Advances in the Development of a WCl6 CVD System for Coating UO_2 Powders with Tungsten

NASA Advanced Exploration System (AES) Project:
Nuclear Cryogenic Propulsion Stage

NETS 2013
27 February 2013

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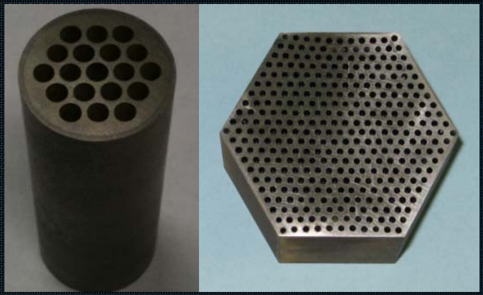
Background

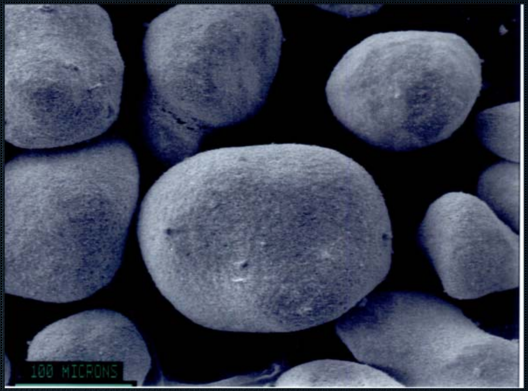
- NTP fuels under development
  - W-60vol%UO_2 CERMET



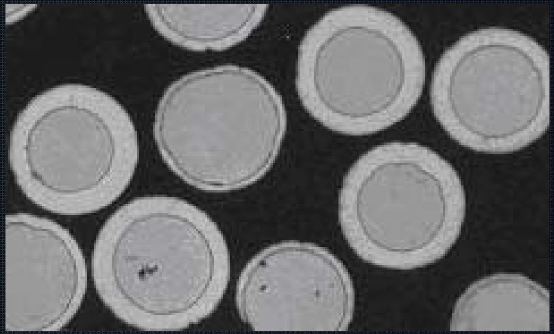
- Minimize erosion
  - Prevent H_2 propellant (2850-3000 K) from reducing UO_2 fuel kernels
  - Clad each fuel kernel in tungsten
- Coat spherical dUO_2 powders with 40 vol% W
- Coated spherical powders advantageous for HIP
  - Higher powder packing %TD
  - Minimize powder segregation

Problem & Objectives

- WF_6 process
  - Residual F exacerbates fuel loss
  - HF bi-product
- WCl_6 process
  - Minimal Cl contamination
  - More complex than WF_6 process (solid-to-vapor vs. gaseous reagent)
- Vendor cost to coat dUO_2 excessive
- Develop a lab-scale prototype that utilizes the WCl_6 process that enables cost effective coating of spherical dUO_2 powders



SEM Micrograph of spherical uncoated particles



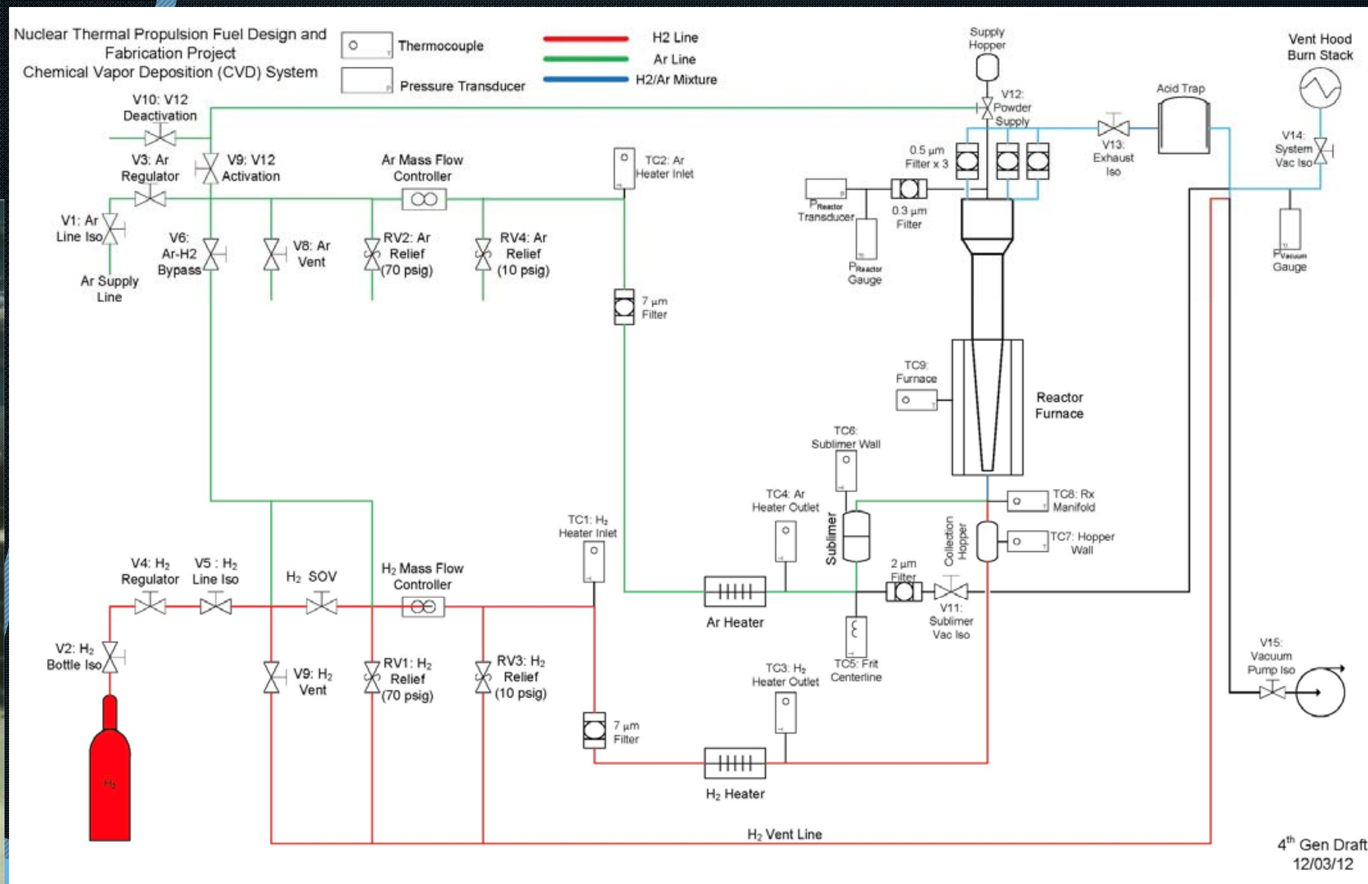
SEM micrographs of spherical coated particles

CVD Apparatus & Procedure

- WCl_6 process
  - Fluidized bed reactor
  - Raining feed system
  - H_2/Ar 10:1 ratio
  - 25 g batches
  - 30 to 60 min

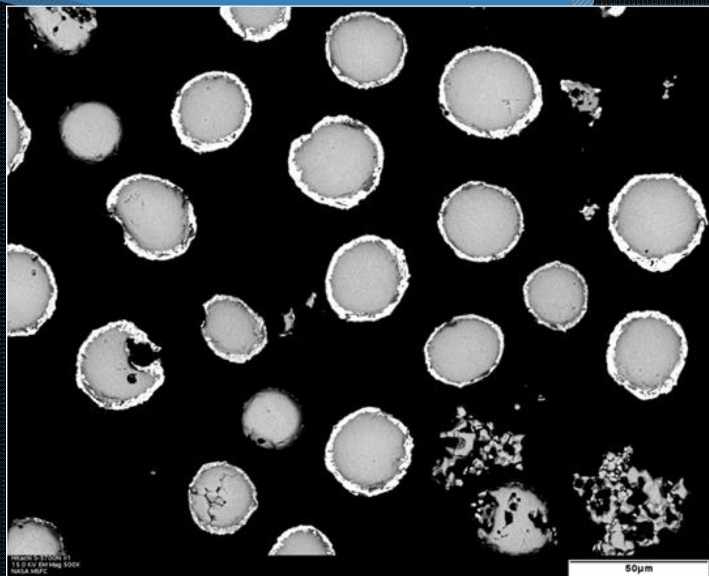
$$WCl_6 + 3H_2 \xrightarrow{Ar,\, xs\, H_2,\, 930^\circ C} W + 6HCl + Ar + xs\, H_2$$

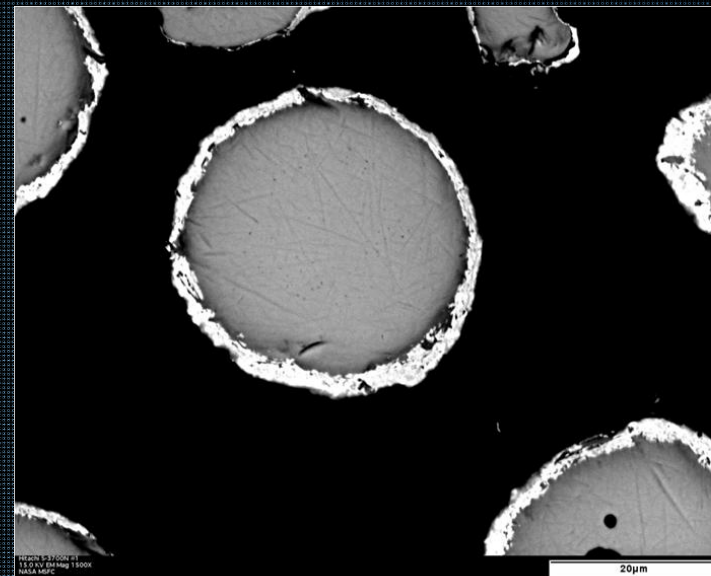
CVD Apparatus



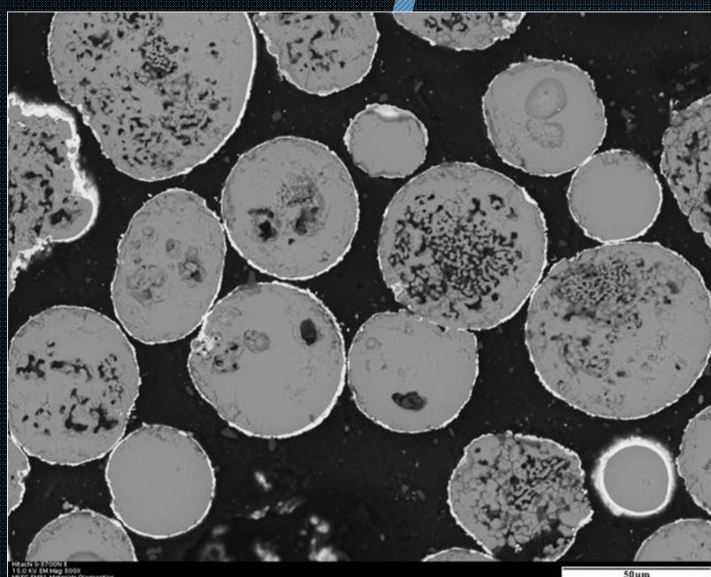
CVD System Schematic

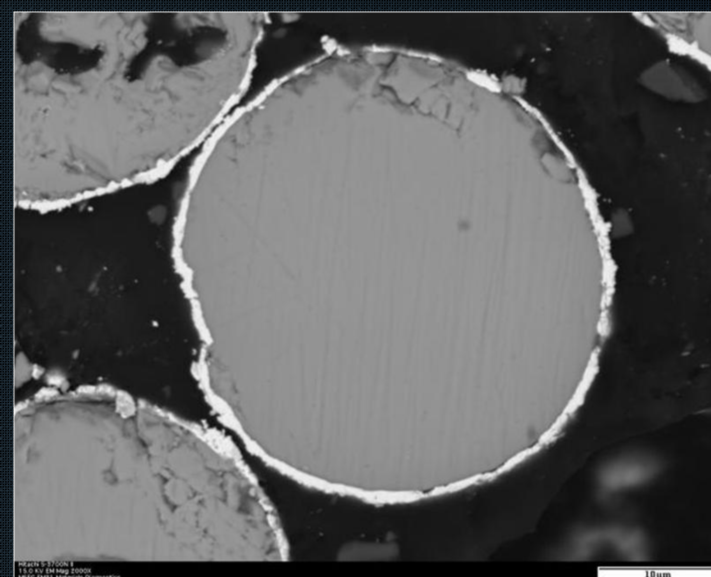
CVD Results





CVD Run 4: 60 minutes. W coated ZrO2, average particle OD 31.0 µm, average coating thickness 1.76 µm.





CVD Run 5: 30 minutes. W coated ZrO2.

Performance Improvement

- Vapor yield optimization
- Flow Line Blockage
  - Indications of temperature dependence
  - Continued blockage results in line leakage
- Component optimization
- Materials optimization
- System control and monitoring

H_2 and WCl_6/Ar mixture junction at reactor inlet

Sublimer outlet line blockage

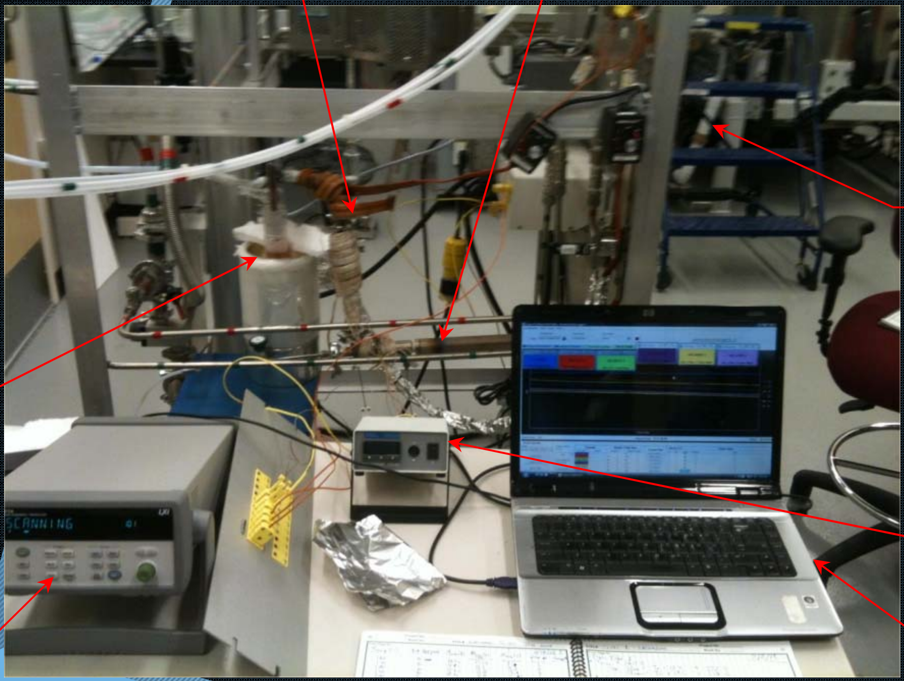
WCl_6 and W coated ZrO2 blockage

Sublimer outlet ball joint vacuum grease blow by location

Sublimer Characterization & Optimization

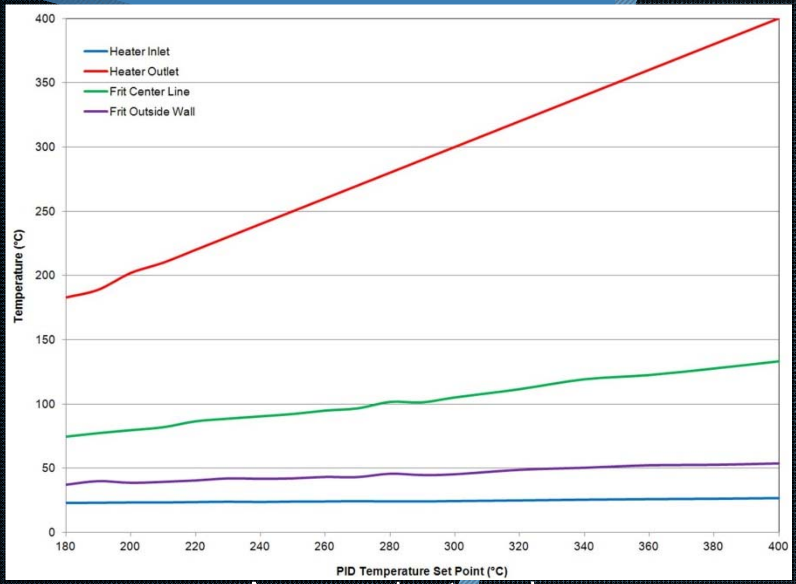
- Increase WCl_6 vapor yield
- Determine min/max sublimation temperatures
- Characterize yield vs. temp and carrier gas flow rate
- Optimize WCl_6 vapor yield

					Initial	Final	
T_{FCL} (°C)	t (min)	Vial No	M_V (g)	M_{V+WCl6} (g)	M_{WCl6} (g)	M_{WCl6} (g)	ΔM (g)
160	30	1	16.0	21.1	5.1	2.6	2.5
170	30	2	15.9	21.1	5.2		
180	30	3	15.6	21.0	5.4		
190	30	4	15.9	21.0	5.1		
200	30	5	16.0	21.2	5.2		
210	30	6	15.7	20.9	5.2		
220	30	7	15.7	21.0	5.3		
230	30	8	15.6	20.8	5.2		

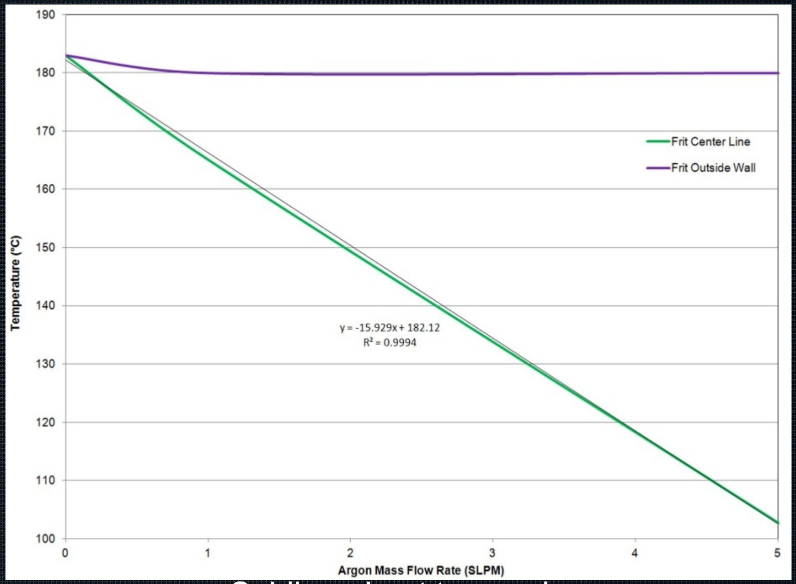


Instrumented sublimer and manifold

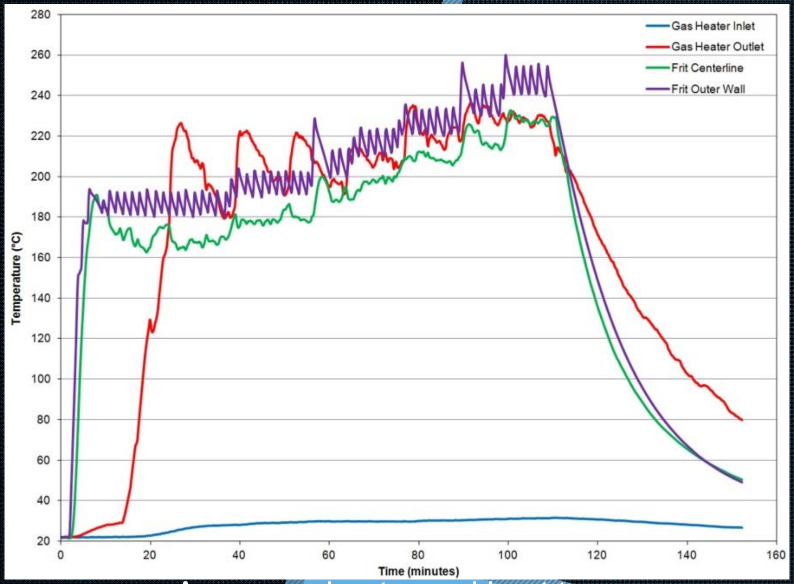
Sublimer Temperature Profiles



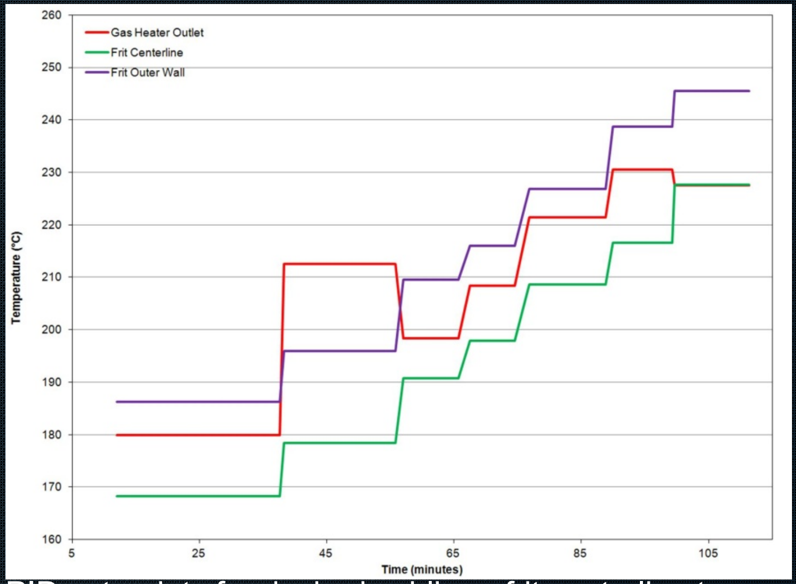
Argon pre-heater only



Sublimer heat tape only

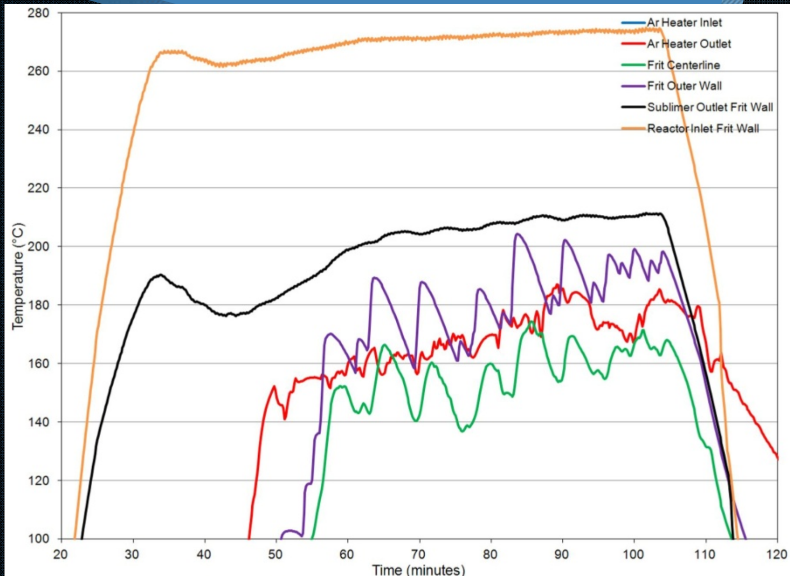


Argon pre-heater and heat tape



PID set-points for desired sublimer frit centerline temp.

Sublimer Characterization: 160 °C Run



Sublimer Temperature Profile

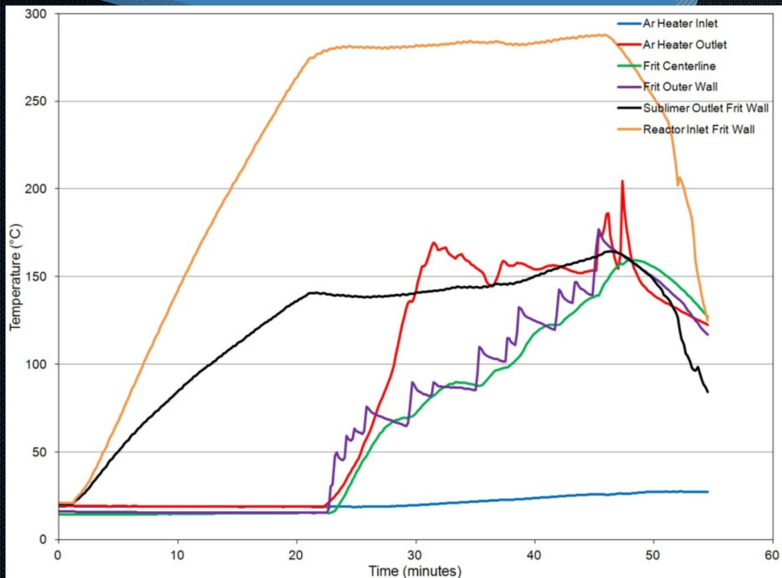
Sublimer (post test)

Sublimer outlet line (post test)

Sublimer outlet frit 1 up stream (post test)

Vacuum cryo trap (post test)

Sublimer Characterization: 170 °C Run



Sublimer Temperature Profile


Sublimer (post test)

Failed run due to “cotton candy” blockage.

Blockage a function of temperature schedule and entrained volatiles (cleaning solutions and water)


Sublimer outlet ball joint (post test)


Sublimer outlet frit 1 up stream (post test)

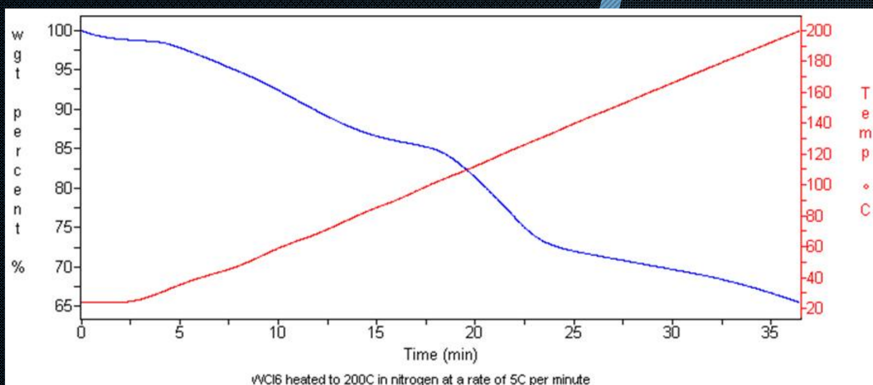
Sublimer are now baked to 150 °C for 1 hour to drive off volatiles in the frit immediately before a run.

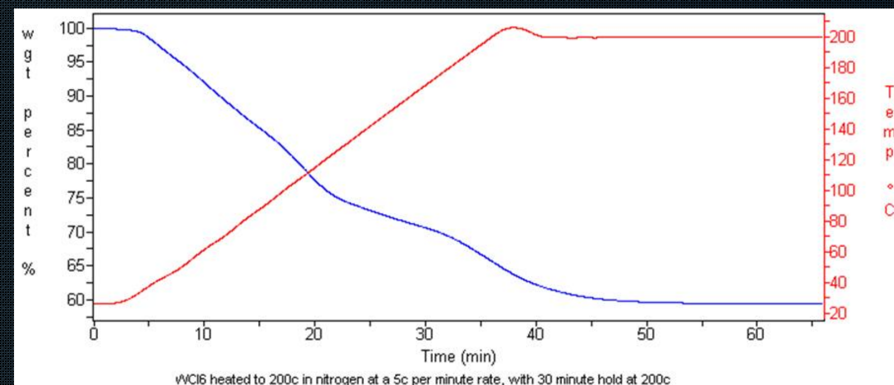
Reactor manifold frit should be maintained above 210 °C to prevent blockage.

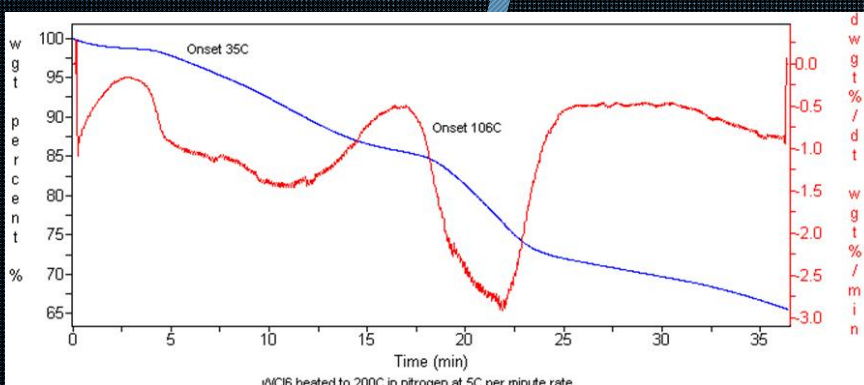
Sublimer Characterization: TGA

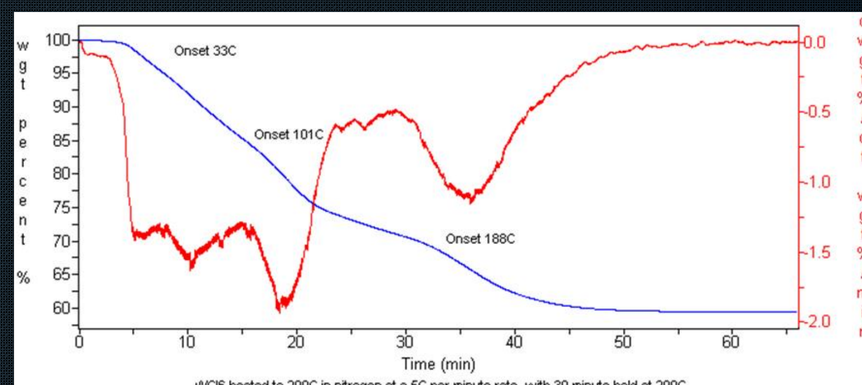
- Observation of sublimation inflection points using Thermal Gravimetric Analysis (TGA)
- Objective: Quantify WCl_6 onset sublimation temperature and sublimation rate

Thermo-Cahn Versa–Therm TGA





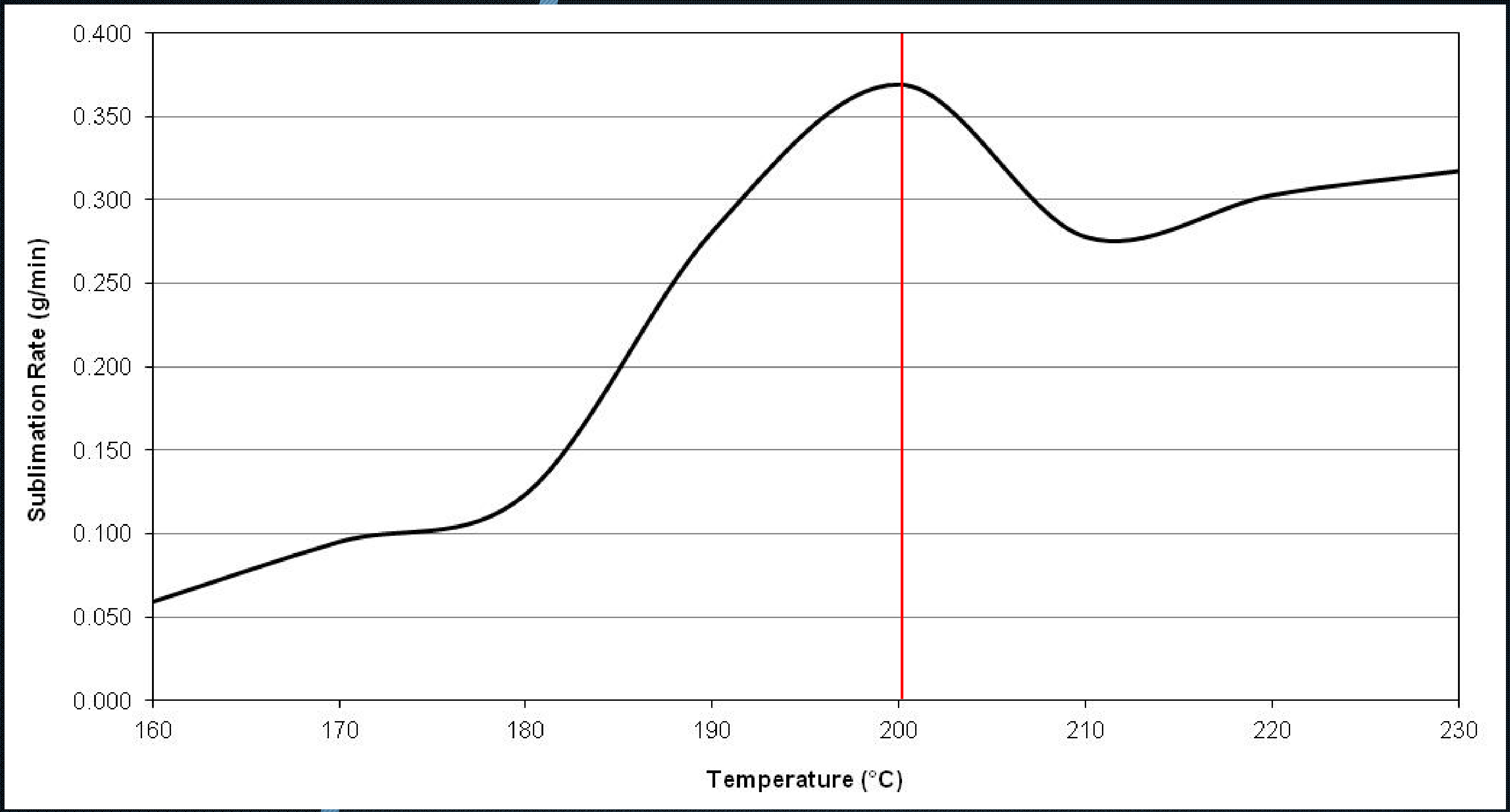




Conclusion: Sublimation onset at 33-35 °C, 101-105 °C, and 188 °C. Retained 200 °C nominal temperature.

Sublimation Rate

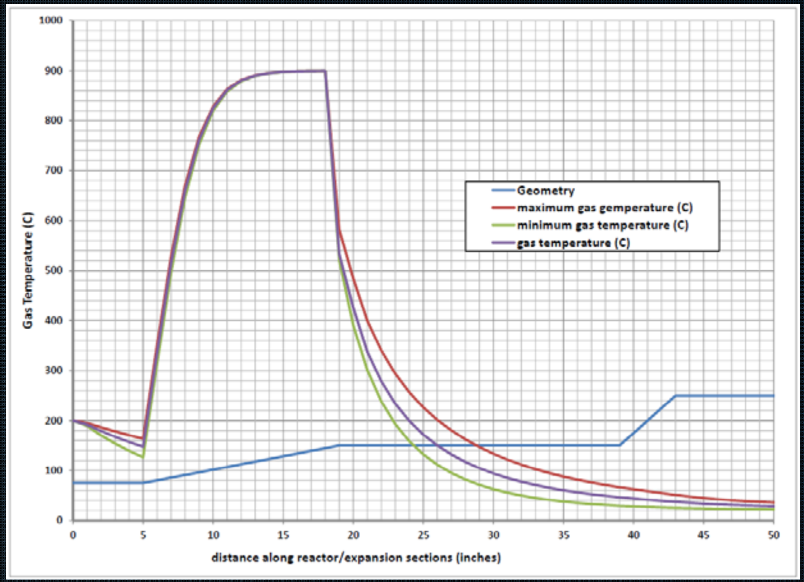
- Based on coarse sublimer characterization data
- Higher fidelity rates obtained using TGA

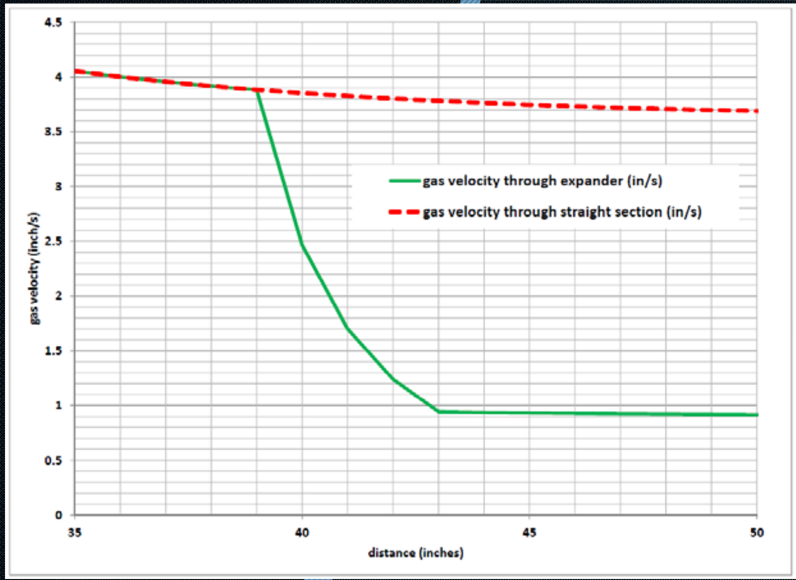


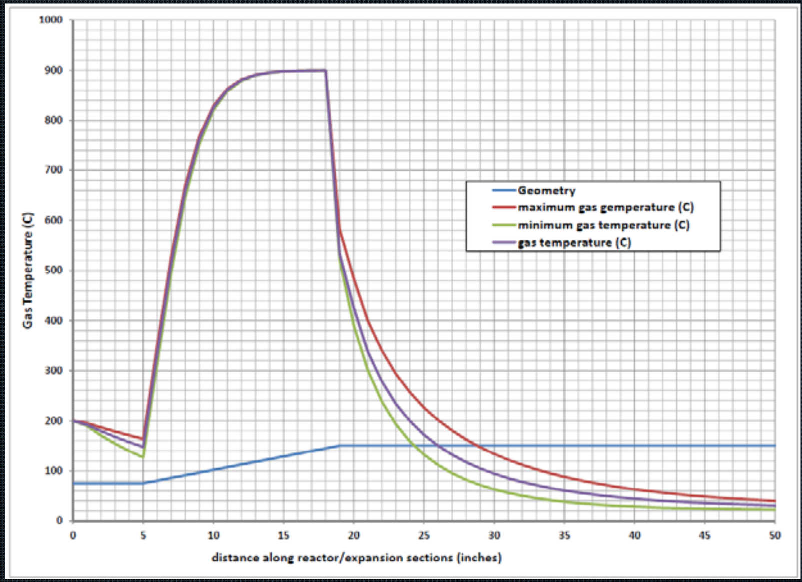
- CVD runs at 200 °C exhibited excessive vapor yield
- 160 °C selected as optimal sublimer frit center-line operating temperature

Reactor Temp/Flow Modeling

- Assumptions
  - Ar & H2 flow-rates 1 & 10 SLPM respectively
  - Gas mixture enters at 200 °C and 20 psia
  - Glass surface temperature of 900 °C
  - Furnace starts at ~ 5” and ends at 17”
  - Axial conduction through the glass is neglected
- Results
  - Gas at low flows, through un-insulated glass, is rapidly cooled by outside
  - No thermal reason for expander
  - Particle velocity reason for expander (retain fines)







- Conclusion: Reactor and expander sections too long. Shorten reactor 4 inches, shorten expander 10.5 inches.

Materials Compatibility Study

- Glass (Pyrex/quartz)-to-304 SS seals
  - Significant corrosion in CVD environment
- Corrosion resistant candidate materials
  - Ti 6-4, Inconel 600, Inconel 718, Hastelloy C-276
- Exposed coupons in sublimer and expander
- Larson Electronic Glass provided with material samples to determine seal suitability
  - Samples torch annealed on a glass lathe
  - Seals frozen then immersed in hot water
  - Heated in oven to observe strain
  - Cleaning (removing oxide layer from metal)

Sample	Seal	Strain Test	Strain (rel. to 304 SS)	Thermal Shock Test	Post Test Cleaning
Hastelloy C-276	Fail	Fail (fell apart)	Higher	N/A	N/A
Inconel 600	Good	Low	Lower	Minor internal separation (like 304 ss)	Cleaned up well
Inconel 718	Good	Slighly > Inconel 600	Lower	Fail (fell apart)	N/A
Titanium 6-4	Good	Low	Lower	No change	Unsuccessful without abrasive

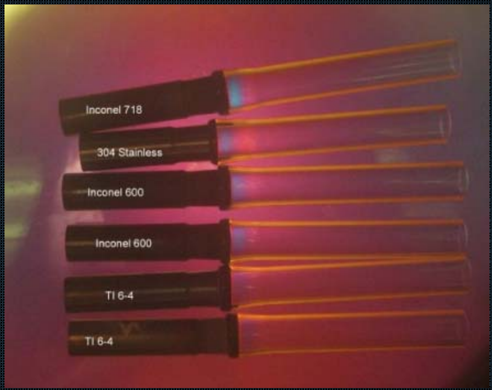
- Inconel 600 selected over Ti 6-4 due to corrosion resistance, weldability, and cost
- Sublimer will remain Pyrex while expander and metal-to-glass transitions made of Inconel 600

Pre run sublimer samples

Post run sublimer samples

Post run expander samples

Hastelloy C-276 | Inconel 600 | Inconel 718 | Titanium 6-4



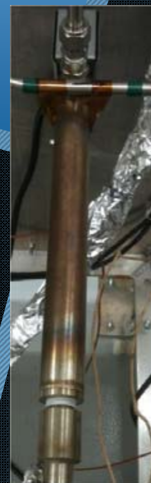
Heated Strain Visualization

Failed C-276 Seal

CVD Upgrades

Gas line simplification, valve sequence, ball/socket joints

Pneumatic powder fill pinch valve



Ar & H_2 pre-heaters

Collection Hopper

Burn-stack hinge & nichrome flame arrestor

H_2 and Ar Reactor Inlet Bellows

Markez Z1028 O-rings

Lexan Containment

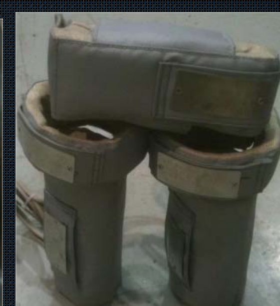
Inconel 600 Expander (optimum height)

Inconel 600-to-Quartz Reactor Seals

H_2 Area Monitor

DAQ System

Manifold Filter



Heating Jackets

Sublimer Bore Scope

Conclusions

- Demonstrated viability and utilization of:
  - Fluidized powder bed
  - WCl_6 CVD process
  - Coated spherical particles with tungsten
- The highly corrosive nature of the WCl_6 solid reagent limits material of construction
- Indications that identifying optimized process variables with require substantial effort and will likely vary with changes in fuel requirements

Future Work

- Optimize process variables in order to produce coating properties that meet requirements
- Characterize coatings as a function of substrate microstructure and process variables
- Design CVD system to process large quantities of power required for engine scale fuel fabrication

Acknowledgements

- Funding was provided by the “Advanced Exploration Systems – Nuclear Cryogenic Propulsion Stage” project.

- The authors would like to thank Grace Belancik, Richard Booth, Andrew DeSomma, Roger Harper, Stan MacDonald, Tim Nelson, Ronald Renfroe, Adam Kimberlin, Gabriel Putnam, Zachary Koch, Eric Stewart, Frank Zimmerman, Mike Houts, Jim Martin of NASA MSFC, Dave Bradley of YetiSpace, Jeff Ogle of Alloy Engineering, Chuck Larson of Larson Electronic Glass and Gene Nelson of AG Scientific Glass.

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