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**SODIUM MASS TRANSFER: III
THE APPLICATION OF LIQUID
AMMONIA AS A SODIUM
LEACHING AGENT**

By
H.W. Alter
P.A. McManus

U.S. Atomic Energy Commission
Contract AT(04-3)-189
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ATOMIC POWER EQUIPMENT DEPARTMENT
GENERAL ELECTRIC
SAN JOSE, CALIFORNIA

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Prepared under the
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1.0 ABSTRACT

A technique is presented for liquid ammonia leaching of metallic sodium from corrosion coupons, filter elements, and sodium samples to reveal contaminants and impurities. The advantages of the method in preserving the physical form of corrosion or mass-transfer deposits are demonstrated. A possible application to the determination of trace oxygen in sodium is mentioned.

2.0 INTRODUCTION

The high-temperature sodium mass-transfer loops being operated by the Atomic Power Equipment Department for the AEC produce a variety of samples. Analysis and characterization of these samples represent an important phase of the loop program. Types of samples include bulk sodium, corrosion coupons, screen filters and trap deposits. Characterization consists of chemical and radio-chemical analysis and x-ray diffraction and metallographic identification of materials.*

A prime objective of the program is the measurement of quantity and type of material transported through the loops by mass transfer or other mechanisms and deposited in colder portions of the system. Evidence of such deposition is the persistent plugging of the test loops by deposits in narrow annuli in all "cold leg" sample holders. Samples are located at the 1100, 1000, and 700 F areas of the decreasing-temperature region (cold leg) of the loop.

All loop samples contain sodium. The conventional practice has been to dissolve and remove such sodium by reaction with alcohol. While the alcohol technique is well adapted to the dissolution of bulk sodium, the

*For details see GEAP-3726, Screening Test Data and Analysis.

vigor of the alcohol-sodium reaction can affect the structure of deposits on coupons or other samples and leave no clue as to the nature of the original in-loop deposit. In the plugging example cited above, alcohol and water washes of cold leg coupons left surfaces with an apparent adherent thin film but free of any gross coating. In some cases a small alcohol-insoluble residue was found, but its relation to the plugging problem could not be established because initial flow conditions were obtained when washed samples were returned to the loop.

The importance and urgency of the plugging problem led to the present work with liquid ammonia as an alternate leaching agent.

The high solubility of the alkali metals, including sodium, in liquid ammonia has long been known. The solution mechanism involves the formation of solvated sodium ions and electrons. The reaction proceeds without gas evolution or appreciable release of heat. These mild conditions implied the possibility of removing sodium without changing underlying deposits.

The solubility of alkali metals in liquid ammonia is not shared by other metals and compounds of specific interest in the mass-transfer loop program. A literature survey on the solubilities of some typical materials was kindly made available to us by Professor George Watt of the University of Texas. Solubilities and references are given in the Appendix. The solution of sodium by liquid ammonia is a truly selective process, leaving other material essentially unchanged.

The purpose of this study was to investigate liquid ammonia as a leaching agent for loop samples to permit undistorted examination of nonsodium residues.

3.0 DISCUSSION

It was found from preliminary work that the equipment for ammonia washing had to fulfill several requirements:

1. Tank ammonia had to be purified by removing particulate material and water vapor.
2. Samples should have minimum contact with air before washing to prevent further oxidation of sodium.
3. Samples after washing should have minimum contact with air to avoid subsequent change due to the hygroscopic nature of the deposits.
4. Washing had to be conducted in such a way that liquid ammonia did not boil on the sample. The sample had to be thoroughly contacted with fresh ammonia. The characteristic deep blue color of sodium in liquid ammonia provided a convenient check on the completeness of washing.

With these requirements in mind the sodium extraction apparatus shown in Figures 1 and 2 was developed. The apparatus was designed to allow condensing the ammonia directly from the cylinder and then refluxing from the same vessel. Earlier work on the apparatus had shown the necessity of immersing the sample completely. Washing the sample on a filter led to splashing and each new contact of the liquid on the sample produced some boiling so that washing on a filter was not desirable. On the other hand, flowing a stream of fresh ammonia over the sample in a cup did not effect complete removal of sodium in a reasonable length of time. Condensing into a syphon type receiver was the best solution. The collector provided for accumulation of liquid until the sample was entirely immersed followed by syphoning

SCHEMATIC DIAGRAM OF LIQUID
AMMONIA LEACHING APPARATUS
FIGURE 1

LIQUID AMMONIA LEACHING APPARATUS
FIGURE 2

off in a slug. This method washed the sample very efficiently with no significant removal of material, other than sodium, from the samples.

Another problem was regulating the rate of addition of coolant, liquid nitrogen, to the condenser. Irregular addition caused pressure fluctuation and, in turn, boiling both in the still pot and around the sample. The boiling, again, was detrimental to the purpose of preserving the physical character of the deposit. An insulating cover of glass wool between polyethylene sheets was fitted around the sample changer to reduce temperature gradients. Future designs will include continuous circulation of coolant to the condenser.

The sample chamber was fitted with a ball and socket joint and could, therefore, be used conveniently for transporting the sample, before and after washing, without excessive contact with air. It was, of course, desirable to minimize oxidation of the sample prior to washing. After washing it was necessary to keep the residue of whatever oxide film had formed from absorbing atmospheric moisture and spoiling the appearance of the sample.

The sodium mass transfer loops make use of a small coupon of the loop structural material to study weight loss and weight gain between the hot and cold sides of a circulating system. The coupons are long with a rectangular cross-section. They are accurately machined to fit diagonally into a larger rectangular tube. The resulting triangular passageway is about 0.040 by 0.100 inch, and is a region of high flow rate compared to the rest of the circulation path. Each loop has seven sample holders. During recent operation, the increasing-temperature region (hot leg) of the

type 316 Stainless Steel Loop was operated with one holder at 1100 F, one at 1200 F, and two at 1300 F. In the "cold leg" of this loop the holders were operated at 1200, 1100, and 800 F.

It was found that all loops developed a gradual rise of pressure differential across the cold-leg sample holders. This pressure rise indicated the growth of some kind of plug in the narrow, high velocity, part of the path. Pressure differentials across plugged sample holders have gone as high as 40 psi, compared to an initial level of about 2 psi.

As part of this investigation special filter assemblies were placed in cold leg sample holders of Loop 1 (loop and filter material 316 stainless). The assemblies consisted of two folded strips of 60 mesh screen, 1/8 inch x 2 inches, on either side of a strip of micro-metallic filter. They were placed across the tops of the sample holders so all flow passed through each of them. When the loop had been operated for a sufficient length of time for flow degradation to occur, the assemblies were carefully removed and transported to the laboratory with a minimum of contact with air.

The first test loop sample washed with ammonia consisted of a portion of the screen-micrometallic filter assembly taken from the coldest sample holder (800 F) in the cold leg. The washed sample showed a thick layer of black crystalline deposit covered by a thin film of sodium oxide. The sodium oxide (plus possibly NaOH and Na_2CO_3) formed by exposure of the sample to air remained almost intact during the ammonia washing operation.

The photograph in Figure 3 shows the resultant deposit on the screen and micrometallic filter. A place is apparent on each piece where the film has flaked off. Microscopic examination showed that these places had

65 MICRON FILTER (LEFT) AND 60 MESH SCREEN SAMPLE HOLDER C3
 RUN 1-1F 80 ppm O₂ 960 HOURS EXPOSURE AT 800 F
 8X;
 FIGURE 3

60 MESH SCREEN 18X; SAMPLE HOLDER C3
 RUN 1-2 10 ppm O₂ 1400 HOURS EXPOSURE AT 700 F

FIGURE 4

originally been covered by thicker layers of sodium than had the surrounding areas and when the sodium was leached out the film easily broke off. The examination also disclosed the physical nature of the deposits: black crystalline needles with some perpendicular orientation relative to the surface on which they were found. The appearance of both deposit and film in this sample illustrate the effectiveness of the liquid ammonia washing in removing sodium without disturbing the deposit.

Figure 4 illustrates the initial stages of the plugging process. This screen was exposed in the same test loop as the screens shown in Figure 3. However, the test conditions were modified, including longer exposure, lower oxygen impurity level, and a loop temperature pattern 100 F lower than the previous fouling-test run. The fact that there were more corrosion samples upstream from the screen may have affected the amount of deposit.

Figure 5 shows a screen exposed at the same time as the screen in Figure 3, but located in the 1200 F zone (sample holder C-1) where the deposition was not as extensive. The higher magnification clearly reveals the appearance of the deposit after cleaning with liquid ammonia. The original screen is shown for comparison.

Chemical and x-ray diffraction analyses showed the black crystalline deposit to be α -iron with stainless steel components (Ni, Cr, Mn). The crystals were readily washed off with water. The particle size was in the 5- to 10-micron range.

60 MESH SCREEN BEFORE (LEFT) AND AFTER EXPOSURE
RUN 1-1F 80 ppm O₂ SAMPLE HOLDER C1
EXPOSURE: 960 HOURS AT 1200 F
18X;

FIGURE 5

The method has also been applied to bulk sodium samples and plugging materials that powdered when the metallic samples were cleaned in alcohol and water.

4.0 CONCLUSIONS

This work has demonstrated the usefulness of liquid ammonia washing of samples of deposit in sodium in cases where isolation of the sample and preservation of its physical form are desirable. By comparison, ethanol washing produces violent agitation. Where a deposit contains sodium throughout its internal voids, as did those handled in this work, alcohol solution would produce large forces tending to break the sample apart.

In the study of the plugging problem, given as an example, the deposits provide a straightforward illustration of the mass transfer phenomenon as indicated by nucleation and crystal growth on exposed cold leg surfaces.

The applicability of liquid ammonia washing to the analysis of other impurities in sodium, such as oxygen or carbon, should not be ignored in further studies.

APPENDIX
(Tables and References Supplied
by Prof. George Watt, Univ. of Texas)

Solubilities in Liquid Ammonia

<u>Solute</u>	<u>Temp. °C</u>	<u>Solubility</u>	<u>Refs.</u>
Na	22	6.14 moles NH_3 /23 g. Na	1
	0	5.87 moles NH_3 /23 g. Na	1
	-33.5	5.37 moles NH_3 /23 g. Na	2
	-50	5.39 moles NH_3 /23 g. Na	1
	-70	5.20 moles NH_3 /23 g. Na	1
	-70	19.2 g. Na/100 cc. of Solution	3
NaOH	-45	2.5 mg./1000 g. NH_3	4, 5
	-45	1.8 mg./liter of NH_3	4, 5
(1) Na_2CO_3	-38	"Insoluble"	6
Na_2O	-33.5	Ammonolyzes $\rightarrow \text{NaOH} + \text{NaNH}_2$	7, 8
(2) NaNH_2	25	0.004 g./100 g. NH_3	9
NaH	-40	"Insoluble"; very slow reaction at -35 is probably $\text{NaH} + \text{NH}_3 \rightarrow \text{NaNH}_2 + \text{H}_2$	10
(3) NaCl	25	4.35 g. NaCl /100 g. NH_3	11, 12
	0	12.80 g. NaCl /100 g. NH_3	11
	-30	4.20 g. NaCl /100 g. NH_3	13
	-60	0.63 g. NaCl /100 g. NH_3	13

<u>Solute</u>	<u>Temp.</u> <u>°C</u>	<u>Solubility</u>	<u>Refs.</u>
Ca	-33	< 0.1 gram-atom Ca/liter (dilute phase)	14
CaO	-38	"Insoluble"	6
Ca(NH ₂) ₂	---	"Very Slightly Soluble"	15
CaCO ₃	-38	"Insoluble"	6
Ca(OH) ₂		No Data (probably < NaOH)	
CaH ₂		No Data (probably like NaH but at lesser rate)	
Ca ₃ N ₂		No Data [probably << Ca (NH ₂) ₂]	
CaCl ₂	-35 ± 3	"Insoluble"; forms CaCl ₂ · 8 NH ₃	6, 15-19

- (1) Slow reaction — carbamates (?).
- (2) There are conflicting data; e.g., from 1 g. to 1 mole/liter.
- (3) Solubility maximum at -9.5°, at and below which temperature the solid phase in equilibrium with the saturated solution is NaCl · 5 NH₃.

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