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Program: Sodium Technology

ERDA Task: 1 - Sodium Removal and Decontamination of Components

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MASTER

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I. PROJECT OBJECTIVES

The objectives of this program are to devise, develop, test, and evaluate techniques for sodium (Na) removal from test specimens and components by evaporative and local heat gun techniques, and 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) sodium-alcohol reaction chemistry and alcohol regeneration studies, (4) quality control and inspection technique development, and (5) sodium-alcohol 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 sodium-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. In May 1975, the objectives were expanded further to include the development of data on the removal of sodium-water reaction products, using the alcohol process.

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II. TECHNICAL PROGRESS DURING FISCAL YEAR 1975

The major part of the effort in GFY 1975 was directed at sodium removal process development, which included three activities:

- 1) Development of a process to remove sodium by the use of alcohol
- 2) Development of vacuum distillation as a sodium removal process
- 3) Development of a hot gas lance for the removal of sodium.

This work will terminate, early in GFY 1976, with a demonstration of the Alcohol-Sodium Removal Pilot Plant Facility and the preparation of the final revision of the process specification.

The new activities which were initiated during the last quarter of GY 1975 to:

- 1) Provide support to the CRBRP use of an alcohol process for the removal of sodium
- 2) Investigate the use of the alcohol process for the removal of sodium-water reaction products

will continue through GFY 1976.

A. SODIUM REMOVAL-STORAGE

Twelve long-term storage bolt specimens which were wetted with sodium, cleaned, and then stored (6 in bags with no atmosphere control, and 6 in an nitrogen-filled bell jar with 50 ppm water vapor and 50 ppm O_2) for 1 year, were examined. None of the bolt specimens, regardless of the material, cleaning method, or storage method exhibited residues which would indicate the presence of sodium products. However, one of the Type 304 stainless steel spacers of specimen No. 106 did have a small deposit of fine white crystalline particles. Table 1 summarizes the observations on the bolt specimens. The next group of specimens will be removed and examined in July 1975.

TABLE 1
OBSERVATIONS ON BOLT SPECIMENS AFTER 1-YEAR STORAGE

Bolt Specimen Number	Cleaning Method			Storage Method		Comments
	Type Material	Dowanol	Moist N ₂	Air-Filled Bag	N ₂ +50 ppm H ₂ O+50 ppm O ₂	
4-2	RDT Type 304 SS	X		X		Oxidation discoloration on upper 4 bolt threads
6-2	ASME Type 316 SS	X		X		Light rust spots on middle 5 threads of bolt
106	RDT A286	X		X		Two rust spots on lower threads of bolt
4-6	RDT Type 304 SS	X			X	Discoloration on upper bolt threads and rust spots on bolt shank
6-6	ASME Type 316 SS	X			X	Surface oxidation on upper 4 bolt threads
110	RDT A286	X			X	Spotty surface discoloration
4-12	RDT Type 304 SS		X	X		Few scattered rust spots on bottom 2 bolt threads
6-12	ASME Type 316 SS		X	X		Rust areas under head of bolt
116	RDT A286		X	X		Lower 3 threads of bolt lightly oxidized
4-16	RDT Type 304 SS		X		X	Rust on lower end of bolt
6-16	ASME Type 316 SS		X		X	Rust on tip of bolt, under-side of bolt head, and last 2 bolt threads
120	RDT A286		X		X	Discoloration on bolt threads

B. ALCOHOL-SODIUM REMOVAL PROCESS DEVELOPMENT

1. Alcohol Process Investigation

a. Reaction Rate Tests – Cylindrical Specimens

The measurements of the reaction rates of sodium, cast as specimens in cylindrical glass tubes, with a denatured ethanol (Jaysol SS)^{*} and Dowanol PM,[†] was initiated in FY 1974, using two AI-designed and -built test fixtures (Figures 1 and 2), and a specially developed procedure to provide dense, uniform sodium specimens. Figure 3 shows two different diameter tubes after the initial filling with sodium. The photo also shows the same size specimens after a process of remelting, recasting under vacuum, followed by directional freezing, from the bottom upward, to produce a relatively crack-free, void-free specimen. During the preparation of these specimens, three Chromel-Alumel thermocouples (0.020-in. OD, stainless steel sheathed) were installed in the sodium to measure the specimen temperature.

These instrumented specimens were installed in one of the two test fixtures, and alcohol (Jaysol SS or Dowanol PM) was introduced at the desired test temperature. The recession rate of the sodium column was measured in order to determine a reaction rate, in in./hr. Temperatures were recorded in the sodium, in the alcohol, and at the reaction interface (at each of the three thermocouple junctions). These latter temperatures, which were identified as the interface temperatures, were the maximum observed temperatures. Figure 4 shows a schematic arrangement of the specimen and the thermocouples.

The reaction rate of sodium in an 0.85-in. ID tube with Jaysol SS is shown in an Arrhenius-type plot in Figure 5, which indicates the mean recorded temperatures in the sodium and alcohol, and at the reaction interface. The maximum ΔT between the sodium-alcohol and the interface is $\sim 25^{\circ}\text{F}$, and occurs at the higher temperature tests.

^{*}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.

[†]Propylene glycol methyl ether

Figure 1. Alcohol-Sodium
Removal Vessel

6507-40416A

Figure 2. Alcohol-Sodium Reaction
Rate Apparatus

6507-40418

Figure 3. Sequence of Sodium Sample Preparation for Reaction Rate Tests

6507-40466A

Figure 4. Schematic of the Alcohol-Sodium Reaction Rate Apparatus

74-07-56-1

Figure 5. Reaction Rates of Sodium With Jaysol SS, 0.85-in. ID Cylindrical Specimen

74-07-56-2A

When the test was run with the alcohol at the maximum temperature, $\sim 160^{\circ}\text{F}$ (boiling point, $\sim 170^{\circ}\text{F}$), the peak temperature increased $\sim 10^{\circ}\text{F}$, but the reaction rate remained constant, indicating a self-controlling or self-limiting effect, probably caused by a hydrogen gas blanketing over the sodium surface, acting as a rate control mechanism. Figure 6 illustrates the results from the test.

The series of reaction rate tests was conducted on sodium and Dowanol PM, which showed the Dowanol to be $\sim 1/3$ as reactive as Jaysol SS. Figure 7 shows a comparison of the reaction rates of the two alcohols.

The effect of water additions on the reaction rate of Jaysol SS is illustrated, in Figures 8a, b, and c, for three different specimen sizes (0.375, 0.85, and 4 in. diameter). In all cases, the rate values for each size of specimen at a particular temperature agreed quite well (e. g., the reaction rates at 100°F were ~ 1.5 , 1.2 , and 1.3 in./hr, respectively, for Jaysol SS containing 5 vol % water). Figure 9 plots the relationship between the reaction rate and the vol % water for the 0.85-in. diameter specimen at several peak reaction interface temperatures. A slight decrease from the linear relationship is noted for the 20 vol % water test, where the reaction rate is very high. This decrease is probably the result of a "self-regulating" action, caused by the rapid formation of bubbles, preventing free access of the surface by the water-alcohol solution.

The effect of water additions on the reaction rates of sodium with Dowanol PM also was established for two different size specimens (Figure 10a and 10b). These values did not agree as well as the corresponding tests for Jaysol, but the water was shown to increase the reaction rate significantly.

Not all the sodium to be removed from the reactor components will be easily accessible, but may remain in cavities in various orientations. Figure 11 shows reaction rates of Jaysol SS reacting with sodium in a horizontal specimen to be the same as the rates for a vertical specimen. Rotating the 0.85-in. diameter specimen to a position 45° to the vertical, with the open end up, raised the reaction rates at the lower temperatures, but reduced the rates slightly at the higher temperatures (Figure 12a). The reason for these changes is not understood; but, since the changes were not large, no further investigation was made. However,

Figure 6. Self-Limiting Reaction of Sodium-Jaysol With Increased Temperature

Figure 7. Reaction Rates of Sodium With Jaysol SS and Dowanol PM, 0.85-in. Diameter Specimens

a. 0.375-in. Diameter Specimens

b. 0.85-in. Diameter Specimens

c. 4-in. Diameter Specimens

Figure 8. Reaction Rates of Sodium With Jaysol SS Containing Different Amounts of Water

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Figure 9. Reaction Rate of Sodium (0.85-in. diameter specimen) With Jaysol SS as a Function of Water Content and Temperature

a. 0.85-in. Diameter Specimens

b. 0.375-in. Diameter Specimens

Figure 10. Reaction Rates of Sodium With Dowanol PM Containing Different Amounts of Water

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Figure 11. Reaction Rates of Sodium With Jaysol SS, 0.85-in. Diameter Tubes, Vertical and Horizontal Attitudes

a. 0.85-in. Diameter Specimens

b. 0.375-in. Diameter Specimens

Figure 12. Reaction Rates of Sodium With Anhydrous Jaysol SS — Variation With Orientation

when similar tests were conducted on 0.375-in. diameter specimens, a similar change in rate was found to occur at almost the same temperature. In this latter case, the horizontal rate was found to be slightly lower than the vertical rate, and roughly midway between the vertical and the 45°-to-the-vertical position (Figure 12b).

Two rate tests have been conducted using 0.85-in. ID specimens in the inverted position, one with denatured ethanol at 140°F and the other with Dowanol PM at 99°F. In both cases, the reaction proceeds until a layer of hydrogen gas builds up, preventing the liquid from reaching the sodium. From that point on, the reaction proceeds as sodium vs alcohol vapor. Reaction rates were determined to be 0.11 in./hr for ethanol at 140°F during the first 10 hr. From 10 hr to 50 hr, the rate slowed to 0.018 in./hr. The rate for Dowanol PM was 0.024 in./hr for the first 18 hr at 99°F. After 18 hr, the reaction appeared to stop. Table 2 lists other reaction rate tests conducted in the inverted position.

TABLE 2
REACTION RATE OF SODIUM WITH JAYSOL SS AND DOWANOL PM
AT VARIOUS TEST CONDITIONS (Inverted Specimens)

Alcohol	Sample Diameter (in.)	Water (vol %)	Mean Sodium-Alcohol Temperature (°F)	Peak Interface Temperature (°F)	Rate (in./hr)
Jaysol SS	0.85	0	140	140	0.018
Jaysol SS	0.85	5	73	73	0.016
Jaysol SS	0.375	10	75	75	0.023
Jaysol SS	0.375	10	137	137	0.024
Dowanol PM	0.85	0	99	99	0.024

As may be seen from these data, the reaction rates are not particularly sensitive to the reaction temperature or the reacting alcohol, and probably are controlled by diffusion rates of the vapor to the sodium surface.

To demonstrate the effect of alcohol flow to the sodium surface on the reaction rate, the specimen tested in ethanol at 140°F was further tested in the same fixture, except that the flow of ethanol was directed, by a small nozzle, upward onto the sodium surface. A reaction rate of 2.69 in./hr was measured, accompanied by a peak interface temperature of 144°F. Figure 12a indicates a reaction rate of ~2.4 in./hr should be obtained with a specimen of the same diameter and same peak temperature, reacting with ethanol in the normal manner. The good correlation between the two rates indicates that the circulation of alcohol over the surface of the sodium specimen in the normal or upright position in the test fixture is very good. In other words, the turbulence produced by the rising hydrogen bubbles effectively stirs the alcohol, and prevents stagnation from occurring.

One 2-in. diameter sodium specimen, 4 in. deep, was reacted with anhydrous denatured ethanol. The reaction rate was 0.32 in./hr at a mean sodium-alcohol temperature of 78°F and a reaction interface peak temperature of 86°F. This agrees quite well with the 0.27 in./hr for a 4-in. diameter specimen under the same conditions.

An alcohol vapor - sodium reaction rate test was conducted on a sodium specimen in a 0.85-in. ID glass tube that was oriented open end up above a pool of 140°F anhydrous Jaysol SS. The observed rate was 0.0115 in./hr. Condensed drops of alcohol which fell onto the sodium were felt to contribute significantly to the reaction rate.

It was concluded from these tests that, within reasonable limits, the reaction rates of sodium with anhydrous Jaysol SS were the same for all specimen sizes from 0.375 to 4 in. ID in the horizontal and vertical orientations for each reaction interface temperature from 60 to 180°F. A modified Arrhenius Law equation was calculated for Jaysol SS:

$$R = 3.345 \times 10^{-6} \exp(-4869/T) \pm 25\%, \quad \dots (1)$$

where R is expressed in in./hr and T = °K. A similar equation was calculated for Dowanol PM:

$$R = 2.587 \times 10^{-6} \exp(-4993/T) \pm 20\% \quad \dots (2)$$

From these equations, the heat of activation for the Na-ROH reaction is ~ 2.5 Kcal/mole. It was further concluded that the reaction rates for specimens oriented 45° to the vertical were slightly lower than the rates for vertical and horizontal specimens, and that the rates for inverted specimens were considerably lower, although directional liquid flow to the inverted surfaces could be used to increase the rate to that of a normal specimen.

b. Reaction Rate Tests - Crevice Specimens

Determination of the reaction rate of sodium in crevices was initially conducted using glass specimens to visually observe what occurs during the sodium removal reaction. The specimens consisted of a standard tapered element, sealed at the bottom, a glass stopper, and three 1-mil stainless steel shims (Figure 13). The shims were placed $\sim 120^\circ$ apart, against the wall of the joint. When the element was filled with molten sodium, the stopper was pressed firmly into the tapered opening until stopped by the shims, thus producing a crevice of ~ 1 mil.

The first specimen was reacted with anhydrous denatured ethanol at $\sim 100^\circ\text{F}$ (38°C) for ~ 34 hr. About 90% of the sodium was removed from the crevice. The reaction rate was calculated to be ~ 0.03 in./hr. Additional glass specimens were tested under other conditions, as shown in Table 3, but the results appeared to be erratic, probably because the sodium did not effectively wet the glass.

The remainder of the tests were conducted using the metal crevices specimens shown in Figures 14a and b. These specimens were wetted with sodium at 1050°F for ~ 48 hr, and then reacted with Jaysol SS at several temperatures and in the vertical, horizontal, and inverted attitudes. Table 4 summarizes the test data, and Figure 15 shows two typical specimens after being pulled apart to measure the depth of sodium removal.

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.

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Figure 13. Glass Crevice Specimens

TABLE 3
REACTION RATE OF SODIUM IN GLASS CREVICE SPECIMENS

Alcohol	Water Content (wt%)	Crevice Size (mil)	Alcohol Temperature (°F)	Specimen Attitude	Reaction Rate (in./hr)
Ethanol	0.2	1	100	Vertical	0.03
Ethanol	0.2	6	140	Inverted	0.035
Ethanol	10	1	80	Vertical	0.011*

*0.025 in./hr during first 15 hr

a. Schematic

b. Photograph

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Figure 14. Metal Crevice Specimens

TABLE 4
METAL CREVICE — SODIUM REMOVAL RATE
(Jaysol SS)

Temperature (°F)	Orientation								
	Vertical			Horizontal			Inverted		
	Size (mils)								
	1	6	13	1	6	13	1	6	13
	Rate (in./hr)								
140	0.015 (250)*	0.66 (3)	2.36 (1.5)	0.013 (250)	0.34 (4)	1.05 (2)	—	0.29 (3)	0.81 (1.5)
120	0.013 (237)	0.275 (4)	1.07 (1.5)	0.0105 (237)	—	—	—	—	—
90	0.0026 (250)	—	—	—	—	—	0.0039 (250)	—	—
80	0.0042 (312)	0.056 (8)	0.13 (3)	0.0054 (312)	—	—	—	—	—

*The number in parentheses shows the hours the test was run.

Figure 15. Crevice Specimens, Jaysol SS

Three tests were run on the 1-mil crevice specimens in the vertical position at 140°F; the reaction rates were 0.016, 0.015, and 0.015 in./hr for 125, 165, and 250 hr, indicating that the removal rate is not a function of time, up to 250 hr, and with crevices nearly 4 in. deep.

The reaction rates for Jaysol SS with sodium in crevices of 1, 6, and 13 mils, and larger specimens up to 4-in. diameter, are summarized in Figure 16, which shows that, in crevices smaller than 13 mils, the reaction rates drop significantly.

The removal of sodium from shrink-fit crevices could not be accomplished using Jaysol SS. Figure 17 shows a -4 mil shrink fit after cleaning with anhydrous Jaysol SS for 158 hr at 140°F. The sodium had been removed to a depth of 1/16 in. or less.

c. Reaction Rate Tests — Bolt Specimens

The initial tests to establish the reaction rate of sodium imbedded in large bolt-spacer-nut assemblies with 0- and 1-mil gaps between parts were reported in the Annual Report for GFY 1974, AI-AEC-13132. Forty-six hours of exposure to 140°F denatured ethanol effectively cleaned the bolt specimen with the 1-mil gap, except for a small amount of sodium on the bolt threads. The assembly with 0-mil gap showed partial cleaning in denatured alcohol at 140°F after ~40 hr.

Four additional assemblies were prepared, two with 0-mil gaps, and two with 1-mil gaps between the parts. After ~100 hr of cleaning in denatured ethanol at 140°F, one specimen of each type was removed, disassembled, and examined. Both specimens were found to be clean of sodium and sodium compounds (Figure 18). The second pair, which had originally been planned for a longer exposure, was removed, and also was found to be clean.

Additional bolt specimens were prepared; and, to provide uniformity, all assemblies were torqued to 50 in.-lb. The results of the sodium removal tests are summarized in Table 5.

From these data, it is indicated that cleaning of bolt specimens with "0" or small gap (~1 mil) spacing between components is easily accomplished in 100 to 150 hr in 140°F anhydrous Jaysol SS. The difficult regions to clean are the

Figure 16. Composite Reaction Rate Data for Sodium and Anhydrous (0.2 wt% water) Jaysol SS

Figure 17. Shrink Fit (-4 mil) Specimen After Cleaning With Anhydrous Jaysol SS for 158 Hr at 140°F

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Figure 18. Bolt Specimen Cleaned of Sodium,
Using Jaysol SS, 99.5 hr at 140°F

(hr)			
	0 Gap	1-mil Gap	
40	20	90(3)*	Shut down overnight, drained
60	35	95(2)	Shut down overnight, drained, torqued
80	50	98(1)	Shut down overnight, drained, torqued
100	92(3)	90(4)	Continuous test, torqued
100	—	95(2)	Continuous test, torqued
150	80	95(2)	Continuous test, torqued

*() Indicates number of bolt threads uncleaned.

threads of the bolt and nut, where the torquing action provides areas of high contact loadings which form effective "seals" to prevent the entry of the liquid. Because of the unpredictability of the stresses, significant bolt-to-bolt variation is to be expected.

Four additional sodium-wetted bolt specimens, with 1 mil spacers and torqued to 50 in.-lb, were cleaned in ambient temperature Jaysol SS until all bubbling ceased. The bolts then were rinsed in 180°F water for 100 hr. The bolts were found to be free of sodium, and no sodium compound residues were visible, although rust spots and powdery black deposits were found between almost all of the spacers (Figure 19). These specimens demonstrate the efficiency of a hot water rinse, but also emphasize the potential rusting of sensitized stainless steel components in the water rinse.

d. Reaction Rate Tests - Sodium Frost

A sodium frost generating apparatus was designed and built to produce specimens of sodium frost for reaction rate tests. Figure 20 shows a schematic view of the apparatus. The sodium pool is in the heated base of the retort, and the sodium vaporizes and collects on the cool frost collection region.

The initial run was made with a 925°F sodium pool for 220 hr. The apparatus was transferred to the drybox, and opened under dried argon. The majority of the sodium had volatilized from the heated pool, and had collected on the horizontal discs as molten sodium, forming large plates of sodium on the discs upon freezing. A small amount of frost was found on the cover plate and some pieces, $\sim 3/8$ in. in diameter, were removed, and dropped into room temperature denatured ethanol. The frost reacted actively, but not violently, with the ethanol, indicating that no problems should be expected with the presence of sodium frost when components are cleaned with alcohol.

The frost generating apparatus was cleaned of sodium with denatured ethanol by filling the retort from the bottom. The ethanol was not circulated during the cleaning operation. A maximum temperature of 180°F was recorded which agrees well with the maximum temperature observed in the specimen tests. The apparatus was then assembled, and refilled with sodium. The heater power was lowered to give a 550°F sodium pool. The retort was opened after ~ 670 hr, and

Figure 19. Sodium Removal From Bolted Assemblies,
Using Jaysol SS and Water

Figure 20. Sodium
Frost Generating
Apparatus

a light layer of frost was found on all of the discs, the inside of the vessel, etc. No frost-alcohol reactions were tried, because it was believed the layer was too thin to give a reasonable temperature rise. The frost rig was reassembled, and the test restarted with a sodium pool temperature of 750°F. After 670 hr of operation, the apparatus was shut down, and transferred to the argon atmosphere drybox and opened. Only a small deposit of frost was found on the cover, but a heavy deposit of frost was present on the side of the vessel near the top. The lower collection discs were covered with a heavy layer of sodium (Figure 21). Each succeeding disc above it was covered with less and less metallic sodium, in the form of globules which were increasingly smaller as the top was approached. The two uppermost discs (Figure 22) were covered with a fragile sheet of metallic sodium frost which had not wet the stainless steel disc.

The reaction of the loose frost with the anhydrous Jaysol SS (Figure 23) was moderately active, similar to the reaction of Alka-Seltzer in water. A stainless sheathed, Chromel-Alumel thermocouple, 0.02-in. diameter, was inserted into several pieces of frost, prior to placing it in the alcohol. Temperature increases of 35, 44, and 57°F were measured.

Three of the instrumented frost covered discs were immersed in 300 ml of anhydrous Jaysol SS. The most common thermal behavior recorded was an initial upward jump as the frost reacted, a slight drop of ~5°F, followed by a slow climb to a peak temperature as the more solid particles of sodium reacted, and then a slow decrease in temperature. In particular, the first disc showed a rapid rise of 37°F, followed by a slight peaking, and then a temperature decrease. The second and third discs exhibited initial jumps of 22 to 24°F, a drop of ~5°F, a climb to a peak temperature which about equalled the original jump in temperature, and then a slow, linear cooling. A motion picture film was made of the frost-alcohol reaction for further detailed study.

The apparatus was cleaned of sodium and reassembled, with additional plates added along the sides of the cylinder near the top to obtain more frost specimens. One final temperature iteration was made to 675°F, and the apparatus was heated for 670 hr. When the lid of the retort was removed, the entire upper end was found to be filled with frost, with a thickness of 6 to 7 in. The frost was a spongy, porous mass of a light grey-brownish color (Figure 24).

Figure 21. Sodium Frost Test, 670 hr, 750°F, Sodium Pool

a. Uppermost Disc

b. Second Disc

Figure 22. Sodium Frost Deposits on Upper Two Discs

a. First Stage

b. Second Stage

c. Third Stage

Figure 23. Successive stages of sodium Frost Reaction with Anhydrous Jaysol SS

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Figure 24. Sodium Frost Produced by the 675°F - 670 hr Run

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Figure 25. Piece of Sodium Frost From Run No. 4, Formed on Steel Disc (No adherence), 675°F Pool Temperature, ~500°F Temperature Gradient, 670 hr

The instrumented stainless steel discs were covered with frost, but the frost did not adhere firmly to the discs (Figure 25). Samples of frost were removed from the apparatus, and 0.02-in. diameter thermocouples shoved into the mass. The frost samples were reacted with both anhydrous Jaysol SS and Dowanol PM.

The peak recorded sodium frost temperatures in eight Jaysol SS tests ranged from 150 to 211°F, and the reaction rates ranged from 0.0081 to 0.0299 gm/sec at room temperature, which was 20 to 70 times faster than the rate measured for sodium pellets in Jaysol SS. Generally, a temperature peak was observed, followed by a slow temperature decrease until the frost was completely reacted.

The peak recorded sodium frost temperatures in six Dowanol PM tests ranged from 128 to 213°F, and the reaction rates ranged from 0.0050 to 0.0066 gm/sec, which were, as expected, less than the rates measured for Jaysol SS. Generally, a temperature peak was observed, followed by a drop of 20 to 30°F, and then a second peak occurred which was 10 to 30°F below the first peak. The temperature then slowly decreased until the frost was completely reacted. In both cases, the reactions were gentle, and again resembled the action of an "Alka-Seltzer" with water. Table 6 summarizes the temperature data. Because of the non-homogeneity of the samples, wide variations in reaction rates were observed.

Frost pieces also were dipped into either Jaysol SS or Dowanol PM, and then removed from the alcohol. Bubbling continued as the "soaked-in" alcohol continued to react. Localized melting of the frost surface occurred in 6 to 8 sec. Occasionally, some molten drops fell into the alcohol, flattened and froze on impact, and then reacted slowly with the alcohol. The melting was extensive after the Jaysol SS immersion, indicating a more vigorous reaction. Frost was stored in an evacuated desiccator for further testing.

It was concluded, from these initial tests, that the reaction of sodium frost, either highly metallic or containing appreciable amounts of sodium compounds, is vigorous but not hazardous when conducted in a protective atmosphere of inert gas (nitrogen, argon, etc.). Small-to-moderate ($\leq 40^\circ\text{F}$) temperature increases were observed in the alcohol, depending upon the size of the frost sample. Peak temperatures in the sodium, up to the melting point, were observed, but the high heat capacity of the sodium and the alcohol prevented excessive temperature increases.

TABLE 6
SODIUM FROST - ALCOHOL REACTION TEMPERATURE DATA
(300 ml Alcohol Sample)

Type Alcohol	Weight of Sodium Frost Sample (g)	Initial Alcohol Temperature (°F)	Final Alcohol Temperature (°F)	Alcohol Temperature Increase (°F)	Peak Sodium Temperature (°F)	Rate (gm/sec x 10 ⁴)
Jaysol SS	1.02	—	—	—	178	133
Jaysol SS	1.82	—	142	—	211	185
Jaysol SS	1.25	87	91	4	150	—
Jaysol SS	1.85	112	148	36	171	10
Jaysol SS	0.85	95	97	2	187	80
Dowanol PM	2.65	80	120	40	184	197
Dowanol PM	0.48	130	135	5	213	31
Dowanol PM	1.60	135	160	25	193	89
Dowanol PM	1.05	86	98	12	128	57
Dowanol PM	1.85	102	110	8	169	65

e. Sodium Removal from the IVHM Mockup

A small-scale mockup of the IVHM, which incorporated two plates and numerous bolts, was fabricated by HEDL and cleaned by the Water Vapor - Nitrogen process. Upon completion of their test program, the mockup was shipped to AI for sodium removal by the Alcohol Process.

A series of four sodium removal tests was conducted. Each test cycle underwent the following procedure:

- 1) Assemble unit and torque all bolts 25 ft-lb
- 2) Wet with sodium at 1050°F, 48 hr minimum
- 3) Remove from sodium system and transfer to cleaning vessel under inert gas cover
- 4) Remove sodium by selected media
- 5) Remove from cleaning vessel
- 6) Disassemble, examine, and photograph.

Table 7 summarizes the results of the four sodium removal operations.

TABLE 7
SUMMARY - CLEANING OF THE SODIUM-WETTED IVHM MOCKUP

Run	Time (hr)	Temperature (°F)	Conditions	Results
1	140	140	Jaysol SS	Incomplete cleaning
2	200	150	Jaysol SS	Slightly greater cleaning
3	150	180	Bulk - Jaysol SS Crevices - Water	More complete cleaning; much sodium on bolts
4	145	140	Jaysol SS + 1 vol% H ₂ O and 1 vol% Additive	No improvements over Run 1

Examination of the IVHM mockup after cleaning with Jaysol SS at 140°F for 140 hr revealed the threads of many of the bolts and the mating threads in the plates to contain sodium. Sodium also was found under the narrow plate (Figure 26a).

6507-40538A

a. Run No. 1

6507-40546A

b. Run No. 2

Figure 26. Cleaning of the Sodium-Wetted IVHM Mockup
(Sheet 1 of 2)

75-MA19-53-5

c. Run No. 3

75-JU9-53-37

d. Run No. 4

Figure 26. Cleaning of the Sodium-wetted IVHM Mockup
(Sheet 2 of 2)

The mockup was cleaned, rewetted with sodium, and recleaned with Jaysol SS at 150°F for 200 hr. Some improvement was found, but the cleaning of the bolts was still incomplete (Figure 26b).

The third run was made by reacting the bulk of the sodium with ambient temperature Jaysol SS until the bubbling stopped. The Jaysol SS was replaced with water, and the IVHM was soaked at 180°F for 150 hr. Again, improvement was found, but the five bolts which entered the narrow plate from the top still were covered with large amounts of sodium. The space between the plates was almost clean (Figure 26c).

A fourth run was made, using Jaysol SS containing 1 vol % additive and 1 vol % water at 140°F for 145 hr. The appearance of the IVHM mockup was about the same as observed for Run 1, indicating that the presence of a small amount of an additive and water does not improve the cleaning efficiency of the Jaysol SS (Figure 26d).

It was concluded, from these tests, that sodium-wetted assemblies having highly torqued, medium-to-fine threaded bolts cannot be cleaned of sodium by extensive soaking in 140 to 150°F anhydrous Jaysol SS or Jaysol SS containing 1 vol % of an additive and 1 vol % H_2O , or by 180°F water in 140 to 150 hr.

It is believed that the bolt torque is a critical factor in sodium removal by either alcohol or water (i. e., the bolt deformation under high stress provides a very effective seal, preventing the entrance of the cleaning liquid). Further, it is concluded, from these tests that bolted hardware must be disassembled to insure complete removal of sodium.

f. Reaction Side Effects

A constant-temperature bath was procured and set up (Figure 27) to conduct sodium reaction rate tests on pellet specimens. These tests were planned to establish the sodium-alcohol reaction rate as a function of temperature, sodium alcoholate concentration, water content, etc.

Pellets of sodium were produced by casting a sheet of sodium in a flat dish, and cutting discs from the sheet with a brass cork borer (Figure 28).

6507-40501

Figure 27. Constant-Temperature Bath for Sodium-Alcohol Reactions

6507-40516

Figure 28. Sodium Pellets

The pellets of sodium were dropped into a flask containing ~ 300 ml of anhydrous (0.2 wt % water) denatured ethanol, and the time for the pellet to completely react was measured. Each pellet weighed ~ 1 gm.

Figure 29 shows the data recorded at 80, 100, 120, 125, and 140°F. The reaction rate is seen to drop off sharply at 3 to 4 wt % Na, and approach "zero" at ~ 6 wt % Na. If the reaction rates (extrapolated to a "zero" concentration of sodium) are plotted as a function of temperature on an Arrhenius plot, as shown in Figure 30, for anhydrous denatured ethanol, a straight line is obtained which has the same slope as the line shown in Figure 5, indicating that the change of the reaction rate with temperature is not influenced by specimen geometry. However, as described in an earlier section, orientation of the tube does influence the reaction rate of the cylindrical specimens, probably because the flow of hydrogen bubbles is altered, and it retards the flow of alcohol to the reacting interface.

Table 8 presents the reaction rate data, converted to a common basis of grams reacted per second, for the pellet and the 0.85-in. diameter rod specimen, and the relationship between the two rates. The pellet-to-rod ratio is seen to be 0.42 (as stated earlier, the slopes of the two Arrhenius plots are the same). With this value and the reaction rate for a pellet, the corresponding reaction rate, in in./hr, can be calculated for the corresponding 0.85-in. diameter cylindrical specimen. (Note: A corresponding ratio can be calculated for the 0.375-in., the 4-in., etc. specimens.)

Reaction rate tests were conducted on sodium pellets with anhydrous Jaysol SS containing 2 vol % of an additive. Figure 30 also shows the results of these rate tests. It can be seen, from this plot, that the addition of a small amount of the additive increases the reaction rate by $\sim 50\%$ at the lower temperatures tapering off to $\sim 30\%$ increase at the higher temperatures. The reaction was well controlled, and similar to the ethanol reaction, although slightly faster.

The addition of 2 vol % of an additive to the Jaysol SS helps eliminate the possibility of caustic stress corrosion cracking. The additive apparently has negligible effect on stainless steel.

Figure 29. Sodium Pellet
Reaction Rate vs
Concentration of Sodium
in Jaysol SS

Figure 30. Reaction Rates
of Sodium Pellets With
Denatured Alcohol as a
Function of Temperature

TABLE 8
RELATIONSHIP BETWEEN THE REACTION RATES OF
SODIUM PELLETS AND ROD SPECIMENS (0.85 in.
Diameter) WITH ANHYDROUS
DENATURED ETHANOL
(Jaysol SS)

Temperature (°F)	Reaction Rate (gm/sec x 10 ⁴)		Pellet-to-Rod Ratio (0.85 in. diameter)
	Pellet	Rod*	
80	4.4	10.4	0.42
100	7.6	18.3	0.42
120	13.0	32.0	0.41
140	23.0	55.0	0.42
160	35.1	87.7	0.41

* $\frac{\text{in./hr} \times 9.02 \text{ gm/in.}}{3600 \text{ sec/hr}}$, for a 0.85 in. specimen

An ethanol, denatured with methanol (4.72 vol %), ethyl acetate (4.72%), and methyl isobutyl ketone (0.94%), which is marketed as Jaysol SCS, has been reported to maintain an acidic system, by the presence of the ethyl acetate, when reacted with sodium. A supply of Jaysol SCS was obtained, but only as a solution containing 5 vol % water. The presence of the 5 vol % water increases the reaction rate significantly

The ethyl acetate apparently has the ability to act like a buffer and help control the pH of the system, although the action is slow. It was found that the addition of a very small amount of sodium immediately forms a basic medium; but, after several hours, the solution turns acidic. It was concluded, from these tests, that the ethyl acetate addition was not as advantageous as the previous addition.

A reaction rate test of Dowanol PM with sodium pellets, to establish the condition of significant rate decrease, was conducted at 120°F, using Dowanol + 2 vol % water. Figure 31 shows the test results, which indicate that the reaction rate decreases markedly at 10 gm Na/l of Dowanol PM, whereas a similar

6507-47192

Figure 31. Sodium Pellet Reaction Rate vs
Concentration of Sodium in Dowanol
PM With 2 vol % Water 49°C (120°F)

decrease did not occur until ~ 30 gm Na/l of Jaysol SS. Comparing these data with the data presented earlier on the reaction rate of sodium pellets with anhydrous Jaysol SS, it is found that the Dowanol PM plus 2 vol % water at 120°F has the same reaction rate as anhydrous Jaysol SS at 100°F. This relationship also agrees quite well for the cylindrical specimen reaction rates.

2. Pilot Cleaning Facility

a. Facility Assembly

The Pilot Cleaning Facility was assembled. All major items have been delivered and installed. The facility will be operational following the leak check and systems checkout.

b. Jaysol SS - Alcoholate - Elastomer Compatibility

An alcohol cleaning solution - elastomer compatibility test was conducted to assure that the O rings and gaskets used to seal the cleaning vessel during the sodium removal process would not be damaged.

Eight samples of various elastomers were placed in a glass flask with the lower portion of the sample covered with the Jaysol SS - alcoholate solution and the upper portion exposed to Jaysol SS vapor. Table 9 shows the hardnesses and weights after 8 and 31 days.

Based upon these observations after 1 month, it was concluded that the silicone elastomers should not be used with hot, caustic Jaysol SS. The Butyl (B318 compound) and the EPR elastomers appear to be satisfactory. The remaining elastomers appear to be usable on a "limited" basis.

c. Process Safety

An extensive review of the Occupational Health and Safety Administration (OHSA) Codes, the National Fire Codes, and other pertinent documents relative to the handling of alcohol was conducted, and an alcohol cleaning process safety report, SRR-707-830-001, "Operational Safety Report for the Cleaning of Non-Radioactive Sodium-Wetted Reactor Components with Ethyl Alcohol," was released.

TABLE 9
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	0	8	31	0	8	31
Neoprene*	9.9367	8.8106	8.7037	47	59	61	47	64	68
Nitrile (336Y)†	3.1748	3.5809	4.0937	70	65	60	70	62	49
Nitrile (N741)§	3.3231	3.9624	4.4885	77	76	73	77	71	70
EPR (559N)†	3.3574	3.1598	3.1628	68	79	74	68	73	77
EPR (E692)§	3.0415	3.0168	3.0246	73	77	78	73	75	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	67	69	67	67	69	67

*Kirkhill Inflatable Seal

†Minnesota Rubber

§Parker Seal

**Dissolved

A companion safety specification, "Preliminary Safety Specification for the Cleaning of Non-Radioactive Sodium-Wetted Reactor Components with Ethyl Alcohol," TI-707-830-007, also was released.

d. Process Specification

A preliminary alcohol cleaning process specification, "Preliminary Specification for a Sodium Removal Process Using Ethanol," TI-707-830-008, was released in September 1974. This initial draft of the specification was based upon information currently available. The specification was revised in November 1974, and released as ST0110NA0021, "Sodium Removal Using Ethanol."

3. Process Quality Control and Inspection

a. Process Control

A survey of process control instruments was conducted to define the equipment for the new, pilot cleaning facility which could be adapted and expanded for use in future, large cleaning facilities. Table 10 summarizes the results of the survey. It shows that equipment suitable for industrial application is available.

TABLE 10
INSTRUMENTS FOR CONTROL OF THE ALCOHOL PROCESS

Principle of Detection	Manufacturer
Hydrogen and/or Alcohol in Inert Gas	
Palladium membrane-ion gauge	Perkin-Elmer, Veeco, Varian
Silicone membrane - RGA mass spectrometer	Beckman, Perkin-Elmer
Thermal Conductivity	Gow Mac
Catalytic	MSA
Gas Chromatograph	Many
Semiconductor	Figaro Engineering
Water in Alcohol, Alcoholates	
Karl Fisher Reagent	Photovolt Corporation
Sodium in Alcohol	
Flame Photometer	Many
Atomic Absorbtion	Many
Specific Electrode	Orion Research
pH electrode	Many
Refractometer	Pharmacia
Oxygen in Inert Gas	
Electrolytic Cell	Westinghouse, Thermco
Fuel Cell	Teledyne
Paramagnetic Detector	Beckman
Water in Inert Gas	
Al ₂ O ₃ sensor	Panametrics
Quartz Crystal	DuPont Instruments

As a result of this survey, the following instruments were selected and procured for the sodium-Alcohol Pilot Plant Facility:

H₂ and/or Alcohol – Gas Chromatograph

Water in Alcohol – Karl Fischer apparatus

Sodium in Alcohol – Differential Refractometer

Oxygen in Inert Gas – Paramagnetic Type (high levels)
– Fuel cell (low levels)

b. Evaluation of the Karl Fischer Apparatus

Process studies have indicated that the water content of the alcohol solutions will need to be controlled at the following stations: (1) incoming alcohol, (2) alcohol after storage, and (3) alcohol after reprocessing, to provide good reaction rate control. The Karl Fischer method was chosen as ideally suited for all these applications. A Labindustries Model No. 1321 apparatus (Figure 32) was purchased for evaluation, and a program to determine the suitability of this type of apparatus for the determination of water in alcohol-alcoholates was established. It includes: (1) a laboratory evaluation program, involving making water determinations on alcohol and alcoholates over the range of operating conditions expected for the alcohol removal process, and (2) an investigation of commercially available equipment suitable for process control in an industrial plant. The investigation of the Karl Fischer method was completed, and the following observations and conclusions were made:

- 1) The Karl Fischer technique can determine water additions to alcohol solutions in increments of 0.5 mg/ml with a precision of $\pm 5\%$. The Karl Fischer technique is able to distinguish between two samples of "anhydrous" Jaysol that were 1.24 mg H₂O/ml (0.158 wt %) and 2.3 mg H₂O/ml (0.29 wt %), respectively. This indicated that the Karl Fischer technique can be used to verify that the alcohol meets anhydrous specification requirements.
- 2) Water absorption by alcohol (denatured ethyl alcohol) from the atmosphere at room temperature was 4.6×10^{-2} mg/ml-in.²-hr after 2.5 hr, decreasing to 3.3×10^{-2} mg/ml-in.²-hr in 20-1/4 hr. This test

Figure 32. Karl Fischer Apparatus

indicated both the sensitivity of the Karl Fischer apparatus in determining changes in water content and the ability of alcohol to absorb water from the atmosphere. This finding indicates care will be necessary during sampling to obtain representative results.

- 3) An alcoholate solution that had been made up with a known amount of water (50 mg/ml) and a known amount of sodium (10 gm/l) was tested, and the Karl Fischer apparatus indicated 54.6 mg/ml of water, demonstrating that the presence of sodium at the maximum anticipated process concentration does not compromise the water detection technique.
- 4) Two alcohol solutions which contained identical amounts of sodium, 43 gm/l, were tested for water content. One solution was light orange, and the other dark brown. It has been hypothesized that the color results from the condensation of resinous aldehyde compounds. The more condensation, the darker the color; and the more condensation, the more water produced in the alcoholate solutions. The Karl Fischer technique indicated that the light orange solution contained 2.63 mg H₂O/ml, which was 0.71 mg H₂O/ml less than that of the dark brown solution. Thus, this technique may possibly be used to measure the amount of water produced by these chemical reactions.

The investigation of the Karl Fischer apparatus for use as process control instrument was summarized in two reports:

- 1) OP-707-830-004, "Operational Procedure for the Measurement of Water Content of Alcohol Type Compounds," R. Bowman (January 8, 1975)
- 2) TR-707-810-007, "Effectiveness of Karl Fischer Technique in Determining Water Content of Jaysol SS," R. Bowman (January 27, 1975).

Based upon these tests and evaluation, an Automatic Karl Fischer instrument was procured for use. This instrument is automated and thus eliminates the operator judgment required by the simpler Labindustries model.

c. Inspection

A test plan for developing inspection techniques for components which have been cleaned by the alcohol process was issued as TP-707-830-004, "Special

Methods for Detecting Sodium Residues for Cleaned Reactor Components." The plan is based on the approach of making proof-of-principle tests of several chemical and instrumental techniques to establish a method of go/no-go screening for the inspection of components. Specimens which are known to have been completely cleaned and specimens which have a known sodium residue will be utilized in these studies.

d. Process Reliability and Repeatability

A major activity in the Alcohol Sodium Removal Program is an evaluation of the process with respect to its effect on the hardware being processed. The reaction of alcohol with sodium forms sodium alcoholate, a strongly alkaline compound, and trace amounts of water in the alcohol react with sodium to form caustic soda. During the cleaning process, these materials may be present at temperatures up to the boiling point of alcohol (173°F or 78°C). Furthermore, there is a possibility that a misapplication of the process could result in the deposition of significant residues of these materials on parts which would later be installed in sodium systems operating at temperatures up to 1000°F (538°C). The test procedures documented by this report simulate conditions to which parts might be exposed, both intentionally and accidentally, during and subsequent to the sodium removal operation.* Particular interest is focused on the area of caustic stress corrosion cracking, to which the sensitized austenitic stainless steels used in reactor components are known to be susceptible. For the foregoing reason, the specimens employed in this evaluation (Figure 33) were fabricated from Type 304 stainless steel, and were devised to maintain tensile stress on the tensile bar, which constitutes the significant element of the specimen assembly, during all test sequences. They were either sensitized prior to testing or attained that condition during testing.

The environments and temperatures to which the specimens were subjected were selected to simulate, as realistically as possible, those which an actual part will encounter. As regards the residues left on the parts, a worst condition, with no rinsing at all, was tested. The incorporation of a tight-fitting

*Test Procedure DTP-707-810-009, "Procedure for the Stress Corrosion Testing of Standardized Sodium Removal Specimens," October 2, 1974

sleeve over the reduced section of the tensile bar was rigorous simulation of a narrow crevice in a stressed area. It is extremely unlikely that any part in actual service will encounter, as a direct consequence of alcohol removal of sodium, any conditions more severe than those imposed by this test.

All specimens and associated hardware were fabricated by the Hanford Engineering Development Laboratories (HEDL) to their drawing, as shown in Figure 33, for testing and evaluation at AI, while similar specimens were being tested and evaluated at HEDL, as a part of their Water Vapor - Nitrogen Sodium Removal Program.

The initial 10 sets of half sleeves furnished to AI were fabricated to provide a nominal 10 mil gap between sleeve and specimen. The remainder were fabricated to provide a nominal "0" gap. Tensile specimens for the initial test series were delivered sensitized, whereas the specimens for the Group 3 specimens were delivered unsensitized, and attained a sensitized condition by their initial sodium immersion.

All specimens were identified as to the specific test and sequence, and the components were assembled as shown in Figure 33. Stress was applied to the specimens by torquing the end nuts until micrometer measurements indicated that the overall length of the tensile bar had been extended 0.0045 in. This extension was calculated by HEDL to produce a stress level equivalent to 100% of the 0.2% offset yield. For the first two sections of the test, this stress was applied immediately following specimen assembly. For the third section, it was not applied until after the specimen had been wetted with sodium at 1050°F. These assembly instructions also were supplied to HEDL to maintain uniformity between the test programs.

Four groups of specimens were tested as outlined in Figures 34 to 37. The Group 1, Group 2, and the Modified High-Caustic Residue tests were designed to simulate out-of-control alcohol-sodium removal process, such as the presence of alkaline residues, improper storage conditions, high humidity storage conditions, and combinations of these conditions. The Group 3 tests were designed to simulate an in-control alcohol-sodium removal process, and to establish the reliability of the removal process.

5 SENSITIZED AND STRESSED SPECIMENS – 10 mil SLEEVE GAP

NOTE: ALL SPECIMENS TO HEDL DRAWING H-3-37683

74-07-56-11B

Figure 34. Process Reliability and Repeatability Tests – Group 1 Specimens

10 SENSITIZED AND STRESSED SPECIMENS – 5-10 mil GAP, 5-0 mil GAP

IMMERSE 3-10 mil GAP AND 3-0 mil GAP SPECIMENS IN ETOH + 1% Na. DRY OVERNIGHT AT ROOM CONDITIONS. REMAINING 4 SPECIMENS (2-10 mil, 2-0 mil) ARE NOT IMMERSSED – USED AS CONTROLS.

4 SPECIMENS	6 SPECIMENS
2-10 mil GAP 1 TEST (NO. 211) 1 CONTROL (NO. 211C) 2-0 mil GAP 1 TEST (NO. 212) 1 CONTROL (NO. 212C) STORE AT 360°F INERT ATMOSPHERE 168 hr	<div>NO SPECIMEN</div> <div>3-10 mil GAP 2 TEST (NO. 221, 222) 1 CONTROL (NO. 222C)</div> <div>3-0 mil GAP 2 TEST (NO. 223, 224) 1 CONTROL (NO. 224C)</div> <div>STORE IN 10 ppm H₂O ROOM TEMPERATURE 168 hr</div> <div>STORE IN 50% H₂ ROOM TEMPERATURE 168 hr</div>

- HEAT IN INERT ATMOSPHERE
- IMMERSE IN Na AT 375 ± 25°F
HOLD AT 375 ± 25°F – 168 hr
- HEAT TO 600°F AT 50°F/hr
HOLD AT 600°F – 48 hr
- HEAT TO 800°F AT 50°F/hr
HOLD AT 800°F – 48 hr

- HEAT TO 1050°F AT 50°F/hr
HOLD AT 1050°F – 48 hr
- COOL TO 350°F AT 50°F/hr
REMOVE FROM SOLUTION
- REMOVE SODIUM BY ALCOHOL
PROCESS
- EVALUATE

NOTE: ALL SPECIMENS TO HEDL DRAWING H-3-37683

74-07-56-12B

Figure 35. Process Reliability and Repeatability Tests – Group 2 Specimens

Figure 36. Modified High-Caustic Residue Tests

(UNSENSITIZED AND UNSTRESSED)

- HEAT TO 350°F IN ARGON
- IMMERSE IN Na AT 350°F
- HEAT TO 1050°F AT 50°F/hr
HOLD AT 1050°F – 48 hr
- COOL TO 350°F – 50°F/hr
- REMOVE FROM SODIUM
- COOL IN ARGON TO ROOM TEMPERATURE
- STRESS TO 0.2% YIELD
- REMOVE SODIUM BY ALCOHOL PROCESS (SPECIMENS 36 AND 327 REMOVED)
- STORE AT ROOM TEMPERATURE AND 50% H_r – 120 hr
- HEAT IN ARGON AT 400°F FOR 120 hr (SPECIMENS 37 AND 328 REMOVED)
- REIMMERSE IN SODIUM AT 350°F
- HEAT TO 1050°F AT 50°F/hr
HOLD AT 1050°F – 48 hr
- COOL TO 350°F AT 50°F/hr
- REMOVE FROM SODIUM (SPECIMEN 312 REMOVED)
- REMOVE SODIUM BY ALCOHOL PROCESS (SPECIMENS 314, 321, AND 323 TENSILE TESTED WITHIN 24 hr OF SODIUM REMOVAL)
- EVALUATE

NOTE: ALL SPECIMENS TO HEDL DRAWING H-3-37683

74-07-56-14B

Figure 37. Process Reliability and Repeatability Tests – Group 3 Specimens

In those cases where the assemblies were wetted with sodium, the sodium was removed following the procedure outlined in the Alcohol Process Specification.*

The evaluation process consisted of the following operations. All tensile bars were thoroughly examined under 45-diameters magnification following sodium removal. All suspect areas were then examined at 200 diameters. The specimens were subjected to liquid penetrant inspection by trained Quality Control personnel. They were then stressed to failure in a tensile machine. Rate of load application was 0.002 in./in./min to the yield point, and then 0.02 in./in./min. The 0.2% yield strength, ultimate strength, elongation, and reduction in area were measured. Following this, they were reexamined microscopically. Areas of interest, plus a random sampling of the population, were metallographically mounted, sectioned, and subjected to detailed examination at 500 diameters. Documentation was accomplished by photographs of areas of interest.

To provide control data at interim steps in the Group 3 specimen processing, specimens were removed at various steps in the process, as noted on Figure 37, to identify at what point deleterious changes, if any, were occurring. Figure 38 shows Specimen 327, taken out of the process after the initial sodium removal, and indicates complete removal of sodium under the sleeve, although traces of sodium were present on the threads. Specimens 37 and 328 were removed after the argon soak at 400°F, and Specimen 312 was removed after the second sodium wetting, to assure that the sodium fully wetted the assembled component. Figure 39a shows the specimen with the sleeve in place, and Figure 39b shows the sodium to have fully penetrated under the sleeve.

Following completion of the test exposures, all tensile bars were subjected to thorough examination under a binocular microscope at 45 diameters. No evidence of surface damage or of any anomaly was discovered on any specimen. Typical appearance at this point is illustrated by Figure 40a, which shows the surface stains resulting from the test environments.

With the exception of those three specimens which were tensile tested immediately after sodium removal, all specimens were examined by liquid

*Rockwell International Process Specification ST0110NA0021, "Sodium Removal Using Ethanol," November 13, 1974

6507-40524

Figure 38. Group 3 Specimens After Initial Sodium Removal

6507-40525

a. Sleeve in Place

6507-40526

b. Sleeve Removed

Figure 39. Sodium-Wetted Specimens No. 312, Prior to Sodium Removal

6507-40519

a. After Sodium Removal

6507-40518

b. After Pull Testing

Figure 40. Tensile Specimens

penetrant techniques per RDT F 3-6T. This examination was performed by experienced Quality Assurance Inspectors, using specification procedures and materials. No cracking indications could be observed on any of the specimens.

All specimens were tensile tested to failure, as illustrated by Figure 40b. The resulting data are displayed in Tables 11 and 12. No particular pattern is evidenced by these data, except that they indicate a superior lot of Type 304 stainless steel. The specimens exposed to the test environments show no obviously significant variation in properties from each other, or from those of the two specimens which were tensile tested as received.

Metallographic examination of the failed specimens revealed the expected severe mechanical damage in the area adjacent to the fracture. This condition is illustrated by Figures 41a and b, which show sharp discontinuities as a result of strain which exceeded the ultimate strength of the material. Elongation of the individual grains can be readily observed. Since both specimens exhibit the same pattern of behavior, and since these specimens were specifically selected as being representative of high-strength and low-strength specimens, nuances of mechanical strength were eliminated as a variable in the formation of the small tensilely formed microcracks. Similar tears or microcracks also were found to be present in specimens tested in the as-received condition with no environmental exposure (Figure 42).

Moving away from the fracture area itself, the tears become less severe, until they become notch-type discrepancies, as indicated by Figure 43. These were found both in controls (Figure 44) and test specimens (Figures 45a through j). Location of the furthest discrepancy of this type from the point of fracture is recorded in Table 13. None were located further away than $3/8$ in., and grain elongation was still apparent in the immediate area of the discrepancy. On one specimen, as illustrated by Figure 46, similar type discrepancies were located on the shoulder, a full inch away from the break; but they appear more rounded, and to have more resemblance to corrosion pits than to mechanical damage.

Three specimens were removed at random from the group of 28 tensile specimens which completed the process qualification sequence. These specimens were examined metallographically. Photomicrographs were made of

TABLE 11

SODIUM REMOVAL PROCESS EVALUATION TENSILE TEST DATA
(Groups 1 and 2 and Modified Test)

Specimen No.	Test Conditions	0.2% Yield Strength (psi)†	Ultimate Strength (psi)	Elongation (%)	Reduction in Area (%)
S*	As received — sensitized	47,600	98,900	52	64
NS	As received — nonsensitized	49,700	100,000	51	68
111	Boiled in EtOH + 1% sodium	46,800	95,500	61	69
112	Boiled in EtOH + 1% sodium	47,800	94,800	60	74.5
113	Boiled in EtOH + 1% sodium	48,300	94,100	60	73.5
121	Boiled in EtOH + 1% sodium + 5% H ₂ O	49,700	95,100	57	76
122	Boiled in EtOH + 1% sodium + 5% H ₂ O	44,700	95,600	58	71.5
211	Exposed to ethoxide — stored at 360°F in N ₂	46,800	93,800	60	71
212	Exposed to ethoxide — stored at 360°F in N ₂	46,600	94,100	59	72
211C	Control — not exposed — stored at 360°F in N ₂	46,200	93,200	60	72
212C	Control — not exposed — stored at 360°F in N ₂	50,000	98,200	54	69
221	Exposed to ethoxide — stored at 50% H _r	51,400	101,700	49	66
222	Exposed to ethoxide — stored at 50% H _r	54,900	103,600	46	64
223	Exposed to ethoxide — stored at 50% H _r	51,900	93,800	58	77
224	Exposed to ethoxide — stored at 50% H _r	44,700	93,200	58	72
222C	Control — not exposed — stored at 50% H _r	46,700	93,600	59	72
224C	Control — not exposed — stored at 50% H _r	47,900	94,300	57	71
225	Exposed to ethoxide — heated at 400°F in argon following exposure to 50% H _r	50,300	99,100	53	72
226	Exposed to ethoxide — heated at 400°F in argon following exposure to 50% H _r	46,000	96,100	57.5	72
226C	Triple ethoxide concentration — heated at 400°F in argon following exposure to 50% H _r	56,700	105,300	45	58

*Specimen which exhibits 0.0022 in. fissure

†Strain rate, ambient conditions — 0.002 in./in./min to yield, then 0.002 in./in./min to ultimate

TABLE 12
SODIUM REMOVAL PROCESS EVALUATION TENSILE TEST DATA
(Group 3)

Specimen No.	0.2% Yield Strength* (psi)	Ultimate Strength (psi)	Elongation (%)	Reduction in Area (%)	Test Sequence
31	43,300	91,400	57	74	Heat to 350°F in argon
32	42,300	91,500	56	73	Immerse in sodium at
33	48,100	96,400	51	72	1050°F - 48 hr
34	44,400	90,800	58	71	Stress to 0.2% yield
35	56,900	101,700	43	61	Remove sodium by alcohol
36†	42,300	91,200	57	70	process
37§	44,500	91,700	56	70	Store at room temperature
38	43,300	91,500	55	72	in 50% humidity air - 120 hr
39	47,100	94,100	55	72	Heat in argon at 400°F -
310	42,200	91,100	56	67	120 hr
311	45,600	91,900	56	69	Immerse in sodium at
312**	54,300	99,400	48	66	1050°F - 48 hr
313	43,600	91,500	57	71	Remove sodium by alcohol
314††	44,400	90,900	55	71	process
315	46,300	92,300	56	70	
316	43,400	91,700	57	71	
317	44,100	91,900	56	72	
318	47,700	92,600	55	71	
319	45,100	92,700	55	71	
320	44,000	92,000	56	73	
321††	42,200	90,400	58	72	
322	46,700	91,800	55	72	
323††	45,600	92,400	57	71	
324	46,300	93,100	57	72	
325	53,800	101,400	43	62	
326	43,000	91,700	58	72	
327†	42,600	91,200	55	73	
328§	43,300	91,300	55	69	
329	47,200	90,900	55	71	
330	46,100	92,100	58	71	
331	45,500	91,900	55	73	
332	45,700	92,300	53	72	

*Strain rate, ambient condition: 0.002 in./in./min to yield, then 0.02 in./in./min to ultimate

†Removed and tested following initial sodium removal

§Removed and tested following humidity exposure and bake

**Disassembled before final sodium removal

††Tested within 24 hr of final sodium removal

Etched

500X

75-J20-11-17

a. Specimen No. 34

Etched

500X

75-J20-11-16

b. Specimen No. 35

Figure 41. Fractured Tensile Test Specimens
(High-stress region adjacent to fracture)

a. As Polished

500X
74-N7-56-113

b. Etched

500X
74-N7-56-113

Figure 42. Fractured Tensile Test Specimen — Sensitized Specimen, Tested As Received (High stress region adjacent to fracture)

500X
74-N7-56-110

a. As Polished

500X
74-N7-56-100

b. Etched

Figure 43. Fractured Tensile Test Specimen No. 211, Showing Notch-Type Discrepancy Further From Fracture Area (High Stress Region)

a. As Polished

500X
74-N7-56-112

b. Etched

500X
74-N7-56-112

Figure 44. Fractured Tensile Test Specimens — Control for Ethoxide Residue Test (Subjected to all test parameters except exposure to sodium ethoxide) (High-stress region adjacent to fracture)

500X
75-A2-11-53A

a. Specimen No. 31, 1/8 in. From Fracture
(Mount 9954-1)

500X
75-A2-11-53A

b. Specimen No. 33, 3/16 in. From Fracture
(Mount 9954-2)

Figure 45. Fractured Tensile Test Specimens
(Furthest discrepancies from points
of fracture)
(Sheet 1 of 5)

500X
75-A2-11-54A

c. Specimen No. 313, 1/8 in. From Fracture
(Mount 9954-3)

500X
75-A2-11-54A

d. Specimen No. 315, 3/16 in. From Fracture
(Mount 9954-4)

Figure 45. Fractured Tensile Test Specimens
(Furthest discrepancies from points
of fracture)
(Sheet 2 of 5)

500X
75-A2-11-55A

e. Specimen No. 317, 3/16 in. From Fracture
(Mount 9954-5)

500X
75-A2-11-55A

f. Specimen No. 320, 5/32 in. From Fracture
(Mount 9954-6)

Figure 45. Fractured Tensile Test Specimens
(Furthest discrepancies from points of fracture)
(Sheet 3 of 5)

500X
75-A2-11-56A

g. Specimen No. 324, 1/16 in. From Fracture
(Mount 9954-7)

500X
75-A2-11-56A

h. Specimen No. 325, 1/8 in. From Fracture
(Mount 9954-8)

Figure 45. Fractured Tensile Test Specimens
(Furthest discrepancies from points of fracture)
(Sheet 4 of 5)

500X

75-A2-11-57A

- i. Specimen No. 330, 9/32 in. From Fracture
(Mount 9954-9)

500X

75-A2-11-57A

- j. Specimen No. 332, 1/8 in. From Fracture
(Mount 9954-10)

Figure 45. Fractured Tensile Test Specimens
(Furthest discrepancies from points of fracture)
(Sheet 5 of 5)

TABLE 13

PROCESS RELIABILITY AND REPEATABILITY TEST LOCATION OF DEFECTS

Mount No.	Specimen No.	Furthest Discrepancy From Point of Fracture (in.)	
			Group 3 Test Conditions
9954-1	31	1/8	Heat to 350°F in argon
-2	33	3/16	Immerse in sodium at 1050°F - 48 hr
-3	313	1/8	Stress to 0.2% yield
-4	315	3/16	Remove sodium by alcohol process
-5	317	3/16 (plus small pits in shoulder)	Store at room temperature in 50% humidity air - 120 hr
-6	320	5/32	Heat in argon at 400°F - 120 hr
-7	324	1/16	Immerse in sodium at 1050°F - 48 hr
-8	325	1/8	Remove sodium by alcohol process
-9	330	9/32	
-10	332	1/8	
9947-1	34	1/4	
-2	35	1/16	
			Modified CSCC Test Conditions
9942-2	226	1/16	Immerse in ethyl alcohol + 1% sodium
			Dry overnight - ambient air
			Store in room-temperature air, 50% relative humidity - 168 hr
			Heat in argon at 400°F - 120 hr
			Heat in sodium at 400°F - 120 hr
			Heat in sodium at 1050°F - 48 hr
			Remove sodium by alcohol process
			Group 2 Test Conditions
9943-1	211	3/8	Immerse in ethyl alcohol + 1% sodium
-2	221	1/16	Dry overnight - ambient air
			Store in room-temperature air, 50% relative humidity - 168 hr
			Immerse in sodium at 375°F - 168 hr
			Heat in sodium at 600°F - 48 hr
			Heat in sodium at 800°F - 48 hr
			Heat in sodium at 1050°F - 48 hr
			Remove sodium by alcohol process

a. Overall View of Mounted Specimen
(Mount 9954-5)

Pits on Shoulder, ~1 in. From
Point of Fracture

Figure 46. Pit-Type Defects on Specimen No. 317, Removed From Tensile Fracture

Specimen No. 32 (which appeared typical) in areas not near the fracture zone, to determine whether any evidence of caustic stress corrosion cracking (CSCC) could be found. This examination confirmed the earlier conclusion that no CSCC was present. Figure 47a shows a view of the specimen at the end of the sleeve, where a concentration gradient might have been present; and Figure 47b a view of the shoulder area, where the specimen changes diameter. Figure 47c is a view in the threaded area of the tensile specimen.

It is concluded, based on these tests and the examination of the 52 specimens and controls, that the alcohol-sodium removal process, per se, neither initiates nor promotes stress corrosion cracking. Exposure to process solutions for extended periods of time, at temperatures beyond those which would be encountered in actual practice, and with several process repetitions, have produced no adverse effects on specimen appearance or properties.

It may also be concluded that residues left on parts cleaned by this process, as a result of an accidentally insufficient rinse following such cleaning, do not contribute to stress corrosion cracking. Aqueous caustic residues on parts inserted in liquid sodium apparently dehydrate before any attack can take place. This is certainly true for parts processed within the boundaries explored by this test.

From the foregoing, a final conclusion may be synthesized – that stainless steel hardware can be cleaned of sodium by the Alcohol Process with zero probability of stress corrosion initiation or promotion. A test report, TR-707-830-004, "Testing and Evaluation of Stressed Stainless Steel Tensile Specimens After Removal of Sodium by the Alcohol Process," was released, covering the details of the activity.

4. Reagent Chemistry and Regeneration

a. Reagent Products Solubility

Although data are available on the solubility of many compounds in ethanol, no data exist on their solubility in the multi-component Jaysol SS. The compounds of interest were sodium hydroxide (NaOH), sodium oxide (Na_2O), sodium hydride (NaH), sodium ethoxide (NaOC_2H_5), sodium carbonate (Na_2CO_3), and sodium bicarbonate (NaHCO_3).

Etched 500X
6507-40548
a. Area at End of Sleeve
(Mount 9949-1A)

Etched 500X
6507-40548
b. Shoulder Area (Mount 9949-1B)

c. Thread Area
(Mount 9949-1C)

Etched 100X
6507-40549

Figure 47. Fractured Tensile Test Specimen No. 32

The Na_2O and NaH compounds were eliminated when they were found to react vigorously with the Jaysol SS. The dissolution of sodium monoxide, Na_2O , in denatured ethanol is an exothermic reaction which rapidly produces a dark brown solution. A precipitate forms upon setting, preventing a true solubility from being determined. NaH also reacts with ethanol, according to Equation 3, preventing a true solubility from being measured.

The solubility of sodium hydroxide (NaOH) in denatured ethanol was determined at several temperatures, as noted in Table 14. The dissolution of the NaOH produces a slightly exothermic reaction, and the solution discolors gradually to a dark brown. Because of this discoloration, a fresh NaOH solution was prepared at each temperature.

TABLE 14
SOLUBILITY OF NaOH IN
DENATURED ETHANOL

Temperature		Solubility [mg/ml (gm/l)]
(°F)	(°C)	
73	23	113.0
86	30	95.7
104	40	107.1
118	48	134.6
140	60	113.0 (= ~ 8.3 wt % Na)

The test data, although not linear with temperature, shows that a significant amount of NaOH will dissolve in ethanol. As reported by Sidgwick,* a solution of NaOH in ethanol consists largely of Na^+ and OC_2H_5^- ions plus molecular water, according to Equation 4,

*N. V. Sidgwick, Chemical Elements and Their Compounds, Volume II (Oxford University Press, London, 1951) p 1352

which lies strongly to the right. It is apparent, from this reaction, that a true solubility value will not be obtained, as would be if NaOH were to be dissolved in water (H_2O).

Two measurements have been made of the solubility of sodium ethoxide ($NaOC_2H_5$) in denatured ethanol at room temperature. The measured values were 192 and 203 mg/ml at 69°F (20°C), which are equivalent to ~8.7 wt % Na. These solubility data for NaOH and $NaOC_2H_5$ confirm the equilibrium condition which exists, as shown in Equation 4 (i.e., the same amount of sodium is present in the alcohol, independent of whether the starting material was NaOH or $NaOC_2H_5$).

The solubilities of sodium carbonate and sodium bicarbonate are indicated in Tables 15 and 16, respectively. The bicarbonate was found to be more soluble than the carbonate.

TABLE 15
SOLUBILITY OF Na_2CO_3 IN
DENATURED ETHANOL

Temperature		Solubility [mg/ml (gm/l)]
(°F)	(°C)	
68	20	0.09
82	28	0.17
99	37	0.06
117	47	0.12
114	62	0

TABLE 16
SOLUBILITY OF $NaHCO_3$ IN
DENATURED ETHANOL

Temperature		Solubility [mg/ml (gm/l)]
(°F)	(°C)	
68	20	0.29
86	30	0.29
98.6	37	0.41
117	47	0.44
156	69	0.41

b. Radiation Stability of Cleaning Materials

A search of the available literature was conducted to gain information on the effects of radiation on alcohols and related organic compounds. This survey approaches the topic with a goal of determining the types of physical and molecular changes that may take place when such compounds are irradiated during the sodium removal from radioactive reactor components. Typical compounds being investigated are light alcohols, carboxylic acids, aldehydes, ketones, esters and esters and ethers, since many of these compounds are used as denaturants for ethanol.

Radiation quality is of interest in this search; γ -rays, x-rays, α particles, β -rays, positrons, ${}^4\text{He}^{2+}$, and fast electrons are examples. A significant amount of information was found on ethanol, methanol, isopropanol (plus other alcohols), light carboxylic acids, ethyl, propyl and butyl ethers, and simple ketones.

It has been found that: (1) the dose rate, electron volts per gram (eV/gm), will determine the quantity of radiation-induced products, (2) gaseous forms of the hydrocarbons tend to form more radicals than liquid forms, when exposed to equal dose rates, and the amounts are a function of temperature, pressure, and energy absorbed, and (3) concentrations of air, mineral acids, and halogen compounds drastically increase ion and radical formation.

Typical bonds attacked by radiation are:

Alcohols	C-H, C-COH
Aldehydes-Ketones	C-H, C-C O
Esters	C-H, C-OR O
Acids	C-H, C-COH O
Halogen Compounds	(F ₂) C-H, C-C (Others) C-H, C-X
Ethers	C-H, C-OR

Using the CRBRP and a component package with a 25r/hr radiation level as a model, plus the G-values* shown in Table 17, it was calculated that $\sim 1.7 \text{ ft}^3$ /week of H_2 would be formed in 40,000 gal. of alcohol, and $\sim 62 \text{ gm}$ /week of alcohol would be destroyed. These amounts were concluded to be trivial, except that the small amount of H_2 formed might cloud the H_2 determinations in the low-ppm range. A report, TI-707-830-010, "Radiation Stability of Organic

*The G-value is the number of molecules changed (formed or destroyed) per 100eV of energy absorbed.

Cleaning Reagents Used in Sodium Removal from Liquid Metal Fast Breeder Reactor Components," was issued, describing the study.

TABLE 17
ORGANIC REAGENT FINAL PRODUCT YIELDS
(Gamma Radiation)

Type of Product	G Yields (molecules/100 eV)		
	Ethyl Alcohol		
H ₂	5.0*	5.0†	4.87
CH ₃ CHO	2.8	3.2†	3.14
(CH ₃ CHOH) ₂	2.2§	1.7†	
CH ₄	0.6	0.6†	0.58
CO	0.06		0.26
CO ₂		0.3†	
H ₂ O	0.5	0.11†	Trace
C ₂ H ₆	0.24		Trace
C ₂ H ₄	0.14		Trace
C ₂ H ₂	≤0.02		
(CH ₂ OH) ₂	0.01		
CH ₂ O	0.13	0.4†	
CH ₃ CH(OH)CH ₂ CH ₂ OH	0.13		
HO(CH ₂) ₄ OH	0.01		
C ₃ H ₈	0.009		

*Dose = 10 x 10¹⁸ eV/gm

†Dose = 1 x 10¹⁸ eV/gm

§Dose = 100 x 10¹⁸ eV/gm

c. Solvent Recovery-Filtration

It was reported, in the previous annual report,* that sodium could be precipitated from the Jaysol SS solution by the addition of CO₂ to form sodium ethyl

*AI-AEC-13132, "Annual Technical Progress Report Sodium Technology and Cover Gas Seal Development Programs Government Fiscal Year 1974" (August 15, 1974)

carbonate, according to Equation 5:

A solvent recovery test was conducted on a sample of Jaysol SS containing 6.1 gm Na/l. The precipitation was done by bubbling carbon dioxide (CO₂) through the solution, which changed in appearance from a clear, red wine color to an opaque, muddy brown. A voluminous precipitate was formed in the 5 gal. of Jaysol SS, and CO₂ was added until the solution pH was 7. Filtration was through a Commercial Filter's Cartridge No. B100438 which had a particle size retention of 5 μ and a filter area of 810 in.² One and a half gallons of solution were pumped through the filter before flow ceased completely. Disassembly of the equipment revealed that the cessation of flow was not caused primarily by plugging of the filter, but rather by complete filling of the filter case with a thick, buttery cake of sodium ethyl carbonate, as shown in Figure 48. The filtrate from the operation was clear, but still reddish colored by the aldehyde

Figure 48. Sodium Ethyl Carbonate Filter Cake

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*AI-AEC-13132, "Annual Technical Progress Report Sodium Technology and Cover Gas Seal Development Programs Government Fiscal Year 1974" (August 15, 1974)

condensation products. A determination of the water content, using the Karl Fischer apparatus, showed the filtrate to contain 1.1 wt % water, and the reaction rate of the filtrate with sodium pellets at 80°F was found to be $\sim 5.5 \times 10^{-4}$ gm Na/sec, compared to a reaction rate of $\sim 4.4 \times 10^{-4}$ gm Na/sec for anhydrous Jaysol SS. The slight increase in rate was attributed to the increased water content.

It was concluded that the method was feasible, although the production of the bulky, adherent precipitate could complicate handling procedures, if the sodium being removed was radioactive; and, for this reason, the investigation was discontinued.

d. Solvent Recover-Distillation

Alcohol which has been used for sodium removal can be recovered by a distillation procedure. Table 18 shows the percent recovery of Jaysol SS as a function of the original sodium ethoxide content.

TABLE 18
RECOVERY OF SOLVENT
BY DISTILLATION

NaOEt Content mg/ml (gm/l)	Solvent Recovered (%)
5.1	89.9
24.4	55.3
43.6	35.5
66.5	31.5
92.4	32.3
98.4	26.1
126.4	15.1
155.2	17.2
192.2	9.6

During the distillation, the boiling point of the solution was $\sim 78^\circ\text{C}$ (172°F). The solutions were not discolored when initially prepared by reacting sodium with the Jaysol SS, but discolored very rapidly during the distillation, as the alcohol content decreased. The sodium ion content of the distillate was determined by flame photometry, and was found to be about equal to the sodium content of the original Jaysol SS sample. As the alcohol concentration decreased, the boiling point gradually increased. At $\sim 80^\circ\text{C}$ (176°F), a pungent odor was noticeable, which was ascribed to the aldehydic condensation products which cause the discoloration of the alcohol, and the dis-

tillation was discontinued to prevent the distillation of undesirable products. The recovery of alcohol under these conditions would be limited to $\sim 40\%$, if the

sodium content did not exceed the 30 gm $\text{NaOC}_2\text{H}_5/\ell$ (10 gm Na/ ℓ), as specified in the process specifications.

Since sodium ethoxide is reported to crystallize out of ethyl alcohol solutions with 2 moles of alcohol of crystallization, the the theoretical recovery was calculated on that basis; and, to verify the data, a sample of Jaysol SS, containing ~ 90 gm $\text{NaOC}_2\text{H}_5/\ell$, was evaporated to dryness. About 95% of the Jaysol SS was recovered. This high yield indicates that the sodium alcoholate does not precipitate out of solution with 2 moles of alcohol of crystallization during distillation. Figure 49 shows comparison of yields for the 2°C temperature rise cut off, evaporation to dryness to 2 moles of alcohol of crystallization, and evaporation to dryness without alcohol of crystallization. The 95% yield data point at 90 gm sodium ethoxide per liter of Jaysol SS is shown for comparison.

An analysis of the distillate from this latter test is being made to determine what compounds are present and to what extent, since it may be advantageous to use the higher recovery yields.

e. Solvent Recovery-Distillation-Incorporation of an Additive

A 100 ml sample of Jaysol SS containing 10 gm Na/ ℓ and 22.5 gm $\text{H}_2\text{O}/\ell$ (2.25 vol % water) was distilled (boiling point of 78°C or 172°F) in an all-glass apparatus in the laboratory. Two samples of distillate were removed and analyzed for water content. The first 30 ml of alcohol was found to contain 21.0 gm $\text{H}_2\text{O}/\ell$ (2.1 vol %). The sample of alcohol removed near the end of the distillation was found to have 19.8 gm $\text{H}_2\text{O}/\ell$ (1.98 vol %). The original solution was a very dark, reddish brown color, but the distillate was a clear, water-white liquid. To the remaining 22 ml of distillation bottoms, which were dark brown and viscous, were added 2.5 ml of an additive. The distillation was continued at 78°C (172°F), and 17 ml of additional clear distillate was obtained. The residual material was a damp, discolored crystalline mass. The total recovery of alcohol was calculated to be in excess of 95%.

Solvent recovery was measured on a sample of denatured anhydrous ethanol (Jaysol SS) containing 2 vol % of an additive, to which had been reacted sodium to form a concentration of 4 gm/ ℓ . The solution was heated to boiling (76.5°C or 170°F), and 96% of the original 250 cc of Jaysol was recovered. A white

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Figure 49. Recovery of Jaysol SS by Distillation

needle-like precipitate was formed as the solution was evaporated to dryness. The residue, on continued heating, formed a hard, dry cake. The solubility of the sodium derivative of the additive in boiling Jaysol SS (76.5°C or 170°F) was determined to be 20.5 gm/l.

It was concluded, from these distillation tests, that, if the additive were incorporated with the Jaysol SS prior to the sodium removal operation, no condensation byproducts would be formed during the removal operation and subsequent storage, and that at least 95% of the alcohol could be recovered, leaving a clean, dry precipitate of the sodium derivative of the additive, which is readily soluble in water.

f. Solvent Recovery - Bulk Distillation

A PER Corp. solvent still was installed, and a series of trial distillations began. The unit uses pressurized steam at ~40 psig, and is capable of 7 to 8 gal./hr. A 55-gal. drum of alcohol, previously used for reaction rate tests and to clean components, was run through the still. The water content of the clear distillate was 6 gm/l (0.8 vol %), whereas the water content of the original solution was 5.5 gm/l (0.75 vol %).

The reaction rate of the distillate with sodium pellets was determined at 38°C (100°F), and found to be $\sim 5.0 \times 10^{-4}$ gm Na/sec, compared to 7.7×10^{-4} gm Na/sec for fresh Jaysol SS. The planned analysis of the distillate components may explain the slight decrease in reaction rate.

C. CRBRP ALCOHOL-SODIUM REMOVAL PROCESS SUPPORT

In April 1975, a new activity was added to the Alcohol-Sodium Removal Process Program, to provide direct support for the CRBRP by establishing specific information not covered by the general program. A program plan, PP-707-830-001, "Program Plan for the CRBRP Alcohol Process for Sodium Removal Support Activity," was prepared describing the six activities:

- 1) Cleaning Vessel Vapor Effluent Processing
- 2) Cleaning Alcohol Regeneration-Separation
- 3) Waste Materials Solidification
- 4) Alcohol-Water Separation

5) Alcohol Process Additives Investigation

6) Process Demonstration.

The test data and literature information gathered since the inception of the program, in April 1975, is presented in the following sections.

1. Cleaning Vessel Vapor Effluent Processing

The basic effort of this activity will be to establish the Alcohol-Sodium Removal Pilot Facility process parameters, to define the quantity and composition of the vapors carried past the condenser in the alcohol facility during sodium removal, and to establish methods for minimizing the vapor carryover, if the amount of carryover is too high to be handled by the planned CRBRP Radioactive Gas System.

In addition, the activity will identify the radioactive species which might be present in the vapor when contaminated parts are cleaned, and determine the amount of carryover by aerosols or other means.

The major effort in this activity has been deferred until the construction of the Alcohol-Sodium Removal Pilot Facility is completed and data can be generated on the large condenser in operation during a typical sodium removal procedure. In the interim, supplementary data have been generated and a test plan prepared.

a. Determination of the Vapor Pressure Curve for Jaysol SS

Jaysol SS is compounded according to a Federal formula which consists of 100 gal. of SD3A alcohol, (where SD3A alcohol is made of 100 gal. of anhydrous ethanol and 5 gal. of methanol), to which 10 gal. of isopropyl alcohol and 1 gal. of methyl isobutyl ketone have been added. Table 19 gives the volume and molar percents of each compound in this formulation.

TABLE 19
COMPOSITION
OF
JAYSOL SS

Alcohol	Volume Percent	Molar Percent
Ethanol	85.80	86.43
Methanol	4.29	6.23
Isopropyl alcohol	9.01	6.92
Methyl isobutyl ketone	0.90	0.42

Since all components are very similar in molecular structure, Raoult's Law can be expressed by Equation 6:

$$P_i = X_i P_i^* , \quad \dots (6)$$

where

P_i = partial pressure of the i^{th} species

P_i^* = partial pressure of the pure i^{th} species

X_i = mole fraction of i present in the system.

Equation 6 can be rewritten as:

$$P_t = \sum_{i=1}^n X_i P_i^* , \quad \dots (7)$$

where

P_t = the total pressure.

Equation 8 can then be written for Jaysol SS where, at any temperature (T), the total pressure (P_t) is expressed as:

$$\begin{aligned} P_t = & 0.8643 P_{\text{ethanol}}^T + 0.0623 P_{\text{methanol}}^T + 0.0692 P_{\text{isopropanol}}^T \\ & + 0.00425 P_{\text{MIBK}}^T \end{aligned} \quad \dots (8)$$

where P_{ethanol}^T = partial pressure of ethanol at temperature, T . Vapor pressure data were obtained from the Chemical Engineering Handbook.^{*} For example, the total pressure of Jaysol SS at 0°C is:

$$\begin{aligned} P_t = & 0.8643 (12.0 \text{ mm Hg}) + 0.0623 (29.5 \text{ mm Hg}) + 0.0692 (8.5 \text{ mm Hg}) \\ & + 0.00425 (1.12 \text{ mm Hg}) . \end{aligned} \quad \dots (9)$$

^{*}J.H. Perry, Editor, McGraw-Hill Book Co.

or

$$P_t = 12.80 \text{ mm Hg} \quad \dots(10)$$

The calculated vapor pressures of Jaysol SS at various temperatures are listed in Table 20. The vapor pressures of the various components of Jaysol SS are shown for comparison. Since the vapor pressures of Jaysol SS and ethanol are approximately equal, as shown in Table 20, the graphical representation in Figure 50 can be used for either component with minimal error.

b. Sodium-Jaysol SS Reaction Rate Factor Equation

The reaction rate data of sodium in anhydrous Jaysol SS was compiled for 0.375-, 0.85-, 2.1-, and 4-in. ID specimens in both the horizontal and vertical orientations. The data in the 70 to 140°F range were found to fit a single Arrhenius equation with a variation of 25% (see Section II-B-1-a). These data were converted from a linear regression rate of in./hr to a surface area corrected form of gm/hr-in.². The reaction rate factor equation for F, the factor expressed in gm/hr-in.², and T, expressed in °K, is:

$$F = 1.664 \times 10^8 \exp (-5198.9/T) \pm 25\% \quad \dots(11)$$

This equation, coupled with the specified allowable hydrogen concentration in the effluent gas, may be used to determine the condenser flow rate and duty for various components. This equation is not valid for application to the reaction of sodium from crevices.

c. Radioactive By-products

Elements or their compounds which may be found in the sodium retained on the components at the time of the sodium removal operation have been identified as: iodine, cesium, rubidium, molybdenum, technicium, and yttrium, plus quantities of iron, nickel, cobalt, chromium, and manganese, and trace amounts of many other elements.

Most of these elements, or a suitable chemical compound, have been procured, and will be added to typical sodium removal operations, and the condenser condensate and the escaping effluent collected and analyzed to determine the extent of carryover of these elements.

TABLE 20
VAPOR PRESSURE OF JAYSOL SS AND ITS COMPONENTS

Component	Temperature (C°)							
	-40	-20	0	20	40	60	80	100
	Vapor Pressure [torr (mm Hg)]							
Jaysol SS	0.38	3.0	12.8	44.5	135	356	828	—
Ethanol	0.32	2.8	12.0	42.0	130	345	810	1630
Methanol	1.45	7.4	29.5	94.0	250	610	1300	—
Isopropanol	0.2	1.8	8.5	33.0	104	280	680	—
Methyl isobutyl ketone	—	0.15	1.12	5.3	19	59	153	355

Figure 50. Vapor Pressure vs Temperature for Ethyl Alcohol and Jaysol SS

75-MA19-53-3A

2. Alcohol Regeneration-Separation

The basic thrust of this activity to solve the problem of the recovery of the alcohol used to remove the sodium, creating a minimal amount of waste materials for eventual disposal, will be to:

- 1) Evaluate candidate separation processes, and select a promising method for further study
- 2) Establish the decontamination ratios to be expected, if distillation is selected as a candidate process
- 3) Determine the limits of the process
- 4) Establish the characteristics of the residual materials, the process "bottoms," and how they may affect the waste materials handling system.

a. Process Evaluation

Several processes were evaluated for recovery of the alcohol from the cleaning process, including distillation, vacuum distillation, precipitation and filtration, etc.

The process which appears the most attractive from the waste management approach will be that approach which will not add additional material for disposal, and which will remove the alcohol, leaving behind a dry or semi-dry residue containing the process nonvolatiles.

A vacuum distillation unit of the wiped film evaporator type was concluded to best meet these criteria, and steps have been taken to obtain a pilot plant size model for evaluation.

b. Distillation - Decontamination Ratio

An extended distillation run was performed with the PER Corp. solvent still using the denatured alcohol, Jaysol SS, which had been used for sodium-alcohol reaction rate tests and sodium removal operations. The Jaysol SS feed was regularly added to the still to replace the distillate, but the sodium ethoxide concentration was allowed to build up in the liquid in the boiling chamber. Of particular interest were the effect of the ethoxide film on the heat transfer, and

the maximum ethoxide concentration which could be tolerated. Any difference between the relative components of the denatured alcohol and the distillate also was of interest.

It was discovered that, at a concentration of 120 gm Na/l in the boiling liquid, any further increase produced a persistent foam, which, if permitted, would completely fill the boiling chamber and carry over into the distillate. This concentration is ~ 10 wt % Na, and is an effective limiting parameter for this operation.

The material, at this concentration, remained a drainable fluid near boiling temperature. Upon cooling, it becomes semi-solid, although it still exhibits the low shear strength of a liquid.

At this point in the run, the bottoms were drained, as indicated by the arrow on Figure 51. The run then was resumed, with no immediate drop in distillation rate. As the buildup of an insulating film on the heat exchange surface continued, this rate began to drop; and, when a steady decline became apparent, coupled with a rise in boiling temperature ($\sim 173^\circ\text{F}$), the run was terminated.

The still was drained of the bottoms, opened, and cleaned by hard scrubbing with a brush and rinsing. If radioactive Jaysol SS solutions were being reclaimed, it is believed that a pressurized hot water - detergent spray would adequately remove any film on the heat exchanger surface. The test run also indicated that, if the sodium level in the alcohol is held to 5 gm/l or less, the alcohol can be 96% reclaimed. Complete data on the composition of the reclaimed alcohol are not yet available, but preliminary information indicates no significant change. Other data resulting from this run are summarized in Table 21.

Another distillation run has been performed on alcohol containing 1 vol % of an additive and 1 vol % water. To this solution, measured quantities of iodine, cesium, rubidium, yttrium, cobalt, nickel, iron, and manganese ions were added. Samples of this feed and of the distillate from it are being analyzed for the concentrations of these ionic species. Comparison of the concentration of each species in the feed and in the distillate will establish the decontamination ratio which would be possible, if these materials were radioactive.

Figure 51. Jaysol SS - Sodium Alcoholate Distillation Rate-Temperature Relationship

TABLE 21

ALCOHOL DISTILLATION PROCESS STUDY USING JAYSOL SS WITH SODIUM ALCOHOLATE AND CONDENSATION PRODUCTS

Alcohol Feed (gal.)	~350
Alcohol Distillate (gal.)	~340
Distillation Rate (gal./hr)	4.6
Power Consumption (kwh/gal.)	1.08
Efficiency (%)	66
Sodium Concentration of Feed (wt %)	0.63
Sodium Concentration of Distillate (wt %)	0.005 (50 ppm) max. 0.001 (10 ppm) min.
Water Content of Feed (wt %)	6.8
Water Content of Distillate (wt %)	4.0
Distillate Appearance	Clear, water-white

c. Process Limits

Preliminary data from distillation tests on Jaysol SS containing sodium alcoholate indicate that an effective distillation process can be developed to recover at least 95% of the alcohol with minimal carryover of nonvolatiles.

The distillation temperature appears to be an excellent process limit, in that a fairly small increase in temperature will indicate a depletion of alcohol in the bottoms, and signal a process termination.

Current tests on material carryover and composition changes will provide further data to define the process limits.

d. Solidification Behavior of Bottoms

The composition of the distillation bottoms will differ, dependent upon the nature of the Jaysol SS feed. The Jaysol SS with the additive will have distillation bottoms consisting largely of Jaysol SS, the additive, the sodium derivative of the additive, and probably smaller concentrations of water, and ethyl and methyl derivatives of the additive.

The Jaysol SS without the additive will have distillation bottoms consisting largely of Jaysol SS, sodium alcoholate, water, and various condensation by-products. The latter components are produced by the reactions shown in Equations 12 and 13.

where the presence of small amounts of oxygen in the systems produces acetaldehyde, which, in turn, undergoes a condensation reaction

producing an unstable aldehyde which loses water to form crotonaldehyde. The reaction proceeds similar to Equation 13 condensing the crotonaldehyde to a larger molecule and more water. Eventually, an oily liquid or solid is formed, orange to dark brown in color. This condensation reaction requires an alkaline medium, and does not occur in the Jaysol SS with the additive.

Three different batches of bottoms were obtained from the distillation of used Jaysol SS. The first batch of 2 gal., was obtained from the initial distillation of ~120 gal. of Jaysol SS during the checkout of the equipment. The second batch of bottoms was removed during the second distillation, after ~150 gal. of used Jaysol SS were processed. The still was drained of bottoms, and the distillation resumed. Two hundred more gallons of Jaysol SS were processed to obtain a third batch of bottoms. Table 22 summarizes the test conditions and results.

TABLE 22
DISTILLATION BOTTOMS PROPERTIES

	Batch No.		
	1	2	3
Volume of Bottoms (gal.)	2	4.5	6.5
Volume of Feed Jaysol SS (gal.)	120	150	200
Sodium Content of Bottoms (wt %)	5.3	10.6	4.6
Viscosity (cp)	15,000	8000	5830
Specific Gravity (gm/ml)	~1.0	1.15	1.29

Although all bottoms were drainable liquids when hot, their properties were quite different, and are probably highly dependent upon the sodium concentration in the feed Jaysol SS, the total volume percent reduction, and the time and temperature of storage (the condensation reaction continues during the storage period, prior to recovery).

3. Waste Materials Solidification

The cleaning of sodium-clad CRBRP components via the alcohol or alcohol-additive reagents requires a means of isolating the generated radioactive wastes from biological systems until decay to innocuous levels is achieved. These wastes will include Na^{22} as the sodium derivative of the additive or sodium alcoholate (e.g., sodium ethoxide), radionuclide corrosion products from fuel cladding (oxides or carbides of Fe, Co, and Mn) and failed fuel pin wastes (Cs, I, Sr, etc).

The objective of this activity is to investigate methods of immobilizing these wastes in stable forms for long-term storage. This includes testing of existing "fixation" methods and development of processes directly applicable to alcohol system.

The most widely used method for waste product solidification has been "fixation" in hydraulic cements. The initial phases of the activity are therefore designed to determine the feasibility of using these cements to contain wastes from the Alcohol Cleaning Process.

A test plan for the activity has been released as TP-707-830-005, "Solidification Studies for Disposal of Radioactive Waste from the Alcohol Cleaning Process."

a. Preliminary Screening Tests

The preliminary test work performed in the activity centered on determining whether the hydraulic cements would enter into alcohol of crystallization reactions with various Jaysol SS solutions. Portland cement, for example, is composed of calcium silicates, calcium aluminates, and calcium aluminoferrite, and "sets" by hydration reactions of these ingredients with water. The formation of an alcohol of crystallization would allow substitution of the alcohols in Jaysol SS for water in cement mixing. The conversion of the liquid waste stream from the cleaning system (alcohol and dissolved sodium derivative of the additive or sodium ethoxide) to a solid medium would then be possible.

Lab tests, whereby alcohol was substituted for water in cement mixes, are illustrated in Table 23 and Figure 52. These tests indicated that Jaysol SS does not undergo a solvation-type reaction with the cement ingredients, since no "set" occurred with the various alcohol and alcoholate solution mixes. Additional tests were run in which Jaysol SS was added in increasing quantities to a Portland cement mix at a constant W/C (water to cement ratio by weight). These tests substantiated information* that alcohol is retained in hydraulic cements only as a diluent (Table 24). The Portland Cement Association has indicated that insufficient cement hydration would occur if the alcohol-to-water volume percent ratio exceeds 30:70. The samples shown in Figure 52 verify this information.

*F. M. Lea, The Chemistry of Cement & Concrete (Edward Arnold Ltd, 1970)

TABLE 23

DETERMINATION OF EFFECTS ON CEMENT BY SUBSTITUTION
OF ALCOHOL FOR WATER IN PORTLAND CEMENT

	Test Number			
	1	2	3	4
Liquid/Cement Ratio	0.50	0.50	0.50	0.50
H ₂ O (vol % of liquid)	100	50	0	50
ROH* (vol % of liquid)	0	50	100	0
ROH-NaOR† (vol % of liquid)	0	0	0	50
Observations	Complete set after 24 hr	No set; moist cake-like mass, partial set to brittle aggregate after ROH evaporation	No set; sedi- mentation of cement, ROH layer, crum- bled residue after ROH evaporation	No set; moist cake-like mass, brittle residue after ROH evapora- tion

*ROH = Jaysol SS

†NaOR = Sodium alcoholate

TABLE 24

DETERMINATION OF EFFECTS ON PORTLAND CEMENT
BY ALCOHOL ADDITION WHEN W/C RATIO IS CONSTANT

	Test Number					
	1	2	3	4	5	6
W/C* Ratio	0.50	0.50	0.50	0.50	0.50	0.50
ml ROH†/100 ml H ₂ O	0	10	20	30	50	50
Mixing Method	Cement and H ₂ O mixed; then ROH added					H ₂ O and ROH mixed; then added to cement
Observations	Complete set after 24 hr	Complete set, but rate retarded; set after ~3 days	Complete set, but rate retarded; set after ~5 days	No set; alcohol remained as layer above cement up to 12 days after mixing	No set; brittle residue after ROH evaporation	No set; brittle residue after ROH evaporation
					No difference by mixing method	

*W/C = Water to Cement Ratio by Weight

†ROH = Jaysol SS

6507-40618

a. 100% Water at 0.5 Water/Cement
Weight Ratio

6507-40611

b. 50% Water + 50% Jaysol SS at
0.5 Fluid/Cement Weight Ratio

6507-40610

c. 100% Jaysol SS at 0.5 Fluid/Cement
Weight Ratio

6507-40612

d. 67% Water + 33% Jaysol SS at
0.5 Fluid/Cement Weight Ratio

Figure 52. Mixture of Portland Cement With Water and Jaysol SS

More short-term tests, performed to gain information on the effects that various waste constituents would have on the setting characteristics of Portland cement, are shown in Table 25. Figure 53 shows the sodium alcoholate "still bottoms" and a cement sample from this group.

For more comparative evaluation, compressive strength was selected as the test property to quantify the effects of various wastes on the set of cement samples. Cylinders, 2 in. in diameter by 2 in. high, were used to form the cement specimens, which were crushed after set, in the compressive mode of an Instron tester (Figure 54).

b. Effect of Water/Cement Ratio

Before extended runs with waste additives were performed, the effect of water content on strength was determined for both Portland and Lumnite (calcium aluminate) cements. The data from these runs are plotted in Figures 55a and b. Water to cement ratios by weight (W/C) at 0.40 for Portland cement and 0.25 for Lumnite cement represent the greatest strength for nonaggregate mixes which still provide workable samples. Since these were comparative nonfilled tests, both sets were aged only two days.

c. Effects of Jaysol SS Content on Portland Cement

Since the Alcohol-Sodium Removal Process wastes will contain residual alcohol concentrations, a test set of Portland cement with increasing Jaysol SS quantities was run. The results are shown in Figure 56. These data indicate that the strengths decrease to a "no set" mix of 30 ml Jaysol SS/100 ml H₂O at 0.50 W/C.

d. Effect of "Bottoms" Content on Portland Cement

If Jaysol were to be used as the system reagent, sodium ethoxide would be the prime waste constituent. A series of test samples were mixed in which "still bottoms" residue from distillation of spent Jaysol SS reagent was added in increasing quantities to Portland cement. These bottoms contained ~10 wt % NaOC₂H₅, or ~3.4 wt % Na. The compressive strengths decrease with increasing "bottoms" concentration to a "no set" condition at 20 gm "bottoms"/100 ml H₂O (Figure 57). This "no set" condition was valid up to 25 days after mixing.

*F. M. Lea, The Chemistry of Cement & Concrete (Edward Arnold Ltd, 1970)

TABLE 25
PORTLAND CEMENT WITH VARIOUS ADDITIVES

	Test No.			
	1	2	3	4
W/C Ratio	0.5	0.5	0.5	0.5
ml ROH/100 ml H ₂ O	20	0	0	0
gm Alcoholate Bottoms 100 ml H ₂ O	0	25	25	0
gm Sodium Salt of Additive 100 ml H ₂ O	0	0	0	10
gm CaCl ₂ /100 ml H ₂ O	10	10	0	0
Observation	Only partial set; CaCl ₂ hydrate formation preferential to alcohol reaction	No set; crumbled residue	No set; crumbled residue	Complete set; retarded rate

6507-40602

a. "Still Bottoms" From Distillation of Spent Jaysol SS Reagent After Reaction With Sodium

6507-40615

b. Portland Cement Mixed With 100% H₂O and 25 gm NaOC₂H₅ "Still Bottoms" / 100 ml H₂O at 0.5 W/C

Figure 53. Test of Effects of Waste Constituents on Setting Characteristics of Portland Cement

6507-40603

a. Specimen Mold

6507-40604

b. Molded Specimen

6507-40606

c. Specimen During Test

Figure 54. Compressive Strength Test

a. Portland Cement

b. Lumnite Cement

Figure 55. Effect of Water Content on Strength

Figure 56. Effect of Alcohol Content on Strength of Portland Cement

Figure 57. Effect of Sodium Alcoholate "Bottoms" on Strength of Portland Cement ("Bottoms" contain ~10 wt % alcoholate)

e. Effect of Content of Sodium Derivative of Additive on Portland Cement

Since the current conceptual design for the Sodium Cleaning Process favors the use of the alcohol reagent with a additive, the sodium derivative of the additive is the major waste constituent to be contained. Recent studies have therefore centered on its compatibility with the hydraulic cement mixes.

An anhydrous sodium derivative of the additive (NaAd) was added to Portland cement mixes at 0.40 W/C, in concentrations up to 40 gm/100 ml H_2O . The compressive strength results are plotted in Figure 58.

Although crystals of the sodium derivative - sodium derivative trihydrate formed on the surface of the 30 gm/100 ml H_2O sample after crushing and in the container of the 40 gm/100 ml sample, as shown in Figures 59a and b, it is felt that the use of asphalt-lined drums would eliminate concern over this phenomenon. It is therefore concluded that the upper limit for "fixation" of the anhydrous sodium derivative is in excess of 30 gm/100 ml H_2O .

f. Effect of Sodium Derivative Plus Jaysol SS on Portland Cement

A series of tests on Portland cement was completed with mixtures of Jaysol SS - sodium derivatives with the sodium derivative in concentrations from 5 to 25 gm/100 ml H_2O , and Jaysol SS concentrations from 0 to 20 wt %. This simulates the waste product from the wiped film evaporation proposed to concentrate the waste stream. Since this product will probably not be anhydrous, but will contain residual alcohol, the Jaysol SS is added to determine the combined effects of the sodium derivative and alcohol on cement strength and set.

The strength of Portland cement was found to diminish more rapidly with inclusion of Jaysol SS in the cement - sodium derivative mixes. Figures 60a through d represent tests with 5, 10, 15 and 20% (wt % of sodium derivative + Jaysol SS), respectively. It was concluded, from these tests, that:

- 1) Portland cement mixes at 0.4 W/C will exhibit compressive strength properties exceeding 1000 psi for sodium derivative concentration up to 25 gm NaAd/10 ml H_2O , if the alcohol content of the NaAd is ≤ 10 wt %.

Figure 58. Effect of Sodium Derivative of Additive on Strength of Portland Cement (Aged 5 days)

6507-40609
a. 30 gm NaAd/100 ml H₂O - Crystals on Surface After Crushing

6507-40608
b. 40 gm NaAd/100 ml H₂O - Crystals in the Container

Figure 59. Portland Cement Mixed With Sodium Derivative of Additive (NaAd)

a. 5 wt % Jaysol SS Added to Sodium Derivative

b. 10 wt % Jaysol SS Added to Sodium Derivative

c. 15 wt % Jaysol SS Added to Sodium Derivative

d. 20 wt % Jaysol SS Added to Sodium Derivative

Figure 60. Effect of Jaysol SS Sodium Derivative of Additive Mixture on Strength of Portland Cement

- 2) In order to maintain 1000 psi compressive strength for mixes containing up to 20% Jaysol SS, the sodium derivative concentration should not exceed 20 gm/100 ml H_2O .
- 3) Sodium derivative and sodium derivative trihydrate crystals form on the surface of crushed samples, if the sodium derivative concentration is ≥ 20 gm/100 ml H_2O , regardless of the residual Jaysol SS concentrations.
- 4) The crystal formation is accompanied by a drop in compressive strength, which is most apparent at high alcohol concentrations.

g. Effect of Sodium Derivative on Lumnite Cement

Lumnite (calcium aluminate) cement is being actively considered as a solidification medium for the subject wastes, 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 cement mixes.

A series of Lumnite cement samples was prepared and tested, in which anhydrous sodium derivative was added, in concentrations from 0 to 40 gm/100 ml H_2O at 0.30 W/C. All of the samples exceeded 1000 psi compressive strength, but an anomalous response condition occurred with the samples at sodium derivative concentrations >20 gm/100 ml H_2O (Figure 61). Despite cracks at the surface of these samples, the compressive strengths increased slightly with increasing derivative concentrations. The test will be repeated to verify these results, and the ends of the samples will be capped with recently acquired capping equipment and capping compound used in concrete compression testing, to produce uniformly flat, parallel ends.

h. Effect of Jaysol SS on Magnesium Oxychloride Cement

Preliminary tests were conducted on a magnesium oxychloride cement. Table 26 shows the results. The cement was found to be of low strength, but does seem to be capable of retaining a moderate amount of Jaysol SS.

Figure 61. Effect of Anhydrous Sodium Derivative of Additive on Strength of Lumnite Cement

TABLE 26

EFFECT OF JAYSOL SS ON THE SETTABILITY OF A MAGNESIUM OXYCHLORIDE CEMENT

	Test Number		
	1	2	3
	0.50	0.5	0.5
Liquid/Cement Ratio			
Water (vol % liquid)	100	50	0
Jaysol SS (vol % liquid)	0	50	100
Observations	Cement is of Low Strength		
	Complete Set	Moderate Set	No Set

i. Preliminary Conclusions

Based on the results obtained to date, the following conclusions are made concerning the Waste Material Solidification Program:

- 1) Hydraulic cements do not enter into solvation reactions with alcohols (i.e., alcohols cannot be substituted for water in cement mixes).
- 2) When sufficient water is present to complete the hydration reaction, ~25 ml Jaysol SS/100 ml H₂O can be added to the cement mix without preventing the "set" of the mix.
- 3) A W/C of 0.40 for Portland cement and 0.25 to 0.30 for Lumnite cement provides the maximum strength while maintaining a workable mix.
- 4) About 20 gm of "still bottoms" residue from distillation recovery of spent Jaysol SS can be fixed in Portland cement. These bottoms contained only 10 wt % NaOC₂H₅ or 3.4 wt Na.
- 5) An anhydrous sodium derivative of the additive can be fixed in Portland cement, in concentrations of ~30 gm/100 ml H₂O, while maintaining a compressive strength of 1000 psi.
- 6) Adding Jaysol SS to the sodium derivative reduces the amount of sodium derivative which can be "fixed" from ~30 gm without Jaysol SS to ~20 gm with Jaysol SS addition of 15 and 20 wt %.

Table 27 summarizes the data generated to date on the maximum amounts of various materials which may be added to Portland cement, yet form a settable material with a compressive strength of at least 1000 psi.

4. Alcohol-Water Separation

The Alcohol-Sodium Removal Program has been conducted on the basic premise that the alcohol would be nominally anhydrous (containing <0.2 wt % water). In the event of accidental contamination of the alcohol during storage or use, a process must be available for removing water from the alcohol.

The separation of water from ethyl alcohol is a well-established, commercial process; but the alcohol selected for this cleaning process is a denatured ethyl alcohol, Jaysol SS, containing four components. In addition, if the alcohol

TABLE 27
AMOUNTS OF VARIOUS MATERIALS WHICH MAY BE ADDED
TO PORTLAND CEMENT WHILE STILL RETAINING
A SETTABLE MATERIAL WITH A MINIMUM
COMPRESSIVE STRENGTH OF 1000 psi

Material	Water/Cement Ratio by Weight	Concentration per 100 ml Water
Jaysol SS	0.5	20-25 ml
Bottoms	0.4	18-20 gm
Sodium derivative	0.4	~30 gm
Sodium derivative (5 wt % Jaysol SS)	0.4	~25 gm
Sodium derivative (10 wt % Jaysol SS)	0.4	~25 gm
Sodium derivative (15 wt % Jaysol SS)	0.4	~20 gm
Sodium derivative (20 wt % Jaysol SS)	0.4	~20 gm

has been used previously for sodium removal and the sodium removed by a distillation operation, the Jaysol SS may contain more than the specified maximum amount of water, plus trace amounts of radioactive contamination, including sodium and other metal ions, and tritium- and iodine-containing organic compounds.

The multicomponent alcohol and the traces of radioactive materials may complicate the use of commercial water removal processes, and require the development of other type water removal processes.

The approach to the objective of providing a method for the removal of water from Jaysol SS is to:

- 1) Evaluate and select an optimum process
- 2) Demonstrate the water removal process on a small scale.

In this preliminary investigation of water removal processes, two types of conditions were considered:

- 1) Jaysol SS plus ~6 wt % H_2O , which represents an accidental contamination with water

- 2) Jaysol SS plus ~ 6 wt % H_2O and 5 gm Na/l, which represents a used Jaysol SS containing water, either by accident or formed during use.

If a water removal process could be developed which also removed sodium, the two processes of alcohol regeneration and alcohol drying could be combined with an inherent process simplification. Since the latter process is the most difficult, the emphasis was placed on the combined process.

In the search for potential drying - sodium removal process, two general methods are available:

- 1) Physical methods, where only a change of state occurs
- 2) Chemical methods, where a change of some type occurs in the chemical composition.

Examples of the physical methods include:

- 1) Vacuum distillation
- 2) Azeotropic distillation
- 3) Extractive distillation
- 4) Addition of anhydrous Jaysol SS and distillation.

Examples of the chemical methods are:

- 1) Formation of hydrated sodium salts which are insoluble in alcohol, such as the sulfates, sulfites, and phosphates
- 2) Formation of hydrates of salts which do not contain a sodium ion, such as calcium sulfate, magnesium perchlorate, barium oxide, etc (these compounds would not remove sodium from the alcohol, only water)
- 3) Absorption on complex silicates (molecular sieves).

a. Physical Methods for Separating Water from Alcohol

Physical methods for separating water from alcohol are well documented, and detailed engineering data are available in technical publications. Azeotropic distillation of ethanol-water with an added hydrocarbon compound is the process in commercial use. Comparison of some of these methods has been made by

Gerster,^{*} and details of the process for ethanol using benzene are available in Perry.[†] Off-the-shelf designs also are commercially available.

However, none of the developed processes take into account the effects of sodium, sodium corrosion products, and radioactivity. It can be stated with certainty that a preliminary step to remove some of these interferences would be necessary to prevent fouling of heat transfer surfaces, and changes in vapor-liquid equilibria. With the exception of the denaturants, the removal of interferences should be possible with developed chemical processes.

The presence of the denaturants undoubtedly would complicate the standard benzene-type azeotropic distillation, and would require a distillation process development with pilot-plant scale equipment, before the process could be accepted for CRBRP use.

The vacuum distillation process for ethanol has been briefly investigated, and the vapor-liquid equilibria which apply at room temperature are shown in Figures 62 and 63. They show that a 0.2 % water distillate can be obtained at 20 to 25°C at a pressure of 50 to 100 mm Hg. Such pressures are easily attained by commercial steam jet ejectors. Detailed engineering designs are not available for this process.

The extractive distillation process, using ethylene glycol, has also been evaluated, and it does not seem to merit any further consideration, based on an economic evaluation by Black, Golding, and Destler, of Shell Development Co.,[§] who showed the extractive distillation with ethylene glycol to be more expensive than an azeotropic distillation with n-pentane.

One additional process was found which might merit consideration. This process consists of adding anhydrous alcohol to the alcohol-water mixture in a sufficient quantity to move the composition beyond the azeotropic minimum boiling point (78.15°C and 89.43 mole % ethanol), as shown in Figure 64. With this composition, an atmospheric pressure distillation, using a fractionating column, will remove the water from the alcohol. This process, as well as the vacuum distillation, may be complicated by the denaturants, as well as by the sodium, if present, but both processes appear to have merit.

^{*}J. A. Gerster, *Chemical Engineering Progress*, 65, (9) 43 (1969)

[†]*Chemical Engineers Handbook*, J. H. Perry, Editor (McGraw-Hill Book Co.)

[§]C. Black, R. A. Golding, and D. E. Destler, *Advances in Chemistry Series*, 115 p 64.

Figure 62. Percent Water in Azeotropic Mixture of Ethanol and Water as a Function of Absolute Pressure at 20°C

Figure 63. Vapor-Liquid Equilibrium Curve for Ethanol-Water System at 50 mm Hg Pressure

Figure 64. Vapor-Liquid Equilibrium Curve for Ethanol-Water System

The conclusion from these preliminary investigations of physical processes is that removal of water from ethanol can be accomplished in several ways, and, of these methods, the commercial benzene-type azeotropic distillation is the most attractive. If interfacing substances, including sodium, are present, these substances might have to be removed prior to the drying operation.

The three denaturants in Jaysol SS may produce different liquid-vapor equilibria than that found for ethanol alone, requiring distillation development work prior to adaption of the process for CRBRP usage.

b. Chemical Methods for Separating Water from Alcohol

(1) General Considerations

The formation of hydrated sodium salts which are insoluble in alcohol is a particularly attractive process, since they could thus perform the multiple

functions of drying and regeneration. They could remove the sodium by precipitation, and probably occlude many of the insoluble radioactive corrosion products. Some of these precipitates could be converted into glasses for easy waste disposal. The maximum amount of water which can be precipitated is ~ 50 wt % of total salt, of which $\text{Na}_3\text{PO}_4 \cdot 12 \text{H}_2\text{O}$ is an example.

The theoretical requirement of such a salt to reduce the water concentration can be calculated with reasonable accuracy.

By Raoult's Law, the following equations apply:

$$P_{\text{hydrate}} = P_{\text{H}_2\text{O}} X \text{ at } T^\circ\text{C} \quad \dots (14)$$

where

P_{hydrate} = vapor pressure of the hydrate at $T^\circ\text{C}$

$P_{\text{H}_2\text{O}}$ = vapor pressure of water at $T^\circ\text{C}$

X = mole fraction of water in alcohol

and

$$\frac{\text{wt } \%}{100} = \frac{18X}{18X + (1 - X) 46} \quad \dots (15)$$

where, at 0.2 wt %, $X = 0.00517$; and, at 25°C , $P_{\text{hydrate}} = 0.12$ mm of Hg.

Likewise, the free energy change required for a hydrate to remove water to any level is:

$$-\Delta F = RF \ln \frac{1}{P_{\text{hydrate}}} - RT \ln \frac{1}{P_{\text{H}_2\text{O}}} \quad \dots (16)$$

where P is in atm and ΔF is cal/mole. To achieve a 0.2% water content at 25°C , $-\Delta F = 3275$ cal/mole. This is the free energy change required to achieve a maximum residual water content of 0.2% at room temperature, regardless of the method used to achieve it.

Based on the preceding calculations, the following materials are capable of reducing the water content of alcohol to 0.2 wt %, although some may be

undersirable for actual use, for other reasons: P_2O_5 , $Mg(ClO_4)_2$, BaO , $CaSO_4$, and the molecular sieves. There are likely to be other suitable materials for which thermodynamic data has not been found.

(2) Experimental Results

Preliminary laboratory evaluations of chemical dehydrating agents have been carried out. Most experiments have been made with denatured alcohol (Jaysol SS) containing 5 gm Na/l and varying amounts of water, up to ~ 7.5 wt %.

Sodium sulfate is insoluble in alcohol, and forms two hydrates which showed not to be stable in alcohol containing 6% water, according to the preceding calculations. The experiments confirm both these properties, the precipitate being unhydrated Na_2SO_4 . Complete precipitation of the sodium occurred without a reduction in the water content.

The removal of water from alcohol, or alcohol containing sodium alcoholate, is being investigated, using additions of sodium phosphate or phosphoric acid, respectively, according to the following general reactions.

These phosphates have more stable hydrates than sodium sulfate, although quantitative data were not found. Sodium monohydrogen orthophosphate dihydrate, $Na_2HPO_4 \cdot 2H_2O$, has been precipitated to date from the Jaysol SS - sodium

alcoholate - water solution, but some side reaction, probably esterification, also takes place which prevents the reduction of the water content. The sodium content can be reduced successfully.

Four types of molecular sieves have been evaluated for water and sodium removal: 3A, 4A, 5A, and 13X.

The crystal structure of molecular sieves (MS) is like a honeycomb with cavities of different sizes. When placed in contact with mixtures of materials with different-sized molecules, they selectively absorb the molecule having a molecular size nearest that of the cavity. For a water-alcohol mixture molecular sieve, 3A should be best, since the cavity size most closely matches the water molecule size.

The results of preliminary experiments at an alcohol to MS ratio of 2:1 by volume and a 5 gm/l sodium content are given in Table 28.

TABLE 28
MOLECULAR SIEVE WATER REMOVAL FROM SODIUM
ALCOHOLATE - JAYSOL SS SOLUTIONS
(Alcohol/MS Ratio = 2:1 by Volume,
Sodium Content = 5 gm/l)

Contact Time (hr)	Molecular Sieve Size			
	3A	4A	5A	13X
	Water Content (wt %)			
0	7.6	7.6	7.6	7.6
24	1.9	2.2	3.4	4.1
48	1.8	2.0	3.4	3.6
72	1.9	2.0	3.2	3.6

However, in addition to water removal, the molecular sieves also removed sodium. These results are shown in Table 29.

TABLE 29
SODIUM ION REMOVAL BY MOLECULAR SIEVES
(Alcohol/MS Ratio = 2:1 by Volume)

Contact Time (hr)	Molecular Sieve Size			
	3A	4A	5A	13X
	Sodium Content (gm/l)			
0	5.0	5.0	5.0	5.0
72	0.68	0.34	0.34	0.17

Molecular Sieve 13X removed 96% of the original sodium in 72 hr, and a little over one-half the water. Molecular Sieve 3A removed ~75% of the water and 86% of the sodium in 72 hr at the 2:1 volume ratio of alcohol to MS used in these tests. Additional tests will be required to determine whether these materials can be regenerated by heat alone, as in its normal regeneration process, or whether the added sodium content will need to be removed to maintain their water absorption capacity.

(3) Conclusions

The conclusion, at this stage of development, is that none of the chemical methods for separating water from alcohol is free of additional complications and none can be recommended for use without additional experimental studies. However, the phosphate and molecular sieves offer an effective method for removing sodium in a form which could simplify the alcohol and sodium disposal when radioactive, and may be of interest as combined water-sodium removal agents.

5. Process Development

No work is planned on the additive activity until the experimental data are formalized and the process solutions, etc are selected. A report, TR-707-830-006, "Interim Data Report on the Alcohol Process for the Removal of Sodium in Support of the CRBRP Design," was released.

D. HOT GAS LANCE STUDY

The basic design of the argon heat exchanger, initiated last year, was simplified from a three-pass system to a single-pass device, using an electric heating

element of special manufacture. In addition to a considerable simplification of the air flow circuit, the new configuration minimizes thermal stresses in the shell by permitting the end to expand freely.

A computer program to calculate the bulk temperature rise and heater wall temperatures for an annular passage, using temperature-dependent fluid properties, was developed to support the design effort. Calculations with the new program indicated that the single-pass configuration can raise the gas outlet temperature 300 to 400°F higher than could the multipass configuration.

An analysis was made of the feasibility of using an argon-powered jet pump to provide suction for a vacuum pickup system. It was found that an argon flow rate of 25% of the main heating jet flow could provide a system pressure rise of 5.0 psi with an induced velocity pressure of 1.0 psi at the suction line inlet. It was concluded that the jet pump would be a feasible device to provide suction for the pickup tube.

The design of the new, high-power (6000 w) hot gas lance was completed, and incorporated a vacuum pickup feature for removal of the molten sodium. The device is illustrated in Figure 65a.

The hot gas lance was assembled (Figure 65b) and given a preliminary run. The jet pump device was found to provide inadequate suction. Minor changes in orifice size were made, but the efficiency could not be brought up to desired level. In order not to delay the demonstration testing of the hot gas lance, the jet pump was disconnected, and a positive displacement pump was installed downstream, beyond the cyclone separator. Utilization of a bypass line and throttling valve permitted the inlet and outlet flows of argon to be balanced, allowing the atmosphere box pressure to be stabilized at less than ± 1 in. H_2O .

The "hot" trial run was begun, using a sheet of scrap sodium which was melted successfully and drawn into the exhaust line, although a considerable amount of the low-density sodium escaped the suction nozzle and was blown into the box. In another test, sodium was melted and blown out of a 4-in. diameter vessel. Again a portion of the sodium escaped the suction nozzle and was blown in the box. The hot gas lance then was tested on a piece of chain from

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a. Schematic

Figure 65. Hot Gas Lance Test Device

WORKING GAS	ARGON OR HELIUM
ELECTRICAL POWER (w)	6000 (max.)
HEATED GAS FLOW RATE (ft ³ /hr)	1200
SUCTION FLOW CAPACITY (ft ³ /hr)	2000
JET PUMP FLOW RATE (DRIVER) (ft ³ /hr)	400
GAS OUTLET TEMPERATURE (°F)	1200 (1400 max.)
SODIUM REMOVAL RATE (lb/hr)	100 (max. theoretical)
WEIGHT (lb)	12.5

6507-1828A

b. Photograph
Figure 65. Hot Gas Lance Test Device

the CRBRP EVTM chain and grapple test which had been wetted with sodium. The gas lance successfully melted the sodium, and vacuumed the majority of the sodium into the exhaust line.

During the hot test phase, the sodium cyclone separator and the scrubber unit worked satisfactorily, preventing sodium compounds from being vented into the atmosphere.

A report, TR-707-830-005, "Final Report - Hot Gas Lance Testing," was prepared, summarizing the activity and recommended needed design changes to improve the vacuum pickup efficiency of the unit.

E. EVAPORATIVE REMOVAL OF SODIUM

In order to safely store, inspect, and/or reuse components which have been used in the sodium loops of liquid metal cooled fast breeder reactors, it is necessary to remove the sodium which generally wets and clings to all surfaces which have been immersed in the sodium. If the part is exposed to the atmosphere before this sodium is removed, it can generate hazardous concentrations of hydrogen, and the reaction products formed may preclude the reuse of the component.

Components have been cleaned by a number of techniques, but the most common involve reacting the sodium with some material which would convert it to a compound which is soluble in excess reagent. Water, steam, and alcohol are typical reagents. However, all these reagents have several disadvantages, including waste disposal problems, hydrogen generation (with a consequent safety problem), and the possibility that the process will induce stress corrosion cracking when the part is returned to the reactor.

The removal of sodium by vacuum evaporation has been evaluated by other investigators. However, most prior work was conducted at temperatures in the 1000°F range, using simple mechanical vacuum pumps. Since heating large components to this temperature is difficult in a vacuum system, and may also damage some components, it was desirable to evaluate the removal of sodium in the lower temperature range of 400 to 800°F, using a vacuum system more representative of that available as a result of advances in vacuum technology.

1. Theoretical Considerations Applying to Sodium Evaporation

Knudson^{*,†} and Langmuir[§] showed that the general equation describing the rate of evaporation in vacuum is:

$$M = \frac{PtA}{\left(\frac{2\pi RT}{M}\right)^{1/2}} \quad \dots(21)$$

where

m = mass of vapor (gm)

M = molecular weight of the gas species

A = area of evaporation (cm²)

t = time (sec)

R = gas constant

T = absolute temperature (°K)

P = vapor pressures of the species (atm)

This simplifies to the following expression for sodium metal:

$$Q = 5.85 \times 10^{-2} P \left(\frac{23}{T}\right)^{1/2} \quad \dots(22)$$

where

Q = rate of evaporation (gm-cm⁻²-sec⁻²)

P = vapor pressure of sodium (torr) at T (K°).

Data from various sources^{**,††} indicate that the amount of sodium clinging to wetted reactor components depends upon conditions of time and temperature following their withdrawal from the reactor. However, the extreme values are generally 1 to 5 x 10⁻³ gm-cm⁻².

*M. Knudsen, Ann. Phys., 28 (1909) p 75

†M. Knudsen, Ann. Phys., 29 (1909) p 179

§I. Langmuir, Phys. Rev., 27 (1913) p 329

**Egleme and Michel, Progress in Heat Transfer V7, 1st Ed. (Pergamon Press, 1973) p 503-515

††HEDL Report TC-133, "Sodium Removal, Disassembly and Examination of Fermi Secondary Sodium Pump"

Some preliminary calculations show that, even at temperatures as low as 400°F (205°C), a 2-mil surface film could theoretically be removed in ~2000 sec, if a relatively modest vacuum of 2×10^{-4} torr were maintained at the surface of the wetted specimen.

These data for evaporation are shown in Figure 66, in comparison with data from the literature on the evaporation of sodium in heated argon.* The required time to remove the same amount of sodium at the same temperature is 1000 times less for the vacuum process than the heated argon. Although these data indicate rapid evaporation of sodium from an open surface, the rate-limiting parameter was believed to be the removal of sodium from small crevices. A study of the process of evaporation from small tubes has led to the tentative conclusion that the rate-limiting process is the maximum rate that sodium atoms can leave the crevice opening. This is given by the Langmuir efflux equation:

$$\nu A = 3.51 \times 10^{22} \frac{PA}{(MT)^{1/2}} \quad \dots (23)$$

where

ν = rate at which atoms strike area, A

P = vapor pressure of sodium

M = atomic weight of sodium

T = absolute temperature (°K).

This becomes

$$S = 3.64 \left(\frac{T}{M} \right)^{1/2} A \quad \dots (24)$$

where

S = flow (l/sec at STP)

The quantity, Q, of sodium removed is expressed in Equation 25:

$$Q = S \times P \quad \dots (25)$$

*Egleme and Michel, op cit

Figure 66. Time to Remove 5 mg/cm^2 (2-mil thick layer) of Totally Exposed Sodium by Evaporation in Argon, and by Vacuum Distillation at 2×10^{-4} torr - Maximum Theoretical Rate

The time to remove all the sodium from a full crevice, 0.001 in. in diameter and 6 in. deep, has been calculated from Equation 25 for three different evaporation temperatures and equivalent sodium vapor pressures. The results are given in Table 30.

TABLE 30
CALCULATED RATE OF SODIUM REMOVAL FROM
A CREVICE, 0.001 in. OD by 6 in. DEEP
(7.6×10^{-2} mg Na)

Temperature (°F)	Pressure (torr)	Time (hr)
392	1.5×10^{-4}	330
575	1.5×10^{-2}	25
732	3.7×10^{-1}	1.1

It appeared, from these data, that, although the time to remove sodium from crevices is much longer than from exposed surfaces, the process might be accomplished in 1 to 2 days at a temperature $<600^{\circ}\text{F}$.

Another factor, which is known to influence both evaporation rate and cleaning efficiency, is the presence of sodium impurities, such as sodium oxide, sodium carbonate, and sodium hydroxide. These impurities may be introduced by the exposure of the sodium-wetted component to the atmosphere at any time after it is removed from the reactor. Poor storage conditions may also introduce these nonvolatile contaminants.

There is no acceptable method for calculating the effect of such impurities on the evaporation rate. However, since these impurities are known to form a "skin" on molten sodium, and since evaporation is a surface phenomenon, there can be no doubt that impurities will greatly retard sodium evaporation. Substantially all impurities will remain on the component after the sodium is evaporated.

2. Test Data

The initial activities were exploratory in nature, with the general objective of establishing the feasibility of removing sodium from reactor components at

relatively low temperatures, using a vacuum system with the capability of reaching pressures in the range of 1×10^{-6} torr.

Specific objectives were to:

- 1) Determine the time required to remove sodium from bolt specimens, similar to those used in evaluating the alcohol process for sodium removal, over the temperature range of 400 to 800°F
- 2) Measure the rate of evaporation from horizontal surfaces, and compare this rate with calculated theoretical rates of evaporation
- 3) Observe the behavior of sodium in crevices during evaporation
- 4) Measure the total pressure of the system, and identify some individual gases evolved during the evaporation of sodium.

The initial evaporation experiments were carried out with the equipment shown in Figure 67, which is a Model PMC-720 diffusion-pumped vacuum system with an 18-in. OD glass bell jar. The rated speed of the diffusion pump is 750 l/sec.

The sodium samples were protected from contamination by storage in an inert atmosphere in a closed bottle after removal from the sodium loop. This closed bottle was placed on the base plate of the vacuum apparatus, and the system was evacuated and backfilled with argon two times. The bottle was opened with the bell jar in its raised position, using the glove bag shown in Figure 67 to remove the samples from the bottle and place them in the sample holder. One thermocouple was attached to one sample, and additional thermocouples were attached to each radiation shield. The bottle was then withdrawn into one glove, and the bell jar lowered and the system evacuated.

The sodium sample was heated by a 2800-w, bare-wire heater centered in combined condenser-radiation shields, as shown in Figure 68. When the pressure reached the 10^{-5} torr range, heat was turned on, and the sample was brought to the experimental temperature as rapidly as possible without over-run — usually, in ~ 30 min. Pressure measurements were made with thermocouple gauges down to 1×10^{-3} torr, and with a calibrated Bayer-Alpert ionization gauge in the 10^{-5} torr and lower pressure ranges. In some experiments, a Model GA-4 Veeco residual gas analyzer (RGA) was used to record the mass spectrum from mass 12 to 300.

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Figure 67. Test Equipment Used for Sodium Removal Evaporation Studies

Figure 68. Heating and Condensing System

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The endpoint of most experiments was determined by an arbitrary decision, since, in the early experiments, there was no known way to determine when the sodium was all evaporated. In later experiments, a lighted observation hole allowed visual estimation of the endpoint. Although the pressure trace and the mass scan may eventually be useful as a means for determining the point of completion of sodium evaporation, they were not so used in any of these experiments.

a. Bolt Specimens

Three series of experiments were run using the bolt specimens, which were made of Type 304 stainless steel, 3-1/2 in. long by 1/2 in. in diameter with three spacers, 5/8 by 1 in. The spacer faces had a 32- μ in. or better finish.

The nut was tightened, before immersion in the sodium, with a torque of 50 in.-lb. One-half of the specimens had 1-mil shims placed between each spacer before tightening, and one-half had no shims.

Series I was a series of exploratory runs made without visual observations. Series II was a similar set of experiments with visual observation. Series III was intended to verify that visual observation could be used to determine the point of 100% sodium removal.

Table 31 includes the results of the three series of tests. Figure 69, shows photographs of typical bolt specimens after evaporation.

In addition to the data reported in Table 31, complete temperature-time records were obtained for the specimens and condensers, and pressure-time records were made, based on the ion gauge readout.

The residual gas analyzer was used in a variety of scanning modes during the Series III runs. Visual observations were made periodically during Series II and Series III runs. Table 32 summarizes the result of visual observations.

Figure 70 shows smoothed plots of the time required for 90 and 100% sodium removal in bolt specimens. These curves illustrate the fact that no real difference in removal time exists between the specimens with a 1-mil gap and a zero gap crevice, because the bulk of the sodium in the crevices is not removed by evaporation. Most of the sodium is forced out of the crevices by either sodium vapor or dissolved gas pressure; and, since this sodium does not rewet the specimen, it drops off the vertical surfaces and falls to the unheated support plate.

TABLE 31
RESULTS OF SODIUM EVAPORATION TESTS ON BOLT SPECIMENS

Temperature (°F)	Evapo- ration Time (hr)	Sodium Remaining (gm)				Sodium Removed* (~%)
		Nut	Bolt	Spacers	Total	
"Zero" Gap Between Spacers						
400	30	0.05	0.06	0.05	0.16	79.5
450	30	-	-	-	-	100
500	20	-	-	-	0.06	92.3
550	5.5	-	-	-	-	100
650	5	0.004	0.001	0.007	0.011	98.6
650	5.5	-	-	-	-	100
800	20	-	-	-	ND	100
1-mil Shim Between Spacers						
400	30	0.04	0.04	0.04	0.12	84.5
450	30	-	-	-	-	100
500	20	-	-	-	0.06	92.3
550	5.5	-	-	-	-	100
650	5	0.004	-	0.006	0.01	98.7
650	5.5	-	-	-	-	100
800	20	-	-	-	ND	100

ND - Not detected

*Based on average weight of sodium on representative bolt

a. 500°F, 20 hr

b. 800°F, 20 hr

Figure 69. Vacuum Distillation of Sodium From Bolt Specimens

TABLE 32
OBSERVATIONS DURING VACUUM EVAPORATION –
BOLT SPECIMENS

Original film of sodium on the outside was quickly removed in ~1/2 hr.

Sodium sweats out of crevices, but will not rewet the outside surface.

Balls of sodium dropped to the cold floor of the support, and froze.

Sometimes, sodium vapor recondenses on the outside of specimens when evaporation rate is high.

A periodic pressure fluctuation pattern occurs near the end of the evaporation test, continuing until evaporation is complete.

Dissolved impurities are carried from the crevices to the exterior surfaces, and deposited there.

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Figure 70. Time to Remove Sodium From Bolt Specimens
(Pressure range, 1×10^{-5} to 1×10^{-6} torr;
zero gap and 1-mil gap crevices)

This greatly reduces the time required to clean a crevice, and also reduces the condenser load. This observation suggests a commercial design approach for an evaporation vessel. The part to be cleaned could be supported on a heated open-mesh grid plate. The cold condenser could be below the part, so that run-off sodium would fall into the condenser, and would not re-evaporate. This would also simplify the design of the vacuum vessel, so that it could be loaded from the top.

b. Rate of Evaporation Tests

In order to compare the calculated maximum evaporation rates with those attainable in practice, it was necessary to provide sodium specimens having a known constant surface area during evaporation, and containing a known weight of sodium. This was done by preparing small, Type 304 stainless steel crucibles, 0.824-in. ID by 0.125-in. deep, and filling them with sodium at 1050°F. Evaporation tests were run in the equipment shown in Figure 67. The end of evaporation was judged visually by observing when the last observable trace of metallic sodium shine disappeared from the crucible. This endpoint observation was not extremely precise, because of visual interference by the skin of impurities, and because the bottom of the crucible had a metallic shine similar to sodium. Rate of evaporation tests were run on duplicate samples at 450, 550, and 650°F. The results are summarized in Table 33.

TABLE 33
EXPERIMENTAL SODIUM EVAPORATION RATES

Temperature (°F)	Evaporation Time (hr)	Evaporation Rate (gm-cm ⁻² -hr ⁻¹)	Calculated Evaporation Rate (gm-cm ⁻² -hr ⁻¹)
450	38	8.3×10^{-4}	4.1×10^{-2}
550	2	1.6×10^{-2}	4.3×10^{-1}
650	0.6	5.2×10^{-2}	2.9

As expected, the rate of evaporation, in practice, is much slower than calculated. The maximum theoretical rate was found to be ~ 50 times higher than the experimentally determined rate. The presence of impurities, which form a strong skin over the sodium, greatly retards the rate of evaporation, particularly at 450°F , where it remains relatively undisturbed during evaporation. Another factor which influences these experiments is the unheated large support plate beneath the samples, which cooled the flat bottom of the crucibles by radiation. Since the effect of temperature is exponential, small temperature differences can cause large variations in evaporation rates. Consequently, these rates could probably be improved upon in a well-designed commercial evaporation vessel.

c. Crevice Specimens

The Crevice Specimens were the same as those used during the evaluations of the alcohol process (Figure 14), and only those specimens having a -0.001 in. shrink fit between the pin and sheath were used.

The evaporation process was conducted in the same equipment, using the handling techniques developed for the bolt specimens. However, in order to separate the pin and the sheath after the evaporation of the sodium, it was necessary to chill the entire assembly in liquid nitrogen, and then torch heat the sheath while pulling the assembly apart using an Instron tensile test apparatus.

It was not possible to move the pin in the control sodium-wetted specimen, which was not subjected to vacuum evaporation. The pin was moved only $\sim 1/4$ in. in the specimen evaporated at 450°F , and sodium was still in the crevice. It was possible to completely remove the pins from the specimens evaporated at 550° and at 650°F . The entire assembly was free of sodium in both tests, except for a small amount in the groove of the tapered bottom. Table 34 summarizes the test results, and Figure 71 shows the specimen from the 650°F test, illustrating the completeness of removal from the crevice. The stains on the specimen are from the water bath used to cool the specimen after torch heating.

d. The IVHM Mockup

The single experiment using the IVHM mockup was performed in a large, water-cooled, metal vacuum chamber, ~ 30 in. OD by 48 in. long, pumped by a

TABLE 34
RESULTS OF THE EVAPORATIVE REMOVAL OF SODIUM
FROM -1 mil SHRINK FIT CREVICES

Evaporation Temperature (°F)	Evaporation Pressure (torr)	Time (hr)	Results
450	1×10^{-5} to 6×10^{-7}	51	Pin could be moved ~1/4 in.
550	1×10^{-5} to 5×10^{-7}	24	Pin removed. Free of sodium.
650	1×10^{-5} to 1×10^{-6}	6	Pin removed. Free of sodium.
Control	-	-	Pin could not be moved.

Figure 71. Stainless Steel Crevice Specimen, -1 mil Shrink Fit, ~6 in. Long, After Evaporative Removal of Sodium at 650°F

1500 l/sec diffusion pump. This system is capable of being pumped into the 1×10^{-7} torr range when empty and cold. A specially built Nichrome wire heater chamber was used to heat the 53 lb assembly. The stainless steel cover for the heater chamber was built with a viewing hole centered over the IVHM mockup, and the completed assembly was placed under a vacuum chamber viewport to enable the evaporation process to be observed.

The desired test conditions were 24 hr at 650°F. However, the conditions attained were 9 hr at ~500°F, and 4 hr at 650°F. The indicated pressure varied from 1×10^{-3} to 5.5×10^{-5} torr during the heating cycle.

The part had been used in several cleaning cycles, with both water vapor at HEDL and alcohol at AI, and appeared to contain an exceptionally high gas content. During the evaporation cycle, the vacuum was lost twice — once when the ion gauge broke, and again when the viewport glass cracked — but it was felt that only the surface sodium would be affected, and the test cycle was not interrupted, except to make repairs.

When the chamber was opened and the mockup removed, sodium was found between the flat plate of the mockup and the unheated support plate. Sodium was observed in several places on the surface of the mockup, apparently trapped under heavy surface oxides. However, there was no sodium in the crevices, the bolt threads, the bolt holes, or on the bolts. Figure 72 shows the disassembled IVHM mockup after sodium evaporation.

3. Conclusions

It was concluded, based on the series of tests on sodium-wetted bolts, crevice specimens, and the IVHM mockups, that sodium can be removed from reactor components in the temperature range of 450 to 650°F, using modern vacuum pumping systems which are capable of achieving pressures in the range of 1×10^{-6} torr. The process is particularly attractive for removal of sodium from crevices which cannot be cleaned by any developed chemical method. The process is also faster than typical chemical cleaning processes.

It further was concluded that the evaporative process is well suited for the removal of sodium from either large or small reactor components, and the application of the process is only limited by the size and pumping capacity of the process equipment. The possible application of this process to the removal of

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Figure 72. IVHM Mockup After Evaporative Removal of Sodium

sodium from failed fuel elements should also be considered, since this appears to be the only process which may be capable of removing sodium which has leaked into the interior of fuel pins.

A report, TI-707-830-011 "Evaporative Removal of Sodium from Liquid Metal Fast Breeder Reactor Components - Interim Progress Report," March 15, 1975, was prepared describing all of the test work except the recently completed crevice specimens and the IVHM mockup, which are described in a separate, to-be-released report.

F. SODIUM-WATER REACTION PRODUCTS REMOVAL

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 sodium and sodium-water reaction products from components without causing harm to the component, using the current alcohol process techniques or a modified alcohol process.

Specific objectives of the activity are:

- 1) Prepare typical sodium-water reaction product mixtures
- 2) Characterize the reaction products, and their physical state, relative composition, etc
- 3) Select candidate cleaning materials (alcohol-water-additive mixture)
- 4) Determine the removal rates for the selected solution
- 5) Evaluate the impact of the removal process on the Alcohol Cleaning Process developed for the removal for sodium from components.

The initial phase of the activity was a review of the literature, to characterize the reaction products which might be produced from the potential reactions shown in Table 35.

It was concluded, based upon review of the literature and the observations of the investigators, that the sodium-water reaction products will probably have the following characteristics:

- 1) The reaction products will probably consist of NaOH, hydrated NaOH, Na_2O , and NaH.

- 2) Residual sodium may be mixed with the reaction products.
- 3) Fe, Cr, and Mo, and their Na-O compounds may be found in the product mass.
- 4) The reaction product mass will be hard at room temperature, although portions may be melted at elevated temperatures to form a viscous liquid.
- 5) The majority of the reaction products will be water soluble (NaOH), or will react readily with water (Na_2O and NaH). The Na-O compounds of Fe, Cr, and Mo also may be water soluble, or may decompose in water. The unreacted Fe, Cr, and Mo will be insoluble in water.
- 6) The composition of the products probably will be mostly NaOH and NaO_2 (roughly equal amounts), a lesser amount of NaH, and small amounts of the other types of materials. Unknown amounts of residual sodium will be present in varying extents dependent upon the particular sodium-water reaction event (temperature-pressure of the sodium and water, size of leak, velocity of the reaction products, extent of mixing, etc).

TABLE 35
POTENTIAL REACTIONS RESULTING FROM THE
INTERACTION OF SODIUM AND WATER

	Heat of Reaction (kcal/mole)
$\text{Na}(\ell) + \text{H}_2\text{O}(\ell) \rightarrow \text{NaOH} + 1/2 \text{H}_2$	-35.2
$\text{Na}(\ell) + \text{H}_2\text{O}(\text{g}) \rightarrow \text{NaOH} + 1/2 \text{H}_2$	-45.0
$2\text{Na} + \text{H}_2\text{O} \rightarrow \text{NaOH} + \text{NaH}$	-47.4
$\text{Na} + 1/2 \text{H}_2 \rightarrow \text{NaH}$	-13.7
$\text{Na} + \text{NaOH} \rightarrow \text{Na}_2\text{O} + 1/2 \text{H}_2$	+ 2.6
$2\text{Na} + \text{H}_2\text{O} \rightarrow \text{Na}_2\text{O} + \text{H}_2$	-31.1
$2\text{Na} + \text{NaOH} \rightarrow \text{Na}_2\text{O} + \text{NaH}$	-11.1

A Program Plan, PP-707-810-001, "Program Plan for the Sodium-Water Reaction Products Removal Activity," was prepared, outlining the proposed work. The report also included the results of the literature survey.

A test program was initiated to produce batches of simulated sodium-water reaction products in the laboratory, while a test rig was being designed and fabricated.

Two batches of simulated reaction products were made by two slightly different methods:

- 1) By melting sodium in an argon atmosphere glove box containing small amounts of oxygen and water vapor. Because of the difference in densities between melted sodium and the products (Na_2O and NaOH), and the inability of the hot sodium to wet the compounds, the mixture remained as two phases, solid and liquid, until the sodium was allowed to cool to the freezing point. As the sodium began to freeze to a mushy consistency, the mixture was stirred. The sodium appeared to wet the solid components, and a semi-homogenous solid was formed.
- 2) By melting sodium in a dry box atmosphere containing a small amount of oxygen and adding powdered NaOH to the mixture. The same freezing-mixing technique was again used to produce a solid mix.

The first batch was remelted, flattened into a sheet, and small discs punched (with difficulty) from the sheet for reaction rate tests.

Five pellets were added, one at a time, to 90°F Jaysol SS, and the reaction rate measured. The pellet weight varied from 0.4 to 0.8 gm, and the reaction rate varied from 4.1 to 13.3×10^{-4} gm/sec. This compares to a sodium - Jaysol SS 90°F reaction rate of 5.5×10^{-4} gm/sec

It is believed that the reaction rate will vary from the high rate exhibited by the high surface area of the metallic sodium frost to the slow dissolution rate of NaOH in Jaysol SS. The rate will be highly dependent on the composition of the mixture, the surface area, and the density of the products.

It appears, based upon the literature and the initial tests, that the sodium-water reaction products, except the metallic elements "wasted" from the component by the reaction, will be readily soluble in the Jaysol SS. Also, the use of

additives, appears feasible, if it is desirable to reduce alcohol causticity, or to aid in reprocessing and waste handling.

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 development of local sodium removal tools and techniques, (4) the development of sodium removal by evaporation via vacuum chambers, (5) the preparation of procedures to direct the various sodium cleaning operations, (6) an evaluation of the cleaning and decontamination of sodium-wetted components, (7) providing support for the use of the alcohol process for the CRBRP, and (8) investigating the removal of the sodium-water reaction products by the alcohol process. The information is directly applicable to the FFTF, the CRBRP, and the LMFBR activities.

SCHEDULE

Description	Proposed Activities							
	1975				1976			
	1st Q	2nd Q	3rd Q	4th Q	1st Q	2nd Q	3rd Q	4th Q
A. Alcohol - Glycol Ether Process								
1. Reaction Rate Investigation			1			3		
2. Scale-up Testing				2				4
3. System Safety Report and Specification	5			5		8		
4. Process Specification		6		7			9	
5. Alcohol Recovery-Regeneration				2		8		
6. Process Additive Development								
7. Vapor Effluent Processing								9
8. Waste Materials Solidification								9
9. Alcohol-Water Separation								
10. Sodium-Water Product Removal				2				5
B. Hot Gas Lance								
C. Sodium Evaporation Tests								
D. Decontamination Development								

1. Complete Tests
2. Start Tests
3. Complete Initial test phase
4. Complete final test-demonstration
5. Issue report
6. Issue preliminary specification
7. Issue revised specification

8. Issue final specification revision
9. Issue data package
10. State-of-the-art report
11. Select candidate process
12. Issue interim decontamination procedure
- * Issue preliminary data package for CRBRP Alcohol Process design