NOVEL HYDROGEN-FREE TREATMENT OF SODIUM METAL MIXED WASTE BY METAL OXIDE MITIGATION OF SODIUM (MOMS) PROCESS

David L. Baldwin, Glenn W. Hollenberg, Stanley J. Bos
Pacific Northwest National Laboratory[a]
Richland, Washington

ABSTRACT

The chemical stabilization of mixed-waste sodium metal resulting from the decommissioning of sodium-cooled breeder reactors, as well as other sources, is a present and future concern for the U.S. Department of Energy and other countries. Standard treatments are reviewed and generally produce the flammable byproduct hydrogen or other flammable gases causing a possible safety concern. A novel hydrogen-free process was developed at the Pacific Northwest National Laboratory in Richland, Washington for treating sodium metal wastes. The process called Metal Oxide Mitigation of Sodium, or MOMS, converts the alkali metal into a non-hazardous, or less hazardous product for solid waste disposal.

Candidate metal oxide feed materials were selected for testing based on thermodynamic data. Laboratory testing resulted in selecting magnetite and silica as the most promising candidate feed materials. These two have been demonstrated to react to completion under optimized conditions, with no trace of sodium metal remaining in the solid reaction product. The magnetite reaction forms a sodium iron oxide compound plus iron metal while the silica feed material forms a sodium silicate plus silicon metal as the resulting product. The reactions are as follows:

- $8\ Na + 2\ Fe_3O_4 \rightarrow 4\ Na_2FeO_2 + 2\ Fe$
- $4\ Na + 3\ SiO_2 \rightarrow 2\ Na_2SiO_3 + Si$

Either solid product is ready for disposal as either non-hazardous, or possibly still hazardous mixed waste, but no longer with a Reactive Metal hazard designation. Alternatively, the product could provide feedstock to another process or product. The MOMS process may be conducted in either batch mode for smaller quantities, or *in situ* for residual sodium within piping or vessels, or the process may be operated in continuous mode for bulk scale operations.

INTRODUCTION

In the future, the U.S. Department of Energy (DOE) will face the problem of treating and stabilizing mixed-waste sodium metal resulting from the early testing and decommissioning of sodium-cooled breeder reactors. Presently, there is no definite path, in all states, for full treatment, processing, or stabilization of radioactive alkali metal to a less-hazardous or non-hazardous waste form, as regulations vary from state to state. Present methods for alkali metal treatment are generally hydrogen-generating methods, forming copious quantities of flammable gas as a byproduct. These methods are reviewed; they include reaction with water, steam, caustic, alcohol, or some other hydroxylated organic, as well as some other non-hydrogen-forming methods.

The flammable nature of the byproduct hydrogen or other fumes is a large drawback. In France in 1994, one technician was killed, four others injured, and a building destroyed in a sodium-processing accident of long-archived RAPSODIE reactor coolant sodium, when "large quantities of hydrogen and other gases were produced, leading to ... an explosion of the gaseous mixture..."[1,2].

This paper presents a demonstrated, novel method for the safe, hydrogen-free stabilization of sodium metal, or other alkali metals, to a non-hazardous, or less-hazardous product or waste form. The method involves the oxidation-reduction reaction of sodium with a metal oxide feed material, resulting in a product containing no trace of metallic sodium, with no generation of hydrogen. The resulting product can be considered either a final waste form with no reactive metal characteristics and suitable for disposal, or material as feedstock for further processing. The Metal Oxide Mitigation of Sodium (MOMS) process may be operated in either batch mode or continuous mode, providing a simple hydrogen-free process for safe disposal of alkali-metal mixed waste. It can also provide an alternate, safer D&D approach for sodium-cooled reactors, located on DOE sites, or in France, Russia, Japan, or elsewhere.

BACKGROUND

Sodium was used as a coolant in numerous sodium-cooled U.S. reactors, such as Fermi-I, the Experimental Breeder Reactor (EBR-II), and the Fast Flux Test Facility (FFTF), as well as others around the world. Coolant sodium, contaminated with radioactive constituents and itself activated, is designated as mixed waste because of the hazard classification of "reactive metal" for metallic sodium. Over 1.8 million kg (nearly 500,000 gal) of low-level radioactive sodium exist in the DOE complex.

Table I indicates the location of major quantities of radioactive sodium from reactors and from other miscellaneous sources within the DOE complex [3, 4]. This sodium is presently in the vessels, primary loops, secondary loops, and other piping and components of the reactors, or in long-term storage within drums or storage vessels. Tritium, sodium-22, cesium-137, and possibly other radioactive contaminants, result in this sodium being classified as a mixed hazardous waste.

Table I: DOE Sodium Inventories

Origin	Location	Amount (kg)	Activity (nCi/g)
FERMI	ANL-W	290,000	<1
EBR-II	ANL-W	347,000	50
FFTF	Hanford	905,000	20
SRE	Hanford	37,000	<1
HALLAM	Hanford	275,000	<0.5

There are several baseline methods or newer approaches for treating sodium metal [3, 5–8], which have been either firmly established in practice or are in various stages of development for specific applications. The purpose of these methods, shown Table II, is to convert the waste sodium to more stable solid or liquid forms that are more suitable for either disposal or further processing with the metal-reactivity issue eliminated.

Table II: Baseline or Developmental Sodium-Treatment Approaches

Method	**Description**
Reaction with steam, water vapor, or water	$Na + H_2O \rightarrow NaOH + 1/2H_2$
Reaction with alcohol-based organic	$Na + R\text{-}OH \rightarrow NaO\text{-}R + 1/2H_2$
Reaction with molten NaOH, followed by steam purge	$2Na + NaOH \rightarrow Na_2O + NaH$ $NaH + Na_2O + 2H_2O \rightarrow 3NaOH + H_2$
Combustion or calcining in air	$4Na + O_2 \rightarrow 2Na_2O$
Reaction with CO_2 gas, with optional added water vapor.	$2Na + CO_2 + H_2O \rightarrow Na_2CO_3 + H_2$

Reaction with steam or water vapor, typically in an inert gas stream, is a standard method to mitigate and stabilize sodium metal within components, particularly residual sodium adhering to walls or in crevices in enclosed storage vessels or reservoir tanks. The hydrogen generated from this exothermic reaction, particularly within the enclosed space, is generally considered a manageable issue, but the safety concern is ever present.

The Sodium Processing Facility (SPF) was constructed at ANL-W in Idaho, which uses the well-established process of reacting sodium with water or caustic to form a sodium hydroxide product. Large quantities of hydrogen are exhausted from the facility stack during operation. The final product may be either 50 wt% sodium hydroxide solution or the solid product of 70 wt% sodium hydroxide for planned burial in Idaho. However this solid product is not acceptable for burial in all states.

Alcohol or hydroxylated-organic-based reactions require use of large quantities of organic since the reaction slows considerably after 3 wt% concentration has been reached. In addition, the organic may also be flammable, creating a known, but considered manageable, fire and explosion hazard. During the 1994 accident in France described earlier, the treatment used ethylene glycol as reactant.

Sodium treatment by combustion has proven to be a standard method used by commercial vendors for disposal of non-radioactive sodium only and for sodium-contaminated piping and hardware. Containment would be a major problem for extension of this process to radioactive sodium.

The carbon dioxide gas-phase approach was developed originally in Japan [8] to stabilize thin coatings of residual sodium in vessels, tanks, and piping. Sodium residue has been stabilized on a small scale with the carbon dioxide-based system. The sodium carbonate forms a passivation coating on the sodium metal that limits the rate of reaction, requiring moisture to be pulsed into the system to permit penetration of this residual coating. The gaseous products of this reaction are carbon monoxide and hydrogen. In another carbon dioxide process, Stewart and Navratil [3] describe injecting sodium and excess carbon dioxide and oxygen into a sparged bed of sodium carbonate at very high temperature for a bulk disposal method.

DESCRIPTION OF MOMS CONCEPT

The objective of the present investigation was to develop an alternative hydrogen-free process for chemical stabilization of legacy mixed-waste sodium metal, or other alkali metal. Developing a hydrogen-free process, with resulting non-hazardous or less-hazardous solid disposal forms, could minimize safety and disposal issues normally resulting from the conventional reaction of sodium with water or alcohol. The MOMS process was developed to meet this need.

The method involves the oxidation-reduction reaction of sodium with a selected metal oxide feed material, resulting in no hydrogen or other gases being evolved. A fundamental part of the MOMS approach was to establish a controllable reaction between sodium metal and a metal oxide that yields stable, oxidized sodium compounds mixed with a benign metal slag product. The development effort was guided by targeting the following attributes for a treatment process for the sodium.

- **Hydrogen Evolution:** The process should produce no hydrogen.
- **Completeness:** The process should go to completion and hence eliminate the reactive metal hazardous characteristics of sodium.
- **Control:** The process should reliably limit temperatures and pressures within the reaction vessel during processing.
- **Disposition:** The final product should ideally be non-hazardous so that the resulting product is no longer a mixed waste, providing a solid for burial or as feedstock to another process.

Thermodynamic considerations drove the selection process. Candidate metal-oxide feed materials, described in the next section, were selected based on their published thermodynamic standard free energies of formation. Scoping tests were conducted on the candidate feed materials, and the two best materials having the characteristics based on the above four attributes were selected.

The MOMS process, when performed batch-wise, involves several steps. These are 1) blending the molten sodium and dried metal oxide at a selected mixing temperature, 2) wetting occurs resulting in gradual self-heating, 3) the wetted mixture initiates the full exothermic reaction creating the thermal spike, and 4) the final product immediately cools down. A continuous-mode version of the MOMS process, described later, would modify these four steps.

EXPERIMENTAL

Seven candidate metal-oxide feed materials were selected based on their published thermodynamic standard free energies of formation. These candidate materials tested included hematite (Fe_2O_3), magnetite (Fe_3O_4), stannous oxide (SnO), chromic oxide (Cr_2O_3), manganese monoxide (MnO), zinc oxide (ZnO), and silicon dioxide (SiO_2). The candidate materials, along with their thermodynamic data, are shown in Table III.

The experimental testing was conducted in two phases: scoping tests of all candidate metal oxides and larger-scale, more prototypic crucible tests of the two final candidate materials. All testing was conducted within an inert-atmosphere glovebox. All metal oxide feed materials tested were reagent grade, including the sodium.

Scoping Tests

Scoping tests were conducted with 3–4-mm-diameter spherical beads of molten sodium placed on a heated bed of the dried oxide feed material. Bed temperatures were measured by an embedded thermocouple with sodium beads placed in contact with the thermocouple. The reaction temperatures and thermal spike were recorded as well as the change in bead shape as an indication of wetting. The purposes of the scoping tests were to 1) establish compatibility for safety reasons, 2) determine wetting characteristics as the bead wetted the oxide material, 3) measure the reaction thermal spike, 4) conduct post-test chemical analysis on the byproducts, and 5) determine the likely best-candidate materials for further study.

Thirteen scoping tests were conducted. Figure 1 shows a typical scoping test of sodium beads being heated on a bed of MnO. The sphericity of the beads indicate wetting has not yet occurred. Scoping test results coincided well with literature predictions. See Table III for a summary of scoping-test results. The standard free energy of formation tends to roughly rank the oxides in terms of their oxidation/reduction driving force for reaction with sodium, based on the following generic reaction:

$$M_xO_y + 2y\ Na \rightarrow x\ M + y\ Na_2O \qquad \text{(Eq. 1)}$$

Post-reaction investigations included examining the reaction product by x-ray diffraction (XRD) to identify product compounds, gravimetric mass balance determination, and addition of water with detection for hydrogen to confirm completeness of reaction.

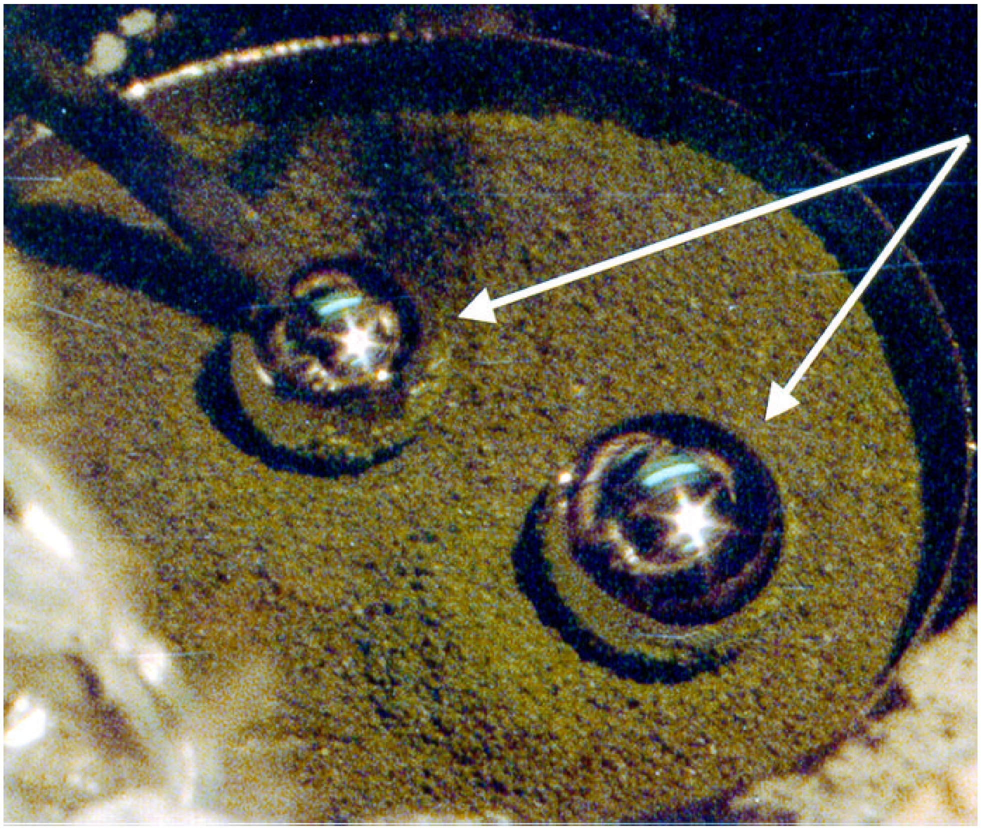

Fig. 1: Typical scoping test of sodium beads heated on a bed of MnO.

The most promising candidate materials resulting from the scoping tests were magnetite and silica. The basic reaction for magnetite as feed material, resulting in the binary product, is

$$8\ Na + Fe_3O_4 \rightarrow 4\ Na_2O + 3\ Fe \qquad \text{(Eq. 2)}$$

The selection of the most promising feed materials was based on initiation temperature, exothermicity, vigor of reaction, and extent of reaction. The magnetite and silica were the only feed materials to both react completely and also to possess controlled reaction kinetics and therefore were the basis for all of the scale-up testing that followed.

Prototypic Crucible Tests

There were larger-scale, more prototypic crucible tests in the second phase of testing. Selected stoichiometric ratios of sodium and candidate feed material were mixed together in the reaction vessel at mixing temperature and ramped via self-heating to initiation temperature, simulating actual treatment conditions. In these tests, heated stoichiometric or hyperstoichiometric quantities of dried feed material were added to and mixed with the molten sodium in a stainless steel crucible at mixing temperature, the mixture self-heated to initiation temperature, and the exothermic reaction was allowed to go to completion. Figure 2 shows a 1:1 stoichiometric ratio mixture of sodium with feed material at mixing temperature, being mixed with tongs, slowing ramping to initiation temperature.

Fig. 2: Shows 1:1 stoichiometric ratio mixture of sodium with feed material at mixing temperature, slowing ramping to initiation temperature.

Twenty-eight crucible tests were conducted, with initial tests starting with limited gram-size quantities of sodium reacting with stoichiometric amounts, or multiples, of feed material oxide. The tests were systematically increased to 35 g sodium. Figure 3 shows a typical final disposal product formed by 35 g sodium reacted with a 3:1 stoichiometric mixture of magnetite. The rock-hard "hockey puck"-like product was fractured to show the interior. The solid product was shown by XRD to contain a mixture of Fe metal plus sodium iron oxide compounds, with no sodium metal remaining.

Of the two final candidate feed materials tested in the prototypic crucible tests, five forms of the two materials were tested. Three types of magnetite included two sieve sizes of a mined magnetite from the Pea Ridge Mine in Missouri and a synthetic, spherical, consistent-sized magnetite. The Pea Ridge materials tested varied from a mean diameter of 35 to 150 µ with wide particle size distribution. The synthetic magnetite was from PowderTech Corporation, Valparaiso, IN, and consisted of sintered spheres of Fe_3O_4-$MnFe_2O_4$ (10% MnO) solid solution, with particle sizes between 75 and 100 µ.

Fig. 3: Shows the final product,"hockey puck" formed by magnetite in a 3:1 stoichiometric mixture with 35g sodium, cracked to show the interior of metallic Fe, Na_2FeO_3, Na_2O, and excess Fe_3O_4.

For SiO_2 feed material, commercial purified sea sand (mean diameter of ~1000 μ) and sub-micron reagent-grade silica were tested. The results in Table III are those for the PowderTech magnetite and the sea-sand silica. These coarse-grained powders appeared to wet better and tended to generate more controllable reactions than the finer powders.

DISCUSSION

Observations Versus Predictions

In Table III, the initiation temperature of the reaction and the maximum temperature achieved is shown. The agglomerated products were isolated and examined by XRD and for residual metallic sodium. Any residual sodium was measured by submersing a sample of the product in water and detecting resulting hydrogen.

Hematite, Fe_2O_3, and stannous oxide, SnO_2, were found to be too exothermic with spewing and spitting of glowing particles even in these bead-sized tests. In both cases, the solid metal (Fe or Sn) was formed along with the ternary oxides (sodium iron oxide or sodium tin oxide). The extremely exothermic behavior was anticipated based on the large difference in standard free energy of formation of these two materials. Although chromic oxide, Cr_2O_3, possesses a much lower free energy of formation similar to that of sodium oxide, it was nearly as energetic as the first two oxides, forming Cr metal and sodium chromium oxides. The likely reason for the very energetic reaction is the very favorable formation of the ternary oxide.

Table III: Candidate Feed Material Test Results

Oxide	**DG_o (kcal /mole)**	**Start Temp (°C)**	**Max Temp (°C)**	**Products Identified (XRD)**	**Comments from Scoping Tests**
Fe_2O_3	90	420 to 540	>1000	$Fe + Na_4FeO_3$	Very exothermic; with spitting, too reactive.
SnO_2	63	300 to 400	>700	$Sn + Na_2SnO_3 + Na_4SnO_3$	Too vigorous, with spitting; wets and reacts on contact.
Fe_3O_4	57	350 to 370	700-800	$Fe + NaFe_2O_3 + Na_4FeO_3 + Na_2O$	Controlled reaction; wets then later reacts.
ZnO	25	NA	350	$NaZn_{13} + Na_6ZnO_4$	Incomplete reaction; wetting and initiation occur at 200°C; major product is $NaZn_{13}$.
Cr_2O_3	11	450 to 500	>700	$Cr + NaCr_2O_3 + Na_2CrO_2$	Difficult to initiate, wetting occurs with difficulty; but reaction too exothermic.
MnO	2	NA	320	None	No reaction, wetting only.
SiO_2	neg	500	700-800	$Si + Na_2SiO_3$	Controlled reaction, not too vigorous.

ZnO did not completely oxidize the sodium metal, but interestingly formed a well-characterized sodium zinc intermetallic compound, $NaZn_{13}$, and sodium zinc oxide. It was found that 30 to 80% of the sodium in these experiments was unreacted. As would be inferred by its free energy of formation, manganese monoxide, MnO, did not extensively oxidize the sodium metal as was indicated by its minimal temperature rise and XRD results.

Considering only the standard free energy of formation to form the binary sodium monoxide, sodium metal should not be expected to reduce silica to silicon metal by itself with the resulting Na_2O. However, the competing reaction forming the ternary sodium silicate is more thermodynamically favorable, and when an excess of silica is present, the added energy from the formation of the ternary sodium silicate makes the reaction favorable. XRD results on the silica product included Si metal and the ternary Na_2SiO_3, indicating that the reaction occurred as shown in Equation 3. Figure 4 shows the final disposal product formed by sodium reacted with silica, according to Equation 3. The product has a slightly crumbly exterior compared to the rock-hard magnetite product, due to the less-dense silica feed material. The sodium silicate nature of this reaction product may make this product an ideal feedstock to other processes such as glass vitrification or grout.

$$4\ Na + 3\ SiO_2 \rightarrow 2\ Na_2SiO_3 + Si \qquad \text{(Eq. 3)}$$

Multiple product compositions were observed with several of the candidate feed materials, including magnetite and hematite, as shown in Table III, depending most likely on the availability of excess feed material to form these compounds and on the available local oxygen. For the iron oxides, the observed products always include metallic iron, but also the ternary $NaFeO_2$, Na_4FeO_3, Na_2FeO_3, and the simple binary Na_2O when excess iron oxide was not available.

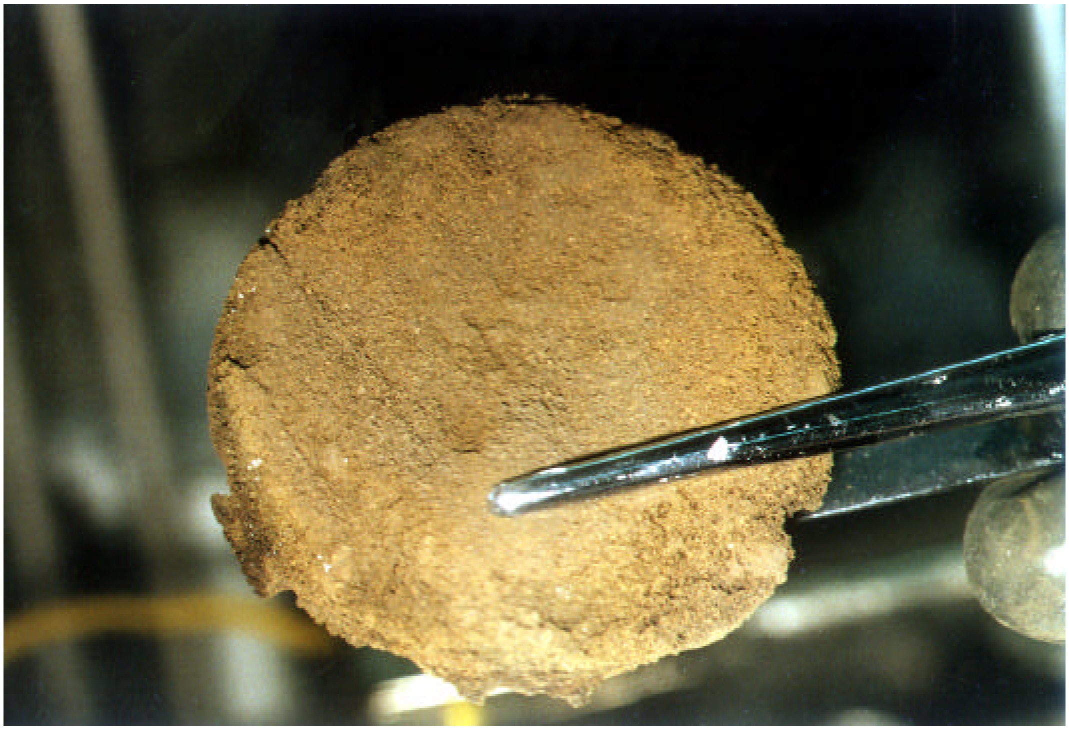

Fig. 4: The crumbly disposal product of silica reacted with sodium, containing elemental Si, Na_2SiO_3, and excess SiO_2.

Mixing and Wetting

The temperature of mixing the sodium and the metal oxide was important in determining the time of self-heating before initiating full reaction. In a four-test series of 1:1 stoichiometric Fe_3O_4 tests, shown in Table IV, the effect of mixing temperature on the time to reaction initiation is shown. Mixing temperatures of 325°C to 200°C resulted in self-heating times to initiation, ranging from 10 sec to 7.5 min, respectively, at which times the full exothermic reaction occurred. The explanation for this time of self-heating to initiation of reaction is that the thermally dependent process of wetting of the oxide begins occurring at mixing and continues, causing the gradual self-heating. The full exothermic reaction initiates when complete wetting has occurred. The selection of mixing temperature allows complete control over the wetting and time of initiation and onset of full exothermic reaction.

Table IV: Four-Test Series Showing Effect of Mixing Temperature

Mixing Temperature (C)	**Time to Initiation**	**Initiation Temperature (C)**	**Maximum Temperature (C)**
325	10 sec	~400	715
300	25 sec	~400	650
250	95 sec	~300–400	720
200	7.5 min	~300–400	680

Though mixing was always considered important, the potential for proceeding with no premixing provided unique processing opportunities. For example, unmixed MOMS processing (pouring excess feed material over the sodium) could be useful for *in situ* treatment for residual sodium within piping or crevices where access for delivering feed material is possible, but the possibility for mixing is not achievable. Tests were conducted that involved no premixing, but only using excess magnetite and heating to normal initiation temperatures. These tests did go to completion and resulted in only the binary Na_2O being formed rather than the ternary oxides. This formation of the binary sodium oxide only was due to the local unavailability of adequate magnetite. The unmixed case goes to completion because of the exothermicity of the reaction, propagating through the sodium to completion, provided there is excess metal oxide. For magnetite, the binary Na_2O may only formed, not just when unmixed, but also when the reaction is metal oxide-limited, for instance at 1:1 stoichiometric mixtures.

Mixing Stoichiometry

XRD results for both magnetite and silica were found to correlate to mixing stoichiometry. Batches were always prepared on the basis of the stoichiometric reactant mass ratio, which indicates the amount of excess oxide, in multiples, as shown in the following examples. The mass ratio is defined as the molar quantity of feed material oxide tested divided by the stoichiometric quantity of oxide just required for the reaction. Hence, a mass ratio of 2 indicates twice the molar quantity of feed material oxide added than is stoichiometrically required to exactly oxidize the sodium to Na_2O. Therefore in the following examples, shown in Table V, the first test case formed only the binary Na_2O because of a reactant mass ratio of 1. In the second test case, with a reactant mass ratio of 3 indicating large excess metal oxide, the ternary Na_2SiO_3 was formed. Similarly, for the third test case, a reactant mass ratio of exactly 1 allowed only sodium oxide to be formed, whereas in the fourth test case, the excess metal oxide allowed the ternary compound to be formed.

Table V: Effect of Reactant Mass Ratio on Product Composition

Test Case	Reactant Mass Ratio	Reaction
1	1	$4\ Na + SiO_2 \rightarrow 2Na_2O + Si$
2	3	$4\ Na + 3SiO_2 \rightarrow 2Na_2SiO_3 + Si$
3	1	$8\ Na + Fe_3O_4 \rightarrow 4\ Na_2O + 3\ Fe$
4	2	$8\ Na + 2Fe_3O_4 \rightarrow 4Na_2FeO_2 + 2\ Fe$

The mass ratios investigated ranged from 1.0 to 3.0. The metallic sodium tended to react incompletely when the mass ratio was less than 2.0 and produced only binary Na_2O with little or no ternary product. It was found that ratios greater than 2.6 consistently eliminated all trace residual metallic sodium in the product and primarily resulted in the ternary product plus the elemental metal.

Thermodynamics

The thermodynamics of the process provides insights into which of the metal oxides can theoretically react with sodium and at what exothermic energy level. Some metal oxides were predicted to be extremely exothermic and were experimentally found to be too vigorous, with temperatures reaching greater than 1000°C along with spitting and spewing of molten material, even in very small tests. In contrast, others were predicted to generate little exothermic reaction, and were experimentally found to become only wetted with no reaction. The intermediate energetic oxides were found to have intermediate characteristics between the two extremes noted above.

Using thermodynamic situations described in Barin [9], final adiabatic temperatures of the selected reactions were predicted by calculating the enthalpy of the reactants at a starting temperature of 527°C and then determining the total enthalpy for the proposed products that are provided by Barin. The temperature at which the sum of the enthalpies of the products equals the sum of the enthalpies of the reactants at 527°C, is the adiabatic temperature that the products would be expected to reach with no local heat loss.

In Table VI [9, 10], the first reaction with silica to form only the binary sodium oxide was determined to be endothermic and hence would not be expected to occur, consistent with the simplistic assessment in Table III. However, the second reaction with silica to form the ternary sodium silicate with excess silica is thermodynamically viable and is expected to result in a temperature rise of 745°C with a final adiabatic temperature of almost 1300°C. This prediction is consistent with the experimental fact that only the ternary sodium silicate plus the elemental Si was found in the products. However, due to nominal heat losses to the surroundings, the maximum temperatures measured have been about 800°C.

Table VI: Calculated Adiabatic Temperatures for Several Potential MOMS Processes

Reactions	Ratio	Adiabatic Temperature Increase
$4\ Na + SiO_2 \rightarrow 2\ Na_2O + Si$	1:1	No reaction expected
$4\ Na + 3\ SiO_2 \rightarrow 2\ Na_2SiO_3 + Si$	1:3	745°C rise to 1272°C
$3\ Na + 2\ Al_2O_3 \rightarrow 3\ Na\ AlO_2 + Al$	1:4	51°C rise, no reaction expected
$8\ Na + Fe_3O_4 \rightarrow 4\ Na_2O + Fe$	1:1	646°C rise to 1173°C

Treatment Scenarios

There are several proposed treatment scenarios. Hydrogen-free batch-mode processing of smaller quantities of radioactive-sodium mixed waste in either the original storage container or in a secondary disposal container is one ideal use. Convenient quantities for batch-mode processing may involve up to 40-80 kg sodium batches in 55-gal drums, or special reaction containers. The thermal-spike heat generation of the MOMS process should allow safe treatment in such scenarios, with the processing conducted in an inert atmosphere. The resultant product is ready for disposal or as feedstock to another application.

Hydrogen-free *in situ* treatment of residual sodium in reactor piping and crevices, storage tanks, or low lying areas is another application. If the residual sodium location is accessible, excess feed-material oxide can be applied with no mixing, the region heated to initiation temperature by wrapped heaters, and the MOMS reaction allowed to go to completion. The result would be the MOMS reaction product in the piping, crevices, and low areas in the place of the metallic sodium.

For continuous-mode processing, the authors have a conceptual plan for the MOMS process for large-scale, bulk quantities of sodium, again with no generation of hydrogen or other flammable gases. The process is based on fluidized-bed design, with a fluidized-bed of metal oxide feed material at selected temperature, in specific-sized particle form, with injection of sodium at specific feed rate. The design lends itself to plant-sized operation, with a major benefit being that no inert-atmosphere containment, outside the fluidized-bed reaction vessel, is required. This processing would generate the product directly into disposal containers, ready for disposal as less-hazardous or non-hazardous waste, or providing feedstock material to a follow-on process.

CONCLUSIONS

Hydrogen-generating methods for the mitigating treatment of sodium metal waste are well-established with generally acceptable risk, but the safety issue is ever present, as the 1994 death confirmed. The presented novel method for mitigating sodium by reaction with metal-oxide feed material has been demonstrated in the laboratory. Seven candidate materials, selected based on their free energies of formation, have been tested by reaction with sodium, resulting in the two best candidate feed materials of magnetite and silica. The batch-mode or continuous-mode reaction product can be considered for further processing or for disposal as a solid waste product consisting of sodium metal oxides.

FOOTNOTE

[a] Pacific Northwest National Laboratory is operated for the U.S. Department of Energy by Battelle under Contract DE-ACO6-76RLO 1830.

REFERENCES

1. "Cadarach Accident Yields Lessons for Decommissioning," *Nucleonics Week*, Page 12, July 28 (1994).
2. "Non-Nuclear Accidents Kill 11 in French Nuclear Facilities," *Nucleonics Week,* Page 3, April 7 (1994).
3. A.E. Stewart and J.D. Navratil, "Treatment of Waste Sodium/NaK; Decommissioning Hardware and Facilities," *Nukleonika* Vol. 43, No. 1 115–130 (1998).
4. W.F. Brehm, and W.J. Schuck, "Trip Report, 1996," 96-002, Westinghouse Hanford Company (1996).

5. R.D. Wolson and C.C. McPheeters, "Methods of Sodium Waste Disposal," *2nd International Conference on Liquid Metal Technology,* Richland, WA (1980).
6. G. Lussiez and J. Dziewinski, "Development of a Process to Neutralize Water-Reactive Wastes," *Techno. Programs Radioact. Waste Manage. Environ. Restor.,* Vol. 2, 863–868 (1994).
7. F.J. Keneshea, S.A. Hobart, C.S. Pohl, M.T. Kelly, D. Riley, "Sodium Conversion Experiments if the Inert Carrier Process Demonstration Plant," *Nucl. and Chem. Waste Management,* Vol. 4, 189–199 (1983).
8. M. Sumi, T. Sano, M. Ueda, Y. Soma, "Method for the Treatment of Metallic Sodium Adhering to Instrument Surfaces," JP 62075396 A2 (1985).
9. I. Barin and G. Platzki, "Thermochemical Data of Pure Substances," 3rd Edition, VCH Publishing, NY, NY (1995).
10. R.A. Swalin, "Thermodynamics of Solids," John Wiley and Sons Inc, New York, New York (1967).