

### III.B.2 Hydrogen Storage: Radiolysis for Borate Regeneration

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#### Objectives

The goal of this project is to develop both a viable and an economical method for regenerating sodium borohydride from sodium borate and meet DOE's fuel cost target of \$1.50/kg H<sub>2</sub>. The following objectives were pursued during FY 2004 to achieve this goal:

- Demonstrate radiological methods of converting borate to borohydride
- Validate earlier results demonstrating the conversion of borate to borohydride and hydrogen generation
- Initiate processes for identifying, qualifying and quantifying conversion mechanisms
- Estimate production capability of process

#### Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- A. Cost
- C. Efficiency
- G. Life Cycle and Efficiency Analyses
- Q. Regeneration Processes for Irreversible Systems
- R. By-Product Removal

#### Approach

The project approach uses radioactive waste as an energy source for off-board regeneration of spent vehicle fuel – specifically to convert sodium borate to sodium borohydride. Economic drivers may make this approach an efficient alternative to current techniques and put radioactive waste to good use. Using ionizing radiation to modify chemical compounds is well known. When applied to sodium borate, it appears to efficiently change borate compounds into other chemical species. By applying the proper combination of controls, stable borohydride compounds may be produced and used as hydrogen fuel storage medium. The approach involves the following major focus areas and steps:

- Prepare and document exposure samples and control samples
- Expose samples to ionizing radiation sources
- Generate, control, and stabilize products
- Document and analyze samples
- Estimate process economics
- Estimate production capacity based on available resources

## Accomplishments

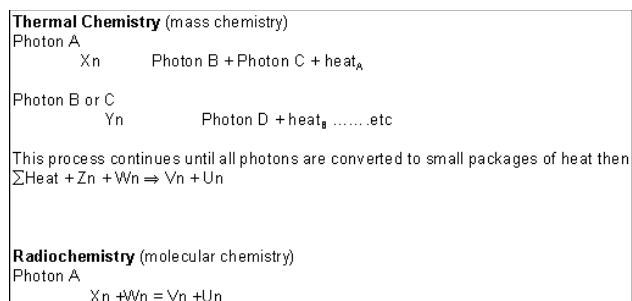
- Duplicated FY 2002 tests in January and March/April 2004
- Duplicated the ability to generate hydrogen from borate solution: the same yield efficiency was obtained three times in FY 2004
- Developed analytical methods and processes
- Estimated absorbed radioactive energy
- Performed analytical studies that indicate possible borate to borohydride changes
- Started a systematic study by varying parameters to increase ability to detect borohydride (i.e., nuclear magnetic resonance, x-ray diffraction) and to estimate conversion efficiency
  - Vary borate/water concentrations over a broad range
  - Vary radioactive intensity and duration
  - Seek methods for stabilizing aqueous solutions of borohydride
  - Evaluate methods for dehydrating borohydride solutions
  - Estimated a 53% conversion efficiency based on hydrogen produced and available photolytic energy

## Future Directions

- Complete unambiguous verification of the formation of borohydride
- Continue investigating methods of improving efficiency and yield
  - Identify methods to control back reactions of borohydride
  - Quantify the impact of different radiation sources
  - Investigate the impact of catalysts
- Qualify the conversion mechanism
- Determine the applicability of this process to other chemistries

## Introduction

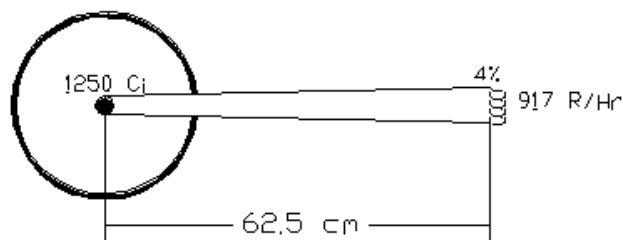
One problem that prevents borohydride from having widespread use for on-board hydrogen storage is its cost of production. The current process for creating borohydride is inefficient and expensive. One advantage of using borohydride as a supply for hydrogen is that during the process of releasing hydrogen, the borohydride is converted to borate. If borate could be recycled, converted to borohydride, and reused at economical cost, we would have a cost-effective recyclable fuel supply. In FY 2002, the Idaho National Engineering and Environmental Laboratory (INEEL) conceived and tested a unique borohydride production and recycling process. This process shows promise for economically producing hydrogen fuel. The purpose of this project is to validate the initial tests and quantify the results.



**Figure 1.** Thermal Chemistry Versus Radiochemistry

## Approach

The INEEL approach uses radiolysis to modify chemical bonds and allow chemical reconfiguration to produce the desired compounds. Figure 1 shows graphically the difference between thermal chemistry and radiochemistry and implies possible differences in processes. The earlier basic proof-of-concept test



**Figure 2.** Illustration of a Point Source Used in the Irradiation of Samples and the Percent of Radiation Absorbed by Each Sample

was conducted to verify that radiolysis does convert borate into borohydride. Exposure to ionizing radiation creates chemical ‘free-radicals’ in solutions that are highly reactive. Some of these radicals recombine to form borohydride. To enhance this process, a number of techniques are used to bias the chemistry toward forming borohydride. The initial laboratory test exposed a sample to a 230 curie, Cs-137 source. Exposure was estimated to be 36,000R. In that initial test, a small amount of borohydride was generated. Several large bubbles and numerous small bubbles of gas were generated upon exposure to ruthenium chloride. Based on the probable reaction and a set of control samples, it is believed that the gas generated was hydrogen.

It is well known that radiation with ionizing potential (i.e., beta, gamma, alpha, neutron) can interact with molecules and atoms and promote chemical changes. Figure 2 shows the percentage of radiation absorbed by each sample assuming a point source. Of particular interest in the subject reaction is the beta and gamma radiochemistry. The electron or photon can react with water, borate, or both. The reaction causes a shift in the electronic molecular structure, and this creates a molecular radical. During a subsequent chemical reaction, this radical (e.g., electron) will resolve to a stable configuration. A sufficient concentration of radicals is formed such that either a substitution or replacement reaction occurs. The radical constituents of the reactants collide or attack the neutral molecule, whereupon the resolution reaction occurs. Managing this reaction to efficiently form borohydride is the object of this research. Radioactive waste materials that must otherwise be processed and stored at great expense can be used for the radiation required for this

process. The approach and purpose of this project is to expand the proof-of-concept testing successfully completed at the INEEL, and to further verify the use of radiochemistry to convert borate to borohydride.

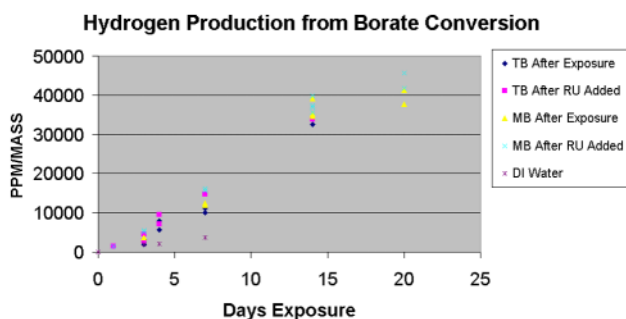
## **Results**

Testing and evaluation in FY 2004 duplicated FY 2002 scoping tests and verified the results. This was achieved when a ruthenium salt added to an irradiated sodium metaborate solution generated hydrogen above prior levels.

The project execution requires a number of steps that include the following:

1. Identify analytical methods with the potential of differentiating between sodium borate and sodium borohydride and quantifying any sodium borohydride generation.
2. Verify parameters and technologies that can detect sodium borohydride [e.g., nuclear magnetic resonance (NMR), x-ray diffraction (XRD)].
3. Vary the concentration of sodium borate to maximize detection of sodium borohydride. This may include the use of solids or pastes.
4. Identify methods that provide stable solutions for sodium borohydride and minimize the tendency for reverse reactions.
5. Consider methods to dehydrate sodium borate/sodium borohydride solutions without enhancing the tendencies for a reverse reaction.
6. Verify that radiolysis of sodium borate solutions shows 53% conversion efficiency where hydrogen generation is the metric.
7. Analytically and experimentally quantify the amount of radioactive energy absorbed during any given exposure period.
8. Vary the radioactive energy intensity and exposure time and correlate them.

The analytical methods used thus far in this study are NMR and quantitative hydrogen generation. The generation of hydrogen was first used as a metric for its ability to indirectly quantify the amount of stable sodium borohydride created during the irradiation process. It was discovered that the level of refinement for accurately estimating the quantity depends on knowing the nature of the species



**Figure 3.** Hydrogen Production from Borate Conversion

generated by the process. This suggested looking into other methods of characterizing the actual species created. In addition to the thermal conductivity gas chromatograph (TCGC) used for measuring the quantity of hydrogen generated, two other methods were considered: NMR and XRD.

The level of sensitivity of both methods is about the same, and the ability to identify the desired chemical species exists for both techniques. Ease of sample preparation, however, does differ, and for this reason NMR is the preferred method for identification.

Figure 3 is a graph of hydrogen production results obtained by TCGC. The samples include controls for exposed and non-exposed solutions, and solutions before and after introduction of the ruthenium chloride. Based on these results, the presence of sodium borate has significant impact on creating hydrogen using a photolytic process. It also shows additional hydrogen released after the introduction of ruthenium chloride. This revealed the need to verify that the mechanism of storage providing the additional hydrogen is sodium borohydride, and not some other chemical creation.

At this point in the project, the results of the NMR study are preliminary and inconclusive. Because of sample size and production rates, the amount of sodium borohydride being created is at or below the detection limits of NMR and is easily masked by the presence of sodium borate at much higher concentrations. One series of tests indicates the presence of sodium borohydride, but experimental replication is yet to be performed.

Use of XRD will be considered in future studies. It is more difficult to prepare samples for analysis when the aqueous solutions must have the water removed, with only solid phase remaining. The drying process must be reasonably rapid and occur at low temperature in order to prevent any reverse reaction of the sodium borohydride to sodium borate.

The efficiency of hydrogen generation is calculated at 53%. This efficiency is the ratio between the measured hydrogen production and the estimated amount of hydrogen produced when the available energy is absorbed. The results indicate 53% conversion efficiency based on an analytical estimation of energy absorbed. The available energy absorbed was obtained from MicroShield calculations. The conversion efficiency based on experimentally measured energy absorption is to be determined in the FY 2005 phase of this study.

### Conclusions

- The photolysis of sodium borate solutions, though not optimized, demonstrates a very high production rate for hydrogen.
- The sodium borate to sodium borohydride to sodium borate process yields high hydrogen generation efficiency.
- NMR analytical measurement has shown trace amounts of sodium borohydride; duplication of this result needs to be completed and production yields increased to fully validate conversion effectiveness.
- Stable reaction intermediaries do exist and could indicate the presence of sodium borohydride during the irradiation process.
- The quantity of photolytic energy available from nuclear radiation sources is useful for generating hydrogen for storage.

### FY 2004 Publications/Presentations

1. Dr. Dennis Bingham, Kraig Wendt, "Radiolysis Process for the Regeneration of Sodium Borate to Sodium Borohydride", FreedomCAR Hydrogen Storage and Vehicle Interface Technical Team, February 19, 2004.

2. Dr. Dennis Bingham, Kraig Wendt, Bruce Wilding, "Radiolysis Process for the Regeneration of Sodium Borate to Sodium Borohydride", 2004 DOE Hydrogen Program Review, May 25-26, 2004.

**Special Recognitions & Awards/Patents Issued**

1. Bruce Wilding, Kerry Klingler, Dennis Bingham, Thor Zollinger, Kraig Wendt, Patent Pending, "Method to generate borohydride from borate using radiolysis".