

TECHNICAL ASSESSMENT AND ANALYSIS OF HYDROGEN R&D PROJECTS

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Abstract

Energetics performs independent site-visit-based assessments of projects associated with the DOE hydrogen program for the purpose of providing the Hydrogen Peer Review Panel with in-depth independent information on the individual R&D projects. This can be used by the Panel to augment the information that they obtain from the Principle Investigators prior to and during the Peer Review itself. In addition, a more general, abbreviated version of the site-visit reports are made available as information to the public.

During the period May 1998-April 1999, Energetics performed a total of eight site visits on Hydrogen production and storage R&D projects. While the details of these visits, which were presented in writing to the Review Panel are competition-sensitive, this paper contains some more generic general comments about these site visits.

Energetics is also performing an analysis of the feasibility of using a low-rank coal as a carbon source for the regeneration of hydrides being used as an on-board, slurry-based hydrogen storage/hydrolysis process. The hydride process is one that is being developed by Thermo Power Corp. For this particular analysis, Wyodak (Wyoming) sub-bituminous coal has been selected as the carbon source and the Thermo Power laboratory in Massachusetts has been selected as the refueling site. In the analysis, a comparison is made between: 1) shipping Wyodak coal to Massachusetts as a carbon source for regeneration, 2) shipping spent hydroxide slurry from Massachusetts to Wyoming to perform the regeneration process at the mine mouth and shipping

the regenerated hydride slurry back to Massachusetts, and 3) using a baseline “char” material (in Massachusetts) proposed by Thermo Power as the regeneration carbon source. The analysis shows that the cost of shipping the coal makes it more expensive than using the char, and that shipping the slurries are cheaper than using the char only if the carbon-conversion rate is low.

Introduction

Part of the role that Energetics plays in the DOE Hydrogen Program is to provide independent technical assessments of ongoing hydrogen R&D projects. In addition, Energetics performs analyses on hydrogen-related processes and systems. During the period May 1998–April 1999, Energetics visited eight laboratories in order to perform assessments on hydrogen production and storage R&D projects. In addition, Energetics has analyzed an alternative regeneration scheme for a hydrolysis-based metal hydride storage system. This paper discusses these topics.

Technical Assessment of R&D Projects

Background/Approach

Over the past three years, Energetics has performed site visits at the laboratories of fourteen projects that have been part of the DOE Hydrogen Program. This work adds a new dimension to the review process: it provides the reviewers with in-depth information that they cannot get from once-a-year 20 minute presentations. It also provides for more continuity in the interfacing between the Program and the projects, helping to establish ongoing dialogs with the Principle Investigators (PI).

Once a project is chosen for technical assessment, a literature review is performed on the subject. This includes a review of the last two or three years of Annual Operating Plan submittals, monthly reports, the Annual Review paper, reviewers’ consensus comments from the past few years, publications in journals, and journal publications on the same or similar topics by other researchers. The PI is then contacted, and an on-site visit is arranged. A set of topic questions or discussion points is then drawn up and sent to the PI about two weeks prior to the visit. These questions are meant to be used as a basis for a large portion of the discussion during the site visit.

During the site visit a tour, preferably with a demonstration of the experimental set-up, is requested whenever possible. The PI then makes a formal or informal (according to the PI’s own preference) presentation on the project and its current status. The majority of the visit is spent in discussions based on the topic questions and on any other items that may come out of the tour, demonstration, and presentation. The on-site visit lasts anywhere from a half-day to a full day, a little longer on some occasions.

Following the site visit, two reports are written. The first is a detailed report that discusses the project and its strengths and weaknesses in a thorough manner. This report is provided to the Peer Review Team as part of their information package prior to the Peer Review Meeting. A copy is also provided to the Hydrogen Program Manager. The second report is a condensed

narrative that discusses the technology but provides no critique. This second report is made available to the public.

Assessments Performed

Prior to May 1998 (the start date of this Annual Report), Energetics had performed a total of six site-visit technical assessments of hydrogen R&D projects. These assessments are identified in Table 1. During the period of this current report (May 1998 – April 1999) a total of eight technical assessments were completed. These are shown in Table 2.

Table 1. Technical Assessments Performed Prior to May 1998

Project	Performing Laboratory	Date of Visit
Enzymatic Conversion: Biomass-Derived Glucose to Hydrogen	Oak Ridge National Laboratory	Feb. 1996
Hydrogen from Catalytic Cracking of Natural Gas	Florida Solar Energy Center	Feb. 1996
Hydrogen Manufacture by Plasma Reforming	Massachusetts Institute of Technology	April 1996
Photovoltaic Hydrogen Production	U of Miami	May 1996
Hydrogen Storage in Carbon Nanofibers	Northeastern U	Dec. 1996
Carbon Nanotubes for Hydrogen Storage	National Renewable Energy Laboratory	June 1997

Table 2. Technical Assessments Performed May 1998 – April 1999

Project	Performing Laboratory	Date of Visit
Storage and Purification of Hydrogen Using Ni-coated Mg	Arthur D. Little, Inc.	June 1998
Hydrogen Transmission and Storage with a Metal Hydride Organic Slurry	Thermo Power, Inc.	June 1998
Thermal Management Technology for Hydrogen Storage	Oak Ridge National Laboratory & Materials and Environmental Research, Inc.	August 1998
Improved Metal Hydride Technology	Energy Conversion Devices, Inc.	August 1998
Hydride Development for Hydrogen Storage	Sandia National Laboratories (CA)	Sept. 1998
Biomass to Hydrogen via Fast Pyrolysis and Catalytic Steam Reforming	National Renewable Energy Laboratory	Dec. 1998

Hydrogen Separation Membrane Development	Savannah River Technology Center	March 1999
Hydrogen Production by Photosynthetic Water Splitting	Oak Ridge National Laboratory	March 1999

Results/Conclusions

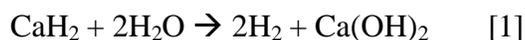
The outcome of the individual technical assessments cannot be reported in this document due to the competition-sensitive nature of much of the results. However, several broad conclusions can be reported here:

- Steady progress is being made in renewable hydrogen production, carbon storage, and hydride systems.
- It is very easy for PIs to lose sight of the fact that these are hydrogen projects. For example, on-board reforming is not a goal of the Hydrogen Program, yet it has appeared as a goal of at least one project.
- Not enough effort is being directed at CO₂ removal. Carbon balances and centralization of CO₂ emissions or processes that do not emit CO₂ need to be looked at more closely.
- Use of magnesium hydride-based storage systems is likely limited to niche applications; R&D in this area has likely run its course. More promise comes from alanate systems and metal hydride hydrolysis systems.
- R&D on alternatives to pressure swing adsorption (i.e., membrane research) is needed.
- Some R&D projects appear to be working in a vacuum, having little or no communication with the mainstream program.

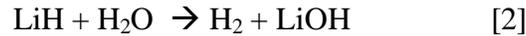
Feasibility of Using Low-rank Western Coal as a Carbon Source for Hydride Regeneration

Introduction and Background

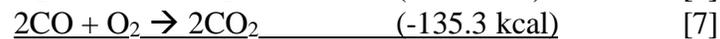
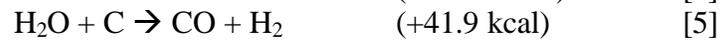
One of the storage systems that is being considered for hydrogen, both on-board and in stationary applications is a system being proposed by Thermo Power Corporation. In this system, a reactive metal hydride such as LiH or CaH₂ is transported in slurry form, using mineral oil as the carrier fluid, to its point of use. After the hydrogen is recovered by reacting with water, the spent material is in the form of an hydroxide. For example:



or:



Thermal Power then proposes to take the hydroxide and reconvert it to the hydride through the following series of steps:



Or for the lithium analog:



Considering reactions [1] and [8] for the calcium system, and reactions [2] and [12] for the lithium system, it can be seen that in both cases, one mole of carbon leads to one mole of hydrogen.

Thermo Power, has proposed that they can obtain a “char” which has a heating value of about 14,000 Btu/lb. Thermo Power further states that the char can be obtained on site in a regeneration plant located on the East Coast for no more than \$1.67/MMBtu (Breault *et al*, 1999). It has been proposed that an alternative low cost process might be to use a low-rank Western coal as a carbon source. The purpose of this analysis is to consider this option and determine under what conditions, if any, such a process would be feasible.

If one were to use a low-rank coal as a carbon source, and the hydrogen is being used in the eastern part of the country, the options open are:

- Move the spent hydroxide west
- Move the low-rank coal east

The cost of these transportation processes as compared with the on-site use of the char is then considered. Note that the cost of regenerating the hydride from the hydroxide is not part of this analysis, as this process would have to take place regardless of the location or carbon source.

However, the *efficiency* of this process is needed in order to estimate the amount of coal or char that needs to be transported.

The coal that was chosen for this exercise is Wyodak sub-bituminous coal from Campbell County, Wyoming. The coal was picked to coincide with that being used by another project involving low-rank Western Coals that is being co-funded by DOE/EE and DOE/FE, and is being performed at the National Renewable Energy Laboratory (Golden, CO) and the Federal Energy Technology Center (Pittsburgh, PA). The proximate and ultimate analyses for Wyodak coal are shown in Table 3.

Table 3: Proximate and Ultimate Analyses of Wyodak Coal (As received)

Proximate Analysis (%)	
Moisture	26.6
Volatile Matter	33.2
Fixed Carbon	34.4
Ash	5.8
Ultimate Analysis (%)	
Sulfur	0.6
Hydrogen	6.5
Carbon	50.0
Nitrogen	0.9
Oxygen	36.2
Heating Value (Btu/lb)	8630

Since Thermo Power at this point is considering Massachusetts (the site of their laboratory) as the potential site for hydride dispensing, the calculation will include: 1) the cost of moving Wyodak coal from Wyoming to Massachusetts, 2) alternatively, the cost of moving spent hydroxide in slurry form, from Massachusetts to Wyoming (where the regeneration process would occur) and then moving the hydride slurry back to Massachusetts, and 3) a comparison with the cost of using Thermo Power's char.

Cost for Transporting Western Coal to Massachusetts

In order to estimate the cost of transporting coal from the western U.S. to Massachusetts it is important to understand that western coal is not currently used in Massachusetts electric power plants. Therefore, no real data exists with organizations such as FERC for what it would actually cost to transport Western coal to Massachusetts by rail. A methodology has been developed that estimates the hypothetical cost of transporting western coal to Massachusetts. This is a

preliminary estimate only to be used for comparing different scenarios and it should not be used for detailed engineering assessments of these options.

Wyodak is the most productive coal bed in Wyoming, with Campbell County being the largest coal producing region in Wyoming (Energy Information Administration, Dec. 1998). However, since no Wyoming coal is shipped to Massachusetts, in order to calculate the transportation cost of sending coal by rail from Wyoming to Massachusetts the following methodology is used:

The average mine-mouth price of coal in Wyoming (nominal dollars, 1997) = \$6.00/short ton (Energy Information Administration, May 1998, p. 154, Table 80). The delivered cost of coal is defined as the mine-mouth price + transportation + taxes + commissions + insurance + equipment lease costs. Since we only have data on mine-mouth price and delivered price of coal, our definition of aggregate transportation cost includes transportation, taxes, commissions, insurance and equipment lease costs. Table 4 shows delivered and aggregate transportation cost for coals from Wyoming for 1997. Table 4 also shows approximate distances for each state from Wyoming. Figure 1 plots the aggregate transportation cost as a function of distance from Wyoming.

Table 4. Aggregate Transportation Cost of Wyoming Coal, 1997

Destination state	Delivered cost (\$/ton)	Distance from WY (miles)	Transportation cost (\$/ton)
AL	19.49	1,080	13.49
AZ	18.99	690	12.99
AR	28.56	860	22.56
CO	14.95	300	8.95
FL	24.59	1,630	18.59
GA	26.29	1,160	20.29
IL	30.70	790	24.70
IN	19.89	900	13.89
IA	15.31	580	9.31
KS	16.69	580	10.69
KY	21.60	1,010	15.60
LA	25.82	1,120	19.82
MI	18.59	960	12.59
MN	19.04	540	13.04
MS	23.22	1,020	17.22
MO	15.56	780	9.56
MT	9.24	240	3.24
NB	10.06	500	4.06
NV	18.79	620	12.79
NC	31.80	1,290	25.80
ND	11.02	420	5.02
OH	21.63	1,040	15.63
OK	15.80	670	9.80

OR	19.95	630	13.95
TN	15.67	1,090	9.67
TX	26.18	1,010	20.18
UT	22.68	320	16.68
WI	16.64	780	10.64
WY	14.16	210	8.16

Sources:

Mine-mouth cost = \$6.00/ton (Source: Energy Information Administration, May 1998, p. 154, Table 80)

Delivered cost: Source: Energy Information Administration, 1995, p. 35 – 38, Table 23.

Distance = Measured roughly from Wyoming to major urban center of each state.

Transportation cost = Delivered cost – mine mouth cost

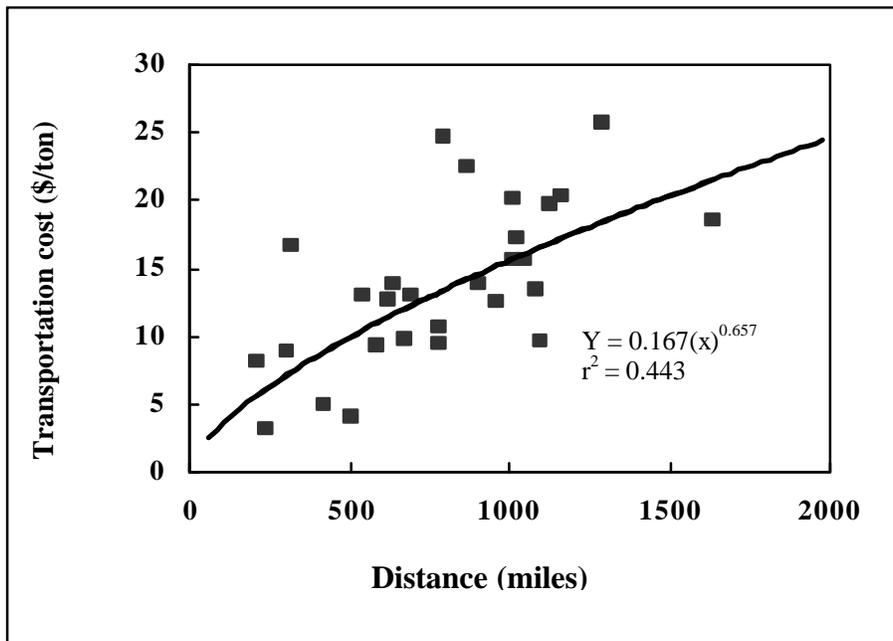


Figure 1. Aggregate Transportation Cost of Wyoming Coal

As can be seen from Figure 1, while there is an upward trend with increasing distance, there is also considerable scatter in the data. This is due to the fact that what is being plotted here is not the real transportation cost only but an aggregate transportation cost which includes the rail cost and other factors such as taxes, commissions, insurance and equipment lease costs.

Nonetheless, using the best-fit regression equation in Figure 1, the cost of transporting the coal from Wyoming to Massachusetts can be calculated. Assuming the distance from Wyoming to Massachusetts to be 1,490 miles (approximate distance from Campbell County, Wyoming to

Boston, Massachusetts) the aggregate transportation cost from Wyoming to Massachusetts would be: $0.167(1490)^{0.657} = \$20.30/\text{ton}$. **Delivered cost for coal from Wyoming to Massachusetts would be: $\$20.30 + \$6.00 = \$26.30/\text{ton}$ (aggregate transportation cost + mine-mouth cost).** It should be pointed out that the transportation cost assumes that the coal cars would be returned empty to the mine. In some cases it is possible that a second product could be identified for the return trip. This would act as a credit, and reduce the cost of coal transportation.

According to the ultimate and proximate analyses as indicated in Table 3, the Wyodak coal has a carbon content of 50% on an as-received basis. Thus, the cost of delivered carbon is $\$26.30/0.5 = \52.60 per ton. Even more important is the fact that the useful carbon – that which would be used in the regeneration process shown in equations [8] and [12] would likely be the fixed carbon. This as shown in Table 3, makes up 34.4% of the coal by weight. The cost of delivered fixed carbon is $\$26.30/0.344 = \76.45 per ton. Right now, due to the state of development of the Thermo Power process, no data is available on what percent of the fixed carbon can be utilized by the regeneration reactions (equations [8] and [12]). Clearly, the process economics would depend significantly on the level of carbon conversion that could be achieved and further data in this area (on the basis of pilot plant tests for example) is essential to deriving meaningful conclusions from this analysis.

The delivered cost of coal on a Btu basis can be calculated simply from the as-received heating value and the delivered cost per ton:

$$\$26.30/\text{ton} / (8630 \text{ Btu/lb} \times 2000 \text{ lb/ton}) = \$ 1.52/\text{MMBtu}$$

On a fixed carbon basis, this is equivalent to:

$$\$ 1.52/\text{MMBtu} / 0.344 = \$4.43 /\text{MMBtu}$$

compared with the reported cost of the delivered char, $\$1.67/\text{MMBtu}$, without even considering the cost of converting the coal to char.

Remembering that one mole of carbon produces one mole of hydrogen (or 12 pounds of carbon produces 2 pounds of hydrogen), and that hydrogen has a heating value of 61,000 Btu/lb, the cost of delivered Wyodak-based fixed carbon to produce one million Btu of hydrogen can be calculated:

$$(\$76.45/ \text{ton C} / 2000 \text{ lb C/ton C}) \times (12 \text{ lb C}/2 \text{ lb H}_2) \times (1 \text{ lb H}_2 /0.061\text{MM Btu H}_2) = \$3.76/\text{MMBtu}.$$

The cost of delivered char to produce the same amount of hydrogen is calculated by:

$$(\$1.67/\text{MMBtu C} \times 0.014 \text{ MMBtu C/lb} \times (12 \text{ lb C}/2 \text{ lb H}_2) \times (1 \text{ lb H}_2 /0.061\text{MM Btu H}_2) = \$2.30/\text{MMBtu}.$$

Cost for Transporting Hydroxide from Massachusetts to Wyoming, and Hydride from Wyoming to Massachusetts

Next, the alternative path of transporting the hydroxides to the mine mouth is considered. First, the weight of hydroxide that must be moved as a function of the hydrogen energy that it will eventually become is calculated. The hydroxide will be converted back to a hydride by reactions [8] or [12], and then used to make hydrogen by reactions [1] or [2], respectively. One mole of LiOH leads to one mole of hydrogen; one mole of $\text{Ca}(\text{OH})_2$ leads to two moles of hydrogen. If 61,000 Btu is used as the energy content of one pound of hydrogen, one pound of LiOH leads to 5080 Btu of hydrogen, and one pound of $\text{Ca}(\text{OH})_2$ leads to 3297 Btu of hydrogen.

Next, the state of the hydroxide as it is collected from a storage area in Massachusetts is considered. Thermo Power is considering using water to wash the spent hydroxide out of the reaction chambers (where hydrogen is made), and then turning the mix into a manageable slurry with more water. R. Breault has indicated that a 60-65 weight % slurry could be made from LiOH and water, and a 70 weight % slurry could be made from $\text{Ca}(\text{OH})_2$ and water (Breault, 1999). The following assumptions to obtain a best-case scenario for this preliminary assessment will be made:

- The degree of difficulty of shipping will not be increased by a lack of slurriability of the hydroxide. That is, we will assume that the slurry is mixable, stable, and pumpable under the loadings designated above.
- There is no residual, unreacted hydride in the hydroxide material (this would react with the water upon slurrying).
- The hydroxide will not need grinding or further processing to make it slurriable.
- The surfactant's cost and concentration will not be included at this time.

The densities for LiOH and $\text{Ca}(\text{OH})_2$ respectively are 1.46 and 2.24 grams/cc. About 11% by weight LiOH is soluble in water, while $\text{Ca}(\text{OH})_2$ is virtually insoluble (less than 0.2%). Using these values, the relationships between the volume of hydroxide/water slurries and MMBtu of hydrogen are shown in Figure 2 for 25-95% by-weight hydroxide slurries. The analogous weight relationships are shown in Figure 3. These data show, for example, that 30.75 gallons of a 60% by-weight LiOH slurry would need to be regenerated to eventually produce 1 MMBtu of hydrogen. This amount of slurry would weigh 329 pounds. For a $\text{Ca}(\text{OH})_2$ slurry, a 70% slurry would require 31.9 gallons, and would weigh 434 pounds.

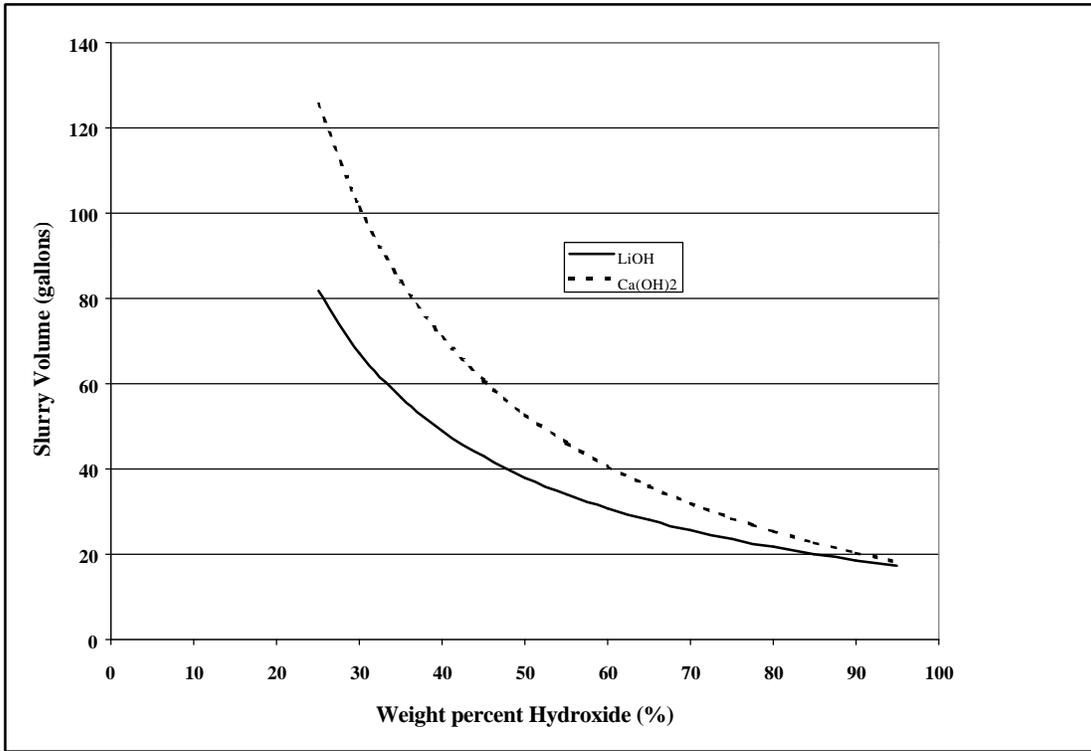


Figure 2. Hydroxide Slurry Volume Resulting in 1MMBtu Hydrogen

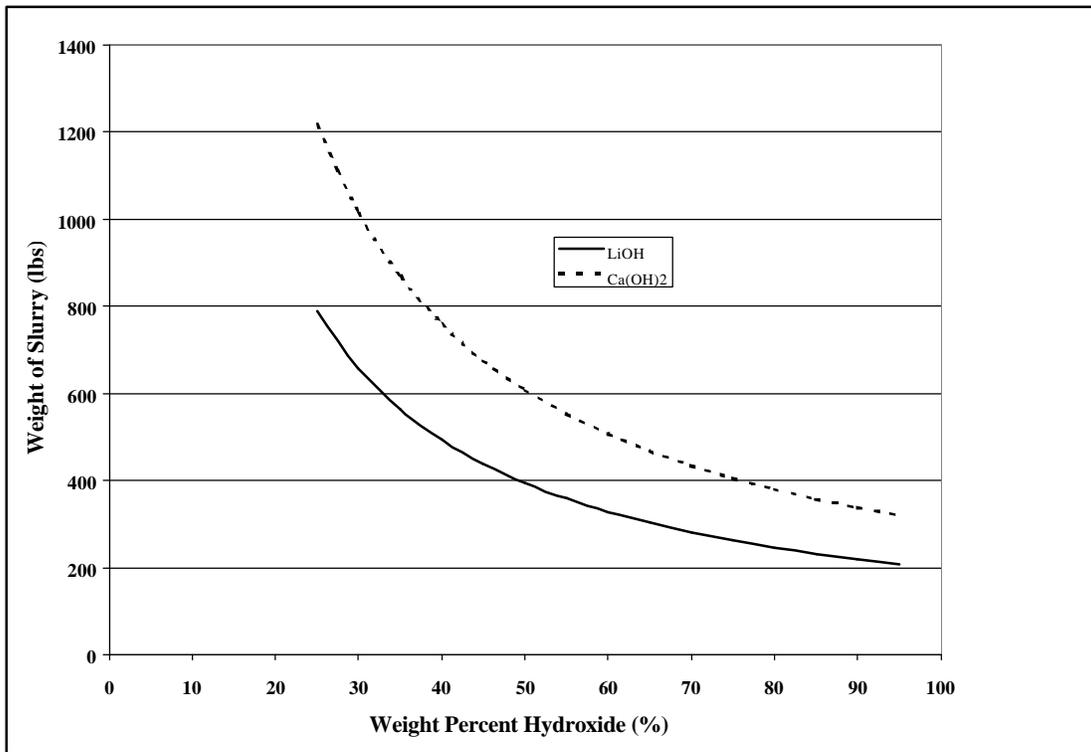


Figure 3. Weight of Hydroxide Slurry Representing 1MMBtu Hydrogen

If it is then assumed that the hydrides are regenerated by the aforementioned processes in Wyoming, and then slurried in mineral oil and shipped back to Massachusetts, analogous calculations can be performed on these hydrides. The densities of LiH and CaH₂ are 0.82 and 1.7 grams/cc, respectively. The hydrides are slurried in mineral oil, having a density of 0.82 (Breault, 1999). The hydrides are, of course, insoluble in the mineral oil. The volume and weight relationships between the hydride/mineral oil slurries and MMBtu of hydrogen are shown respectively in Figures 4 and 5. These data show, for example, that 16.03 gallons of a 60% by-weight LiH slurry would need to be regenerated to eventually produce 1 MMBtu of hydrogen. This amount of slurry would weigh 110 pounds. For a CaH₂ slurry, a 70% slurry would require 23 gallons, and would weigh 247 pounds.

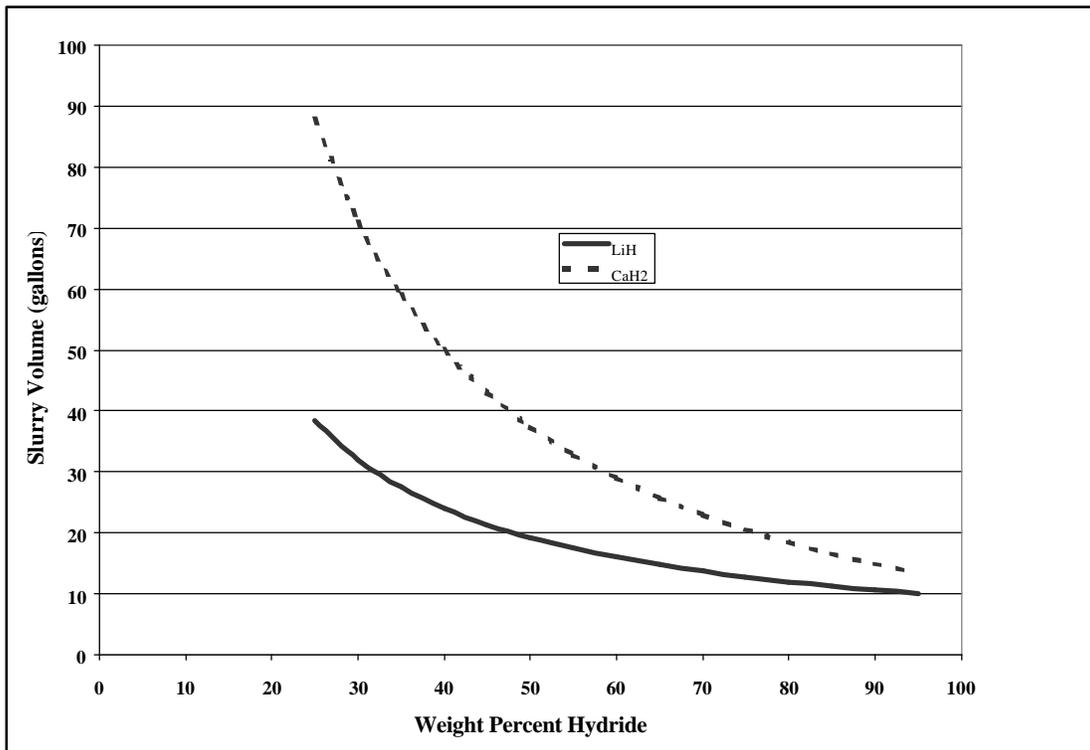


Figure 4. Hydride Slurry Volume Resulting in 1 MMBtu Hydrogen

In considering the cost of transporting the hydroxide and hydride slurries, an assumption will be made that the cost of transporting slurry is the same as transporting coal. This represents a lower limit of the cost. This is because coal transportation is assumed to occur on open rail cars with no cover, the rail cars are not lined with any material to protect them from corrosion, and there is no pre-treatment of the coal to reduce dust or exposure along the way. Transporting the slurries would presumably have to involve some protection of the rail-cars from the slurry and may necessitate other types of controls such as covers or sealed vessels to minimize exposure to the elements. Thermo Power has suggested (Breault, 1999) that the slurries could be carried in a tarp-covered rail car. The equivalency of the coal cost to the slurry transportation cost allows us

to evaluate the economics of this option under highly optimistic conditions. If the economics under these favorable conditions do not turn out to be attractive then it is difficult to see how the cost could be improved to make this option competitive with the cost of transporting the coal from west to east.

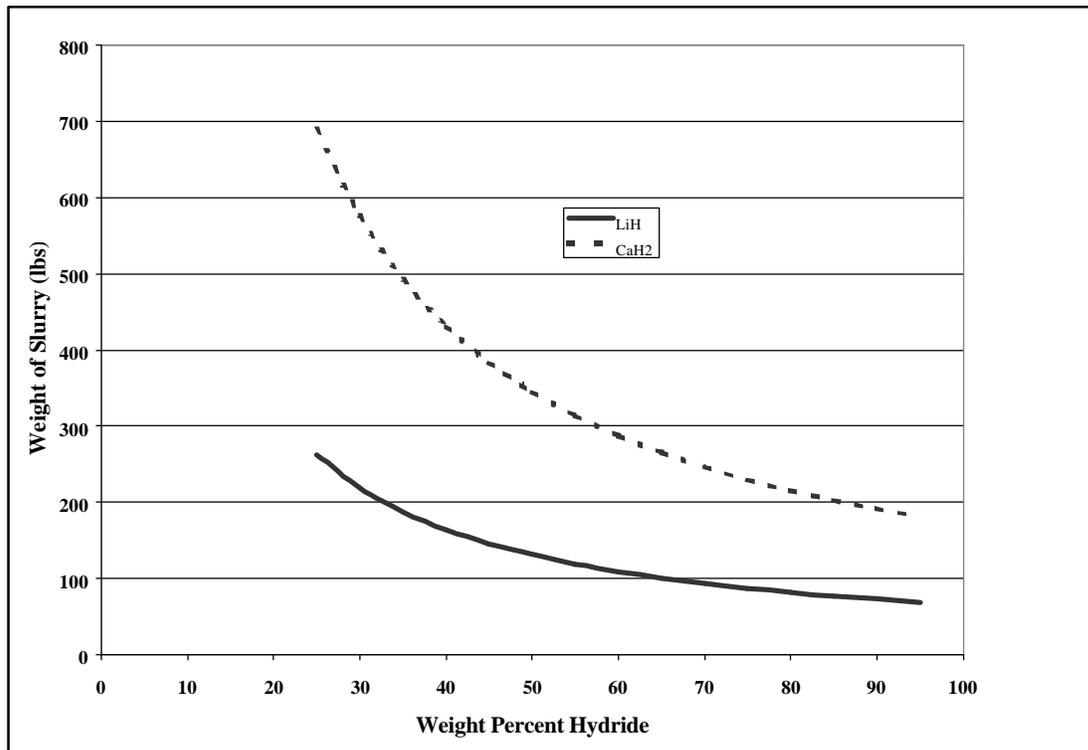


Figure 5. Weight of Hydride Slurry Representing 1 MMBtu Hydrogen

Recall that the cost of shipping coal from Wyoming to Massachusetts was \$20.30 per ton (not including the cost of the coal at the mine mouth). So this number, \$20.30 per ton, can serve as the lower limit of the shipping cost of the slurries. It has been estimated (Breault, 1999) that the relative slurriabilities of the hydrides and hydroxides are about the same; LiH will produce a slurry with about the same ease as LiOH, etc. Using this, the weight of the hydroxide slurry can be added to that of the hydride slurry at any particular loading to get an estimate for the round-trip weight requirement per Btu of hydrogen. The curves relating slurry loading to the equivalent hydrogen cost are presented in Figure 6. Again, looking at the base cases, the 60% lithium slurries would incur a transportation cost of \$4.45/MMBtu hydrogen, and the 70% calcium slurries would incur a transportation cost of \$6.91/MMBtu.

Comparison of Costs/Conclusions

Finally, comparisons can be made of moving slurries back and forth to Wyoming from Massachusetts with the options of moving the Wyodak coal east, and using the “char” that

Thermo Power initially proposed. Recall, that if all the fixed carbon in the coal is converted to hydrogen, the cost of moving the coal east is \$3.76/MMBtu hydrogen. This would then be less expensive than the cost of either the 60% lithium slurry or the 70% calcium slurry. The \$2.30/MMBtu hydrogen cost for the char is cheaper yet. However, if the conversion rates of the carbons are less than 100%, the slurry transportation option becomes more feasible. This is because a slurry transportation cost is not a function of carbon conversion.

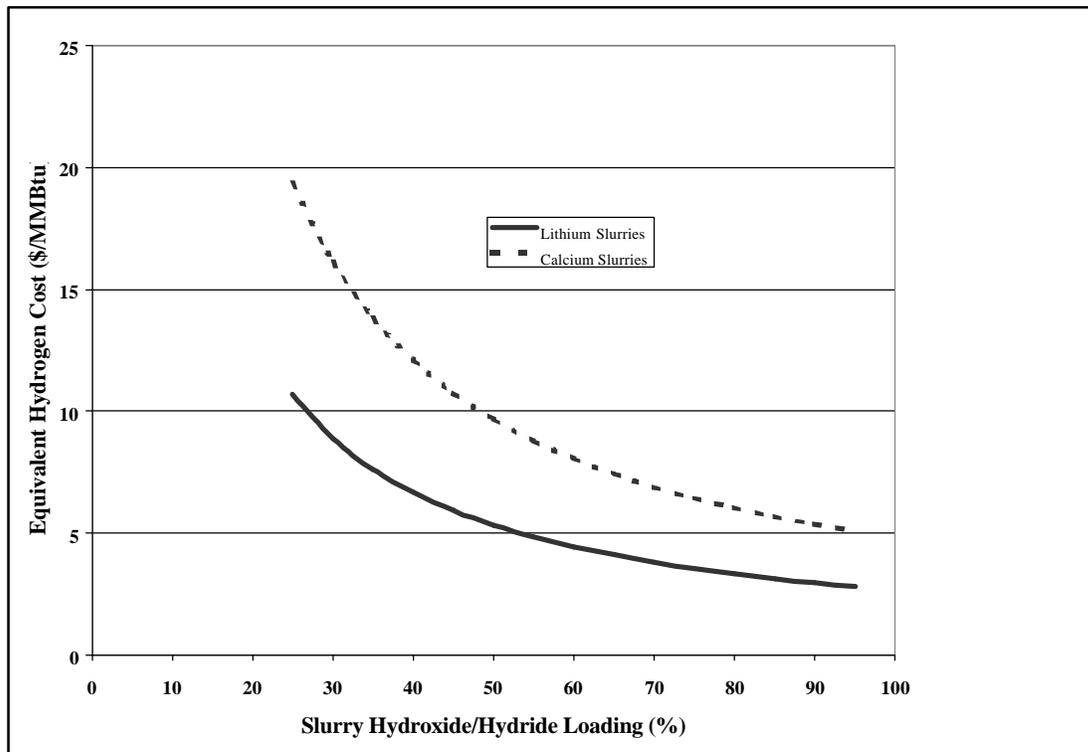


Figure 6. Cost of Round Trip Transport of Lithium and Calcium Slurries

Figure 7 presents the sensitivity to carbon-conversion efficiency of the equivalent transportation costs of Wyodak coal and “char” as compared to 50, 60, and 70% lithium and calcium slurries. As can be seen, transport of 60% lithium slurries become the less expensive option for conversion efficiencies of less than 85% of the Wyodak fixed carbon, and for less than 55% of the char. For the 70% calcium slurries to become the less expensive option, the conversion efficiency of the Wyodak fixed carbon would have to be less than 57%, and the char conversion would have to be less than 35%.

If the carbon-conversion level is low, the process is likely not economical. Thus it would be less likely that shipping slurries is a good option. This is especially true when one considers the fact that this analysis does not consider any additional transportation-related costs involving making the slurries or shipping them under optimal conditions. If these factors are added, the slurry lines

in Figure 7 move upward, making the intersections occur at even lower values of carbon conversion.

It would seem then, that using the char would be the least expensive option. Recall, however, that we are only dealing with transportation costs or equivalent transportation costs. Further analysis would include information on the conversion processes. For instance, if a high conversion percentage were possible for the Wyodak coal at the mine mouth, and this conversion – presumably a pyrolysis process – also produced salable hydrogen (or another salable product), the net cost of transporting the slurries including the hydrogen “credit” may be lower.

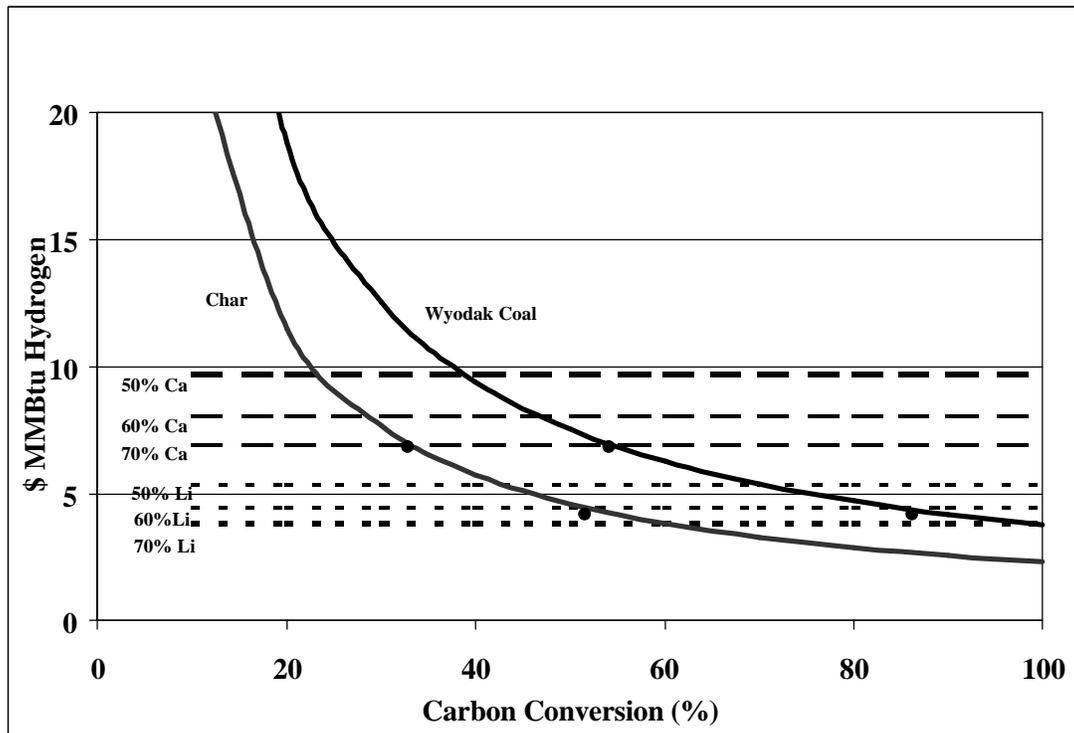


Figure 7. Comparison of Transport Cost as a Function of Carbon Conversion

It should also be noted that this analysis only deals with long-range transportation cost: 1490 miles. Since delivered coal prices are so dependent on transportation, shorter distances will likely present a different picture.

Future Work

Technical Assessments

Two more technical assessments will be performed during the balance of Fiscal Year 1999. Following this, it is planned to continue the assessments, perhaps on a somewhat increased basis.

It is also time to begin revisiting some of the projects that have not been visited for two or three years.

Low-rank Coal Analysis

The low-rank coal analysis is not nearly completed yet. Several more variables need to be looked at. Thus, the analysis will be continued to consider:

- variable transportation distances,
- a process for converting the low-rank coal to a char, and the cost of this process,
- a cost of the char as a function of transportation distance, and
- the incremental cost of an inefficient regeneration process.

Acknowledgements

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