Aluminum Hydride

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BROOKHAVEN NATIONAL LABORATORY

Project ID # ST 034

Overview

Timeline

- Project start date: FY10
- Project end date: Continuing

Barriers

MYPP Section 3.3.4.2.1 On-Board Storage Barriers:

- Weight & Volume
- Efficiency
- Durability/Operability
- Charge/Discharge Rates

Budget

- Funding received in FY11
  - $300K (DOE)
- Planned Funding for FY12
  - $150K (DOE)

Target

Formulate 60% by wt. AlH_3 slurries that have viscosities less than 1500 (cP) centipoise, and capable of meeting DOE's fuel cell vehicle target of a three minute refuel.

Relevance: AlH_3

– High capacity: **10.1 wt%** and **149 g/L**

– Low decomposition enthalpy:

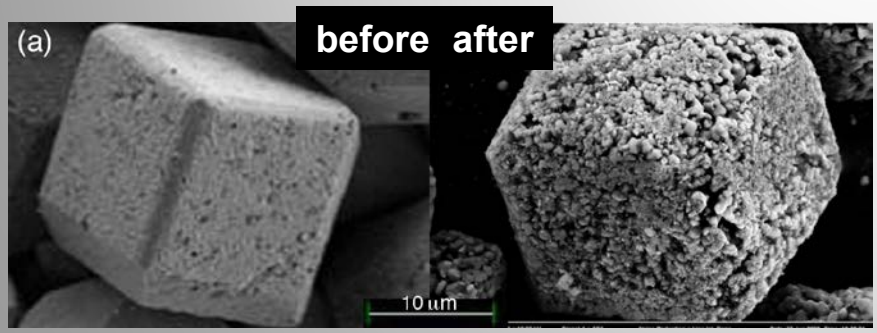
$\Delta H \approx 7$ **kJ/mol** H_2 ($\approx 1/5\ \Delta H_{NaAlH4}$)

– Rapid H_2 evolution rates at low T

Meets DOE target (0.02 gH_2/s) at <100°C

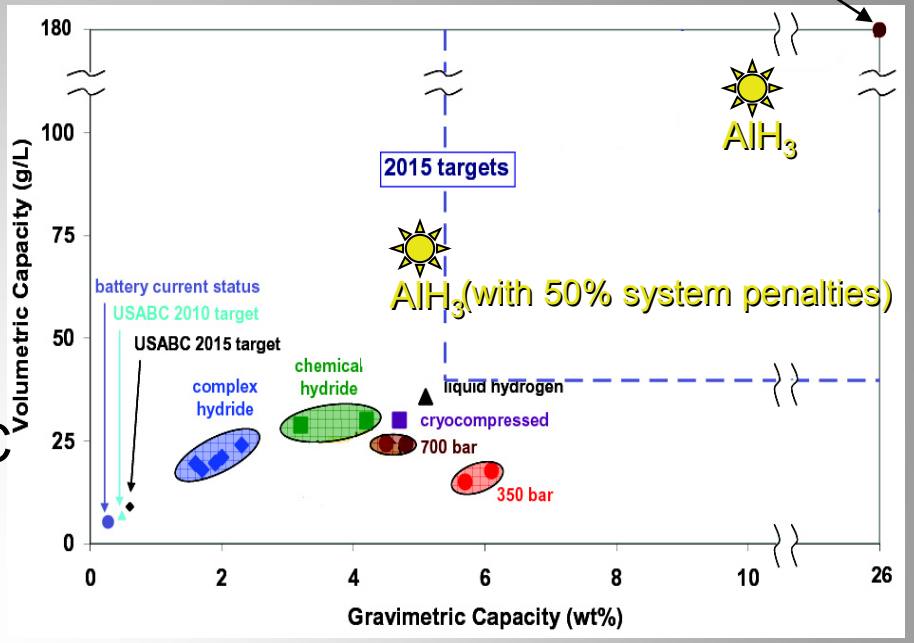
– Decomposition rates can be tuned through catalyst additions

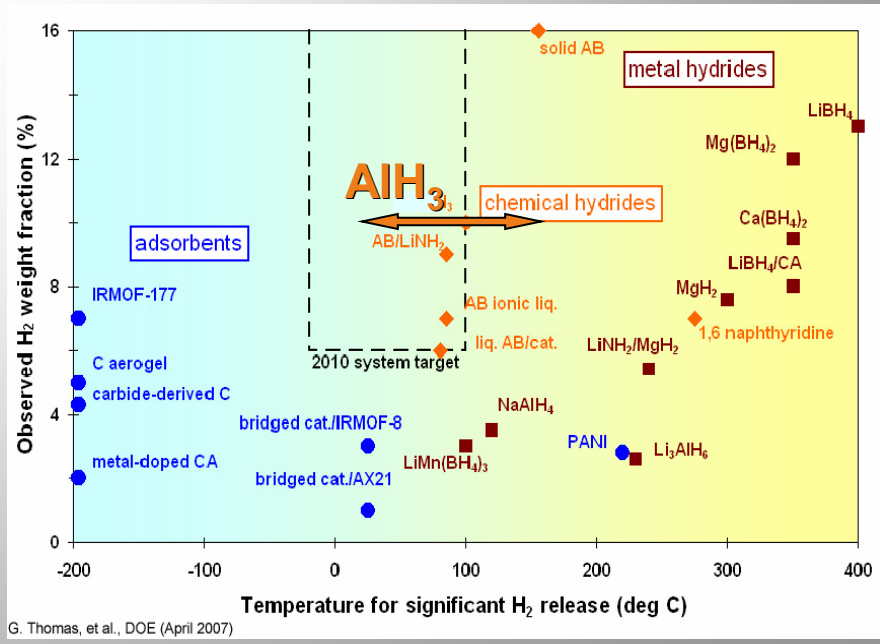
– High purity H_2 - AlH_3 decomposes to Al and H_2 (no side reactions)



Challenge: AlH_3 not "on-board" reversible and decomposition cannot be controlled by H_2 overpressure

today's vehicle systems



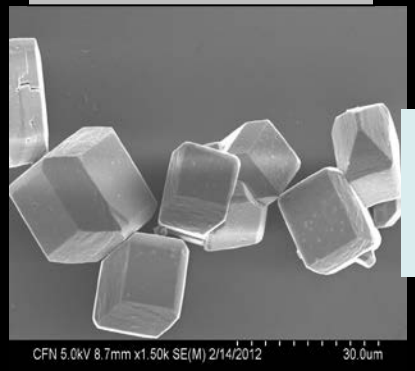


Objective: Meet DOE's 3 minute refueling target with 60% by wt. AlH_3 slurries.

Challenge: Formulate ATK-AlH_3 slurries with viscosities of 1500 centipoise or less, and determine their hydrogen desorption rate as a function of slurry formulation, catalyst loadings and temperature.

Techniques for preparing various types of AlH_3 slurries

As-received ATK AlH_3 Particles



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(5) Solvents
(1) Surfactant
(2) Catalysts

Diethylene glycol dibutyl ether (DGDE)
Dibenzyltoluene (H350)
Polydimethylsiloxane (C50S)
Mineral oil (isoeicosane)
Vacuum pump oil
Triton X-100 (surfactant)
Titanium butoxide
Lithium hydride

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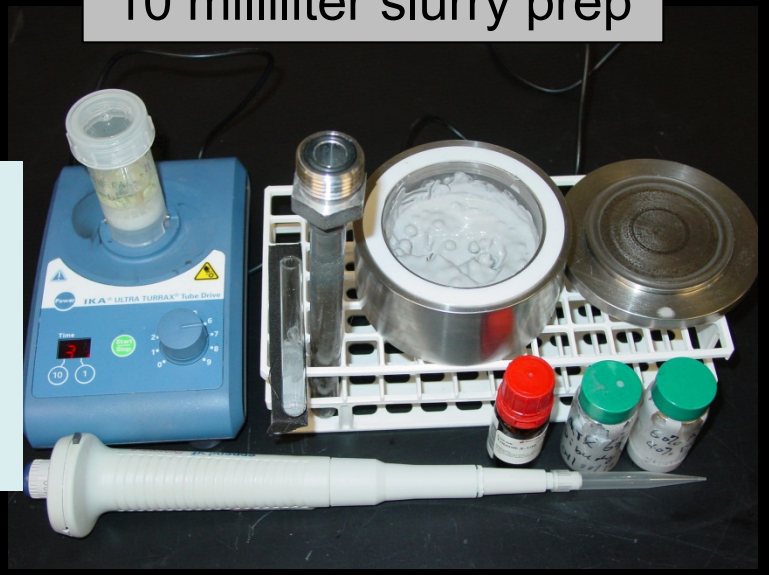
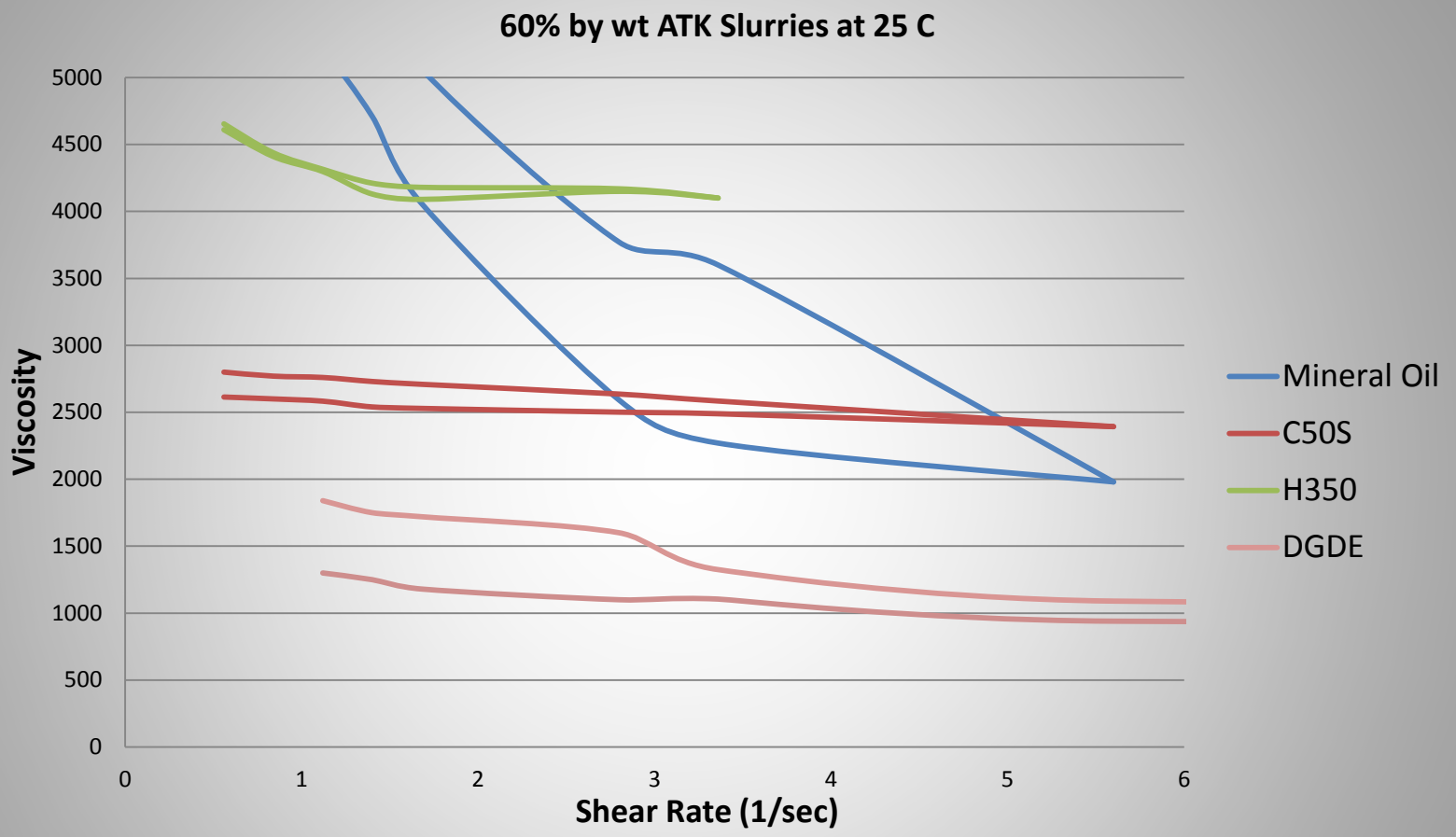
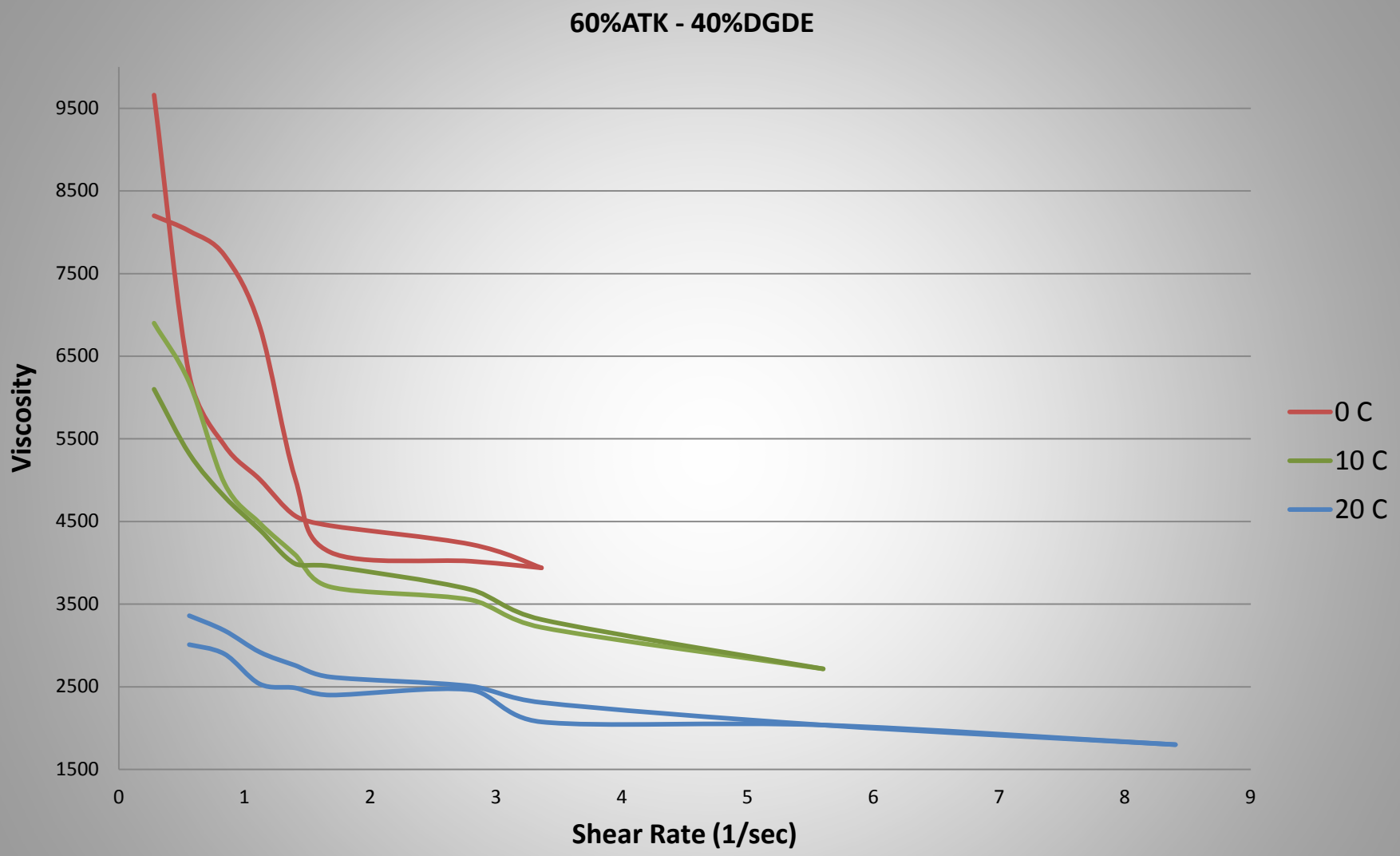
10 milliliter slurry prep

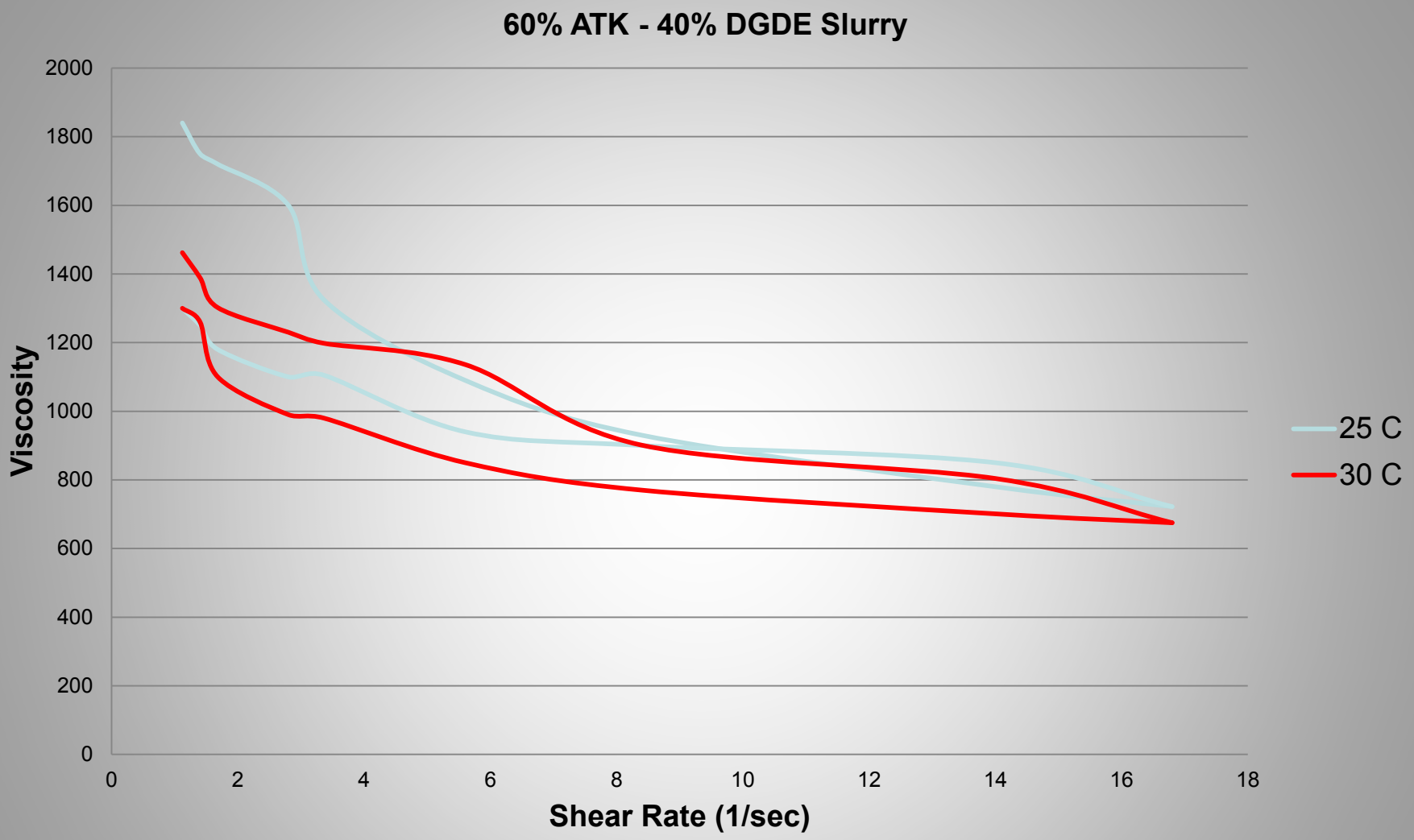




Slurry Viscosities at 25°C for Four Different Solvents



60/40-ATK/DGDE Slurry Viscosities as Function of Temperature and Shear Rate



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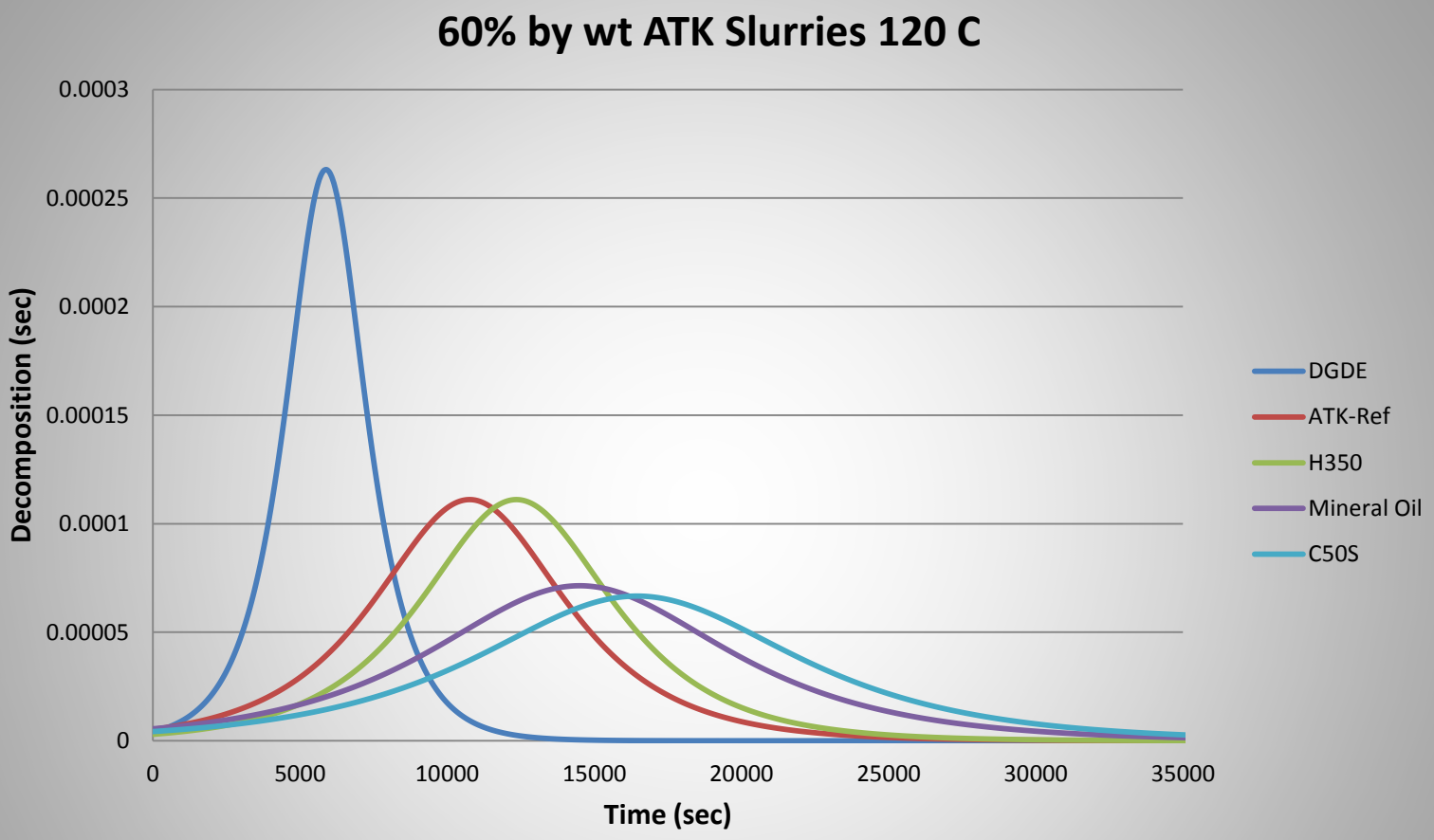
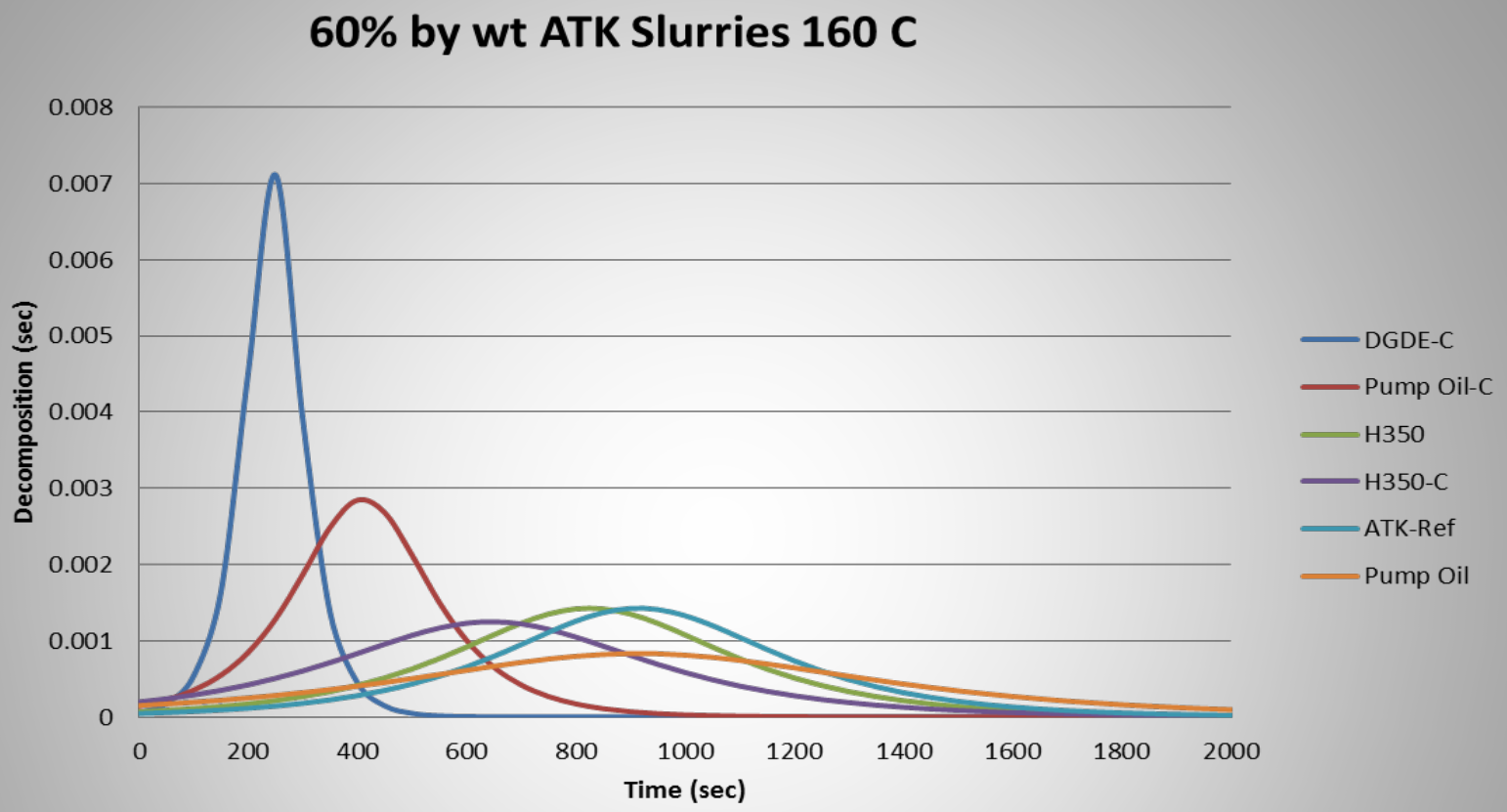
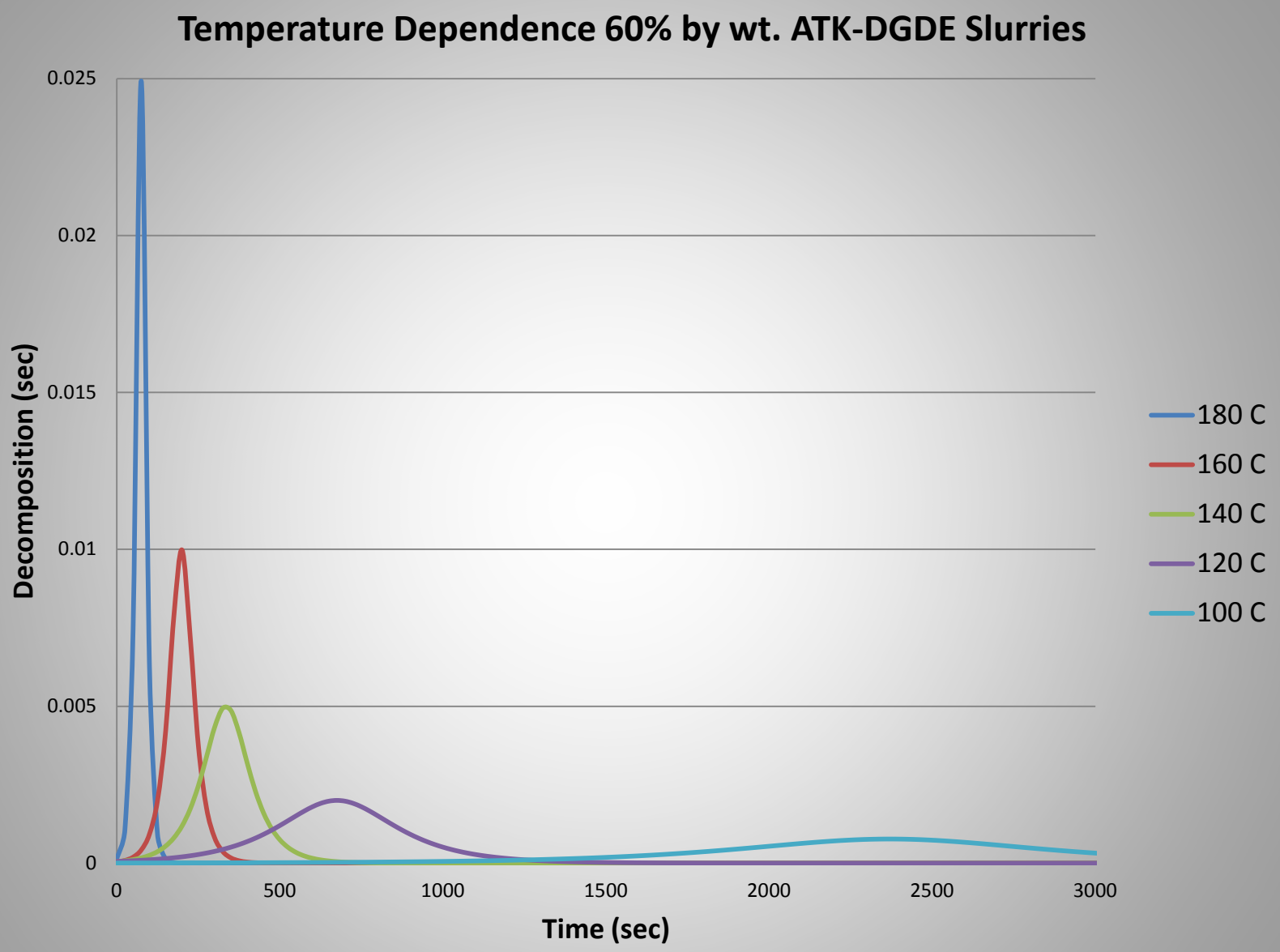


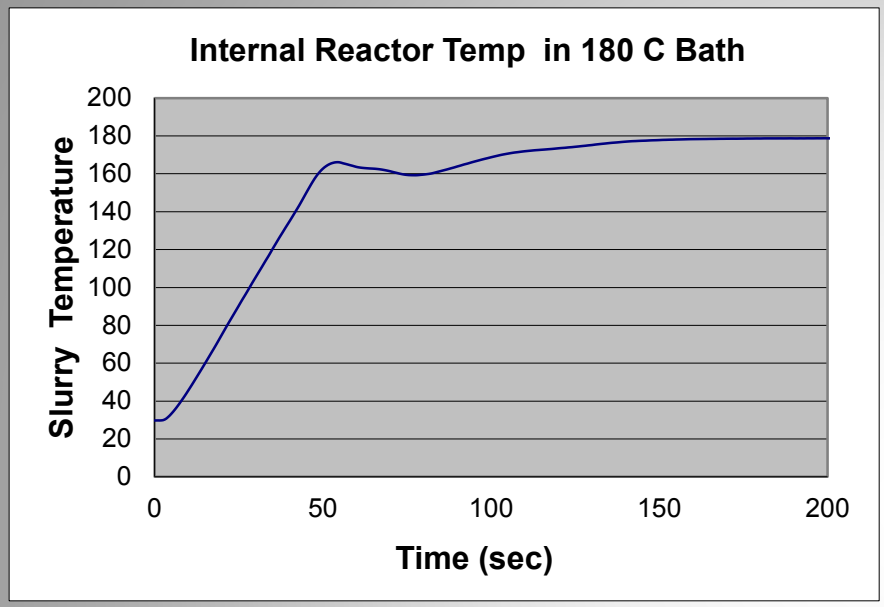
Note: ATK-Ref is the as-received dry AlH_3 particles. At 120°C only the DGDE slurry shows faster decomposition kinetics than the reference material

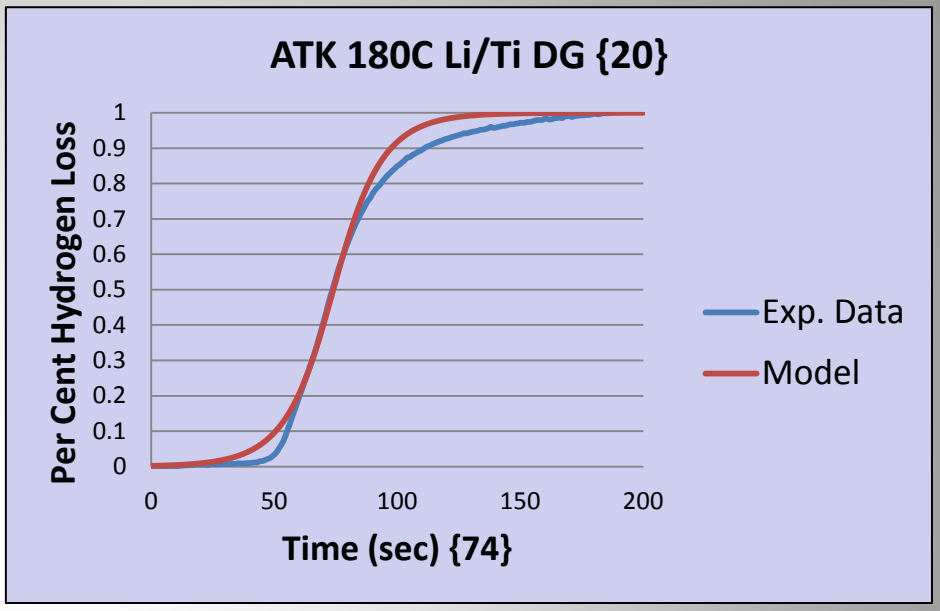


Note: At 160°C both catalyzed DGDE and catalyzed pump oil showed marked improvements over the reference dry ATK particles


Temperature Dependence 60% by wt. ATK-DGDE Slurries
Decomposition (sec)
0.025
0.02
0.015
0.01
0.005
0
0
500
1000
1500
2000
2500
3000
Time (sec)
180 C
160 C
140 C
120 C
100 C

Hydrogen Desorption Data at 180°C





The temperature rise within hydrogen desorption reactor as the AlH_3 slurry is placed in a 180°C oil bath. Note the effects of endothermic cooling after 50 seconds.

Experimental plot of the time release of hydrogen at 180°C for 60% by wt ATK slurry activated with Ti and LiH

$$\text{Model} = (2/\pi)\tan^{-1}(\exp[(\pi/2)(t-t_m)/t_k])$$

where t_k= 20 seconds

t_m= 74 seconds

& max desorption rate = $1/(2t_k)$ at $t=t_m$

Summary of Accomplishments

-Measured the viscosities for five different ATK/Solvent slurries as a function of composition, shear rate and temperature

-Identified a 60% by wt ATK in a 40% by wt diethylene glycol dibutyl ether (DGDE) slurry as having viscosities less than 1500 centipoise at 25°C

-Demonstrated 96% hydrogen release in 88 seconds at 180°C

-Demonstrated 96% hydrogen release in 2860 seconds at 100°C

Other Observations

-Overnight settling of the 15 micron ATK particles in DGDE

-Loss of solvent from bursting of hydrogen gas bubbles

Future Work

-Develop a 100 gram/week capability for synthesizing 1-10 micron AlH_3 particles.

-Improve the stability of AlH_3 slurries by lowering slurry sedimentation rate by reducing particle size from 15 to 5 microns.

-For the lower temperature range ~ 0°C maintain slurries viscosities < 1500 cP.

-Optimize procedures for activating AlH_3 slurries for enhanced hydrogen release.

Oil bath - H_2 Desorption Experiment

Acknowledgement: Special thanks to Savannah River National Laboratory for supplying 500 grams of ATK-AlH_3 used in this study.