Controlled Conversion of Sodium Metal From Nuclear Systems to Sodium Chloride

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A series of three bench-scale experiments was performed to investigate the conversion of sodium metal to sodium chloride via reactions with non-metal and metal chlorides. Specifically, batches of molten sodium metal were separately contacted with ammonium chloride and ferrous chloride to form sodium chloride in both cases along with iron in the latter case. Additional ferrous chloride was added to two of the three batches to form low melting point consolidated mixtures of sodium chloride and ferrous chloride, whereas consolidation of a sodium-chloride product was performed in a separate batch. Samples of the products were characterized via X-ray diffraction to identify attendant compounds. The reaction of sodium metal with metered ammonium chloride particulate feeds proceeded without reaction excursions and produced pure colorless sodium chloride. The reaction of sodium metal with ferrous chloride yielded occasional reaction excursions as evidenced by temperature spikes and fuming ferrous chloride, producing a dark salt-metal mixture. This investigation into a method for controlled conversion of sodium metal to sodium chloride is particularly applicable to sodium containing elevated levels of radioactivity—including bond sodium from nuclear fuels—in remote-handled inert-atmosphere environments.

Keywords: Sodium metal, Sodium chloride, Ferrous chloride, Ammonium chloride, Sodium metal deactivation, Bond sodium

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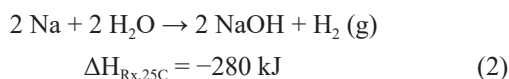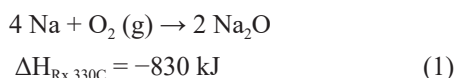|			
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1. Introduction

The use of sodium metal in nuclear systems is a double-edged sword. As a nuclear reactor coolant, sodium metal has a substantially higher thermal conductivity than that of pressurized water, and it functions at ambient pressure. However, its reactive pyrophoric nature introduces hazards that require mitigation while in use, including isolation from air and water, and suitable deactivation prior to disposal. Sodium metal is renowned for its reactivity in air and with water [1-5] per the following reactions, respectively [6].

$$4\ Na + O_2\ (g) \rightarrow 2\ Na_2O$$
$$\Delta H_{Rx,330C} = -830\ kJ \qquad (1)$$

$$2\ Na + 2\ H_2O \rightarrow 2\ NaOH + H_2\ (g)$$
$$\Delta H_{Rx,25C} = -280\ kJ \qquad (2)$$

Once ignited, sodium metal burns readily in air with sufficient heat at the sodium-air interface to volatilize the metal and expand its ability to oxidize in the vapor phase, forming a sodium oxide aerosol. If the aerosol were properly contained and directed to a wet scrubber, the sodium oxide would react with water to form a sodium hydroxide solution per the following reaction [6].

$$Na_2O + H_2O \rightarrow 2\ NaOH$$
$$\Delta H_{Rx,25C} = -151\ kJ \qquad (3)$$
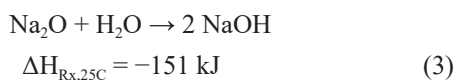
Indeed, the above approach was used for deactivation of a portion of sodium-potassium (NaK) coolant from Experimental Breeder Reactor–I. Specifically, the NaK was burned in air and the resultant aerosol was collected in a wet scrubber, forming a hydroxide solution that was subsequently carbonated with carbon dioxide gas and solidified into a cementitious mixture [7] (Note: The reactions of potassium metal in NaK occurred analogously to those identified for sodium metal in Eqs. 1 and 3).

The reaction of sodium directly with water could lead to a violent reaction if the generated hydrogen gas subsequently ignited in air by the heat evolved from the sodium-water reaction. This could lead to the following explosive hydrogen-oxygen reaction [6].

$$2\ H_2\ (g) + O_2\ (g) \rightarrow 2\ H_2O$$
$$\Delta H_{Rx,25C} = -572\ kJ \qquad (4)$$
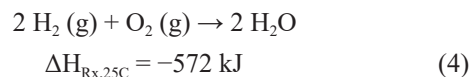
If air were excluded from a sodium-water reaction, the explosive hydrogen-oxygen reaction could be eliminated. The resulting sodium-water reaction would still be considered vigorous with sufficient heat evolved to boil the resultant sodium hydroxide solution. However, if sodium metal and water were metered into a concentrated sodium hydroxide solution under a nitrogen atmosphere, deactivation of the metal to sodium hydroxide could proceed in a controlled fashion. Indeed, the above approach was used to deactivate and dispose of 330,000 liters and 50,000 liters of sodium metal primary and secondary coolant, respectively, from Experimental Breeder Reactor–II (EBR-II) in what was termed a caustic injection process [8].

The above-described methods for deactivation of bulk NaK and sodium metal coolants occurred in separate facilities dedicated to these types of alkali metal treatments. Even though the NaK and sodium coolants were slightly radioactive, the treatment equipment was manually operated and did not require significant radiological shielding. In contrast, bond sodium from EBR-II driver and blanket fuel is in contact with nuclear fuel, and some migration of fission products (particularly ^{137}Cs) into the sodium has occurred. Deactivation of separated bond sodium would likely need to be accomplished remotely, due to elevated radioactivity levels. Currently, portions of the bond sodium in used EBR-II fuel are deactivated upon immersion of the chopped fuel elements in uranium electrorefining salt via reaction with uranium trichloride, per the following generalized reaction mechanism for metal chlorides.
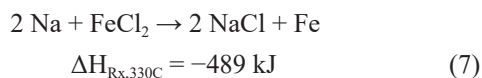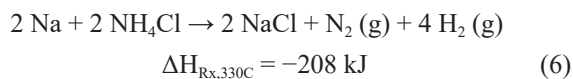
$$x\ Na + MCl_x \rightarrow x\ NaCl + M \qquad (5)$$

Table 1. Operating conditions for series of sodium metal deactivation runs

Run	Mixture	Heating	Sampling
1	Na, NH$_4$Cl (100% of stoichiometric)	300–330°C, 400°C	n/a
	+ NH$_4$Cl (10% of stoichiometric)	400°C	mid-run sample of loose particulate product
	+ FeCl$_2$ (for eutectic mixture with NaCl)	700°C	crushed final sample of consolidated product
2	Na, NH$_4$Cl (100% of stoichiometric)	300–330°C, 400°C	n/a
	+ NH$_4$Cl (10% of stoichiometric)	400°C	mid-run sample of loose particulate product
	No addition	850°C	crushed final sample of consolidated product
3	Na, FeCl$_2$ (100% of stoichiometric)	300–330°C, 400°C	n/a
	+ FeCl$_2$ (10% of stoichiometric)	400°C	n/a
	+ FeCl$_2$ (for eutectic mixture with NaCl)	700°C, 850°C	crushed final sample of consolidated product

Where: M = metal

Depletion of uranium trichloride from bond sodium in a uranium electrorefiner electrolyte is undesirable, however, as it necessitates periodic replenishment. Furthermore, sodium chloride formation in the electrolyte impacts the melting point and consequent useful lifetime of a uranium electrorefiner electrolyte. Therefore, deactivation of plenum sodium (i.e., bond sodium above the fuel column in an EBR-II driver fuel element that is not included in the uranium electrorefining process) requires a separate deactivation method. Researchers at Idaho National Laboratory (INL) have investigated deactivation options for bond sodium, including reaction with metal chlorides [9].

The objective of this study was to expand the investigation of deactivation methods for bond sodium by using a non-metal chloride in combination with, or separate from, a metal chloride. Specifically, the deactivation of molten sodium metal at bench-scale with ammonium chloride and ferrous chloride per the following reaction mechanisms was investigated [6].

$$2\,Na + 2\,NH_4Cl \rightarrow 2\,NaCl + N_2\,(g) + 4\,H_2\,(g)$$
$$\Delta H_{Rx,330C} = -208\,kJ \tag{6}$$

$$2\,Na + FeCl_2 \rightarrow 2\,NaCl + Fe$$
$$\Delta H_{Rx,330C} = -489\,kJ \tag{7}$$

Once formed, the sodium chloride (melting point of 801°C) was consolidated "as is" or it was mixed with sufficient ferrous chloride to form a eutectic mixture of ferrous chloride and sodium chloride with a melting point of 374°C [10].

2. Experimental Aspects

2.1 Approach

The approach for this experimental study was to load 1 g of sodium metal into a 10-ml boron nitride crucible (Kurt J. Lesker Co.) and heat it on a hot plate (Cole Parmer, StableTemp) to a nominal temperature range of 300–330°C. Ammonium chloride or ferrous chloride particulate was incrementally added to the molten sodium on the hot plate and stirred with a 6-mm diameter glassy carbon rod (SIG-RADUR). Periodically the sodium-salt mixture was placed in a box furnace (Thermo Scientific, Thermolyne) for several minutes at 330°C.

After an accumulated stoichiometric addition of ammonium chloride or ferrous chloride, the salt-metal mixture was placed in the furnace and heated to 400°C for approximately 30 minutes to gasify any remaining ammonium chloride (sublimation point of 338°C), as applicable. Additional ammonium chloride or ferrous chloride, amounting

to 10% of the stoichiometric value for the initial sodium loading, was then stirred into the reaction product on the hot plate. The mixture was then placed in the furnace at 400°C for approximately 2 hours, after which the furnace was de-energized and allowed to cool to ambient. A mid-run sample of the loose particulate product was taken, after which sufficient ferrous chloride was added, as applicable, to the product and heated to 700°C to form a eutectic mixture with the generated sodium chloride.

Otherwise, the loose particulate product was heated to consolidation at 850°C for approximately 1 hour. The consolidated products were allowed to cool to ambient, after which they were crushed and ground to a powder for sampling. The procedure was repeated for the series of three runs, as outlined in Table 1.

The series of runs was performed in an argon atmosphere glovebox (MBRAUN LABmaster dp) with a purification system that maintained oxygen and moisture concentrations over the course of the experiments below 10 ppm and 0.1 ppm, respectively.

2.2 Materials

The sodium metal loading for each deactivation run was cut from a block (Alfa Aesar, 99.8%) and further sized to remove oxidized surfaces. Ammonium chloride is hygroscopic and was not available in a high-purity anhydrous form from suppliers. Consequently, the ammonium chloride (Alfa Aesar, 99.999%, Puratronic) used in this study was dried and sieved to a desired particle size using a bench-top box furnace in a separate argon atmosphere glovebox. Specifically, the procured granular ammonium chloride was loaded into trays and heated to 120°C for at least 20 hours, followed by heating at 140°C for at least 4 hours. The dried material was crushed and sieved to particle sizes below 20-mesh. Ferrous chloride (Sigma Aldrich, 99.99%) was procured as anhydrous -10 mesh beads packaged under argon. It was crushed to approximate the size of the ammonium chloride for sodium deactivation.

Fig. 1. Progression of sodium metal deactivation for run 1 from left to right, top to bottom.

2.3 Sample Characterization

Product samples from the series of deactivation runs were ground into fine powders and characterized using X-ray diffraction (XRD) (Rigaku SmartLab, Cu Kα, 40 kV and 44 mA). The XRD data were collected between 10–80° with a step of 0.04° at 4° per min.

3. Results

In the first run, sodium metal was loaded into a boron nitride crucible, heated, and deactivated as described. Initially, the molten sodium metal contacted the crucible bottom and wall. Upon addition of ammonium chloride particles to the surface of the sodium, no sputtering or other signs of a vigorous reaction were observed. Upon stirring, the ammonium chloride particles moved through the sodium to the bottom of the crucible. Upon continued additions and stirring of ammonium chloride, the molten sodium metal soon formed a ball atop a bed of loose particulate reaction product. The ball of sodium gradually decreased in size upon continued ammonium chloride additions and stirring. No bulk sodium metal was observed after the last addition of ammonium chloride, leaving behind a loose particulate with a violet hue. However, the violet hue subsided after

Table 2. Summary of feed material masses for series of deactivation runs

Run	Na (grams)	NH$_4$Cl (grams)	FeCl$_2$ (grams)
1	1.003	2.387 + 0.265 = 2.652	4.022
2	1.012	2.355 + 0.266 = 2.621	n/a
3	1.002	n/a	2.762 + 4.599 = 7.361

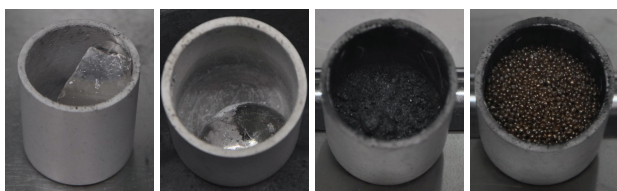Fig. 2. Final consolidated products for runs 1–3 from left to right.

Fig. 3. Progression of sodium metal deactivation for run 3 shown from left to right: cut sodium, molten sodium, mid-run product, and mixture before consolidation.

adding additional ammonium chloride (10% of stoichiometric) and heating the product at 400°C. The progression of sodium metal deactivation for run 1 is shown in Fig. 1.

A mid-run sample of the loose fill product was taken, after which the product was blended with ferrous chloride and heated for consolidation. A molten product with slight, reddish-brown fuming was observed at 700°C, prior to de-energizing the furnace. After cooldown, a consolidated product was observed that was fixed to the boron nitride crucible. Dark material was also observed adhering to the inner and outer walls of the crucible, as shown in Fig. 2.

The second run proceeded similarly to the first run with the exception that the mid-run product was transferred from the boron nitride crucible to a glassy carbon crucible (SIG-RAGUR) for consolidation at 850°C. The consolidated product from run 2 separated from the crucible in translu-cent colorless shards, as shown in Fig. 2.

Upon early additions and stirring of ferrous chloride in molten sodium in run 3, a dark precipitate formed, and the sodium metal pool took on a concave shape, wetting the walls of the boron nitride crucible. Midway through the incremental ferrous chloride additions, a slurry consis-tency formed. The mixture was placed in the furnace for several minutes. A temperature spike on the furnace control thermocouple was observed along with significant reddish-brown fumes. Upon returning the mixture to the hot plate, the sodium's metallic sheen was gone. Addition of the bal-ance of ferrous chloride was difficult due to the increasingly hardened consistency of the product. Given the question-able homogeneity and hardness of the product, no mid-run sample was taken. The eutectic addition of ferrous chloride was added to the product, but not well mixed before pro-ceeding with consolidation. Some fuming of the product in the furnace was observed at 700°C, but the product was not completely molten. Consequently, the furnace temperature was raised to 850°C, at which point significant fuming was observed along with a molten product. The furnace was de-energized, and the product was allowed to cool to ambient. After cooldown, a dark consolidated product with some loose reddish-brown exfoliated material on the surface was observed. The product was fixed to the boron nitride crucible, and material was observed on the inner and outer walls of the crucible, as shown in Fig. 2. A progression of the sodium deactivation for run 3 is shown in Fig. 3. A sum-mary of feed material masses for the series of runs is shown in Table 2.

The consolidated products for runs 1 and 3 were broken and separated from their respective boron nitride crucibles.

Table 3. Summary of identified compounds in product samples for series of deactivation runs

| Run	Sample	Identified Compounds
1	Mid-run	NaCl
	Final	NaCl, FeCl$_2$, Fe, Na, Na$_3$Cl$_2$, Na$_2$Cl
2	Mid-run	NaCl
	Final	NaCl
3	Final	NaCl, FeCl$_2$, Fe, Na, Na$_3$Cl$_2$, Na$_3$Cl

The products from all three runs were crushed and ground to a powder, from which random grab samples of the homogenized materials were taken and analyzed via XRD. The XRD patterns for each of the sample products are shown as a combined plot in Fig. 4. Identified compounds for the respective XRD patterns are summarized in Table 3.

4. Discussion

Ammonium chloride decomposes upon reaching its sublimation point at 338°C into its component gasses, hydrogen chloride and ammonia, via the following reaction.

$$NH_4Cl \rightarrow HCl\ (g) + NH_3\ (g) \qquad (8)$$

In contact with sodium metal, hydrogen chloride reacts to form sodium chloride and hydrogen gas, while ammonia reacts to form sodium amide and hydrogen gas via the following reactions.

$$Na + HCl\ (g) \rightarrow NaCl + \tfrac{1}{2}\,H_2\ (g) \qquad (9)$$

$$Na + NH_3\ (g) \rightarrow NaNH_2 + \tfrac{1}{2}\,H_2\ (g) \qquad (10)$$
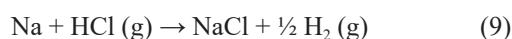
Sodium amide has some interesting properties with a reported melting point of approximately 200°C and decomposition to its elements above 400°C per the following reactions [11].
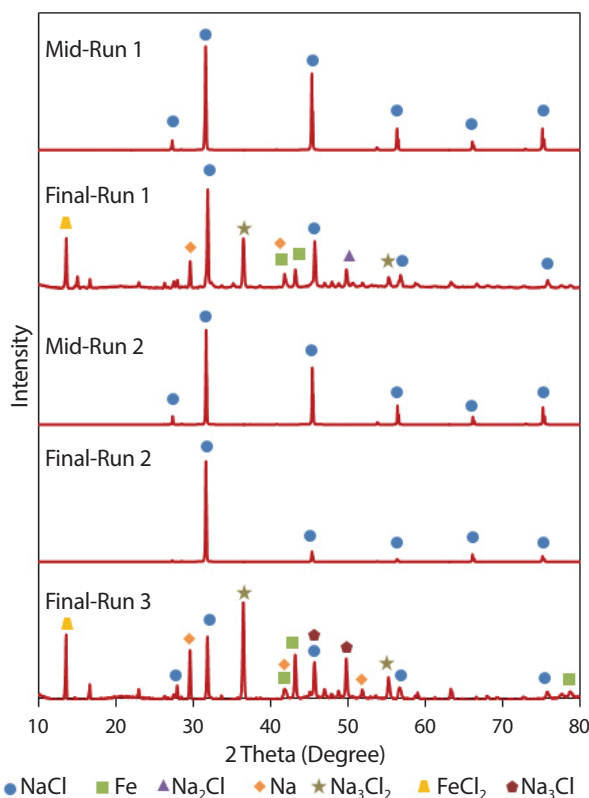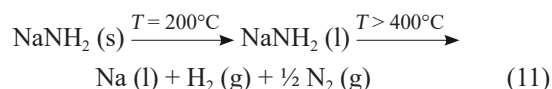

Fig. 4. XRD patterns for sample products.

$$NaNH_2\ (s) \xrightarrow{T=200°C} NaNH_2\ (l) \xrightarrow{T>400°C}$$
$$Na\ (l) + H_2\ (g) + \tfrac{1}{2}\,N_2\ (g) \qquad (11)$$

Indeed, the cracking of ammonia gas in a sodium metal-sodium amide system per the following reaction mechanism has been proposed as a way of storing and delivering hydrogen for a hydrogen-based energy sector [12].

$$2\,NH_3\ (g) \xrightarrow{Na + NaNH_2} N_2\ (g) + 3\,H_2\ (g) \qquad (12)$$

However, in the presence of hydrogen chloride gas, sodium amide reacts to form sodium chloride along with hydrogen and nitrogen gasses per the following reaction.

$$2\,NaNH_2 + 2\,HCl\ (g) \rightarrow 2\,NaCl + N_2\ (g) + 3\,H_2\ (g)$$
$$(13)$$
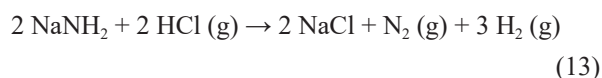
Given the formation of sodium amide as an intermediate compound in the reaction between sodium metal and ammonia chloride, the combination of Eqs. 8, 9, 10, and 13 becomes Eq. 6.

The deactivation of sodium metal (with a melting point of 98°C) in a temperature range of 300–330°C was selected to provide sufficient superheat for a molten sodium phase while precluding the flash sublimation of ammonium chloride. This operating temperature range along with a metered and stirred addition of ammonium chloride resulted in a controlled reaction of sodium metal per the foregoing reaction mechanisms. A subsequent addition of a 10% stoichiometric excess of ammonium chloride and exposure to 400°C produced a pure loose sodium chloride particulate, as evidenced by XRD analysis of the mid-run products for runs 1 and 2 (see Fig. 4).

The addition of ferrous chloride to the mid-run 1 product served to lower the melting point needed to consolidate the sodium-ferrous chloride product. Some reddish-brown fuming was observed during the consolidation step, which was attributed to ferrous chloride with a vapor pressure at 700°C of 1,700 Pa compared to 3 Pa for pure sodium chloride [6]. The melting point suppression from a ferrous chloride addition to sodium chloride comes at an expense, as the theoretical volume and mass of the consolidated product are roughly double and triple those, respectively, of pure sodium chloride. Furthermore, the possible presence of sodium and iron metal in the consolidated product via XRD (see Fig. 4) is troubling, which would require further investigation to determine its validity and origin. On the other hand, the consolidation of the mid-run 2 product at 850°C yielded a pure sodium chloride (see Fig. 4) that separated readily from a glassy carbon crucible.

The deactivation of sodium metal with ferrous chloride (melting point = 677°C) was performed in a temperature range of 300–330°C for direct comparison to the ammonium chloride runs. As described, the intermediate product was a dark thick slurry, which made further mixing of the reactant difficult. Furthermore, uncontrolled reaction of the mixture occurred upon heating in a furnace, as evidenced by spikes in furnace thermocouple readings and reddish-brown fuming. With a melting point of 677°C it is likely that surfaces of ferrous chloride particles became passivated without completely reacting upon their addition and stirring in molten sodium at approximately 300–330°C on a hot plate. After heating in a furnace at 330°C, the passivation layers were likely breached, allowing the ferrous chloride-sodium metal reaction to proceed at an accelerated rate. As shown in Eqs. 6 and 7, the heat of reaction from ferrous chloride and sodium metal is substantially higher than that from ammonium chloride and sodium metal. Specifically, the former heat of reaction could have led to melting, accelerated reaction with sodium, and fuming of ferrous chloride along with an accompanying temperature spike of the furnace thermocouple.

The formation of an iron product in run 3 likely contributed to the spreading of sodium as it wetted the metal product, which was in stark contrast to the balling of molten sodium upon reaction in runs 1 and 2. The stiff consistency of the mid-run 3 product also contrasted sharply to the loose particulate midway through runs 1 and 2. The stiff consistency precluded the mixing of additional ferrous chloride prior to consolidation of the run 3 product, which necessitated stepping the operating temperature from 700°C to 850°C to obtain sufficient superheat to melt the mixture. Characterization of the run 3 final product identified the possible presence of sodium metal, suggesting an incomplete conversion of the feed material to its chloride.

5. Conclusions

A series of three runs was performed to assess the conversion of sodium metal to sodium chloride separately with ammonium chloride and ferrous chloride. Metering and stirring a stoichiometric addition of ammonium chloride into molten sodium at a temperature range of 300–

330°C successfully produced a loose particulate product with a violet hue and no observable sodium metal in two separate runs. Deactivation of the sodium metal in these two runs proceeded without sputtering or other signs of reaction excursion. Mixing a 10% stoichiometric excess of ammonium chloride into the violet particulate products and heating to 400°C formed colorless loose particulate products, which were characterized as pure sodium chloride.

One batch of loose sodium chloride particulate was successfully consolidated upon heating to 850°C, forming pure translucent sodium chloride. The other was successfully consolidated upon blending with ferrous chloride and heating at 700°C, although some fuming of the product was observed. Further investigation into the makeup of the latter product is needed to assure the complete absence of sodium metal.

It proved challenging to deactivate sodium metal with ferrous chloride using the same approach as with ammonium chloride, as evidenced by (1) the inability to adequately blend the reactant with the sodium metal and its attendant reaction products and (2) reaction excursions and the accompanying fuming of the product. Consolidation of the product in the third run required a higher-than-anticipated temperature (i.e., 850°C in lieu of 700°C), resulting in significant fuming of the product. Furthermore, characterization of the final product from the third run exhibited the possible presence of sodium metal. Consequently, it is not recommended to deactivate sodium metal directly with ferrous chloride under the operating conditions applied in this study. In fact, the benefit of adding ferrous chloride to pure sodium chloride particulate to afford a slightly lower consolidation temperature is questionable. In short, deactivation of sodium metal with ammonium chloride in this study identified a controlled conversion of the metal to its chloride. This method lends itself well to deactivating bond sodium, which may contain high levels of radioactivity and are consequently handled in remotely operated inert-atmosphere environments.

Acknowledgements

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