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The reactivity of sodium alanates with O_2, H_2O, and CO_2

An investigation of complex metal hydride contamination in the context of automotive systems

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ABSTRACT

Safe and efficient hydrogen storage is a significant challenge inhibiting the use of hydrogen as a primary energy carrier. Although energy storage performance properties are critical to the success of solid-state hydrogen storage systems, operator and user safety is of highest importance when designing and implementing consumer products. As researchers are now integrating high energy density solid materials into hydrogen storage systems, quantification of the hazards associated with the operation and handling of these materials becomes imperative. The experimental effort presented in this paper focuses on identifying the hazards associated with producing, storing, and handling sodium alanates, and thus allowing for the development and implementation of hazard mitigation procedures. The chemical changes of sodium alanates associated with exposure to oxygen and water vapor have been characterized by thermal decomposition analysis using simultaneous thermogravimetric modulated beam mass spectrometry (STMBMS) and X-ray diffraction methods. Partial oxidation of sodium alanates, an alkali metal complex hydride, results in destabilization of the remaining hydrogen-containing material. At temperatures below 70°C, reaction of sodium alanate with water generates potentially combustible mixtures of H_2 and O_2. In addition to identifying the reaction hazards associated with the oxidation of alkali-metal containing complex hydrides, potential treatment methods are identified that chemically stabilize the oxidized material and reduce the hazard associated with handling the contaminated metal hydrides.

Keywords:

Complex metal hydrides, sodium alanates, contamination, safety, engineering properties, thermal decomposition, reaction kinetics, thermochemistry

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NOMENCLATURE

A_xB_x	Hydride compounds resulting from combining a stronger hydride-forming element with a weaker hydride-forming element
OxAE	Experiments is to determine how sodium alanate is altered when exposed to water and oxygen
REMKIN	Reaction modeling and kinetics compiler
RoE	Rate of evolution
SEM	Scanning electron microscopy
SNL	Sandia National Laboratories
STMBMS	Simultaneous thermogravimetric modulated beam mass spectrometry
UN/DOT	United Nations and Department of Transportation
US DOE	United States Department of Energy
XRD	X-ray diffraction

1. INTRODUCTION — SAFE SOLID-STATE HYDROGEN STORAGE SYSTEMS

Efficient and appropriate hydrogen storage is a significant challenge inhibiting the use of hydrogen as a primary transportation energy carrier. US DOE goals for on-board automotive hydrogen storage systems do not describe or imply a specific technology [1], however, current hydrogen storage technologies, including liquid and compressed gas, are insufficient with respect to energy density (see Figure 1). Additionally, the potential for significant energy density performance improvement of current liquid and gas technology is limited, even when considering the most clever engineering designs. Hydrogen storage technologies that are efficient, low cost, and robust must be developed to enable the use of hydrogen fuel in transportation applications. Although current hydrogen sorption technologies demonstrate low energy densities, solid-state hydrogen storage solutions are theoretically able to store more hydrogen per unit volume than pure liquid hydrogen [2]. Given this potential for high energy density reversible hydrogen storage, significant effort has been applied to develop and enhance solid-state hydrogen storage technology. As technology scale-up is realized, system designers now must consider the operational safety of these solid-state storage systems.

Sandia National Laboratories and General Motors Corporation entered a research agreement in 2003 to develop hydrogen storage systems based on sodium alanates. The developed system contains large-scale quantities of sodium alanates that were produced, stored, and utilized at Sandia National Laboratories, Livermore, CA, USA. This report details the research undertaken during the agreement to understand the reaction processes associated with the exposure of sodium alanates to oxygen and water. Sandia maintains unique capabilities to characterize the reactions of high energy density solids and was able to perform initial characterization of the reaction of sodium alanates during atmospheric contamination.

1.1. SOLID-STATE HYDROGEN STORAGE SYSTEMS FOR AUTOMOTIVE APPLICATIONS

Metal hydride systems have been proposed and demonstrated as potential high energy density hydrogen storage solutions [2]. Metals that form hydrides can reversibly absorb and release hydrogen when appropriate temperatures and pressures are applied. In general, the reaction expression can be described as

$$M + \frac{x}{2} H_2 \leftrightarrow MH_x \qquad \text{(R1)}$$

where M is the metal or metal alloy. Traditionally, metal hydrides have been classified into two main categories: alloys and complexes. Intermetallic alloys, including AB5, AB2, AB, and A2B materials form hydride compounds resulting from combining a stronger hydride-forming element with a weaker hydride-forming element to attain appropriate thermodynamic characteristics.

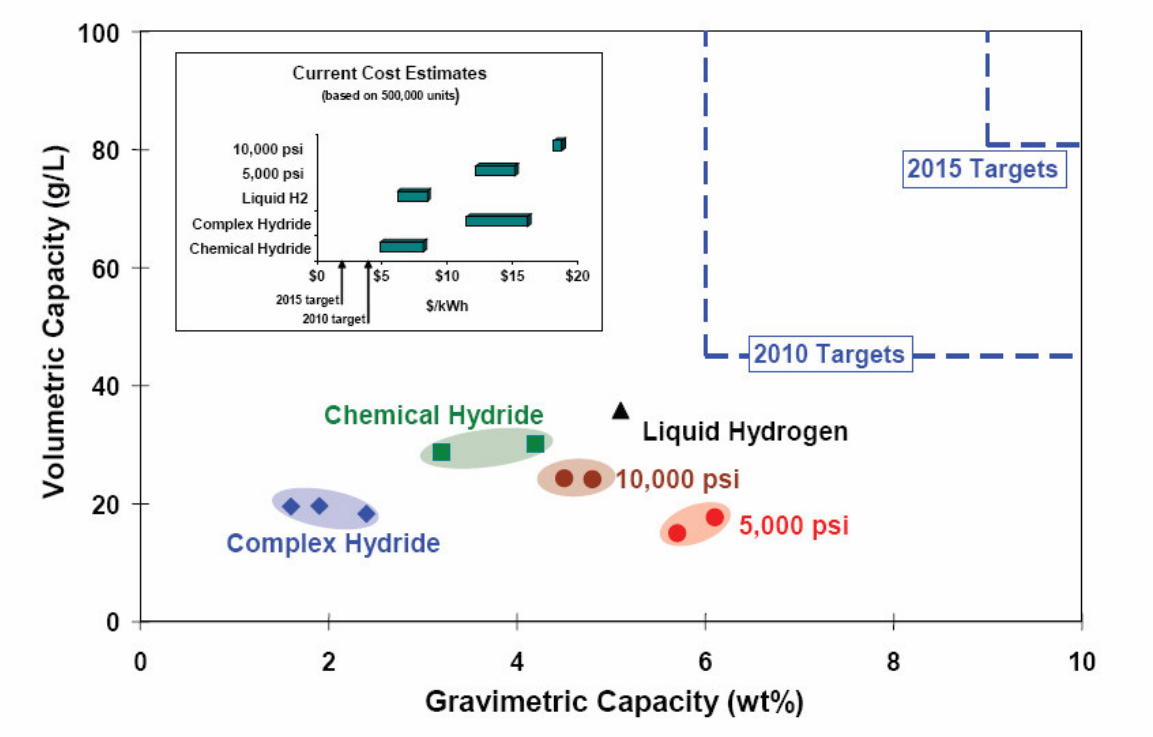


Figure 1 - The current status of hydrogen storage technologies indicates that significant performance improvements must be realized prior to attaining 2010 and 2015 goals [3].

Complexes, on the other hand, are comprised of metal elements that exchange electrons to stabilize higher-ordered hydrogen coordination. Complexes are the focus of this paper since these materials typically exhibit higher hydrogen storage capacities relative to other materials. Prior to building full-scale automotive hydrogen storage systems based on complex metal hydrides, the behavior of these materials in the dynamic automotive environment must be fully understood.

1.2. REQUIREMENTS FOR SOLID-STATE HYDROGEN STORAGE SYSTEM SAFETY

Although energy storage performance properties are critical to the success of solid-state hydrogen storage systems, operator and consumer safety is of the highest importance among engineering-related properties. Safety properties are defined as the health and safety effects of the products, pathways, and rates of reactions occurring between hydrogen storage materials and their potential contaminants. These properties have direct implications on the health and well-being of the vehicle worker and operator. Due to the enormous impact of the US motor vehicle market (approximately 17 million new motor vehicles sold every year within the US), robust and safe systems must be developed. High-energy-density fuel storage systems are intrinsically capable of releasing significant amounts of the stored energy and present a potential hazard.

Although it is improbable that this hazard can be eliminated entirely, engineering controls and appropriate protocols can minimize the potential hazard to an acceptable level. In the case of metal hydrides, the reaction processes with contaminants, especially air and water vapor, must be understood to enable the implementation of engineering controls and the definition of appropriate protocols.

The automotive platform is a dynamic hydrogen fuel storage application intrinsically subject to a highly variable operating environment, uncertain hydrogen refueling quality control, and potentially accidents, such as collisions or externally-fueled fires. The nature of this operating environment increases the likelihood that the storage materials or containment structures may be somehow compromised during the lifetime of the hydrogen storage system. In an accident or contaminated refueling scenario, the hydride material may be exposed to air, water and other contamination. Due to the requirements for high energy density hydrogen storage solutions, complex hydrides comprised of light metal elements are of specific interest - including, but not limited to, lithium (Li), sodium (Na), magnesium (Mg), calcium (Ca), boron (B), and aluminum (Al). Hydrides and complexes synthesized from these elements are typically found in the form of finely divided powders that can be pyrophoric and water reactive. Additionally, the oxidation reaction products may also present hazards. In the case of alkali-metal based materials, the oxidation products include, but are not limited to, hydroxides, oxides, peroxides, and superoxides. Some of these materials may present a health hazard and form hydrates in a humid environment that can decompose rapidly as a result of friction or heat. The associated chemical pathways must be identified and their associated reaction rates must be quantified to enable the design and implementation of safe hydride-based automotive hydrogen storage systems. In addition, chemical hazard mitigation methods must be developed to enable the safe handling of hydride materials during the entire life cycle of the storage system.

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2. SODIUM ALANATES — PROTOTYPICAL COMPLEX METAL HYDRIDES

Sodium aluminum tetra-hydride ($NaAlH_4$) is a complex hydride historically used as a reducing agent in chemical synthesis, which was found to reversibly release and accept hydrogen in a two-step phase change process in 1997. This discovery of kinetic enhancement by titanium doping made sodium alanates ($NaAlH_4$, Na_3AlH_6) promising materials for hydrogen storage systems [4,5].

2.1. THE THERMOCHEMISTRY OF SODIUM ALANATES

Sodium alanates are complex hydrides that release and absorb hydrogen in a two step decomposition and recombination reaction shown in reaction 2.

$$NaAlH_4 \Leftrightarrow 1/3Na_3AlH_6 + 2/3Al + H_2$$
and,
$$1/3Na_3AlH_6 + 2/3Al + H_2 \Leftrightarrow NaH + Al + 3/2H_2 \quad \text{(R2)}$$

Sodium alanate based systems are currently under development for use as high energy density reversible hydrogen storage [6,7]. Reversible hydrogen storage materials are characterized by endothermic decomposition and exothermic recombination and the thermodynamics of these reactions are well characterized [8,9]. It should be noted that sodium alanates will not meet the current US DOE goals for hydrogen storage performance; however, they are currently the leading low temperature complex hydride, and similar higher energy density complexes are actively being investigated that may have structural and chemical reactivity characteristics similar to that of sodium alanates. Sodium alanates exhibit typical metal hydride morphological behavior and are high surface area materials that undergo significant structural changes during hydrogen sorption. Figure 2 illustrates this morphological change using Scanning Electron Microscopy (SEM) imaging of the highly crystalline sodium aluminum tetra-hydride (uncycled hydrogen charged phase, A) compared to the disorderly form of the fully decomposed material (hydrogen released phase, B).

Sodium alanates are pyrophoric and react violently with water, partially due to the high surface area of these porous materials. Some reactive safety investigations of sodium alanates have been reported. Notably, United Technologies Research Center has presented reactivity testing of sodium alanates based on standardized testing procedures [10]. Testing during this effort was qualitative in nature and based on UN/DOT testing for classification of flammability, water contact, and dust explosion. Additional qualitative testing was performed at FZ Karlsruhe in 2005 [11]. Intuitively, it would be expected that the sodium alanate system reacts exothermically to form NaOH and Al_2O_3 upon exposure to an oxidizing species. Despite these relatively benign oxidation products, some researchers have observed samples becoming apparently friction sensitive after uncontrolled oxygen exposure. Researchers as early as Ashby in 1969 [12] reported sensitivities of oxidized potassium alanates to friction.

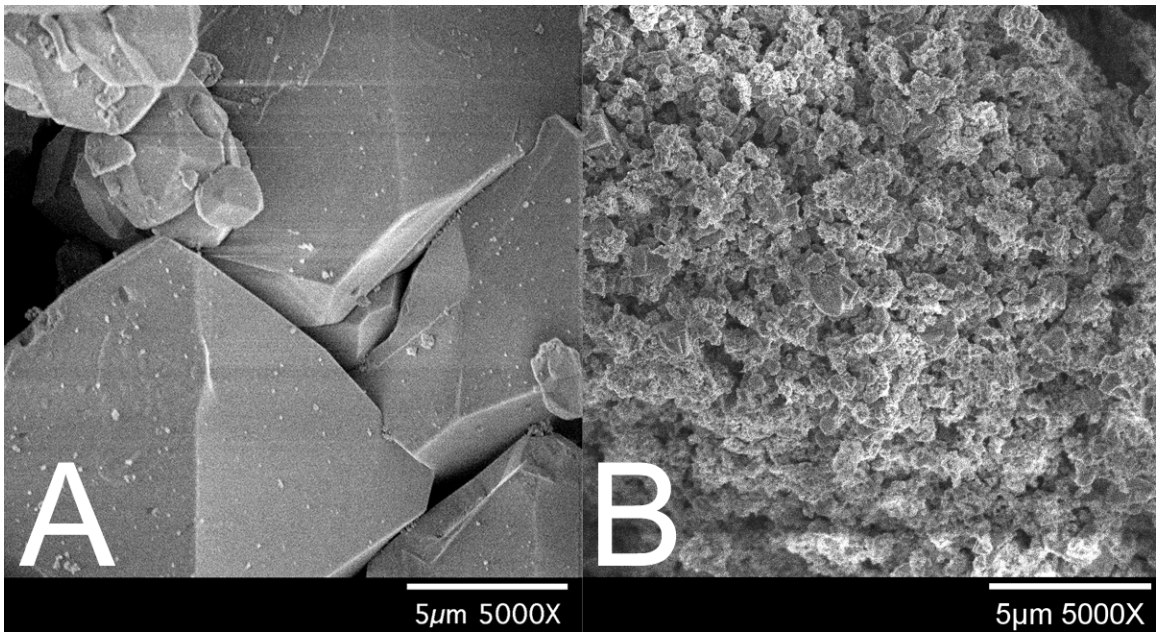


Figure 2 - SEM images of the highly crystalline un-cycled sodium aluminum tetra-hydride (A) compared to the disorderly form of the cycled and fully decomposed material (B).

This behavior suggests that reactions other than the above could occur, perhaps resulting in the formation of sodium oxides, such as sodium superoxide, as determined by Desreumaux [13]. Clearly, the oxidation reaction is not fully understood, which creates difficulties when designing safe and effective controls for storage systems. Since large quantities of reactive sorption materials must be integrated into the automotive platform, the hazards associated with contamination and environmental exposure must be fully understood and quantified so that appropriate codes, standards, and engineering controls can be designed and integrated.

A large number of oxidation reactions are possible between sodium alanates and the gases present in the atmosphere (oxygen and water vapor). Most such reactions are thermodynamically favorable as shown by the calculations presented in Table 1 describing free energy and enthalpy changes for a number of possible oxidation reactions. The thermodynamic property data presented here were obtained from Barin, Knacke and Kubachewski [14]. Reactions that yield sodium oxides are of particular interest as some of these compounds exhibit instability with regard to frictional disturbance. The oxidation of sodium alanate by oxygen to yield various Na-O compounds and either hydrogen or water vapor are an interesting class of reactions considered during this study. The latter product is also capable of further oxidizing either the remaining alanates or the oxidation products of the initial reactions. Oxidation reactions resulting in sodium oxides such as peroxide, Na_2O_2, and superoxide, NaO_2, are both favorable according to the free energy changes although less so than to sodium oxide, Na_2O. Another general class of reactions considered was oxidation of sodium alanate by water vapor to yield various Na-O compounds and hydrogen.

Table 1 - Thermochemistry properties and volumetric changes of reactions of $NaAlH_4$ with oxygen (O_2) and water (H_2O).

Calculated properties	ΔG kJ/mol	ΔH kJ/mol	ΔV %
Oxidation by O_2 to Na-O compounds and H_2			
$1/2\ O_2 + 2\ NaAlH_4 = Na_2O + 2\ AlH_3 + H_2$	-94.516	-107.52	-10.4
$O_2 + 2\ NaAlH_4 = Na_2O_2 + 2\ AlH_3 + H_2$	-129.78	-155.14	-10.1
$O_2 + NaAlH_4 = NaO_2 + AlH_3 + 1/2\ H_2$	-123.67	-159.20	5.6
Oxidation by O_2 to Na-O compounds and H_2O			
$O_2 + 2\ NaAlH_4 = Na_2O + 2\ AlH_3 + H_2O$	-209.11	-228.78	-10.4
$3/2\ O_2 + 2\ NaAlH_4 = Na_2O_2 + 2\ AlH_3 + H_2O$	-244.38	-276.39	-10.1
$5/2\ O_2 + 2\ NaAlH_4 = 2\ NaO_2 + 2\ AlH_3 + H_2O$	-238.32	-280.45	2.8
Oxidation by H_2O to Na-O compounds and H_2			
$H_2O + 2\ NaAlH_4 = Na_2O + 2\ AlH_3 + 2\ H_2$	20.12	13.72	-10.4
$2\ H_2O + 2\ NaAlH_4 = Na_2O_2 + 2\ AlH_3 + 3\ H_2$	99.45	87.32	-10.1
$2\ H_2O + NaAlH_4 = NaO_2 + AlH_3 + 5/2\ H_2$	167.40	162.88	5.6
Oxidation to Al_2O_3 as one product			
$4\ O_2 + 2\ NaAlH_4 = Na_2O + Al_2O_3 + 4\ H_2O$	-1389.67	-1417.75	-19.0
$4\ H_2O + 2\ NaAlH_4 = Na_2O + Al_2O_3 + 8\ H_2$	-472.75	-447.90	-19.0
Oxidation to NaOH			
$4\ O_2 + 2\ NaAlH_4 = 2\ NaOH + Al_2O_3 + 3\ H_2O$	-1467.37	-1515.57	-12.7
$H_2O + NaAlH_4 = NaOH + AlH_3 + H_2$	-57.57	-84.10	-8.3

Notes: Free energy and enthalpy changes are given per mol of $NaAlH_4$. Volumetric changes refer to the solid compounds only and are percentages based on $NaAlH_4$.

Calculations of volumetric changes of the solid compounds associated with these reactions were also performed to determine potential effects on the bed, such as consolidation or unpacking, or expansion that might affect the container. These results were obtained from published values of the bulk density of the various solid oxidation products and data for the phases of sodium alanates [14]. The volumetric calculations are also summarized in Table 1. The volumetric changes are percentages based on the presence of only $NaAlH_4$ initially. In general, significant volumetric changes are not realized during bed oxidation, with the prevailing trend toward volumetric reduction.

The rates of the oxidation reactions are not known. However, as most of these reactions are exothermic, the rate of the above described oxidation processes must be controlled to avoid rapid heating and, possibly, ignition of the metal hydride. In the case of the thermodynamically aggressive postulated process,

$$4\ O_2 + 2\ NaAlH_4 \Rightarrow 2\ NaOH + Al_2O_3 + 3\ H_2O \qquad \text{(R3)}$$

the heat of reaction is -1516 kJ/mol-$NaAlH_4$. For a sodium alanate-based system that reversibly stores 5 kg of hydrogen, the total quantity of heat removal required is

approximately $5x10^9$ J – an equivalent amount of energy released when burning 38 kg of hydrogen. If the majority of this heat is not removed, it is plausible that ignition could result. In a postulated event in which the oxidation process is active for 4 hours (a relatively protracted oxidation scenario), the average heat rate is 333 kW. Since this is a significant amount of energy and flux to manage during an automotive accident scenario, controls must be in place to limit the impact of such an oxidation event to avoid ignition.

2.2. ENABLING SAFE AND EFFECTIVE SYSTEMS BASED ON COMPLEX METAL HYDRIDES

Considering the above oxidation thermochemistry examples of complex metal hydrides, some effort is required to quantify and address the hazards associated with the production and operation of the automotive-scale solid-state hydrogen storage systems. The authors have begun the following three-part investigation to enable safe systems based on reactive solids:

- *Identify chemical processes* and hazards associated with hydride exposure to air, water vapor, and other relevant contaminants, and build validated chemical reaction models as a function of reaction conditions (especially pressure and temperature).
- *Predict chemical processes* during system contamination scenarios by applying chemical reaction models to full scale analysis of heat and mass transfer.
- *Identify hazard mitigation strategies* to allow for handling and disposal of contaminated materials

The resulting data will enable the system designer to identify and implement safety controls and standards to reduce the hazard associated with the operation of solid-state hydrogen storage systems.

3. EXPERIMENTAL INVESTIGATIONS OF THE CONTAMINATION REACTIONS OF SODIUM ALANATES

The goals of the experimental investigations undertaken during this program were focused on identifying the hazards associated with producing, storing, and handling bulk quantities of sodium alanates, and thus allowing for the development and implementation of hazard mitigation procedures. The reaction processes associated with the exposure of sodium alanates to oxygen and water have been characterized with the use of simultaneous thermogravimetric modulated beam mass spectrometry (STMBMS) and X-ray diffraction.

3.1. SIMULTANEOUS THERMOGRAVIMETRIC MODULATED-BEAM MASS SPECTROMETRY

The Simultaneous Thermogravimetric Modulated Beam Mass Spectrometer (STMBMS) instrument was originally designed and operated by Richard Behrens at Sandia National Laboratories in the 1980s to investigate the contamination reactions of hydrogen storage materials [15]. The capabilities were further enhanced and coupled with new data analysis algorithms to investigate condensed-phase reaction processes of propellants and explosives [16-19]. Eventually, the system was coupled with new numerical algorithms to model and simulate complex reaction processes that control the behaviors of propellants and explosives under various safety and aging scenarios [20]. This instrument was identified as an appropriate tool to characterize the complex processes that may be present during the oxidation and contamination of sodium alanates. Specifically, the instrument was used in the current study to investigate the reaction of sodium alanates with O_2 and H_2O and CO_2. Experiments were conducted to (1) identify the reaction products, (2) determine and elucidate the reaction scheme, (3) determine the rates of oxidation and (4) understand how oxidation affects the rate of hydrogen evolution and the corresponding effect on rate of hydride decomposition. Reaction products were also identified to understand the hazards associated with handling of oxidized sodium alanates and to develop strategies to mitigate these hazards.

During typical experiments, a small reaction cell containing the sodium alanate was placed on the top of a thermocouple probe that is seated in a microbalance (Figure 3). The entire instrument was then evacuated and the sample was heated by a bifilar wound tantalum or tungsten wire on an aluminum oxide furnace tube. As the sample is heated, all gas generated from the sample evolves, fills the reaction cell, and the mass loss due to gas leaving the cell is recorded with the microbalance. Gas exiting the reaction cell flows through a small (2 to 1000 μm) orifice and is formed into a molecular beam, which is modulated, and then detected with a quadrupole mass spectrometer, using electron bombardment ionization. The force due to the gaseous species within the cell is measured with the microbalance and the mass spectra of the species in the molecular beam are measured with the mass spectrometer. The force data and mass spectra are both collected as a function of time during the experiment.

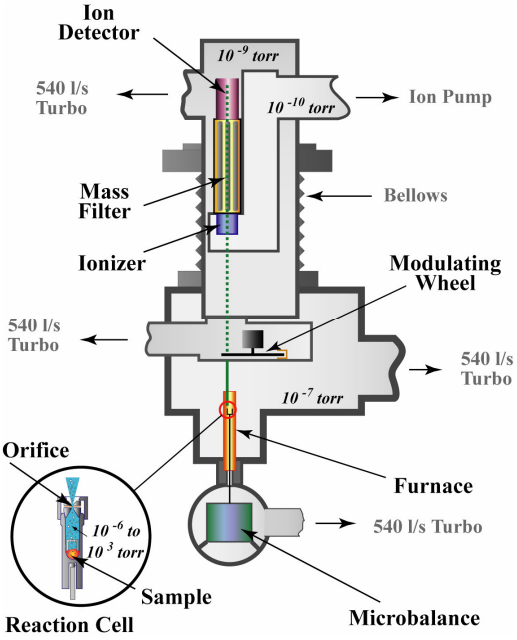


Figure 3 - Schematic cross section of the STMBMS instrument.

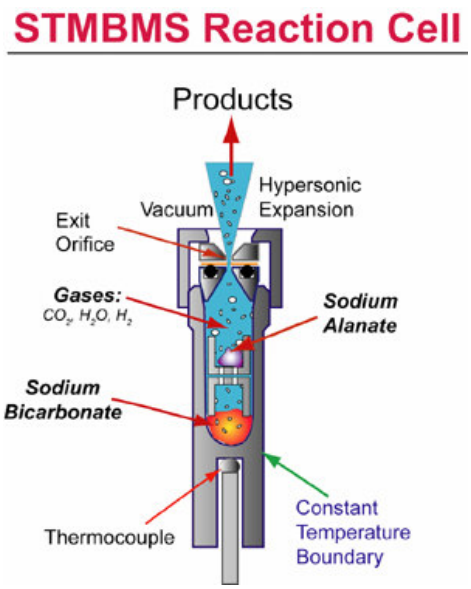


Figure 4 - Oxidation study operation of the STMBMS reaction cell includes the sample in proximity to a contamination-emitting material.

This data is then used to identify the gaseous species and to determine their number density within the reaction cell as a function of time [15-17]. The number densities can then be used to calculate the partial pressures of species within the cell and their rate of evolution from the sample. (Note that the force measured with the microbalance consists of the mass of the sample and a component due to the thrust generated by the gas within the cell.) The combination of the force data and mass spectra are then analyzed to provide the identities and partial pressures of each gaseous species within the reaction cell as a function of time. This information can then be used to determine vapor pressures and rates of reactions of chemicals or materials of interest. The sequence of species evolution is used to determine the reaction mechanisms. A reaction modeling and kinetics compiler (REMKIN) and analysis tool can be used to rapidly postulate and test reaction models and of the underlying reaction kinetics using data to determine parameters of various reaction processes in the postulated reaction scheme.

For the sodium alanate studies, the STMBMS was operated in two modes. In the *hydride decomposition operation mode*, the instrument was used to heat sodium alanate samples in the as-hydrided (unoxidized) condition, samples oxidized by various gases, and oxidized samples that were subsequently CO_2-treated to determine the identities and amounts of gaseous species that evolve. The samples were heated from room temperature to approximately 1000°C at 2°C/minute to determine the identities and temperature range over which various products evolve as the sample is heated.

In the *oxidation study operation mode*, the STMBMS apparatus was configured to examine the rate of oxidation of sodium alanate samples over a range of different conditions. In these experiments, materials that evolve oxygen or water are placed in the reaction cell in combination with the hydride materials of interest. The materials are loaded at room temperature and are separated by a set of baffles, as shown in Figure 4. The STMBMS instrument requires a vacuum ($< 10^{-6}$ Torr) external to the reaction cell to operate. Thus gases must be generated within the cell to participate in oxidation reactions. As the system is heated, the contaminant-containing material decomposes, filling the reaction cell with the gaseous contaminant, and exposing the sample of sodium alanate to the gaseous species. For example, sodium bicarbonate ($NaHCO_3$) decomposes to form sodium carbonate (s), H_2O (g) and CO_2 (g) over a temperature range of interest (see Appendix B for characteristics of $NaHCO_3$ decomposition.

Due to the pyrophoric nature of the sodium alanates, all samples were loaded in an argon glove box (O_2 and H_2O levels maintained below 1 ppm) and transferred in the STMBMS instrument under a stream of nitrogen gas.

3.2. X-RAY DIFFRACTION LABORATORY

Identification of the condensed-phase reaction products was assisted by crystal structure determination using a theta 2-theta Scintag XDS 2000 powder diffractometer located in the X-Ray Diffraction Laboratory at Sandia National Laboratories. This instrument allowed researchers to verify the inferred contamination reaction products observed in the experiments with the STMBMS.

3.3. RESULTS OBTAINED FROM THE STMBMS EXPERIMENTS

The primary objective of the STMBMS experiments was to determine how oxidizers, such as oxygen and water react with sodium alanate and whether hazardous products, such as peroxides, may be formed under certain subsets of reactive conditions. To achieve this objective a series of different experiments were conducted with the STMBMS instrument. The experiments may be divided into the following four categories, each having a specific objective:

1. *Baseline experiments*. These experiments focus on characterizing the products that evolve from sodium alanate samples as they are heated from ambient temperature to 1000°C. Samples charged with hydrogen or deuterium are examined. The objective of these experiments is to provide the baseline with which to compare the results from experiments in the other categories.
2. *Oxidation experiments*. These experiments focus on determining how different types of oxidation conditions (e.g., dry air vs. moist air) affect the sodium alanate samples. The objective of these experiments is to make a broad search of the parameter space for oxidation of sodium alanates to find those regions that are likely to form thermodynamically stable products and those regions that are likely to form less stable reaction products.

3. *Decomposition of salts*. These experiments focus on obtaining the thermal decomposition characteristics of various types of salts that may be formed when sodium alanate is oxidized. The objective of these experiments is to provide the reference data needed to interpret the results from the oxidations experiments with sodium alanate.
4. *Oxidation rate experiments*. These experiments focus on collecting data on the rate of oxidation of sodium alanate by water, oxygen and CO_2. The objective of these experiments is to collect data that can be used to develop a reaction mechanism of the oxidation process and mathematical models to represent the reaction kinetics of the process.

The results from the experiments in each of these categories are presented and discussed below. A list summarizing the objectives and general conditions used in experiments to assess each of these issues is presented later in Table 5 (Appendix A).

3.3.1. Sodium alanate sample preparation

All sodium alanate samples were produced using direct synthesis of non-stoichiometric amounts of sodium hydride (NaH), aluminum powder (Al), and titanium chloride ($TiCl_3$) within a Fristch P6 planetary ball mill. The resulting molar mixture proportionality was:

$$100\ NaH\ +\ 127\ Al\ +\ 4\ Ti\ +\ 12\ NaCl \qquad (R4)$$

After applying hydrogen at pressure and temperature, the first sodium alanate phase (sodium aluminum hexahydride) is formed,

$$33\ Na_3AlH_6\ +\ 94\ Al\ +\ 4\ Ti\ +\ 12\ NaCl \qquad (R5)$$

Another increase in pressure results in the fully hydrided sodium alanates that contain nearly 4.5% reversible hydrogen by weight (lower than maximum theoretical capacity of sodium alanates due to salts and excess aluminum present within the sample

$$100\ NaAlH_4\ +\ 27Al\ +\ 4Ti\ +\ 12\ NaCl \qquad (R6)$$

The samples were repeatedly cycled between a hydrided and dehydrided state to ensure that relevant end-use morphologies and particle sizes were attained prior to reactivity testing. Several samples were charged with deuterium, which allows the source of hydrogen in the products of reaction to be determined.

3.3.2. Baseline experiments

The identities and rates of evolution of various products that evolve from the sodium alanate as it is heated from 20 to 1000°C are shown for samples charged with hydrogen and deuterium (Figure 5). The rate of evolution of each species is plotted in moles/sec. As the sample is heated, chemical species evolve in the following sequence:

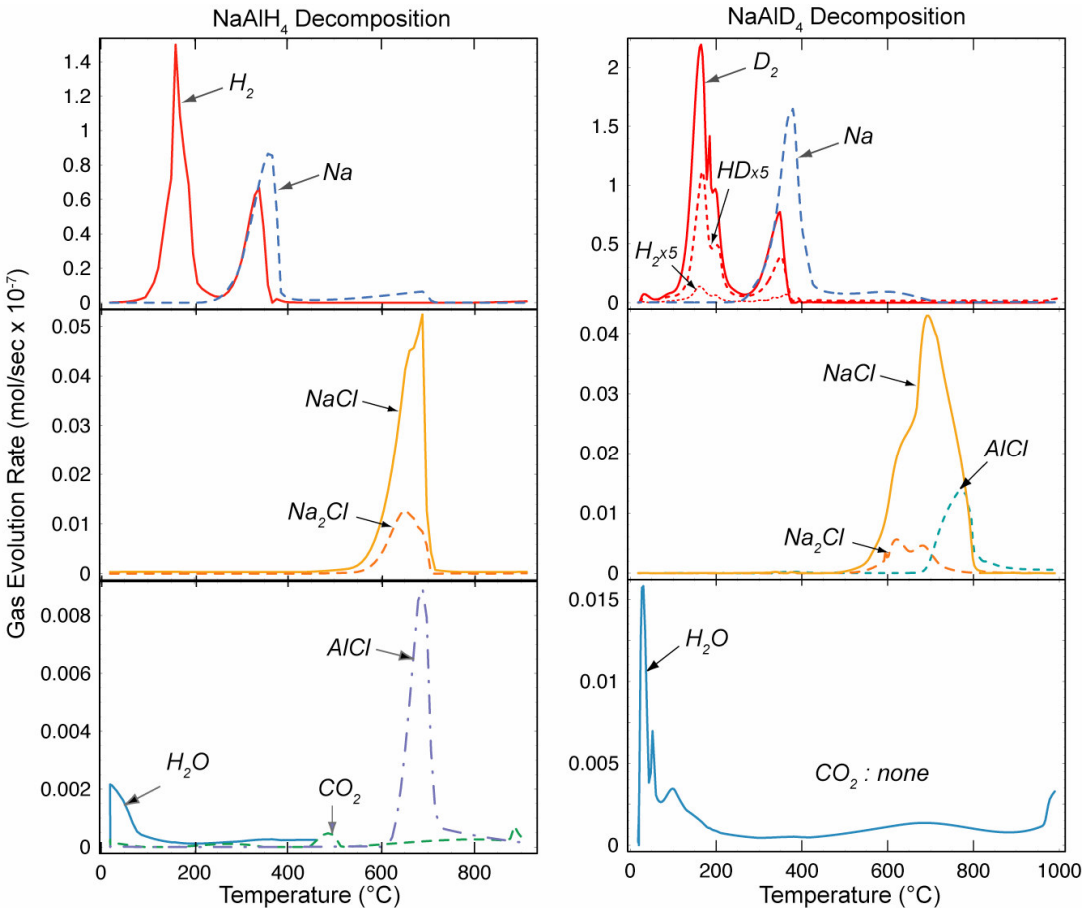


Figure 5 - Gas evolution rates of compounds released from sodium alanate samples ($NaAlH_4$ and $NaAlD_4$) as they are heated to 1000°C.

1. Water (H_2O) evolves from the sample as it is heated between 20 and 100°C. Note that H_2O evolves from the deuterium labeled sodium alanate, not HDO or D_2O. This small amount of water is presumably due to adsorption during transfer of the reaction cell.
2. Hydrogen evolves from the samples in two distinct temperature ranges: 100 to 220°C and 250 to 400°C. Evolution of hydrogen in the lower temperature range consists of contributions from two sources. Contribution from the first source occurs between 100 and ~180°C, and is due to the conversion of $NaAlH_4$ to Na_3AlH_6. Contribution from the second source overlaps with the first and appears as a shoulder at ~190 to 200°C. This is due to the decomposition of Na_3AlH_6 to NaH and aluminum. Note that a small amount of hydrogen evolves as HD and H_2 in the deuterium charged sample. This may be attributed to the use of NaH (vs. NaD) as the starting material in making the deuterium charged sodium alanate.

3. As the sample is heated between 250 and 400°C, hydrogen and sodium evolve from the sample. In this region, the NaH apparently decomposes to form H_2 and sodium and then the sodium evaporates from the sample. The evolution of sodium lags the evolution of hydrogen. Thus, molten sodium is present in the reaction cell for a period after all the hydrogen has evolved. Quantitative analysis of the data suggests that all of the sodium eventually evolves from the sample.
4. Above 400°C, titanium, aluminum and NaCl remain in the reaction cell. Between 550 and 800°C, sodium chloride and an aluminum chloride species evolve from the remaining sample. Aluminum has a melting point of 660°C suggesting that the sample may be molten aluminum. However, the presence of 2 to 3% of titanium will raise the liquidus point above 1000°C. The Na_2Cl species is probably formed by electron bombardments ionization of a NaCl dimer in the mass spectrometer. All of the sodium and chlorine evolve during the course of an experiment. Titanium and aluminum remain in the reaction cell after the sample is heated to 1000°C.
5. A small amount of CO_2 evolves from the $NaAlH_4$ sample near 500°C.
6. Comparison of the amount of hydrogen and deuterium that evolves from the deuterium loaded sample shows that about 3.5mol% of the sample evolves as hydrogen and the remainder evolves as deuterium. Thus, the series of hydriding/dehydriding cycles replace most of the hydrogen that was originally loaded into the sample as NaH.

The thermal decomposition of the sodium alanate sample as it is heated to 1000°C may be summarized by the sequence of events listed in Table 2. At the end of the thermal decomposition experiment a solution of titanium and aluminum remains.

Table 2 – Solid sample transformation during thermal decomposition of sodium alanate.

#	Molar ratios of starting material	Molar ratios of ending material	Range (°C)
1	100 $NaAlH_4$ + 27Al + 4Ti + 12 NaCl	33 Na_3AlH_6 + 94 Al + 4 Ti + 12 NaCl	100 - 180
2	33 Na_3AlH_6 + 94 Al + 4 Ti + 12 NaCl	100 NaH + 127 Al + 4 Ti + 12 NaCl	150 - 220
3	100 NaH + 127 Al + 4 Ti + 12 NaCl	100 Na + 127 Al + 4 Ti + 12 NaCl	250 - 375
4	100 Na + 127 Al + 4 Ti + 12 NaCl	127 Al + 4 Ti + 12 NaCl	250 - 420
5	127 Al + 4 Ti + 12 NaCl	~125 Al + 4 Ti	550 - 800

3.3.3. Oxidation experiments

The objective of the oxidation experiments is to determine how sodium alanate is altered when exposed to water and oxygen. To achieve this objective a series of experiments (type OxAE listed in Table 5) were conducted in which a sodium alanate sample ($NaAlD_4$) was loaded into a sample container, mounted on a gas manifold, and exposed to various types of oxidizing atmospheres. The oxidizing atmospheres used to expose the sample included: (1) moist air, (2) dry air, and (3) O_2 at 300 ppm and 56 ppm in argon.

3.3.3.1. Moist air – full oxidation

A sample of $NaAlD_4$ was exposed to ambient laboratory air for four hours and then analyzed. The exposure to moist air resulted in a nearly total loss of available deuterium and a significant uptake of water. The identities and rates of evolution of products from the sample are shown in Figure 6. There are significant changes in the identities and the temporal behaviors of the compounds that evolve from the sodium alanate samples that have been exposed to moist air. The change in these features may be summarized as follows:

1. *Hydrogen.* The amount of hydrogen that evolves from the sample has decreased by approximately a factor of ten when compared to the baseline experiments. For the sample of $NaAlD_4$, other isotopomers* of hydrogen, H_2 and HD, now evolve from the sample at rates comparable to D_2. H_2 and HD both start to evolve when the sample is first heated from 20°C. This indicates that the samples react with water to incorporate some of the hydrogen from the water into the sample. When the sample is heated, some of the hydrogen from water evolves as hydrogen gas (H_2 and HD). The temperature dependence of the thermal desorption of hydrogen from the sample is quite different from the baseline experiments.

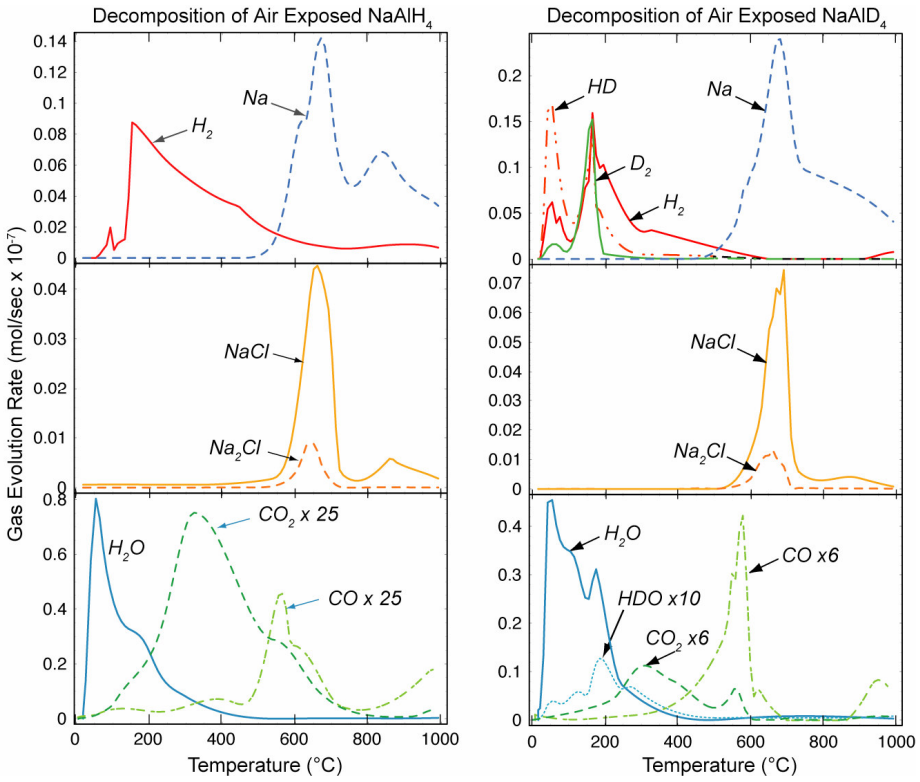


Figure 6 - Gas evolution rates of compounds released from sodium alanate samples ($NaAlH_4$ and $NaAlD_4$) that were exposed to moist air.

* Molecules having different isotopes at specific positions of a given element in a molecule.

2. *Sodium.* The sodium starts to evolve at ~500°C - a higher temperature than observed in the baseline experiment. This indicates that a sodium compound that starts to decompose at ~500°C was formed when the sample was exposed to air.

3. *Carbon oxides.* As the sample is heated, CO and CO_2 evolve. These carbon-containing compounds are not observed in the baseline experiments. Thus, the sample apparently reacts with carbon dioxide in the air. The carbon dioxide evolves between 100 and 600°C, with the greatest rate of evolution occurring between 300 and 400°C. The CO evolves at a higher temperature than CO_2. It starts to evolve at approximately 400°C and its rate of evolution increases significantly between 500 and 600°C. The CO evolves slightly ahead of sodium. This suggests that the sodium is part of a compound that decomposes to form CO. The compound may be composed of the carbon oxides and sodium, or it may also include aluminum and/or titanium. The compound does not appear to be pure sodium bicarbonate ($NaHCO_3$) or sodium carbonate (Na_2CO_3), since the rate of gas evolution from these two compounds is quite different from that observed in these experiments (see Appendix B).

4. *Water.* Water is the most abundant product that evolves from the sample. As can be seen from the experiment with $NaAlD_4$, most of the water that evolves is H_2O. Only a much smaller fraction of the water evolves as HDO. Almost no water evolves as D_2O. This indicates that almost all of the water that evolves from the sample originates from the air to which the sample was exposed. The water evolves from the sample over a wide temperature range (20 to 400°C). The water that evolves between 20 and 100°C most likely originates from water adsorbed on the sample. The water that evolves at higher temperatures suggests that some of the water may be present as hydrates, or possibly hydroxides. The rate of evolution of HDO rises as the sample is heated. This suggests that the water is reacting with some of the residual deuterium remaining in the sample.

5. *Salts.* The sodium chloride evolves over approximately the same temperature range as in the baseline samples. The AlCl species that was observed in the baseline samples is not observed in this sample, which was exposed to moist air. This would be consistent with the aluminum existing as aluminum oxide in air exposed samples.

One of the more interesting features of exposing the sodium alanate sample to air was the affinity of sodium alanate and/or its oxidation products for carbon dioxide in air. This affinity was later exploited to stabilize an oxidized sodium alanate sample as discussed in sections below.

Measurements using XRD confirmed the presence of sodium hydroxide (NaOH), some form of sodium bicarbonate (Na_2CO_3) and aluminum oxide hydrate ($Al_2O_3 \cdot 3H_2O$). Another sodium complex was observed, possibly, sodium peroxide hydrate ($NaO_2 \cdot XH_2O$), however phase identification from X-ray diffraction data of hydrated hydroscopic samples is difficult due to the number of phases present and the resulting peak overlap.

3.3.3.2. Dry air & oxygen – partial oxidation

The initial experiments in which the samples were exposed to moist air demonstrated that sodium alanate reacts readily with water, but its interaction with O_2 was less obvious. To determine how sodium alanate reacts with O_2, $NaAlD_4$ samples were exposed to atmospheres of dry air (< 6 ppm H_2O) and oxygen at concentrations of 300 and 56 ppm in argon. The samples were exposed to the various atmospheres for 4 hours and then examined with STMBMS and X-ray measurements. The STMBMS results from the three experiments are shown in Figure 7. The gas evolution rates of the compounds that evolve from the samples as they are heated to 1000°C are quite different from the results with the sodium alanate samples that were exposed to moist air.

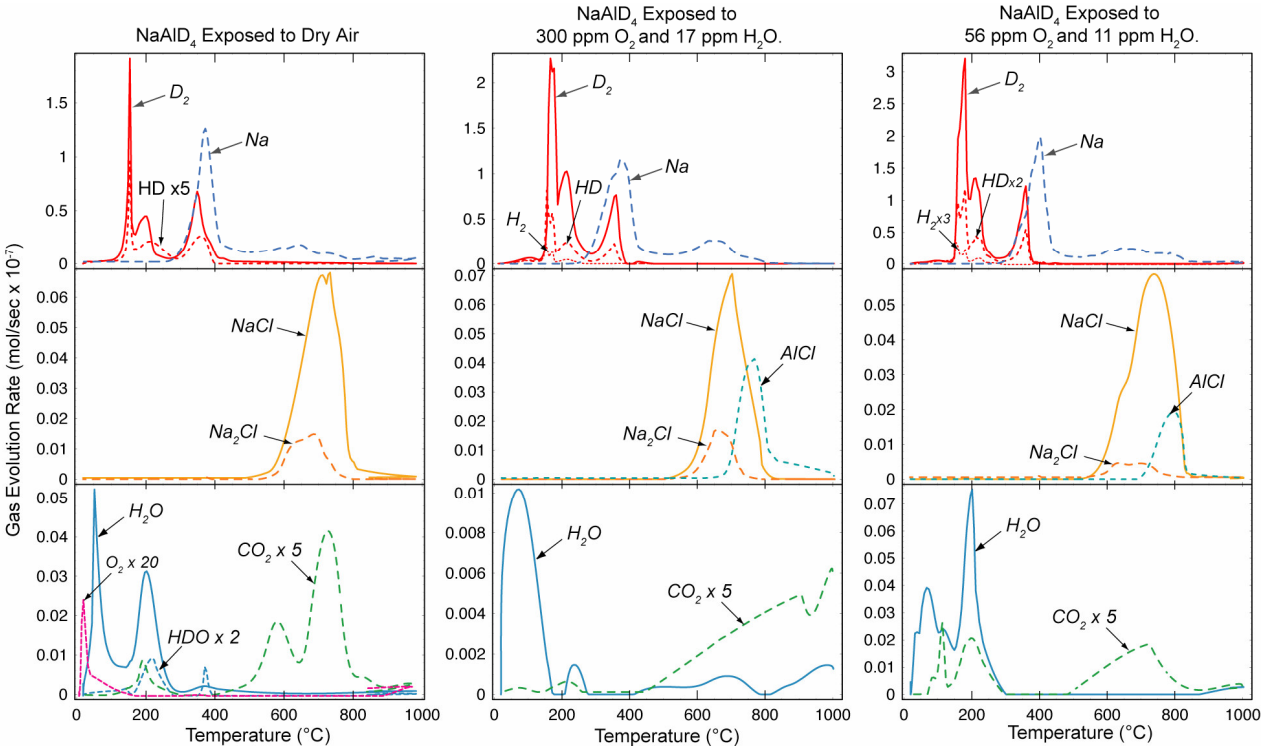


Figure 7 - Gas evolution rates of compounds from sodium alanate samples that were first exposed to dry air and two different concentrations of oxygen.

The features of the various compounds that evolve from the samples are as follows:

1. *Hydrogen*. The amount of hydrogen, its rate of evolution, and the general temperature dependence of its evolution from the samples exposed to oxygen are similar to the baseline experiment. The hydrogen evolves in two temperature regions as was describe above for the baseline samples. The main hydrogen isotopomer that evolves from the $NaAlD_4$ is D_2. The amount of HD that evolves from any of the three samples is a factor of five to ten lower than for the samples fully oxidized with moist air. The ^1H in the HD apparently originates from the small amount of water that is present in the "dry" samples. The one notable difference between the samples exposed to dry air or oxygen is the more abrupt change in the rate of release of hydrogen from the samples that have been exposed to oxygen. Note the rapid rise of the rate of evolution in D_2 in the three experiments as it is heated. This results in a significant contribution of a thrust term to the force measured by the microbalance, similar to the thrust created by the gas in a rocket motor. This behavior is illustrated with comparison of the mass data from two experiments shown in Figure 8, where the more rapid release of D_2 from the sample exposed to dry air results in an apparent gain in mass.

2. *Sodium.* The sodium evolves from these samples in a manner that is very similar to the baseline experiments. The NaD decomposes to form D_2 and sodium. The D_2 evolves rapidly from the reaction cell. This is followed by the evolution of the majority of the sodium from the reaction cell as it sublimes from the sample. This behavior shows that exposure to O_2 does not result in a significant formation of a more thermally stable sodium oxide salt.

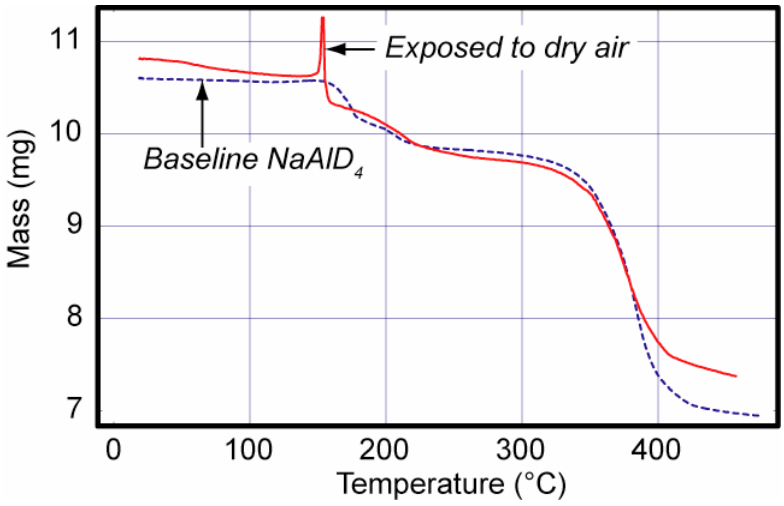


Figure 8 - Comparison of mass loss data from $NaAlD_4$ exposed to dry air and the baseline data.

3. *Water.* The amount and rate of evolution of water from the three samples exposed to oxygen is much lower than samples exposed to moist air. The primary water isotopomer that evolves is H_2O. This indicates that most of the water that evolves originates from the minor amount water that was present in the gases used to expose the samples and not from the reaction of oxygen with deuterium in the $NaAlD_4$ sample. There is a small amount of HDO that evolves as the samples are heated to higher temperature. This suggests that H_2O exchanges some of hydrogen with deuterium as the $NaAlD_4$ sample decomposes and releases D_2. The smaller amount of water present on the sample also suggests how the water is bound to the $NaAlD_4$ sample. The water evolves over two distinct temperature ranges. Between 20 and 100°C most water likely originates from adsorbed water on the sample. Evolution between 150 and 300°C suggests that this water is more strongly bound to the sample, possibly as a hydrate.

4. *Oxygen.* Oxygen gas (O_2) evolves from the sample exposed to dry air as shown in Figure 7. Oxygen gas appears when the sample is first heated and then its evolution falls as heating of the sample continues. Further insight into the process responsible for the appearance of O_2 is provided in the section below on oxidation rates.

5. *Carbon oxides.* The only carbon oxide that evolves from the sample is CO_2. The amount and rate of evolution of CO_2 is much lower than in the sample that was exposed to moist air. Carbon monoxide does not evolve from the samples as was observed in the sample that was exposed to moist air.

6. *Salts.* The sodium chloride salts evolve over the same temperature range as was observed in experiments with both the baseline samples and samples exposed to moist air. The evolution of the AlCl species from the samples exposed to 300 and 56 ppm oxygen is similar to that observed for the baseline experiments. However, AlCl does not evolve from the sample exposed to dry air. This suggests that the oxygen in the sample exposed to dry air was sufficient to alter the state of aluminum in the sample so that it could not react with the available chlorine in the sample. Sodium peroxide (Na_2O_2) was identified by XRD measurements as a dominant species resulting from dry air exposure.

The most important change in the samples due to exposure to dry air or small concentrations of O_2 is the alteration of the rate of evolution of deuterium as illustrated in Figure 9. As mentioned above, the evolution of deuterium from the samples exposed to oxygen is similar to its evolution from the baseline sample (black curve). The majority of the deuterium evolves between 100 and 220°C and the remainder evolves between 300 and 400°C as the NaD decomposes. However, careful examination of the rate of evolution of D_2 from the sample between 100 and 150°C shows that the onset of D_2 evolution occurs at higher temperatures in the samples exposed to oxygen. In addition, when it does start to evolve, the rate of change in the evolution rate with temperature is more rapid. This manifests itself in the abrupt release of gas from the reaction cell.

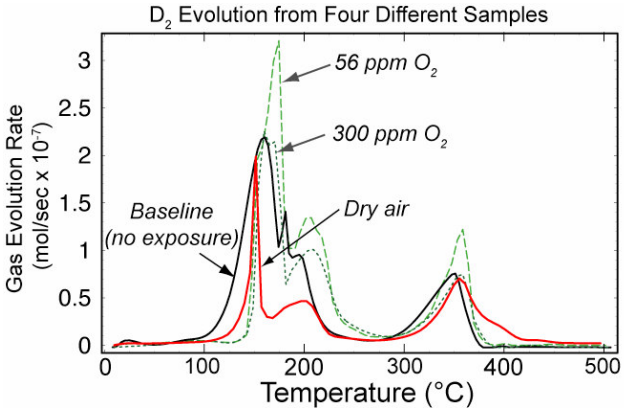


Figure 9 - The gas evolution rate of D_2 from samples of $NaAlD_4$ that have been exposed to various levels of oxygen.

In the development of sodium alanates for storage of hydrogen it was found that the addition of titanium facilitated the movement of hydrogen in and out of the sample [5]. The delayed onset of release of D_2 from the samples used in our experiments may indicate that the titanium has been partly oxidized and is no longer available to facilitate the movement of gas between the solid and gaseous phases as effectively.

3.3.3.3. Salt decomposition characteristics

During the oxidation of sodium alanate it may be possible to form sodium salts that have limited stability. The presence of these salts may create a material that could undergo further reaction if ignited. Such materials may have similarities to thermites (Fe_2O_3 + 2Al → Al_2O_3 + 2Fe). To help identify whether these types of salts may be formed during the oxidation of sodium alanate, the thermal decomposition characteristics of a selected set of salts were determined using the STMBMS apparatus. The characterized salts include: $NaHCO_3$, Na_2CO_3, NaOH, and Na_2O_2. The sodium bicarbonate and sodium carbonate were selected for characterization based on the observation of the evolution of carbon monoxide and carbon dioxide from sodium alanate samples exposed to moist air. The sodium hydroxide was selected because hydroxides are one class of compounds that may be formed by the interaction of sodium alanate with water. The sodium peroxide was selected because it has been reported in the literature that this may be formed in sodium containing systems. In addition, it has been reported as being sensitive to ignition by impact [21].

The qualitative characteristics (i.e., the identities of the products and the temperature range over which they evolve) of the thermal decomposition of these four compounds are summarized in Appendix B of this report. The main features of the decomposition of each compound are summarized in Table 3. The main products that evolve from the decomposition of NaOH, Na_2O_2, and Na_2CO_3 are H_2O, O_2 and CO_2, respectively. The sodium bicarbonate undergoes two distinct decomposition processes.

Table 3 - General qualitative decomposition characteristics of salts.

Compound	Reaction*	Temp (°C)
$NaHCO_3$	$2\ NaHCO_3(s) \rightarrow Na_2CO_3(s) + H_2O(g) + CO_2(g)$	90 - 180
Na_2CO_3	$Na_2CO_3(s) \rightarrow Na\text{-}O\text{-}Na(int) + CO_2(g)$	850 - 980
	$Na\text{-}O\text{-}Na(int) \rightarrow 2\ Na(g) + 1/2\ O_2(g)$	900 - 980
	$Na\text{-}O\text{-}Na(int) \rightarrow Na_2O(s)$	900 - 980
NaOH	$2\ NaOH(s) \rightarrow Na_2O(s) + H_2O(g) + Na_xO_y(int)$	400 - 570
	$NaOH(s) \rightarrow NaOH(g) + Na_2OH(g)$	400 - 570
	$Na_xO_y(int) \rightarrow x\ Na(g) + y/2\ O_2(g)$	750 - 1000
Na_2O_2	$2\ Na_2O_2(s) \rightarrow 2\ Na_2O(s) + O_2(g)$	400 - 600
	$2\ NaOH(s) \rightarrow Na_2O(s) + H_2O(g) + Na_xO_y(int)$	550 - 750
	$Na_xO_y(int) \rightarrow x\ Na(g) + y/2\ O_2(g)$	800 - 950
All salts	$Salt \cdot xH_2O \rightarrow Salt + x\ H_2O$	20 - 100

* Nomenclature: s – solid; g – gas; int – reaction intermediate.

The first converts the sodium bicarbonate to Na_2CO_3 and releases H_2O and CO_2. This occurs over a temperature range between 100 and 200°C. The remaining sodium carbonate decomposes in the same manner as observed for the Na_2CO_3 sample.

It is interesting to note that, for each of the salts, the high temperature (>750°C) decomposition behavior involves the formation of a reaction intermediate of the form Na-O-Na that apparently reacts along two competing pathways. One forms the stable $Na_2O(s)$, which remains in the reaction cell at 1000°C. The other results in the formation of O_2 and the release of O_2 and sodium vapor from the reaction cell.

While these results of the decomposition of these sodium salts provide a basis for comparison with the evolution of gaseous compounds from the sodium alanate samples, analysis of the gas evolution from the sodium alanate samples do not exhibit gas evolution that can be directly matched with the results from these sodium salt reference materials. This suggests that oxidation by H_2O or O_2 may create compounds involving aluminum and titanium in addition to the sodium.

In addition to providing baseline data on the decomposition of various salts, the experiments with sodium bicarbonate suggested that it would be a good source for generating H_2O and O_2 within the reaction cell over a temperature range in which we are interested in examining the details of the reaction of sodium alanate with these two gases. Hence, a set of experiments were run to explore this method of examining the detailed reaction kinetics of sodium alanate.

3.3.3.4. Oxidation rate experiments

While thermal decomposition experiments of sodium alanate samples exposed in the laboratory to various atmospheres are useful for evaluating the effect of various oxidizing environments on the reaction of sodium alanate, greater insight may be obtained if the rates of oxidation may be probed by *in situ* measurements of the gases formed and consumed during the reaction process. Important features of complex reaction mechanisms may be determined from the sequence of disappearance and appearance of different species involved in the reaction process [22]. In addition, by making quantitative measurements of the concentration of various gases within the reaction cell as a function of time, data may be obtained that can be used to determine reaction kinetics parameters of the various steps on the reaction mechanism.

Experiments were conducted to investigate how sodium alanate reacts with water and carbon dioxide. This was implemented by conducting STMBMS experiments in which sodium bicarbonate was loaded into the bottom of the reaction cell and the sodium alanate sample was placed in a separate "cup-like" baffle located above the sodium bicarbonate (Figure 4). As the reaction cell is heated, gaseous compounds evolve from each compound and fill the internal free volume of the reaction cell. The gaseous compounds may interact with both solid samples, as well as each other, within the reaction cell. The water and CO_2, which evolves from $NaHCO_3$, may interact with the sodium alanate. The deuterium evolving from the $NaAlD_4$ may interact with the sodium bicarbonate/sodium carbonate.

To examine the reaction process, a set of two experiments is conducted on each sodium alanate sample ($NaAlD_4$). In the first experiment, the reaction cell containing both sodium alanate and sodium bicarbonate was heated from 20°C to temperatures ranging up to 300°C. The gases emanating from the reaction cell are measured during this process. The time-dependent rates of evolution of the various gaseous compounds provide the data for determining the reaction mechanisms and the associated kinetics. After the first experiment is complete, the sodium alanate sample is removed from the reaction cell and placed in a clean reaction cell. This sample is then heated from 20 to 1000°C and the products that evolve are determined from the data.

In the first set of experiments the sample was heated from 20 to 300°C. It was observed that all three isotopomers of hydrogen evolved from the sample at temperatures between 100 and 150°C. In the second experiment, alane (AlH_3) evolved from the sample, which was not observed in the samples exposed to moist air and oxygen. Based on the results from this initial set of experiments, another set of experiments was conducted in which the temperature of the sample was carefully heated through a set of sequentially increasing heating/cooling cycles.

Data from the first experiment in which the sample is heated through a set of sequentially increasing heating/cooling cycles reveals new insight into the reaction of sodium alanate with water and carbon dioxide. Data from this experiment, along with data from sodium

bicarbonate by itself heated through a similar set of heating/cooling cycles, is shown in Figure 10 and Figure 11. The sodium alanate sample, exposed to H_2O and CO_2 in this set of heating/cooling cycles, was examined further by measuring the gas evolution rate of products from this sample as it was heated to 1000°C (Figure 11B). Careful examination of the data from these experiments shows the following interesting features of both the sodium alanate reaction process and the experimental method:

1. <u>*Oxidizer generation*</u>. The decomposition of the sodium bicarbonate ($NaHCO_3$) can be tracked by the rate of evolution (RoE) of H_2O and CO_2. Note that the RoE of these two compounds is the largest of all the gases, as expected. The rate of evolution of H_2O and CO_2 from $NaHCO_3$ by itself is approximately equal in cycles two through four (Figure 10 graphs C and D). During the first cycle in which the sample is heated to 70°C, adsorbed water evolves from the sodium bicarbonate. Note the rapid increase in its rate of evolution above 60°C. The evolution of H_2O and CO_2 effectively ceases during the fourth heating/cooling cycle because the $NaHCO_3$ has decomposed completely leaving Na_2CO_3 in the reaction cell.

2. <u>*Reaction with water*</u>. Examination of the data from the first two heating/cooling cycles (Figure 10B and D) provides new insight into the reaction of water with sodium alanate.

    a. *Hydrogen*. The following features are observed in the release of hydrogen from the sample:

        i. H_2 and HD evolve from the sample indicating that hydrogen gas is formed via reaction of water (the source of H atoms) with the $NaAlD_4$.

        ii. Examination of the hydrogen evolution in the first two cycles shows that the H_2, HD and D_2 evolve in a ratio of approximately 1:2:1, which would be expected for statistically random mixing of equal amounts of the two isotopes. This suggests that each water molecule may transfer its oxygen atom to the $NaAlD_4$, which in turn results in the release of two hydrogen atoms from the water and two deuterium atoms from the $NaAlD_4$.

        iii. The rate of evolution of the hydrogen isotopomers increases rapidly above 60°C during the first reaction cycle (Figure 10*B*). This rapid rise in the RoE of hydrogen correlates with the increased amount of water available for reaction within the reaction cell (Figure 10*D*). The close tracking of the RoE of hydrogen with that of water indicates that the reaction rate of $NaAlD_4$ with water is quite rapid at temperatures below 70°C. This type behavior is also observed during the second heating/cooling cycle.

    b. *Water*. H_2O evolves from the $NaHCO_3$ sample as it decomposes. The water fills the internal volume of the reaction cell and comes in contact with the $NaAlD_4$, where it deposits on the sample surface and may diffuse into the interior of the sample. Examination of the data in Figure 10 and Figure 11 exhibit the following features:

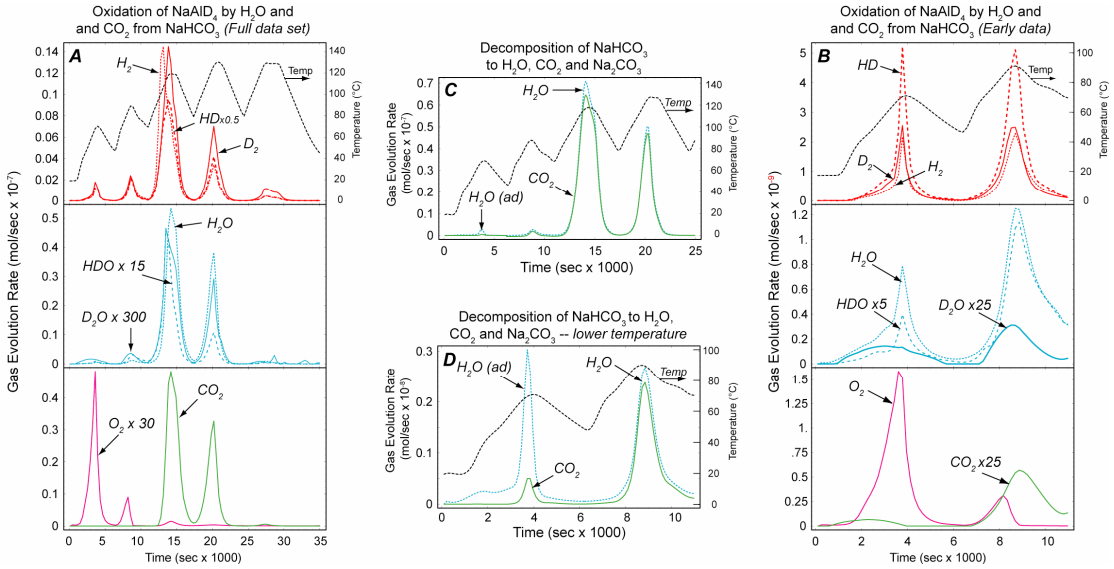


Figure 10 - Gas evolution rates of products from the reaction of $NaAlD_4$ with H_2O and CO_2 formed by the decomposition of $NaHCO_3$ (graphs *A* and *B*). Gas evolution rate from a $NaHCO_3$ sample by itself as it is heated through the same thermal profile is shown in graphs *C* and *D*. The temperature profile is shown on each graph. Note different units on the ordinates (A & C: 10^{-7} mol/sec; B: 10^{-9} mol/s; D: 10^{-8} mol/s).

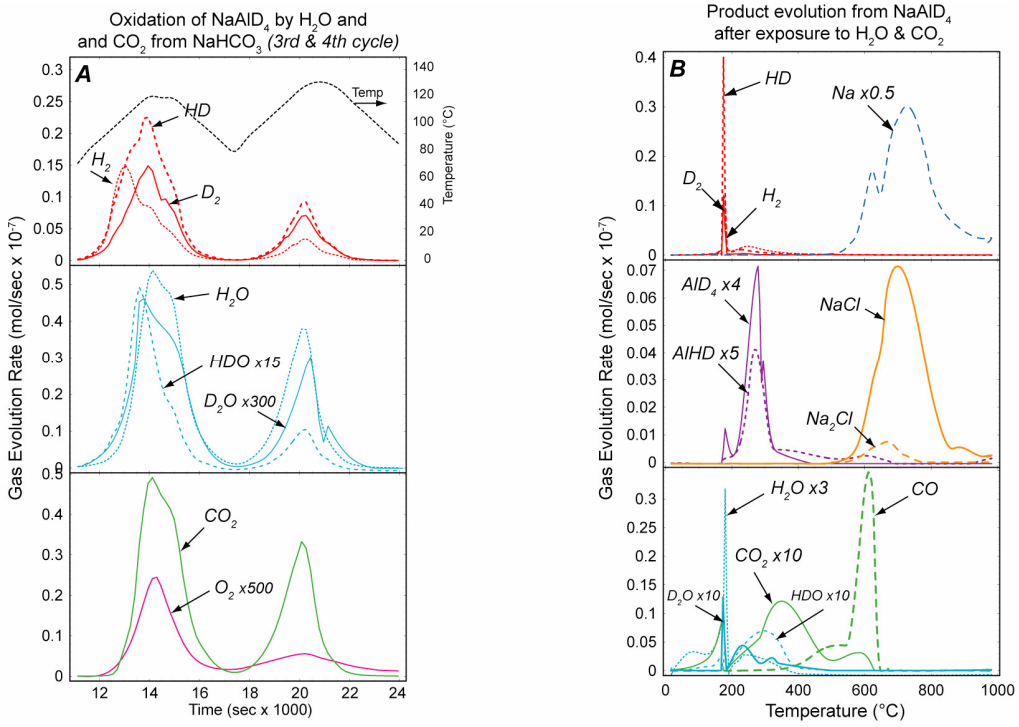


Figure 11 - *A*. Expanded view of the 3rd and 4th heating/cooling cycles in reaction of $NaAlD_4$ with H_2O and CO_2 generated by the decomposition of $NaHCO_3$. *B*. Gas evolution rate of products from $NaAlD_4$ sample that was exposed to H_2O and CO_2 from $NaHCO_3$.

i. During the first two heating/cooling cycles (Figure 10*B*) ~ 80% of the water evolves as H_2O, ~ 20% of the water evolves as HDO and ~ 1% evolves as D_2O. Since the only source of deuterium is the $NaAlD_4$ sample, this indicates a relatively extensive interaction occurs between H_2O and the $NaAlD_4$ sample, which results in the exchange of deuterium for hydrogen in the water molecules.

ii. A comparison of the temporal behaviors of the RoEs of the hydrogen and water isotopomers during the 1st and 2nd cycles shows that the temporal behaviors of the RoE of H_2O from $NaHCO_3$ by itself (Figure 10*D*) and the three hydrogen isotopomers from the $NaAlD_4$ (Figure 10*B*) are quite similar. In contrast, the temporal behavior of the RoE of the water isotopomers is quite different from the other two. This suggests that the primary reaction involves a global reaction such as
$2\ H_2O(abs) + NaAlD_4(s) \rightarrow H_2 + 2\ HD + D_2 + NaAlO_x(?) + (1 - x/2)\ O_2$.
A slower reaction involves the exchange of hydrogen between the $NaAlD_4$ and water $H_2O(abs) + NaAlD_4(s) \rightarrow NaAlD_3H(s) + HDO(abs)$.
Thus, during the first two reaction cycles the amount of H in the outer regions of the $NaAlD_4$ particles should become enriched in the ^1H isotope.

iii. Examination of the RoEs of the hydrogen isotopomers in the 3rd cycle, as the sample is heated to 120°C, shows that the sequence of evolution of the three isotopomers is: H_2, HD and then D_2. This is consistent with the outer regions of the $NaAlD_4$ particles becoming enriched in ^1H due to the hydrogen exchange reaction with H_2O.

c. *Diffusion limitations*. As expected, the rate of reaction of water with the sodium alanate sample is limited by diffusion. This is illustrated by the fall-off of the hydrogen isotopomer and HDO RoEs in the 3rd heating/cooling cycle (Figure 11*A*). The maximum rate of evolution of HD, D_2 and HDO occurs when the sample first reaches an isothermal temperature of 120°C. Their RoEs decrease as the sample is held at this constant temperature. This behavior is consistent with evolution of gases out of particles that comprise the sample. As time progresses the gases must diffuse from regions of a particle further from its surface, which results in a slower rate of evolution of the gases.

d. *Oxygen.* The evolution of O_2 from the sample provides a possible explanation for why sodium alanate samples have been observed to explode while being handled during laboratory experiments. Dioxygen evolves from the sample at significantly different rates during the first three heating/cooling cycles (Figure 10 and Figure 11A). While one might expect that the oxygen from water would react with the sodium alanate to form some type of salt, below 70°C the water appears to react with the sodium alanate to form O_2 gas. The following features of the data show when O_2 may be formed in the reaction of H_2O with $NaAlD_4$:

i. The RoE of O_2 is greatest during the 1st cycle. Its RoE starts to rise as the amount of water in the reaction cell first starts to rise (Figure 10*B*). This starts between 30 and 40°C. While the rate of formation of the hydrogen isotopomers tracks the rate of evolution (and thus the partial pressure within

the reaction cell) of water, the RoE of O_2 appears to rise gradually after its first appearance. This suggests that the rate of formation of O_2 may depend on (1) the presence of a supply of water on the surface of the $NaAlD_4$ particles and (2) the rate of reaction between the H_2O(abs) and the underlying $NaAlD_4$.

ii. When the temperature nears 70°C the RoEs of O_2 and the hydrogen isotopomers are comparable. This could possibly make an explosive mixture.

iii. When the sample starts to cool during the 1st cycle, the RoE of O_2 drops rapidly. This is similar to the behavior of the hydrogen isotopomers. In contrast, the RoE of HDO falls off more gradually as the sample is cooled.

iv. As the sample is heated in the 2nd cycle the RoE of O_2 again starts to rise. However, when the sample attains a temperature of ~70°C the RoE of O_2 falls toward zero as the sample continues to heat. It is possible that this falloff is due to the depletion of the sample constituents that are necessary to form O_2. However, a more plausible explanation may be that above 70°C the oxygen atoms formed in the reaction with water (or possibly CO_2) are consumed in reactions with titanium, aluminum and sodium to form stable oxides. Thus, little O_2 is released from the reaction cell above 70°C.

v. The RoE of O_2 during the 3rd heating/cooling cycle is very low compared to the earlier cycles. This suggests that the reaction that leads to the formation of O_2 still occurs, but at higher temperatures reactions of O_2 with other constituents in the sample lead to the formation of stable oxides leaving less O_2 present in the free volume of the reaction cell.

3. *Reaction with carbon dioxide.* As mentioned in descriptions of the reaction of sodium alanate samples with moist air, it was found that sodium alanate reacts with CO_2 to form compounds that release CO and CO_2 when heated between 100 and 600°C. The data from the interaction of $NaAlD_4$ with H_2O and CO_2 provide some insight into the when and how fast the CO_2 reacts with the sodium alanate. Since our present analysis of the data does not reveal a gaseous product that is formed by the reaction between CO_2 and $NaAlD_4$, it is more difficult to track the interaction between these two compounds. However, some insight is gained into their interaction by comparing the rates of evolution of CO_2 from the sodium bicarbonate sample by itself to its evolution from the mixture of $NaHCO_3$ and $NaAlD_4$ in this experiment. The following observations and interpretations may be gleaned from the data:

   a. The main features may be obtained from a comparison of the RoE of CO_2 from the $NaHCO_3$ sample (Figure 10*D*) and the $NaAlD_4/NaHCO_3$ mixture (Figure 10*B*) during the first two heating/cooling cycles of each experiment. The data from the experiment with $NaHCO_3$ shows that CO_2 first evolves from the sample at ~60°C (the first cycle). The 2nd cycle shows that CO_2 and H_2O evolve from the reaction cell at about the same rate (0.25×10^{-8} mol/s -- Figure 10*D*). Examination of the data from the 1st and 2nd cycles in the experiment with $NaAlD_4/NaHCO_3$ shows that the evolution of CO_2 during the 1st cycle is negligible and the RoE during the 2nd cycle is ~ 0.2×10^{-10} mol/s, which is about a factor of 100 lower than in the decomposition of $NaHCO_3$ by itself. Thus, the sodium alanate sample during the

initial stages of its decomposition reacts very rapidly with the CO_2, essentially removing it from the reaction cell atmosphere as fast as it is generated.

b. A comparison of the RoE of CO_2 in the 3rd cycle of both experiments shows that the rate of CO_2 evolution from the $NaAlD_4/NaHCO_3$ experiment is ~25% lower than from the $NaHCO_3$ by itself. In a rough approximation, if we assume that 25% of the available CO_2 is consumed in the reaction with the $NaAlD_4$, then the reaction consumes 1 mole of CO_2 for every 2 moles of sodium alanate. The products formed by this reaction are unknown at present.

4. *Decomposition of the $NaAlD_4$ reacted with H_2O and CO_2*. The sodium alanate sample was removed from the reaction cell after being exposed to H_2O and CO_2 in the thermal cycling experiment and placed in a clean reaction cell for subsequent analysis. The reaction cell was fitted with a 1000µm diameter orifice and the sample was heated from 20 to 1000°C at 2.5°C/min. The identities and gas evolution rates of the various compounds are shown in Figure 11*B*. The evolved compounds have many features in common with the compounds evolved from the samples exposed to moist air (Figure 6). The most notable difference is the evolution of AlH_xD_y species from the $NaAlD_4$ exposed to only H_2O and CO_2, whereas these species are not observed in the sodium alanate samples exposed to moist air. The general features of the various compounds that evolve from the sodium alanate sample are:

   a. *Hydrogen*. The evolution of the hydrogen isotopomers is very abrupt. This is similar to the change in the RoE of hydrogen in the samples exposed to dry air and different concentrations of O_2 (Figure 7 - Figure 9).

   b. *Water*. The rate of water evolution from this sample is very low compared to the samples exposed to moist air (Figure 6). This suggests that the water that evolves from the samples exposed to moist air contain water that was adsorbed on the sample after it reacted with H_2O and CO_2. The rapid evolution of hydrogen gas from the sample appears to correspond to a similar rapid release of water from the sample. The origin of the water that evolves rapidly cannot be determined from the current data set. It may originate from water adsorbed in the sample or it may originate from the reaction with an oxide in the sample.

   c. *Alanes*. The rapid evolution of hydrogen gas is followed by the onset of evolution of alanes from the sample. The evolution of alanes indicates that the aluminum within the sample has not been fully oxidized. About 5% of the aluminum evolves from the sample as alanes. Ion signals associated with all of the hydrogen isotopomers of alane and an AlD_4 species are observed in the mass spectra. The observation of an AlD_4 species (m/z=35) appears somewhat unusual. This signal is not attributed to Cl as no correlated signal is observed for the mass 37 Cl isotope.

   d. *Carbon oxides*. Both CO_2 and CO evolve from the sample as it is heated. However, CO is the dominant product. It starts to evolve from the sample starting at ~400°C and its RoE becomes very rapid from 500 to 620°C. As CO is released from the sample, the release of sodium commences. This suggests that exposing the sample to a mixture of H_2O and CO_2 at lower temperature results in the

formation of a compound that decomposes to form CO and some free sodium. Approximately 75% of the sodium is released from the sample as either sodium vapor or the sodium chloride salts. The release of CO from the sample is very similar to one of the sample exposed to moist air (Figure 6).

e. *Sodium*. Sodium is released from the sample as sodium vapor starting at ~500°C. This coincides with the onset of the release of CO from the sample. Thus, the compound formed by the reaction with CO_2 inhibits the evolution of sodium, when compared to the baseline experiments (Figure 5).

The oxidation rate experiments provide information on the sequence of species consumption and evolution in the reaction between $NaAlD_4$ and H_2O/CO_2. The results have shown that the following localized global reactions control the interaction of $NaAlD_4$ with H_2O and CO_2:

$$2\ H_2O(abs) + NaAlD_4(s) \rightarrow H_2 + 2\ HD + D_2 + NaAlO_x + (1 - x/2)\ O_2 \quad (R7)$$

$$H_2O(abs) + NaAlD_4(s) \rightarrow NaAlD_3H(s) + HDO(abs) \quad (R8)$$

$$NaAlO_x + O_2 \rightarrow NaAlO_{x+2} \quad (R9)$$

$$CO_2 + NaAlO_x \rightarrow NaAlO_x \bullet CO_2. \quad (R10)$$

Reaction R7 and R8 are reasonable global reactions and are consistent with the data. Reaction R9 represents the reaction of H_2O with $NaAlD_4$ above 70°C, where O_2 is no longer formed and the oxygen is most likely consumed in reactions to form oxides with sodium, titanium or aluminum. Reaction R10 simply represents that some unknown compound is formed in a reaction between the sodium alanate and CO_2. It is possible that reaction R7 must occur prior to reaction of CO_2 with the sample via interaction with the $NaAlO_x$ species. Further experiments examining the interaction of $NaAlD_4$ without the presence of water would help to further elucidate the details of the reaction mechanism involving Reaction R10.

3.3.4. Discussion of oxidation-induced rapid-kinetic events

These experiments have shown that the exposure of sodium alanates to rather low concentrations of oxygen and water vapor (<100 ppm) may result in significant destabilization of the hydrided material during subsequent thermal decomposition. Aggressively oxidizing the materials seems to result in a relatively benign substance while partial oxidation results in a less stable hydrogen-containing structure. These are qualitative observations given the many factors of sample geometry, extent, type and distribution of oxidation products that can be expected to affect these preliminary studies. Future experiments can refine the quantification of such factors.

Additionally, exposure of sodium alanates at temperatures below 100°C results in the simultaneous generation of O_2 and H_2 gas in nearly equivalent concentrations. If the reaction proceeds to ignition, combustion of these gasses is possible.

4. REACTIVE HAZARD MITIGATION

The oxidation reactions of sodium alanate by either oxygen or water vapor yield one of the three sodium oxides or sodium hydroxide, among other compounds. Sodium peroxide and superoxide are reported to be friction-sensitive precursors to highly energetic oxidation reactions [13, 21]. As such, these sodium oxides create the possibility that an atmospherically contaminated hydride bed could evolve hydrogen rapidly during an exothermic event, if initiated. Because the oxidation products are caustic, an apparently simple means to neutralize them, in-situ, would be to expose a partially oxidized sodium alanate bed to an acidic gas. Gases can readily be distributed throughout the bed to contact compromised material regardless of where it is located. Although any acidic gas could be used for this purpose (for example, SO_2, NO_x, CO), CO_2 has obvious advantages of availability, ease of handling, stability and lack of hazards at low atmospheric concentrations.

Carbon dioxide reacts with alkali-metal oxides to form carbonates. For example, the free energy changes (ΔG) of the reactions below (R11–13) are favorable to forming sodium carbonate.

$$Na_2O + CO_2 = Na_2CO_3 \qquad \Delta G = -274.60 \text{ kJ/mol} \qquad \text{(R11)}$$

$$Na_2O_2 + CO_2 = Na_2CO_3 + 1/2 \qquad \Delta G = -204.01 \text{ kJ/mol} \qquad \text{(R12)}$$

$$2\ NaO_2 + CO_2 = Na_2CO_3 + 3/2\ O_2 \qquad \Delta G = -216.19 \text{ kJ/mol} \qquad \text{(R13)}$$

The sodium carbonate resulting from a gaseous neutralization treatment is stable and non-hazardous, reducing the overall risk of handling and disposing of the compromised material. Although the reaction of the higher sodium oxides also yield oxygen during the proposed treatment, an excess of CO_2 will dilute the oxygen formed, and neutralize any additional oxidation products that might result from such secondary reactions.

4.1. IMPLICATIONS OF CO_2 TREATMENT FOR HYDRIDE-BASED SYSTEMS

Treatment of oxidized metal hydrides may be useful for minimizing the hazards associated with the handling compromised or end-of-life materials. In practice, a bed could be treated in whole or in part prior to handling or disassembly. The enthalpies of carbonate formation are significant, but manageable, especially if the CO_2 can be administered in a slow, controlled manner. For example consider the following postulated process (R14) which is the most thermodynamically aggressive of the reactions considered above:

$$Na_2O + CO_2\ (+ Al_2O_3) = Na_2CO_3\ (+ Al_2O_3) \qquad \text{(R14)}$$

$\Delta H = -319$ kJ/mol Na_2O $\Delta G = -275$ kJ/mol

For a system that stores 5kg of hydrogen, the quantity of heat produced during treatment would be on order of approximately $5x10^8$ J which is equivalent to burning 4 kg of H_2. If the process was conducted at a constant rate over 4 hours, the required heat removal would be modest 33 kW. If necessary, the CO_2 treatment protocol could be adjusted, e.g., using a variable CO_2 pressure, to reduce the oxidation rate to a level commensurate with heat dissipation. Temperature sensors in the hydride bed and container walls would provide the necessary control information. Although the reaction of sodium alanate and CO_2 is thermodynamically favorable, these compounds did not measurably react at room temperature, as confirmed by XRD measurements.

Volume and mass changes of the sorption material should also be considered when evaluating a CO_2 treatment process. In the case of the treatment of sodium hydroxide and disodium oxide, mass changes are significant but the volume changes are small (see Table 4 below). In the case of the volumetric expansion, care must be taken to avoid containment vessel failure during treatment. The volume changes shown in Table 4, fall within the void space limits indicating that the vessel will not be compromised during treatment.

Table 4 - Molar mass and volume changes due to the treatment of NaOH and Na_2O with CO_2.

Initial species	Treated Species	Products	Mass change	Volume change
$2NaAlH_4$	$2\ NaOH + Al_2O_3$	$2\ NaHCO_3 + Al_2O_3$	+150%	+21%
$2NaAlH_4$	$Na_2O + Al_2O_3$	$Na_2CO_3 + Al_2O_3$	+93%	-19%

4.2. EXPERIMENTAL INVESTIGATION OF CO_2 TREATMENT

The results from experiments examining sodium alanate samples that were exposed to moist air showed that compounds are formed by reaction between sodium alanate and carbon dioxide in the air (see Figure 6 and Figure 7). This suggested that one method to prevent the formation of reactive oxides such as Na_2O_2 and NaO_2 is to expose the sodium alanate to CO_2. These experiments focus on determining whether carbon dioxide can be used to stabilize a bed of sodium alanate and render it safe for disposal. The objective is to provide insight into how carbon dioxide reacts with sodium alanate and sodium alanate that has been partially oxidized.

To examine how a sodium alanate sample is transformed when exposed to carbon dioxide, two experiments were performed. The samples were first exposed to moist air for 4 and 24 hours. After exposure to moist air, they were exposed to CO_2 at 170 psia for 12 hours. The identities and rates of evolution of the products from these samples were then determined using the STMBMS instrument. The data from the experiment in which the sample was exposed to air for 24 hours and then CO_2 is shown in Figure 12A. Data from the experiments in which sodium alanate was exposed to moist air (Figure 12B) and

the mixture of H_2O and CO_2 generated from $NaHCO_3$ (Figure 12C) are also shown for comparison. Comparison of the sample exposed to moist air (Figure 12B) with the sample exposed to air/CO_2 (Figure 12A) shows the following significant differences:

1. The rate of hydrogen release from the sample exposed to CO_2 is about a factor of three below the sample exposed only to air. Note that the rate of release of hydrogen from the sample exposed to moist air is already a factor of ten below that of the baseline experiments (Figure 5).

2. The carbon oxides, CO and CO_2, evolve over the same temperature range in each experiment, but the rate of evolution of CO_2 is much higher in the sample exposed to CO_2 than it is in the sample exposed to moist air.

3. The CO_2 evolves from the sample over three distinct temperature ranges in the sample exposed to CO_2 compared to only one peak observed in the evolution of CO_2 from the sample exposed to moist air.

    a. The first peak occurs over a temperature range of 100 to 150°C. This corresponds to the temperature range over which $NaHCO_3$ decomposes to Na_2CO_3 plus H_2O and CO_2 (see Appendix B for $NaHCO_3$ decomposition behavior). Note that there is also an increase in the H_2O gas evolution rate over this same temperature range. This shows that $NaHCO_3$ was formed by exposing the sodium alanate sample to a high pressure of CO_2.

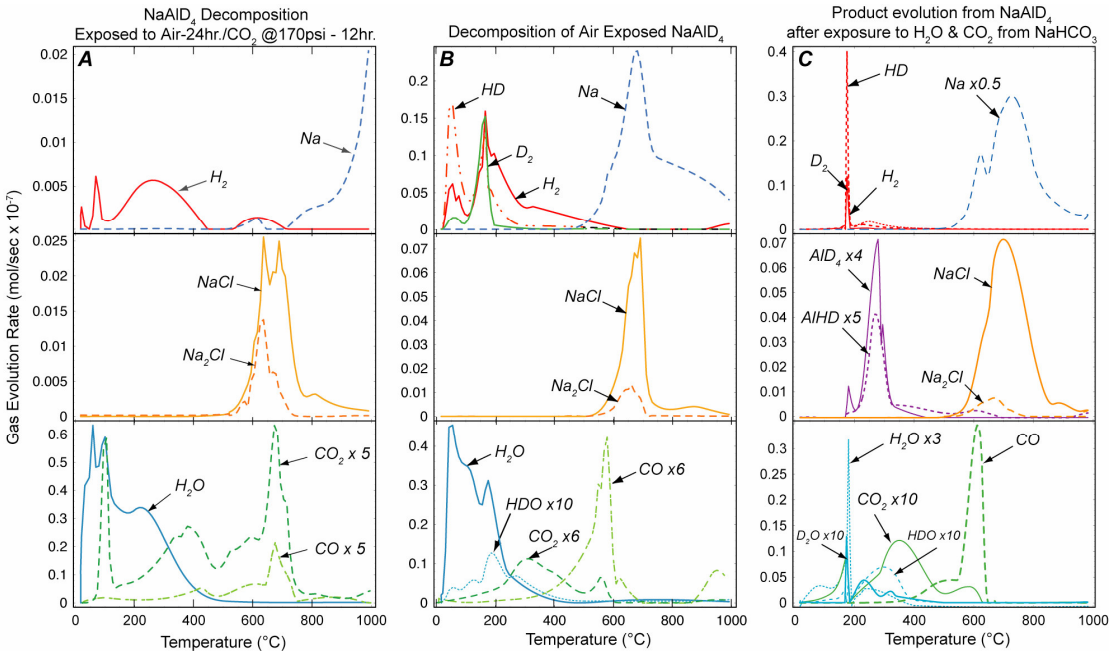


Figure 12 - Identities of products and their gas evolution rates from (A) $NaAlD_4$ sample exposed to air for 24 hours followed by CO_2 @170ps for 12 hours, (B) $NaAlD_4$ exposed to moist air, and (C) $NaAlD_4$ exposed to H_2O and CO_2 generated from $NaHCO_3$.

b. The decomposition of $NaHCO_3$ to form Na_2CO_3 suggests that the CO_2 and O_2 should be observed evolving from the sample between 800 and 1000°C due to the decomposition of Na_2CO_3 (see Appendix B for features of Na_2CO_3 decomposition). The data in Figure 12A shows that this is not the case.

c. The second peak is broad and evolves between 200 and 500°C. It is observed in all three experiments.

d. The third peak is the largest and it evolves between 600 and 700°C. This large CO_2 peak is only observed in the sample exposed to air and 170 psia of CO_2. In the other two experiments, the rate of evolution of CO_2 is low in this temperature range and the rate of evolution of CO is quite large. This suggests that at lower pressures of CO_2 some sort of carbonyl complex may be formed with the sodium and aluminum in the sample.

4. The amount of sodium that evolves from the sample exposed to air and 170 psia CO_2 is quite small compared to the other two experiments. A small amount of sodium evolves from the sample above 800°C. In the samples exposed to air and the mixture of H_2O and CO_2 from $NaHCO_3$, the rate of evolution of sodium is quite high after CO evolves from the sample. This is not the case for the evolution sodium after the CO_2 has been released in the sample exposed to air and 170 psia CO_2.

In summary, exposing sodium alanate to carbon dioxide results in the formation of compounds that more effectively bind sodium in the sample. In the baseline experiments, sodium evolves from the sample when the NaH starts to decompose at ~250°C. When the sodium alanate is exposed to low pressures of H_2O and CO_2 a compound is formed that decomposes between 550 and 650°C, eliminating CO and leaving sodium in the sample, which rapidly sublimes. When the sodium alanate is exposed to higher pressures of CO_2, the sodium is more effectively bound in the sample and little sodium vapor evolves from the sample. It might be expected that by exposing the sample to higher pressures of CO_2 sodium carbonate will be formed in the sample. However, sodium carbonate decomposes between 800 and 1000°C, releasing CO_2 and smaller amounts of sodium and O_2 in the process (Appendix B). Since this is not observed in the decomposition of the sodium alanate exposed to air and 170psia CO_2, it is likely that at higher pressures the carbon dioxide forms some other stable compound that may also contain aluminum and/or titanium.

Measurements using X-ray diffraction verified the formation of some form of carbon containing salt. The structure appeared very similar to sodium carbonate (Na_2CO_3) although it is likely a modified form of sodium carbonate since the thermal decomposition behavior of the treated sodium alanate sample varies from that of pure sodium bicarbonate/carbonate (see Appendix B). Regardless, the presence of the carbon-containing salt indicates that the treatment process converts the sodium to a more stable form.

This CO_2 treatment technology could be applicable to various oxidized alkali-based metal hydrides including potassium and lithium compounds. This chemical process could be used to enable the safe handling and disposal of oxidized metal hydrides. Optimized

treatment process conditions including pressure, temperature, and reaction time have not yet been defined, as further technology development is required. Significant testing is required to apply this technology to large scale systems since the treatment reaction could be diffusion limited thus reducing its applicability. Additionally, direct measurement of exerted pressure during treatment must be undertaken prior to implementing CO_2 treatment as a safety protocol.

4.3. RECOMMENDATIONS FOR HANDLING OF SODIUM ALANATES AND SIMILAR MATERIALS

Several controls and practices are recommended to minimize the hazards associated with handling contaminated alkali-based metal hydrides, given the observations of simultaneous generation of oxygen and hydrogen during low-temperature water exposure and rapid evolution of hydrogen from partially-oxidized alanate material exposed to oxygen and water vapor reported here.

- *Monitor and ensure use of high-purity hydrogen.* At this time the long-term cumulative effect of oxygen and water exposure is unknown. Our results have shown a significant decomposition rate enhancement from very small oxygen and water exposure levels. It is important for the user/operator of these systems to ensure that the contamination exposure is minimized.

- *Understand oxidation hazards.* Recognize that exposure of sodium alanate to water below 70°C may generate combustible mixtures of H_2 and O_2.

- *Perform positive pressure operation.* It is recommended that the system designers ensure that a positive pressure will always be maintained during the operation of reactive metal hydride systems. This eliminates the possibility of contamination in the case of a minor system leak.

- *Use of non-destructive pressure relief devices (PRDs).* It is imperative that self-closing PRDs are utilized to avoid contamination following a system over-pressurization event.

- *Removal of hydrogen and water from oxidized materials.* If oxidized materials must be handled, the user should attempt to remove as much reversible hydrogen and added water content as possible. This can be accomplished using heating and purging methods depending on chemistries involved.

- *Availability of CO_2 for in-situ treatment.* Prior to handling potentially oxidized material, it may be prudent to treat the bed with 1-10 atm of CO_2 at room temperature for several hours. Although the details of this process need to be determined, our testing demonstrated effective stabilization of the alkali metal containing species within the oxidized system.

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5. CONCLUSIONS AND FUTURE WORK

These studies have shown that the exposure of sodium alanates to even low levels of oxidants results in a significant destabilization of the hydrided material. This effect has been observed for both oxygen and water vapor contamination and a variety of exposure conditions including low concentrations of oxidants (<100 ppm). Fully oxidizing the materials seems to result in a relatively benign substance while partial oxidation results in a less stable hydrogen-containing structure. The results of in-situ measurements of sodium alanate reaction with mixtures of H_2O and CO_2 show that below 70°C both H_2 and O_2 may be formed at comparable rates. Above 70°C that oxygen apparently reacts with the sodium, aluminum and titanium, forming more stable oxides.

The destabilization caused by the oxidation of the complex metal hydrides can be partially mitigated with acidic gas treatment. Carbon dioxide readily reacts and alkali-metal oxides to form carbonates. The resulting carbonates are stable and non-hazardous compared to the initial oxide species, reducing the overall risk of handling and disposing of the compromised material. Although the higher oxides of sodium produce oxygen during the above processes, an excess of CO_2 can further neutralize any additional oxidation products that might result from such secondary reactions. This CO_2 treatment technology could be applicable to various oxidized alkali-based metal hydrides including potassium and lithium compounds. This chemical process could be used to enable the safe handling and disposal of oxidized metal hydrides.

This work and future efforts are required to understand the reaction processes of reactive hydrogen storage materials with contaminants, especially air and water vapor. The quantification of these safety properties enables the implementation of engineering controls and the definition of appropriate protocols to provide safe and effective hydrogen storage solutions for a variety of commercial and consumer markets. Future work will focus on identifying the elemental mechanisms of the contamination reactions and extend these methods to newly developed hydrogen storage materials.

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APPENDIX A – LIST OF EXPERIMENTS

Table 5 - List of experiments.

Exp	Type*	Material	Mass (mg)	Description	Fig	DB #
1	Bas	$NaAlH_4$	10.6	Baseline – decomposition of sodium alanate. HR: 2.5°C/min	Figure 5	SA004
2	Bas	$NaAlD_4$	9.1	Baseline – decomposition of deuterium labeled sodium alanate. HR: 2.5°C/min	Figure 5	SA053
3	OxAE	NaAlH4	11.0	$NaAlH_4$ sample exposed to moist laboratory air overnight.	Figure 6	SA007
3	OxAE	$NaAlD_4$ & air	20.9	$NaAlD_4$ sample exposed to moist air	Figure 6	SA008
4	OxAE	$NaAlD_4$, dry Air	10.8	$NaAlD_4$ sample exposed to dry air for 4 hours. (< 5 ppm H_2O)	Figure 7	SA047
5	OxAE	$NaAlD_4$, 300 ppm O_2		$NaAlD_4$ sample exposed to 300 ppm O_2, 17 ppm H_2O in nitrogen for *** hours.	Figure 7	SA048
6	OxAE	$NaAlD_4$, 56 ppm O_2	14.6	$NaAlD_4$ sample exposed 56 ppm O_2, 11 ppm H_2O for *** hours.	Figure 7	SA049
7	OxAE	$NaAlD_4$, dry Air		$NaAlD_4$ sample exposed to dry air. Heated at slower rate: 0.5°C/min. (Not summarized)	NA	SA054
8	OxTr	$NaAlD_4$, Air, CO_2	25.3	$NaAlD_4$ sample exposed to moist air for 24 hours, followed by CO_2 @ 170 psi for 12 hours	Figure 12	SA037
9	OxTr	NaAlD4, Air, CO_2	25.8	NaAlD4 sample exposed to moist air for 4 hours, followed by $_{CO2}$ @???	NA	SA034
10	Kin	$NaAlD_4$, $NaHCO_3$	9.5, 37.0	$NaAlD_4$ sample exposed to H_2O & CO_2 generated from $NaHCO_3$. Heating: 20 to 300°C @2.5°C/min.	Figure 10	SA013
11	Kin	$NaAlD_4$ from SA013	?	Decomposition of $NaAlD_4$ sample that was exposed to H_2O and CO_2 in SA013.	Figure 11	SA014
12	Kin	$NaAlD_4$, $NaHCO_3$	13.7, 35.7	$NaAlD_4$ sample exposed to H_2O & CO_2 generated from $NaHCO_3$. Heating: 5 cycles	NA	SA017
13	Kin	$NaAlD_4$ from SA017		Decomposition of $NaAlD_4$ sample that was exposed to H_2O and CO_2 in SA017	Figure 12	SA018
14	Kin	$NaAlD_4$, $NaHCO_3$	9.9, 34.9	$NaAlD_4$ sample exposed to H_2O & CO_2 generated from $NaHCO_3$. Heating: 5 cycles	NA	SA044
15	Kin	$NaAlD_4$ from SA044	?	Decomposition of $NaAlD_4$ sample that was exposed to H_2O and CO_2 in SA044	NA	SA045
16	Salt	$NaHCO_3$	10.21	$NaHCO_3$ decomposition. 20 to 1000°C. Has both $NaHCO_3$ and Na_2CO_3 decomposition.	Appdx B	SA011
17	Salt	$NaHCO_3$	36.5	$NaHCO_3$ decomp. 20 to 130°C. Multiple cycles. 10µm orifice.	Appdx B	SA020
18	Salt	Na_2CO_3	9.6	Na_2CO_3 decomposition. 20 to 1000°C.	Appdx B	SA012
19	Salt	NaOH	~18	NaOH decomposition. 20 to 1000°C.	Appdx B	SA022
20	Salt	Na_2O_2	12.2	Sodium peroxide decomposition. 20 to 1000°C	Appdx B	SA024

* Bas – baseline experiment; OxAE – oxidation with air exposure; OxTr – oxidation and treatment (typically CO_2).

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APPENDIX B – SALT DECOMPOSITION DATA

The qualitative decomposition characteristics of several sodium salts are presented in this appendix. The data presented for each salt includes: (1) the thermogravimetric weight loss data, and (2) the temporal behaviors of the ion signals that represent the evolution of various compounds from the samples as they are heated and decompose. An approximate estimate of the relative amounts of the various products that evolve may be made be considering the mass loss and the relative intensities of the ion signals representing the evolving compounds in the temperature region of interest in each experiment.

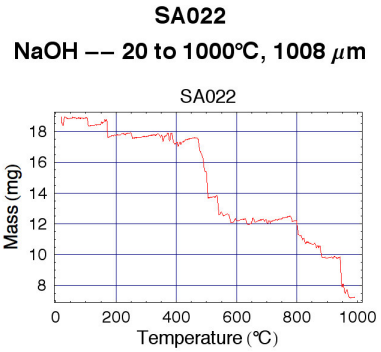
SODIUM HYDROXIDE (NAOH)

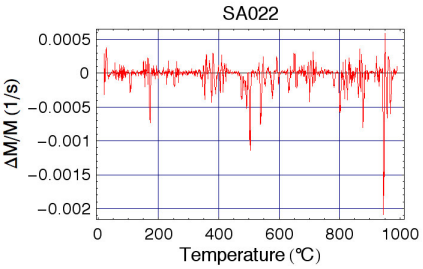
The thermogravimetric data shows that the sample decomposes in two primary temperature regions: (1) 400 to 600°C and (2) above 800°C. The data in this experiment is somewhat noisy due to improper positioning of the reaction cell within the furnace. The following products are observed in the decomposition of NaOH: H_2O (m/z=18), NaOH (40), Na_2OH (63), O_2 (32 & 16), and Na (23).

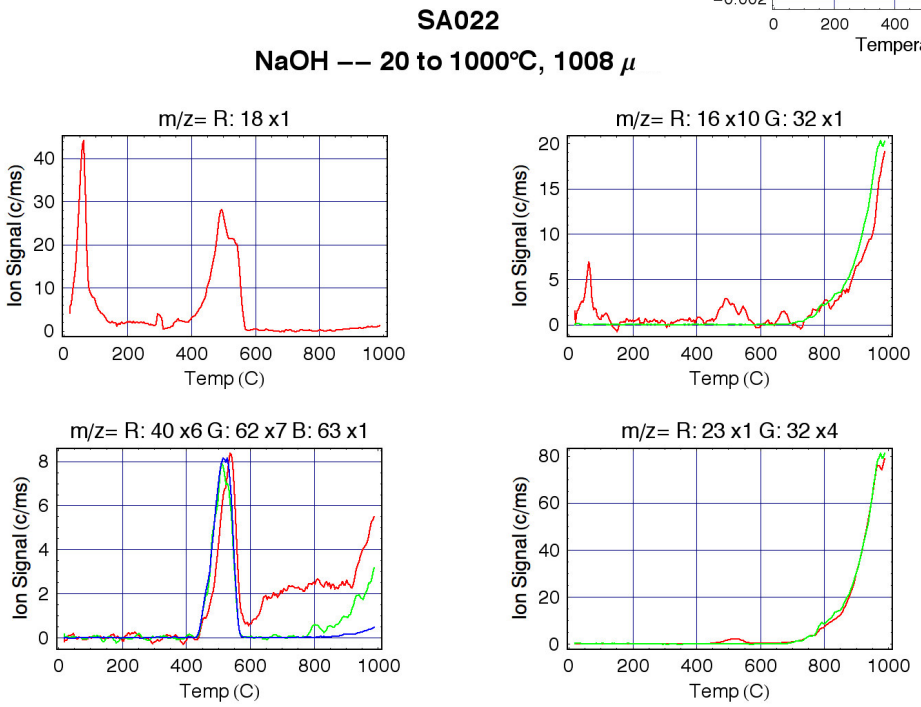
The decomposition reactions are summarized in the table.

Table 6 - Sodium hydroxide decomposition.

Reaction	Temp (°C)
$NaOH \cdot xH_2O(s) \rightarrow NaOH(s) + H_2O(g)$	20 – 100
$2\ NaOH(s) \rightarrow Na_2O(s) + H_2O(g) + Na_xO_y(int)$	400 – 570
$NaOH(s) \rightarrow NaOH(g) + Na_2OH(g)$	400 – 570
$Na_xO_y(int) \rightarrow x\ Na(g) + y/2\ O_2(g)$	750 – 1000







SODIUM PEROXIDE (NA_2O_2)

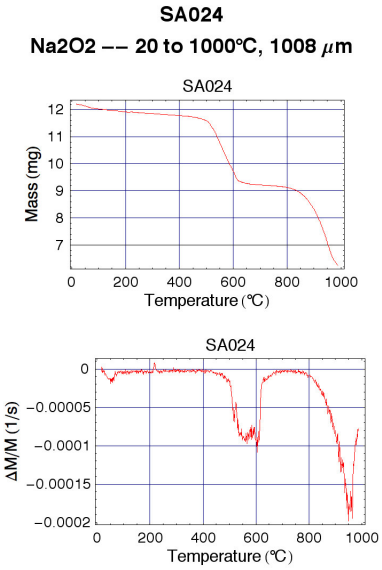
The thermogravimetric data shows that the sample decomposes in three primary temperature regions: (1) a gradual mass loss from 100 to 500°C, (2) 500 to 600°C, and (3) above 850°C.

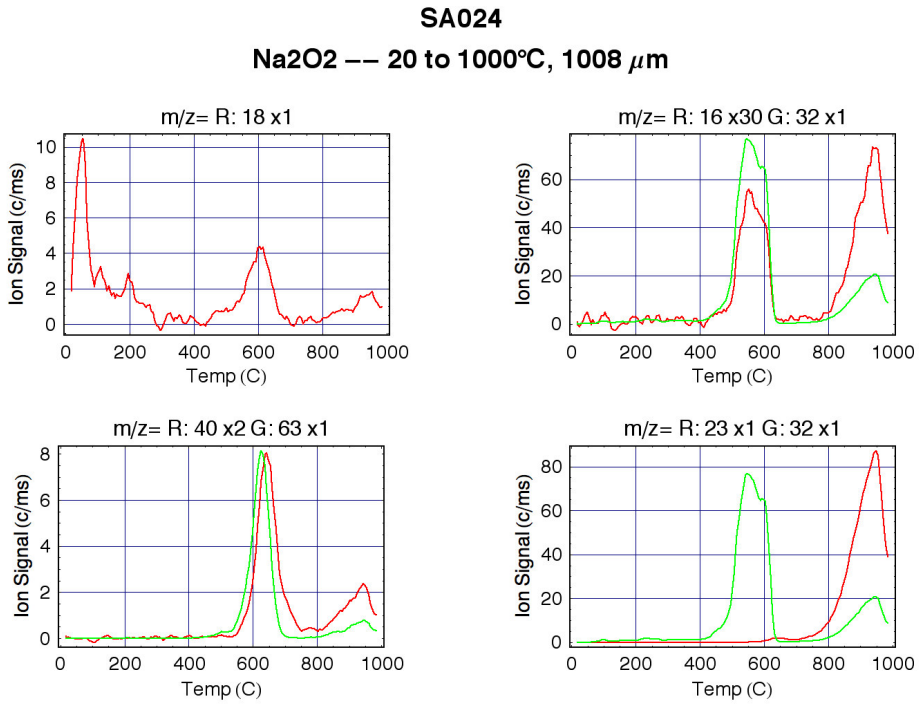
The following products are observed in the decomposition of Na_2O_2: H_2O (m/z=18), NaOH (40), Na_2OH (63), O_2 (32 & 16), and Na (23).

The decomposition reactions are summarized in the table.

Table 7 - Sodium peroxide decomposition.

Reaction	Temp (°C)
$Na_2O_2 \cdot xH_2O \rightarrow Na_2O_2(s) + x\ H_2O(g)$	20 – 100
$2\ Na_2O_2 \rightarrow 2\ Na_2O + O_2(g)$	400 – 600
$2\ NaOH(s) \rightarrow Na_2O(s) + H_2O(g) + Na_xO_y(int)$	550 – 750
$Na_xO_y(int) \rightarrow x\ Na(g) + y/2\ O_2(g)$	800 – 950





SODIUM CARBONATE (NA_2CO_3)

The thermogravimetric data shows that the sample decomposes in one primary temperature region: a gradual mass loss starts at ~800°C and then increases rapidly at ~900°C. The rate of reaction begins to slow when the sample reaches ~950°C. The sample also has adsorbed water that evolves between 20 and 100°C.

The following products are observed in the decomposition of Na_2CO_3: H_2O (m/z=18), CO_2 (44), O_2 (32 & 16), and Na (23).

The decomposition reactions are summarized in the table.

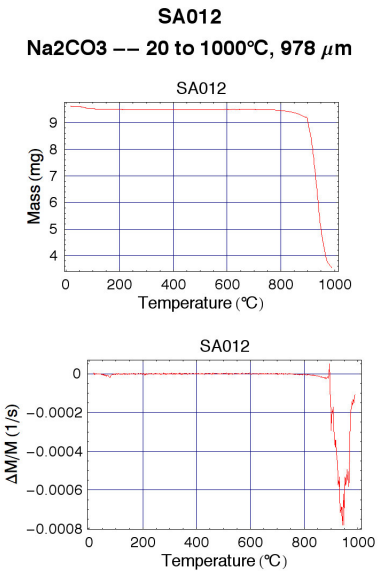
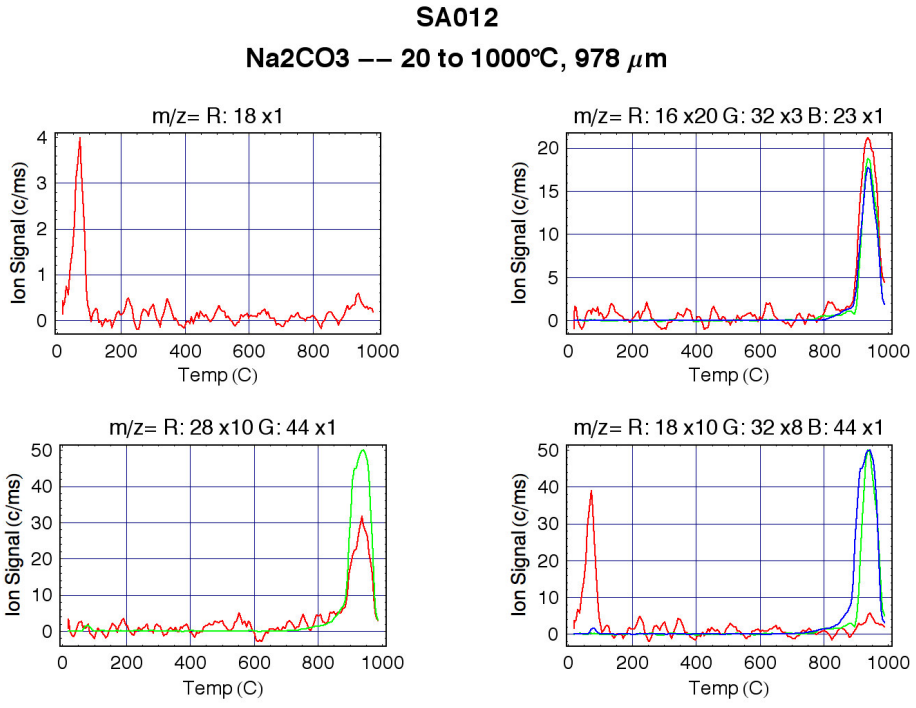


Table 8 - Sodium carbonate decomposition.

Reaction	Temp (°C)
$Na_2CO_3 \cdot xH_2O(s) \rightarrow Na_2CO_3(s) + x\ H_2O$	20 – 100
$Na_2CO_3(s) \rightarrow$ Na-O-Na(int) + $CO_2(g)$	850 – 980
Na-O-Na (int) → 2 Na(g) + 1/2 $O_2(g)$	900 – 980
Na-O-Na (int) → $Na_2O(s)$	900 – 980



SODIUM BICARBONATE ($NAHCO_3$)

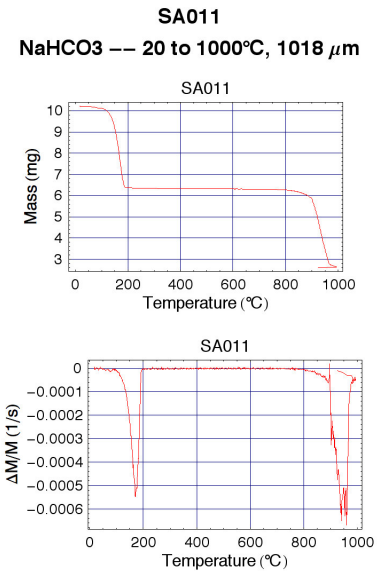
The thermogravimetric data shows that the sample decomposes in two primary temperature regions: (1) One occurs between 100 and 200°C, and (2) the second starts with a gradual mass loss starts at ~800°C and then increases rapidly at ~900°C. The rate of reaction begins to slow when the sample reaches ~950°C. The sample also has adsorbed water that evolves between 20 and 100°C.

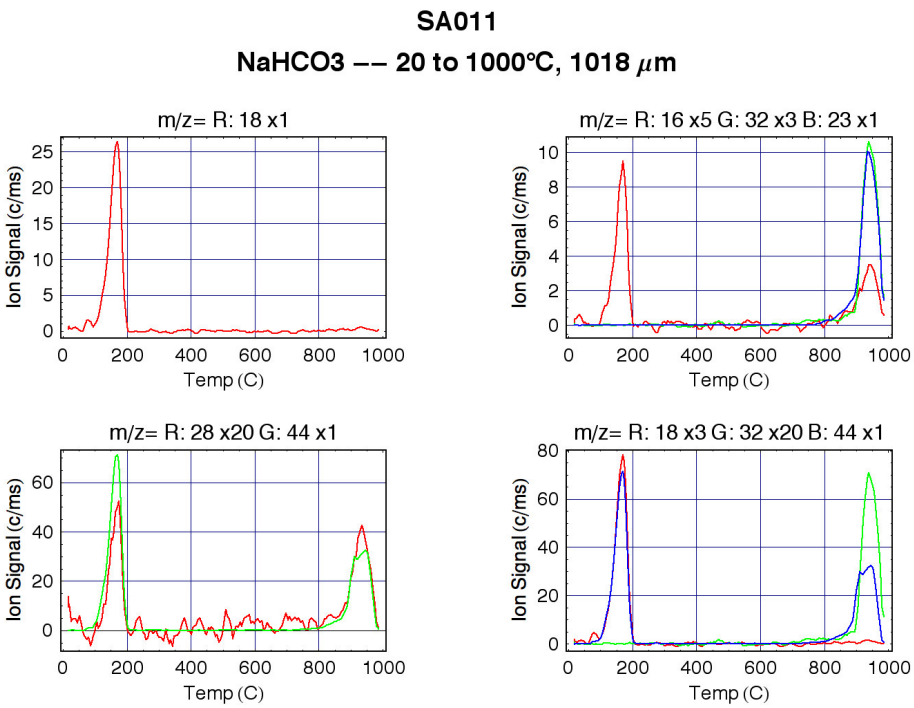
The following products are observed in the decomposition of Na_2CO_3: H_2O (m/z=18), CO_2 (44), O_2 (32 & 16), and Na (23).

The decomposition reactions are summarized in the table.

Table 9 - Sodium bicarbonate decomposition.

Reaction	Temp (°C)
$NaHCO_3 \bullet xH_2O(s) \rightarrow NaHCO_3(s) + x\ H_2O$	20 – 100
$2\ NaHCO_3(s) \rightarrow Na_2CO_3(s) + H_2O(g) + CO_2(g)$	90 – 180
$Na_2CO_3(s) \rightarrow Na\text{-}O\text{-}Na(int) + CO_2(g)$	850 –980
$Na\text{-}O\text{-}Na(int) \rightarrow 2\ Na(g) + 1/2\ O_2(g)$	900 – 980
$Na\text{-}O\text{-}Na(int) \rightarrow Na_2O(s)$	900 – 980





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