SANDIA NATIONAL LABORATORIES HYDROGEN STORAGE DEVELOPMENT PROGRAM

QUARTERLY PROGRESS REPORT FOR OCTOBER-DECEMBER 2007.

TASK 1.2 COLLABORATIVE WEBSITE SUPPORT (STORAGE CENTERS & PROJECTS QUICKPLACE)

AUTHOR: MARCINA MORENO

At the request of DOE, Sandia National Laboratories developed the Storage Centers & Projects QuickPlace (QP) in May 2005 for the purpose of sharing information among hydrogen storage colleagues in a password protected environment. Sandia maintains the membership list as approved by DOE and provides posting services upon request for each of the restricted member private rooms. Marcina Moreno (mamore@sandia.gov) is the point of contact for DOE and room managers for membership authorizations, training and other concerns.

Since the user tracking website commenced February 2006 (https://sierra-nk.son.sandia.gov/QuickPlace/h2storage-sl/Main.nsf/h_Toc/9883355257F03FD280256CFB005221E3/?OpenDocument), the site has recorded 1091 hits from its primary membership base.

TASK 2 DOE ROUND ROBIN TESTING PARTICIPATION

There was no activity under this task during Q1 of FY 2008.

TASK 3: IEA AND OTHER DOE DUTIES –GARY SANDROCK

AUTHOR: GARY SANDROCK

SUBTASK 3.1 IEA(HIA)/DOE/SNL HYDRIDE DATABASES

Reference: http://hydpark.ca.sandia.gov

The Hydride Information Center, a US contribution to the IEA HIA, was established in 1995 with DOE funding and a Sandia National Laboratories web server. It has been a widely-used and well-known tool of the hydride community ever since. It is my job to peruse the hydride literature and periodically update the databases, as well as answer user inquiries on the contents. The Meetings & Symposia database, especially useful for travel planning purposes, was updated once during this reporting period. Bimonthly Meetings updates will continue during FY2008, but all other updating will be suspended during my upcoming Detail at DOE HQ (see Subtask 3.2). George Thomas will be working with SNL on revising the operational properties of HYDPARK. He will represent the IEA Project at the next two Experts' Workshops.

SUBTASK 3.2 IPHE AND OTHER AD HOC ASSISTANCE TO DOE

This effort has covered a number of miscellaneous activities performed for DOE and/or SNL. All work under this Subtask was to be suspended during FY2008 because I was slated be spending that period on an on-site Detail to DOE HQ (HFCIT Storage) as a limited-term-employee of Oak Ridge National Laboratory. However, a personal health problem and incomplete DOE approval have resulted in a postponement of the start of the Detail until the second Quarter of FY2008. During the last Quarter, I participated in the MHCoE meeting held at SNL/CA December 11-12, 2007.

TASK 4 STORAGE CONSULTATION – GEORGE THOMAS

AUTHOR: DR. GEORGE J. THOMAS

Contribution unavailable

TASK 5 IEA / IPHE PARTICIPATION

SUBTASK 5.1 HYDROGEN MATERIALS: COMPLEX ANIONIC HYDRIDES

AUTHOR: EWA RONNEBRO

The objective of this subtask is to support participation at the IEA HIA Task 22 Experts Meetings and report on progress on the search for new light-weight, high-capacity complex metal hydrides for reversible on-board hydrogen storage guided by theory. We are participating with Project H-31: Borohydride Materials Discovery and Development.

Novel, light-weight, high-capacity metal hydrides have been determined to be potential candidates for on-board materials that will shrink the growing gap between experimental result and the desired goals. For our project, the discovery process involves preparation methods in the solid state; mainly ball milling and the high-pressure sintering technique ($P < 140MPa$, $T < 773K$). By utilizing different ball milling approaches in collaboration with our MHCoE partners, we are able to control the size of the particles which is crucial for creating diffusion paths for hydrogen. The high-pressure vessel that enables six sample holders has been proven to be an effective tool for discovering/screening for new hydrides in different ternary systems.

We have decided to abandon our attempts in the ternary Si and Ge systems because these new materials phases only contained very small amounts of hydrogen, thus not worthwhile to pursue. Instead, we are focusing our new materials effort on new bialkali borohydrides and mixed alkali transition metal borohydrides.

<u>Calcium borohydride</u>

We are continuing our work on calcium borohydride which has potential to be absorbed/desorbed by a specific reaction route, resulting in theoretical 9.6wt% hydrogen. We are underway to characterize thermodynamics, kinetics and cycle life to understand how useful this material is for reversible on-board storage at more moderate temperatures and pressures.

By ball milling for a longer time before heat treating under high-hydrogen pressures, we were able to increase the yield of $Ca(BH_4)_2$ using the previously patented reaction route of reacting CaB_6 with CaH_2 and catalyst.

We prepared pure, crystalline $Ca(BH_4)_2$ as earlier described by heating up a sample of $Ca(BH_4)_2(THF)_2$ in vacuum. We submitted a manuscript to PRB in December 2007 which describes three different polymorphs of $Ca(BH_4)_2$ at different temperatures, as revealed by *in-situ* synchrotron data (ESRF). We are underway characterizing decomposition products in collaboration with our MHCoE partners and other collaborators: NMR & in-situ NMR (JPL/Caltech), in-situ XRD (GE) and neutron vibrational spectroscopy (NIST). Moreover, at Sandia, we are currently performing desorption/absorption experiments and in our first attempt, we observed desorption in vacuum starting at ca315C and thereafter partial absorption (re-hydrogenation) starting at ca 315C under 90bar H-pressure. We are currently reproducing this experiment and will perform XRD on desorbed and re-hydrided samples, as well as calculate weight percent hydrogen.

Monte Carlo - DFT structure prediction for new materials searching

A publication has been submitted to Physical Review Letters on the discovery of a low energy crystal structure for Mg(BH4)2, titled "First-principles prediction of a ground-state crystal structure of magnesium borohydride." The prototype electrostatic ground state (PEGS) search technique, using distance scaling method (DSM) Monte Carlo (MC) identified the lowest energy structure (I-4m2). First-principles calculations indicate the PEGS structure to be 5kJ/mol lower in total energy at 0K than the observed P61 structure, indicating a potential new ground state.

The PEGS method has also identified NaK(BH4)2 and LiK(BH4)2 compounds as potentially stable materials. First-principles T=0K calculations indicate decomposition into mono-cation borohydrides is weakly exothermic. The four highest symmetry crystal structures from the PEGS search for NaK(BH4)2 are, from lowest to highest symmetry, R3, R-3, P3m1, and R-3m. Remarkably, all generated structures are trigonal, belonging to the same fundamental lattice type. The total DFT energies, at T=0K, of the four structures are ordered monotonically with the crystal symmetry, with the highest symmetry R-3m having the lowest energy. The P3m1, R-3, and R3 structures have a T=0K total energy of 76, 80, and 110 meV per formula unit above the R-3m structure, respectively. Using the lowest energy R-3m structure for NaK(BH4)2, and ignoring the phonon contribution to the total free energy, we have calculated the energy for the decomposition reaction of NaK(BH4)2 into NaBH4 and KBH4 to be near -3kJ/mol formula unit at T=0K. This indicates that the decomposition will proceed spontaneously. However, zero point energy (ZPE) phonon contributions can be in the range of 5kJ/mol for these compounds due to low Z elements and resulting high vibration frequencies, and the potential for a stable compound could not be ruled out initially.

Samples of NaK(BH4)2 were prepared by mechanical milling of NaBH4 and KBH4 using a SPEX high energy ball mill. Raman spectra of prepared material indicated BH4 anion vibrations. X-ray diffraction (XRD) peaks not belonging to NaBH4 or KBH4 from prepared materials indicated the existence of a new phase. Correlation of the peak positions with those of the predicted structures suggested a Rietveld refinement of the XRD data was necessary, and suggests that R3 may be the correct structure. Time resolved XRD also indicated that the material spontaneously decomposed into NaBH4 and KBH4 after approximately 14-24 hours. Interpretation of the data is ongoing, and a publication is in progress. The PEGS method has correctly predicted the existence of a metastable NaK(BH4)2 compound.

Exploration of new bialkali borohydrides

Objective: We are exploring bialkali borohydrides to find new high-capacity hydrogen storage materials by solid state reactions predicted by the above described PEGS method.

$NaK(BH_4)_2$

A new bialkali borohydride of $NaK(BH_4)_2$ has been predicted, as described above, to be almost stable by the Monte-Carlo technique (Eric Majzoub, UMSL) and was recently synthesized via a ball milling technique to introduce a potential candidate for a hydrogen storage material. The material was previously characterized using X-ray diffraction and Raman spectroscopic techniques. The proximity of the values of the Raman and XRD peaks of $NaK(BH_4)_2$ to peaks associated with KBH_4 indicates this new compound has crystalline features more similar to KBH_4 rather than $NaBH_4$.

From an experimental evaluation of the above proposed potential structures of $NaK(BH_4)_2$, it is clear that $R3$ give the best fit between the observed and calculated patterns, judging from the considerably lower R_B-value and better fit between observed and calculated diffraction patterns as compared to R-3 and R-3m. The plot from the Rietveld refinements is shown in Figure 2. The R_B values for $R3$, R-3 and R-3m respectively were: 26%, 44% and 40% refined to obtain the same unit cell parameters. The difference plots (not shown here) of R-3 and R-3m are very similar, and so are their respective R_B values. The cell parameters for $NaK(BH_4)_2$ were refined between $2\theta = 0.3\text{-}75°$ in space group $R3$ ($Z = 3$) to: $a = 4.615(2)$ and $c = 22.39(2)$ Å. R-values of $R_B = 25.6$ and $R_F = 21.4\%$ were obtained for the metal atom structure. It was to some extent possible to refine displacement factors and atom coordinates.

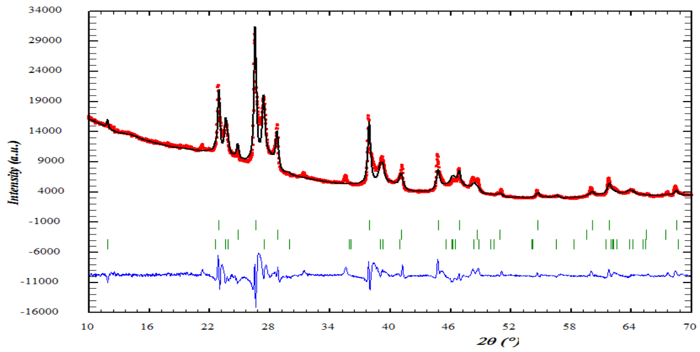

Figure 2. Difference plot from Rietveld refinements of from top to bottom: KBH_4, $NaBH_4$ and $NaK(BH_4)_2$. $NaK(BH_4)_2$ was refined in *R*3 with unit cell parameters a = 4.615(2) and c = 22.39(2) Å.

However, the calculated peaks at 2θ = 11.83° and 22.56° cannot be observed in the X-ray pattern. Thus, a new attempt was made to refine the structure in a unit cell with half the *c*-axis, similar to a suggestion from TREOR. The procedures were the same as described above. This resulted in considerably lower R-values (%) for all the three space groups: *R*3; R_B = 15.4 and R_F = 12.6, *R*-3; R_B = 11.0 and R_F = 9.49, *R*-3*m*; R_B = 13.4 and R_F = 10.1. In average, this gives: R_B = 11-15% and R_F = 9.5-12.5% which is acceptable for a pattern of amorphous character and without hydrogen atoms completing the true structure. It was possible to refine atom coordinates, but the displacement factors were not stable and had to be locked. The sample contains 33% of $NaK(BH_4)_2$, 56% of KBH_4 and 10% of $NaBH_4$.

The difference plots are identical, so it was not possible to distinguish between the three rhombohedral structures, since the metal atom structures are very close to each other. Figure 3 shows one of the plots from the Rietveld refinements. Neutron diffraction data would bring clarity in the true structure, but since the sample is metastable it would be difficult to collect data. It's important to note that the bonding distances become unreasonable short in the smaller unit cell, and thus it is more likely that the larger unit cell better describes the crystal structure.

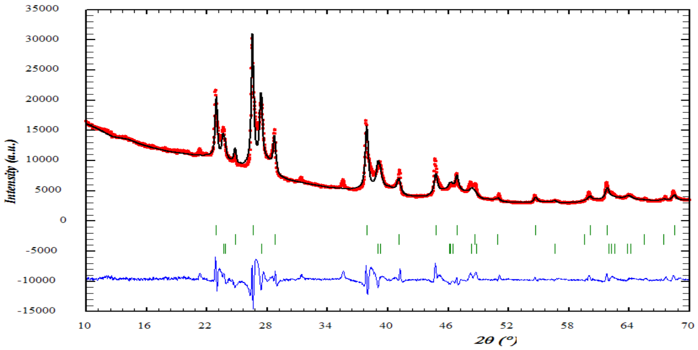

Figure 3. Difference plot from Rietveld refinements of from top to bottom: KBH_4, $NaBH_4$ and $NaK(BH_4)_2$. The plots of *R*3, *R*-3 and *R*-3*m* are similar, so here only one of them is shown. The unit cells were refined to a = 4.612(2) and c = 11.193(8) Å.

LiK(BH₄)₂

We also successfully prepared $LiK(BH_4)_2$ by ball milling $LiBH_4$ and KBH_4 in a similar way to preparing $NaK(BH_4)_2$. Powder X-ray diffraction and Raman spectroscopy (Figure 4 a) confirmed formation of a stable phase which has also been reported by Prof. Edwards group at U. Oxford, UK (Poster by Nickels et al at ISHE, Richmond, VA, Nov-07). We also collected Neutron Vibrational Spectra in collaboration with Terry Udovic (NIST) and NMR in collaboration with Bob Bowman (JPL)/Son-jong (Caltech). Figure 4b) shows TGA and DSC curves. DSC shows endothermic phase transitions at 100 and 110C and one major exothermic transition at 450C and a minor at 430C, the latter associated with a minor weight loss, according to the TGA curve. It doesn't seem like there is a major hydrogen loss within 500C, so this is not a promising material for reversible H-storage. We are underway summarizing the results for publication.

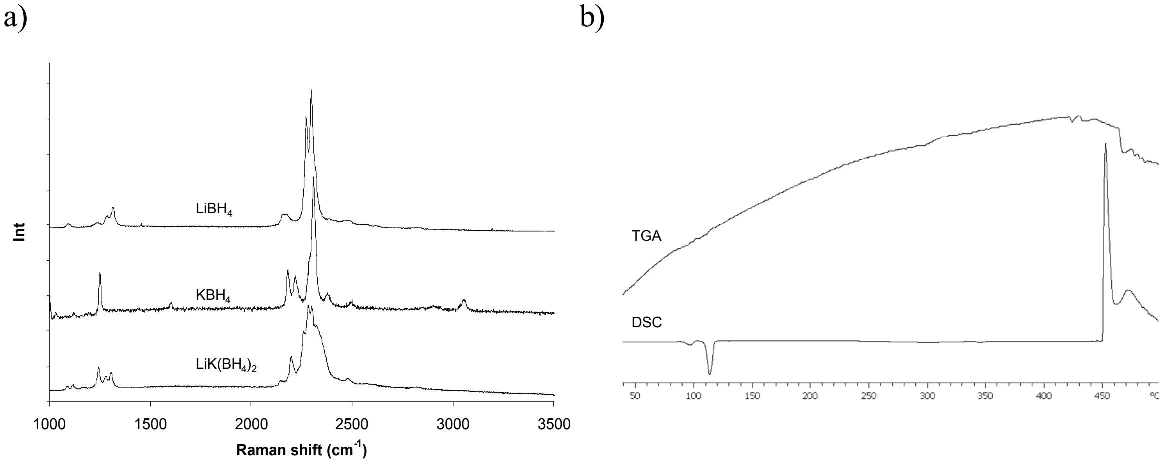

Figure 4. a) Raman Spectroscopy of $LiBH_4$, KBH_4 and $LiK(BH_4)_2$ and b) TGA and DSC curves of $LiK(BH_4)_2$.

Mg-containing Materials

In collaboration with U. Geneva and Stockholm University we are investigating Mg-containing materials. We are planning on submitting an abstract to MH2008 on a new high-yield route to prepare Mg_2FeH_6 (work done in 2004 at SNL) and how dopants effect kinetics (work done at U. Geneva).

TASK 6 – DEVELOP GENERALIZED METHODS AND PROCEDURES TO INVESTIGATE SAFETY PROPERTIES OF HIGH ENERGY DENSITY STORAGE MATERIALS (PHASE I)

AUTHOR: DANIEL DEDRICK

Program background

This program is structured to develop generalized methods and procedures that are required to quantify the contamination reaction properties of hydrogen storage materials to enable the design, handling and operation of effective hydrogen storage systems for automotive applications. The project is divided into two phases; during Phase I, generalized analysis methods and procedures will be developed and validated based on current state-of-the-art materials. During Phase II, new materials will be identified and modifications, additions, and/or deletions to the capability will be integrated with the developed methods and procedures. Each phase is organized into four tasks: Task 1 focuses on quantifying chemical processes and kinetics of contamination reactions. Task 2 will seek to quantify the hazards associated with low-level life-cycle contamination. Task 3 will predict processes during accident scenarios by developing validated highly coupled physical process numerical models. Task 4 seeks to identify and demonstrate hazard mitigation strategies that are appropriate for a broad spectrum of hydrogen storage materials. This program was initiated in Q4 of FY07.

Summary of accomplishments

The first quarter of FY08 included efforts in three task areas as summarized below.

Task 1 – Baseline decomposition measurements were made on two new hydrogen storage materials in preparation for oxygen and water contamination experiments. A new method was developed for characterizing the reactions between oxygen gas and solid-state hydrogen storage materials.

Task 2 – The operation of the cycling station assembled in Q4 of FY07 (Figure 3 below) was validated utilizing a complex metal hydride with well-characterized hydrogen sorption properties.

Task 3 – The flow-through reaction manifold was completed and prepared for testing. Calculations were carried out to determine tube lengths required to mix contaminants with air before entering the sample. Estimates were made for the permeability of AlH_3 and the pressure differential required to drive a gas flow through it. Initial calculations were performed to predict particle trajectories in reactive dust clouds utilizing Fuego, a code developed at SNL.

Detail of results in each task

First quarter efforts in ***Task 1*** utilized the Simultaneous Thermo-gravimetric Modulated-Beam Mass Spectrometry (STMBMS) Laboratory. Baseline decompositions of two samples of α -AlH_3 were performed in preparation of oxygen and water exposure testing. The decomposition of the de-stabilized BNL alane formulation was compared to the DOW Chemical sourced alane. It was determined that the time-dependence of the rate of evolution of hydrogen from the BNL alane is more complex than for the Dow alane. Additionally, hydrogen evolves from BNL alane at a temperature that is ~50°C lower than that of Dow alane as predicted by literature (Figure 1). Various combinations of sodium and lithium salts evolve at higher temperatures. The temporal behavior of the hydrogen evolution from the BNL alane indicates that a least two different processes may be controlling the rate of release. Baseline decomposition experiments were also performed on another new material synthesized at SNL, $2LiBH_4 + MgH_2$. Results of these baseline measurements will be compiled in Q2 of FY08.

A new method was developed to quantify oxygen contamination reactions. The new method involves decomposing Ag(II)O in the presence of the hydrogen storage materials to investigate the reactions associated with oxygen gas. The thermal decomposition of Ag(II)O is shown in Figure 2. Utilizing the newly developed reaction cell, the oxygen evolving from the Ag(II)O can be utilized to quantify the oxidation reaction rates. This method will be combined with the previously identified sodium bicarbonate method to isolate and quantify the reactions of hydrogen storage materials with oxygen and water. Second quarter efforts will focus on demonstrating these methods on the new hydrogen storage materials.

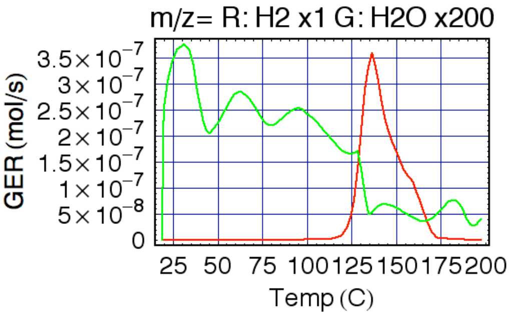

Figure 1 - Baseline decomposition of BNL sourced α - AlH_3 in preparation for contamination experiments

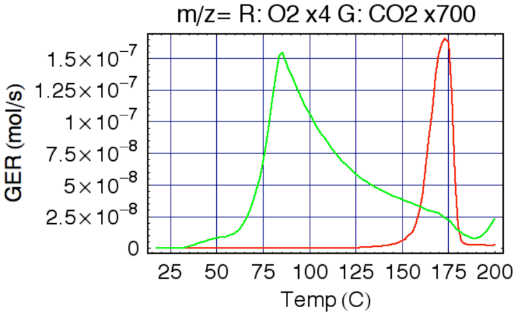

Figure 2 - The decomposition of silver oxide (II), AgO was identified as an appropriate method of insitu oxygen exposure

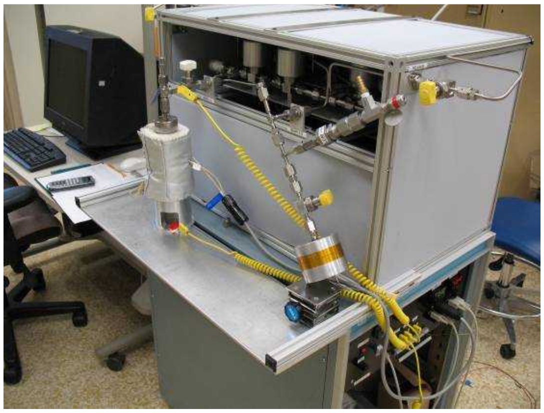

Figure 3 - Automatic Sieverts-style apparatus dedicated to the production of contaminated and un-contaminated samples

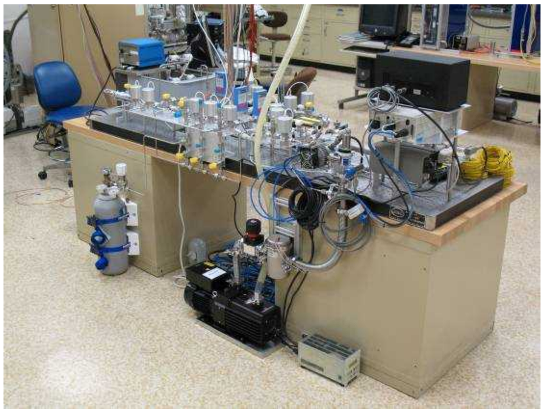

Figure 4 - Flow-through manifold utilized to characterize bulk contamination reaction processes

The operation of the ***Task 2*** Sieverts cycling apparatus assembled in FY07 Q4 was validated utilizing sodium alanates in the first quarter of FY08. The system is utilized to produce highly-cycled contaminated materials (e.g., Li_3AlH_6+3$LiNH_2$) and uncontaminated hydrogen storage materials of appropriate hydrogen content and morphology. The PI, Daniel Dedrick, visited Dhanesh Chandra at the UNR this quarter to coordinate with cycling performance degradation efforts at UNR. Sandia will evaluate reaction products resulting from highly cycled samples produced by UNR.

Efforts in ***Task 3*** were two-fold in the first quarter of FY08: the flow-through reactor system was completed and prepared for testing, and scoping calculations were performed considering reactive dust clouds. The completion of the flow-through reactor (Figure 4) allows for initial testing in Q2 which will focus on gas flow through a bed of α - AlH_3 followed by air and humid air reactivity testing. For the operating conditions considered here a tube length of 50 cm was found through calculations to be required to adequately mix air with water vapor before entering the sample bed. Based on the characteristics of the Brookhaven Alane (AlH_3), which has a very small particle size, the estimated permeability of an Alane bed is very small. This means that containing an alane sample, and forcing a gas flow through it will be a major challenge that this program must overcome. This manifold will also be utilized to quantify the CO_2 mitigation reactions proposed in ***Task 4***.

The ***Task 3*** dust jet modeling effort continued in this quarter in preparation for reactive hydrogen storage material modeling efforts. During this quarter a two-phase flow consisting of a turbulent, isothermal, particle-laden jet was modeled with the Sandia massively parallel Navier-Stokes code, Fuego. This code is being used at Sandia currently to predict the transport processes in high pressure hydrogen jet flames and hydrocarbon fuel pool fires, including the radiation heat transfer from the high temperature regions. During the current year the capability to predict transport processes in propellant fires is being included. In preparation for using the code to model metal hydride tank releases, a jet of air and sand with a mass loading ratio of 0.2 was modeled. This problem was studied experimentally by Shuen et al. (1985). Distributions of gas and particle mean velocity as well as gas and particle turbulence quantities along the centerline of the jet and in the radial direction at several axial locations are available for model validation. The distribution of mean particle mass flux along the centerline of the jet was also measured. Flame propagation and potential flame acceleration in a hydride particle release depend to a large extent on the particle concentration and turbulence in the gas-particle flow. Thus it is important to be able to predict the evolution of the gas-particle flow in a turbulent jet. An example of the two-phase turbulent jet flow predicted this quarter using Fuego is shown in Figure 5. The centerline air velocity distribution is compared with the data of Shuen et al. (1985) in Figure 6. New capabilities for representative particle tracking and visualization of average particle properties have been added to Fuego recently; these capabilities will be utilized this quarter to compare particle fluxes and turbulence quantities with the data. Once the isothermal jet validation is completed, a particle-laden jet with heat transfer will be validated.

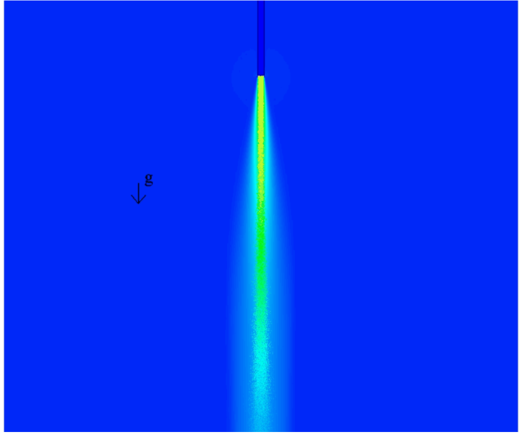

Figure 5 – Turbulent air-sand jet directed vertically downward; particles are colored by axial particle velocity; mass loading ratio of 0.2; jet Reynolds number $Re_d=1.8x10^4$.

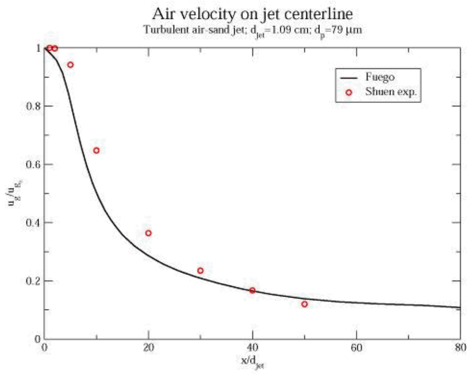

Figure 6 – Distribution of axial component of air velocity along centerline of air-sand turbulent jet; mass loading ratio of 0.2.