Development of Regenerable, High-Capacity Boron Nitrogen Hydrides For Hydrogen Storage

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Intematix

Overview

Timeline

- Project start – 3/15/2005
- Project end – 11/30/2008
- Percent complete - 10

Budget

- Total project funding
  - DOE share - $ 1.6M
  - Contractor share - $ 0.4M
- Funding received in FY04 - 0
- Funding for FY05 - $ 0.2M
- Funding for FY06 - $ 0.15M

Barriers

- A – Storage system and fuel cost
- B – Gravimetric/volumetric hydrogen storage density
- R – Cost effective regeneration processes

Partners

- State Scientific Research Center of Russian Federation (GNIIChTEOS)
- Intematix Corporation

Objectives

Overall – Develop a boron-nitrogen hydride-based hydrogen storage system to meet U.S. DOE's 2015 hydrogen density and cost targets.

Hydrogen Release – Develop an efficient on-board heating system to extract most of the hydrogen from ammonia-borane (NH_3BH_3).

Regeneration – Develop an off-board, energy efficient, integrated process for regenerating spent materials (~ BN) utilizing commodity hydrogen and chemicals.

Technical Barriers Addressed

- A – Storage system and fuel cost (2015 targets: System cost $67/ kg H_2 ; Fuel $2 to 3/GGE (~kg H_2)
- B – Gravimetric/volumetric hydrogen storage density (2015 targets: 0.09 kg H_2/kg and 0.081 kg H_2/L)
- C – Energy efficiency
- D – Durability
- E – Refueling Time
- G – System Life-Cycle Assessment
- R – Cost effective regeneration processes
- S – By-Product/Spent Material removal
- T – Thermal Management for hydrogen extraction

Phase I Program Approach

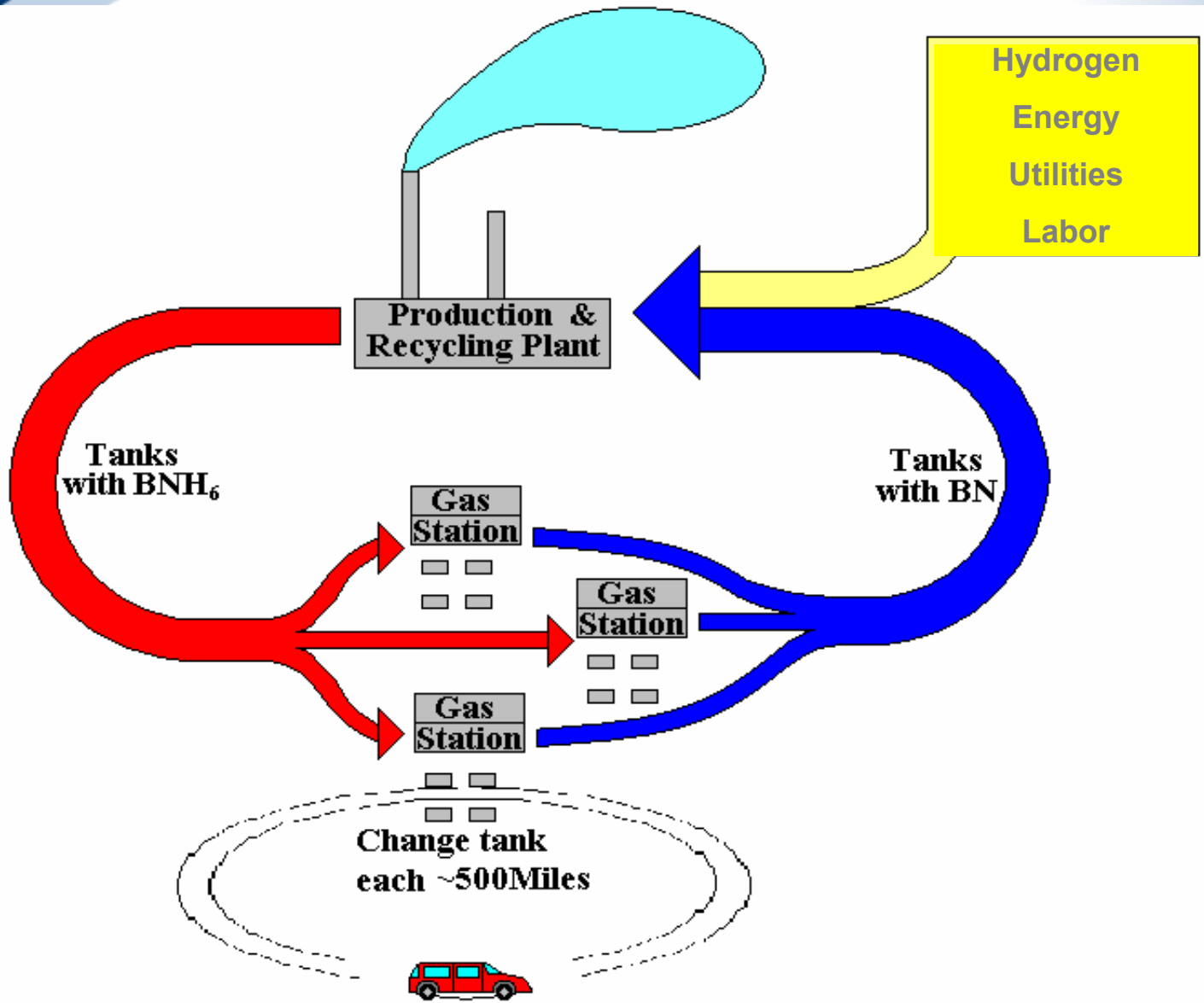
- **Task 1 – Regeneration** - Demonstrate individual chemical steps for converting BN to ammonia-borane.
- **Task 2 - Hydrogen Release –** Ammonia-borane heating approaches for maximum hydrogen yield.
- **Task 3 – Recycle Spent Products –** Regeneration of ammonia-borane decomposition products.
- **Task 4 – Preliminary Storage System Design** Develop a preliminary prototype (1 kg hydrogen capacity) design with >9 wt% hydrogen capacity.
- **Task 5 – Feasibility -** Determine technical and economic feasibility.

Ammonia-borane Properties

- Molecular Formula – NH_3BH_3
- White crystalline solid – stable in ambient air
- Hydrogen Content – 19.6% by weight
- Density - 0.74 g/cm3
- Heat of formation - - 42.54 kcal/mole
- Melting temperature ~ 105^{o}C
- Solubility at 20 ^{o}C is ~ 33.6 g in 100 g of water.
- Water solutions of Ammonia-borane are also very stable during long term storage.

Ammonia-borane for Transportation

- On-Demand Decomposition by Direct Heating.
- Hydrogen combustion or electrical heating powered by Fuel Cell - Net material-based Hydrogen Density > 17% by wt with complete hydrogen release.
- Spent Boron Nitride must be converted to Ammonia-borane (AB) Off-board in a central processing facility utilizing commodity hydrogen.
- Develop AB Distribution / BN Recycling Network.



Aminoborane in close energy transfer cycle

Technical Accomplishments

- **Task 1 – Regeneration** – Initiated BN chlorination studies at laboratory scale – literature search for process conditions, catalysis, reactor materials, product separation and analytical techniques.
- **Task 2 - Hydrogen Release –** Conducted controlled ammonia-borane heating studies. Demonstrated release of 85% of available hydrogen in < 30 seconds; confirmed with elemental analysis of the decomposition residue.

  Material-based hydrogen density achieved ~ **16.5 wt%**
- **Task 4 – Preliminary Storage System Design**
  Identified components for the prototype design.

Task 1 - Ammonia-borane regeneration

Reaction	Reaction Enthalpy
$2\ BN + 3\ Cl_2 \rightarrow 2\ BCl_3 + N_2$	-36.8 kcal/mole BN (1000 C)
$2\ BCl_3 + 6\ H_2 \rightarrow B_2H_6 + 6\ HCl$	+32.1 kcal/mole BCl_3 (400 C)
$B_2H_6 + 2NH_3 \rightarrow 2\ BH_3NH_3$	-20.9 kcal/mole BH_3NH_3 (30 C)

Overall Reaction

$$2\ BN + 3\ Cl_2 + 6\ H_2 + 2NH_3 \rightarrow 2\ BH_3NH_3 + N_2 + 6\ HCl$$

Overall Reaction Enthalpy ~ -25.6 kcal/mole BH_3NH_3 (exothermic)

Task 1 – Activities

- Literature review for conducting BN chlorination; process temperature ~ 1000 C; catalysis – group Ib, VIIb and VIII element chlorides; reactor materials – quartz, alundum; product separation and analysis.
- Diborane synthesis by hydrogenation of boron chloride - the most challenging process step but is industrially practiced.
- Prior experience in synthesizing AB from diborane.
- Laboratory apparatus assembled for studying BN chlorination, product separation, and analysis of gas streams and liquid samples.

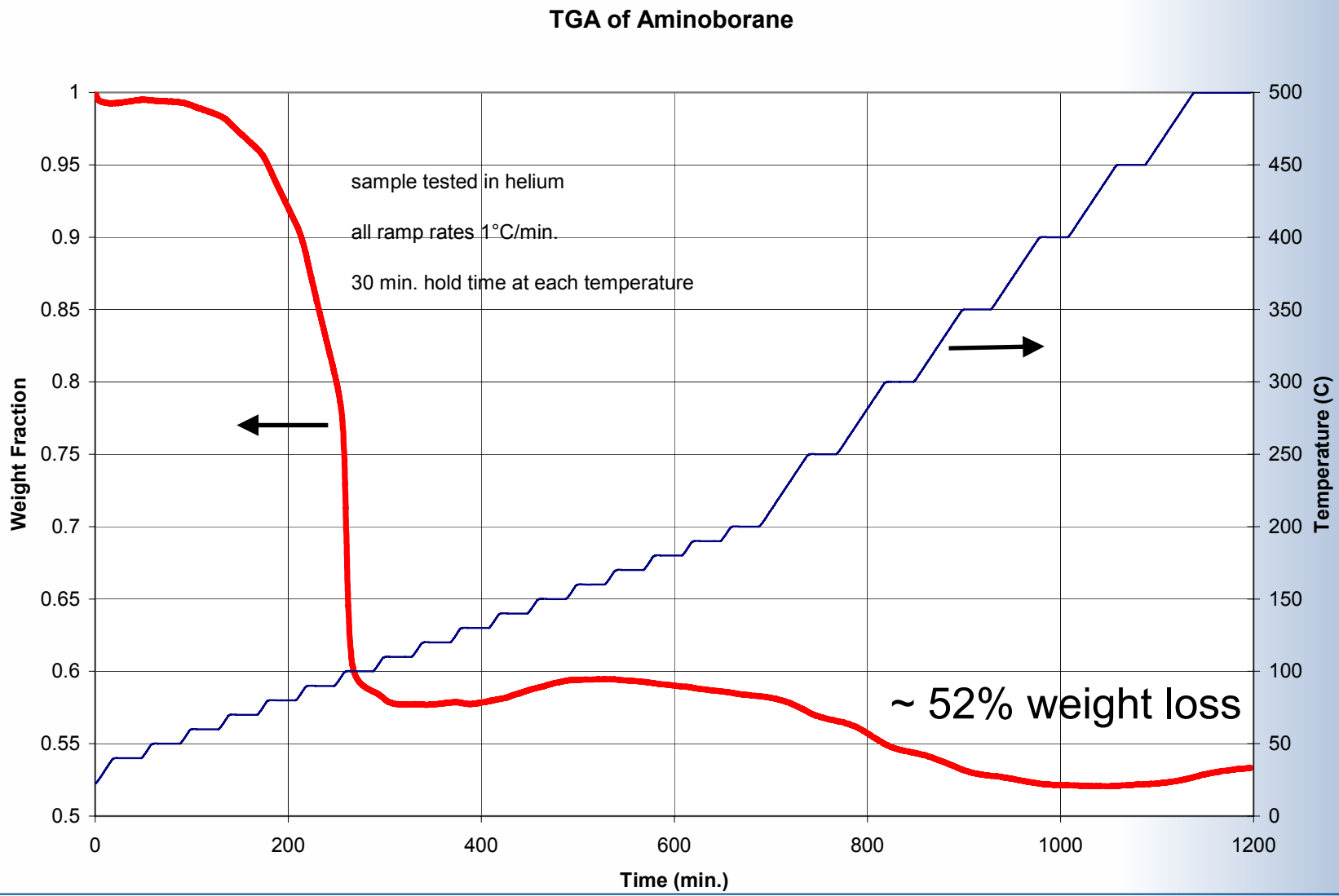
Task 2 - Hydrogen Release

- Two possible modes of supplying heat: direct hydrogen combustion, Resistive heating using fuel cell power.
- AB cartridge design: a) Fixed material cartridge with heat directed to progressive zones – simple compartmentalized cartridge design -- slower heating rate, intermediate products.
- AB cartridge design: b) dispensing in a fixed hot zone – rapid heating rate, need separate product storage and solid powder/pellet dispensing system.

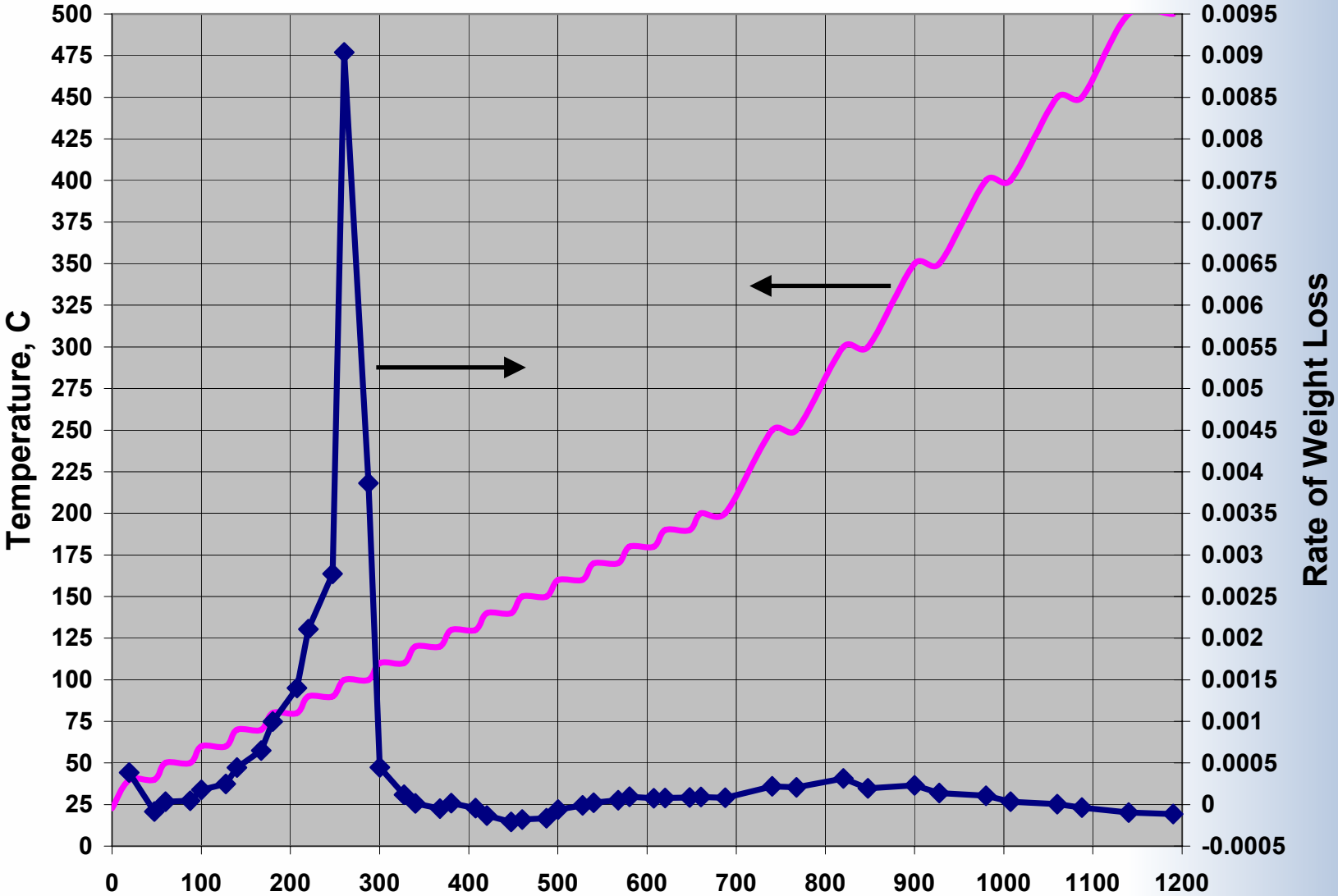
Task 2 – TGA-MS Activities

- TGA studies conducted with controlled heating patterns, ramp rate, hold times and final temperatures.
- All TGA studies experienced mechanical loss of sample due to melting and subsequent gas release through melt regardless of ramp rate.
- Maximum rate of weight loss was at 100 ^{o}C coincident with first stage hydrogen release.
- Exit gas analyzed by online Mass Spectrometer for species identification.

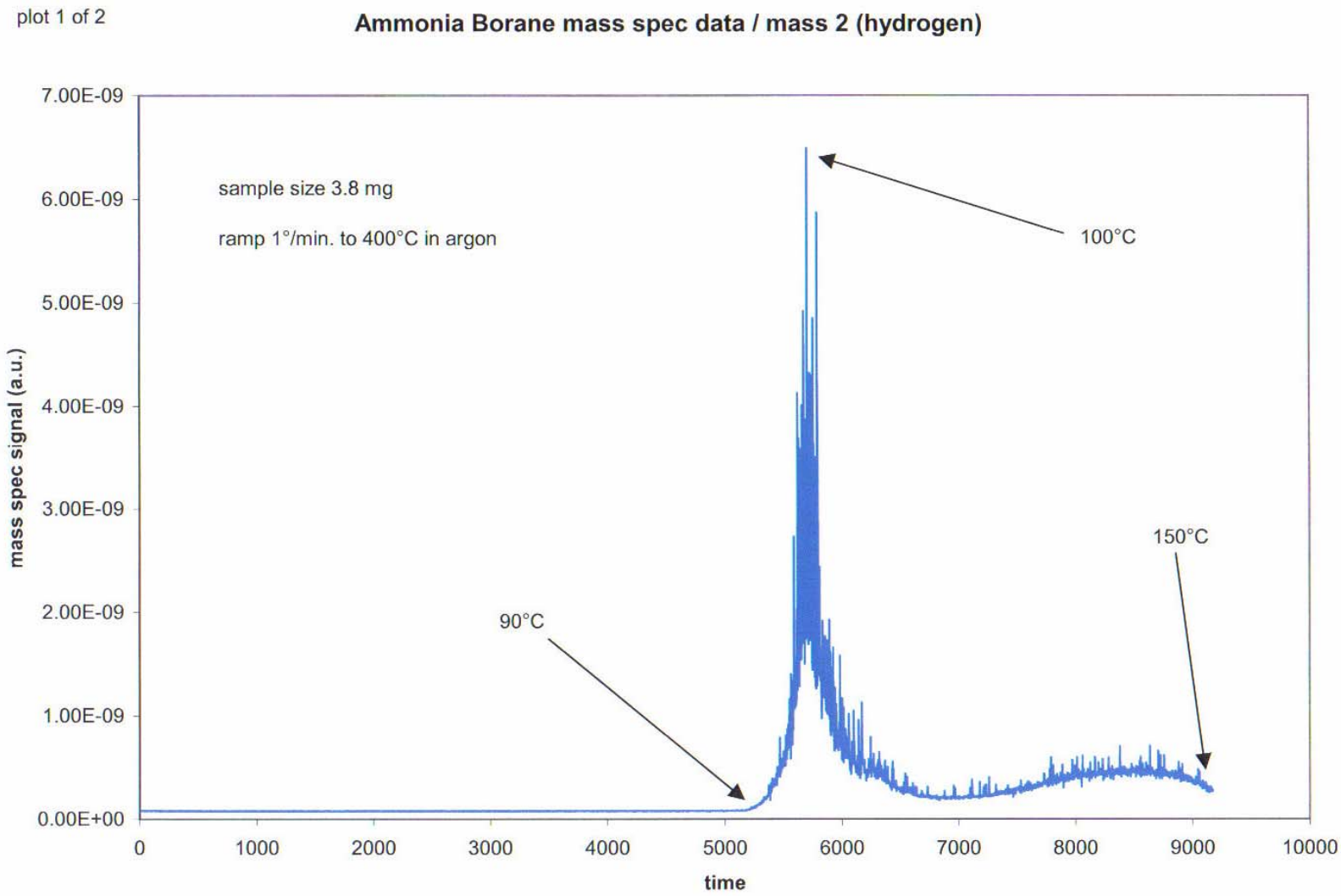
TGA Sample weight loss



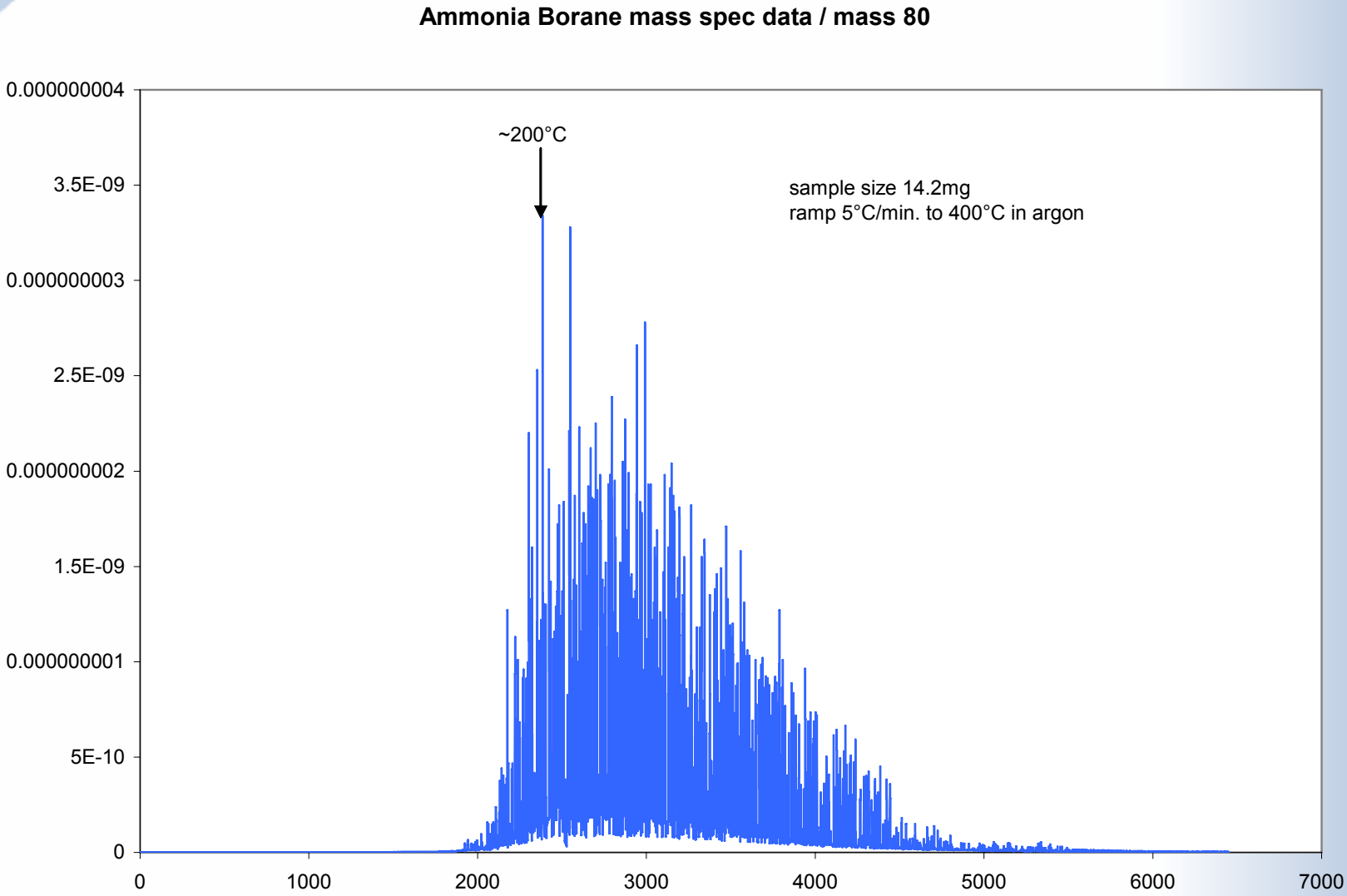
Rate of Weight Loss with Temperature



MS analysis of Gas Released - Hydrogen



MS analysis of Gas Released - Borazine



Conclusions from TGA-MS studies

- First stage hydrogen release occurs at ~ 100 ^{o}C with a second stage release at ~140 ^{o}C. Hydrogen release at < 90 ^{o}C temperature below MS detection limit.
- Melting of ammonia-borane also around 100 ^{o}C caused foaming of sample and mechanical weight loss in TGA studies.
- All of the detectable higher MW emissions occurred after reaching 175 ^{o}C, e.g. MW = 54 ($B_2N_2H_4$) and MW = 81 ($B_3N_3H_6$ - borazine).
- Melting of ammonia-borane and foaming as hydrogen is released – possible problem in progressive heating approach.

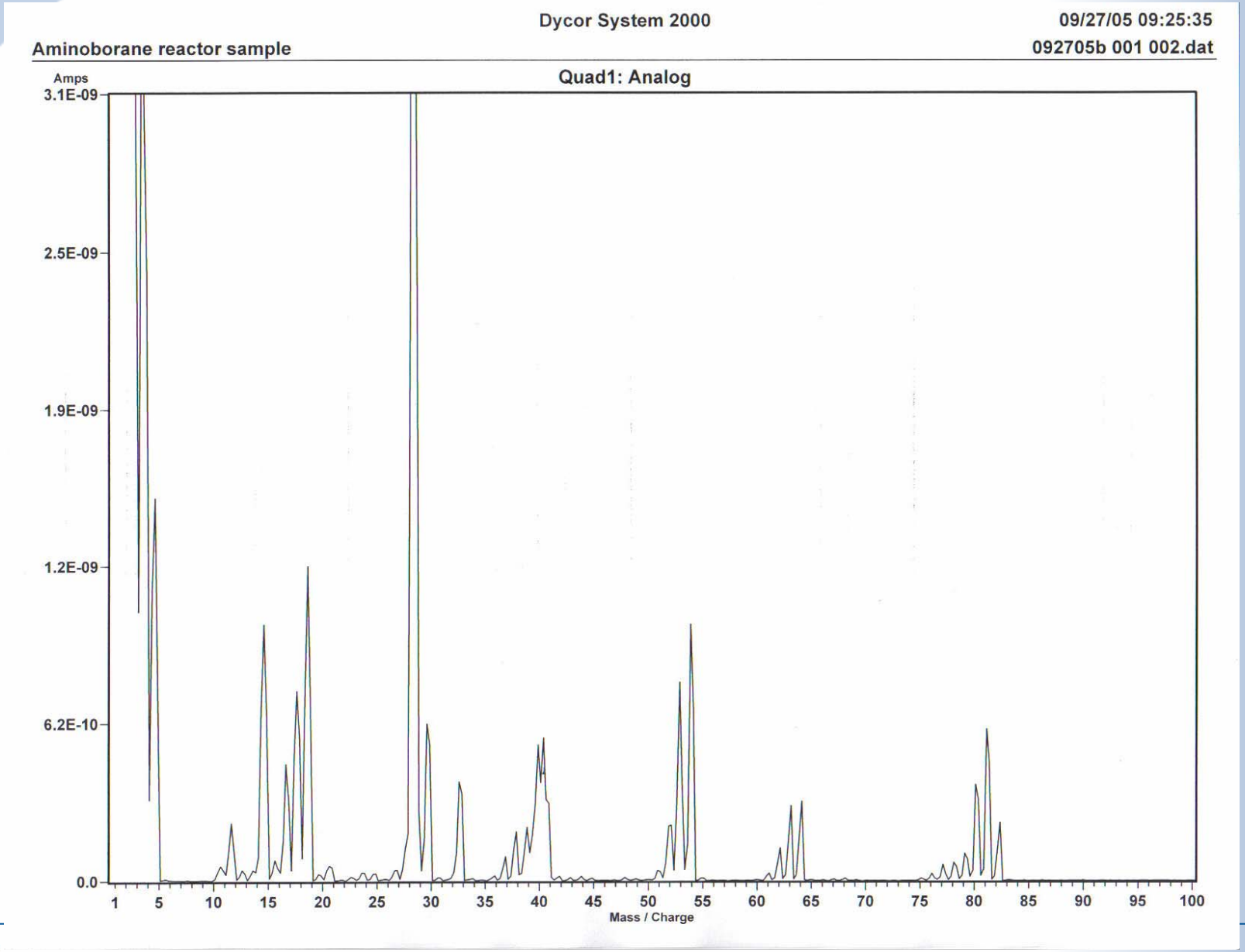
Task 2 – High Temp. Reactor Studies

- High temperature tubing reactor used for quantitative determination of hydrogen released as a function of reactor temperature and sample hold time.
- Reactor temperature was varied from 400 to 500 ^{o}C and sample hold time was varied from 15 sec to 10 minutes.
- Amount of gas generated was measured by direct water displacement.
- Ammonia-borane decomposition residue analyzed for elemental composition.

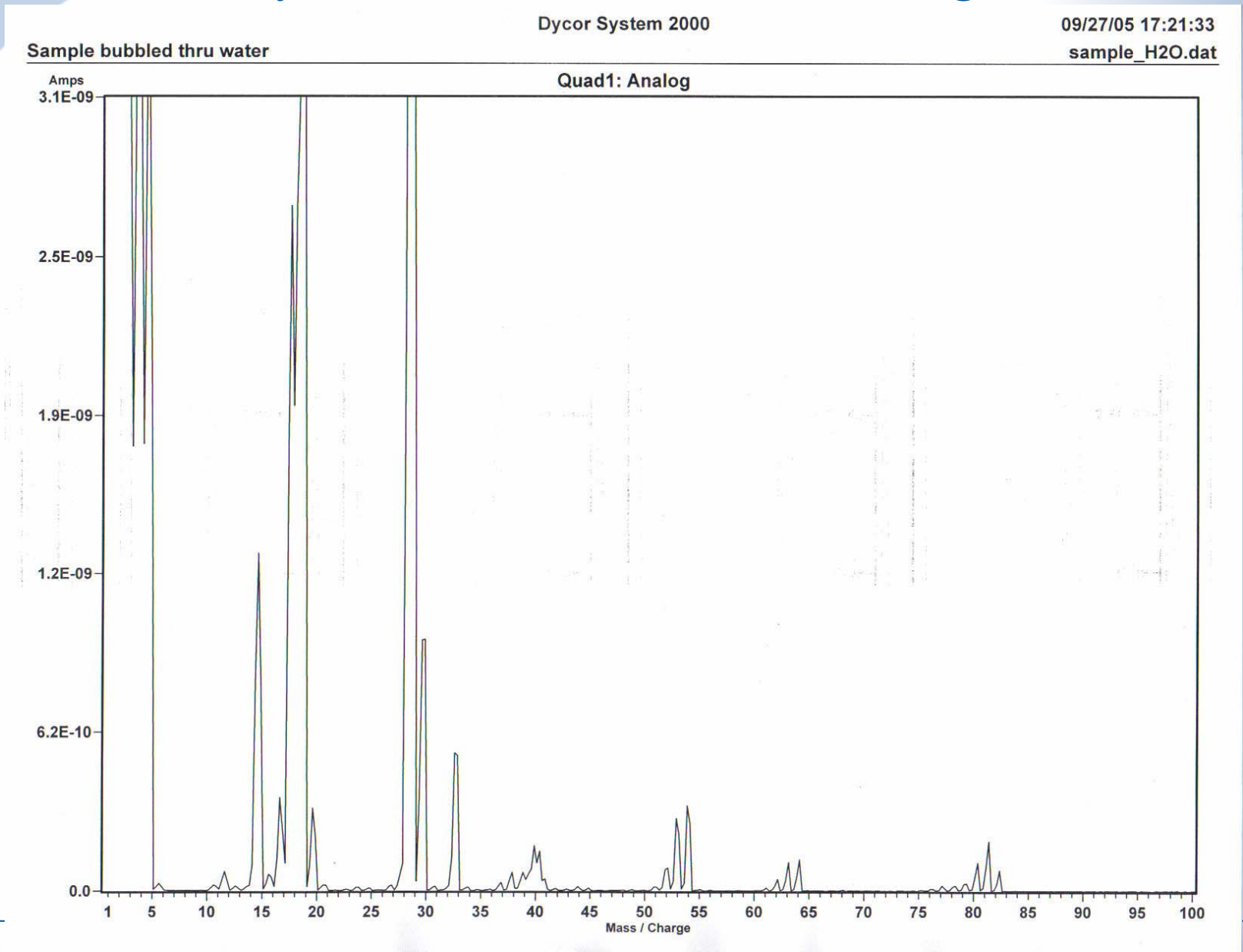
High Temperature Reactor Test Results

- Specific gas release of ~ 1980 cc/g ammonia-borane at 500 ^{o}C. (~ 85% of the maximum possible hydrogen).
- Material-based hydrogen density achieved ~ **16.5 wt%.**
- Specific gas release at 500 ^{o}C ~ 10% greater than at 400 ^{o}C.
- Hold time of 30 seconds is adequate for gas release.
- Elemental analysis of the residue indicated composition of $BN_{0.9}H$ – consistent with observed specific gas release.
- GC analysis of gas indicated hydrogen purity ~ 98.5%.
- The nature of impurities analyzed by Mass Spectrometry.

MS analysis of HT Reactor Gas



MS analysis of Gas bubbled through water



MS analysis of HT Reactor Gas

- MS analysis of the HT reactor gas indicated possible presence of cyclic B,N,H compounds (e.g. MW = 39 (B_2NH_3), 54 ($B_2N_2H_4$), 64 ($B_3N_2H_3$), and 81 ($B_3N_3H_6$) with successive addition of B/N atom).
- Need positive identification of individual species.
- These species appear to be stable even at 500 ^oC.
- Passing the gas through a water bubbler significantly reduced the concentration of these species by a factor of 2 to 3.

Task 4 - Preliminary Storage System design

- Components identified – reagent/product storage chambers, heating system for the reactor chamber, solid feed and extraction system, buffer hydrogen tank, filter/purifier if needed, and pressure sensor-based control system.
- Solid feed with an adequate hold time in the reactor. Allowable design pressure and ammonia-borane feed rate/injection will determine volume of the reactor.
- Buffer tank capacity determined by the startup hydrogen requirements.
- Heat can be supplied by direct hydrogen combustion or electrical heating during startup. The hydrogen release process is expected to be self-sustaining after start-up.

Activities anticipated in FY06

- Task 1 – Continue evaluation of process conditions and catalysts for maximizing product yield in each of the individual reaction steps starting from BN chlorination.
- Task 2 - Continue evaluating direct and catalytic decomposition approaches for hydrogen release.
- Task 3 - Determine additional considerations for starting with decomposition product instead of BN in Task 1, Evaluate catalytic regeneration of decomposition products.
- Task 4 - Develop preliminary design of an on-board hydrogen storage and delivery system.
- Task 5 – Estimate costs of regeneration process, stored hydrogen, and the hydrogen storage system.

Activities anticipated in FY07

- Task 1 - Finalize process conditions and catalysts for maximizing product yield in each individual reaction steps.
- Task 2 - Select a heating system and process conditions for maximum hydrogen yield.
- Task 3 – Demonstrate regeneration of ammonia-borane decomposition products.
- Task 4 - Complete the preliminary design of an on-board hydrogen storage and delivery system using the heating approach and conditions identified in Task 2.
- Task 5 - Update estimates of costs of stored hydrogen and the storage system

Phase I Technical Milestones

- Synthesis of pure ammonia-borane from boron nitride at a laboratory scale.
- Demonstration of a process, suitable for on-board deployment, for extraction of pure hydrogen from AB.
- Demonstrate lab-scale synthesis of pure ammonia-borane starting from AB decomposition products.
- Design a prototype, 1 kg hydrogen capacity, on-board AB-based hydrogen storage system with > 9 wt% H_2 capacity.
- Determine technical and economic feasibility of ammonia-borane-based hydrogen storage system leading to a Go/No Go decision point for continuation to Phase II.

Project Summary

- **Relevance –** Develop a hydrogen storage system to meet DOE's 2015 hydrogen density and cost targets.
- **Approach -** Utilize thermal decomposition of ammonia-borane (19.6 wt% hydrogen) to produce hydrogen on-board. Regenerate spent materials chemically off-board.
- **Technical Accomplishment –** Demonstrated release of 85% of available hydrogen in < 30 seconds. Material-based hydrogen density achieved ~ 16.5 wt%. Identified a chemical route for regeneration of spent products.
- **Future Activities –** Demonstrate efficient ammonia-borane decomposition and regeneration processes.

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Hydrogen Safety

The most significant hydrogen hazards:

- Handling toxic chemicals such as diborane, chlorine, hydrogen and ammonia during evaluation of aminoborane synthesis processes.
- Extreme conditions during synthesis processes, e.g. high and low temperatures (e.g. 1000 C to -200 C).
- Uncontrolled release of hydrogen during evaluation of approaches for hydrogen extraction from aminoborane.

Hydrogen Safety

Our approach to deal with these hazards:

- Safe laboratory practices during handling of chemicals and extreme process conditions eliminating exposure to TLV levels of toxic chemicals involved.
- Limit scale of experiments to assure safety during synthesis experiments, increasing the scale gradually as experience is gained in handling hazardous process conditions.
- Design hydrogen extraction experiments so as to eliminate any possibilities of uncontrolled release as well exposure of hydrogen to any open flame.
- Conduct all experiments in ventilated fume hood areas