:

80 cc/min x (118 hrs x 60 min/hr) = 566.4 liters

The TrimSol solution created a total volume of:

40 cc/min x (118 hr x 60 min/hr) = 283.2 liters

The chloride content of the feed stream is calculated below:

1) TrimSol (30% $C_{20}H_{37}Cl_5$)
Carbon 12
Hydrogen 1
Chlorine 35.453
($C_{20}H_{37}Cl_5$) = (12x20) + 37 + (35.453x5) = 454.265
Chloride 177.265/454.265 = .39
.39 x .3 = 11.77 %
40 cc/min x 118 hr x 60 min/hr = 283200 milliliters
11.77% chloride x 283200 milliliters = 33,332.64 grams of chlorides

2) $CeCl_3$ 140.12 + (35.453 x 3) = 246.479
chloride 106.36/246.48 = .43
.43 x 5400 ppm = 2330 ppm
.002330 grams/ml x 566400 = 1319.7 grams of chlorides

3) $PbCl_2$ 207.19 + (35.454 x2) = 278.1
chloride 70.91/278.1 = .255
.255 x 2250 = 573.69 ppm
.00057 grams/ml x 566400 = 322.85 grams of chlorides

4) $ZnCl_2$ 65.37 + (35.454 x 2) = 136.278
Chloride 70.91/136.278 = .52
.52 x 2200 ppm = 1144.73 ppm
.0011 grams/ml x 566400 = 623.04 grams of chlorides

Total Chlorides:
33,332.64 + 1319.7 + 322.85 + 623.04 = 35,598.24 grams of chlorides

It is important to note that the metal solution contributed 6.36% of the chloride loading. The metals solution did not impact the chloride loading of the system.

The total volume of flow into the system was:

TrimSol	283200 ml
Water/metals	566400 ml
Purge Lines	1,628,400 ml
Annulus	2,124,000 ml

Liquid Effluent:
Chloride 1300 ppm, Sulfate 230 ppm, Chromium 3.9 ppm, Iron .36 ppm, Moly 1.5 ppm, Nickel 7.98 ppm, Potassium 38 ppm, Sodium 2000 ppm, Zinc 17 ppm

1250 cc/min x 59.6 hrs x 60 min/hr = 4,470 liters
Chlorides: 5811 grams
Cerium : 8.08 grams   8.08/643.68 = 1.26%
Zinc: .84 grams   .84/ 236.02 = .36%
Lead 1.92 grams   1.92/ 358.32 = .54%

Composite Rinse: 188 liters
Chloride 170 ppm, Sulfate 2300 ppm, Chromium 1.4 ppm, Iron .38 ppm, Moly 1.5 ppm, Nickel 11.5 ppm, Potassium 140 ppm, Sodium 1400 ppm, Zinc 6.2 ppm

Total	4,602,000 ml

The amount of chlorides entering the system was
35,598.24/4,602,000 ml = .0077 grams/ml = 7,735 ppm of chlorides

In Section 4 the steam was diluted at 350 cc/min or a total flow of 2,478,000 ml. This lowered the concentration of chlorides to:
35,598.24/7,119648 = 5000 ppm of chlorides.

The liquid effluent had a total flow of:
1250 cc/min x 118 hr x 60 min/hr = 8,850 liter
The lab analysis showed a chloride concentration of 1800 ppm
.0018 x 8850000 = 15,930 grams of chloride
The chlorides collected from the various solid samples (see Table 5) was only .3792 grams
15,930.4/ 35,598 = .4475 or 44.75 % mass balance on the chlorides from the effluent. This does not account for the amount of chlorides recovered from the post test rinse or that remained settled in the feed tank as part of the surrogates.
The solids were collected from several locations in the system.(See diagram in Appendix C).
The rod that held the metal coupons became a deposition surface within the casing.
The mass balance for the metals used the following calculations:
1) Cerium calculation
Cerium 140.12
Chloride 35.453
$CeCl_3$ 140.12 + (35.453x3) = 246.479
Cerium 140.12/246.479 = .5679
.5679 x 5400 ppm = <u>3067 ppm cerium = (.003 x 566400) = 1,699.2 grams of cerium</u>

2) Zinc Calculation
Zinc 65.37
Chlorine 35.454
ZCl_2 (65.37) + (35.454 x 2) = 136.28
65.37/136.28 = .48
.48 x 2850 ppm = <u>1367.1 ppm of zinc = (.0014 x 566400) = 774.32 grams of zinc</u>

3) Lead Calculation
Lead 207.19
Chlorine 35.453
$PbCl_2$ 207.19 + (35.454 x2) = 278.1
207.19/278.1 = .745
.745 x 2250 = <u>1676.31 ppm lead = (00167x 566400) = 945.89 grams of lead</u>

The metals mass balance takes into account the amount of surrogates that settled to the bottom of the tank, and the amount found in the post test rinses. The feed contained approximately:
1699 grams of cerium
774 grams of zinc

946 grams of lead

Lab analysis of the metal feeds indicates that only 4500 ppm of cerium instead of 5400, 1230 ppm of lead instead of 2250, and 1840 ppm of zinc instead of 2850, actually went into the system as feed with the remainder left behind at the bottom of the tank. This results in the total metals in the feed as 1447 grams of cerium instead of 1699 grams, 519 grams of lead instead of 946 grams
and 500 grams of zinc instead of 774 grams.

The solids effluent from Table 5 gives the following results:

Cerium	156.86 grams
Zinc	25.09 grams
Lead	14.76 grams

The liquid effluent from Table 6 gives the following results:

Cerium	ND
Zinc	150.45 grams
Lead	2.56 grams

The post test rinses from Table 7 gives the following results:

Cerium	450 grams
Zinc	140 grams
Lead	110 grams

The total cerium regained was 606.86 grams. This is 606.9/1447 = 42%
The total zinc regained was 315.54 grams. This is 315/500 = 63%
The total lead regained was 127.32 grams. This is 127/519 = 24.5%

Observations:

The cerium deposits were seen primarily at the top of the rod, then the middle of the rod and then the titanium liner, with a small amount found in the cyclone, and none in the liquid effluent. It would appear that as soon as the surrogates mix with the oxidant the cerium begins depositing and probably coated most surfaces inside the casing. The recovery of cerium was 42% with most of that from the post test rinses. It can be assumed that the remaining cerium is on the ceramic rings. This resistance to rinsing illustrates the importance of controlling deposition on walls versus relying on post test rinsing to recover deposits. Further investigation is needed of the affect of cerium depositing on the ceramic rings. The SEM analysis shows the cerium showing up on the surface of the ceramic coatings but not being absorbed into the cracks of the coatings. The controlling mechanism for this behavior is not understood.

In the 120 hour run, there were 1447 grams of cerium fed into the system or approximately 12 grams/hour. The amount of cerium that would be captured in the brine of an ongoing system run is not known. A buildup of an actual radionuclide such as plutonium could occur on the scale of several grams/hr. The amount of deposition at the top of the reactor could become an operating constaint.

Deposits of lead were found further downstream than cerium on the titanium liner and in the cyclone. The rinsing process recovered most of the lead while relatively little was found in the top or the middle rod deposits. A brine level in the reactor would most likely increase lead recovery.

The zinc had the highest recovery rate, appearing mostly in the cyclone and rinse processes.

Table 5: Solid Effluent

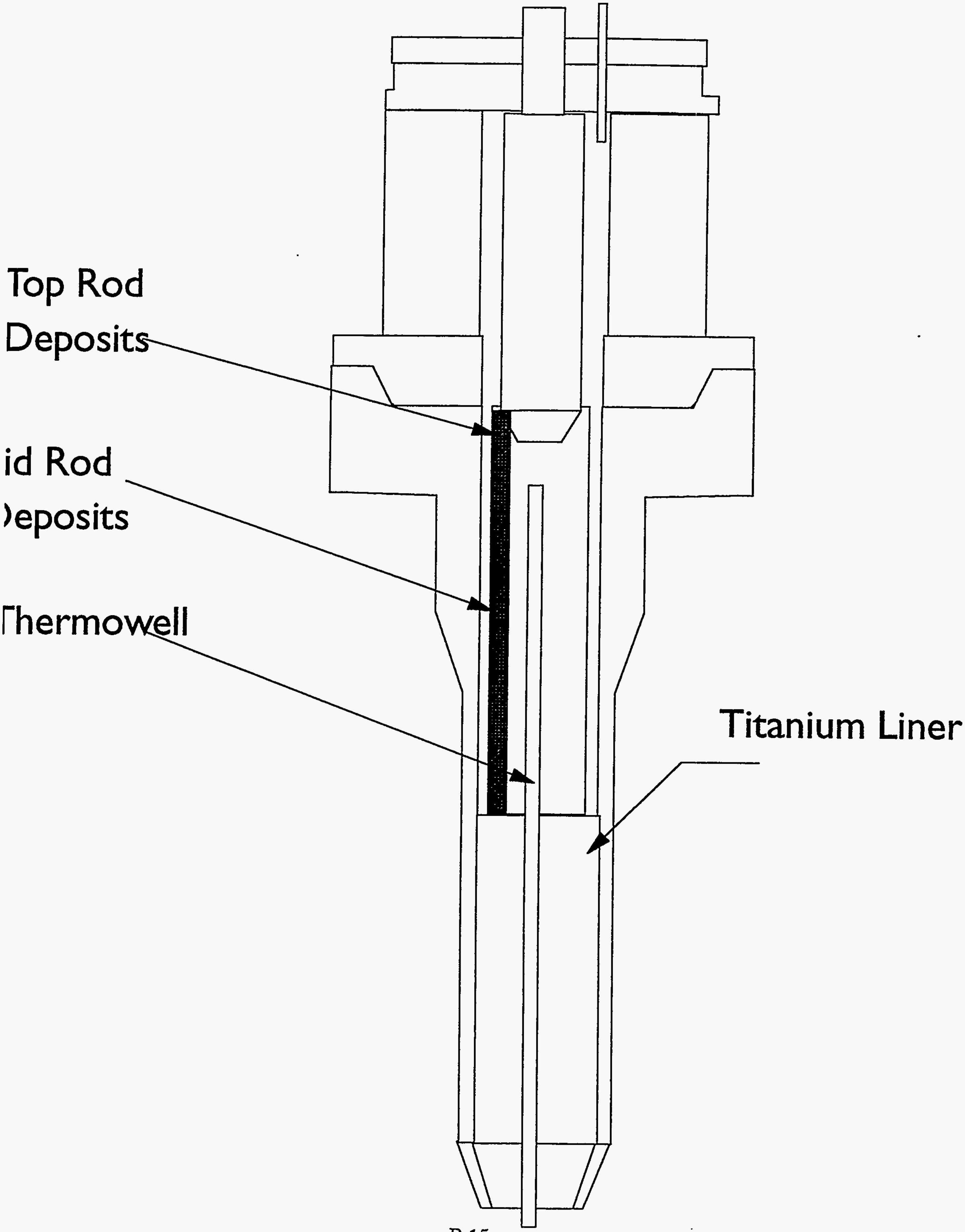
942 Top Rod 70 grams	942 Mid Rod 35 grams	942 Cyclone 16 grams	942 Titanium Liner 568 grams
Sodium 12,000 ppm (.84 grams) Chloride 490 ppm (.034) Nickel 270 ppm (.19 grams) Cerium 50% (35 grams) Lead 3000 ppm (.21 grams) Zinc 380 ppm (.027 grams)	Sodium 66,000 ppm (2.31 grams) Chloride 480 ppm (.0168 grams) Nickel 7400 ppm (.26 grams) Cerium 36% (12.6 grams) Lead 14,000 ppm (.49 grams) Zinc 430 ppm (.015 grams)	Sodium 840 ppm (.0134 grams) Chloride 2400 ppm (.038 grams) Nickel 27000 ppm (.43 grams) Cerium 8.4% (1.34 grams) Lead 27,000 ppm (.43 grams) Zinc 110,000 ppm (1.76 grams)	Sodium 39000 ppm (22.15 grams) Chloride 510 ppm (.29 grams) Nickel 32000 ppm (18.18 grams) Cerium 19% (107.92 grams) Lead 24,000 ppm (13.63 grams) Zinc 41000 ppm (23.29 grams)

Table 6:

Liquid Effluent:	1250 cc/min x 118 hours x 60 min/hr = 8850 liters
Chloride	1800 ppm
Sulfate	300 ppm
Cerium	ND
Chromium	3.2 ppm
Iron	.12 ppm
Lead	.29 ppm
Moly	.53 ppm
Nickel	5.27 ppm
Potassium	20 ppm
Sodium	2500 ppm
Zinc	17 ppm

Table 7: Post Test Rinses

Vessel/Brine Take Off (17 liters)	Rinse #1 (1517 grams)	Rinse #2 (2988 gr)	Supernatant (215 liters)
1 gram of cerium	334 grams of cerium	63 grams of cerium	52 grams of cerium
	73 grams of lead	36 grams of lead	1 gram of lead
	15 grams of zinc	78 grams of zinc	47 grams of zinc


Top Rod
Deposits
id Rod
eposits
Thermowell
Titanium Liner

Attachment 1

INEL Corrosion Test Plan

EGG-WTD-11391

INEL Corrosion Test Plan

G. T. Hong

Published March 1994

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Prepared for EG&G Idaho, Inc.
and for the
U.S. Department of Energy
Assistant Secretary for Environmental Management
Under DOE Idaho Operations Office
Contract DE-AC07-76ID01570

INEL Corrosion Test Plan

EGG-WTD-11391

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ABSTRACT

The process of supercritical water oxidation creates a material challenge in several zones. Ceramics are known to have a high degree of corrosion resistance in many environments. This test will evaluate multilayered ceramics that have been applied by the thermal process. The ceramic will be sprayed to the inside of rings and exposed to the supercritical water oxidation environment.

SUMMARY

The goal of the test is to investigate and identify ceramic coatings for use in supercritical water oxidation (SCWO) environments. The test evaluates three coatings in two different SCWO environments.

The ceramic coatings have been applied to the internal diameter of rings using a thermal spray process. Several different layers are applied to accommodate the thermal expansion of the substrate at operating conditions. The rings will be evaluated in MODAR's SCWO reactor. TrimSol, water, and air will be introduced into the reactor at 3,400 psi and 600°C. The rings will be exposed to 600°C in the top zone of the reactor and 350°C at the bottom of the reactor.

The first test run will be 60 hours with five temperature cycles, the second test run will be for 60 hours with two temperature cycles, and the third test run will be for 120 hours with two temperature cycles. The rings in the center of the reactor could see up to 240 hours of testing. The rings will be visually inspected, then sectioned. Micrographic analysis will be used to define the mechanisms of corrosion and failure of the rings.

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INEL Corrosion Test Plan

1. GENERAL DESCRIPTION

The process of supercritical water oxidation (SCWO) engenders some extremely aggressive environments in the course of treating many wastes of interest. The difficult challenge presented to system materials of construction can sometimes be answered by noble metals such as gold and platinum; however, the high cost of these materials is likely to be prohibitive for most applications. Ceramics are known to have a high degree of corrosion resistance in many environments, are generally modest in cost, and are thus favored candidates for SCWO applications.

The goal of the current project is to investigate and hopefully identify suitable ceramic coatings for use in SCWO environments. The project entails moderate duration testing of three different thermal spray coatings in two different SCWO environments. The chemical composition of these environments is based on TrimSol cutting fluid, and has been described in the Statement of Work (Appendix A). The TrimSol will be diluted to provide a chloride level of at least 5,000 mg/kg on an aqueous basis in the SCWO environments. Neutralization will be carried out only after the process fluid has exited the test zones.

The primary purpose of ceramic coatings in SCWO systems is expected to be the protection of equipment surfaces exposed to the most demanding areas of the process environment. As such, cylinder inside diameters are the most important geometry, and given that the coatings are geometry sensitive, it is this configuration which has been chosen for testing. Furthermore, coating of cylinder inside diameters less than about 4 in. is difficult and would require additional developmental work. For these tests, a cylinder inside diameter of about 7 in. will be used, a size range that is within common practice and very relevant to pilot-scale reactor vessels. The tests will be carried out in MODAR's pilot-scale SCWO system.

2. SYSTEM CONFIGURATION

The system configuration to be used for these tests is shown in Figure 1. One part of TrimSol at about 13 wt% in water is pumped up to system operating pressure of about 3,400 psi and introduced to the reactor through a downward-pointing insulated nozzle. Air and an appropriate amount of water are pumped to pressure, heated to about 600°C with electrical radiant heaters in a "hot box," and introduced to the reactor through an annulus around the cool core feed stream. The two streams mix and reaction commences, achieving a final reaction temperature of about 600°C. Acids and salts form within the reaction zone; some of the salts will adhere to the ceramic coated walls in the reaction zone. The reacted process stream continues in downflow until it enters the cooldown zone, which is maintained by a separate stream of cold water. The process stream continues along its downward path until it reaches the approximate location of the exit tube. At this point, the process stream mixes with cool dilute caustic and is neutralized. The warm mixed stream exits from the vessel and passes through a heat exchanger to be brought to near-ambient temperature. After two stages of insoluble solids removal, pressure is let down to about 1,500 psi and a liquid vapor separation carried out (V-491). The liquid and gas streams drawn off from the separation vessel are reduced to near ambient pressure and then vented, drained, and analyzed online or collected for analysis.

As shown in Figure 1, the reactor vessel possesses horizontal arms. These house either filtration or quenching apparatus for a reversing flow mode of operation, and will not be used in these tests. The axial temperature profile will be monitored by thermocouples located within the central thermowell. Temperature will be monitored at least four axial positions within the internal can.

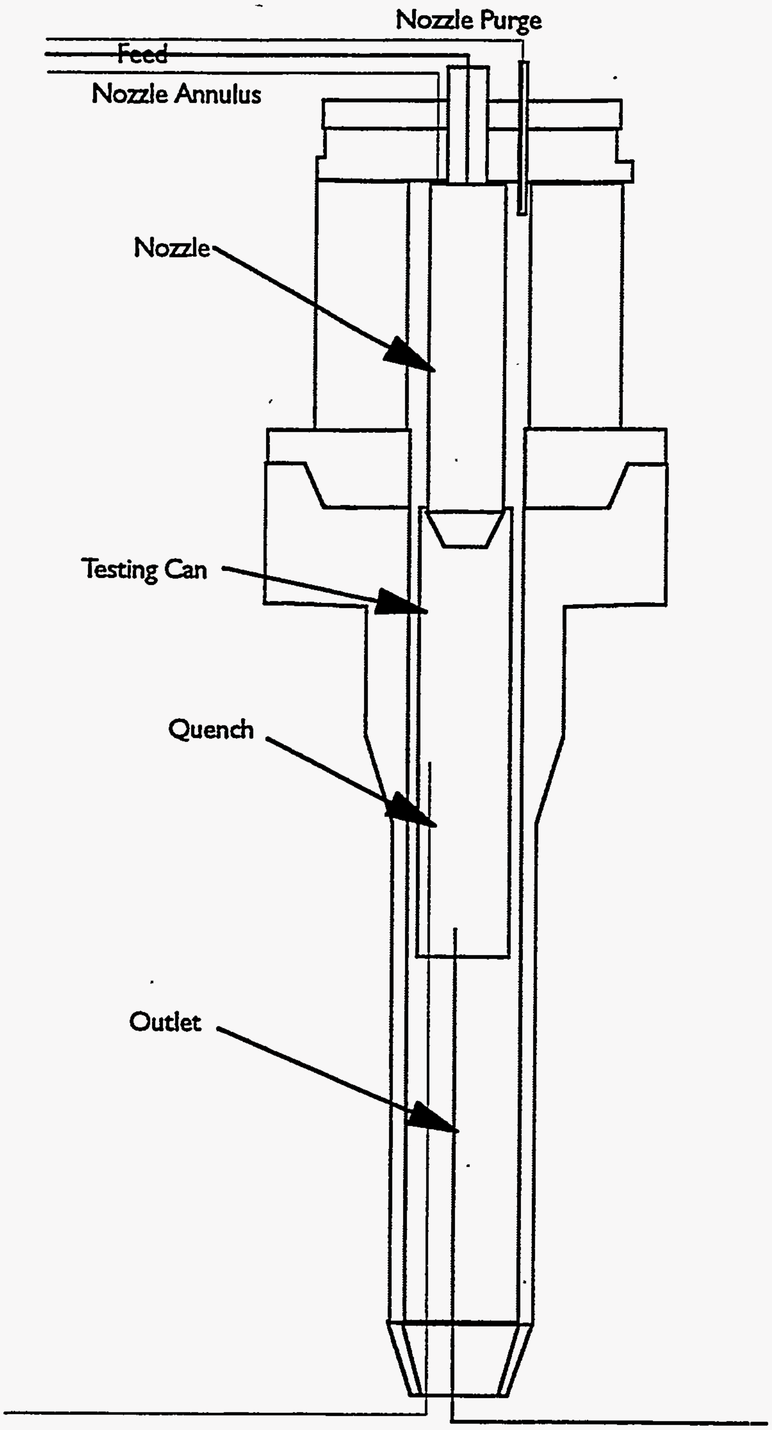

Figure 1. Pilot unit configuration.

3. CORROSION SAMPLE RIG

The detailed setup to be used for the corrosion samples is shown in Figure 2. Fifteen coated rings, 3 in. high and about 7 in. ID after coating, will be stacked and potted with an inert mortar inside a 45-in. high casing. The casing in turn will be mounted within the pilot plant vessel reactor. A cover plate is bolted onto the cylindrical casing and an Alloy 625 rod protrudes down into the stack of rings from its lower surface. A short length of threaded rod is welded onto the main rod at each ring position, allowing the mounting of 1 or 2 metallic corrosion coupons. These coupons will include at least one each of Alloys 625 and C276 in each zone to serve as reference materials, as these alloys have the largest exposure database available from prior studies.

It is believed that the internal can of Figure 2 will provide excellent protection for the reactor vessel walls. A major concern which remains, however, is the survivability of exposed metallic parts, in particular the feed nozzle, the cover plate, the thermowell, and the metallic coupon rack. It is conceivable that these pieces will have to be replaced regularly or, if possible, constructed of more durable materials. As such construction is difficult, it will not be attempted unless early experimental results indicate a need. One possibility is the use of platinum; however, even this metal has questionable survivability under the conditions specified. In their corrosion tests for ARPA, General Atomics found platinum unsuitable for unneutralized mustard agent, a chlorine and sulfur containing organic as is TrimSol. Platinum wires will be included in the test rig of Figure 2 to obtain information in this regard.

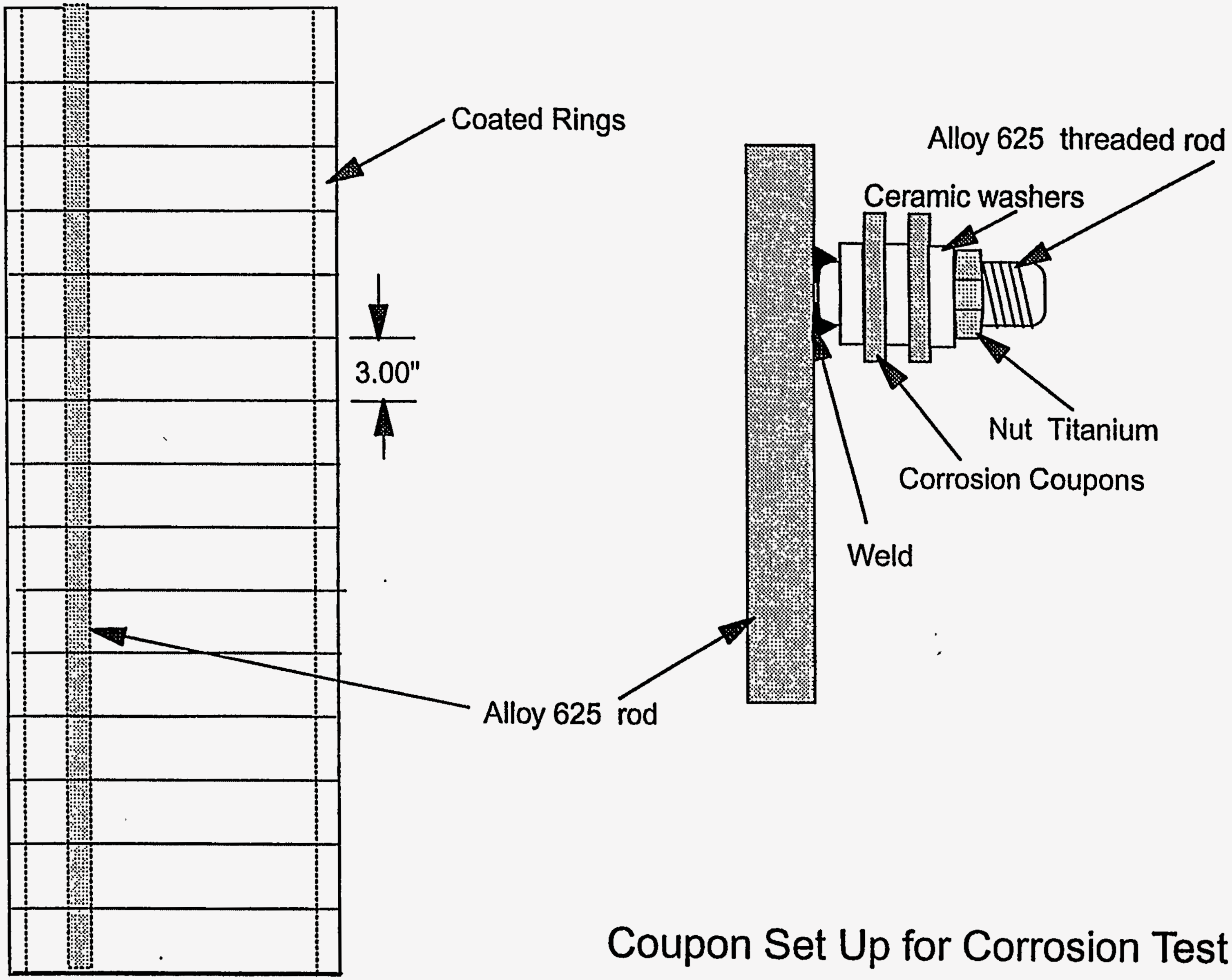

Figure 2. Corrosion sample cartridge.

4. TEST MATRIX AND SCHEDULE

A viable coating must be able to withstand extended periods at operating conditions as well as repetitive thermal cycling. For convenience, samples will be designated as hours/cycles/zone/set (e.g., the first set of samples seeing 60 hours of exposure and five thermal cycles in the reaction zone is designated as 60/5/R/1).

The coatings to be tested are two types of zirconia and one type of titania. The inert mortar is based on calcium sulfate.

The test matrix is comprised of four tests, as follows:

1. Baseline Test

   The down flow mode of operation described in Section 2 has been previously used on the MODAR bench-scale system, but not on the pilot-scale system. The use of an internal "can" with perhaps excellent insulating properties is also a nonstandard arrangement. For these reasons, a baseline test will be required to establish appropriate flow rates for the various streams. The baseline test necessarily involves the full system setup including the corrosion rig, so that the corrosion samples in place will see noncorrosive SCWO exposure time. This time is not counted toward the exposure time with TrimSol feed running. Figure 3a shows the corrosion rings that will be in place for the baseline test as well as the 60-hour test that follows.

2. 60-Hour Test with Thermal Cycles

   Thermal cycling is of importance in materials testing because it involves stresses and environments which are different, and frequently more severe, than those encountered during steady state operation. For example, ceramic coatings may be most susceptible to delamination when subjected to the temperature gradients of a startup procedure. In this test, the 60-hour exposure time will be artificially interrupted five times, and reactor temperatures allowed to drop below 300°C or less. These thermal cycles will not all be evenly spaced because the first run segment will be terminated after about 4 hours to verify that the internal can is indeed protecting the pressure vessel from corrosive attack. Thus, after this first short segment, the reactor head will be removed, the internal can removed, and the equipment visually inspected for corrosion locales. Assuming the equipment is functioning as planned, the reactor will be reassembled and the test continued. Should the equipment not be functioning in the desired fashion, the possibilities for modification will be considered, and implemented if deemed practical. After 60 hours of exposure and five thermal cycles (with the possibility that some of these cycles will comprise full shutdowns with coating and reactor inspections), the reactor will be opened, the internal can removed, and the 60-hour samples removed from the casing. The corresponding metal coupons will also be removed. The rings and coupons will then be replaced with a second set of 60/5 samples. It is unknown how difficult it will be to remove the potted rings from the inert mortar that backs them. In the extreme case, the casing cylinder will have to be cut up. A spare casing cylinder will be kept on hand to avoid schedule delays in this eventuality.

36 rings
11 tests @ 3 rings
1 baseline set

Coupons will be checked after 4 hrs and then thermally cycled for 4 cycles. The first 60 hour rings will be removed and replaced with the second set of 60 hour rings. After 120 hours the second 60 hr rings and the first 120 hour rings will be pulled and replaced with new 120 hour rings.

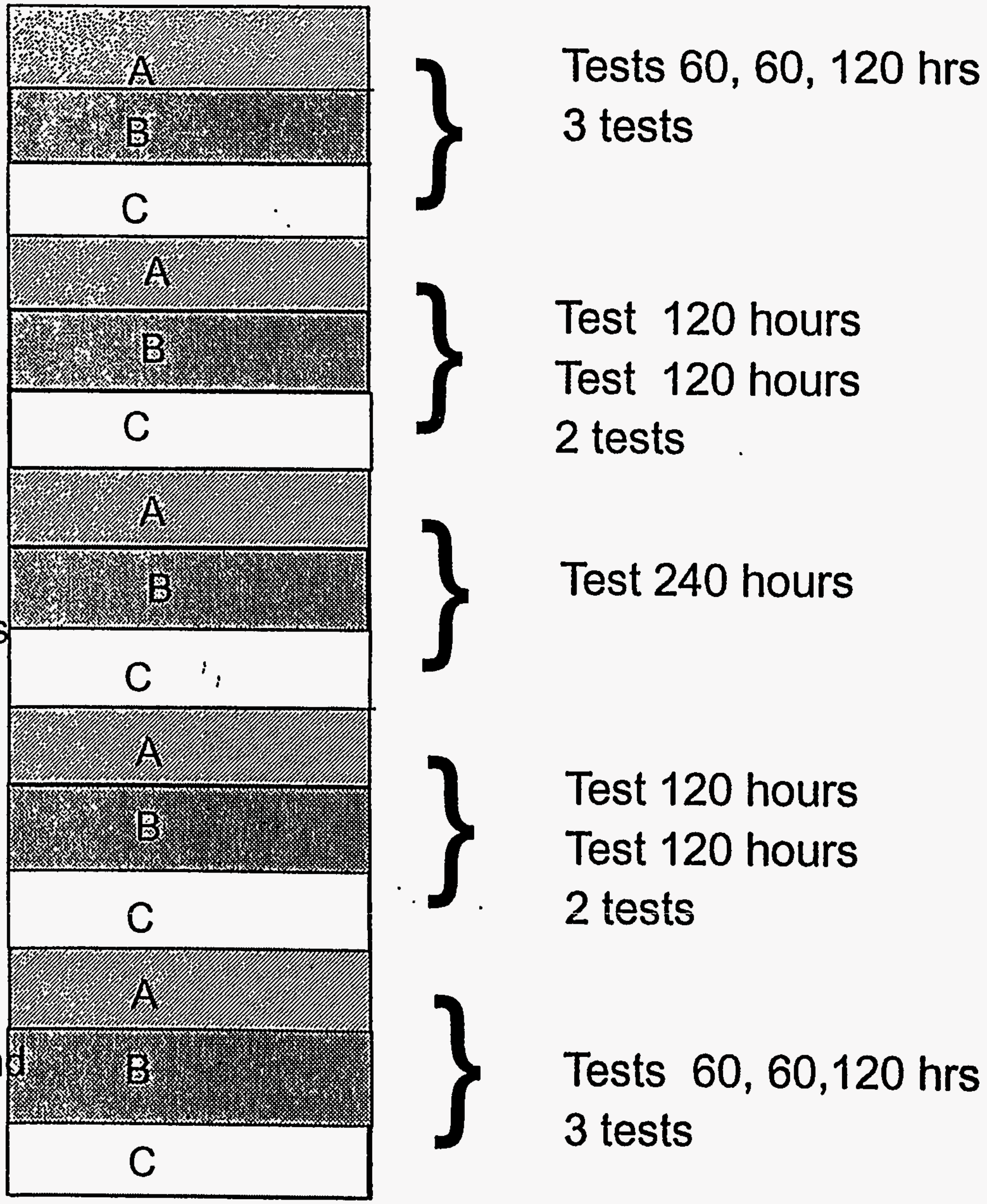

Figure 3. Ring setup for test matrix.

3. 60-Hour Test with Thermal Cycles

Figure 3b shows the test rings as configured for this second 60-hour test. This test should be similar to the first 60-hour test, but with less of a need for full shutdowns because the viability of the setup will no longer be in question. Following this test, the second set of 60/5 samples and the 120/10 set of samples will be removed and replaced with two sets of 120/1 samples.

4. 120-Hour Continuous Test

Figure 3c shows the test rings as configured for this test. The duration of this test is nominal. Should it be found that budgetary limits are being approached, the time may be reduced. Likewise, should the project be proceeding smoothly, an extension of this run will be considered. This test involves only a single thermal cycle.

The test matrix described will require 36 coated rings as follows:

- Twelve 60/5 rings
- Six 120/10 rings
- Twelve 120/1 rings
- Three 240/11 rings
- Three unused reference rings.

The scheme will allow duplicate comparisons to be made between two sets of 60/5 rings tested in different runs and two sets of 120/1 rings tested in the same run. The effect of thermal cycling can also be gauged by comparison of the 120/1 and 120/10 ring sets. It should be noted that the 240-hour exposure time is obtained by having a single set of rings which is in place for all of the tests (60 + 60 + 120), as shown in Figure 3. The number of thermal cycles and exposure times provided for by this scheme are consistent with failure histories of similar ceramics previously tested at MODAR. In these previous tests, coatings have failed at exposure times between 100 and 200 hours.

Analytical procedures for the test project have been described in the proposal Description of Work. The analytical contract has not yet been assigned by EG&G Idaho.

Figure 4 shows the prospective schedule for the test matrix. It should be emphasized that both the test matrix and schedule are success oriented, presuming for example that the samples and system will maintain their integrity for extended periods of time. The number and duration of tests, as well as the schedule and Test Plan, may have to be modified as events dictate.

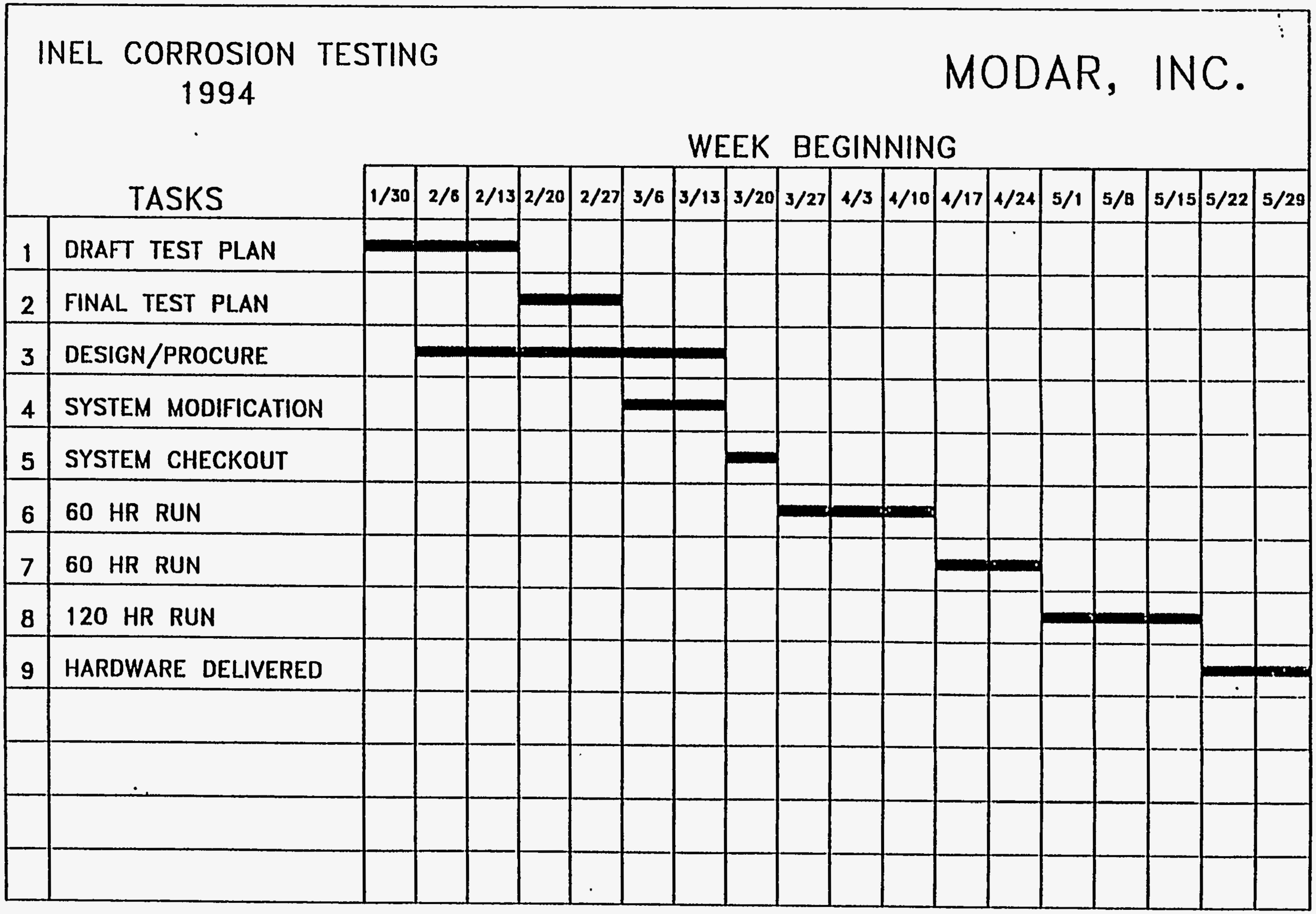

Figure 4. Test schedule.

5. QUALITY PROGRAM

During the execution phase of the project, engineering and technical personnel will continually monitor progress and effectiveness so that any necessary cost saving adjustments can be made to optimize results. Engineering personnel will have the principal responsibility of ensuring the quality of all work performed. Management personnel will provide an appropriate level of independent verification. This verification will rely heavily on performance-based verification methods (as opposed to after-the-fact programmatic audit techniques). This will provide for real-time problem identification and resolution, as well as feedback to the planning process for quality improvement. Deficiencies noted will be reported to and resolved by engineering personnel.

Our approach to quality assurance results from our extensive experience in design, engineering, and construction of SCWO facilities, including three pilot plant configurations and numerous bench-scale projects. It is based on the recognition that quality achievement is the responsibility of those personnel performing work, that quality leads to improved productivity, and that appropriate verification of that quality is an important management tool in preventing and resolving problems, improving work product quality, enhancing performance, and satisfying contractual and regulatory requirements and commitments.

Specific responsibilities for this project are:

• Procurement	Project Technical Director
• Inspection, measuring, and testing equipment	Operations Supervisor
• Document control	Project Technical Director
• Control of SCWO process	Project Engineer
• Control of project nonconformances	Project Manager

As called for in the Scope of Work, our quality assurance and control procedures will be reviewed with and approved by EG&G Idaho in the earliest phase of the contract.

6. PARTS LIST

The following parts are specific to the current project:

- 2 casing cylinders.
- 1 casing cover plate
- 1 bolting ring
- 1 cover plate extension
- 1 raising/lowering cross piece
- 1 feed nozzle assembly
- 1 reactor thermowell assembly
- 6-ft threaded rod, 1/4-20
- 50 ceramic shoulder washers
- 30 titanium nuts, 1/4-20.

In addition, various nonspecific parts such as those listed in Table 1 will be required. No major equipment will be purchased.

Table 1. Generic parts list for SCWO units.

Pipe, tubing, hose (not made of Inconel 625)
  - Includes C-276, C-22, 316 SS, 304 SS, plastic, rubber, PVC, CVPC, carbon steel, brass, copper

Valves (except those made of specialty alloys)
  - Manual, automatic with actuators, relief valves, vacuum breakers, valve trims

Maintenance parts, spare parts

Electrical equipment
  - Enclosures, wiring, contactors, circuit breakers, tie wraps, trays, conduit, junction boxes, fuse holders, fuses, relays, switches, heaters, heating tape, Variacs, terminals, transformers, cable, grounding equipment, lighting

Instrumentation (excluding computer control system)
  - Pressure—transducers, gauges, I/P converters
  - Temperature—thermocouples, thermowells, gauges
  - Level—differential pressure transducers, gauges
  - Flow—differential pressure transducers, dry test meter
  - Safety devices
  - Local temperature controllers
  - Local level controls

Insulation
  - Board, blanket, fiber, powder, molded forms for pipe, aluminum sheathing, tie wire

Structural support
  - Unistrut, angle iron, sheet, guard rails, hangers, clips, square tubing, I-beams, ladders, fittings, plate, walkways, stairs, scaffolding

Fittings
  - High pressure—(e.g., Autoclave Engineers)
  - Low pressure—Swagelok
  - Flanges
  - Seal rings

Miscellaneous items
  - Tools
  - Shielding (e.g., Lexan)
  - Floor drain covers

7. CONSUMABLES

Typical consumables for SCWO testing are given in Table 2.

Table 2. Generic consumables list for SCWO testing.

- Analytical consumables
  - Sample bottles or containers
  - Labels
  - Colorimetric gas analysis tubes
  - Tenax traps
  - XAD resin traps
  - TOCA reagents
  - Calibration gases
  - GC carrier gas
  - pH paper
  - Chloride strips
  - Gas absorption solutions
  - Gases for atomic absorption spectrophotometer
  - Chemicals for wet chemical analyses
  - Chemicals for ion specific electrode analyses
- Carbon traps for vent gas
- Ion exchange resins for feed water and effluent
- Feed chemicals
- Effluent/brine treatment chemicals
- Neutralizing reagent (e.g., NaOH)
- Welding consumables (e.g., wire, gases)
- Propane for torch, fork truck
- Filter elements
- Computer consumables
  - Floppy disks
  - Printer paper
  - Printer ribbons
- Modification materials
- Repair materials
- Batteries
- Lubricants (for pumps, motors)
- Joint sealants
- Cleaning solutions
- Paint, primer, brushes, rollers, thinner, sandblasting materials
- Shipping materials
- Thermocouple wire
- Tool expendables (e.g., drill bits, saw blades)

Appendix A

Statement of Work

Appendix A
Statement of Work

Introduction

Many of the Department of Energy (DOE) sites are generating and/or storing radionuclide contaminated hazardous wastes, i.e. mixed wastes, that are classified as Land Disposal Restricted (LDR) under the Resource Conservation and Recovery Act (RCRA). The Federal Facility Compliance Act of 1992 requires each facility at which the DOE generates or stores mixed waste to generate plans for treatment of all mixed wastes, or, for cases where no treatment technology currently exists, to generate plans for developing such technology. This act, which amends the RCRA, provides the impetus for accelerated efforts to develop, design, and construct facilities that will render DOE mixed wastes into forms that can be legally and inexpensively disposed of.

The Supercritical Water Oxidation (SCWO) technology holds promise of treating a portion of DOE mixed waste. The DOE strategy calls for demonstration of a mixed waste pilot plant designed for handling radioactive and hazardous waste. To support the design of this pilot plant, more data are required to solve the technical constraints of the process. One of these technical constraints is the selection of the materials of construction. Corrosion of SCWO reactors has been identified as a technical constraint to construction. This constraint can be eliminated by either preventing the corrosive elements of the waste stream from coming into contact with the materials of construction, or by identifying materials capable of withstanding the corrosivity of the fluid. Corrosion testing of various materials of construction is needed to identify materials capable of withstanding supercritical conditions.

Purpose

Specific testing will be conducted on a variety of coupons using selected waste streams. The coupons will be analyzed for types and amount of corrosion. A comparison will be made between the corrosion of the Hastelloy C-276, Inconel 625, other selected metals and ceramic lined coupons. The data from these tests will be used to conclude whether ceramic liners or other specialized metals are viable materials to be used in SCWO.

Work Scope

The contractor shall provide a system for demonstrating materials performance under the following conditions:

- 3,500 psi
- 100°C to 650°C
- The ceramic coupons shall at least 2.7 in. in width, 0.125 in. thick, with 0.25 in. of clearance around the coupon.

- The feed to be oxidized shall consist of TrimSol, a chlorinated cutting oil, and selected radionuclide surrogates (see Table 1) diluted to bring the chlorine content down to 5,000 ppm.

- Flow-through pressure vessel containing a coupon tree

    - A test plan shall be written and submitted to EG&G for approval prior to the start of testing. The contractor shall have a quality program that addresses procurement; responsibility and authority of inspection and test personnel; document control; inspection and testing; control of special processes; inspection, measuring and testing equipment; inspection and test status; and control of nonconformances.

    - The design of the test setup shall be submitted to EG&G for approval prior to the start of testing. The design package shall include detailed drawing of the location of the coupons in the system. It is assumed by EG&G that the contractor has an existing system for SCWO and the design would involve modifying the existing system to accept the piping and pressure vessels needed for this particular test.

    - Coupons shall be tested at the three significant temperatures of the process including the transition temperature as the process goes from the supercritical phase to the subcritical phase.

    - The contractor shall propose the approach for mounting and retrieving the coupon tree. Each run shall go for at least 60 hours, with coupons removed at set intervals according to the test plan. Six to eight coupons will be placed in the pressure vessel for each run. Hastelloy C-276 and Inconel 625 coupons shall be included in each run as a reference.

    - The ceramic coated and metal coupons shall be provided by EG&G for the tests. All piping, pressure vessels, and valves exposed to the unneutralized waste stream at high temperatures and pressures shall be considered consumables for the test. The coupons and all hardware acquired for testing such as piping, pressure vessels, and valves shall be delivered to EG&G for analysis.

    - Solid, liquid, and gas effluent from each run shall be collected and analyzed for at least chrome, nickel, chloride, potassium, sodium, molybdenum, iron, sulphate, TOC, TOX, pH, oxygen, carbon dioxide, methane, nitrogen, lead, cerium, and zinc. The lab analysis contract will be let by EG&G under advisement from the contractor.

Table 1. TrimSol with surrogates.

Chlorine	130,000 ppm
Sodium	>700 ppm
Calcium, potassium	>300 ppm each
Iron, titanium, zinc, lead	>100 ppm each
Cerium	3,000 ppm
Total solids	25,000 ppm

Deliverables

1. Draft Test Plan including experiment design, parts lists, consumables, and schedule
2. Final Approved Test Plan
3. All test logs and instrument readings
4. All coupons
5. System hardware procured under contract
6. Effluent data.

Schedule

Draft Test Plan	November 22, 1993
Final Test Plan	December 10, 1993
Procurement	December 10, 1993
System assembled	February 19, 1994
System checkout	March 25, 1994
Testing complete	July 29, 1994
Hardware delivered	August 26, 1994