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Program: Sodium Technology

ERDA Task: 1 - Sodium Removal and Decontamination of Components

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I. PROJECT OBJECTIVES

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MASTER

The objectives of this program are to devise, develop, test, and evaluate techniques for sodium (Na) removal from test specimens and components by the reaction of sodium with alcohol.

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

In April 1975, the objectives were expanded to include the following activities in support of the CRBRP: (1) processing of the cleaning vessel vapor effluent, (2) alcohol regeneration-separation, (3) waste materials solidification, (4) alcohol-water separation, (5) investigation of additives to the alcohol process, and (6) demonstration of the revised cleaning process; but these activities were terminated when funding changes occurred.

A new activity was initiated in the early part of May 1975, with the objective of developing a method or methods for the safe, reliable removal of Na and Na-H₂O reaction products from components without harming them, using the current alcohol process technique or a modified alcohol process.

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A decontamination program was added to Task 1 with the objective of developing well-characterized processes for removing deposited radionuclides from LMFBR primary system components to minimize radiation levels for maintenance operations.

II. MAJOR ACCOMPLISHMENTS DURING REPORT PERIOD

A. SODIUM REMOVAL-STORAGE

Twenty-four long-term storage bolt specimens which were wetted with sodium, cleaned with Dowanol/ethanol or moist nitrogen and then stored for 2 years, either in bags with no atmosphere control, or in a nitrogen-filled bell jar with 50 ppm water vapor and 50 ppm O_2 were examined.* None of the bolt specimens, regardless of the material, cleaning method or storage method, showed residues which would indicate the presence of sodium compounds, although one of the spacers (No. 6-9) did have a small deposit of white crystalline particles.

Table 1 summarizes the observations made during the examination. It is concluded that the type of storage (air or N_2 + 50 ppm H_2O and 50 ppm O_2) has little or no effect on the discoloration or rusting of the bolt, however, in general, those bolts cleaned by moist N_2 exhibited heavier discoloration and rusting than did those bolts cleaned by the alcohol process. This examination concludes the bolt storage tests.

*The results of the examination after 1 year storage are reported in AI-AEC-13138.

TABLE 1
OBSERVATIONS ON BOLT SPECIMENS AFTER TWO YEARS STORAGE

Bolt No.	Type Material	Cleaning Method		Storage Method		Comments
		Dowanol Ethanol	Moist N ₂	Air-filled Bag	N ₂ + 50 ppm H ₂ O + 50 ppm O ₂	
4-3	RDT Type 304 SS	X		X		Moderate rust on 3 threads
4-4		X		X		Shiny and clean
4-7		X			X	Small rust spots on 3 threads
4-8		X			X	Clean, minor surface discoloration
4-9		X			X	Clean, minor surface discoloration
4-10		X			X	Clean, minor surface discoloration
4-13			X	X		Rust on lower 2 threads
4-14			X	X		Moderate rust on 1/4 of lower thread
4-17			X		X	Moderate rust on 1/4 of lower thread
4-18			X		X	Moderate rust on 1/2 of lower thread
4-19			X		X	Scattered rust on lower 2 threads
4-20			X		X	Moderate rust on 1 lower thread
6-3	ASME Type 316 SS	X		X		Clean and shiny
6-4		X		X		Heavy surface oxidation on top 4 threads
6-7		X			X	Scattered spots of surface oxidation
6-8		X			X	Clean and shiny
6-9		X			X	Scattered surface discoloration. White deposits on spacer
6-10		X			X	Scattered surface discoloration
6-13			X	X		Heavy surface discoloration on lower 2 threads. Light rust in lower threads and rust on nut
6-14			X	X		Moderate rust on lower 2 threads. Light rust on 3rd and 4th threads
6-17			X		X	Heavy discoloration on bottom thread
6-18			X		X	Moderate rust on 1/2 of lower thread. Light rust on end of bolt
6-19			X		X	Light rust on bottom thread, heavy discoloration on 2nd thread
6-20			X		X	Heavy discoloration on all threads
107	RDT A286	X		X		Uniform light discoloration
108		X		X		Uniform light discoloration
111		X			X	Light discoloration
112		X			X	Moderate discoloration
113		X			X	Slight discoloration
114		X			X	Very slight discoloration
117			X	X		Heavy discoloration
118			X	X		Light rust on lower 5 threads
121			X		X	Heavy discoloration on lower 4 threads
122			X		X	Heavy discoloration on lower 3 threads
123			X		X	Moderate discoloration on lower 3 threads
124			X		X	Moderate rust on lower thread, light rust on 2nd thread, heavy discoloration on 3rd and 4th threads

B. ALCOHOL PROCESS DEVELOPMENT

1. Reaction Rate Tests - Crevice Specimens

Reaction rate testing of Jaysol SS* with sodium in 1-, 6-, and 13-mil metal crevices at various orientations continued. Table 2 summarizes the test data in matrix form.

TABLE 2
METAL CREVICE - SODIUM REMOVAL RATE
(JAYSOL SS)

Temperature (°F)	Orientation								
	Vertical			Horizontal			Inverted		
	Size (mil)								
	1	6	13	1	6	13	1	6	13
	Rate (in. /hr)								
140	0.015	0.66	2.36	0.013	0.34	1.05	0.014	0.29	0.81
120	0.013	0.275	1.07	0.0105	0.27	0.89	0.013	0.107	0.50
90	0.0026	-	-	-	-	-	0.0039	-	-
80	0.0042	0.056	0.13	0.0054	-	-	-	-	-

Orienting the crevice in the horizontal or inverted position lowers the reaction rate, and, in general, it appears that the order of reaction rates is:

vertical > horizontal > inverted.

These tests complete the planned portion of the crevice cleaning task.

*Jaysol SS is a completely denatured anhydrous ethyl alcohol, containing 85.8 vol % ethyl alcohol, 4.3 vol % methyl alcohol, 9.0 vol % isopropyl alcohol, and 0.9 vol % methyl isobutyl ketone, and is available commercially without an Internal Revenue Service User's Permit from EXXON. It is available also from Union Carbide as Anhydrol PM-4092, and from Shell Chemical as Filmcol.

2. Reaction Rate Tests - Sodium Frost

The new Teledyne Trace O₂ Analyzer was connected to the nitrogen atmosphere box. The frost retort was loaded into the box and the system was purged to ≤ 24 ppm O₂. The frost rig previously had been run for 666 hr at a sodium pool temperature of $\sim 660^{\circ}\text{F}$ and a top flange temperature of $\sim 165^{\circ}\text{F}$, and was stored for 3 months before opening.

The retort was opened and the frost deposits were a very pure white color, indicating that a majority of the sodium had been converted to oxide or hydroxide either during the test or during the long storage (Figures 1 and 2).

About two-thirds to three-quarters of the original sodium remained in the pool, whereas in the previous run under almost the same conditions, no sodium pool remained. Table 3 compares the results of the 5 runs. One difference which might have influenced the results of Run 5 was the method of argon injection. To increase the oxygen level in the retort, the argon was flowed through 20 ft of 3/16-in. ID, 1/16-in. wall thickness Tygon tubing before it was introduced into the retort. This step increased the oxygen level from ~ 10 ppm to ~ 65 ppm.

TABLE 3
SODIUM FROST TEST CONDITIONS AND RESULTS

Run No.	Sodium Pool Temperature ($^{\circ}\text{F}$)	ΔT ($^{\circ}\text{F}$)	Time (hr)	Test Results
1*	925	~ 725	220	Heavy deposits of metallic sodium on plates. Slight deposit of frost on top flange.
2*	550	~ 400	670	Light layer of frost on plates.
3*	750	~ 575	670	Heavy ($\sim 1/4$ in. thick) frost deposit.
4*	675	~ 500	670	Massive frost deposit filling upper end of retort.
5	660	~ 495	666	Moderate ($\sim 1/8$ in. thick) frost deposit - converted to oxide and hydroxide.

*Runs 1 through 4 are discussed in the FY 1975 Annual Report, AI-ERDA-13154.

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Figure 1. Heavily Oxidized
Sodium Frost

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Figure 2. Oxidized Frost
on Stainless Steel Disc

Since the pool temperature and the ΔT of Runs 4 and 5 were almost the same, the increase in oxygen level may have retarded the frost formation as well as converting the metallic frost to an "oxide" frost.

A few small pieces of frost were dropped into anhydrous Jaysol SS where they floated on the surface and reacted very fast. Some fragments sank to the bottom and bubbled slowly, whereas a few sank to the bottom and did not dissolve.

Motion pictures were taken of a frost-coated stainless steel mesh disc being immersed in and reacting with Jaysol SS. The oxide frost reacted very rapidly, disappearing in a puff — even more rapidly than the metallic sodium frost. Sparks were observed. Dark brown to black pieces of an unknown nature formed and sank to the bottom of the alcohol. No temperature readings were taken of the reactions with Jaysol SS because the frost deposits were thin and broken, etc. (Figure 2).

3. Reaction Rate Tests — Sodium Pellets

Jaysol SS is a solution of three alcohols and ketone which has been found to have a reaction rate with ~ 1 gm Na pellets of 4.5×10^{-4} gm/sec at 80°F . To better understand the role of the individual components in the reaction, the reaction rate of sodium was determined for several pure alcohols, as shown in Table 4.

The order of reactivity noted in Table 4, methanol > ethanol > 1-propanol > 2-propanol, agrees well with known organic chemistry reactivity observations.

TABLE 4
REACTION RATE OF VARIOUS
ALCOHOLS WITH SODIUM
PELLETS AT 80°F

Alcohol	Reaction Rate (gm/sec $\times 10^{-4}$)
Methanol	20.2
Ethanol	9.4
1-Propanol	4.5
2-Propanol (isopropyl alcohol)	0.028
Jaysol SS	4.5

Since Jaysol SS is about 90% high reactivity alcohol, it would be expected that its reaction rate would not be too different than the rate for ethanol. However, the presence of the 10% low reactivity isopropyl alcohol and methyl isobutyl ketone has a significant effect, lowering the rate to about one-half the rate of ethanol.

Table 5 compares the effect of an addition of 2 vol % water to Jaysol SS and to ethanol. As may be seen from these data, the 2 vol % water addition to Jaysol SS nearly triples the reaction rate, whereas the same amount of water added

TABLE 5
EFFECT OF ADDITIONS OF WATER TO JAYSOL SS AND
ETHANOL ON THE REACTION RATE WITH
SODIUM PELLETS AT 80°F

Alcohol	Water Content (vol %)	Reaction Rate (gm/sec x 10 ⁻⁴)
Jaysol SS	0	4.5
Jaysol SS	2	12.7
Jaysol SS	5	16.7
Ethanol	0	9.4
Ethanol	2	20.1

to ethanol little more than doubles the rate. These data also emphasize the necessity of maintaining strict water content control on the alcohol solutions used for sodium removal, if reproducible sodium removal rates are desired.

Table 5 also shows that the addition of 5 vol % water to the Jaysol SS increases the reaction rate, but much less significantly than the addition of 2 vol % water.

4. Additive Investigation

The reaction rates of sodium pellets with various alcohol-water-additive solutions were determined to aid in the selection of the "best" additive. Table 6 summarizes the rate data from these tests.

As is evident, there was no really significant difference among the three additives with either Jaysol SS or ethyl alcohol; but significant differences were found in the solubility of the sodium compounds formed, and on that basis Additive No. 2 was selected as the "best" additive.

TABLE 6
REACTION RATES OF SODIUM PELLETS WITH VARIOUS
ALCOHOL-ADDITIVE-WATER MIXTURES AT 80°F

Alcohol	Additive		Water (vol %)	Rate (gm/sec x 10 ⁻⁴)
	No.	Vol %		
Ethyl	1	2	-	7.3
Ethyl	2	2	-	9.8
Ethyl	3	2	-	8.5
Jaysol SS	1	2	-	6.9
Jaysol SS	2	2	-	6.8
Jaysol SS	3	2	-	5.8
Jaysol SS	2	5	-	20.8
Jaysol SS	3	5	-	8.1
Jaysol SS	2	1	1	9.6
Ethyl	2	1	1	16.1

Increasing the additive content to 5 vol % in Jaysol SS increased the reaction rate by a factor of ~3 for Additive No. 2, whereas Additive No. 3 produced little increase — the lower solubility possibly producing a blocking effect.

A 1 - 1 vol % water - Additive No. 2 solution with Jaysol SS and ethyl alcohol showed the water to have more effect on the reaction rate with sodium than did the additive.

A series of tests were made with Jaysol SS containing various water-Additive No. 2 combinations to select an optimum mixture. Table 7 shows these data for four test temperatures.

Based upon these data, the composition chosen for future cleaning operations was 1.5 vol % Additive No. 2, and up to, but preferably less than 0.5 vol % water. This composition relaxes the strict (0.2 vol % water) limit of the sodium Removal Specification, ST0110NA0021.

The solubility of the sodium compounded Additive No. 2 in anhydrous Jaysol SS was measured at 70°F as 3.5 gm Na/l or about 30 lb Na/1000 gal., indicating that, even though the solubility is much less than the solubility of sodium

TABLE 7
REACTION RATES OF SODIUM PELLETS WITH
VARIOUS JAYSOL SS - ADDITIVE NO. 2 -
WATER MIXTURES

Content (vol %)		Reaction Rates (gm/sec x 10 ⁻⁴)			
Water	Additive No. 2	80°F	100°F	120°F	140°F
0	0	4.5	6.8	15.4	23.9
0	2	6.8	13.9	17.1	33.1
2	0	12.7	21	33.1	56.7
0.5	1.5	11.2	20.6	43.3	39.8
1.0	1.0	9.6	19.5	45.4	54.6
1.5	0.5	11.3	25.2	52.8	57.5

alcoholate in Jaysol SS, it is sufficiently high to hold in solution the sodium compounds formed while cleaning future sodium-wetted and drained components.

If ethyl alcohol were to be substituted for the Jaysol SS, using the same additive-water concentrations, it could be anticipated that the reaction rate with sodium would be higher than with Jaysol SS — perhaps $13 - 14 \times 10^{-4}$ gm/sec. From visual observations, a rate of $10 - 11 \times 10^{-4}$ gm/sec appears to be an optimum rate, and to obtain this lower rate, the temperature of the solution could be reduced to $\sim 70^{\circ}\text{F}$.

5. Process Reliability and Control Using Additive Solutions

A drawing(N707000018) was prepared for a tensile bar specimen (Figure 3) which will be used to establish the effects of the Jaysol SS-Additive No.2 solution on a stressed stainless steel specimen wetted with sodium. This specimen is the same type and of the same dimensions as the specimens used for the earlier study on the removal of sodium with Jaysol SS. The earlier specimens were furnished to AI by HEDL to provide direct comparison of specimen behavior.

A single heat of Type 304 stainless steel bar, ASTM A479-72, has been procured and the specimen fabricated for test. A test plan is being prepared.

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Figure 3. Tensile Specimen for Stress Corrosion Test

C. ALCOHOL-SODIUM REMOVAL PILOT FACILITY

1. Facility Assembly

The facility assembly was completed in mid-July, and a system safety review and procedural checkout conducted. The system then was flushed with Jaysol; several minor leaks were found and corrected. The system instrumentation, and the alcohol heating system were checked out and found satisfactory.

The control room of the pilot facility (Figure 4) includes the MSA hydrogen and alcohol detection units, the differential refractometer used for sodium determination in alcohol, the temperature recorder and the gas chromatograph. Figure 5 shows the cleaning loop, consisting of the reaction vessel, the heating tank, the vapor condenser and the associated pump and piping. The outside storage area, with tanks for both fresh and used alcohol, is shown in Figure 6.

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Figure 4. Alcohol-Sodium Removal Process Control Room

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Figure 5. Alcohol-Sodium Removal Process
Cleaning Vessel and Heating Tank

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Figure 6. Alcohol-Sodium Removal Process Alcohol Storage Tanks

2. Initial Facility Operation

The first hardware cleaned in the facility was a sodium-wetted valve, supplied by HEDL, and a NaK-wetted electromagnetic pump.

The valve had been received from HEDL with welded end caps; these caps were cut from the valve in an argon-filled plastic bag. The open ends were sealed with small plastic covers, and the sealed valve and previously sealed pump placed in the loading bag of the cleaning vessel. The entire assembly was purged with nitrogen, the plastic covers removed, and the valve and pump installed in the vessel. About 250 gal. of ambient temperature ($\sim 75^{\circ}\text{F}$) Jaysol SS were pumped into the vessel, and 200 gal. were pumped into the heating tank. After 2 to 3 hr of reaction, heatup of the Jaysol SS was started at a rate of 10 to 15°F/hr until 140°F was reached.

After no evolution of hydrogen had been observed for 12 to 14 hr, the circulating pump and the heater power were shut off and the system was allowed to sit under a protective atmosphere of nitrogen over the weekend. The alcohol was then pumped from the system, the vessel was opened and the components removed. No traces of sodium or sodium-compounds (or NaK, etc.) were visible on either component.

The seal weld on the bellows housing of the valve was ground off and the bellows removed. The bellows convolutions were shiny, clean and free of sodium or its compounds (Figure 7). Residual sodium was found behind the heavy ring next to the seal weld (Figure 8). This sodium was trapped behind the tight-fitting components, and had not been removed during the cleaning cycle. Figure 9 is a schematic showing the location of the residual sodium. Since no drawing accompanied the valve which had been supplied by HEDL, knowledge of the valve internals was not available, and no allowance was made for the cleaning of a tight crevice in planning the test. This effectively points out the need to have full knowledge of the part to be cleaned, if an effective job is to be done.

3. Jaysol SS Recovery-Distillation

Chemical analysis was made of the distillate from a batch of used Jaysol SS, doped with small amounts of elements which might be found in the alcohol after

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Figure 7. Cleaned Bellows of
Sodium Valve

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Figure 8. Close-up of Cavity between Weld and
Sleeve Containing Residual Sodium

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Figure 9. Location of Residual Sodium in the Bellows Valve

cleaning a component in the primary loop of an LMFBR. Table 8 shows the results of the chemical analysis of the feed and two distillate samples. Nickel, iron, chromium and molybdenum showed at least a 200-fold decrease in the distillation, and yttrium showed at least a 50-fold decrease. It is interesting to note that significant quantities of cesium were found in the distillate, indicating the presence of a volatile cesium compound.

Gas chromatographic analyses were performed on six drums of Jaysol SS which had been used for sodium removal and then regenerated by processing through the solvent still. The results are shown in Table 9 with a sample of fresh Jaysol SS and the final sample of distillate included for comparison. These data indicate relatively minor changes in the alcohol composition as a result of the operations through which it has passed. It suggests that the reacted sodium is distributed among the three alcoholates in the same ratio as the original alcohols were present. In any event, the isopropyl alcohol is not selectively depleted as might be anticipated from the fact that it has the least soluble alcoholate.

TABLE 8
CHEMICAL ANALYSIS OF "DOPED" FEED ALCOHOL
AND DISTILLATE SAMPLES

Element Added to Feed	Feed Alcohol (ppm)	Distillate Samples	
		No. 1 (ppm)	No. 2 (ppm)
Nickel	84	<0.3	<0.3
Iron	234	0.2	0.8
Chromium	83	<0.3	<0.3
Molybdenum	81	<0.4	<0.4
Yttrium	50	<2	<2
Cesium	57	6.4	2.4

4. Temporal Effects on Heated Jaysol SS Solutions

During the laboratory tests and sodium removal operations, it has been observed that the Jaysol SS solution rapidly darkens.* Increasing the temperature accelerates the darkening. In addition, the darkened solution seems to be thicker.

A laboratory program was conducted to measure the viscosity and density of Jaysol SS and Jaysol SS plus Additive No. 2 solutions containing various amounts of sodium. Table 10 summarizes these data.

It may be seen that only minor changes in viscosity and density occur in 2 to 4 weeks heating at 140°F. However, Jaysol SS without the additive darkened, and formed medium-to-heavy sediments or precipitates, whereas the presence of the additive prevented the darkening, or at least reduced the color change to a pale yellow.

These observations confirm that during long cleaning cycles or storage after cleaning, Jaysol SS will darken, but the viscosity and density should not change significantly. Small additions of Additive No. 2 will prevent the darkening, which indicates the presence of aldehydic-type condensation products.

*AI-AEC-13132, Annual Technical Progress Report, GFY 1974

TABLE 9

ANALYSIS OF DISTILLATE OF JAYSOL SS/SODIUM
ALCOHOLATE SOLUTIONS (vol %)

Distillation Run No.	Water			Methanol		Ethanol		Isopropanol	
	Chromatograph		KF*	CSUN	AI	CSUN	AI	CSUN	AI
	CSUN†	AI	AI						
1	3.68	5.0	3.95	4.36	4.2	83.25	83.8	8.72	7.4
2	3.41	4.7	3.69	4.24	4.3	83.8	84.2	8.55	7.7
3	2.41	4.0	2.69	3.70	3.4	84.85	85.1	9.04	8.0
4	2.02	3.0	2.21	3.98	3.7	84.8	85.8	9.19	8.2
5	5.92	7.0	5.64	5.60	5.2	81.2	82.8	7.26	5.5
6	5.50	7.3	5.51	3.96	3.2	81.46	82.9	9.07	8.3
Final	28.8	24.3	24.6	0.44	3.2	63.9	63.0	6.9	4.8
Jaysol SS	0.05			4.3		85.8		9.0	

*KF = Karl Fischer

†CSUN = California State University at Northridge

TABLE 10
 VISCOSITY AND DENSITY CHANGES IN JAYSOL SS CONTAINING
 VARIOUS AMOUNTS OF WATER, ADDITIVE NO. 2,
 AND SODIUM ADDITIONS

Composition			Viscosity (cp) at 140°F After Elapsed Time (weeks)				Density (gm/ml) at 80°F After Elapsed Time (weeks)				Observations
H ₂ O (vol %)	Additive No. 2 (vol %)	Na (gm/l)									
			0	1	2	4	0	1	2	4	
0	0	0	0.0630*	0.635	0.785	†	0.780	0.775	0.780	†	Solution remained clear
0	0	5	0.780	0.795	0.833	†	0.789	0.786	0.786	†	Solution turned light brown, sediment forming
0	0	10	1.000	0.915	0.955	1.07	0.800	0.798	0.798	0.797	Solution turned a dark, blackish brown; heavy sediment on the bottom of the flask
0.5	1.5	0	0.740	0.736	0.730	0.730	0.785	0.785	0.785	0.785	Solution turned a yellowish color
0.5	1.5	5	0.930	0.860	0.860	0.862	0.795	0.787	0.787	0.787	Solution turned a pale yellowish color; slight precipitate

*Viscosity of ethanol at 140°F, 0.592 cp

†In process

5. Elastomer-Seal Compatibility

The elastomer-caustic Jaysol SS test was terminated after 115 days exposure; Table 11 summarizes the test data. The behavior of the individual elastomers is summarized as follows:

- 1) Neoprene - large weight loss and significant hardening; surface had checked (cracked) appearance
- 2) Nitrile (366Y) - large weight gain; significant softening and swelling of the liquid exposed elastomer
- 3) Nitrile (N741) - same as 366Y except less softening
- 4) EPR (559N) - slight weight loss, slight hardening
- 5) EPR (692) - essentially no change in weight or hardness
- 6) Silicone (71417) - dissolved in a few hours
- 7) Silicone (S684) - dissolved within a week
- 8) Butyl (B318) - very slight weight loss and softening.

It was concluded that the silicone elastomers should not be used with hot caustic Jaysol SS. The butyl (B318) and the EPR elastomers (559N and E692) are approved for use. The neoprene and the nitrile are useable only for short-time contact.

6. Treatment of the Alcohol-Sodium Removal Process Wastes

Exploratory tests on the fixation of the waste products from the alcohol process continued. These tests were initiated during the fiscal year in support of the CRBRP, but changes in funding have eliminated this activity for FY 1976. The current activity will complete the original matrix of tests and bring the study to a logical conclusion.

A series of tests were conducted using vermiculite as a medium to absorb the Jaysol SS which would be added to Portland cement. Figure 10 shows that about 25 ml of Jaysol SS containing 10 gm Na/l can be mixed in Portland cement yet maintain a settable mixture with a compressive strength of 1000 psi, which had been previously set as an arbitrary minimum value for purposes of comparison.

TABLE 11

COMPATIBILITY OF SOME COMMON ELASTOMERS WITH
BOILING (173°F) JAYSOL SS CONTAINING 10 gm Na/l

Elastomer	Weight (gm)				Hardness, Durometer, Shore							
					Vapor Exposed				Liquid Exposed			
	Time (days)											
	0	8	31	115	0	8	31	115	0	8	31	115
Neoprene [*]	9.9367	8.8106	8.7037	8.6299	47	59	61	76	47	64	68	74
Nitrile (336Y) [†]	3.1748	3.5809	4.0937	4.0387	70	65	60	67	70	62	49	47
Nitrile (N741) [§]	3.3231	3.9624	4.4885	4.6095	77	76	73	75	77	71	70	68
EPR (559N) [†]	3.3574	3.1598	3.1628	3.1486	68	79	74	76	68	73	77	76
EPR (E692) [§]	3.0415	3.0168	3.0246	3.0253	73	77	78	77	73	75	76	76
Silicone (71417) [†]	3.4063	1.1283	**	-	69	69	**	-	**	**	**	-
Silicone (S684) [§]	2.9246	3.9044	**	-	73	67	70	-	73	5	-	-
Butyl (B318) [§]	2.9021	2.9163	2.8963	2.8771	67	69	67	64	67	69	67	62

*Kirkhill inflatable seal

†Minnesota rubber

§Parker seal

**Dissolved

Figure 10. Effect on Strength of Portland Cement of Vermiculite-Jaysol Mixture with 10 gm Na/l Alcohol and Vermiculite Weight at 17% of Jaysol Volume

The test program then concentrated on the use of a Lumnite cement as the fixation medium. This material was selected because it exhibits higher strength, is more "forgiving" to the presence of organics, is a faster "setting" cement, and is more resistant to temperature and corrosive environments than comparable Portland cements.

Figure 11 shows that 80 ml Jaysol SS/100 ml water can be added to Lumnite cement and exceed the 1000 psi minimum. This compares to 20 to 25 ml for Portland cement.

These tests were repeated with 10 gm Na/l Jaysol SS, and 70 to 80 ml Jaysol SS/100 ml water was found to be the limit, as shown in Figure 12.

Figure 11. Effect of Jaysol on Strength of Lumnite Cement

Figure 12. Effect on Strength of Lumnite Cement of Jaysol With 10 gm Na/1l Alcohol

The GFY 1975 Annual Report showed that >40 gm sodium additive No. 2 (NaAd)/100 ml water could be added to Lumnite cement and meet the 1000-psi strength requirements. Tests then were conducted using the NaAd compound plus varying amounts of Jaysol SS to simulate the addition to Lumnite cement of the concentrated waste product containing residual alcohol. Figures 13 to 16 show the test results. It is seen that the amount of NaAd which may be added drops from >>40 gm/100 ml water at 5 wt % Jaysol SS to ~30 gm at 20 wt % Jaysol SS.

Tests with calcium acetate added to Jaysol SS as a gelling agent prior to the addition of the alcohol to the cement were completed using both Portland and Lumnite cements. Figures 17 and 18 give the compressive strengths of the "set" samples, and show that the Portland cement produces a weak material, whereas the Lumnite product is very strong.

Only about 15 ml Jaysol SS/100 ml water can be tolerated by the Portland cement, but it is estimated that 100 to 110 ml Jaysol SS can be tolerated by the Lumnite cement. Similar tests were run using Jaysol SS containing 10 gm Na/l. As shown in Figure 19, 100 to 110 ml of Jaysol SS can be tolerated by the Lumnite cement and maintain a strong, settable mixture.

Figure 13. Effect of Jaysol SS-Sodium Derivative of Additive Mixture on Strength of Lumnite Cement - 5 wt % Jaysol Added to Sodium Derivative

Figure 14. Effect of Jaysol SS-Sodium Derivative of Additive Mixture on Strength of Lumnite Cement - 10 wt % Jaysol SS Added to Sodium Derivative

Figure 15. Effect of Jaysol SS-Sodium Derivative of Additive Mixture on Strength of Lumnite Cement - 15 wt % Jaysol SS Added to Sodium Derivative

Figure 16. Effect of Jaysol SS-Sodium Derivative of Additive Mixture on Strength of Lumnite Cement - 20 wt % Jaysol SS Added to Sodium Derivative

Figure 17. Effect of Calcium Acetate-Jaysol Mixture on Strength of Portland Cement With Sufficient Acetate to Form Gel

Figure 18. Effect of Calcium Acetate-Jaysol Mixture on Strength of Lumnite Cement With Sufficient Acetate to Form Gel

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Figure 19. Effect on Strength of Lumnite Cement of Calcium Acetate-Jaysol Mixture With 10 gm Na/l Alcohol With Sufficient Acetate to Form Gel

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The results of the waste treatment task are summarized in Table 12 which shows the obvious superiority of the Lumnite cement over the Portland cement for alcohol process waste fixation, and indicates that quite large quantities of Jaysol SS and sodium alcoholate can be fixed using a calcium acetate to gel the alcohol prior to mixing with the cement.

This work completes this activity, except for a test report which is in preparation.

7. Cleaning of the IHX Tube Bundle Mockup

Cleaning of the IHX tube bundle mockup is delayed pending installation of a larger test tank in the sodium loop which will permit sodium wetting of the mockup. The test procedure involves the sodium wetting and cleaning of this assembly a total of three times.

Pre-inspection of the IHX tube bundle was completed and the plug welds dye penetrant inspected and photographed. Only several small, pit-type areas were found.

8. Sodium Removal By Alcohol Specification

Revisions were made to the process specification to provide the option for using an additive to the Jaysol SS prior to the inclusion of the process in the Sodium Removal Process Standard currently being prepared.

The AI specification document will be updated next quarter to include these revisions.

D. SODIUM-WATER REACTION PRODUCTS REMOVAL

1. Test Fixture Design and Fabrication

Design of the test fixture was completed and shop fabrication was started. The fixture is designed to inject, on demand, small quantities of water or steam into hot sodium. The sodium will be drained at different periods, and the reaction rate of the $\text{Na-H}_2\text{O}$ reaction products with Jaysol SS and Jaysol SS plus additives measured.

TABLE 12

AMOUNTS OF VARIOUS MATERIALS WHICH MAY BE ADDED TO HYDRAULIC CEMENT
AND RETAIN A SETTABLE MATERIAL WITH A MINIMUM COMPRESSIVE
STRENGTH OF 1000 psi

Materials Added		Amount in grams per 100 gm Water Added to Cement	
		Portland	Lumnite
Sodium Acetate		~30	>40
Sodium derivative of the additive	+ 5 wt % Jaysol SS	~25	>40
	+10 wt % Jaysol SS	~25	>40
	+15 wt % Jaysol SS	20-25	35-40
	+20 wt % Jaysol SS	20-25	~30
Jaysol SS		14-18	80
Jaysol SS + calcium acetate to gel		10-15	100-110
Jaysol SS + 10 gm Na/l		-	70-80
Jaysol SS + 10 gm Na/l + calcium acetate to gel		-	100-110
Still Bottoms		18-20	-
Jaysol SS + 10 gm Na/l + vermiculite binder		~25	-

2. NaOH Dissolution Tests

It was stated in the GFY 1975 Annual Report concerning the dissolution of the Na-H₂O reaction products, "It is believed that the reaction rate will vary from the high rate exhibited by the high surface area of metallic sodium frost to the slow dissolution rate of NaOH in Jaysol SS," and to establish one of the rate parameter a series of simple tests were conducted. Pellets of NaOH were exposed to water, Jaysol SS, and Jaysol SS containing 1.5 vol % additive and 0.5 vol % water under several test conditions. Table 13 summarizes the data.

TABLE 13
NaOH DISSOLUTION RATE TEST

Solution	Reaction Rates (gm/sec)		
	Flask Test, 5 Pellets NaOH in 400 ml Solution		Tube Test 1 Pellet in 20 ml solution
	Unstirred	Stirred	Unstirred
Water at 180°F	633.0×10^{-4}	542.8×10^{-4}	1.3946×10^{-4}
Jaysol SS at 140°F	2.110×10^{-4}	4.520×10^{-4}	0.02347×10^{-4}
Jaysol SS + 1.5 vol % Additive +0.5 vol % H ₂ O at 73°F	Between 0.1113×10^{-4} and 0.3577×10^{-4} (Reaction time between 7 and 22.5 hr)	0.8201×10^{-4}	0.04404×10^{-4}

Water, stirred and unstirred, at 180°F dissolves the pellets 10 to 300 times faster than Jaysol SS at 149°F, but if the pellet is placed in a long tube where access to the solute is minimized, the difference decreases to ~ 70 times. Extrapolating this behavior to NaOH in a deep crevice or crack, it could be postulated that the difference in rates would become much smaller.

The effect of Jaysol SS plus additive on the NaOH dissolution rate was conducted at room temperature, and cannot be compared directly with water. Since it is anticipated that the additive might increase the dissolution rate,

the low rates obtained can only be attributed to the effect of the lower temperature. This test will be conducted at 140°F during the next quarter.

E. DECONTAMINATION STUDIES

Effort this quarter was directed toward performing tests for screening candidate decontaminating agents and completing the design of a loop for preparing deposits for future process evaluation studies.

1. Planning and Procurement

A revised Program Plan, N707-PP-830-002, was issued August 19, outlining the program tasks and schedule of activities for GFY 76 and 77. The revised schedule and milestones are shown in Figure 20.

A Development Test Procedure "Decontamination Studies - Metal Removal Rate Tests," N707-DTP-830-004, was issued September 17, 1975. A procedure for stress corrosion testing of decontamination specimens is in final draft form.

The procurement of test equipment and supplies is complete for Task I.

2. Design and Fabrication of Loops and Test Specimens for Task II

The design of the deposition loops is completed and drawings have been released for fabrication. Tensile specimens have been ordered for use in the deposition loop and for stress corrosion testing. The stress jigs are also being fabricated.

3. Results of Screening Tests on Candidate Decontamination Solutions

The screening program is progressing on schedule, with the tests nearly complete on the original candidate reagents and additives at room temperature and 120°F. The metal removal rates obtained at 120°F are presented in Table 14.

A number of significant observations were made based on the sensitized Type 304 stainless steel test specimens used for these tests. The metal has the maximum carbon content allowed for Type 304 stainless steel, 0.08% by weight. The specimens are 0.016-in. thick and are sensitized at 1250°F for 1 hr.

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Figure 20. Revised Schedule and Milestones for GFY 1976 and 1977

TABLE 14
REMOVAL RATES - WATER SOLUTIONS OF
CANDIDATE REAGENTS AND ADDITIVES
(Sensitized Type 304 Stainless Steel, 120°F)

Reagent	Concen- tration (wt %)	Additive*	Metal Removal Rate (mil/year)					Comments
			24 hr	48 hr	72 hr	96 hr	120 hr	
Formic	5	None	68	48	0.7	-	-	Pitting
		EDTA	1	-	-	-	-	
		NTA	1	-	-	-	-	Slight pitting
Acetic	5	H ₂ O ₂	0	0	0	0	0	See text
		None	0	0	0	-	-	
		EDTA	0	0	0			
		NTA	0	0	0	-	-	
		H ₂ O ₂	0	0	0	0	0	
		HF	220	172	-	-	-	Pitting
		KA	0	0	0	-	-	
Oxalic	10	AN	0	0	0	-	-	
		None	51	0.3	1.4	-	-	
		EDTA	76	0	0	-	-	Slight pitting
		NTA	3.5	2.0	-	-	-	
		H ₂ O ₂	0	0	0	-	-	Reacted together
		HF	108	229	284	357	-	Pitting
		KA	41	169	0	0	-	Pitting
Citric	10	AN	80	0	0	0	-	Pits
		None	0	0	0	-	-	
Phthalic	Satu- rated	None	0	0	0	-	-	
Glycolic	5	None	119	0	0	0	0	Promising
Phosphoric	10	None	0	0	0	-	-	Intergranular attack
Nitric	10	None	0	0	0	-	-	
Sulfuric	1	None	279	1.2	0	0	-	Pitting
Sulfurous	5	None			See text			Completely dis- solves metal
Sulfamic	5	None	263	117	1	0	-	Promising
		EDTA	0	0	0	0	-	
		NTA	X	X	X	X	X	
		H ₂ O ₂	0	0	0	-	-	See text
		KA	39	0	X	X	X	Good surface
(NH ₄) ₂ CO ₃	20	Gl-50	1.6	0	0	1.6	-	Good surface
		EDTA	0	0	0	-	-	
		NTA	0	0	0	-	-	
		H ₂ O ₂	0	0	0	-	-	
		HF	0	0	0	-	-	
		KA	2.7	2	1	1.5	-	Good surface
		None	426	0	0	-	-	Promising if permissible
H C $\overline{O}$ ₄ †	1	None						
Al ₂ (NO ₃) ₃ 9H ₂ O	38	None	0	0	0	-	-	

* Legend

EDTA Ammonium salt of ethylene diamine tetraacetic acid
NTA Ammonium salt of nitrile triacetic acid
KA Kojic acid
AN Aluminum nitrate - nonahydrate
GL-50 50% gluconic acid
X Untested as yet
† Room temperature test only

It was observed that nitric acid did not cause any weight change during the metal removal test, but produced enough intergranular attack to cause the metal to loosen its metallic ring and become limber. Sulfurous acid completely dissolved the test specimen in less than 3 days at room temperature. Several acids produced an acceptable metal removal rate - the program criterion is a rate of 20 mil/year - but caused pitting. The most promising reagents of the original candidate materials are 5% sulfamic acid and 5% hydroxyacetic acid (glycolic). The most promising additive is hydrogen peroxide. Hydrogen peroxide can act as a corrosion inhibitor or as an accelerator and it seems to control pit formation.

Because the aqueous solutions may all have some tendency to cause stress corrosion cracking of sensitized austenitic stainless steel, it seemed desirable to evaluate the possibilities of certain undiluted organic acids. Glacial acetic acid has been tested extensively by the Welding Research Council in a field corrosion evaluation program and was one of the few reagents which caused no intergranular corrosion of any specimen of sensitized stainless steel of the 300 series.

Consequently, testing of undiluted formic, acetic and propionic acid has been initiated with and without additives, with the results to date shown in Table 15. Glacial acetic acid is a very promising reagent, producing the desired average metal removal rate without undesirable side effects which can be visually detected.

The effects of varying the water content and adding chelating agents is now under investigation. Another interesting approach is to remove the metal from the stainless steel test specimen by the vapor of anhydrous acetic acid, as noted in Table 15.

The Test Plan includes screening tests using the candidate reagents at room temperature. Only sulfurous acid caused any metal removal at room temperature and it completely dissolved the test specimen in less than 72 hr (see Table 16).

It is desirable to use a standardized and quantitative test to determine the reproducibility of the sensitization treatment, 1250°F for 1 hr, used for the

TABLE 15

METAL REMOVAL RATES OF ORGANIC ACIDS
(Sensitized Type 304 Stainless Steel)

Acid	Temperature (C°)	Impurities or Additives	Metal Removal Rate (mil/year)					Comments
			24 hr	48 hr	72 hr	96 hr	120 hr	
Formic	101	Up to 3% H ₂ O	—	—	26	76	66	Severe pitting
Propionic	141	None	30	3	3	6		Severe pitting
Propionic	118	Teflon	38	4	3	4	—	
Acetic (liquid phase)	118	0.4% H ₂ O	47	51	7			Good surface
Acetic (liquid phase)	118	1% H ₂ O	1.2	0				1% water lowered metal removal rate
Acetic (liquid phase)	118	Acetic Anhydride	76	55	106	48	113	Sufficient metal removed in 40 hr
Acetic (liquid phase)	118	Kojic Acid	39	113	1	7	86	Some pits, brown
Acetic (Vapor phase)	118	Acetic Anhydride	36	16	13	5	19	Some raised areas on surface

Type 304 stainless steel. The test selected was ASTM G28-72, which is a boiling sulfuric acid-ferric sulfate solution. This test is normally run for 120 hr but for the high carbon, thin sheet specimens the metal dissolves in a very short time. Effort to find a suitable sensitization test continues.

TABLE 16
ROOM TEMPERATURE METAL REMOVAL FROM
SENSITIZED STAINLESS STEEL

10% Oxalic Acid	}	All zero - 24 to 72 hr
Saturated Phthalic Acid		
10% H_3PO_4		
1% $HClO_4$		
38% $AN^\dagger$		
5% Sulfamic Acid		
20% NH_4HCO_3		
20% $(NH_4)_2CO_3$		
5% Formic Acid		
5% Acetic Acid		
10% Citric Acid		
5% SO_2 -Ethanol		
10% Nitric Acid		
1% Sulfuric Acid		
5% Sulfurous Acid		24 hr - 456 mil/year
		48 hr - 1514 mil/year
		72 hr - Complete dissolution

† Aluminum nitrate-nonahydrate

III. 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-glycol ether 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.

IV. NEXT REPORT PERIOD ACTIVITIES

The Sodium Removal Process Specification will be revised to include the use of an additive to the Jaysol SS.

The reprocessing of used Jaysol SS will be initiated in the Building T042 facility.

The process reliability testing using sodium-wetted, stressed tensile specimens cleaned with the Jaysol SS containing the additive will be started.

The sodium-wetted IHX tube bundle will be cleaned of sodium using Jaysol SS containing the additive.

The Na-H₂O reaction products testing will begin.

Work will continue on the early selection of a candidate decontamination process.

V. SCHEDULE

The various activities and milestones of the tasks are shown in Figure 21.

Figure 21. Task 1 Activities and Milestones