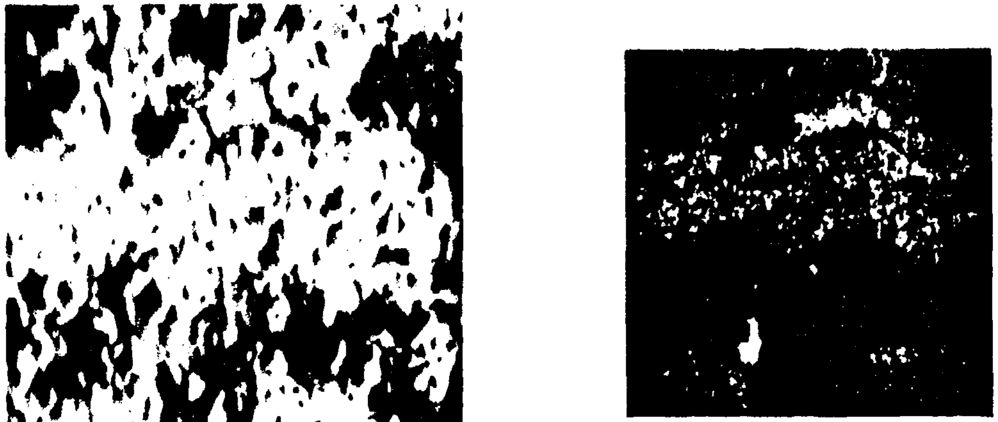
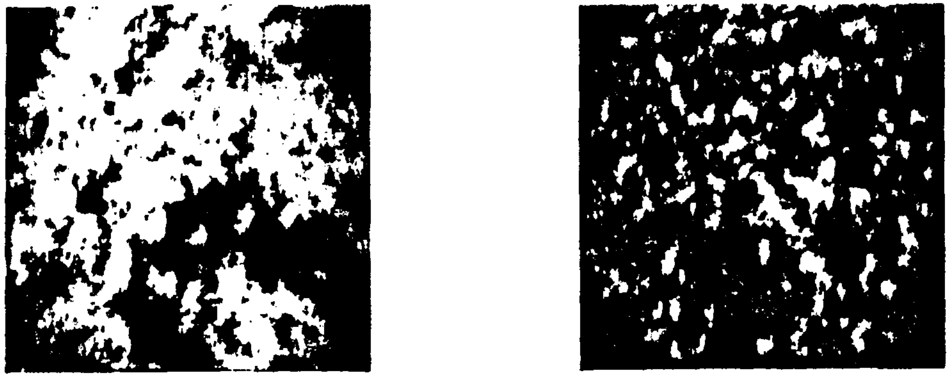


1000X SEM

800X
RED - Mn
GREEN - Fe



800X
RED - Mn
GREEN - Ni

30 m

800X
RED - Mn
GREEN - Cr

FIGURE 8. TYPICAL COLD LEG DEPOSIT (532°C) FROM ARD LOOP MTL-4-8

DEVELOPMENT OF ACIDIC PROCESSES FOR DECONTAMINATING LMFBR COMPONENTS

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I. INTRODUCTION

The objective of the DOE decontamination program is to develop a well-characterized chemical decontamination process for application to LMFBR primary system components that subsequently permits contact maintenance and allows requalification of the components for reuse in reactors.

The paper describes the subtasks of deposit characterization, development of requalification and process acceptance criteria, development of process evaluation techniques and studies which led to a new acidic process for decontaminating 304 stainless steel hot leg components.

II. DECONTAMINATION PROCESS ACCEPTANCE AND REQUALIFICATION CRITERIA

The objective of the decontamination process is to produce a maximum reduction in radioactivity with a minium of damage to the contaminated component. Some damage must be accepted since the high diffusion rate of ^{54}Mn, for example, often results in its penetration to a depth of over 20 μ in a hot leg component fabricated from 304 stainless steel. Thus removal of about this much metal is required to achieve relatively complete decontamination. Cold leg decontamination requires less metal removal for equivalent decontamination.

Precise evaluation of the amount of damage which can be tolerated on a reusable component is not available. For the purposes of this program, it has been estimated that 25 μm of metal removal is an acceptable limit for requalification. On this basis, the process performance criterion for decontaminating 304 SS hot leg components has been set at 19 ± 6 μm metal removal. At the lower limit, acceptable decontamination could be expected in most cases, based on the available penetration profiles for ^{54}Mn. Maximum pit depth has been fixed at 50 μm. Evidence of generalized intergranular attack or cracking is also a basis for elimination of a reagent from consideration.

III. CHARACTER OF SURFACE DEPOSITS AFFECTING DECONTAMINATION

The radioactive deposits which will be transported to the primary system components may originate from 1) fission products released during reactor operation with breached cladding, 2) activation of the sodium and its impurities, and 3) activated corrosion products from the fuel cladding. The activated corrosion products were considered the limiting problem and principal concern for component decontamination. It was assumed the component would be removed from the heat transport system and the sodium would be removed by the standard procedures before application of the decontamination process.

The surfaces of test facilities used to study the release and deposition of activated corrosion products have been characterized with respect to the elemental composition and physical nature of the radioactive deposits as discussed at this conference(1). These analyses indicated two fundamentally different contamination problems exist in the hot leg and cold leg portions of the heat transport system.

In the hot leg, the radioactive deposits will primarily consist of ^{60}Co and ^{54}Mn isotopes diffused into the base metal up to a depth of 20 μm. In the cold leg, the contamination will be predominantly ^{54}Mn contained in small nickel-rich nodules spread over the surface. Radionuclide penetration into the base metal will be limited to only 2 or 3 μm. The nickel-rich deposit phase has a substantially different corrosion behavior than the stainless steel substrate. Consequently, different processes are expected to be required for decontaminating hot or cold components. Efforts in the program so far have been directed mainly at a hot leg process.

IV. METALLURGICAL VARIABLES WHICH AFFECT DECONTAMINATION

It is well known that the character of the corrosion resistance of stainless steel is substantially changed by sensitization, which involves the intergranular precipitation of chromium carbide when austenitic stainless steel is exposed to temperatures in the range of 800°F (427°C) to 1500°F (816°C). Service in a sodium-cooled reactor will normally sensitize 304 SS hot leg materials, making them susceptible to intergranular corrosion in aqueous environments.

In the laboratory screening program it was necessary to standardize on one method of sensitization. Sensitization in air and vacuum were evaluated and vacuum sensitization at 1250°F (677°C) for one hour was chosen as the reference method. The rate of metal removal which will be obtained for LMFBR components sensitized by long-time exposure in sodium service will usually be higher than the rate observed using short-time sensitization. The quantitative relation between the time-temperature history and metal removal rate will need to be known to accurately predict the process time required to any acid-based decontamination process. It was concluded that a standard and reproducible short-time sensitization method can be used as a basis for comparing and selecting reagents for further development.

V. SELECTION OF ACIDIC REAGENTS

Since decontamination of hot leg components cannot be accomplished without metal removal, a reproducible laboratory metal removal procedure is needed. A suitable procedure evolved during the program.

Test specimens comprised five individual sensitized specimens from the same heat, hung on unsensitized stainless steel hooks at the initiation of a test. They were immersed simultaneously in the decontamination solution at temperature. Two specimens were removed from the solution each day, observed and weighed. One of these specimens was returned to the solution immediately. The returned specimen was weighed again next day, along with another specimen which had not been previously removed. This approach continued, (with a three-day interval for week ends), so that at the end of the six-day test, one specimen had been weighed four times and the other specimens only once each. This approach served to evaluate the effect of air exposure on the specimen which was weighed repeatedly.

Metal removal testing showed oxygen control to be essential to avoid passivation. To achieve low oxygen levels, all non-boiling solutions were pre-sparged 16 hours at the specified reaction temperature. A Henry's law calculation indicated that the oxygen level of the solution would be reduced to about 0.5 parts per billion at equilibrium. The sparging was continued during the test. No other stirring was used. Both nitrogen and argon with oxygen concentration varying from 1 to 12 parts per million were used, with similar results.

A large number of common organic and inorganic acids and compatible additives were evaluated during the program. Most failed to meet one or more of the criteria listed in Table I. The two most promising solutions were:

1. 50% acetic acid; 2.5% citric acid. Boiling and 90°C.
2. 2.5% glycolic acid; 2.5% citric acid. 70°C to 90°C.

Boiling 50% acetic acid was eliminated because it was determined that this condition would pose plant scale problems in large process vessels. The remaining candidates gave more or less comparable results, but it was decided to concentrate efforts on the 2.5% glycolic-2.5% citric acid reagent since this system would minimize waste disposal problems. Anions of these acids are also powerful sequestering agents, which should minimize any tendency of dissolved radioactive cations to redeposit.

Typical results of individual tests are given in Figures 1 and 2. Figure 3 shows results of a test in which air exposure caused a stoppage of the reaction on the re-exposed coupon. Conclusions drawn from an extensive series of tests were:

1. The rate of metal removal was linear with time for tests where passivation or oxygen introduction was avoided.
2. Accidental air exposure of solutions could passivate all specimens still in it.
3. The necessary air exposure of a coupon weighed repeatedly could also passivate it.
4. There was no significant difference between metal removal rates for equivalent sodium and vacuum sensitized specimens.
5. Metal removal rates vary significantly among different metal heats, but no correlation with metal compositional variables was apparent.

TABLE I

Decontamination Process Criteria

A. PRIMARY CRITERIA

1. Decontamination Effectiveness on Hot Leg Specimen
2. Minimum Damage to Sensitized 304 Stainless Steel
3. Predictable Process End Point
4. Compatibility with Sodium Removal Process
5. Adaptability to Plant Scale Equipment

B. SECONDARY CRITERIA

1. Minimum Waste Disposal Problem
2. High Solubility of Dissolved Metal Salts
3. Low Cost and Commercial Availability of Reagents

In addition to achieving a satisfactory rate of metal removal, minimum damage to the component is essential. The selected process has not shown any tendency to produce pitting in most tests. Occasional mild intergranular attack was observed but is not considered serious. An example is shown in Figure 4.

Tests were also run on specimens taken from the SPEX-1 loop to evaluate the performance of the process on materials exposed to long sodium service. Results, which confirm the longer term linearity of metal removal with time, are shown in Figure 5. The 304 SS tested had operated in the loop for 6520 hrs at 510°C (950°F). Surface damage was acceptable as shown in Figure 6.

In order to establish the correlation between metal removal and decontamination for the promising reagent, tests were run on hot leg sections of STCL-1 loop from HEDL, with the results shown in Figure 7. These results confirm that metal removal is, in fact, producing decontamination. Based on the results presented above, the final decision was made that the 2.5% glycolic acid - 2.5% citric acid reagent will provide an acceptable decontamination process.

VI. THE GLYCOLIC-CITRIC ACID (GCA) DECONTAMINATION PROCESS

The glycolic-citric acid process (GCA) is based on the use of a water solution of 2.5% by weight of glycolic (hydroxyacetic) acid combined with 2.5% by weight of citric acid monohydrate for the removal of diffused radioactive elements from LMFBR components. It is suitable for use over a temperature range of 70 - 90°C.

It is necessary to maintain a low oxygen concentration in the solution to obtain reproducible metal removal rates and this condition can be attained by continuously sparging the solution with an inert gas such as nitrogen or argon.

The acid treatment time is determined by relating the rate of metal removal which will be achieved for the various metal heats used in manufacturing the component to the diffusion profile of the radionuclides of interest.

After the treatment is complete, the component is passivated by air sparging for 24 hours at the process temperature. The component is then rinsed with high quality water and dried with hot inert gas until an exit gas dewpoint of -40°C is attained.

The final step of the decontamination process is passivation of the cleaned reactor components by air sparging. This is a precaution to avoid any continued corrosive attack from traces of acid solution remaining after rinsing the component. Of particular concern is the potential for serious crevice corrosion which could result from acid remaining in component crevices.

The sensitivity of acid decontamination solutions to air exposure suggested that air could be used to "turn off" the solution, stopping the corrosive attack. Potentiostatic corrosion potential measurements showed that freely corroding coupons in an oxygen-free solution have a potential of about -0.4 V (vs.SCE). If air is admitted to the solution, the corrosion potential immediately jumps to the passive range, + 0.3 V (vs. SCE).

To confirm the process application, a series of tests were conducted in gas-tight flasks containing the GCA reagent. Solutions were continuously sparged with inert gas and maintained at 70°C $\pm$ 0.5°C. Duplicate metal specimens were placed in each flask.

In each test, the glycolic-citric solutions were initially sparged with an inert gas (nitrogen or argon). After etching the metal specimens for 6 to 13 days, the sparge gas was changed to air. The tests were then continued for several days in order to determine the effect of the air sparge.

Without exception, etching of the specimens ceased immediately when the sparge gas was switched to air (Figure 8). The depth of etch, or time in solution, did not influence this phenomenon, nor did the heat or the carbon content of the steel appear to have any effect.

TABLE II

Parametric Tests: Hot Leg GCA Decontamination Process
Reference Conditions: 2.5% Glycolic Acid, 2.5% Citric Acid;
70°C; Sparge Rate: 2.8 x 10^{-2} m^3 hr^{-1} (15 CFM)

METAL REMOVAL RATE, μm/day

		Vacuum Sensitized 1 Hour at 677°C (1250°F			Deposition Loop Sensitized, 3000 hrs at 538°C (1000°F)	
Parameter Varied	Amount	Ht 74821	Ht 74966	Ht 55183	Ht 74966	Ht 55183
Temperature	-3°C	0.94	0.62	0.85	1.34	1.49
	0	0.94	0.56	0.77	1.10	1.21
	+3°C	1.41	0.75	1.06	1.95	2.12
	+10°C	1.81	0.98	1.41	2.54	2.12
	+20°C	2.82	2.82	0.73	3.63	2.12
Acid Concentration	-10%	1.06	0.62	0.91	1.59	1.49
	0	1.49	0.82	1.34	1.69	1.95
	+10%	0.88	0.55	0.69	1.21	1.21
Sparge Rate	-25%	1.02	0.85	0.64	1.49	1.15
	+25%	1.02	0.55	0.73	1.41	1.49

In addition, it was found that the metal specimens "cleaned up" after soaking in the continuously air-sparged solution. Whereas specimens normally had a dull gray finish after decontamination treatment, the specimens surface appeared clean with a shiny surface after air sparging.

VII. PARAMETRIC STUDIES

In order to evaluate the sensitivity of the GCA process to reasonable variations in the important process parameter of temperature, concentration and sparge rate, a series of parametric tests were run using both radioactive and non-radioactive specimens. The radioactive specimens were from the AI deposition loop and had been exposed to 1000°F sodium for 3000 hours. The results are shown in Table II.

These tests show that the temperature of the decontamination solution is the most sensitive parameter which needs to be controlled. Sparge rate and acid concentration control requirements are nominal. The tests also indicate that the metal removal rate for a given heat will be affected by service conditions. This may be related to sensitization or sodium corrosion effects on the surface. The process time required to remove enough metal to achieve the desired degree of decontamination will have to be fixed for each component and specific processing condition. Ideally, "traveler" coupons from the same metal heats used to fabricate the component could be used to monitor the process. It is essential, if this approach is used, that such specimens experience an environmental history equivalent to that seen by the component.

VIII. DECONTAMINATION DEMONSTRATION FACILITY

Scaling up processes from the laboratory requires a pilot plant demonstration facility. At HEDL, a demonstration facility is under construction. The facility has been designed to meet the following objectives:

1. Perform a complete series of operations, including sodium removal, rinsing, hot or cold leg decontamination and inerting in as realistic a manner as possible.
2. Obtain technical data to verify and supplement laboratory data which will define process performance capabilities.
3. Develop operating procedures and control requirements which can be translated to full-scale plant systems.
4. Demonstrate operations on test assemblies of a sufficient size and complexity to permit assessment of process capabilities on plant scale components.

The demonstration facility is being built using equipment developed in the demonstration program for the Water Vapor-Nitrogen (WVN) process for sodium removal. The process vessel is 12 ft high and 24 inches in diameter. The vessel has a full diameter flanged cover and is serviced by an overhead crane, so that articles up to 12 feet long and a maximum span of about 2 feet can be processed. The vessel is jacketed and electrically heated.

Nitrogen is piped to the vessel through a tube furnace and heat traced lines. Water vapor from a small steam generator can be injected into the nitrogen for sodium removal operations. The process vessel is also supplied with a pumped liquid recirculation system. Addition of rinse water or decontamination solutions is through the recirculation lines.

For decontamination operations, chemicals to be used will be dissolved and mixed in a small addition tank. The concentrated solution, containing all reagents in the required amounts, is then added to a mixing-conditioning tank which has the same volume as the process vessel. Here, water is added to produce the final working concentration and the solution is heated to final temperature. Sparging with nitrogen is used to eliminate oxygen and to mix the solution. Either distilled or demineralized water can be used at any stage of the process.

Decontamination is accomplished by pumping the conditioned reagent solution into the process vessel and recirculating at temperature under a continuous nitrogen sparge. The sparge gas can be switched to air to stop the reaction.

Basic instrumentation permits monitoring and control of temperatures and flows throughout the system. The equipment is designed to operate at any temperature up to about 100°C. Because of the apparent sensitivity of the potential hot leg decontamination solutions to dissolved oxygen, two instruments have been included to monitor oxygen concentrations. A recirculating sample line which can sample from either the main circulation system or the conditioning tank is connected to the detectors. One instrument operates on a polarographic principal, the other as a galvanic cell and both are sensitive in the part per billion range.

Monitoring progress of the decontamination reaction is essential. One control method could be the measurement of radioactivity in the solution. While it is planned ultimately to make such measurements, the limited availability and small size of representative contaminated hot leg material limits the utility of this approach in the demonstration program. For this reason an electro-chemical corrosion monitor using a three electrode detector is incorporated in the recirculation line. An attempt will be made to correlate data from this instrument with weight loss data from test coupons.

The demonstration facility includes a number of features for control of radioactivity. Those portions of the equipment expected to become contaminated, the process vessel and the recirculation system particularly, are isolated by check valves from supply systems and are surrounded by a concrete curb capable of containing a spill of the entire contents of the system. The conditioning tank has also been included in this area to permit temporary retention of a radioactive solution from the process vessel if this should prove desirable in the future. The vent lines from both the process vessel and conditioning tank go through condensers which return condensate to the tanks during sparging. The dried vent gas is then heated slightly and passed through HEPA filters to the filtered building exhaust system. Liquid wastes are pumped to a crib retention system for ultimate burial.

It is expected that a substantial amount of activity will be removed in particulate forms, especially during sodium removal. A dual filter is included in the recirculation line to collect particles, both as a clean-up measure and to permit examination of the residues.

IX. REFERENCES

1. R. P. Colburn, "Characterization of Corrosion Product Deposits in Sodium Systems," Hanford Engineering Development Laboratory, SA-January 1978

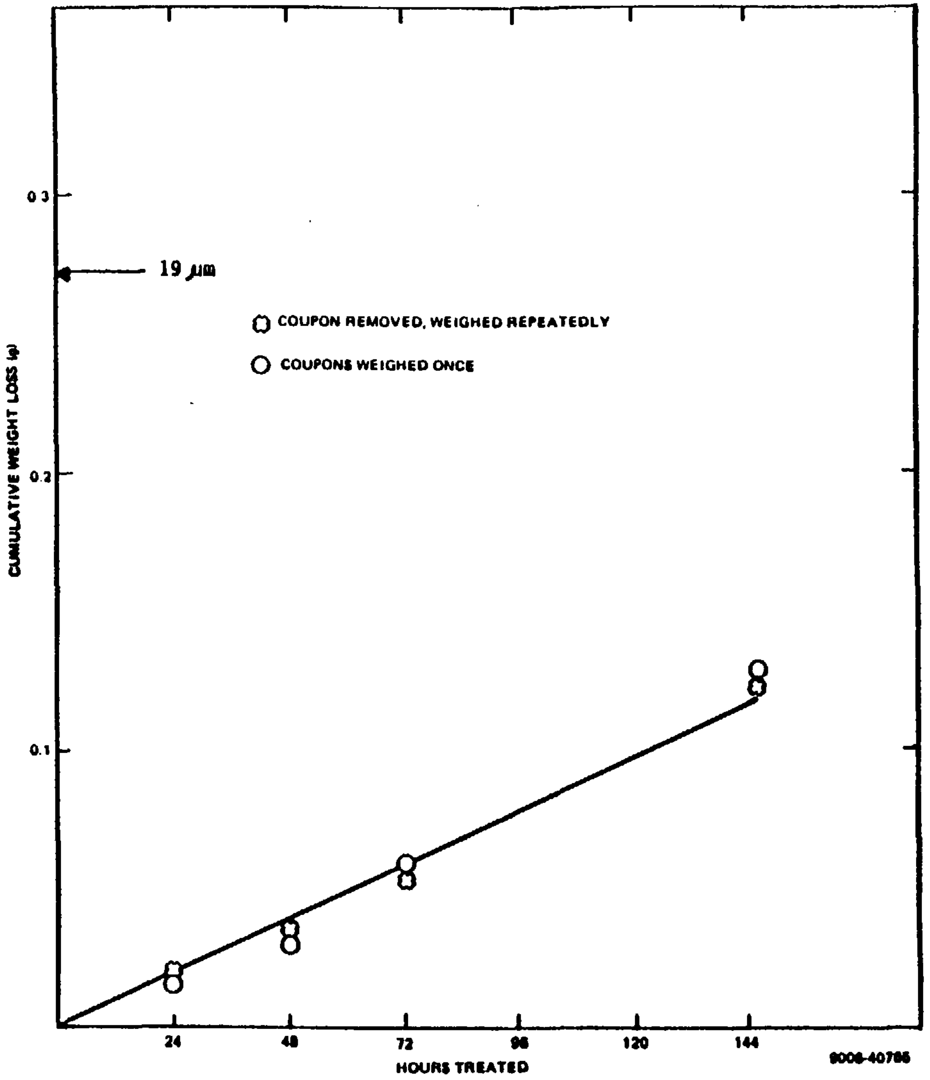

Figure 1. Metal Removal from Sodium Sensitized 304 SS (Ht 55183) by 2.5% Glycolic Acid - 2.5% Citric Acid, 70°C (158°F)

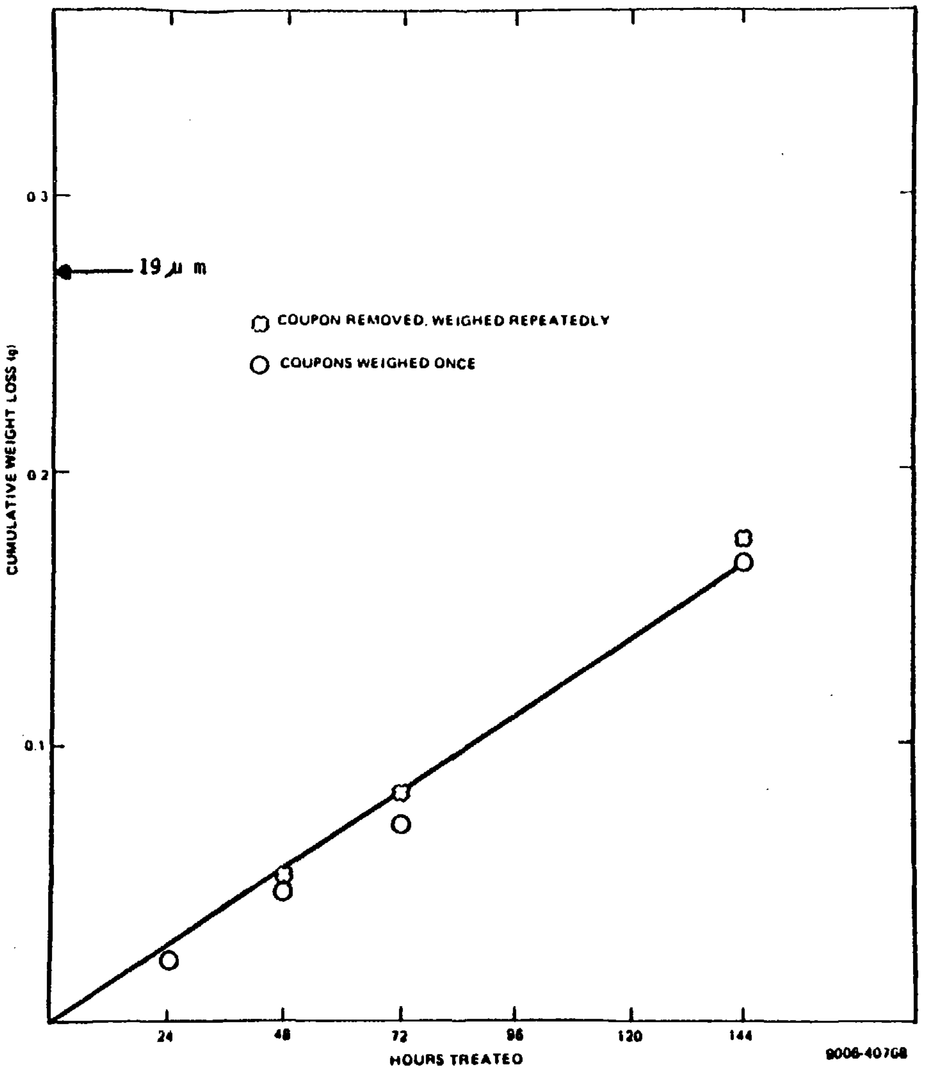

Figure 2. Metal Removal from Vacuum Sensitized 304 SS (Ht 74966) by 2.5% Glycolic Acid + 2.5% Citric Acid, 70°C (158°F)

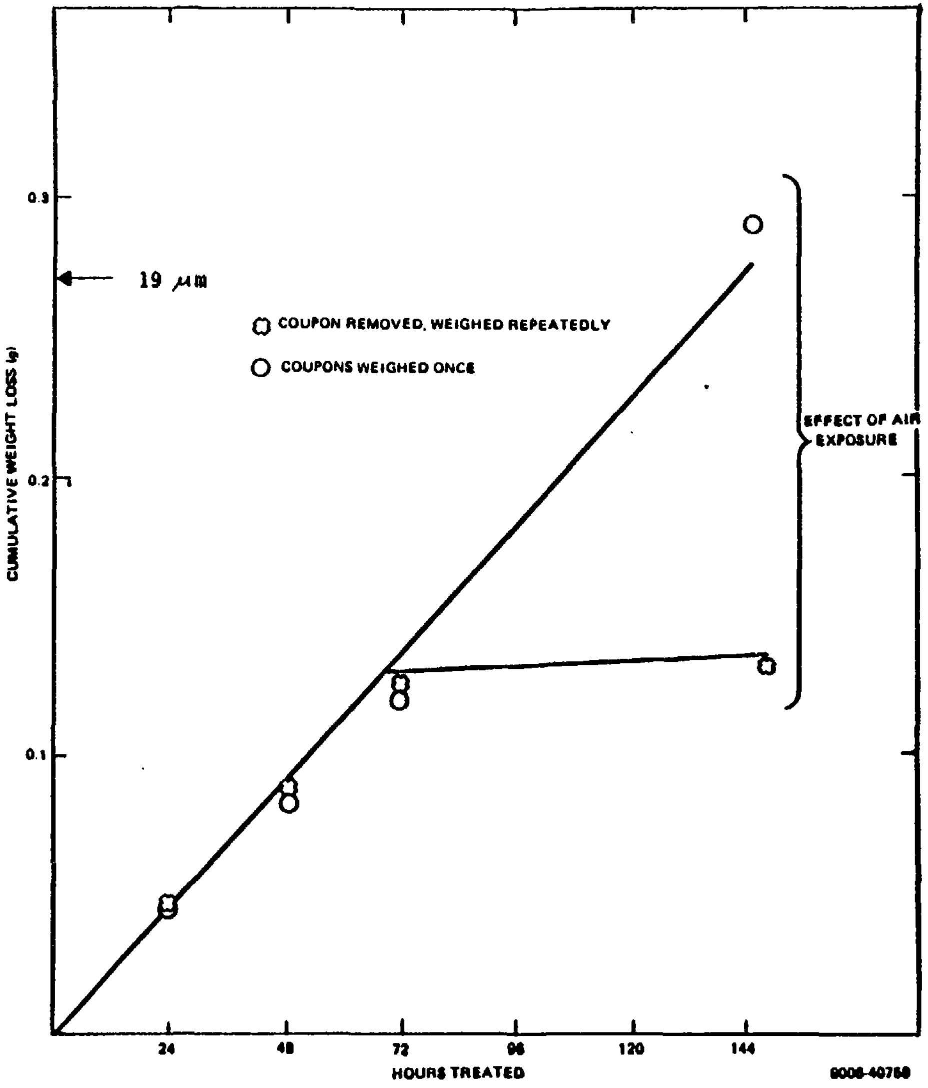

Figure 3. Metal Removal from Sodium Sensitized 304 SS (Ht 55183) by 50% Acetic Acid + 2.5% Citric Acid, Boiling

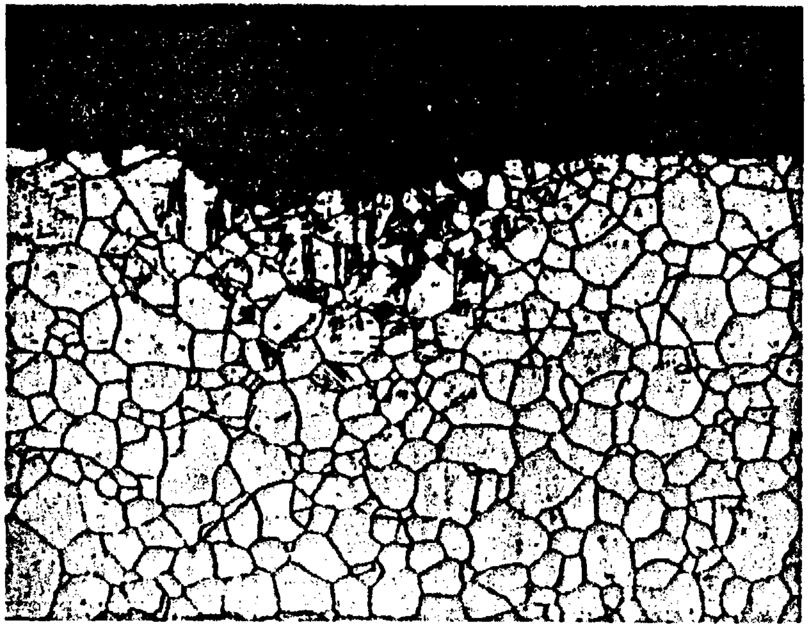

Figure 4. Cross Section of Sensitized Type 304 Stainless Steel Treated with 2.5% Glycolic-2.5% Citric Acids at 70°C (158°F) (250X)

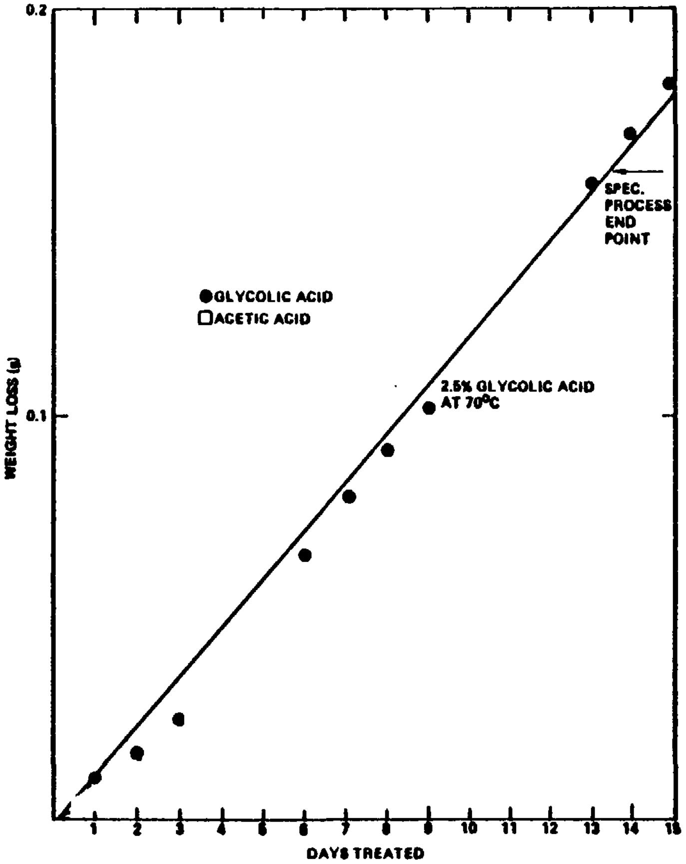

Figure 5. Metal Removal by 2-1/2% Glycolic Acid + 2-1/2% Citric Acid from SPEX-1 Loop Economizer Specimen

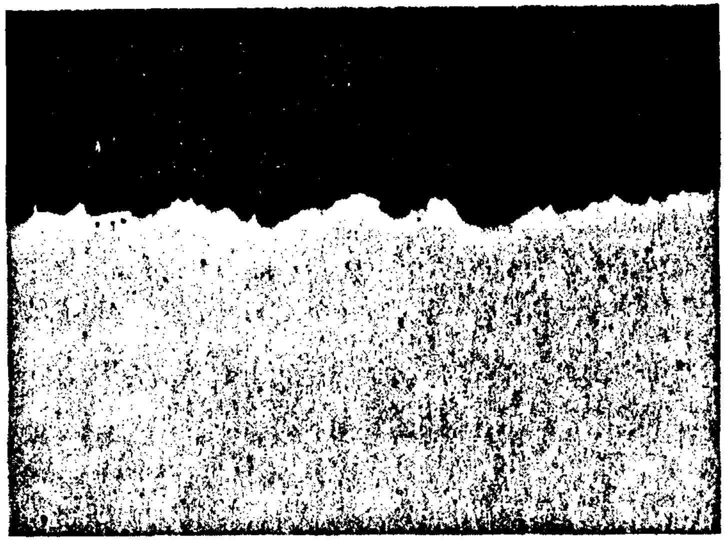

Figure 6. Surface Condition of Hot Leg Specimen from SPEX-1 Loop After 16 days Exposure in 2-1/2% Glycolic Acid + 2-1/2% Citric Acid at 70°C (158°F) (Metal Removed ≅ 25 μm)

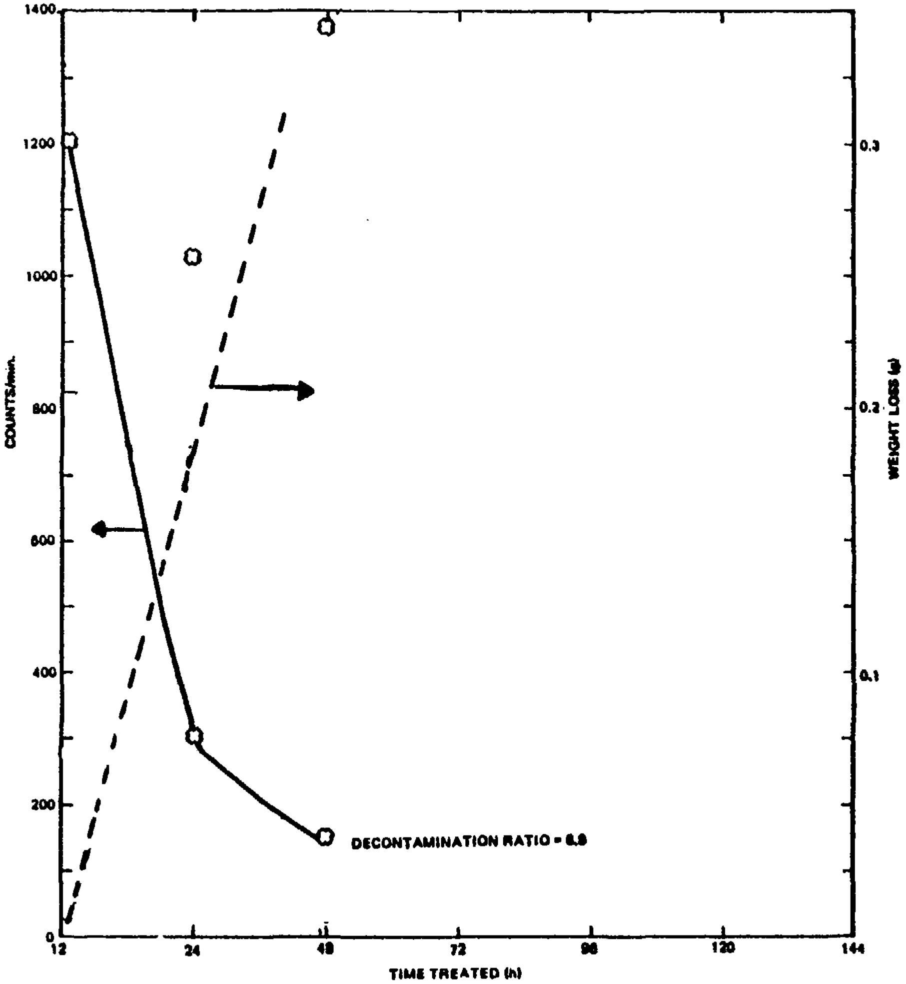

Figure 7. Hot Leg Decontamination by 2-1/2% Glycolic Acid-2-1/2T Citric Acid. ^{54}Mn Removal from HEDL STCL-1 Specimen

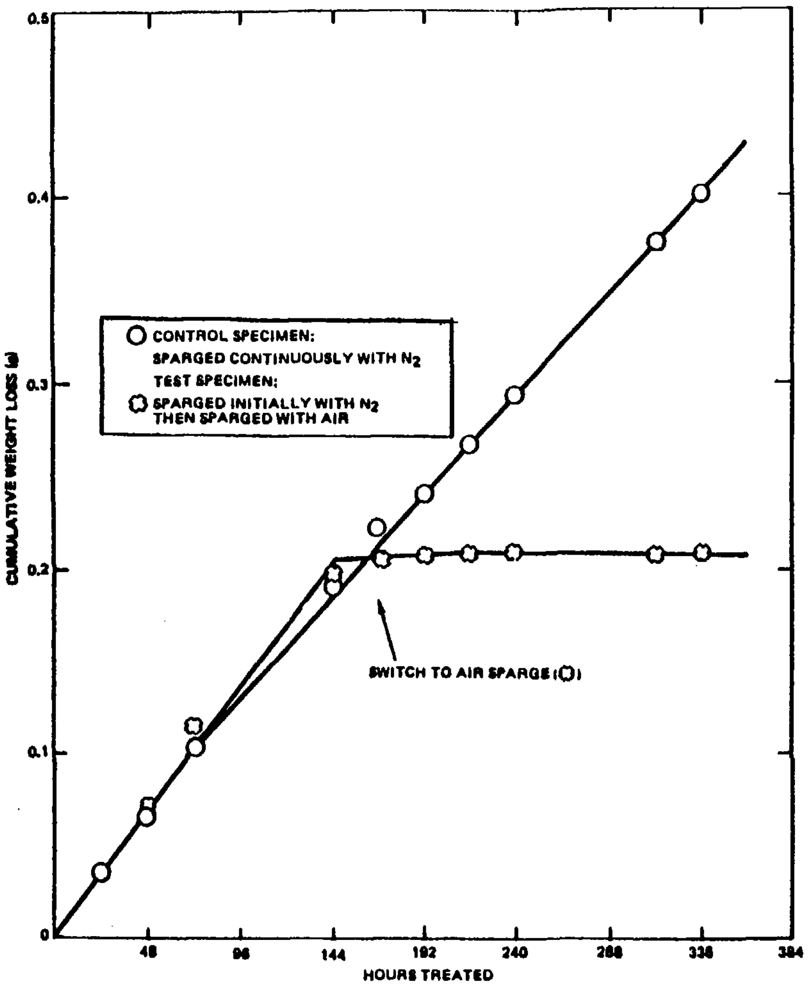

Figure 8. Post Decontamination Corrosion Control Experiment
Metal Removal from Vacuum Sensitized 304 SS (Ht 74821)
by 2-1/2% Glycolic Acid-2-1/2% Citric Acid at 70°C (158°F)

NON-AQUEOUS REMOVAL OF SODIUM FROM REACTOR COMPONENTS

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I. INTRODUCTION

Reactor components from sodium-cooled systems, whether radioactive or not, must have the sodium removed before they can be safely handled for 1) disposal, 2) examination and test, or 3) decontamination, repair, and requalification. In the latter two cases, the sodium must be removed in a manner which will not harm the component, and prevent future use.

Two methods for sodium removal using non-aqueous techniques have been studied extensively in the U.S.A. in the past few years.

a. The Alcohol Process, which uses a fully denatured ethanol to react away the sodium;

b. The Evaporative Process, which uses heat and vacuum to evaporate the sodium from the component.

II. PROCESS DEVELOPMENT

A. The Alcohol Process

Atomics International (AI) was given the responsibility by ERDA (now DOE) for 1) defining the parameters for a process using a denatured ethanol or a denatured ethanol plus 1.5 vol % acetic acid, and 2) qualifying the process to a point where it could be used as a safe, reliable method of sodium removal.

The process, so-defined, uses hot, denatured ethanol to react the sodium, forming H_2 and sodium ethylate. The reaction rate is regulated by controlling