# ANHYDROUS LIQUID AMMONIA AND IODINE – PROGRESS REPORT ON AN IMPROVED PROCESS FOR TREATMENT OF SODIUM IN FERMI-1 BLANKET FUEL

S.A. Ploger, J.A. Snook
Global Technologies, Inc.

G.D. Getman
Consultant

## ABSTRACT

Sodium-bonded spent nuclear fuel (SBSNF) elements pose a potential hazard regarding eventual disposal in a geologic repository because sodium is pyrophoric and water-reactive. An improved process is needed that can extract the sodium from SBSNF elements and render the sodium into a nonhazardous chemical form that is not subject to the Resource Conservation and Recovery Act (RCRA).

Global Technologies, Inc. (GTI) has successfully demonstrated such a process through sodium dissolution in ammonia and conversion to nonhazardous sodium iodide on unirradiated sodium-bonded Fermi-1 blanket fuel elements. Argonne National Laboratories-West (ANL-W) provided the fuel element and cut it between the 35.6-cm slugs of depleted uranium fuel meat to avoid freeing alpha contamination. A secondary objective was to demonstrate that the ammonia and resulting process solutions do not attack the depleted uranium in the fuel. This objective was accomplished. Treated Fermi-1 blanket fuel segments were returned to ANL-W for disposal as non-RCRA low-level radioactive waste, without metallic sodium or loose radioactive contamination from uranium corrosion. The products of the improved GTI process are solid, unregulated sodium iodide and the low-level radioactive depleted metallic fuel elements.

A diffusion-only process with sodium and ammonia had been previously demonstrated by Commodore Advanced Sciences. An in-house experiment verifying the diffusion-based process on Fermi-1 segments was not successful. The diffusion-based process required access for liquid ammonia to continue dissolving sodium in the narrow annulus between the stainless steel cladding and slugs of depleted uranium. Progress of the dissolution front was inhibited by precipitation of insoluble sodium amide ($NaNH_2$) in the annulus. The study described herein overcame the deficiencies noted in the Commodore process by utilizing two enhancements. It was found that pressure cycling—gradually raising the reaction vessel pressure and then abruptly dropping it—forced loose sodium amide from the annulus, which improved ammonia access to the clad metallic sodium. Second, early addition of the elemental iodine was found to convert the resultant sodium amide from a dense, adherent form to a porous, powdery form. The powdery form of sodium amide was much more amenable to removal from the annulus by pressure cycling.

The combination of these two refinements not only overcame plugging by sodium amide, but also produced a substantial increase in dissolution rate. With these enhancements, an ammonia-based sodium removal process is completely viable for treating irradiated Fermi-1 blanket fuel

elements. A patent application has been filed teaching the above described process improvements.

## INTRODUCTION

Sodium-bonded spent nuclear fuel (SBSNF) elements pose a potential hazard regarding eventual disposal in a geologic repository because sodium is pyrophoric and water-reactive. Sodium conceivably could react vigorously with any water, producing heat, dangerous hydrogen gas, and corrosive sodium compounds. Therefore, methods are needed that can extract the sodium from SBSNF elements and render the sodium into a nonhazardous chemical form that is not subject to the Resource Conservation and Recovery Act (RCRA).

In the *Final Environmental Impact Statement for the Treatment and Management of Sodium-Bonded Spent Nuclear Fuel*, the U.S. Department of Energy (DOE) selected electrometallurgical treatment as its preferred alternative for all SBSNF, except for blanket fuel elements from the Fermi-1 Reactor [1]. These elements had very low burnup and low times-at-temperature in the reactor, so DOE selected the no-action alternative to allow for development of more economical treatment techniques. Accordingly, DOE's Idaho Operations Office commissioned Global Technologies, Inc. (GTI) to investigate the viability of a technique developed by Commodore Advanced Sciences, Inc. [2] in the *Proof of Principle Experiments with Anhydrous Ammonia to Demonstrate the Removal of Sodium from Liquid Metal Reactors*. Commodore's process uses solvated electrons to destroy hazardous materials, and includes using ammonia to dissolve metallic sodium and convert it to a nonhazardous form. During this proof of principle study, GTI discovered and improved upon several deficiencies with the Commodore process.

This study has progressed in increasingly sophisticated phases. Phase I proved that ammonia could remove sodium quickly from single-ended mockups [3], whereas Phase II tested longer sodium-bearing mockups with two open ends that better represent pieces of Fermi-1 blanket fuel elements from a head-end chopping process [4]. Phase II also used elemental iodine to convert sodium into nonhazardous sodium iodide without generation of hydrogen. Phase III tested this technology on segments of an unirradiated sodium-bonded Fermi-1 blanket fuel element supplied by Argonne National Laboratories-West (ANL-W). The reclamation products of sodium iodide and low-level radioactive depleted uranium fuel elements are non-RCRA regulated.

### Commodore Process

The technique developed by Commodore destroys hazardous materials using solvated electrons, and includes using ammonia to dissolve metallic sodium. The dissolved sodium is subsequently converted to a nonhazardous form with an ionizable precipitating agent.

The anhydrous ammonia molecule has a tetrahedral structure with one nitrogen atom and three hydrogen atoms on the corners. Metals with low ionization potentials (high electrode potentials) such as the Group I alkali metals are very soluble in ammonia. Sodium is soluble in liquid ammonia up to approximately 20 weight percent (16 mole percent) at 0°C [5], so macroscopic amounts of exposed sodium dissolve within a few minutes, even as solid lumps of centimeter dimensions.

There is a dramatic rise in conductivity when a substantial amount of an alkali metal (such as sodium) is introduced to liquid ammonia and it produces both positive and negative charge carriers according to:

Na (metal) $\Rightarrow$ Na$^+$ (ammoniated) + e$^-$ (solvated)                (Eq. 1)
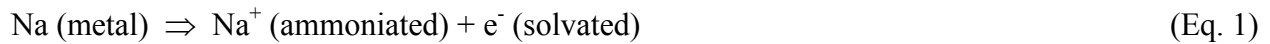
Solvated electrons display a characteristic deep blue color in dilute ammonia solutions. Concentrated solutions (greater than 3 weight percent) are bronze in color [5]. Conductivity is proportional to mobility of the charge carriers and mobility is inversely proportional to their mass. Therefore, the lighter electron, rather than the heavier sodium cation, is responsible for most of the observed conductivity.

Conductivity of such solvated solutions is not static, because sodium ions and solvated electrons are only independent in infinitely dilute solutions. In the concentration range of these experiments, a fraction of the positive ions and solvated electrons join to form electrically neutral "monomers" with the electron outside the shell of NH$_3$ molecules surrounding each sodium cation [6]. The monomers tend to be attracted by their dipole moments into "dimers" and higher order neutral complexes that manifest themselves as decreasing indicated conductivity with time. Indicated conductivity may drop by 50 percent or more in as little as 15 minutes before gradually attaining equilibrium [6].

The process precipitating agent must ionize in ammonia and provide an anion to combine with the sodium cation and produce a sodium salt. The precipitating agents in the Commodore process patent include ammonium chloride, water, hydrogen chloride, copper chloride, ammonium nitrate, sodium nitrate, nitric acid, ammonium sulfate, ammonium chromate, benzoate, and metal halides [2]. Many candidate reagents were initially examined for the proof of principle experiments. Some were not soluble in liquid ammonia, were more hazardous that metallic sodium, or released dangerous hydrogen has when reacting with ammonia. A metal halide, copper iodide, was tested in the initial experiments, but left a potentially pyrophoric copper residue.

**Improved GTI Process**

The Commodore process had been experimentally tested with sodium, ammonia, and various precipitating agents, but not on actual Fermi-1 blanket fuel segments. The proof of principle experiments were designed for testing Fermi-1 blanket fuel segments. The metallic uranium fuel is not considered soluble in liquid ammonia, particularly when the uranium is present as a cylindrical slug. Nevertheless, its resistance to corrosion by solvated electron solution and iodide ions was substantially unknown. Even a small amount of corrosion conceivably could have released alpha contamination. A major objective of the proof of principle experiments was demonstrating that the GTI treatment approach had no adverse effects on the depleted uranium fuel meat. In addition, several problems with the Commodore process became apparent during the experiments. The first problem was finding a suitable precipitating agent, elemental iodine. The second problem was the formation of insoluble sodium amide, NaNH$_2$, which plugged the tight annulus space and prevented the ammonia from reacting with the sodium. This problem was solved by pressure cycling and early addition of iodine.

When iodine is added to a solution of ammonia and sodium, the highly conductive solvated electrons combine with the iodine molecules to form relatively immobile (less conductive) iodide ions [7]:

$$I_2 + 2Na^+ + 2e^- \Rightarrow 2Na^+ + 2I^- \qquad \text{(Eq. 2)}$$

The iodine to iodide ion reaction is extremely rapid, occurring as fast as complete mixing is achieved. As a consequence, there is no opportunity for ammonia and iodine to begin forming any hazardous byproducts such as unstable $NI_3$ [4]. As the solvated electrons combine with the iodine, the characteristic blue color of a solvated electron solution disappears, and the ammonia solution returns to its original transparent color. Sodium and iodine ions are both soluble in liquid ammonia, but non-hazardous sodium iodide precipitates at elevated concentrations as the ammonia evaporates [5].

Solvated electron solutions formed by sodium dissolution are energetically unstable and gradually combine with ammonia (without iodine) to form sodium amide and hydrogen [8].

$$2Na^+ + 2NH_3 + 2e^- \Rightarrow 2NaNH_2(\downarrow) + H_2(\uparrow) \qquad \text{(Eq. 3)}$$

Sodium amide formation is mentioned in the literature as an impurity-catalyzed by-product associated with "fading" of solvated electrons [9]. This reaction is catalyzed by many common impurities, including oxygen, water, and most metals [10]. Thus, sodium amide formation tends to be more rapid in a metallic experimental apparatus than in glassware. Sodium amide is nearly insoluble in liquid ammonia, only 0.004 g per 100 g of ammonia [5]. So, as sodium amide gradually forms and precipitates, it takes both positive ions and solvated electrons (both types of charge carriers) out of solution and decreases solution conductivity [10].

Sodium amide is merely an intermediate reaction product until iodine is added [8], which breaks up the amide and restores charge carriers according to:

$$6I + 6NaNH_2 \Rightarrow 6Na^+ + 6I^- + 4NH_3 + N_2(\uparrow) \qquad \text{(Eq. 4)}$$

Thus, the original bonded sodium reacts completely with the ammonia to form sodium ions, which then precipitate with iodine ions to form sodium iodide. The ammonia is scrubbed and recycled. The GTI process reclamation products of sodium iodide and low-level radioactive depleted uranium fuel elements are not regulated by RCRA.

In the proof of principle experiments, iodine addition alone was not sufficient to overcome the problem of sodium amide plugging the tight annulus space and preventing ammonia access to the sodium. Pressure cycling was used to knock the sodium amide loose from the annulus and reestablish ammonia access with the sodium. In pressure cycling, the reaction vessel was gradually raised to 1.4 MPa by manually using the nitrogen regulator. Then, the pressure was rapidly dropped by partially engaging the 0.7-MPa relief valve. This process was repeated every 30 or 60 minutes throughout the dissolution sequence in the pressure cycling experiments.

An additional process improvement was the early addition of the iodine precipitating agent. Early addition of iodine prevented the sodium amide from becoming densely packed and

adherent in the narrow annulus.  The sodium amide properties changed to a porous, powdery form, which was much more amenable to movement by the improved pressure cycling process.

## PLENUM SEGMENT TREATMENT EXPERIMENTS

### Apparatus

The conceptual design for the Phase III experimental apparatus is shown in Figure 1. The vacuum pump was intended to remove nearly all oxygen and water vapor remaining after nitrogen purging, so these impurities did not interfere with the desired sodium dissolution and iodide conversion reactions. All ammonia also was evaporated through the high efficiency particulate air (HEPA) filter to confine any potential loose alpha-emitting contamination. Semiconductor-grade liquid ammonia of 99.99% minimum purity was used in Phase III to effectively eliminate impurities from that source. The Phase III system was designed to withstand an internal pressure of 1.7 MPa. For select experiments the reaction vessel was pressurized above 1.0 MPa intermittently to investigate effects of pressure cycling on sodium dissolution rates. The pressure was gradually raised to 1.4 MPa by manually using the nitrogen regulator. Then, the pressure was rapidly dropped by partially engaging the 0.7-MPa relief valve. This process was repeated throughout the dissolution sequence in these particular experiments.

The reaction vessel in Figure 1 contains an array of instruments. A stainless steel-sheathed resistance temperature detector (RTD) measured ammonia temperature by direct immersion. A conductivity sensor consisting of two horizontally oriented stainless steel electrodes monitored reaction progress. A digital pressure transducer accurately indicated pressure changes throughout each experiment. Outputs from these sensors were recorded on a data acquisition system (DAS). Ammonia liquid level was determined by observation through a sight glass on a reaction vessel end flange. Temperature, pressure, ammonia level, and solution conductivity were calibrated before experimental trials began.

### General Procedure

ANL-W sectioned the Fermi-1 blanket fuel element between the 35.6-cm slugs of depleted uranium fuel meat to avoid freeing alpha contamination. The element was sectioned in an inert glove box and each segment was encased inside a sealed stainless steel tube.  Each tube was then placed inside a steel outer container also sealed under an inert gas. Consequently, it was a surprise to see corrosion product on the sodium upon opening the tube in an inert glove box. Where possible, the corrosion product was scraped with a sharp knife to expose shiny sodium metal.

Each segment was loaded into the reaction vessel in an inert glove box.  The segment was held in place by centering spiders. The reaction vessel was sealed, transported to, then installed in the GTI fume hood.  The system was allowed to pump down under a vacuum so most gaseous impurities were removed.  Approximately 750 ml of ammonia was then added to the reaction vessel.  The solvated electron solution typically turned opaque almost immediately, then gradually cleared.  When the solution was clear, plumes of solvated electrons and bubbles could occasionally be seen cascading from the segment annulus.  A precipitate was often visible in the
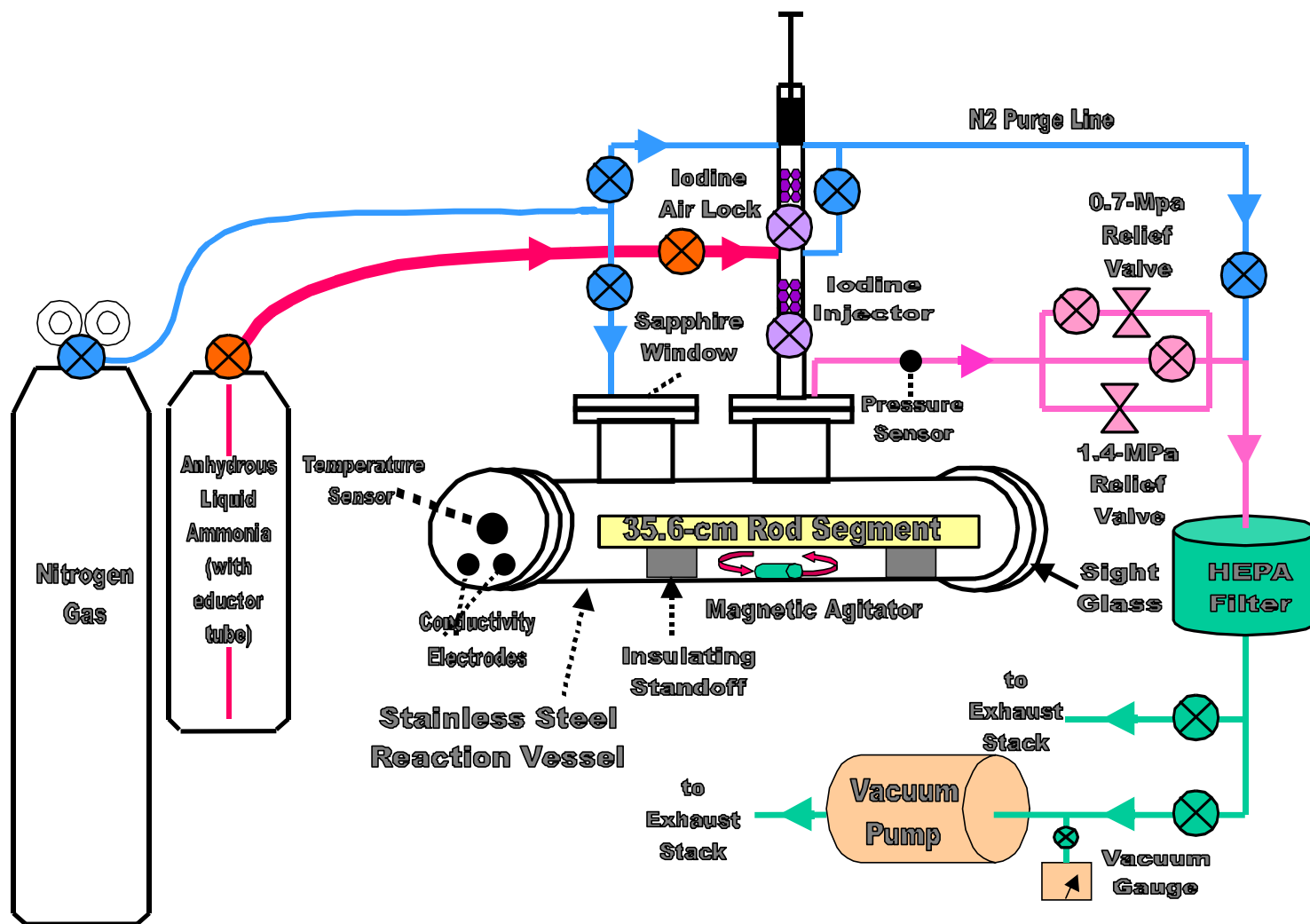
Fig. 1. Conceptual Design of Phase III Apparatus.

reaction vessel. Iodine with an ammonia flush was added when the conductivity appeared to stabilize.  The ammonia was gradually evaporated, leaving a sodium iodide precipitate.

Treatment times were initially estimated to be approximately 10 hours by extrapolating results from previous shorter mock-up segments. It soon became apparent that much longer treatment times were not dissolving all of the sodium in the annulus.  Sodium amide, $NaNH_2$, was forming in the annulus and reaction vessel.  The sodium amide in the annulus prevented ammonia access to the sodium. Periodic pressure cycling was added to later experiments to knock the sodium amide loose from the annulus space. Each pressure cycle typically resulted in an opaque solution, which gradually cleared.  Early addition of iodine was later found to decrease treatment times also.

Following the initial treatment of the Fermi segments, each segment was returned to its stainless steel tube in the steel outer container in the inert glove box. A final rinsing was performed at the conclusion of the treatment process. The original intent of the rinsing process was to ensure that no metallic sodium remained on the cladding or the uranium segment before returning the segments to ANL-W for disposal.  Visual inspection prior to rinsing confirmed the lack of visible sodium on the cladding or the segment.  However, many pieces had a visible sodium amide residue.  Like sodium metal, sodium amide is water-reactive and, thus, a RCRA-characteristic hazardous material.  The rinsing solution consisted of a dilute (0.2%) solution of water in denatured alcohol.  The rinsing solution was very effective in almost instantly removing the gray patches of sodium amide from the cladding and depleted uranium slugs.  This reaction was accompanied by a gentle generation of ammonia bubbles and precipitation of sodium oxide on the base of the tray.  All treated components appeared bright and shiny after the rinse, as shown in Fig. 2.
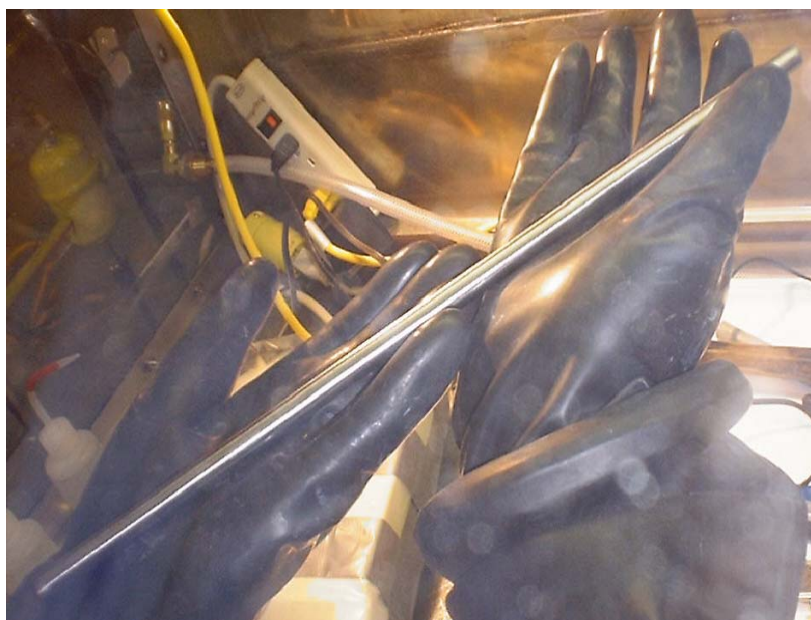


Fig. 2   Shiny uranium fuel segment with no evidence of chemical attack

A brief synopsis of each experimental trial is found in Table I. The top plenum segment, F5, had a shorter 14.6-cm depleted uranium slug, was predicted to contain 7.28 g of sodium, and have a

significantly shorter treatment time than the remaining segments. The bottom segments, F1-F4, were 35.6 cm long and were each expected to contain 4.0 g of sodium. In Table I, the experiment is identified with a FX-Y number. The FX number denotes the plenum segment, with the X ranging from 1 to 5. The Y number is number of times the FX segment has been treated, with 1 being the first treatment. F5-2 would then denote the second experimental treatment of the F5 segment. Experimental condition variations, extenuating circumstances, and total treatment times are also listed in Table I. It should be noted that several experiments had seal failures, which could be prevented by design changes in scale up equipment.

Table I  Experimental trial results

| Experiment | Experimental Conditions | Extenuating Circumstances | Time in ammonia solution | Outcome |
|---|---|---|---|---|
| F5-1 | Commodore process modified with iodine, no pressure cycling | Epoxy degraded in solution | 10 hours | F5 unsuccessful |
| F5-2 | Commodore process modified with iodine, no pressure cycling | Epoxy contamination from previous experiment | 9 hours | F5 successful (19 total hours) |
| F1-1 | Commodore process modified with iodine, no pressure cycling | O-ring failure, ammonia evaporated. Replaced O-ring, experiment resumed. | 42 hours | F1 unsuccessful |
| F1-2 and F2-1 | Commodore process modified with iodine and pressure cycling. Circular cuts in F2. |  | 30 hours | F1 successful (72 total hours) F2 unsuccessful |
| F2-2 and F3-1 | Commodore process modified with iodine and pressure cycling. Circular cuts and lengthwise cuts in F2. | Protruding fuel on F3. Conductivity probe seal failed, ammonia evaporated. No iodine addition. | 17 hours | F2 successful (47 total hours) F3 unsuccessful |
| F3-2 and F4-1 | Commodore process modified with early iodine addition and pressure cycling. | Protruding fuel and sodium amide from previous experiment on F3. Conductivity probe seal failed, ammonia evaporated. | 10 hours | F4 successful (10 total hours) F3 unsuccessful |
| F3-3 | Commodore process modified with early iodine addition and pressure cycling. | Protruding fuel and sodium amide from previous experiment on F3. | 3.5 hours | F3 successful (30.5 total hours) |

**Experimental Comparison**

The basic Commodore process, modified with iodine as a precipitating agent, is best exemplified by the F1-1 experiment. Conductivity and pressure measurements for the 35.6-cm F1 segment are shown in Figure 3. The ammonia solution turned dark very quickly and the conductivity rose gradually.  Sharp conductivity peaks occurred at 270 and 340 minutes of elapsed time. Precipitate was visible at about 300 minutes of elapsed time.  A flange O-ring failed at 840 minutes and all of the ammonia evaporated.  Nitrogen was added to maintain an inert atmosphere and the system was repaired. Ammonia was readmitted to the reaction vessel and the experiment continued.  Two iodine injections, 11.04 g and 4.38 g (0.12 M and 0.15 M, respectively), were added to the reaction vessel at 1810 and 2995 minutes. Iodine addition resulted in sharp conductivity increases.  Four distinct jumps in conductivity occurred after the first iodine addition, with no visible change in the appearance of the solution. Ammonia was evaporated after the segment had been immersed in ammonia for a total of 42 hours. The expected weight loss was 4.0 g of sodium, and the actual weight loss was 3.27 g.  The F1 cladding and fuel rod could not be separated at the conclusion of this experiment, but 2.0 g of white powder was tapped from the annulus. The powder was established as sodium amide by melting point.
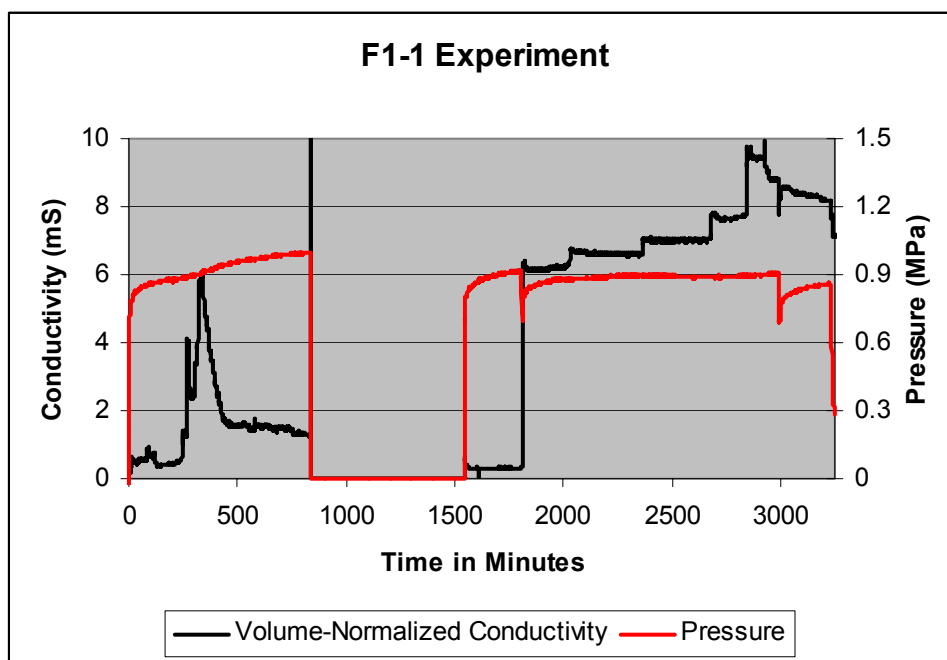


Fig. 3  Conductivity and pressure for F1-1 processing

For comparative purposes, the F3-2 and F4-1 experiment best exemplifies the GTI improved process. The F4 segment was processed at the same time the F3 segment was reprocessed.  The conductivity and pressure measurements are shown in Figure 4. The initial conductivity curve is similar to the conductivity curve for the F1-1 experiment in Figure 3, where the conductivity rose to 6 mS after 340 minutes. In this experiment, the conductivity stepped up to 6 mS after 245 minutes.   Pressure cycling was used in this experiment, but was not used in the F1-1 experiment. Pressure cycling appeared to decrease the reaction time by approximately 36 percent at this point

in the experiment.  The solution was inky with a few bubbles after 12 minutes.  White precipitate was visible after 75 minutes.  The solution turned inky and cleared as the pressure was cycled. The two step increases at 264 and 308 minutes were each the result of iodine addition of 5.50 and 5.52 grams (0.05 M and 0.09 M, respectively).  Iodine was added earlier in this experiment to minimize the sodium amide formation in the annulus and prevent the annulus from becoming plugged with sodium amide.  There was no visible precipitate in the reaction vessel shortly after the second iodine injection. Pressure cycling after the second iodine addition resulted in intermittent plumes and bubbles and a slowly decreasing conductivity curve. A precipitate had again formed at 545 minutes of reaction time. The conductivity connection seal failed at 604 minutes and all of the ammonia was released from the reaction vessel.
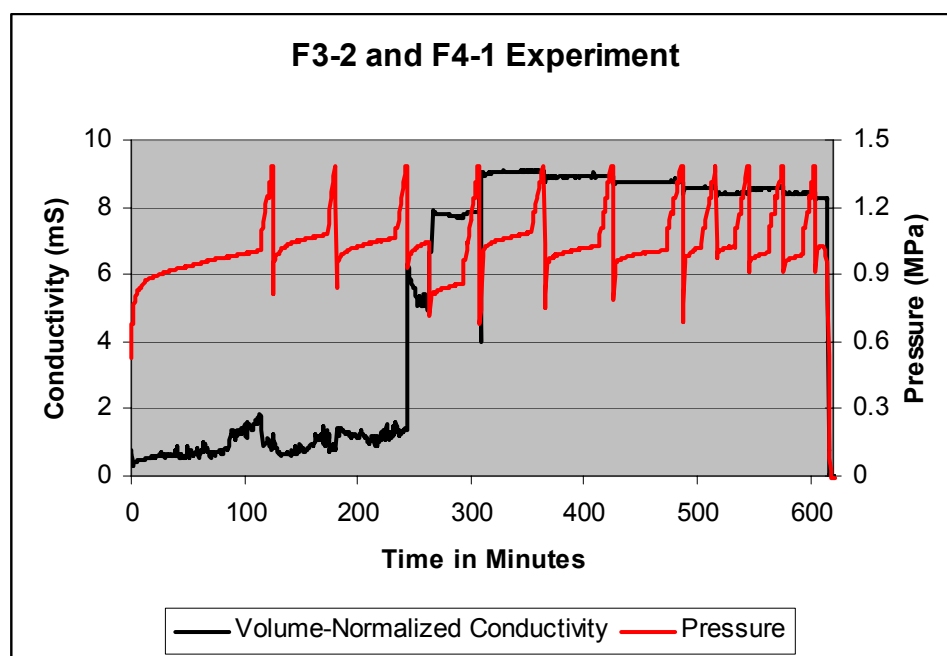


Fig. 4  Conductivity and pressure for F3 reprocessing and F4 processing

Because the reaction time for this F3/F4 experiment was only 10 hours before failure and previous unsuccessful experimental trials had run much longer, the F3 and F4 segments were not expected to be fully treated for sodium removal.  Upon removal from the reaction vessel, this was indeed the case for the previously plugged F3 segment, which did not have any weight loss over the reaction time. However, the weight loss for the F4 segment was 3.42 g out of the expected 4.0 g.  (Some sodium amide remained in the annulus.) When the fuel element was tapped to see if it was possible to extract from the cladding, the cladding and the fuel meat separated.   The pressure cycling and the early addition of the iodine appeared to have appreciably reduced the reaction time for this process down to within 320 minutes, after which there is no indication of dissolving sodium in Figure 3.  This was a significant process improvement and substantially faster than the 560 minute reaction time anticipated by extrapolating Phase II mockup results.

**Radiological Results**

There were several unknowns regarding radiation in the experiment.  The depleted uranium (DU) had been contained within the fuel cladding for a considerable time.  It was anticipated that there could be minor amounts of DU and daughters of the U-238 decay chain that could be contained within the sodium bonding of the fuel rod.  Also, because of the surface impurities that might be contaminating the DU, a small amount of DU compounds could be contained in the sodium. In addition, it was not known if reactions or different operations would cause some degradation of the DU and create small particle contamination of the reaction products. Several experiments had procedures that could have scored the DU rod, as when the cladding was cut with the tubing cutter, which may have released particles of DU to the sodium.

Contamination control was not taken for granted throughout the entire operation; it was assumed that any operation or reaction within the reaction vessel or inadvertently with oxygen could produce DU contamination with the potential for release. Because of these contamination possibilities, checks were made at each step in the procedure to determine if the DU had become dispersed.  Precautions for the steps of the operation involved transfer of the fuel rod to the reaction vessel inside a nitrogen-inerted glove box and checking for contamination at each step where contamination could possibly be released from the fuel rod.  Each of the monitored exhausts from the fume hood and the glove box was filtered to prevent an unacceptable release to the environment.  The possibility of contamination release was checked whenever a new surface of sodium was exposed and especially when a new DU surface was exposed.  When anything was to be removed from the glove box or fume hood, a smear of that object was taken and placed by the door of the enclosure to be removed and counted before the object was removed. The same controls were instituted for the GTI fume hood where the reaction with anhydrous liquid ammonia was performed. Both of the monitored exhausts from the fume hood and glove box were HEPA-filtered to positively prevent an unacceptable release of radioactive particles to the environment.

Early in the performance of the project, the level of sensitivity for detection of DU was established for the instrument that would be used to detect DU in any of the numerous samples that would be taken during the project. The test showed a 10-minute count would be required on all samples taken to detect any additional activity above background, given the natural background level of activity present in the general area. For 10-minute counts the minimum detectable level (MDL) is approximately 20 disintegrations per minute at $2\sigma$ uncertainty. Converting this MDL to micrograms of depleted uranium yields an MDL of approximately 25 micrograms of U-238. Hence, at the limit of sensitivity for the counting instrument used for all of the samples collected during this experiment, 25 micrograms of depleted uranium on any sample would have been detected with a 95% confidence level.

None of the 63 swipes or samples indicated a presence of DU.  The swipes taken before the loading the reaction vessel did not show any indication that DU had become fragmented or that DU had been released to the sodium of the rod. All readings of potential DU spread following cladding cuts failed to show that DU had been released from the rod.  None of the samples of the reaction product or samples taken on the immersed RTD gave indications that the DU had degraded during the reaction such that even minor amounts of DU were included in the reaction product. The hood filters were checked for contamination and showed no indication at any time

that DU had been released within the hoods. During the entire operation, there was no instance of personnel or equipment contamination, nor any indication that there was a measurable release to the environment.

## DISCUSSION

Initial proof of principle experiments determined that sodium could be successfully removed from stainless steel mockups with 100 percent efficiency in an ammonia solution. Additional results concluded that conductivity measurements were an effective means of monitoring reaction progress and adding iodine to the solution rapidly produced non-hazardous sodium iodide as a reaction product. The purpose of the final experiments was to verify bonded sodium could be extracted from segments of an unirradiated Fermi-1 blanket fuel element without adversely affecting the depleted uranium fuel meat.

Sodium was successfully extracted from the Fermi-1 blanket fuel element segments. Table II shows the initial, as-received and final, after-rinsing weights for each of the Fermi segments, along with the sodium removed. The nominal design value of sodium in the F5 segment was 7.28 g, but 8.00 g of sodium was removed. The total expected sodium removal for the 142-cm segments totaling F1 through F4 was 16 grams. The actual sodium removed from these segments was 16.07 grams, a difference of merely 0.4%. The electronic balance used to weigh the segments has a readability/linearity of 0.01 g and a repeatability of 0.007 g. From the minor variation in sodium removed from each segment and protruding fuel element in F3, it appears that the cladding cut point between F2 and F3 was slightly askew.

Table II  Sodium removal

| Segment | Initial Weight (grams) | Final Weight (grams) | Actual sodium removed (grams) | Expected sodium removal (grams) |
|---|---|---|---|---|
| F1 | 542.04 | 538.06 | 3.98 | 4.00 |
| F2 | 544.95 | 540.67 | 4.28 | 4.00 |
| F3 | 543.11 | 539.36 | 3.75 | 4.00 |
| F4 | 542.16 | 538.10 | 4.06 | 4.00 |
| F5 | 258.09 | 250.09 | 8.00 | 7.28 |

In addition to successful sodium removal, the remaining depleted uranium fuel meat was not adversely affected. Radiological results show that the DU was not fragmented, released to the sodium, released during the ammonia reaction, or released during cladding cutting. There was no instance of personnel or equipment contamination, nor any indication that there was a measurable release to the environment. The uranium rods were bright and shiny after the final rinse, with no evidence of pitting.

Another objective was to render the sodium into a nonhazardous chemical form that is not subject to the RCRA. In initial experiments, copper iodide was added to the sodium-ammonia solution to form sodium iodide but left a potentially pyrophoric copper residue. Subsequent experiments added elemental iodine to the sodium-ammonia solution. The iodine to iodide conversion occurred within one minute and the sodium and iodine ions combined with nearly

100 percent efficiency to form non-hazardous sodium iodide. This was confirmed by x-ray diffraction analysis.

Using ammonia to remove sodium from fuel elements involves complex chemical reactions. Actual results do not correlate well to theoretical results because previous studies have not been performed in the confinement of a narrow annulus. Even in theoretical situations, the conductivity of a fixed amount of sodium in an ammonia solution is dynamic, changing rapidly over time. While sodium was successfully removed from Fermi-1 blanket fuel segments, several deficiencies in the Commodore process became apparent during the experimental process.

The first challenge was the formation of a white, scaly substance in the segment annuli. This substance appeared to form at the sodium-ammonia interface, ceasing and blocking further sodium reaction with the ammonia. A sample of the white, scaly substance was collected from the F1 annulus. This sample was heated to determine the melting point. The sample melted at approximately 493 $^{\circ}$K. A list of potential compounds and their melting points are found in Table III. Sodium amide melts at 483 $^{\circ}$K and all of the other potential compounds have melting points at least 100 degrees higher. As expected, the sample appears to be sodium amide. Formation of insoluble sodium amide is catalyzed by metal, so the stainless steel reaction vessel, Fermi-1 cladding, and uranium fuel all increased the likelihood of sodium amide formation. Sodium amide is merely an intermediate reaction product until iodine is added, which breaks up the sodium amide to form sodium ions, iodide ions, ammonia, and nitrogen gas. However, the presence of sodium amide significantly increased the reaction times by blocking the access of ammonia to the sodium interface.

Table III  Sodium Compound Melting Points

| Compound | Formula | Melting Point (K) |
|---|---|---|
| Sodium Amide | $NaNH_2$ | 483 |
| Sodium Carbonate | $Na_2CO_3$ | 1124 |
| Sodium Hydroxide | NaOH | 591 |
| Sodium Iodide | NaI | 934 |
| Sodium Oxides | $Na_2O + Na_2O_2$ | >673 |

Another challenge was determination of complete sodium removal. Initial experiments successfully used visual inspection and conductivity measurements to monitor the progress of the dissolution and conversion reactions. In the Fermi-1 segment experiments, a purple solvated electron solution or cascading purple plumes from the segment were again evidence that sodium was actively dissolving. Conductivity measurements consistently rose during this active period also. Conversely, if no purple plumes were evident and the conductivity was flat, sodium was no longer reacting with ammonia. However, this did not necessarily mean that the sodium reaction was complete. In many instances, sodium amide plugged the annulus and prevented the ammonia-sodium reaction from occurring. Absolute conductivity numbers were not a reliable indication of reaction completion because the conductivity measurements reflected multiple, time-dependent reactions. Unfortunately, reaction time is not a reliable indicator of reaction progress, either. One fuel segment was reprocessed with no weight loss in the same vessel that another fuel element had all of the sodium removed. This difference was primarily due to

whether the sodium amide was porous and powdery or dense and firmly adherent. The only reliable method of determining complete sodium removal was by visual inspection after removing the segment from the vessel at the conclusion of the experiment.

A patent has been filed on the process improvements that were made to overcome the problem of sodium amide plugging [11]. Periodic pressure cycling forced loose sodium amide from the annulus and reestablished ammonia access. Pressure cycling was accomplished by gradually raising the reaction vessel pressure with an inert gas, then abruptly dropping the pressure through a relief valve. Experimental trials without pressure cycling inevitably resulted in a plugged sodium amide annulus and the segments had to be retreated, despite lengthy treatment times. The pressure cycling increased conductivity and bubble production at segment ends, when solution opacity did not prevent observation. As stated previously, increased conductivity is an indication of the ammonia reestablishing contact with the sodium and resulting solvated electrons in solution. Pressure cycling alone could not completely overcome the sodium amide plugging. An additional improvement of early addition of the iodine conversion reagent was found to change the sodium amide from a dense, adherent form to a porous, powdery form. The powdery form of sodium amide was much more amenable to movement by pressure cycling from the annulus. The combination of these two enhancements not only overcame plugging by sodium amide, but also produced a significant increase in dissolution speed.

While this project has demonstrated the feasibility of removing sodium from irradiated Fermi-1 blanket fuel elements, this method can also be used to deactivate sodium or sodium-potassium alloys used as a liquid coolant and/or heat transfer agent in a nuclear reactor system [11]. The alkali metal is dissolved in an ammonia solution to form a reaction mixture of alkali metal cations and solvated electrons. Elemental iodine is then admitted to the solvated electron solution, which combines with the alkali metal cations to form an alkali or alkaline earth metal halide salt. This salt would be separated from the ammonia solution to form a non-hazardous waste product.

Additionally, solidified alkali metal remaining within the coolant system after initial drainage can be dissolved by circulating an ammonia solution within the coolant system [11]. Concurrent pressure fluctuations will aid in the removal of the alkali metal adhered to surfaces and crevices in the system. Once again, iodine is then added to the solvated electron solution, which forms an alkaline iodide salt. This salt would be separated from the ammonia solution by evaporation, leaving a non-hazardous waste product.

**CONCLUSIONS**

- All of the sodium was successfully removed from each Fermi-1 fuel segment without chemically attacking the uranium fuel meat. Each treated component appeared bright and shiny with no evidence of chemical attack before shipment back to ANL-W for disposal as low-level radioactive waste.
- No radioactivity above background was ever found during the proof of principle experiments.
- An ammonia-based process for safely treating sodium-bonded Fermi-1 blanket fuel segments can also avoid generating RCRA mixed wastes by forming non-hazardous sodium iodide.

- Conductivity curve shape, absolute conductivity values, solution color and time are not necessarily reliable indicators of sodium removal completion.
- Reaction surface areas and diffusion distances are critical factors in reaction time needed for complete sodium removal.
- Progress of the dissolution front was inhibited by precipitation in the annulus of insoluble sodium amide ($NaNH_2$).
- Pressure cycling—gradually raising the reaction vessel pressure and then abruptly dropping it—forced loose sodium amide from the annulus and reestablished ammonia access.
- Early addition of the iodine conversion reagent was found to change the sodium amide from a dense, adherent form to a porous, powdery form. The powdery form of sodium amide was much more amenable to movement by pressure cycling from the annulus.
- This method can also be used to deactivate any sodium or sodium-potassium alloy used as a liquid coolant and/or heat transfer agent in a nuclear reactor system.
- This method can also be used for in situ deactivation and recovery of solidified metal coolant from surfaces of a reactor cooler system, process equipment, tool, and any other surface encrusted with alkali metals.

**REFERENCES**

1    U.S. Department of Energy, "Final Environmental Impact Statement for the Treatment and Management of Sodium-Bonded Spent Nuclear Fuel," DOE/EIS-0306, July 1980.

2    G.D. Getman, " Deactivation of Metal Liquid Coolants Used in Nuclear Reactor Systems," US Patent number 6,175,051, January 16, 2001.

3    Global Technologies, Inc., "Final Report for the Proof of Principle Experiments with Anhydrous Ammonia to Demonstrate the Removal of Sodium from Liquid Metal Reactors," January 2001.

4    Global Technologies, Inc., "Final Report for the Phase II Experiments with Anhydrous Ammonia to Demonstrate the Removal of Sodium from Liquid Metal Reactors," June 2002.

5    H.H. Sisler, "Chemistry in Non-Aqueous Solvents," Reinhold Publishing Corp., New York, NY, 1961.

6    C.E. Evers and P.W. Frank, "Solutions of Metals in Amine Solvents. II. A Conductance Function for Dilute Solutions of Sodium in Ammonia," Journal of Chemical Physics, Volume 30, No. 1, page 61, January 1959.

7    C.A. Kraus, "Solutions of Metals in Non-Metallic Solvents: Some of Their Physical and Chemical Properties," Journal of the Franklin Institute, Volume 212, page 559, November 1931.

8    J.W. Mellor, "Mellor's Comprehensive Treatise on Inorganic and Theoretical Chemistry, Volume VIII, Nitrogen and Phosphorus," page 244, Longmans, London, 1947.

9    G.E. Gibson and T.E. Phipps, "The Conductance of Solutions of Alkali Metals in Liquid Ammonia and in Methylamine," Journal of the American Chemical Society, Volume 48, page 312, February 1926.

10   J.L. Dye et al., "Ion Transport in Sodium-Ammonia Solutions," Journal of the American Chemical Society, Volume 82, page 4797, September 1960.

11   G.D. Getman and S.A. Ploger, "An Improved Process for Deactivation of Liquid Metal Coolant used in Nuclear Reactor Systems," US patent application number 60/509785.