Synthesis and Characterization of Alpha Alane

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Overview

- Introduction
- Properties of alane
- Alpha alane & history of alpha alane
- Synthesis of alpha alane at ATK Launch Systems
- Comparison of ATK alane with other materials
- Future plans

Introduction

- Aluminum hydride (a.k.a. – alane, AlH_3) is an extremely attractive material for a number of energetics applications
- Alane possesses extremely high fuel value:
  - High density for a metal hydride (ρ = 1.48 g/cc)
  - Extremely high hydrogen content (10.08% by weight)
  - ΔH_f = -2.8 kcal/mol
  - Calculated performance increase of 5%+ in I_{sp} relative to aluminum-based formulations
  - Lower O/F environments & lower flame temperatures compared to aluminum
- Alane also considered for explosives and hydrogen storage applications

Alpha Alane Polymorph

- Most promising form of alane is the alpha polymorph
  - Cubic or hexagonal crystal form
  - Possesses highest density of the common polymorphs
  - Most stable form thermally and hydrolytically

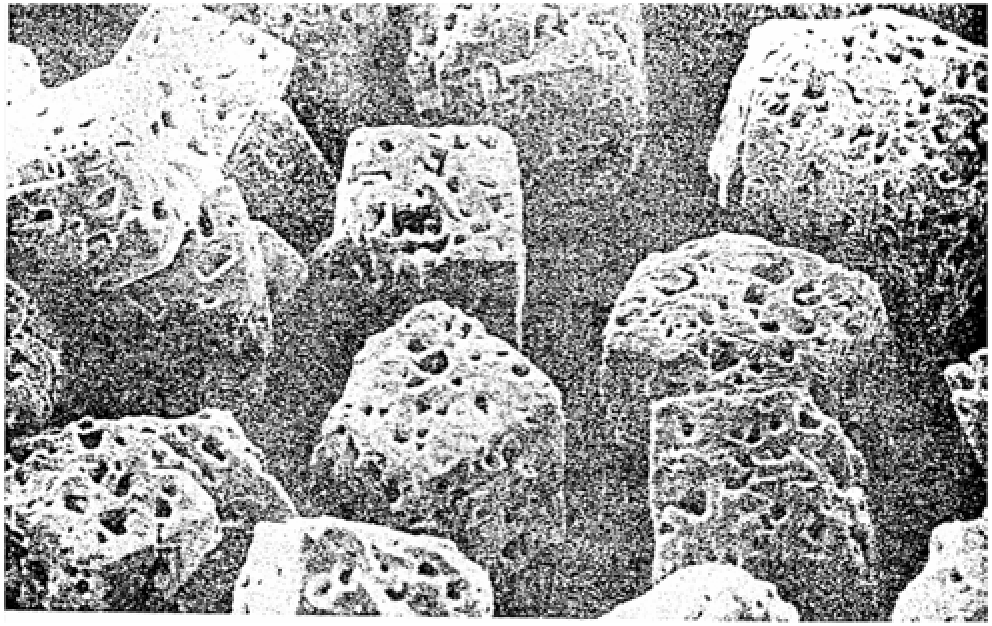
History of Alane Research in US

- Significant efforts have been expended on alane, both in US and abroad
- Dow Chemical (funded by US Air Force) in late-1960's
  - Six polymorphs of alane were identified and described
  - Alpha phase ("light metal hydride" or LMH-1451) was identified as "desired" phase & solid propellant formulations were investigated
  - High *purity* material was produced @ 1000lb/day via continuous process
    - While *pure*, the *quality* of the crystals was lacking
      - Poor morphology (porous, lower overall density (ρ = 1.474 g/cc)
      - Poor long-term stability

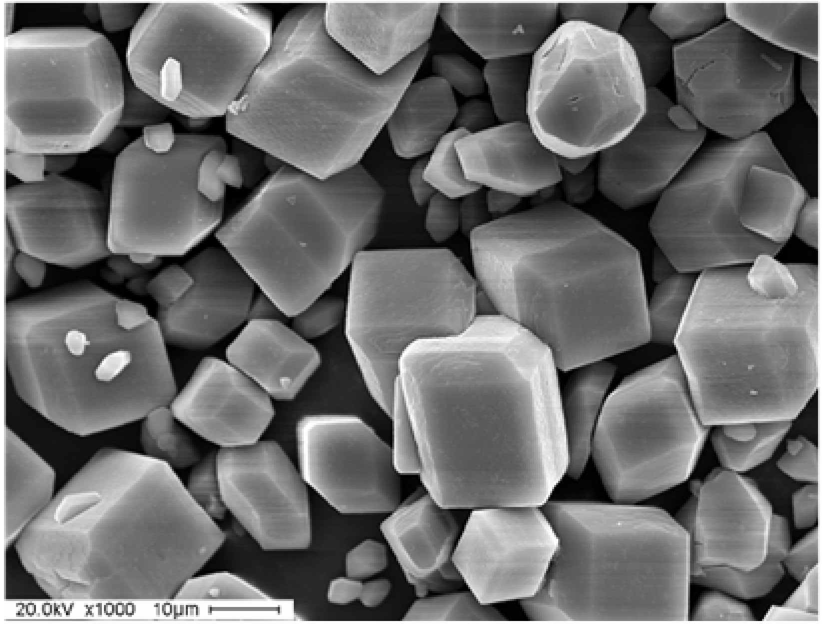
History of Alane Research in FSU

- About same time as Dow efforts, FSU conducted alane research
- Developed a process that afforded high crystal quality as well as high purity alpha alane
- Also developed passivation / thermal stabilization technology
- Successfully deployed solid propellant ballistic rocket motors based on alane
- Many of the process details remain unknown to western scientists
- Material from FSU was obtained in US in 2001

Comparison of Dow and FSU Material



Dow “light metal hydride”



FSU Alpha Alane

- Crystal quality of FSU material is superior to material made in U.S.

Properties of FSU Alane

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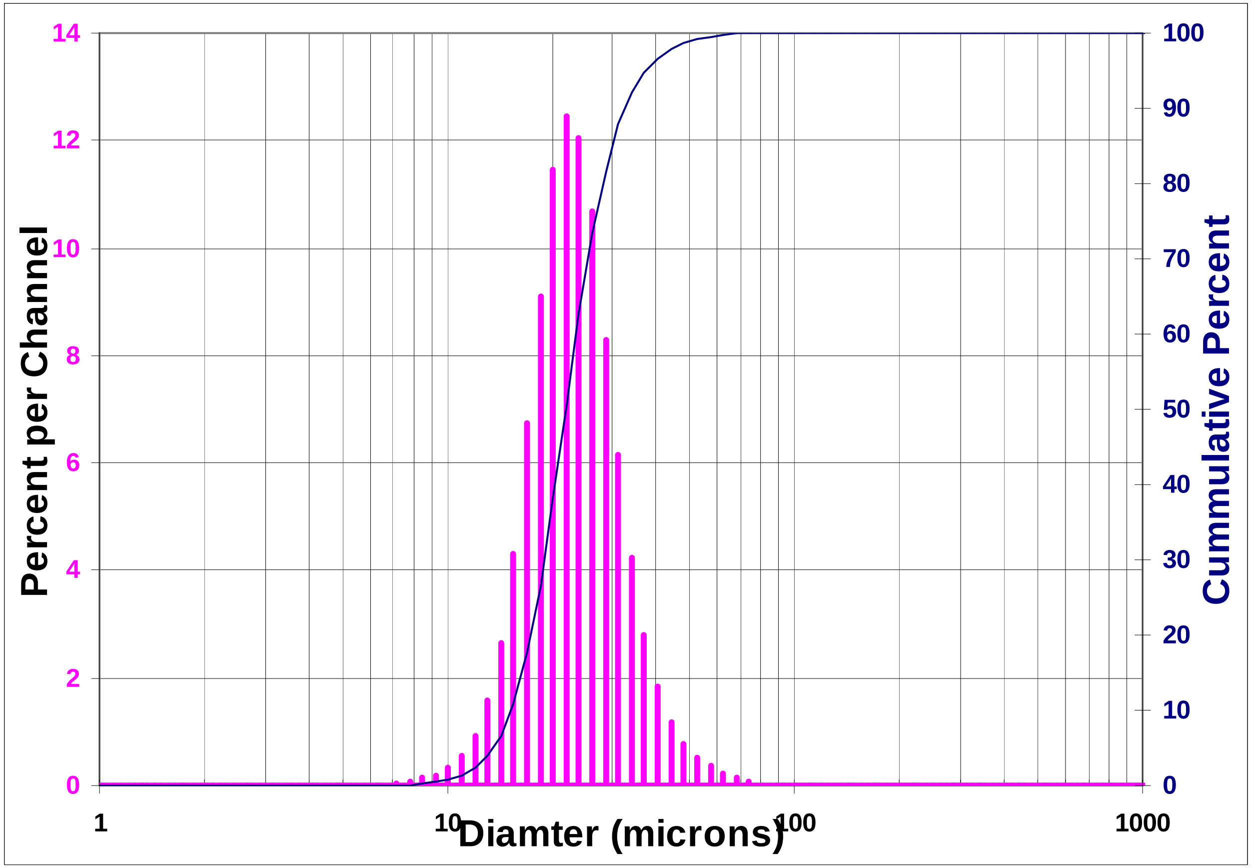

- Particle size distribution centered at 22 microns
- Average hydrogen content is 10.24% by elemental analysis

Safety Properties of Alane vs. Al & RDX

Test	Alane	Nanoaluminum	RDX reference
ABL Modified BOM Impact (TIL)	13 to 17 cm.	80 cm.	1.8 to 11 cm.
ABL Friction (psi, TIL)	100 to 180 lb @ 4 ft/sec	800 lb @ 8 ft/sec	50 to 100 @ 6 ft/sec
TC Impact (50%)	>46 in.	46 in.	28 in
TC ESD	0.03 J	0.05J	0.03 to 1.2 J
SBAT (10 F/hr)	251°F Exotherm, no ignition	>500° F	382°F
DSC (20° C/min)	Exotherm baseline departure @ 157° – 170°C, peak @ 197°C	>300° C	Exotherm baseline departure @ 216°C, peak @ 255°C

- More sensitive than nano-Al (except ESD)
- Less sensitive to impact than RDX, but more friction and ESD sensitive

TGA of Alane

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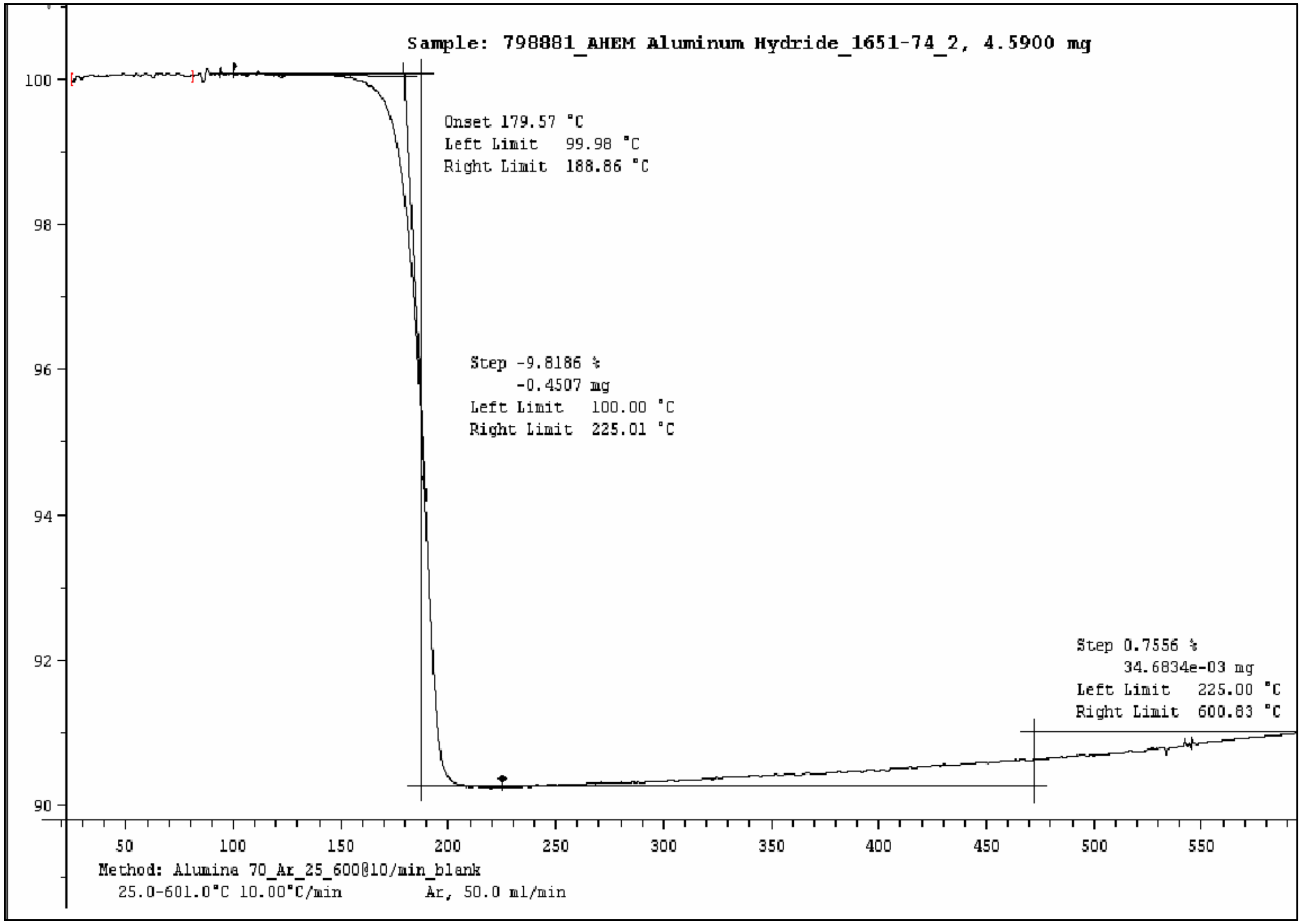
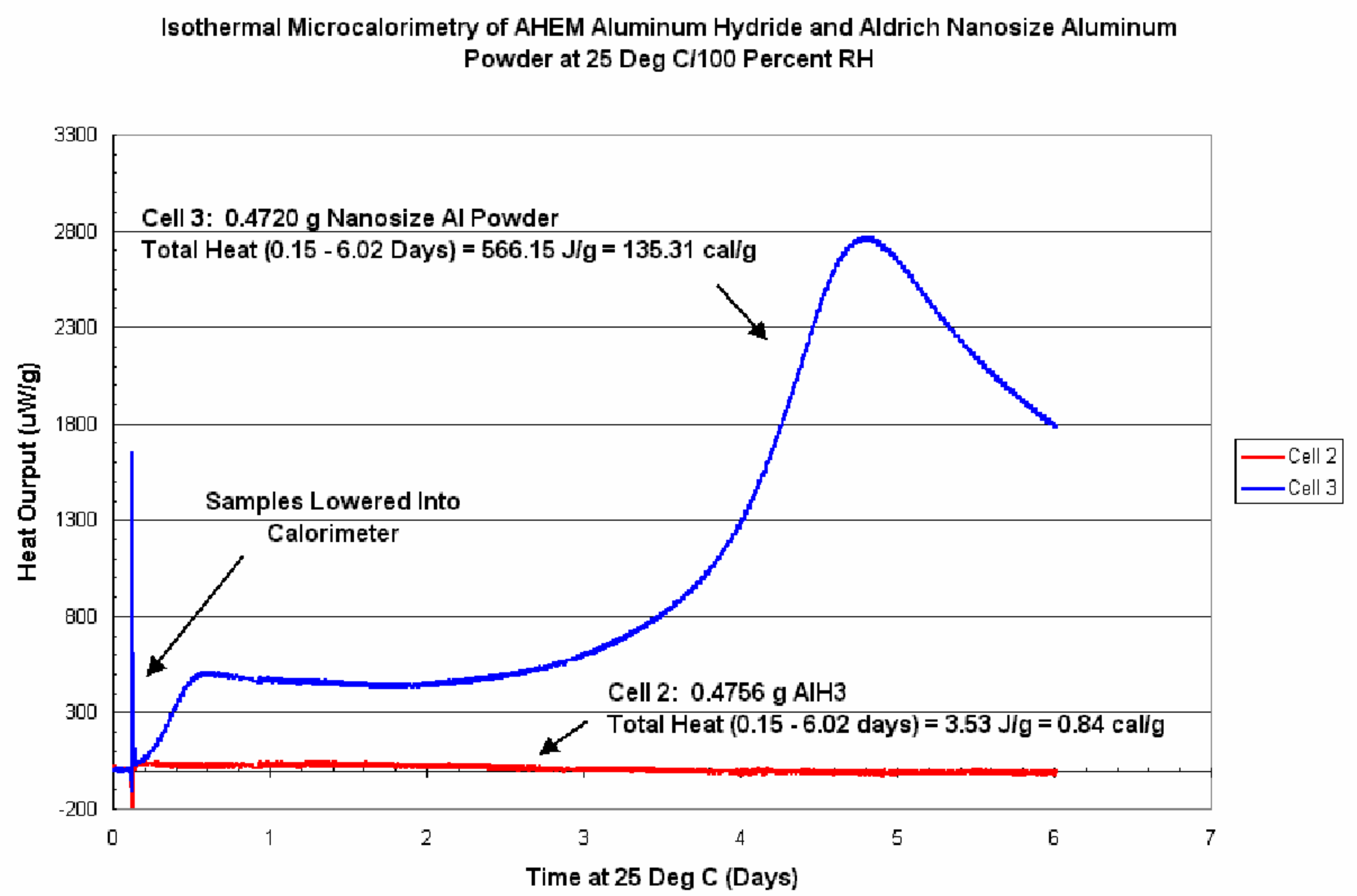


- Rapid & complete desorption of hydrogen starting at ~ 180 °C, accompanied by ~ 10% loss in overall weight

Isothermal Microcalorimetry Alane



- Little reaction after 100% RH at 25 °C for 6 days

Thermal Decomposition of Alane to Al Cubes

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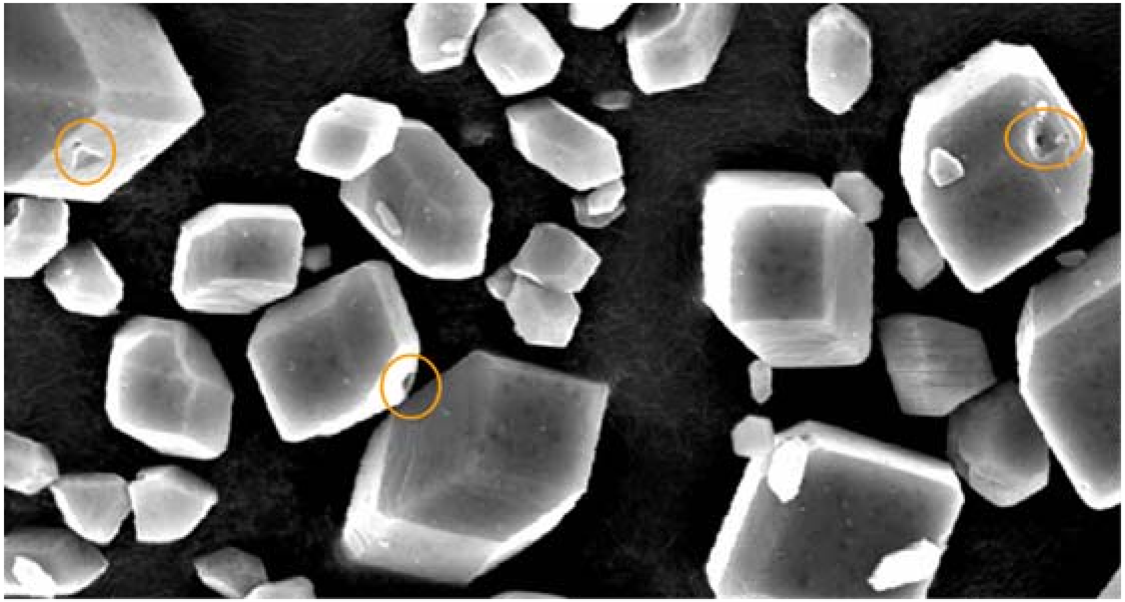
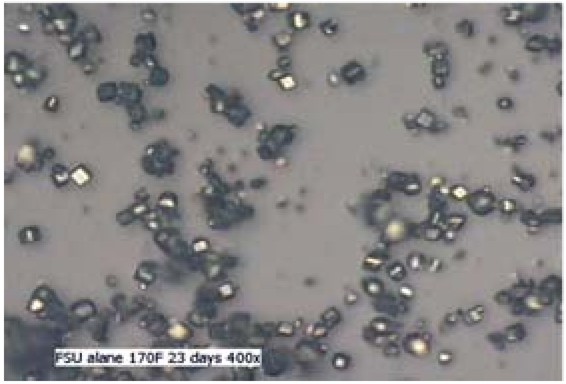
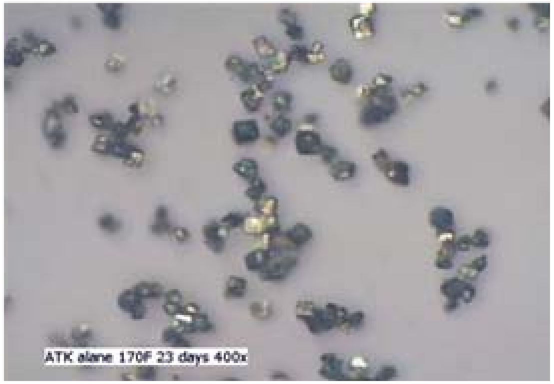






- Decomposition begins at isolated “hot spots” & leaves Al cubes

Synthesis of Alpha Alane at ATK Launch Systems

Reactor

$$3\ LiAlH_4 + AlCl_3 \xrightarrow[Et_2O]{} 4AlH_3{\cdot}Et_2O\ (\text{Complex}) + 3LiCl\downarrow + LiAlH_4$$

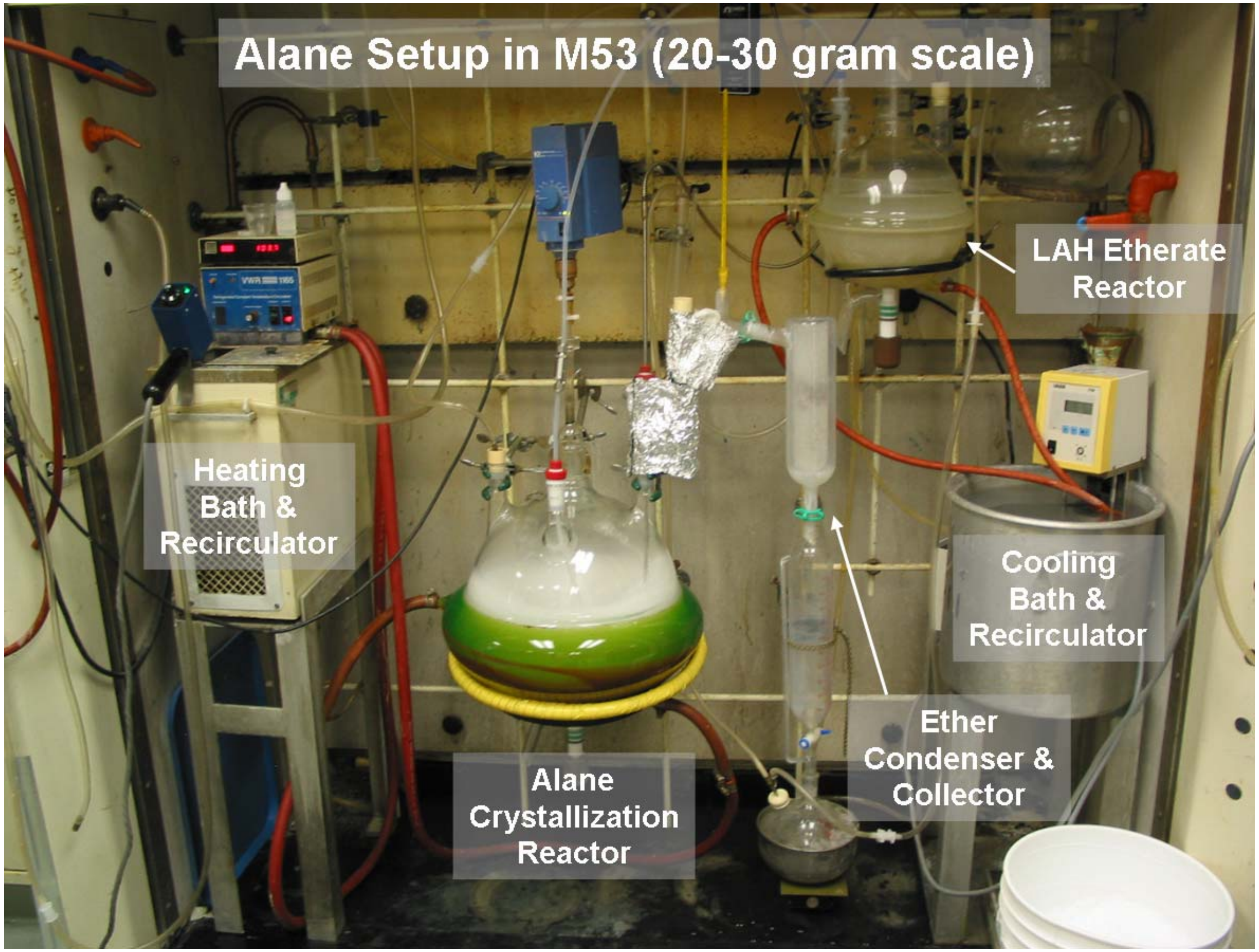
Recrystallization Reactor

$$AlH_3{\cdot}Et_2O\ (\text{Complex}) \xrightarrow[\text{Toluene}]{Et_2O\ (g)\uparrow} AlH_3\ (\text{polymeric crystalline product})$$

(transferred from reactor)

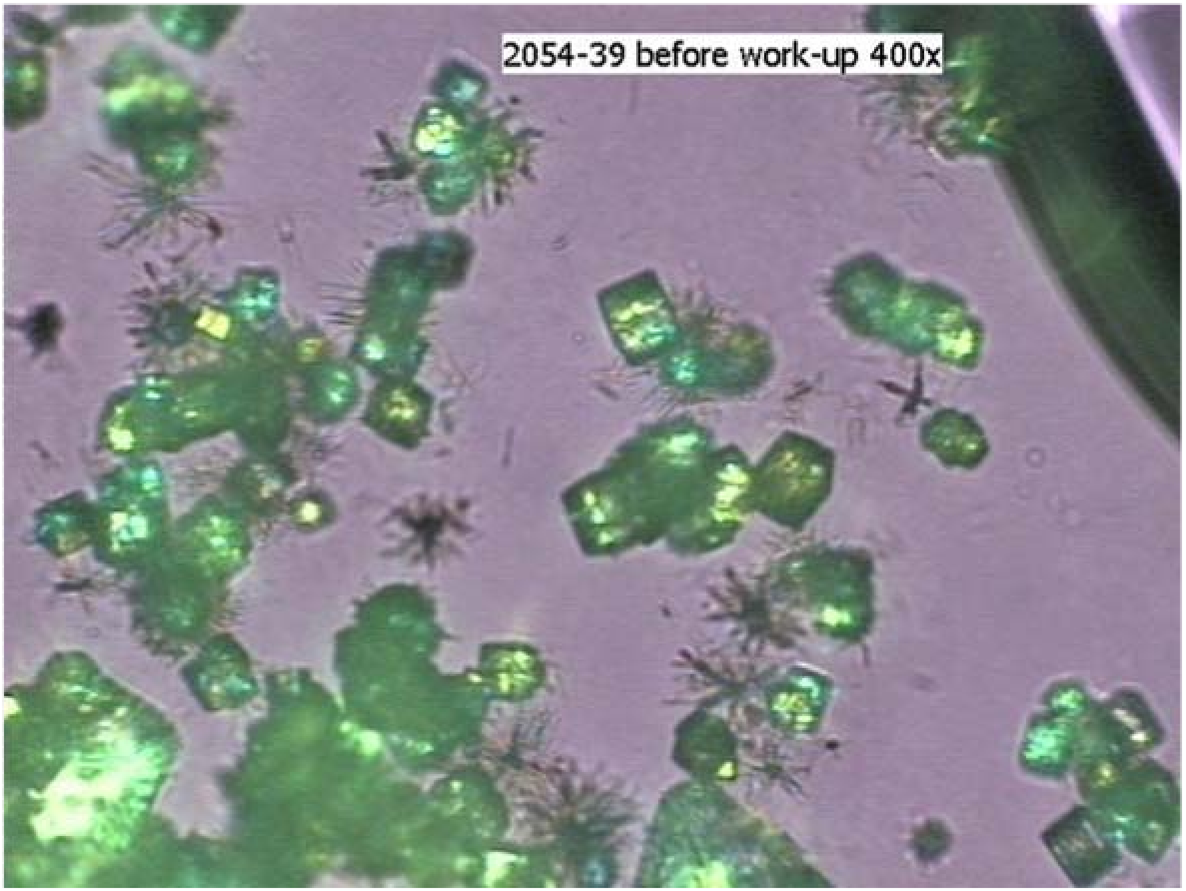
- Synthetic route based on what we know of historically used routes
- Synthesis (Step 1) followed by recrystallization (Step 2)
- Hydride-based additives used in Step 1 with varied degrees of success
- Various “crystallization modifiers” investigated in Step 2 w/ varied success

Setup for 20-30 gram Alane Synthesis



- ATK process has recently been identified which yields alpha alane reproducibly at the 1-gram, 10-gram and 25-gram scales

Visual Examination of Products



- Crude alane is typically examined by optical microscopy prior to workup with aqueous HCl

Polymorphs of Alane Encountered

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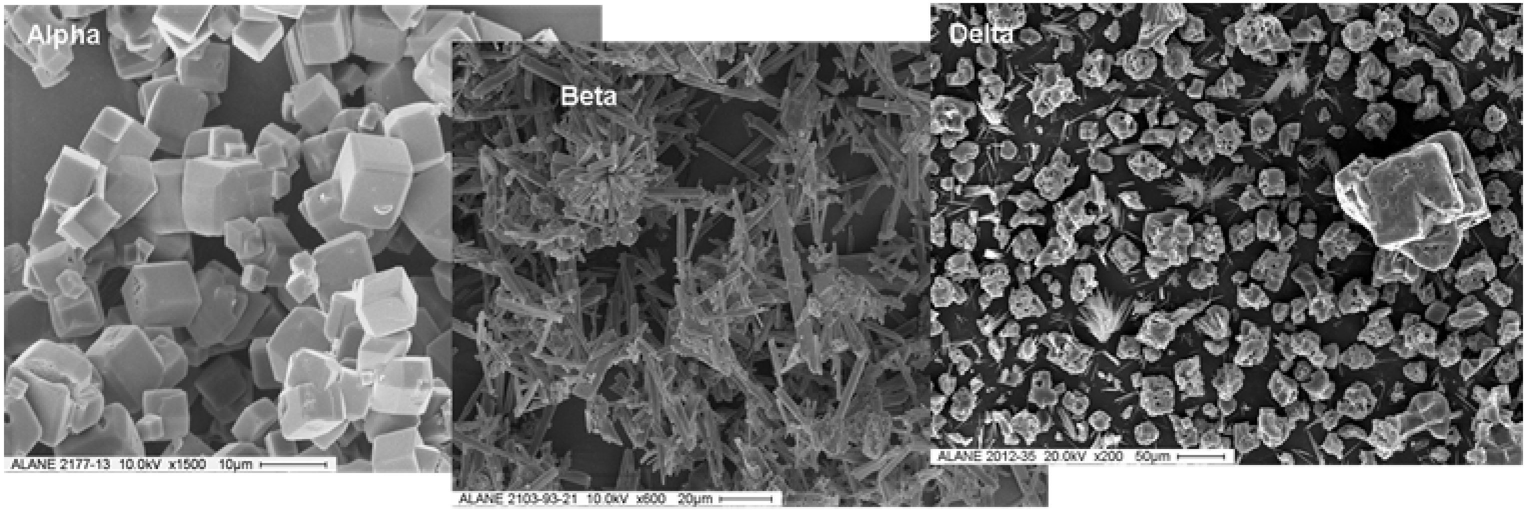
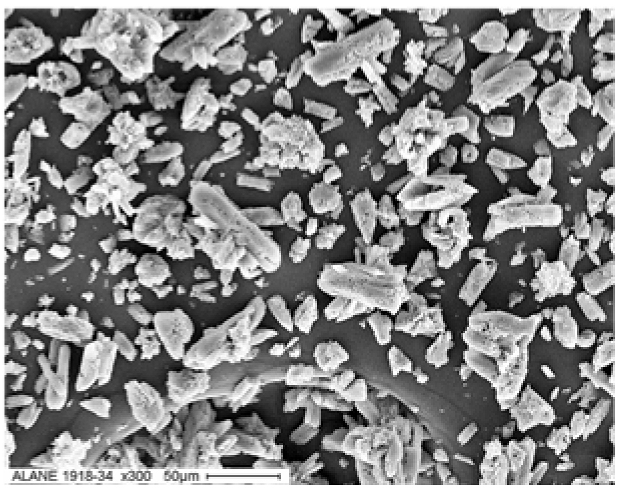
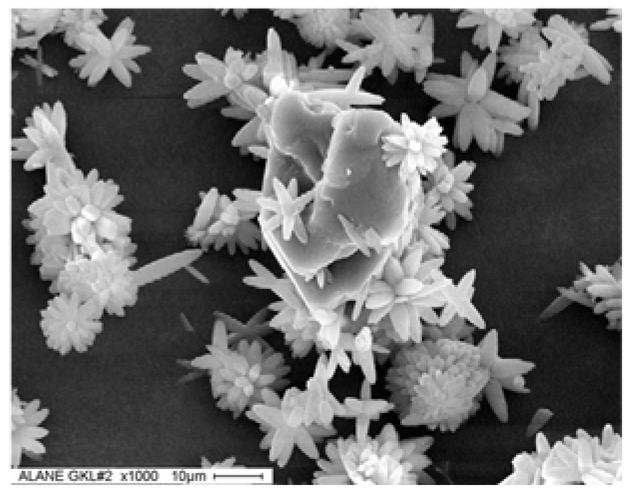
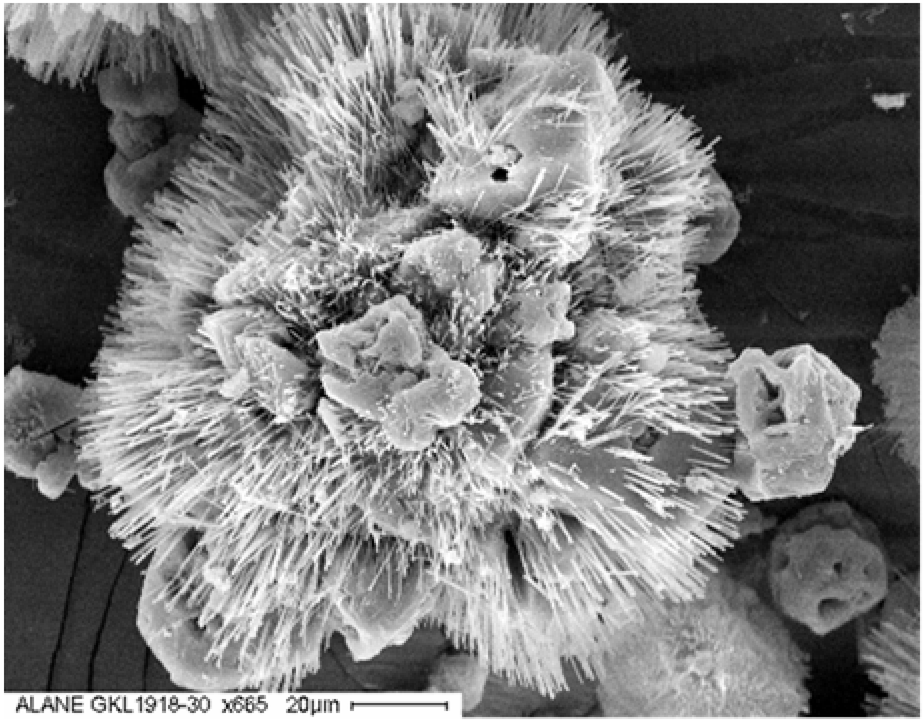


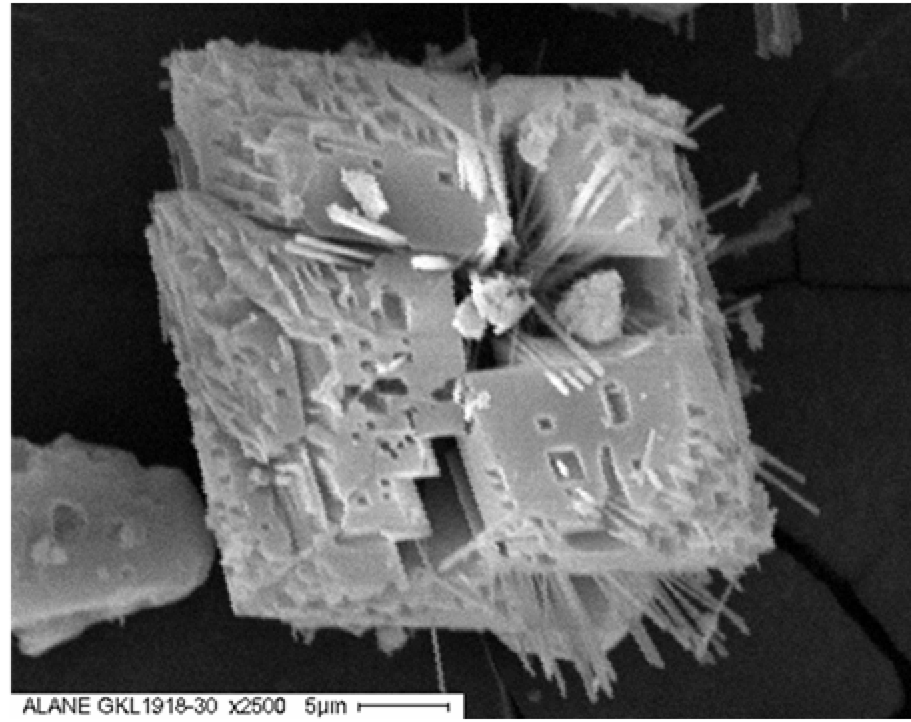




- Several alane polymorphs survive workup and can contaminate alpha phase

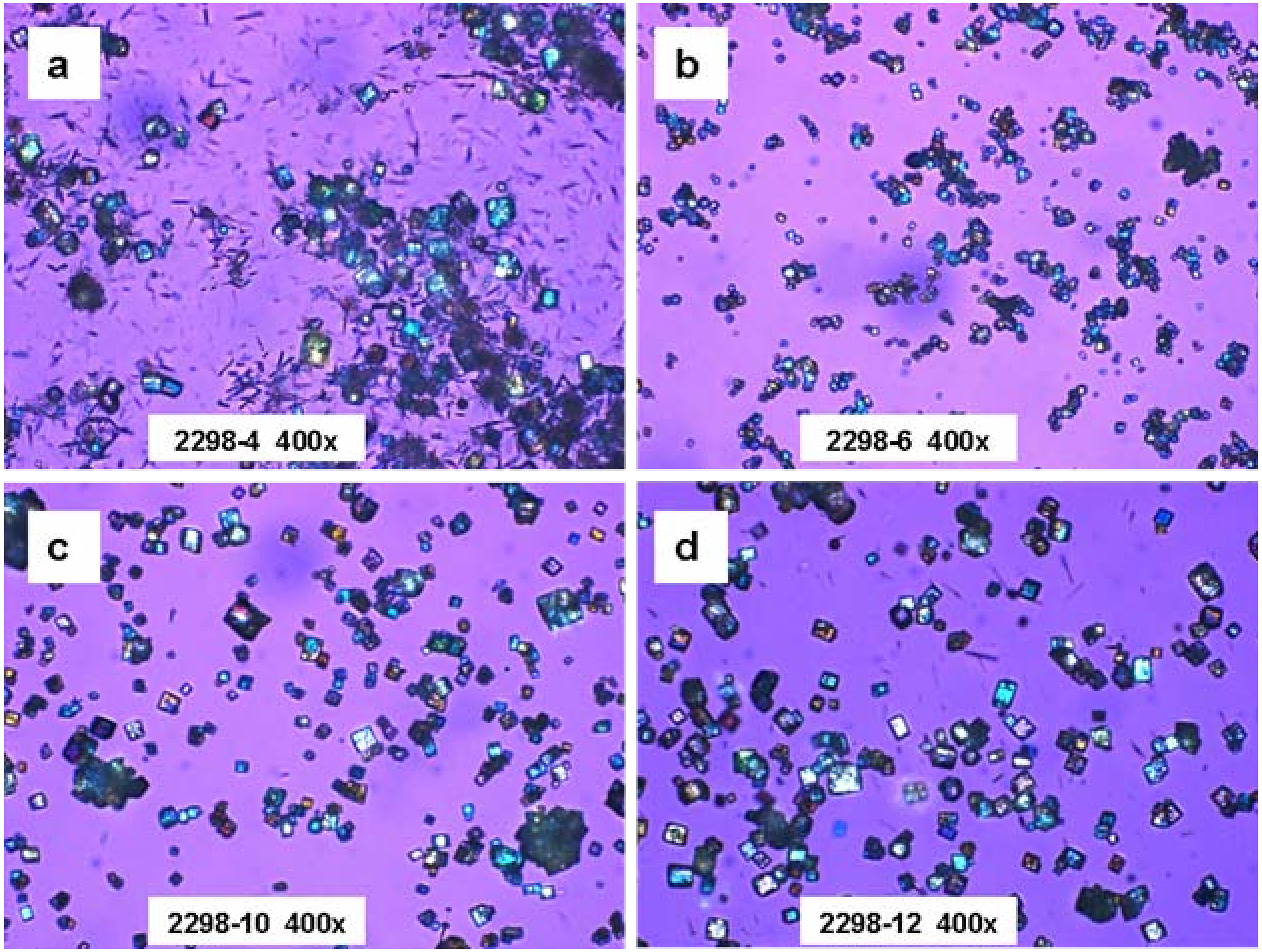
Mixed Polymorphs: Delta in Alpha





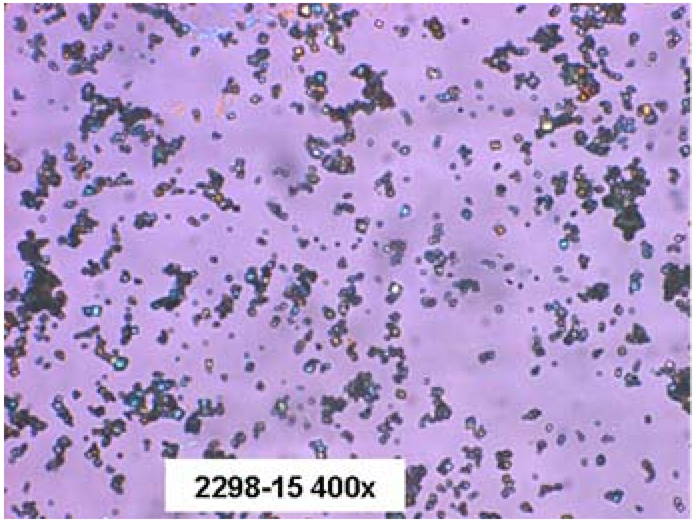
- Multiple polymorph combinations are occasionally observed
- Finding a scaleable, reproducible process has proven challenging

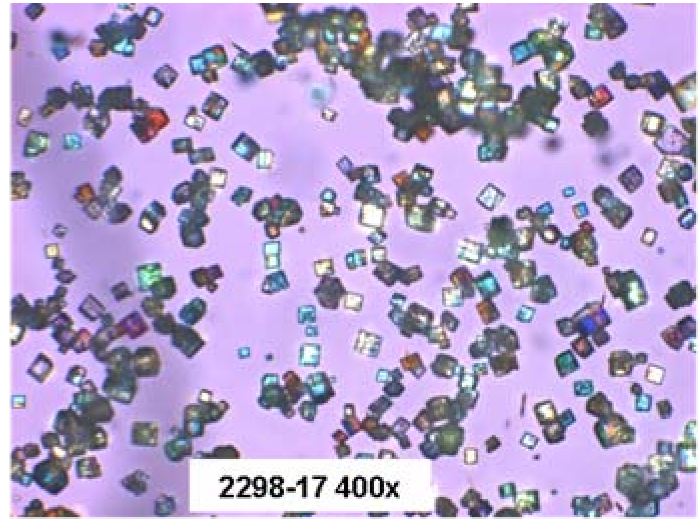
Effects of Process Variability Are Dramatic

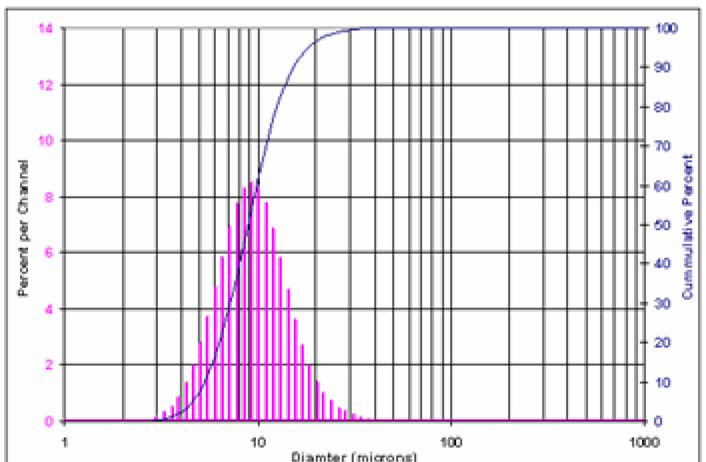


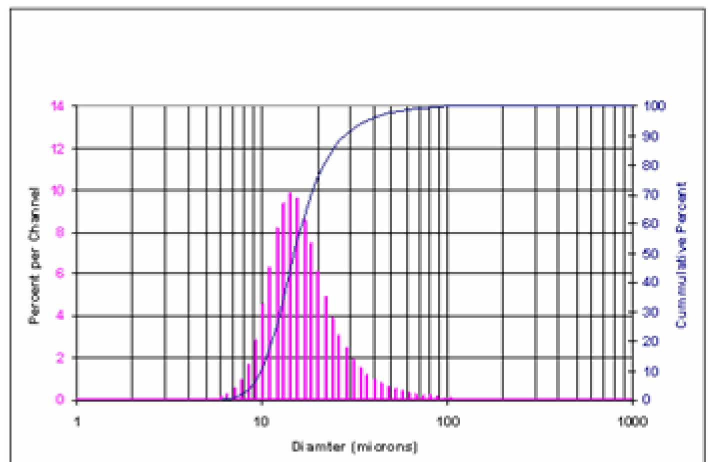
- Products vary dramatically depending on rate of etherate addition, temperature of reactors, pre-conditioning of reactors, etc.

Size of Alpha Cubes Depend on Conditions









- Small cubes average ~ 9 micron, large cubes ~ 15 micron

Safety Properties of Small vs. Large Alane Cubes

	2298-15 (9µm cubes)	2298-17 (15 µm cubes)	FSU (22 µm cubes)
ABL Impact (cm)	64	>80	13 to 17
TC Impact (in)	> 46	46.5	> 46
ABL ESD (J)	< 0.00125	< 0.00125	< 0.00125
ABL Friction (lb)	< 25@ 3 ft/s	50@ 4ft/s	100 to 180 @4ft/s
SBAT Onset (°F)	231 (exo, no burn)	243 (exo, no burn)	251 (exo, no burn)

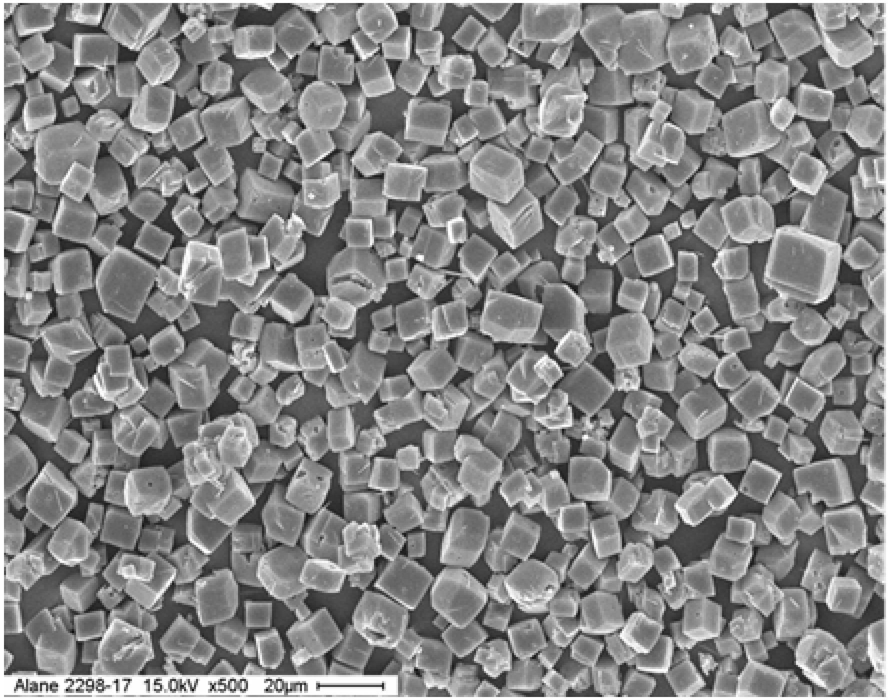
- FSU material more sensitive to impact
- Smaller cubes more friction than larger cubes
- Smaller cubes exhibit lower thermal stability (SBAT = stimulated bulk autoignition temperature)
- Larger cubes are targeted as more desireable

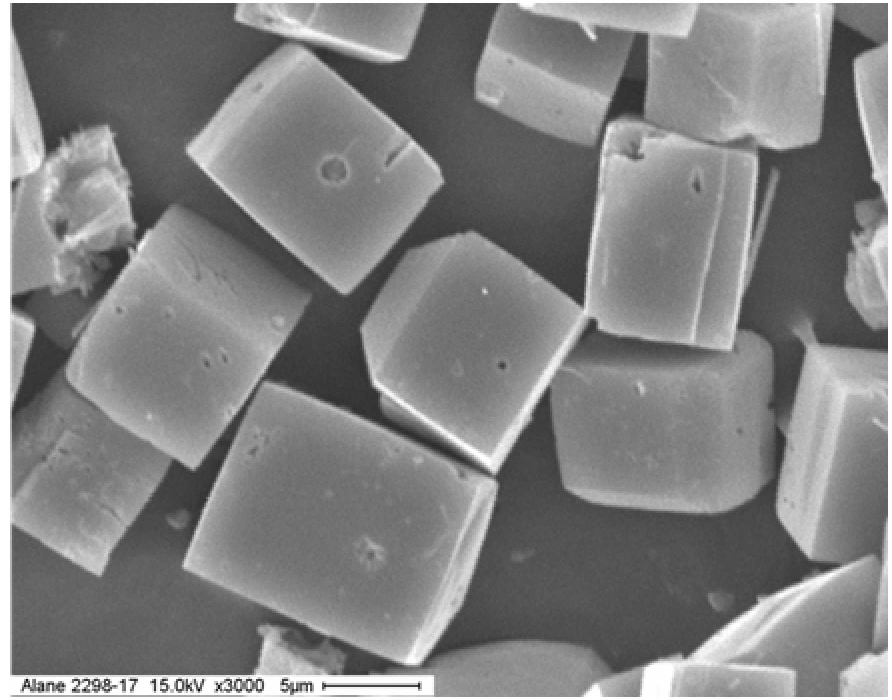
Elemental Analysis of ATK vs. FSU alane

	ATK alane	FSU alane
Hydrogen %	10.22	10.24
Carbon %	0.15	0.14
Nitrogen %	0.00	0.08
Chlorine %	0.018	0.009

- Elemental analyses (chemical purity) compare quite favorably
- Chloride content of ATK material is slightly higher

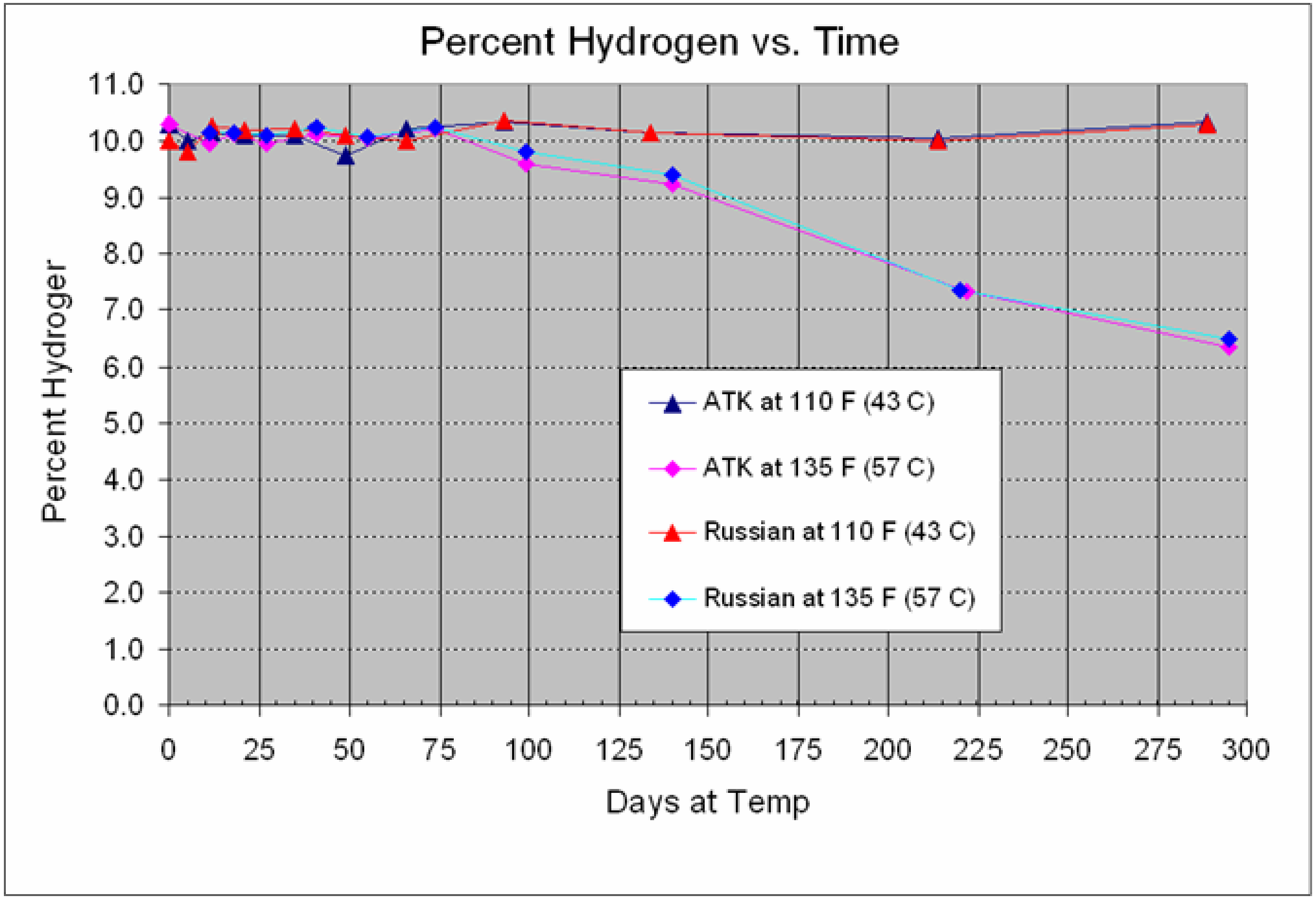
Optical Comparison of ATK vs. FSU Alane





- SEM of ATK material at 500x (left) and 3000x (right) magnification
- Quality compares favorably with FSU material by visual inspection

Thermal Stability: ATK vs. FSU Material



- ATK material behaves similarly to FSU material at elevated temperatures
- Materials are stable at 43 °C; at 57 °C materials show induction period (autocatalytic decomposition)

Conclusions

- Synthesis of stable aluminum hydride has been extensively investigated at ATK under ONR funding
- Repeatable process has been developed at ATK for the synthesis of high purity, high crystal quality alpha alane
- The alane produced at ATK compares favorably to FSU material
  - Compares w/ respect to: crystal morphology, density, chemical composition, sensitivity and thermal stability
  - ATK material is thermally and hydrolytically stable
- Side-by-side comparison of ATK vs. FSU materials in propellant and explosive formulations is in progress

Acknowledgements

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