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AT03-76SF 91001

I. PROJECT OBJECTIVES DOE/SF/91001--T6

DE82 011130

This project has several tasks, each with its own specific objectives. One of these tasks is the Sodium Removal Process Development; the first objective of which is to devise, develop, test and evaluate techniques for sodium removal from test specimens and components by the reaction of sodium with alcohol.

As a part of the alcohol process development, the following activities are being investigated: (1) reaction rate studies, (2) process control and repeatability, (3) sodium-alcohol reaction chemistry and alcohol regeneration studies, (4) quality control and inspection technique development, and (5) alcohol-sodium removal process safety evaluation (Safety Report and Safety Specification). The culmination of this program will be a sodium cleaning process specification incorporating the pertinent data and other information generated by the sodium-alcohol studies.

The second objective of the sodium removal development effort is to determine the process parameters for the removal of sodium from test specimens and components by the use of sodium evaporation techniques. Further development in this area is being held until next Fiscal Year.

A second task of this project is the Decontamination Process Development. The objective of this effort is to develop a well-characterized decontamination process for use on LMFBR primary system components. The process should subsequently permit contact maintenance and allow requalification of the components for reuse in the reactor.

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A third task has the objective of developing a method or methods for safe, reliable removal of sodium and sodium-water reaction products from components without harming them, using the current alcohol process or a modified process.

II. MAJOR ACCOMPLISHMENTS DURING FISCAL YEAR 1976

Examination was completed of bolt specimens stored for 2 years after sodium removal by the alcohol process or the moist nitrogen process. It was concluded that the storage atmosphere of either air or nitrogen containing 50 ppm water vapor and 50 ppm O_2 had little effect on the discoloration or rusting of the bolts; however, in general, those bolts cleaned by moist nitrogen exhibited heavier discoloration and rusting than did those bolts cleaned by the alcohol process.

The reaction rate tests of sodium in thin crevices with Jaysol SS were completed. It was demonstrated that the sodium could be removed from a 1-mil crevice at a rate of 0.015 in. (0.038 cm)/hr with 140°F (60°C) Jaysol SS.

The sodium frost-Jaysol SS reaction rate tests were concluded, and it was observed that the highly metallic, large surface area sodium frost reacted with the Jaysol SS with about the same vigor as an Alka-Seltzer tablet and water. Oxidized frost was observed to react slightly less vigorously.

Reaction rate tests of sodium pellets with various alcohols and additives were completed, and an optimized concentration of Jaysol SS containing 1.5 vol % additive and <0.5 vol % water selected. The solubility of the sodium salt of the additive was measured to be 3.5 g (as Na)/l or 30 lb Na/1000 gal of Jaysol SS.

The process reliability tensile specimens were prepared, wetted with sodium at 1050°F (565.6°C), stressed to 100% of 0.2% yield, and cleaned of sodium using the acidified alcohol process. Visual and dye penetrant examination showed no stress corrosion cracking.

Viscosity and density change tests of Jaysol SS, with and without the additive, were completed. The Jaysol SS, containing sodium alcoholate, showed some increase in viscosity with time, but the presence of the additive prevented a viscosity increase, in addition to retarding the condensation reaction which occurs in the caustic alcohol solution.

The Alcohol-Sodium Removal Pilot Facility was completed and a procedural checkout conducted. The initial cleaning operation was conducted on a sodium-wetted valve.

A facility operating procedure was prepared, and a review of the draft of the "Sodium Removal Process Specification Manual," RDT F 5-9 was completed.

The IHX Tube Bundle Mockup was wetted with sodium and cleaned three times using the alcohol process. Dye penetrant inspection of the weld areas after each cleaning showed no change from the precleaning inspection. The three sodium wetting-alcohol cleaning cycles produced no deleterious effects on the component.

Chemical analysis of the distillate from a batch of used Jaysol SS which had been doped with small amounts of Ni, Fe, Cr, Y, Mo, and Cs showed at least a 200-fold decrease in all metals except Cs, indicating the presence of a volatile cesium compound.

Gas chromatographic analysis of the distillate indicated only minor changes in the relative component (ethyl, methyl and isopropyl alcohols and methyl isobutyl ketone) concentration after reaction with sodium and subsequent distillation.

Elastomer-caustic Jaysol SS compatibility tests were completed after 115 days exposure at 173°F (78.3°C) (bp Jaysol SS containing 10 g Na/l). It was concluded that a butyl (B318) and two EPR (559N and E692) elastomers were satisfactory for long-term service. The neoprene and nitriles were usable for short periods, whereas the silicone elastomers should not be used with the caustic Jaysol SS.

The study on the fixation of the Alcohol-Sodium Removal Process wastes into a cement matrix was completed, and a final report (N707TR830-007) was issued. This work showed that quite large quantities of the alcohol wastes can be fixed in a Lumnite[®] cement. The fixation can be improved by the use of calcium acetate to gel the alcohol prior to addition to the cement.

The Na-H₂O reaction products test apparatus was designed, built and assembled. Tests using 0.5 to 10 ml water samples in sodium at 300 to 600°F (149 to 315.6°C) have been conducted.

The decontamination program was initiated July 1, 1975. A program plan was issued on August 19, 1975, NP707-PP-830-002, and Revision A was issued on November 26, 1975. The revised plan and schedule provide for the following tasks:

- I. Screening of Metal Removal Agents
- II. Specimen Procurement and Characterization
- III. Design, Fabrication and Operation of a Deposition Loop
- IV. Decontamination Process Development
- V. Process Specification

Metal removal rate tests continued under the decontamination activity. Nine different heats of Type 304 stainless steel were obtained to supply test specimens to evaluate a variety of candidate decontaminating reagents, additives and pretreatments.

Metal specimens were selected to provide a wide range of metal carbon contents, since this variable has a major effect on metal removal. The reagents and conditions of use evaluated during this period were those which had been shown to have the most promise in the over 350 evaluation tests which have been run in preliminary screening tests. The objective of the metal removal studies was to select candidate removal agents for detailed process development. These tests also serve to help identify the major process variable which should be controlled.

Acetic acid - both anhydrous and water solutions, glycolic-citric acid mixture, and sulfamic acid reagents were recommended for further development. Hydrogen peroxide was shown to be a promising reagent to inhibit corrosion reactions and perhaps avoid the potential problem of post-decontamination crevice corrosion. Potassium permanganate was recommended for further investigation as a pretreatment material.

The design and construction of a manganese-cobalt deposition sodium loop to provide prototypical deposits for use in future decontamination evaluations was completed.

Preliminary planning was initiated on the handling and storage of radioactive specimens from HEDL sodium loops.

A stainless steel condenser was ordered to convert the alcohol process pilot facility to a pilot plant suitable for operation using acidic decontaminating agents.

III. PROGRESS DURING REPORT PERIOD

A. ALCOHOL PROCESS DEVELOPMENT

1. Process Reliability and Control Using Additive Solutions

The group of stressed tensile specimens, described in the July-September 1975 Progress Report (AI-ERDA-13160), completed the sodium exposures and cleaning sequences using acidified Jaysol SS, as outlined in Figure 1.

Visual examination and dye penetrant inspection did not reveal any evidence of stress corrosion cracking in any of the 67 specimens.

2. Process Reliability and Control Tensile Specimen Test Data

Three tensile specimens were mechanically tested within 24 h of the completion of the sodium removal operation using acidified alcohol. These Type 304 stainless steel specimens had been subjected to conditions, as noted in Table 1, which represented a case where a high concentration of sodium compound was left on the specimens. Visual inspection of the fracture surfaces indicated normal fractures, and the tensile data appear typical of Type 304 stainless steel.

The remaining specimens are currently in test.

B. ALCOHOL - SODIUM REMOVAL PILOT FACILITY

1. Facility Operations

A report was released describing the calibration and use of the gas chromatograph (N707TI830-014), "Calibration and Use of the Carle Model AGC-111 Gas Chromatograph in the Alcohol Process for the Removal of Sodium."

2. Sodium Removal Process Specification Manual, RDT Standard F 5-9

The draft of the Manual was reviewed by the Sodium Removal Working Committee meeting at Atomics International on January 8-9, 1976. The recommended changes are being incorporated in the Manual by HEDL personnel.

TWO AI SPECIMENS
AS REFERENCE

THREE AI SPECIMENS
USED AS CONTROL

27 AI SPECIMENS
18 HEDL SPECIMENS

6507-40655A

Figure 1. Tensile Specimen Conditioning and Testing Sequences

TABLE 1

**MECHANICAL PROPERTIES OF TYPE 304 STAINLESS STEEL SPECIMENS EXPOSED TO
HIGH CONCENTRATIONS OF SODIUM COMPOUND (EARLY TEST)***

Specimen Number	Ultimate Tensile Strength		0.2% Yield Strength		Elongation (%)	Reduction in Area (%)
	(N/m ²)	(psi)	(N/m ²)	(psi)		
R1-4	6.24×10^8	90,500	2.92×10^8	42,400	70	77
R1-6	6.05×10^8	87,700	2.99×10^8	42,800	63	77
R1-10	6.08×10^8	88,200	2.83×10^8	40,500	64	75

***Exposure Conditions:**

- a. Sensitized in vacuum at 677°C (1250°F) for 1 h.
- b. Assembled in their holders and stressed to 100% of 0.2% offset yield.
- c. Soaked for 1 h in Jaysol SS acidified with 1.5 vol % additive containing 3.5 g Na / $1 \times 10^{-3} \text{ m}^3(\ell)$ as sodium compound.
- d. Drained of liquid and stored in 50% relative humidity air for 120 h.
- e. Baked at 204°C (400°F) in argon for 120 h.
- f. Wetted in sodium at 566°C (1050°F) for 48 h.
- g. Cleaned with Jaysol SS acidified with 1.5 vol % additive.

3. The IHX Tube Bundle Mockup Cleaning No. 2

Examination of the Tube Bundle was completed after the second cleaning operation, as described in the last progress report (AI-ERDA-13165). The unit was more free of sodium than after the first cleaning of 80 h, but residual sodium was still present on the deepest bolt threads and in the cavity at the base of the bolt. No other sodium was visible.

The pin weld areas were dye-penetrant inspected, but no evidence of damage was observed. After several days of storage in ambient air, a bleedout of sodium compounds was found around the base of the tie rod, and the junction between the top support bar and the front support bracket. The unit was soaked in hot water, dried, and reassembled. Six of the assembly bolts were drilled out lengthwise to provide a passage for alcohol to the base of the bolt hole. The assembly was wetted with sodium at 566°C (1050°F) for 154 h for the third cleaning cycle.

4. The IHX Tube Bundle Mockup Cleaning No. 3

The sodium-wetted Tube Bundle was installed in the Cleaning Vessel and cleaned with acidified Jaysol SS using the same procedures as in the two prior cleanings. The system was adjusted to run unattended, except for periodic instrument readings during the normal working hours. After 180 h of cleaning with hot [$135 \pm 5^\circ\text{F}$ ($57.2 \pm 3^\circ\text{C}$)] acidified Jaysol SS, the heater was shut off and the system allowed to cool down.

The acidified Jaysol SS was pumped from the vessel, the Tube Bundle drained and dried of alcohol, and removed from the vessel. Upon disassembly and examination, it was found that the unit was free of sodium, except in three places:

- 1) The undrilled bolts had sodium on the threads and in the cavity below the bolt, as noted in the earlier cleanings.
- 2) The drilled bolts had traces of sodium on a thread. The cavity at the base of the bolt was completely free of sodium.
- 3) A trace of sodium was noted under one of the side plates near a bolt hole.

In general, the unit was found to be the cleanest of the three cleaning operations. The cleanliness of the drilled bolts and bolt holes emphasizes the necessity of eliminating all holes or cavities with restricted access where sodium may penetrate.

The unit was shipped to Inspection for dye penetrant inspection which was witnessed by William H. Goodrich of Westinghouse. Twelve pin welds and six tube welds (three tubes selected from each end at random) were inspected and the comments were, as recorded on the Westinghouse ARD Inspection Report:

- 1) One pore of porosity was noted nearer the center of five pin welds
- 2) No indications were noted on the tube welds.

The small pores on the pin welds had been observed on the three previous inspection-precleanings, after Cleaning No. 1 and after Cleaning No. 2. These pores had been attributed to weld electrode pullout.

No cracks or other anomalies were noted during any of the four inspections.

This inspection concludes the activity on the sodium wetting/acidified alcohol cleaning/nondestructive test (NDT) inspection of the IHX Tube Bundle Mockup until further work is requested.

C. SODIUM-WATER REACTION PRODUCTS REMOVAL

1. Sodium-Water Reaction Tests

Using the test fixture and the test procedure described in the October-December 1975 Progress Report (AI-ERDA-13165), a series of sodium-water reaction tests have been conducted. Table 2 summarizes the test conditions and the observations.

As anticipated, the violence of the reaction increases with temperature and water volume. Figure 2 shows the upper half of the specimen holder after the reaction of 10 ml H_2O with sodium. The 1/4 in. (6.3 mm) thick reduced section at the center was found to be bent about 3/16 in. (4.8 mm). The reaction vessel has not been affected by the tests, and apparently could withstand the reaction of larger water samples. The limitation on the test is the strength of the capsule which contains the water (steam) at 600°F (316°C). The 10-ml water sample appears to be the maximum amount which may be contained in the pinched and welded tubing capsule now being used.

TABLE 2
SODIUM-WATER REACTION TESTS - CONDITIONS AND OBSERVATIONS

Specimen Number	Outside Diameter		Water Volume (ml)	Reaction Temperatures		Observations
	(in.)	(mm)		(°F)	(°C)	
1	0.5	12.7	1/2	225	107	No sound heard; sodium droplets on wall of vessel.
2	0.5	12.7	1	355	180	Hissing sound noted, ~1 s duration; sodium droplets on wall of vessel.
3	0.5	12.7	2	300	149	Similar sound noted, 2 to 3 s duration; about 100 g of reaction products collected.
4	1.25	31.75	7	600	316	No sound noted; large pressure surge observed; reaction products widely dispersed.
5	1.25	31.75	10	550	288	Rumbling sound noted in vessel; pressure surge observed; reaction products widely scattered; little on collection screen.

Figure 2. Specimen Holder after Sodium Reaction with 10 ml of Water at 550° F (288° C)

The optimum sample, from the standpoint of collecting a useable reaction products sample, appears at this stage in the test program to be 5 to 7 ml.

2. Reaction Rate Tests of Sodium-Water Reaction Products with Jaysol SS

The initial effort on these tests was to develop a method of producing pellets of a relatively uniform size and density. A punch was made in the laboratory which produces pellets of 0.8 to 1.0 g.

The reaction rate data from the first of the pellets shows the reaction products have a slightly higher rate than metallic sodium with Jaysol SS at 80°F (26.7°C). This difference may be caused by the less compact (more surface area) of the pellets as compared to a pure sodium pellet.

Additional tests are in progress.

D. METAL REMOVAL RATE STUDIES

Metal removal rate studies continued with the following variables and effects under evaluation:

- Reagent concentration, 0.5% to 100 %
- Temperature, room to boiling
- Carbon content of Type 304 Stainless Steel, 0.018 to 0.08%
- Pretreatment, 0.13 M KMnO_4
- Sensitizing atmospheric air, vacuum
- Additives, chelating agents
- Stirring
- Atmosphere, air or nitrogen
- Pitting or intergranular attack
- Stress corrosion cracking
- Redeposition
- Crevice corrosion

Preliminary scoping evaluations have been made of these variables and effects, except for stress corrosion cracking, and possible redeposition of some radioactive species during decontamination. The results obtained to date on these variables and effects are summarized in the following sections.

1. Test Metals Used and Sensitization Results

Nine different heats of Type 304 stainless steel with a range of carbon content covering both 304L and regular 304 were obtained for use in this activity. Sheet stock was selected in several thicknesses varying from 0.016 in. (0.41 mm) to 0.105 in. (2.67 mm). Information on the test metal specimens is summarized in Table 3.

TABLE 3
METAL SPECIMENS USED IN TEST PROGRAM

Manufacturer	Heat Number	Carbon Content (%)	Thickness	
			(in.)	(mm)
McLouth	068650	0.018	0.105	2.67
Metal Mart	18680-4	0.023	0.016	0.41
McLouth	72490	0.027	0.105	2.67
Jones & Laughlin	55183	0.030	0.050	1.27
Republic	8651438	0.065	0.025	0.64
McLouth	74821	0.070	0.105	2.67
Nisshin	53331	0.080	0.016	0.41
McLouth	74966	0.080	0.048	1.21
McLouth	74778	0.080	0.105	2.67

To assure that the metals were sensitized in a reproducible manner, it was necessary to develop a sensitization procedure and a method for evaluating the suitability of the sensitization procedure.

The standard ASTM procedure for sensitization recommends using an air or nitrogen atmosphere. Initially, an air oven was used, but the oxide film was very difficult to remove in a reproducible manner. Experiments showed that vacuum sensitization was easier to control, and this method was selected as the standard sensitization method.

A recommended ASTM sensitization test for Type 304 stainless steel is a 120-h, boiling sulfuric acid-ferric sulfate solution test. This test proved to be too severe, dissolving some of the specimens in less than 1 h. Eventually, a modified boiling nitric acid test (Huey Test) was developed which achieved reasonable reproducibility. The modifications involved changing the acid every 24 h and modifying some details of the equipment. The results obtained with the selected test metals are shown in Table 4. The large effect of metal carbon content is obvious, although it appears that some other variable is also involved in the attack by nitric acid.

2. Effect of Carbon Content on Metal Removal Rate for Promising Decontaminating Agents

An important characteristic desired in a decontaminating agent is that its rate of attack is uniform for all surfaces exposed to the reagent. Otherwise, some parts of a component might have to undergo severe attack in order to remove the required amount of metal from a more resistant part. The results presented in Table 5 show that the more promising reagents differ with respect to this characteristic, but sulfamic, aqueous acetic, and glycolic-citric acids show much less variation with metal carbon content than does nitric acid.

3. Effect of Atmosphere and Stirring

The protective film which chromium forms over the metal surface in the presence of oxygen is the primary reason that stainless steel is corrosion resistant. In "sensitized" stainless steel, the most important effect of sensitization is to reduce the effective concentration of chromium to a level which provides only marginal corrosion protection. It is not surprising, therefore, that oxygen in its various forms can have a potent effect on the metal removal rates observed in these tests. In addition, oxygen can produce two completely opposite effects. At an early stage of corrosion, it can act as an accelerator of the corrosion of iron, but later, the chromium oxide formed may retard or even stop corrosion.

The results of tests to evaluate the effect of atmosphere and stirring show that when acid solutions are exposed to air and stirred with a magnetic stirrer (which pulls air into the solution at the vortex it produces) almost all metal removal occurs in the first 24 h. When stirring by sparging nitrogen through the solution, the corrosion tends to continue over longer periods of time. However,

TABLE 4

SENSITIZATION EVALUATION
(65% Boiling Nitric Acid Test)

Heat Number	Carbon (wt %)	Thickness		Sensitization Method	Sensitization Batch	Metal Removal Rate [mil/yr (nm·s ⁻¹)]			
		(in.)	(mm)			24-h		48-h	
668650	0.018	0.105	2.67	Air	A	20	(140)	22	(154)
18680-4	0.023	0.016	0.41	Air	A	15	(105)	15	(105)
72490	0.027	0.105	2.67	Air	A	20	(140)	28	(196)
55183	0.030	0.050	1.27	Air	A	37	(259)	113	(791)
8651438	0.065	0.025	0.64	Air	A	1045	(7315)	1616	(11312)
74821	0.070	0.105	2.67	Vacuum	B	411	(2877)	1402	(9814)
				Vacuum	C	331	(2317)	1603	(11221)
				Vacuum	C	310	(2170)	981	(6867)
				Vacuum	C	458	(3206)	1296	(9072)
				Air	A	922	(6454)	2443	(1710)
53331	0.080	0.016	0.41	Air	A	210	(1470)	974	(6818)
				Vacuum	B	377	(2639)	1426	(9982)
74966	0.080	0.048	1.22	Vacuum	B	934	(6538)	2100	(14700)
				Air	A	1215	(8505)	2202	(15414)
74778	0.080	0.105	2.67	Air	A	930	(6510)	3037	(21259)

TABLE 5
EFFECT OF CARBON IN TYPE 304 STAINLESS STEEL ON 24-HR METAL
REMOVAL RATE FOR VARIOUS REAGENTS

Reagent	Carbon Content (%)					
	0.018		0.065		0.08	
	Removal Rate [mil/yr (nm·s ⁻¹)]					
2.5% Glycolic Acid at 70°C (158°F)*	—	(-)	0	(0)	0	(0)
3.5% Glycolic at 70°C (158°F)*	—	(-)	0	(0)	0	(0)
5.0% Glycolic at 70°C (158°F)*	—	(-)	87	(609)	1094	(7658)
5.0% Glycolic + 0.13 M KMnO ₄ at 70°C (158°F)*	—	(-)	144	(1008)	785	(5495)
2.5% Glycolic + 2.5% Citric at 70°C (158°F)*	82	(574)	74 [†]	(518)	454	(3178)
2.5% Glycolic + 2.5% Citric + 0.13 M KMnO ₄ at 70°C (158°F)*	—	(-)	168	(1176)	1012	(7084)
50% Acetic Acid at 70°C (158°F)*	—	(-)	214	(1498)	775	(5425)
Boiling 90% Acetic Acid	64	(448)	77 [†]	(539)	77	(539)
Boiling Acetic, 118°C (244°F)	1	(7)	48	(336)	56	(392)
Boiling 30% Acetic + 5% Formic	—	(-)	50	(350)	482	(3374)
1% Sulfamic Acid at 70°C (158°F)*	179	(1253)	219	(1533)	279	(1953)
1% Sulfamic + 0.13 M KMnO ₄ at 70°C (158°F)*	—	(-)	249	(1743)	687	(4809)
Boiling 65% Nitric Acid	19	(63)	1045	(7315)	934	(6538)

*Magnetic stirring, air atmosphere

†0.07% Carbon

a very slight amount of air leakage into the system can often stop the corrosion. Results which illustrate this effect for one reagent tested are shown in Table 6. It is clear from these data that oxygen control can be very important in the decontamination process.

4. Effect of Temperature and Concentration

Both temperature and reagent concentration are important variables in metal removal, but their effects are not linear. In fact, both variables may produce a maximum rate of removal at some point over the range of values under consideration. The magnitude of both effects varies widely for the different reagents, and generalizations are not too useful.

No promising reagent showed any appreciable attack below 70°C (158°F). This temperature may be considered, therefore, a minimum process temperature. Many reagents are most effective at the boiling point, and 118°C (247°F) was the highest temperature required for a promising reagent. Consequently, it is recommended that future designs incorporate enough heating capability to attain this temperature.

Some reagents have a maximum metal removal rate at an intermediate temperature, showing lower values at both higher and lower temperatures. This is illustrated in Table 7 for acetic acid solutions. At 80°C (176°F) the rate of metal removal reaches a maximum for a 30% acetic-5% formic acid solution. The reason for the rate drop at 101°C (214°F) is believed to be the lower solubility of oxygen in the solution at this higher temperature. The increase in rate produced by increasing the temperature from 70°C to 80°C (158°F to 176°F) is the normal thermodynamic effect of temperature.

The effect of acetic acid concentration in the range shown in Table 7 is normal. However, at higher concentrations the metal removal rate drops, as shown in Table 8. As will be shown later, the rate drops still more in anhydrous acetic acid, even at temperatures as high as 118°C (244°F).

The curve of metal removal rate vs concentration differs considerably in shape and magnitude for each of the promising reagents, so plant designs may be affected in terms of storage capacity, mixing, waste disposal, etc.

TABLE 6

EFFECT OF STIRRING 30 WT % ACETIC ACID SOLUTIONS AT 70°C
(Vacuum Sensitization, No Pretreatment)

Heat Number	Carbon (wt %)	Additive (wt %)	Metal Removal Rate [mil/yr (nm·s ⁻¹)]									
			24-h		48-h		72-h		96-h		120-h	
NITROGEN SPARGED												
53331	0.08	None	4	(28)	10	(70)	32	(224)	24	(168)	24	(168)
		Formic (5.0)	213	(1491)	128	(896)	130	(910)	120	(840)	120	(840)
74821	0.07	None	55	(385)	51	(357)	1	(7)	0	(0)	0	(0)
		Formic (5.0)	39	(273)	69	(483)	67	(469)	59	(413)	54	(378)
MAGNETIC STIRRING												
53331	0.08	None	317	(2219)	6	(42)	0	(0)	0	(0)	0	(0)
		Formic (5.0)	55	(385)	1		0		0		0	
74821	0.07	Formic	81	(567)	189	(1323)	3	(21)	0	(0)	0	(0)

TABLE 7

EFFECT OF TEMPERATURE AND CONCENTRATION FOR ACETIC ACID SOLUTIONS
(Magnetic Stirrers, Heat Number 53331, Carbon 0.08 wt %, No Pretreatment)

Concentration (wt %)	Temperature		Additive (wt %)	Sensitization Method	Metal Removal Rate [mil/yr (nm·s ⁻¹)]				
	(°C)	(°F)			24 h	48 h	72 h	96 h	120 h
15	49	120	None	Air	0	0	0	0	0
30	49	120	Formic (5.0)	Air	0	0	0	0	0
50	49	120	None	Air	0	0	0	0	0
75	49	120	None	Air	0	0	0	0	0
50	70	158	None	Air	775 (5425)	70 (490)	2 (14)	0	0
30	70	158	None	Vacuum	371 (2597)	6 (42)	0	0	0
50	70	158	None	Vacuum	365 (2555)	7 (49)	0	0	0
30	80	176	Formic (5.0)	Air	1478 (10346)	508 (3556)	341 (2387)	4 (28)	0
30	80	176	Formic (5.0)	Vacuum	1371 (9597)	45 (315)	0	0	0
30	101	214	Formic (5.0)*	Air	482 (3374)	258 (1806)	263 (1841)	0	0

*Boiling

TABLE 8

EFFECT OF CONCENTRATION OF ACETIC ACID

Concen- tration (wt %)	Temper- ature (C°)	Additive (wt %)	Pre- Treatment	Metal Removal Rate [mil/yr (nm·s ⁻¹)]				
				24 h	48 h	72 h	96 h	120 h
Magnetic Stirrers, Heat Number 74966, 0.08% Carbon, Vacuum Sensitized								
30	Boiling	Formic (5.0)	KMnO ₄	126 (882)	97 (679)	93 (651)	71 (497)	71 (497)
30	Boiling	Formic (5.0)	None	102 (714)	92 (644)	79 (553)	51 (357)	51 (357)
90	Boiling	None	None	77 (539)	55 (385)	50 (350)	13 (91)	13 (91)
Magnetic Stirrers, Heat Number 74821, 0.07% Carbon, Vacuum Sensitized								
30	70 (158°F)	Formic (5.0)	None	81 (567)	189 (1323)	3 (21)	0	0
30	70 (158°F)	Formic (5.0)	KMnO ₄	101 (707)	92 (644)	4 (28)	0	0
30*	Boiling	Formic (5.0)	None	161 (1127)	154 (1078)	165 (1155)	145 (1015)	-
30	Boiling	Formic (5.0)	None	129 (903)	99 (693)	128 (896)	122 (854)	115 (805)
30	Boiling	Formic (5.0)	KMnO ₄	126 (882)	93 (651)	116 (812)	114 (798)	124 (868)
90	Boiling	None	None	29 (203)	34 (238)	20 (140)	0	0

*Metal specimen was air sensitized

5. Additives, Chelating Agents and Pretreatment

All primary metal removal agents evaluated to date exhibit some potentially undesirable effect which might be minimized by the use of an additive. The addition of chelating agents is a particularly attractive idea, since such agents have the potential of increasing the rate of metal solution and of preventing the redeposition of unstable compounds. In decontamination technology as developed for water reactors, a pretreatment with potassium permanganate has been found to be particularly beneficial.

A considerable number of conventional metal chelating agents were tested as additives, but all, except citric, gluconic, tartaric and Kojic acids, were too insoluble in strong acid solutions. Citric acid is the most cost-effective in this latter group, and merited the most evaluation.

Another additive, discovered in the course of the work, which shows a promising effect is hydrogen peroxide. It exhibited the ability at extremely low concentrations, to halt the attack of all reagents in which it was tested. Since small amounts of residual acids left in crevices at the end of the process could cause damaging crevice corrosion, the addition of a small amount of hydrogen peroxide at the end of decontamination treatment may protect the decontaminated part from crevice corrosion during drying and subsequent storage. It is believed that the peroxide enables the metal surfaces which have been depleted in chromium by sensitization to utilize the remaining chromium more effectively so as to reform a protective film.

Pretreatment of the metal test specimens with an alkaline permanganate solution, similar to that used in the decontamination of water reactor components, nearly always produced a significant effect on metal removal rate, sometimes slowing the rate and sometimes accelerating it. Since manganese is the radioactive isotope which presents the major decontamination problem, it is not clear whether a permanganate treatment is desirable. In view of the complex action of permanganate it is recommended that it receive no further evaluation until radioactive specimens are available to allow true decontamination measurements to be made.

6. Stress Corrosion Cracking, Pitting and Intergranular Corrosion

Evidence of pitting and intergranular corrosion was looked for in all metal removal screening tests. Stress corrosion cracking is scheduled for investigation using the deposition loop during FY 77.

Making quantitative measurements of pitting tendency is an extremely difficult technique, since the number of pits, their depth and characteristic shape, varies considerably for different reagents, reagent temperature, and concentrations of reagent. None of the reagents tested yielded metal samples which were free of pitting and which also produced the minimum acceptable metal removal depth. However, the more promising reagents can produce the desired metal removal with pits having a depth of less than 1 mil (0.025 mm).

Intergranular corrosion was not observed in the screening tests for any of the recommended reagents and conditions, but several of the unpromising reagents, discussed later in this report, do produce intergranular corrosion. It will be necessary to make more extensive investigation of this potentially serious problem during more detailed process development phase of work.

7. Unpromising Reagents

A summary of the conclusions regarding unpromising reagents and additives is given in Table 9. A substantial number of individual test results form the basis of these conclusions. Most of these reagents are clearly unsuitable for use in a decontamination process for LMFBR components, based on that data accumulated during the program. However, maleic, gluconic and tartaric acid are potentially desirable additives, or possibly useful as the primary metal removal agent. In other words, these acids were eliminated more due to the time limitations of the immediate program than on the basis of intrinsic lack of merit.

Similarly, hydrofluoric and perchloric acids were eliminated because they are halogen-based acids, which, as a class, are widely considered to be undesirable in LMFBR applications. However, it has not been established that all acids of this broad class are undesirable. Either of these two acids may deserve additional consideration if they become acceptable for use.

The elimination of many commercial chelating agents merits discussion. Chelating agents are widely used with considerable success in decontamination applications where radioactive metal ions are present. Most present applications involve solutions which are only slightly acid, if at all. For LMFBR applications, where surface metal removal is a requirement, acid solutions with a pH below 2 are necessary.

TABLE 9
INEFFECTIVE OR UNPROMISING REAGENTS

Reagent or Additive	Result	Evaluation
Nitric Acid	Intergranular attack	Undesirable effect
Oxalic Acid	Insoluble coating on metal	Undesirable effect
Phosphoric Acid	Low removal rate	Other effects also unfavorable
Phthalic Acid	Low removal rate	Solubility too low
Chelating Agents	Reduction in removal	Low solubility in acid solution
SO ₂	Severe pitting	Undesirable effect
Sulfuric Acid	Severe pitting	Undesirable effect
Ammonium Carbonates	Low removal rate	Can't be increased by higher temperature
Hydrofluoric Acid	Satisfactory metal removal	Halogen based acids are undesirable
Perchloric Acid	Satisfactory metal removal	Same as above
Maleic Acid	Satisfactory metal removal	Moderately expensive
Gluconic Acid	Low removal rate	Undesirable effect
Tartaric Acid	Low removal rate	Undesirable effect
Aluminum Nitrate	Minimal effect	No advantage to use

Most of the commercial chelating agents have low solubility at this pH. Only the acidic chelating agents (citric, gluconic, tartaric and Kojic acids) are useful, and of these, only citric acid was investigated extensively, because it was judged to have a large cost-effectiveness advantage over the other acidic chelating agents.

8. Effective Decontaminating Reagents

The initial criteria for an effective decontaminating agent were established jointly by HEDL and AI, taking into consideration the then existing knowledge of manganese diffusion in sodium loops and an engineering assumption concerning acceptable process time and conditions. As a result, the following criteria were established as a guide in metal removal tests:

- 1) About 0.4 mil (0.01 mm) of metal would need to be removed
- 2) A reasonable process time was 7 days
- 3) Consequently, the minimum acceptable metal removal rate per 24 h was 20 mil/yr ($1.5 \times 10^{-6} \text{ ms}^{-1}$)
- 4) Excessively high metal removal rates, $>500 \text{ mil/yr}$ ($37.5 \times 10^{-6} \text{ ms}^{-1}$) were to be avoided
- 5) Excessive pitting and intergranular corrosion would be a sufficient basis to eliminate reagents from consideration.

Over 350 metal removal tests have been run and a summary of all data is contained in Tables 10 to 17. From these data the following reagents were selected as effective decontaminating agents, since they meet the established criteria and will be the reference reagents in the process development phase of this program. These reagents are acetic acid, both anhydrous and aqueous solutions, glycolic-citric acid mixtures and sulfamic acid.

Data which led to the selection of these reagents are shown in Table 18. Also tabulated are data on an acetic-formic acid mixture and citric acid, which meet some criteria but were eliminated as reference reagents in a final evaluation because of excessive pitting.

Concentrations of 80 to 95% acetic acid in the aqueous solutions are considered promising for future evaluation. Lower concentrations tend to cause excessive pitting. Anhydrous acetic acid is considered to be quite promising. Included in this category is commercial glacial acetic acid and glacial acetic acid to which acetic anhydride has been added to reduce its water content below the 0.4% level of commercial acid.

Glycolic acid (HOCH_2COOH) is hydroxyacetic acid, differing only from acetic acid by having an OH group substituted for a hydrogen atom, causing it to be a considerably stronger acid than acetic acid. Glycolic acid could be suitable for use alone, but it is quite compatible with another hydroxy acid which is a good commercial chelating agent, citric acid. Since Mn^{54} is the radioactive isotope which causes the major decontamination problem in LMFBR components, its chemistry may become critically important in decontamination. It is well

TABLE 10
METAL REMOVAL RESULTS GLACIAL ACETIC ACID, BOILING
118°C (244°F)

Metal Heat Number	Carbon (wt %)	Sensitization Method	Pre-treatment	Additive	Metal Removal Rate (mil/yr)*					
					24 h	48 h	72 h	96 h	120 h	144 h
53331	0.08	Air	None	None	56	52	48	37	—	—
53331	0.08	Air	None	Acetic Anhydrous	114	196	34	34	48	34
53331	0.08	Air	KMnO ₄	None	138	47	3	1	1	1
53331	0.08	Vacuum	KMnO ₄	None	150	261	261	261	228	32
53331	0.08	Vacuum	None	None	167	196	209	127	107	81
53331	0.08	Air	Vapor	Acetic Anhydrous	36	16	13	5	7	6
8651438	0.065	Vacuum	None	None	14	11	5	0	0	0
8651438	0.065	Vacuum	KMnO ₄	None	21	21	21	0	0	0
8651438	0.065	Vacuum	None	None	13	10	10	10	0	0
8651438	0.065	Air	None	None	48	11	1	0	0	0
8651438	0.065	Air	None	Acetic Anhydrous	39	18	18	18	0	0
74821	0.07	Air	None	None	46	32	4	3	3	0
74821	0.07	Air	None	None	34	48	1	1	0	—
74821	0.07	Air	KMnO ₄	None	57	59	10	1	1	—
74821	0.07	Vacuum(A)†	None	None	75	58	52	2	2	2
74821	0.07	Vacuum	KMnO ₄	None	53	42	42	42	0	0
74966	0.08	Air	KMnO ₄	None	40	34	36	44	23	23
74966	0.08	Air	None	None	41	28	26	29	29	29
74966	0.08	Vacuum	None	None	32	8	7	12	12	12

*1 mil/yr = 7 nm·s⁻¹

† Batch No.

TABLE 11
METAL REMOVAL RATES
ACETIC ACID SOLUTIONS
(Magnetic Stirrers)

Heat Number	Carbon (wt %)	Concentration (wt %)	Temperature		Additive (wt %)	Pre- Treatment	Sensitization Method	Metal Removal Rate (mil/yr)				
			(C°)	(F°)				24 h	48 h	72 h	96 h	120
53331	0.08	15	49	120	None	None	Air	0	0	0	0	0
		30	49	120	Formic (5.0)	None	Air	0	0	0	0	0
		50	49	120	None	None	Air	0	0	0	0	0
		75	49	120	None	None	Air	0	0	0	0	0
		50	70	158	Citric (5.0)	KMnO ₄	Air	0	0	0	0	0
		50	70	158	None	KMnO ₄	Air	39	100	4	0	0
		50	70	158	None	None	Air	775	70	2	0	0
		50	70	158	Citric (5.0)	None	Air	0	0	0	0	0
		30	70	158	Formic (5.0)	None	Vacuum	55	1	0	0	0
		30	70	158	None	None	Vacuum	371	6	0	0	0
		50	70	158	None	None	Vacuum	365	7	0	0	0
		30	Boiling		Formic (5.0)	None	Air	482	258	263	0	0
		30	80	176	Formic (5.0)	None	Air	1478	508	341	4	0
		30	80	176	Formic (5.0)	None	Vacuum	1371	45	0	0	0

* 1 mil/yr = 7 nm·5⁻¹

TABLE 12
METAL REMOVAL RATES
ACETIC ACID SOLUTIONS
(Magnetic Stirrers)

Heat Number	Carbon (wt %)	Concentration (wt %)	Temperature (C°)	Additive (wt %)	Pre-Treatment	Sensitization Method	Metal Removal Rate (mil/yr)*				
							24 h	48 h	72 h	96 h	120 h
74966	0.08	30	Boiling	Formic (5.0)	KMnO ₄	Vacuum	126	97	92	71	71
		30	Boiling	Formic (5.0)	None	Vacuum	102	92	79	51	51
		90	Boiling	None	None	Vacuum	77	55	50	13	13
74821	0.07	30	70 (158°F)	Formic (5.0)	None	Vacuum	81	189	3	0	0
		30	70 (158°F)	Formic (5.0)	KMnO ₄	Vacuum	101	92	4	0	0
		30	Boiling	Formic (5.0)	None	Air	161	154	165	145	-
		30	Boiling	Formic (5.0)	None	Vacuum	129	99	128	122	115
		30	Boiling	Formic (5.0)	KMnO ₄	Vacuum	126	93	116	114	124
		90	Boiling	None	None	Vacuum	29	34	20	0	0

* 1 mil/yr = 7 nm · 5⁻¹

TABLE 13
METAL REMOVAL RATES
ACETIC ACID SOLUTIONS
(Nitrogen Sparged)

Heat Number	Carbon (wt %)	Concentration (wt %)	Temperature		Additive (wt %)	Pre - Treatment	Sensitization Method	Metal Removal Rate (mil/yr)*				
			(C°)	(F°)				24 h	48 h	72 h	96 h	120
53331	0.08	30	70	158	None	None	Vacuum	4	10	32	24	2
		30	70	158	Formic (5.0)	None	Vacuum	213	128	130	120	120
74821	0.07	30	70	158	None	None	Vacuum	55	51	1	0	0
		30	70	158	Formic	None	Vacuum	39	69	67	59	5

* 1 mi. /yr = $7 \text{ nm} \cdot 5^{-1}$

TABLE 14

METAL REMOVAL RATE RESULTS
GLYCOLIC ACID SOLUTIONS

(Magnetic Stirring)

Heat Number	Carbon (wt %)	Concentration (wt %)	Temperature		Additive (wt %)	Pre-Treatment	Sensitization Method	Metal Removal Rate (mil/yr)*				
			(C°)	(F°)				24 h	48 h	72 h	96 h	120 h
8651438	0.065	3.5	70	158	None	None	Air	0	0	0	0	0
53331	0.08	4.25	70	158	None	None	Vacuum	0	0	0	0	0
53331	0.08	5.0	49	158	None	None	Air	119	0	0	0	0
53331	0.08	5.0	70	158	None	None	Air	1094	19	0	0	0
53331	0.08	5.0	70	158	None	KMnO ₄	Air	785	12	0	0	0
53331	0.08	5.0	70	158	None	None	Vacuum	738	6	0	0	0
8651438	0.065	5.0	70	158	None	None	Air	87	0	0	0	0
53331	0.08	4.25	70	158	None	None	Vacuum	792	12	0	0	0

* 1 mil/yr = 7 nm · 5⁻¹

TABLE 15
METAL REMOVAL RATE RESULTS
CITRIC ACID SOLUTIONS
(Magnetic Stirrers)

Heat Number	Carbon (wt%)	Concentration (wt %)	Temperature (C°) (F°)	Additive (wt %)	Pre-Treatment	Sensitization Method	Metal Removal Rate (mil/yr)*				
							24 h	48 h	72 h	96 h	120 h
53331	0.08	10.0	49 120	None	None	Air	0	0	0	0	0
53331	0.08	10.0	49 120	Formic (5.0)	None	Air	0	0	0	0	0
53331	0.08	10.0	70 158	None	None	Air	0	0	0	0	0
53331	0.08	2.5	70 158	None	None	Air	0	0	0	0	0
53331	0.08	5.0	70 158	None	None	Air	0	0	0	0	0
53331	0.08	10.0	Boiling†	None	None	Air	142	1	0	0	0
74821	0.07	10.0	Boiling†	None	None	Vacuum	130	0	0	0	0

* 1 mil/yr = $7 \text{ nm} \cdot 5^{-1}$

† No other stirring

TABLE 16

METAL REMOVAL RATE RESULTS
GLYCOLIC-CITRIC ACID MIXTURES

(Magnetic Stirring)

Heat Number	Carbon (wt %)	Concentration (wt %)	Temperature		Additive (wt %)	Pre Treatment	Sensitization Method	Metal Removal Rate (mil/yr)*				
			(C°)	(F°)				24h	48h	72h	96h	120h
53331	0.08	2.5	70	158	Citric (5.0)	None	Air	245	2	0	0	0
53331	0.08	2.5	70	158	Citric (5.0)	None	Vacuum	640	5	1	0	0
53331	0.08	4.25	70	158	Citric (0.75)	None	Vacuum	903	443	8	0	0
53331	0.08	2.5	70	158	Citric (2.5)	KMnO ₄	Air	1012	588	dissolved		
8651438	0.065	2.5	70	158	Citric (2.5)	KMnO ₄	Air	168	10	4	0	0
8651438	0.065	2.5	70	158	Citric (2.5)	None	Air	0	0	0	0	0
53331	0.08	2.5	70	158	Citric (2.5)	KMnO ₄	Vacuum	113	1	0	0	0
53331	0.08	2.5	70	158	Citric (2.5)	None	Vacuum	1011	16	0	0	0
53331	0.08	2.5	70	158	Citric (2.5)	None	Vacuum	1746	47	0	0	0
53331	0.08	2.5	70	158	Citric (2.5)	KMnO ₄	Vacuum	500	3	1	0	0
53331	0.08	2.5	70	158	Citric (2.5)	None	Vacuum	454	5	1	0	0
74966	0.08	2.5	70	158	Citric (2.5)	KMnO ₄	Vacuum	223	4	1	0	0
74821	0.07	2.5	70	158	Citric (2.5)	None	Vacuum	125	2	1	0	0
74821	0.07	2.5	70	158	Citric (2.5)	None	Vacuum(A)**	78	1	0	0	0
74821	0.07	2.5	70	158	Citric (2.5)	None	Vacuum(A)**	210	3	1	0	0
24821	0.07	2.5	70	158	Citric (2.5)	None	Vacuum(A)**	216	4	0	0	0
74821	0.07	2.5	70	158	Citric (2.5)	KMnO ₄	Vacuum(A)**	3	0	0	0	0
74821	0.07	2.5	70	158	Citric (2.5)	KMnO ₄	Vacuum(A)**	157	2	0	0	0
74821	0.07	2.5	70	158	Citric (2.5)	†	Vacuum(A)**	247	245	6	10	0
74821	0.07	2.5	Boiling		Citric (2.5)	None	Vacuum(A)**	147	2	0	0	0
53331	0.08	2.5	70	158	Citric (2.5)	†	Vacuum(E)**	758	11	8	0	0

* 1 mil/yr = 7 nm · s⁻¹

† Nitrogen sparging

** Batch No.

TABLE 17
METAL REMOVAL RATE RESULTS
SULFAMIC ACID SOLUTIONS

(Magnetic Stirring)

Heat Number	Carbon (wt %)	Concentration (wt %)	Temperature		Additive (wt %)	Pre - Treatment	Sensitization Method	Metal Removal Rate (mil/yr)*				
			(C°)	(F°)				24 h	48 h	72 h	96 h	120 h
53331	0.08	0.5	70	158	None	None	Air	644	6	0	0	0
53331	0.08	1.0	70	158	None	None	Air	279	4	0	0	0
53331	0.08	1.0	70	158	None	KMnO ₄	Air	687	32	2	0	0
8651438	0.065	1.0	70	158	None	KMnO ₄	Air	249	4	0	0	0
8651438	0.065	1.0	70	158	None	None	Air	219	4	0	0	0
53331	0.08	1.0	70	158	None	None	Vacuum	530	6	0	0	0
8651438	0.065	1.0	70	158	None	KMnO ₄	Vacuum	99	3	0	0	0
8651438	0.065	1.0	80	176	None	KMnO ₄	Vacuum	240	1	1	1	1
74821	0.07	1.0	70	158	None	None†	Vacuum	189	174	142	14	0
53331	0.08	1.0	70	158	None	None†	Vacuum	101	99	103	86	-
53331	0.08	2.5	70	158	None	None†	Air	1987	14	1	0	1
53331	0.08	2.5	70	158	None	KMnO ₄	Air	500	2	0	0	0
53331	0.08	2.5	70	158	None	None	Air	2277	14	0	0	0
53331	0.08	2.5	70	158	Citric (5.0)	None	Air	1956	647	4	3	-
53331	0.08	5.0	49	120	None	None	Air	263	117	1	0	-
53331	0.08	5.0	49	120	None	None	Air	110	1	0	0	0
53331	1.08	5.0	70	158	None	None	Air	658	3	0	0	0
53331	0.08	5.0	70	158	None	KMnO ₄	Air	619	2	0	0	0
53331	0.08	5.0	70	158	None	None	Air	311	1	0	0	0

* 1 mil/yr = 7 nm · s⁻¹

† Nitrogen sparging for this test

TABLE 18

DATA WHICH LED TO SELECTION OF EFFECTIVE MATERIALS

Reagent	Temperature		Concentration (wt %)	Additive (wt %)	Stirring Method	Metal Heat Number	Metal Removal Rate (mil/yr)*					
	(°C)	(°F)					24 h	48 h	72 h	96 h	120 h	144 h
Sulfamic Acid	70	158	1.0	None	Magnetic	53331	279	4	0	0	0	0
Sulfamic Acid	70	158	1.0	None	Nitrogen sparging	74821	189	174	142	14	0	0
Glycolic Acid	70	158	2.5	Citric (2.5)	Magnetic	53331	454	5	0	0	0	0
Glycolic Acid	70	158	2.5	Citric (2.5)	Nitrogen sparging	74821	247	245	6	10	0	0
Glacial Acetic Acid	Boiling		100	None	None	53331	167	196	209	127	107	81
Acetic Acid	Boiling		90	None	None	74821	29	34	20	0	0	0
Acetic Acid	Boiling		30	Formic (5.0)	None	53331	482	258	263	0	0	0
Acetic Acid	Boiling		30	None	None	8651438	52	32	27	1	1	0
Citric Acid	Boiling		10	None	None	74821	130	0	0	0	0	0

*1 mil/yr = $7 \text{ nm} \cdot \text{s}^{-1}$

known that MnO_2 is practically insoluble in both acidic and basic solutions, so if the dissolved radioactive manganese is allowed to proceed to this compound during the decontamination process, it may reprecipitate on the component with little, if any, resultant decontamination. It is likely that chelating agents such as citric acid, can reduce, or perhaps prevent this reprecipitation. Consequently, glycolic-citric acid mixtures were selected as a combination reference reagent. Pure citric acid can produce good metal removal, but it causes excessive pitting under the conditions where it is effective, as will be discussed later in this report.

Sulfamic acid ($\text{NH}_2\text{SO}_3\text{H}$) is a strong inorganic acid and is widely used industrially in metal plating. It was tested under a variety of conditions with two different heats of sensitized metal, and high metal removal rates were obtained. Under many conditions excessive pitting occurred, but it was found that at a concentration of 1% and a temperature of 70°C (158°F), a reasonable rate was obtained with acceptable pitting. However, because of the complex nature of the concentration-temperature curves, the concentration and temperature selected as best are not necessarily the optimum conditions. It is expected that additional optimization tests will be required during process development. This kind of study is warranted in view of the fact that this acid shows promise of giving a uniform rate of metal removal with stainless steels having a wide range of carbon content.

9. Qualifying Tests on Candidate Decontaminating Agents

The standard screening tests on the decontaminating agents were allowed to run for 1 week. Consequently, the amount of metal removed varied widely. In order to evaluate promising reagents on an equal basis, consistent with the established criteria, it was necessary to run special qualifying tests on the reagents in which the time of immersion of the metal specimens was varied to produce as nearly equal as possible weight removal from each specimen. Based on the results of screening tests, removal times varying from 24 to 144 h were used, with the objective of removing 0.050 to 0.060 g from each metal test piece.

Another change from the standard test was to immerse three test pieces instead of one in 500 ml of solution to obtain reproducibility data, and also to raise the metal-to-solution ratio closer to the ratio which will be encountered in actual use.

Other variables which were included were the effects of atmosphere and stirring. One test of glycolic-citric acid and one of sulfamic acid was open to the atmosphere and was stirred by a glass-enclosed magnetic bar. An equivalent set of tests was run in a nitrogen atmosphere and the stirring was provided by nitrogen bubbling through the solution. Care was taken to bubble the nitrogen through the solution at the test temperature for 1 day before introducing the metal specimens in order to remove the dissolved oxygen in the solution.

The metal removal results obtained are shown in Table 19. For reference, the amount of metal removed by nitric acid on this sensitization test also is listed. The metal heat was selected as being one of the more typical of the nine metals on hand, having an above-average carbon content for Type 304 stainless steel. A metallographic examination showed a duplex structure with areas of residual cold work on the surface from the final sizing operation. The sensitization treatment promoted carbide precipitation throughout the specimen. The carbide precipitation occurred along the grain boundaries in the surface layers with limited precipitation along the slip planes. In contrast, the central section exhibited heavy carbide precipitation along slip planes in the residually cold-worked grains.

Figures 3 through 12* show the appearance of selected metal specimens from the qualifying test. The surface photographs are at a 30X magnification and the cross-sectional photographs are at a 250X magnification.

The photographs show that the metal removal was not accompanied by intergranular corrosion for any of the candidate reagents, although citric acid, 30% acetic acid and 30% acetic-5% formic acids produced an undesirable depth of pitting. The nitric acid from the sensitization test obviously produced excessive intergranular attacks as expected for this acid on fully sensitized stainless steel.

The conclusion from these tests is that glacial acetic acid, strong aqueous solutions of acetic acid, 80 to 95% acetic acid by weight, 1% sulfamic acid, and 2.5% glycolic-2.5% citric acid mixture are reagents which meet all the original criteria for the metal removal phase of the decontamination program.

*Figures 3 through 12 are grouped at the end of this Task for reader convenience.

TABLE 19

QUALIFYING TEST ON CANDIDATE DECONTAMINATING AGENTS
(Type 304 Stainless Steel, Heat Number 74821)

Reagents	Temperature		Reaction Time (h)	Metal Removed (g)		
	(°C)	(°F)		Spec. A	Spec. B	Spec. C
2.5% Glycolic Acid, 2.5% Citric Acid, Nitrogen Sparging	70	158	48	0.063	0.064	0.060
1.0% Sulfamic Acid, Nitrogen Sparging	70	158	24	0.061	0.058	0.062
2.5% Glycolic Acid, 25% Citric Acid, Magnetic Stirrer	70	158	72	0.041	0.038	0.035
1.0 Sulfamic Acid, Magnetic Stirrer	70	158	24	0.053	0.057	0.057
100% Acetic Acid	118 (Boiling)	244	144	0.016	0.017	0.019
90% Acetic Acid	Boiling		144	0.043	0.046	0.044
30% Acetic Acid	Boiling		48	0.056	0.059	0.058
30% Acetic Acid, 5% Formic Acid	Boiling		24	0.053	0.057	0.059
10% Citric Acid	Boiling		24	0.057	0.053	0.057
65% Nitric (standard sensitization test)	Boiling		48	0.868	—	—

These solutions will require additional evaluation to optimize their performance under large-scale operating conditions. They will also need to be evaluated with specimens which have surface deposits of loop corrosion products which most likely will modify their behavior as compared to clean metal specimens. Most importantly, it seems likely that the decontamination ratio will not have a direct correlation with depth of metal removed. If this proves to be true, the relative effectiveness will have to be evaluated on the basis of the selective removal of the deposited radioactive isotopes.

10. Other Additives and Pretreatment

In addition to the primary metal removal agents recommended for further development, as discussed in the preceding section, one additive, hydrogen peroxide, and one pretreatment material, potassium permanganate, produced results which also warrant additional investigation.

Hydrogen peroxide behaved as a powerful corrosion inhibitor for all metal removal agents with which it was tested. The concentration required for inhibition was found to be extremely low, below 0.1% by weight. As stated previously, at the end of the process it is extremely important to stop all corrosion, especially in crevices. It is not certain that rinsing alone can remove traces of reagent which might later contribute to crevice corrosion. It is possible that the addition of hydrogen peroxide at the end of the process may provide considerable protection from crevice corrosion by residual reagent. The discovery of this effect of hydrogen peroxide was first made during the course of this program.

The use of an alkaline solution of potassium permanganate as a pretreatment was briefly investigated during the course of the metal removal screening tests. Sufficient tests were run to show that a permanganate pretreatment produces significant changes in the metal removal rate of a number of reagents. However, the behavior of the permanganate was complex and its uniform application involved too many variables for it to be properly included within the scope of this screening program.

It is recommended that the application of permanganate as a pretreatment be thoroughly evaluated as a part of a continuing program to optimize the decontamination process using one or more of the recommended primary acid reagents.

The permanganate pretreatment may put the deposited corrosion products in an oxidation state where they are more readily removed or can be more readily chelated, minimizing redeposition on the surface of the reactor component.

11. Summary

The reference decontaminating agents are glacial acetic acid, concentrated aqueous solutions of acetic acid (80 to 95% by weight acetic acid), 1% sulfamic acid and a mixture of 2.5% glycolic acid and 2.5% citric acid. The reference additive is hydrogen peroxide and the reference pretreatment is potassium permanganate.

Over 350 metal removal tests were run in the screening phase of this program using a wide range of reagents, additives and test conditions. Many of the reagents tested gave results which fell outside the criteria under the conditions selected for the specific tests. However, it seems likely that some of these reagents might have been acceptable, if tested under other conditions.

E. DEPOSITION LOOP

The fabrication of a small loop to prepare mass transfer deposits was completed. This loop provides a deposition source at 746°C (1375°F) to produce corrosion deposits at an accelerated rate in downstream deposition sections at 566°C and 427°C (1050°F and 800°F). Each section is capable of accommodating over 100 test specimens.

IV. IMPACT ON LMFBR PROGRAMS

This program addresses itself specifically to: (1) the problems of cleaning surfaces exposed to sodium, (2) the investigation and development of the alcohol-sodium removal process and the associated process control (including reagent regeneration), (3) the preparation of procedures to direct the various sodium cleaning operations, and (4) the development of procedures and specifications for the decontamination of sodium-wetted components. This information is directly applicable to the FFTF and CRBRP activities, and the LMFBR Target Plant design program.

V. NEXT REPORT PERIOD ACTIVITIES

Tensile testing of the process reliability specimens, cleaned using the acidified alcohol, will be completed.

The sodium-water reaction tests will be continued, and reaction rate data of the products with Jaysol SS and acidified Jaysol SS will be performed.

The alcohol reprocessing activity will be completed.

Decontamination tests will be initiated using radioactive test specimens from the STCL-1 loop at HEDL. The decontaminating reagents will be those which were selected as most promising from the metal removal results reported this quarter.

Decontamination tests will also be initiated on nonradioactive specimens from the WARD loops.

The interim report on metal decontamination reagent interactions, which will summarize the results of this part of the decontamination program, will be prepared.

VI. SCHEDULE

The various activities and milestones of the tasks are shown in the following schedule.

Task 1 Activities and Milestones

DESCRIPTION	PROPOSED ACTIVITIES									
	1976				1976B	1977				
	1st Q	2nd Q	3rd Q	4th Q		1st Q	2nd Q	3rd Q	4th Q	
A. ALCOHOL-SODIUM REMOVAL PROCESS										
1. ALCOHOL ADDITIVE STUDY										
2. ALCOHOL REPROCESSING										
3. PILOT DEMONSTRATION										
4. SODIUM-WATER REACTION PRODUCTS										
B. DECONTAMINATION PROCESS										
1. CANDIDATE REFERENCE PROCESS										
2. DECONTAMINATION PROCEDURE										
3. PROCEDURE DEMONSTRATION										
C. EVAPORATIVE REMOVAL OF SODIUM										
1. UPDATE SPECIFICATION TO INCLUDE USE OF ADDITIVES										
2. DATA REPORT ON ALCOHOL REPROCESSING										
3. DEMONSTRATION REVISED PROCEDURE										
4. DEVELOP REMOVAL PROCEDURES										
5. SELECT CANDIDATE PROCESS										
6. COMPLETE INTERIM PROCEDURE										
7. INITIATE COLD TRAP RECOVERY PROCEDURE										
8. DEMONSTRATE PROCEDURE										
9. ISSUE FINAL CLEANING AND WASTE TREATMENT PROCEDURES										
10. ISSUE PROCESS SPECIFICATION										
11. FINAL REPORT										
12. ISSUE EVAPORATIVE PROCESS SPECIFICATION

Cross-Section
250X

76-M9-16-13

Figure 3. Original Metal - Heat 14821 (Unsensitized
Type 304 Stainless Steel, 0.07% C)

Surface 30X

Surface 30X

Cross-Section 250X

76-M9-16-15

Figure 4. Vacuum Sensitized Type 304 Stainless Steel (0.07% C)

Surface 30X

Surface 30X

Cross-Section 250X

76-M9-16-16

Figure 5. Boiling, 90% Acetic Acid, 6 Days (Sensitized Type 304 Stainless Steel, 0.07% C)

Surface 30X

Surface 30X

Cross-Section 250X

76-M9-16-14

Figure 6. Boiling, 100% Acetic Acid, 5 Days (Sensitized Type 304 Stainless Steel, 0.07% C)

Surface 30X

Surface 30X

Cross-Section 250X

76-M9-16-18

Figure 7. 70°C (158°F), 2.5% Glycolic, 2.5% Citric Acids, 2 Days
(Sensitized Type 304 Stainless Steel, 0.07% C)

Surface 30X

Surface 30X

Cross-Section 250X

Figure 8. 70°C (158°F), 1% Sulfamic Acid, 1 Day
(Sensitized Type 304 Stainless Steel, 0.07% C)

76-M9-16-20

Surface 30X

Surface 30X

Cross-Section 250X

76-M9-16-21

Figure 9. Boiling, 10% Citric Acid, 1 Day (Sensitized Type 304 Stainless Steel, 0.07% C)

Surface 30X

Surface 30X

Cross-Section 250X

Figure 10. Boiling, 30% Acetic Acid, 2 Days (Sensitized Type 304 Stainless Steel, 0.07% C)

76-M9-16-17

Surface 30X

Surface 30X

Cross-Section 250X

Figure 11. Boiling, 30% Acetic-5% Formic Acids, 1 Day
(Sensitized Type 304 Stainless Steel, 0.07% C)

76-M9-16-19

Surface 30X

Surface 30X

Cross-Section 250X

Figure 12. Boiling, 65% Nitric Acid, 2 Days (Sensitized Type 304 Stainless Steel, 0.07% C)

76-M9-16-22