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Contamination of Complex Metal Hydrides with O_2, H_2O and CO_2

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Sandia
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A Department of Energy
National Laboratory

Sandia National Labs, California


Aerial View of Sandia/California in Livermore, Calif.

Sandia’s origins can be traced to the Los Alamos National Laboratory Z Division, which was created in 1945 for ordnance design, testing, and assembly. As the division grew, it was renamed “Sandia Laboratory” in 1948, and then officially separated from Los Alamos in 1949. Sandia’s California laboratory was established in 1956. Sandia National Laboratories is now managed for the DOE National Nuclear Security Administration by Lockheed Martin. Sandia conducts R&D work to meet national needs in five mission areas:

- energy and infrastructure assurance
- homeland security
- defense systems and assessments
- nuclear weapons, and
- nonproliferation.

Hydrogen storage science and technology has been a major effort at of the lab since its inception.

In 2003, GM and Sandia partnered to address challenges associated with automotive hydrogen storage

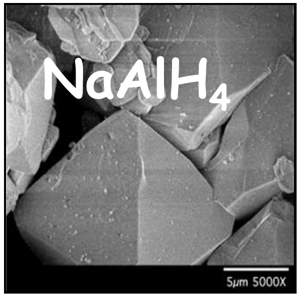
- Effort funded by General Motors
  Scott Jorgensen and Jim Spearot
- 5 year, $10M program, started in 2003
- Overall program goal to develop and demonstrate an automotive scale hydrogen storage system using the complex metal hydrides
- *This poster presents the effort undertaken to understand the hazards associated with the producing, handling and storing large quantities of sodium alanates*

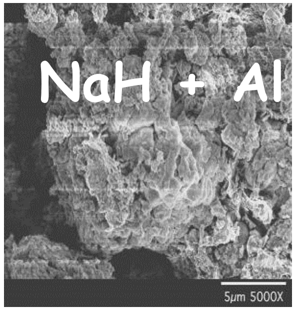
$NaAlH_4 \leftrightarrow 1/3Na_3AlH_6 + 2/3Al + H_2$

$1/3Na_3AlH_6 + 2/3Al + H_2 \leftrightarrow NaH + Al + 3/2H_2$

Sodium alanates are "typical" high energy density complex hydrides

- Finely divided solid-phase powders
- Significant morphological changes experienced
- High surface area - highly reactive
- Contamination sensitive
  - air
  - water



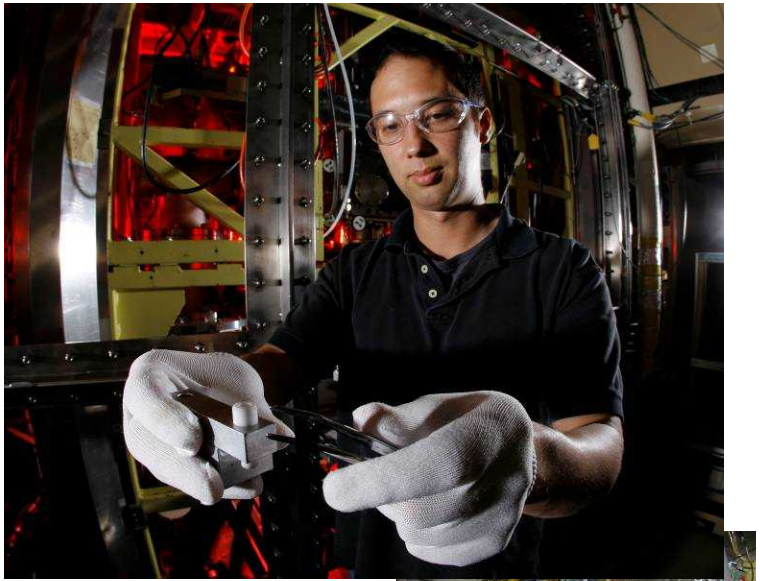


Total Theoretical Capacity = 5.6 wt% hydrogen

$$NaAlH_4 \Rightarrow 1/3\,Na_3AlH_6 + 2/3\,Al + H_2 \Rightarrow NaH + Al + 3/2\,H_2$$

3.7 wt.% - 37 kJ/molH_2 *1.9 wt.% - 47 kJ/molH_2*

Experimental apparatus: The STMBMS



- Simultaneous Thermogravimetric Modulated Beam Mass Spectrometer
- This tool was originally developed for researching the chemical kinetics and contamination properties of energetic materials
- Built in the 1980s based on designs of physical chemistry measurement instruments [1]
- Closely resembles the mass spectrometry instruments that are coupled with Knudsen effusion cells and used to measure thermodynamic properties of molecules (bond energies, etc.) using Second Law methods [2]

[1] Behrens, R., Jr., *New simultaneous thermogravimetry and modulated molecular beam mass spectrometry apparatus for quantitative thermal decomposition studies.* Review of Scientific Instruments, 1987. **58**(3): p. 451-461

[2] Lee, Y.T. et al, Molecular Beam Reactive Scattering Apparatus with Electron Bombardment Detector. Review of Scientific Instruments, 1969. 40(11): P. 1402 - 1408

The STMBMS is an appropriate tool to help quantify complex reaction processes

This is an instrument for used for measuring thermodynamic properties of molecules and studying reaction kinetics of complex systems

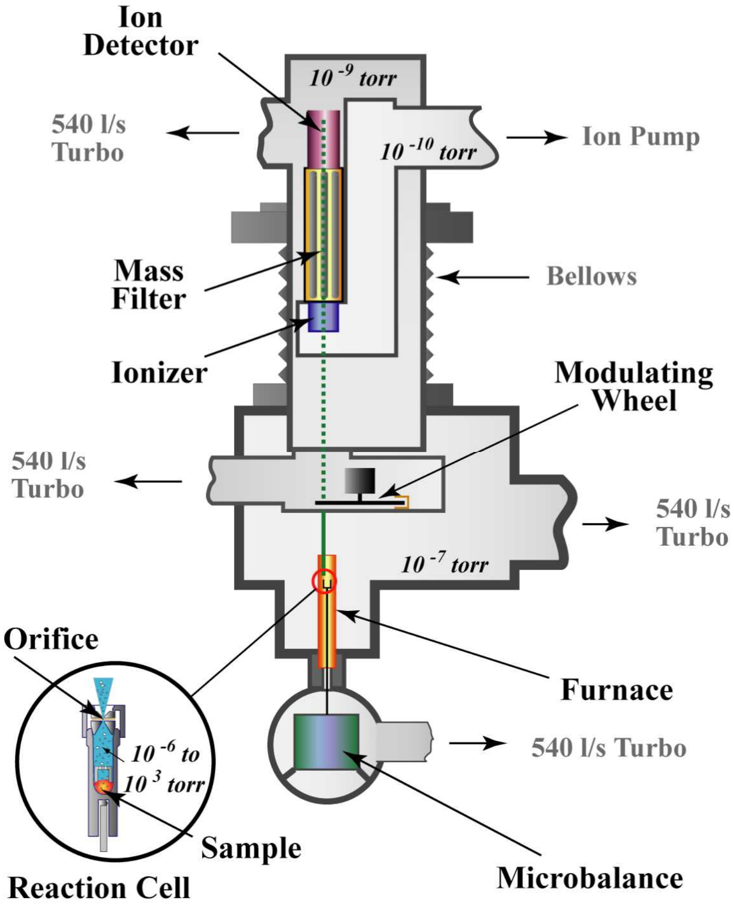
Components:

- Microbalance used to detect change in sample mass
- Tube furnace with sample for molecular beam generation
- High accuracy Ionizer/mass spectra measurement

Data from each of these components is correlated and analyzed to determine reaction processes and kinetics

For metal hydride experiments:

- Hydride decomposition operation: The instrument is used to heat oxidized, un-oxidized, and CO_2 treated sodium alanate samples
- Oxidation study operation: materials that evolve oxygen or water are placed in the reaction cell in combination with the hydride materials of interest



Significant understanding has been accumulated by measuring sodium alanates with the STMBMS

- Material – Fully cycled hydrided/deuterided sodium alanates
- Over 20 individual measurements

Four types of experiments:

- Baseline hydride decompositions
- Pre-oxidized samples
- In-situ oxidation
- Pre-oxidized and treated samples

Exp	*Type**	*Material*	*Mass (mg)*	*Description*	*Fig*	*DB #*	*Notes*
1	Bas	$NaAlH_4$	10.6	Baseline – decomposition of sodium alanate. HR: 2.5°C/min	6	SA004	
2	Bas	$NaAlD_4$	9.1	Baseline – decomposition of deuterium labeled sodium alanate. HR: 2.5°C/min	7	SA053	
3	OxAE	NaAlH4	11.0	$NaAlH_4$ sample exposed to moist laboratory air overnight.		SA007	
3	OxAE	$NaAlD_4$ & air	20.9	$NaAlD_4$ sample exposed to moist air		SA008	
4	OxAE	$NaAlD_4$, dry Air	10.8	$NaAlD_4$ sample exposed to dry air for 4 hours. (< 5ppm H_2O)		SA047	
5	OxAE	$NaAlD_4$, 300ppm O_2		$NaAlD_4$ sample exposed to 300 ppm O_2, 17ppm H_2O in nitrogen for *** hours.		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.		SA049	
7	OxAE	$NaAlD_4$, dry Air		$NaAlD_4$ sample exposed to dry air. Heated at slower rate: 0.5°C/min. (Not summarized)		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		SA037	
9	OxTr	NaAlD4, Air, CO2	25.8	NaAlD4 sample exposed to moist air for 4 hours, followed by CO2 @???		SA034	Not sure about conditions for CO2 exposure.
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.		SA013	
11	Kin	$NaAlD_4$ from SA013	?	Decomposition of $NaAlD_4$ sample that was exposed to H_2O and CO_2 in SA013.		SA014	Main product released is CO.
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		SA017	
13	Kin	$NaAlD_4$ from SA017		Decomposition of $NaAlD_4$ sample that was exposed to H_2O and CO_2 in SA017		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		SA044	Repeat of SA017. Not analyzed.
15	Kin	$NaAlD_4$ from SA044	?	Decomposition of $NaAlD_4$ sample that was exposed to H_2O and CO_2 in SA044		SA045	Not analyzed.
16	Salt	$NaHCO_3$	10.21	$NaHCO_3$ decomposition. 20 to 1000°C. Has both $NaHCO_3$ and $Na2CO_3$ decomposition.		SA011	Has REMKIN model fit to the $NaHCO_3$ and Na_2CO_3 reactions.
17	Salt	$NaHCO_3$	36.5	$NaHCO_3$ decomp. 20 to 130°C. Multiple cycles. 10µm orifice.		SA020	
18	Salt	Na_2CO_3	9.6	Na2CO3 decomposition. 20 to 1000°C.		SA012	No summary sheet. Mass spec data OK.
19	Salt	NaOH	~18	NaOH decomposition. 20 to 1000°C.		SA022	No summary. Plots of ion signal from decomposition products done.
20	Salt	Na_2O_2	12.2	Sodium peroxide decomposition. 20 to 1000°C		SA024	No summary. Weight loss noisy.

Oxidation of sodium alanates significantly alters hydrogen evolution behavior

Gas evolution rate of $NaAlD_4$ and mass spectra as a function of temperature

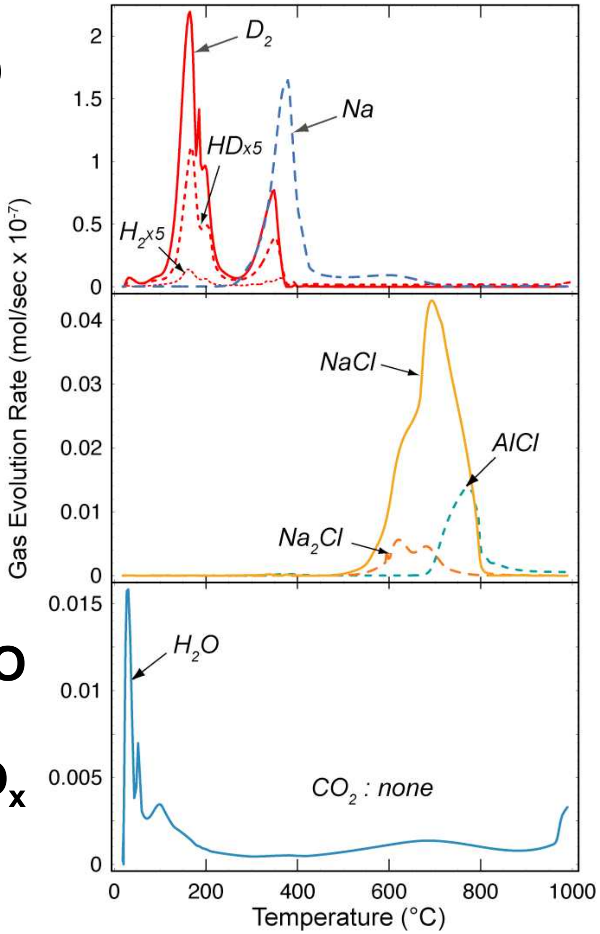
No oxidation **Partial oxidation** **Full oxidation**

H/D Na

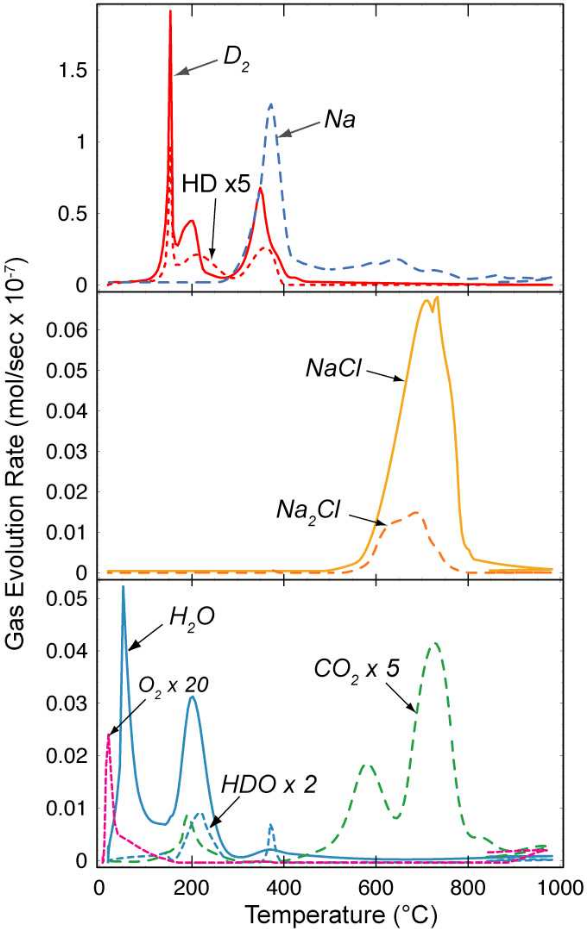
Salts

H_2O O_2 CO_x

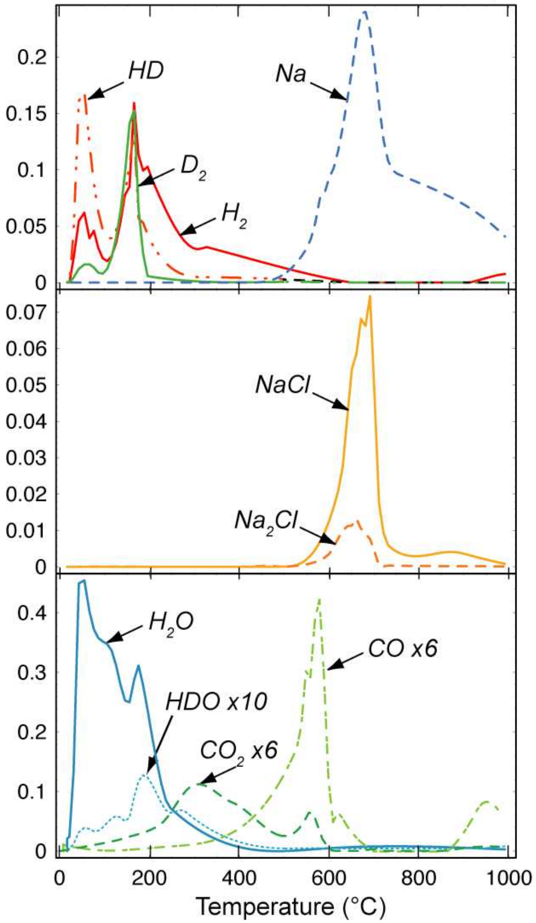
$NaAlD_4$ Decomposition



$NaAlD_4$ Exposed to Dry Air



Decomposition of Air Exposed $NaAlD_4$

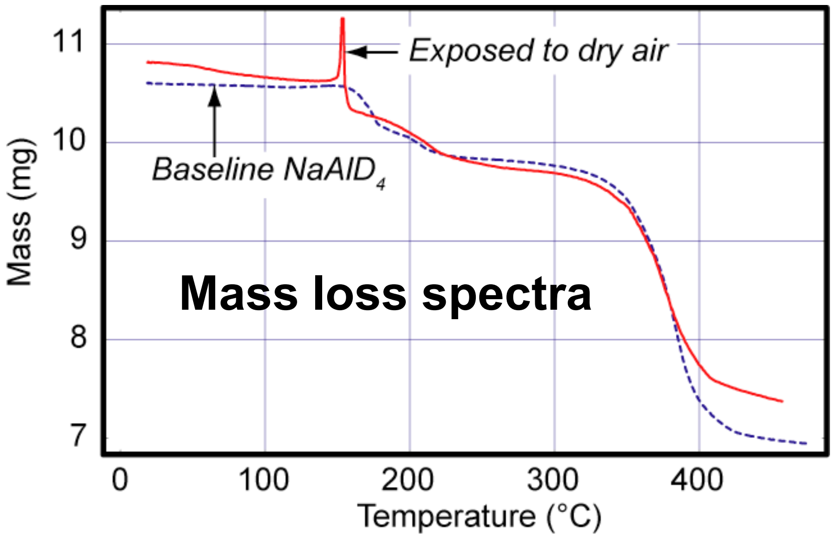


Partial oxidation causes sodium alanates to rapidly decompose

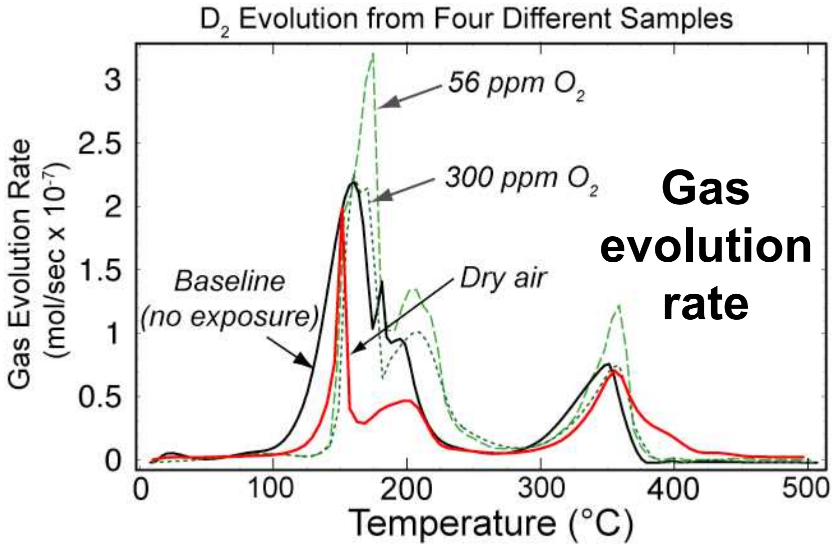
- Samples partially oxidized
  - ✓dry air (<6ppm O2/H2O)
  - ✓56ppm O2
  - ✓300ppm O2
- Subsequently analyzed in STMBMS

Results:

- Decomposition of remaining H2 is very rapid, actually forcing the microbalance downward
- Even very low levels of oxidation causes destabilization



Mass loss spectra



Gas evolution rate

In-situ methods were utilized to fully characterize oxidation processes

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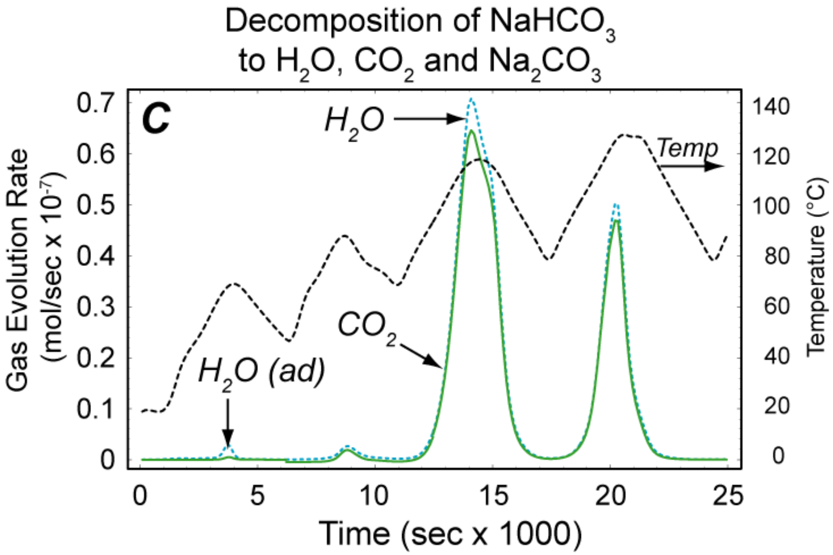
Materials that evolve water or oxygen are placed in the reaction cell in combination with the hydride materials of interest

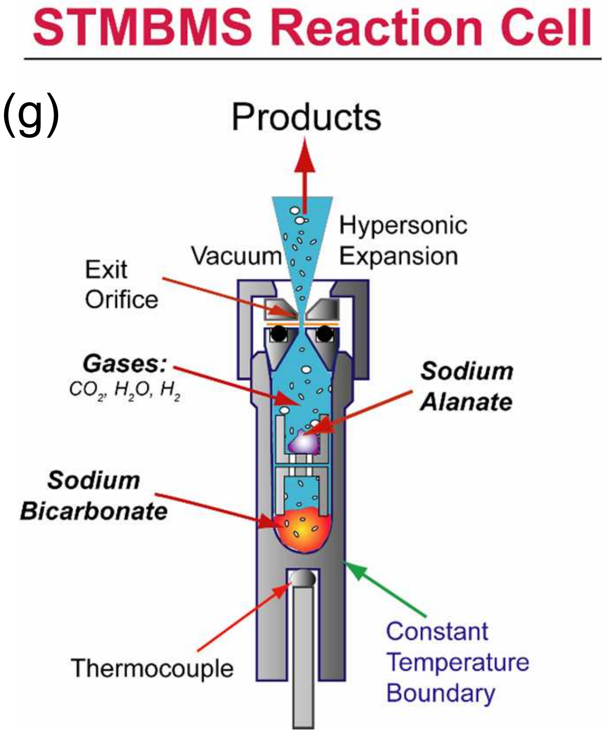
Sodium bicarbonate

90 – 180 °C

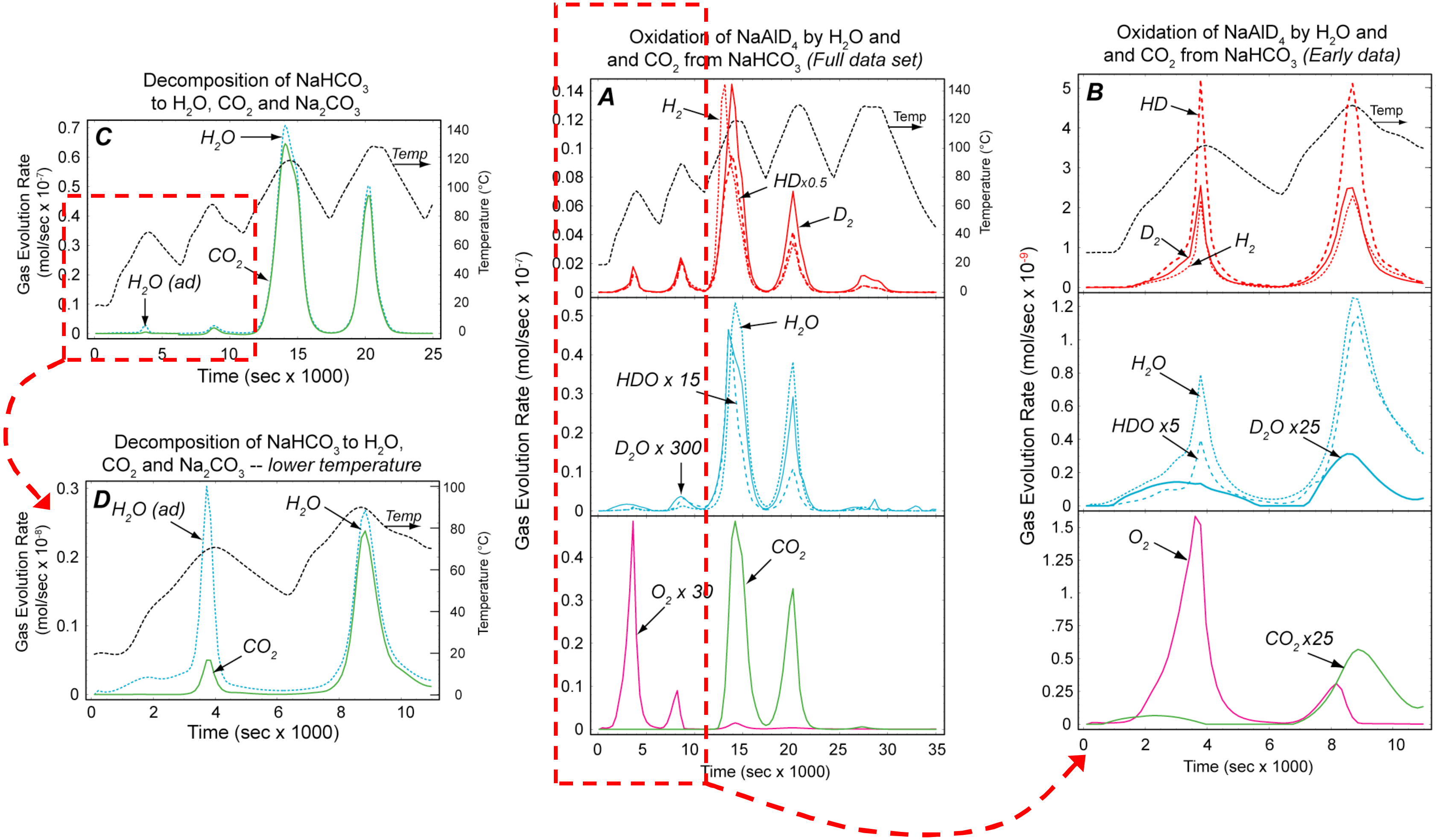
$NaHCO_3(s) \rightarrow Na_2CO_3(s) + H_2O(g) + CO_2(g)$



Decomposition of $NaHCO_3$ to H_2O, CO_2 and Na_2CO_3



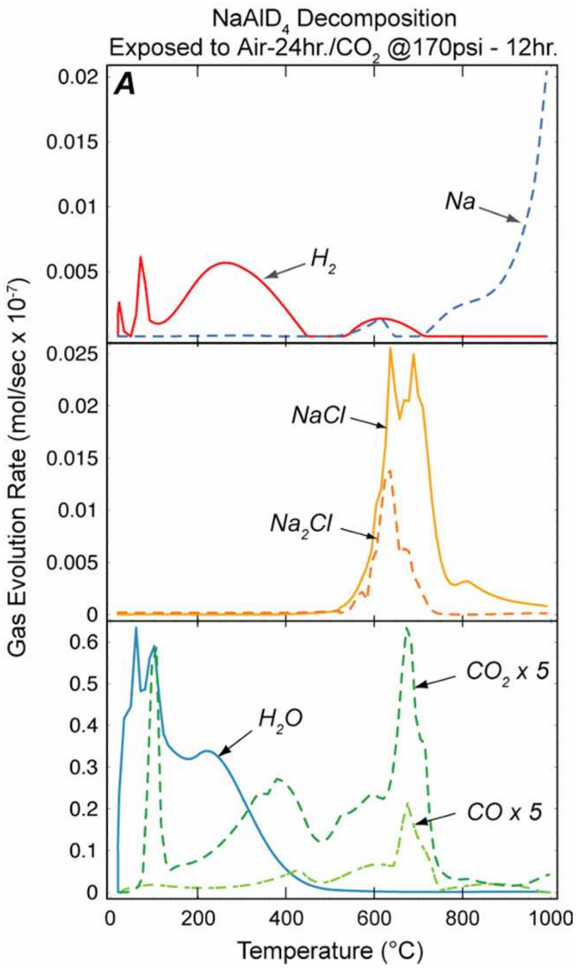
Exposure to H_2O at temperatures <100 °C can result in the production of H_2 and O_2



Exposure to H_2O generates H_2 and O_2 simultaneously in potentially hazardous concentrations

CO_2 hazard mitigation studies

- Carbon dioxide readily reacts with alkali-metal oxides/hydroxides to form carbonates. For example,
  - $Na_2O + CO_2 = Na_2CO_3$
    $\Delta G = -65.63$ kcal/mol
  - $Na_2O_2 + CO_2 = Na_2CO_3 + 1/2\ O_2$
    $\Delta G = -48.76$ kcal/mol
  - $2\ NaO_2 + CO_2 = Na_2CO_3 + 3/2\ O_2$
    $\Delta G = -51.67$ kcal/mol
- STMBMS measurements performed and the formation of carbon-containing salt verified with XRD
- The resulting carbonates are stable and non-hazardous compared to the initial oxide species
- Could reduce the overall risk of handling and disposing of the compromised material



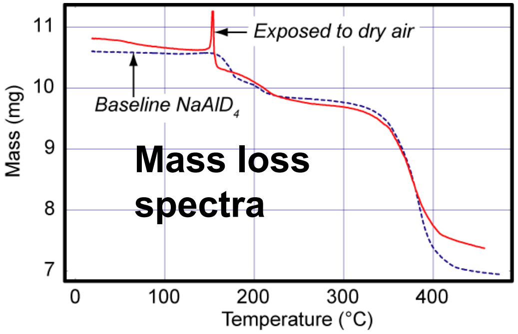
Summary: Two-fold hazard results from the oxidation of sodium alanates

Chemical destabilization

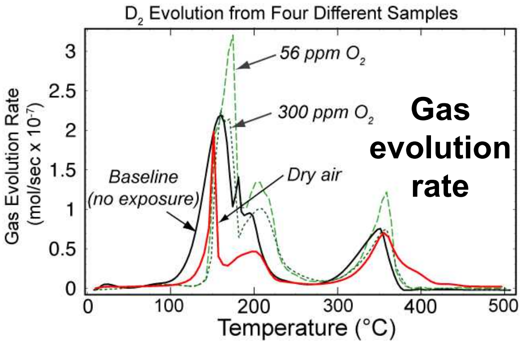
Decomposition of remaining H2 is very rapid, actually forcing the microbalance downward

Partially oxidized samples:

- dry air (<6ppm O2/H2O)
- 56ppm O2
- 300ppm O2



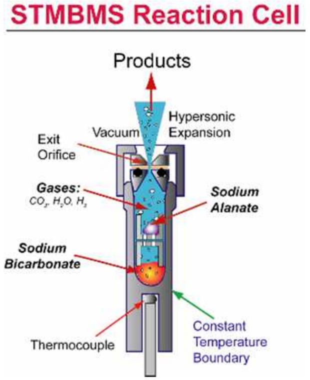
Even very low levels of oxidation causes destabilization

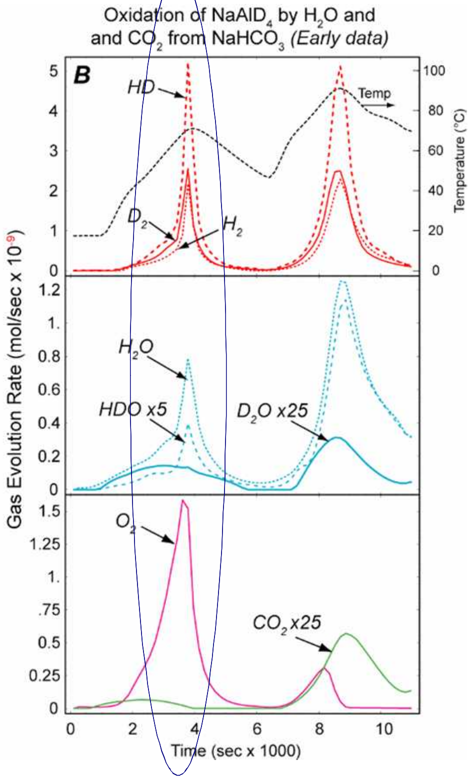


Generation of H_2/O_2 mixtures

Results: Exposure to H_2O at low temperature generates H_2 and O_2 simultaneously in potentially hazardous concentrations

Sodium alanates exposed to H_2O at ~70 °C





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