Development of a Microwave Regenerative Sorbent-based Hydrogen Purifier

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and

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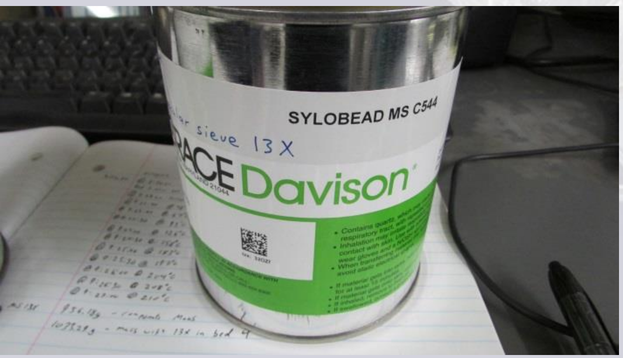
- Development work was performed under a NASA Marshall “Phase 3” contract awarded to UMPQUA Research Company located in Myrtle Creek, Oregon
- Followed a Phase 1 SBIR project demonstrating hydrogen purification using sorbent techniques
- Goal was to develop a Sub-Scale Device Microwave Regenerative Sorbent-based Hydrogen Purifier (MRSHP) –> 0.5 CM target
- Rapid 6-month development schedule: Design, build, test and deliver sub-scale MRSHP to MSFC Technology to support independent validation testing

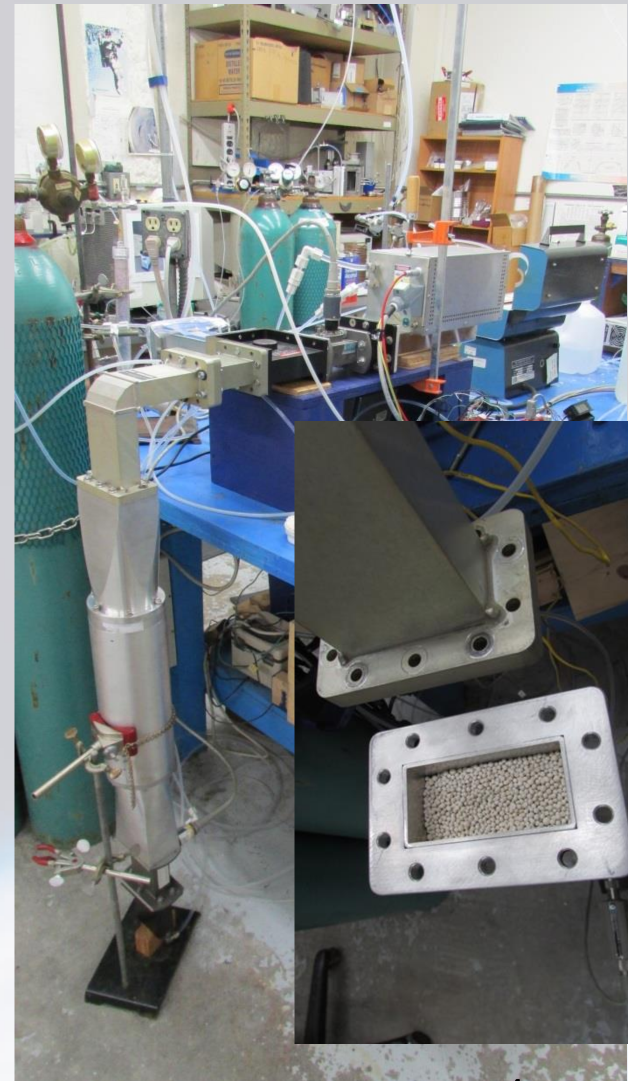
MRSHP Technology Overview:

- **Microwave regenerated 13x molecular sieve allows hydrogen to pass while capturing contaminant gases (acetylene, methane, water, etc.).**
- **Prototype designed for sub-scale demonstration at nominal 0.5-CM scale hydrogen production rate of Plasma Pyrolysis Assembly (PPA) with a targeted 30 minute regeneration required every 8 hours.**
- **Original plan was to have this device serve as an intermediate scale test-bed to support accelerated development of a 4-CM capacity prototype at the end of a Phase 2 effort.**
- **Independent testing to be performed at Marshall would help assure full scale (4-CM) by end of 2 year project.**
- **Phase 3 funding awarded to span the gap between SBIR Phase 1 and Phase 2.**
- **Design, development, fabrication and testing work was accomplished in a 6.5 month time frame (normally requiring 2 years).**
- **Limited performance testing / bed optimization was performed, but fully functional operation confirmed and device ready for independent evaluation when integrated with PPA at Marshall.**
- **Waveguide sorbent bed was refurbished just prior to testing and final verification tests were performed.**
- **Labels were prepared and attached just prior to final photos and crating.**
- **Final Report and a Specifications/Integrations manual prepared.**
- **Shipped device on Sept. 24thand arrived at MSFC on Oct. 5th.**

SBIR Phase I Proof-of-Concept Testing Summary

- **13x media performed best.**
- **Both cylindrical and rectangular waveguides evaluated.**
- **Single ended heating.**
- **Most of sorbent volume not regenerated.**

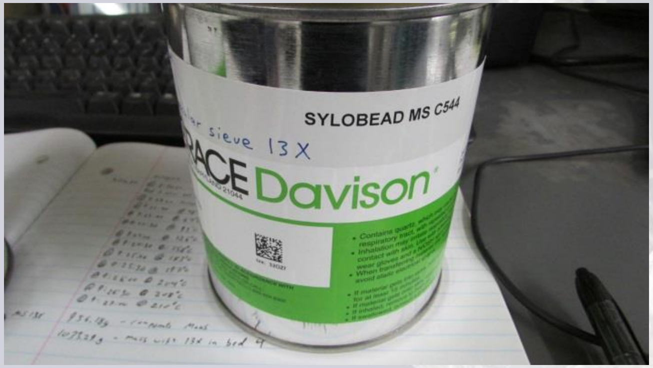


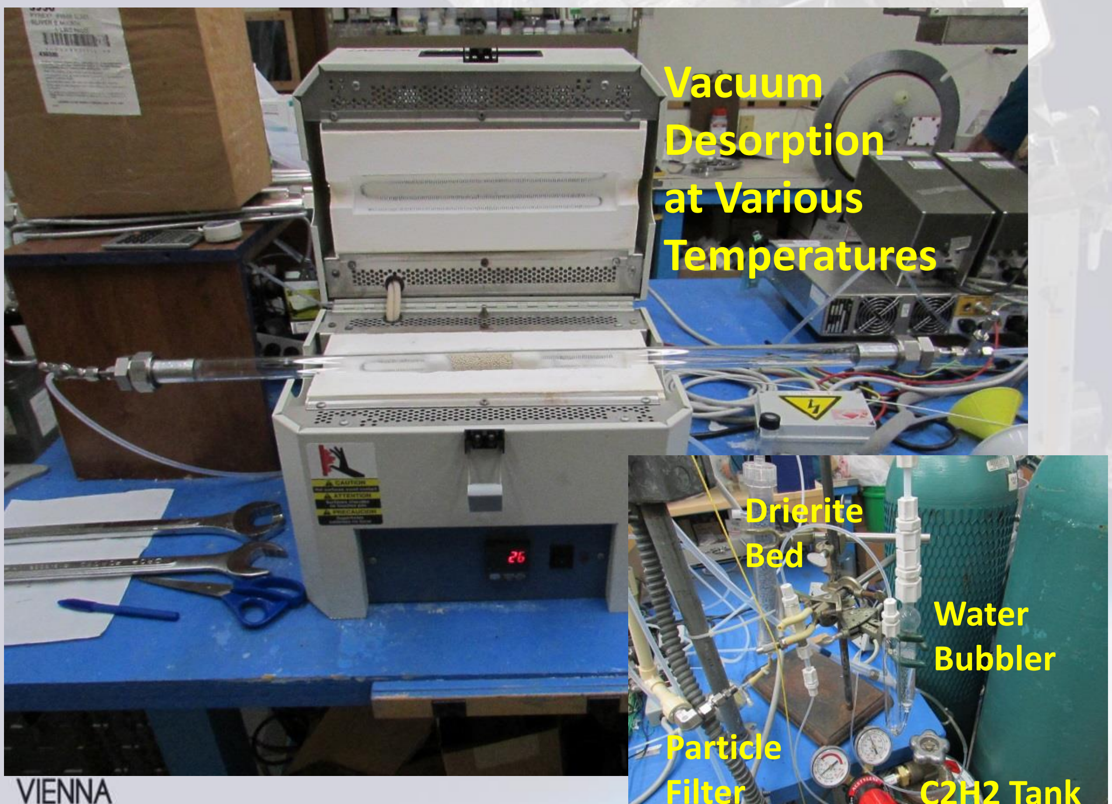


Phase 3 Initial Tasks (1st month):

- Acetylene decomposition study
  - Temperature dependence of decomposition
  - Product (carbon) impact on sorption
  - Impact on microwave desorption
- Preliminary design of sub-scale prototype
- Identify and order long lead-time components
- Dielectric properties measurements
- Temperature profile measurements
- Model preparation and comparisons to test data

Temperature Dependence of Acetylene Decomposition Observed During Thermal Desorption





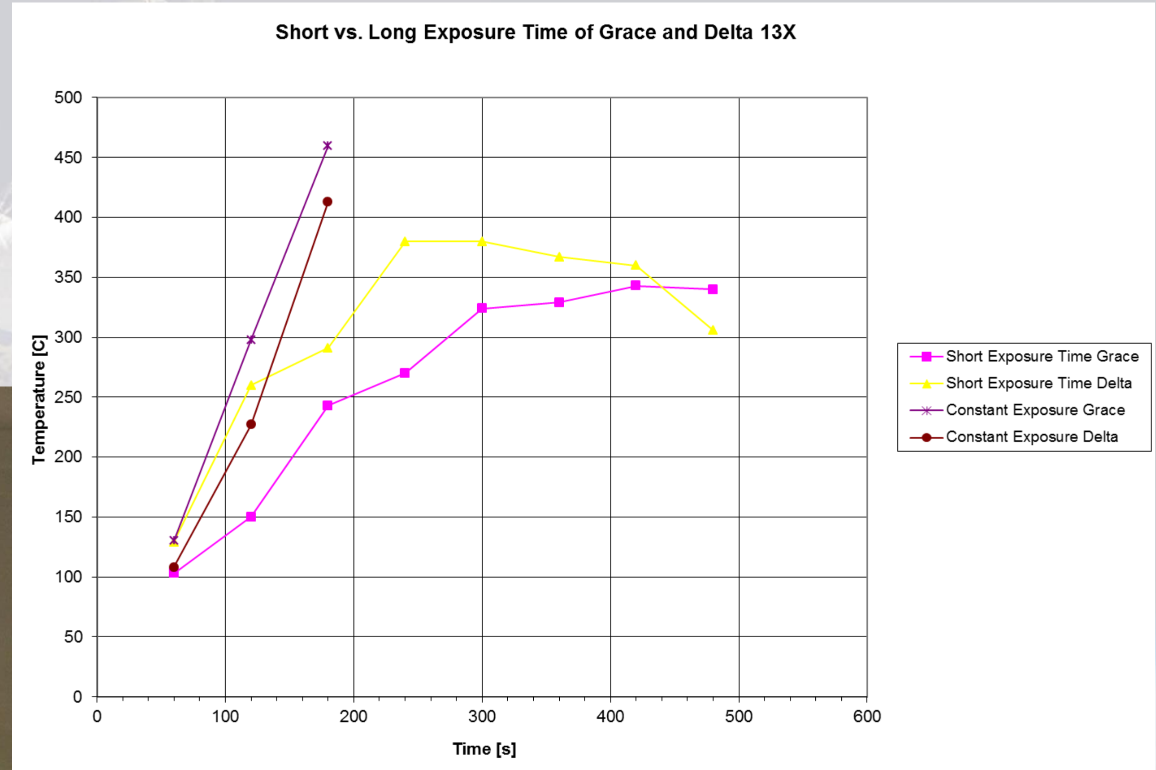
400°C

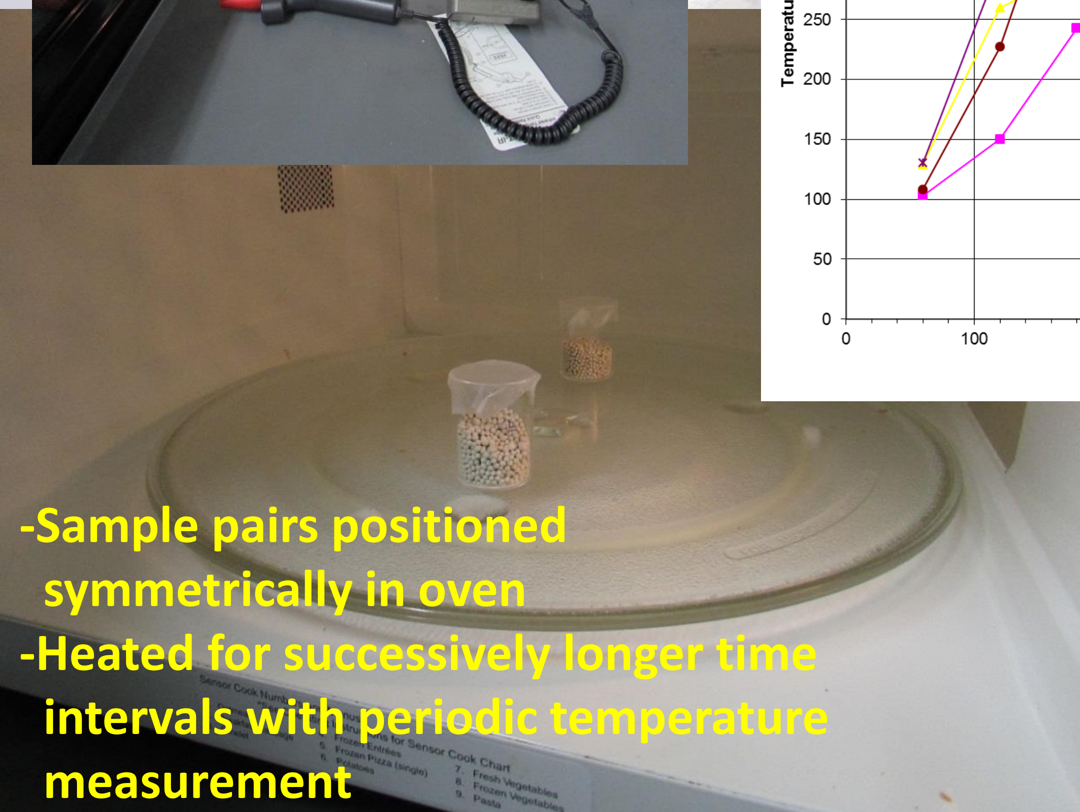
350°C

325°C

210°C

Microwave Heating of 13x as Function of Exposure Time

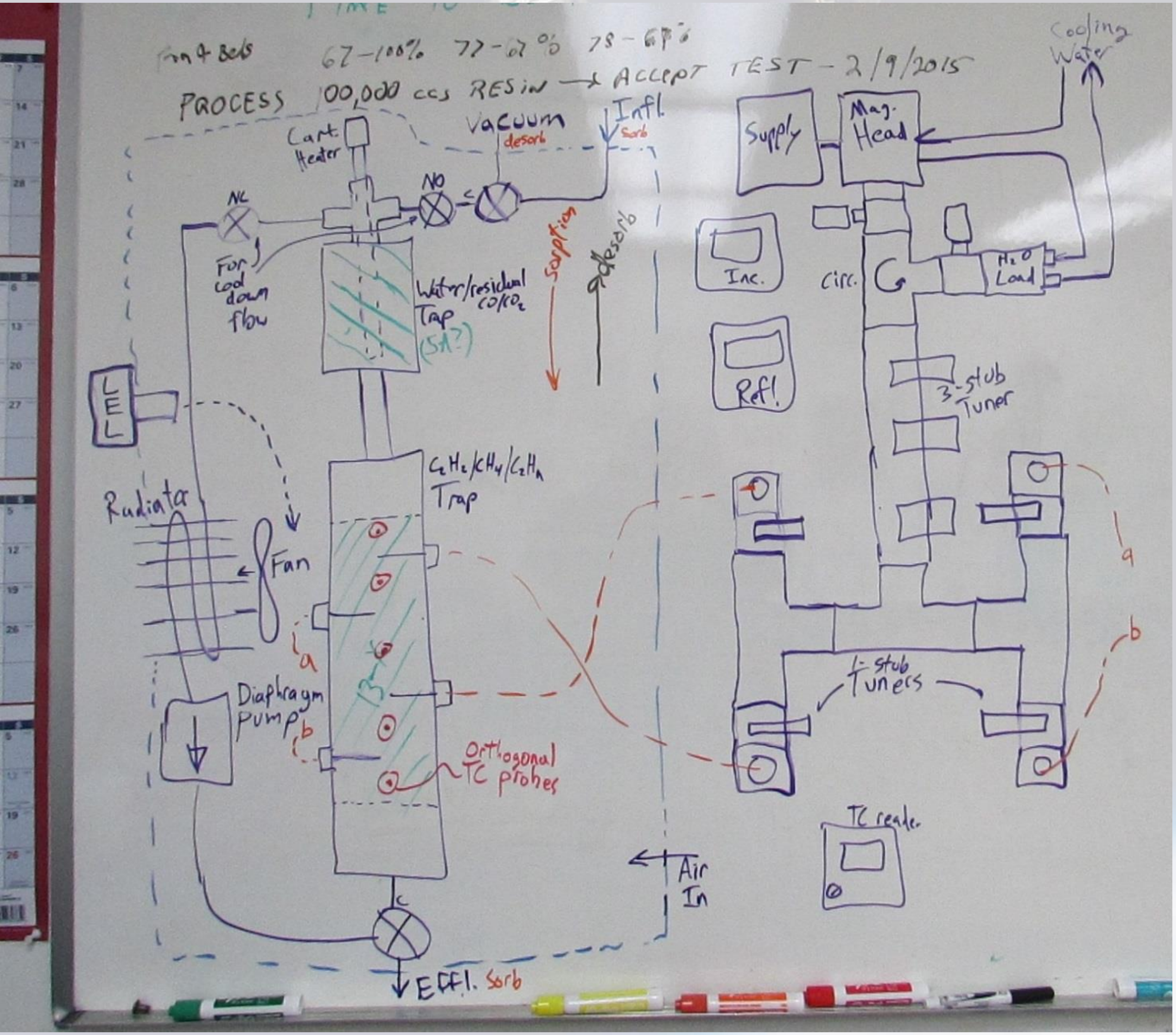




- Sample pairs positioned symmetrically in oven
- Heated for successively longer time intervals with periodic temperature measurement

Virgin Media Duplicates

Phase 3 Preliminary Prototype Design



- **Minimal hardware necessary to demonstrate technology**
  - **Manual push button controls**
  - **Microwave components and meters**
  - **Waveguide sorbent bed**
  - **Temperature probes and reader**
  - **Plumbing and solenoid valves as necessary for basic operation**
  - **External vacuum source, cooling loop and gas flow control required**
- **Microwave power distributed along length of sorbent bed**
- **Coaxial cable feeds to antennae inserted in media**
- **Fan cooled radiator with recirculated gas flow for cooling (not used in final design)**
- **LEL monitors all connections and gas components within a hazardous gas enclosure and removes gas flow on alarm**

Short Project Duration Required that Long Lead-Time Items be Identified and Ordered/Fabricated Early On

- ✓ Microwave Power Source (6-7 weeks)
- ✓ Directional Couplers (8-10 weeks)
- ✓ Waveguide Circulator (8 weeks)
- ✓ Water Load (6-7 weeks)
- ✓ 3-Stub Tuner (6-7 weeks)
- ✓ Waveguide Tees (6-8 weeks)
- ✓ Waveguide to Coax Transitions (6-7 weeks)
- ❑ Single Stub Tuners (6-7 weeks); Custom 3-Stub Tuners Fabricated Instead
- ❑ Coaxial Cables (1-5 weeks)

Dielectric Properties Measurements Required for Design/Modeling Effort

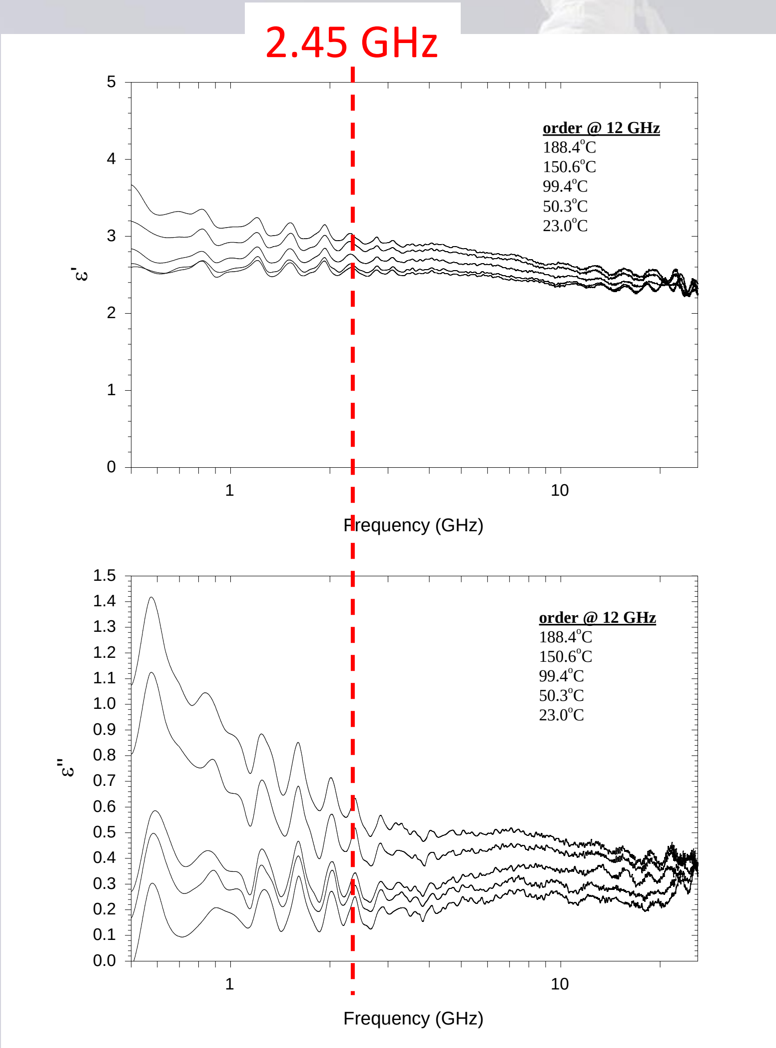
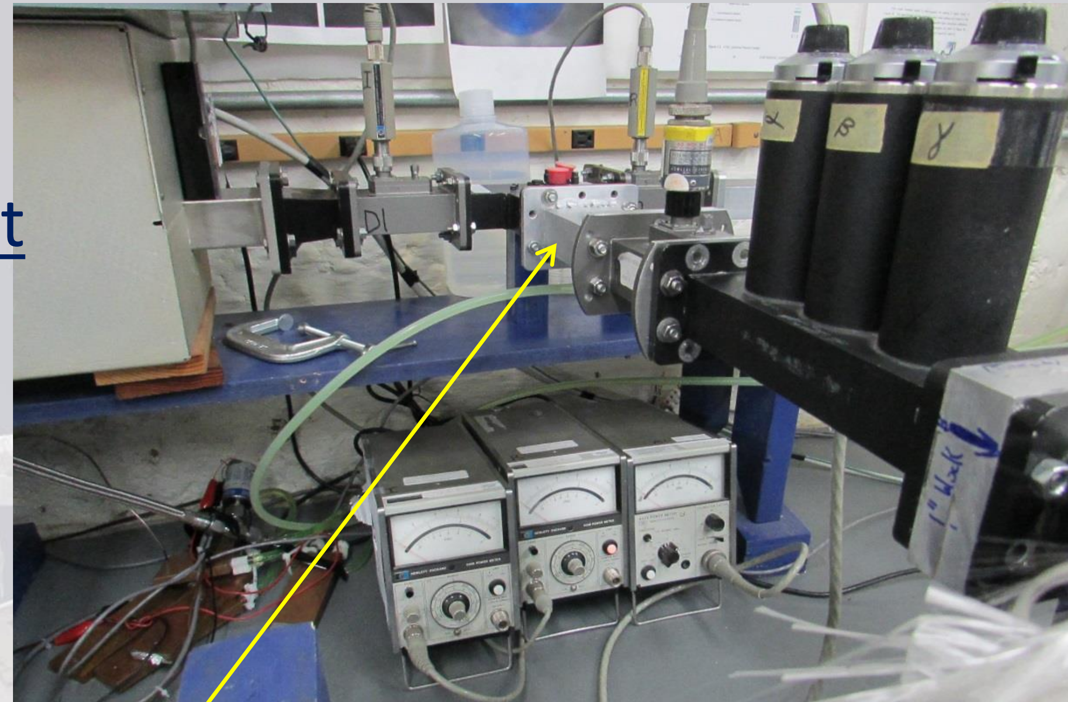


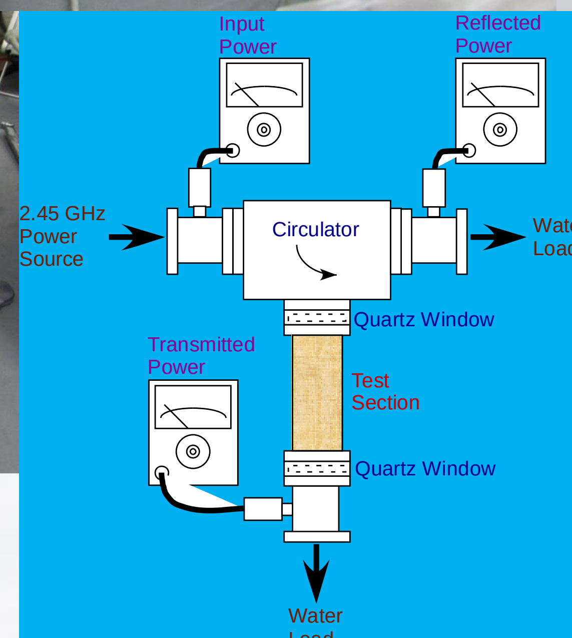
Figure 28. Molecular Sieve 13X with Clay Binder: Real (ε') and Imaginary (ε'') Components of Complex Permittivity. (Excerpt from URC 80851-1, page 33, 1999)



←Old data from previous work.

vs.

New measurement apparatus.→



Temperature Profile Tests

Probes Inserted Centered Along Length of Test Section

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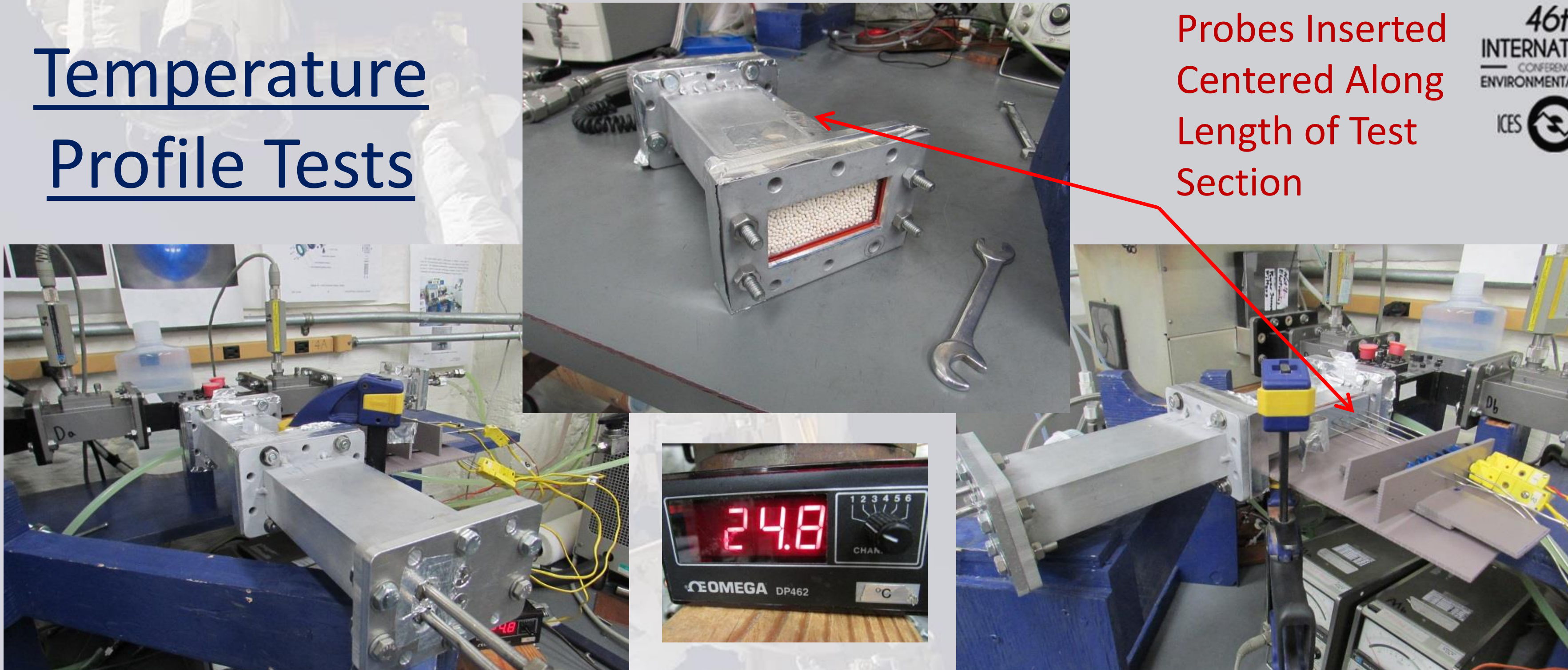
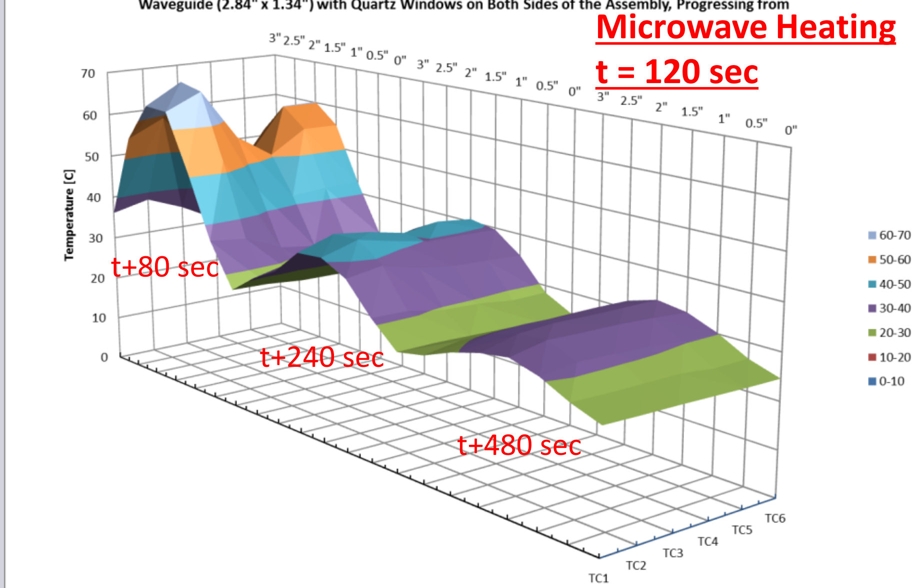
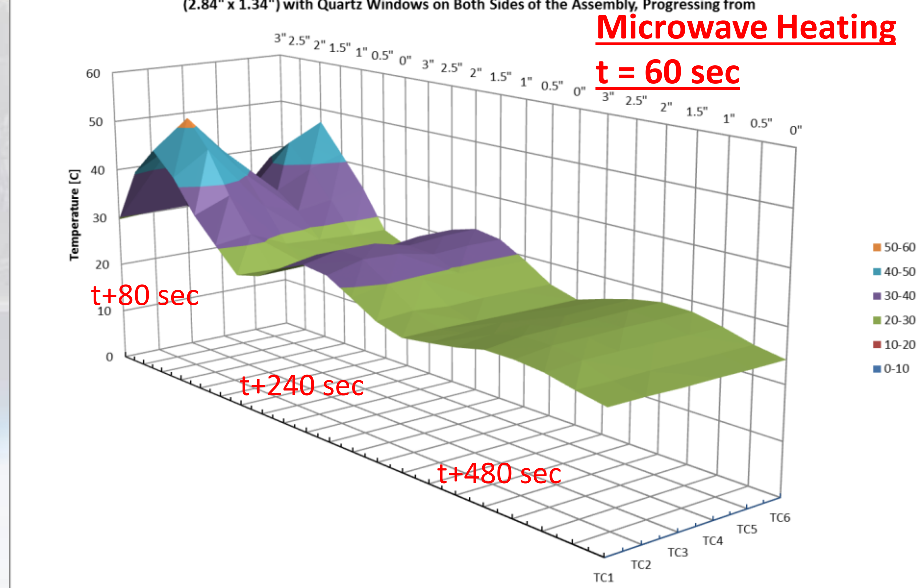




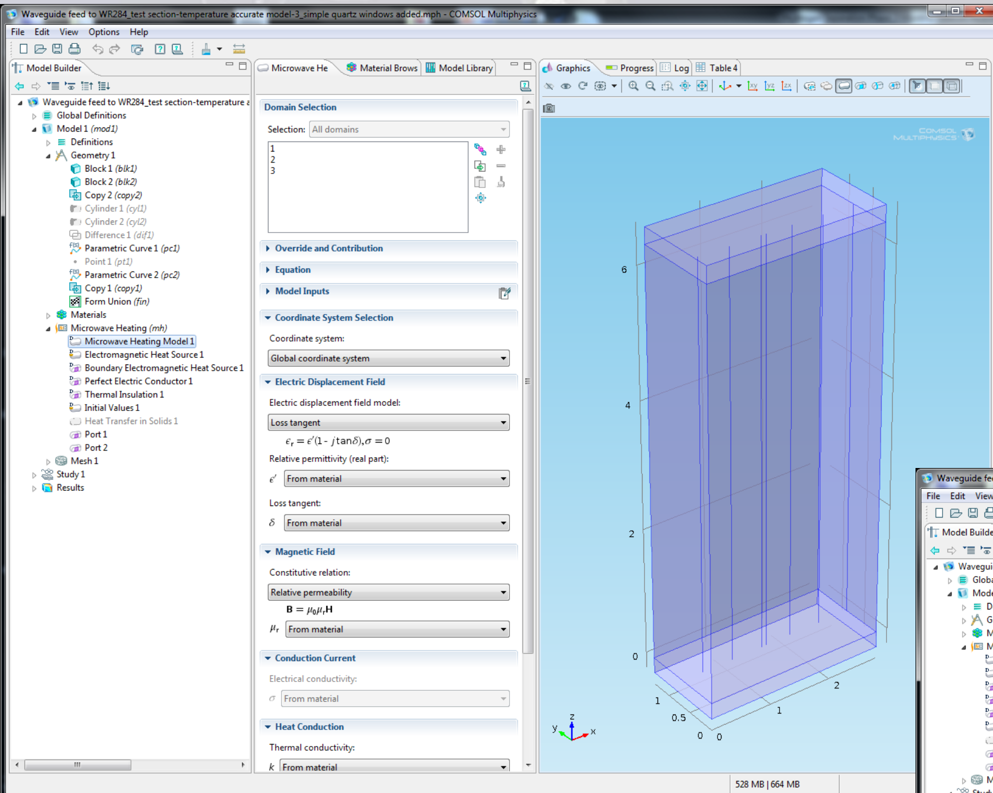
Profile Readings for the Microwave Test Assembly (5th Test on 4/8/15)
120 sec @ 100 W with 20-30% Reflected Power Using 13x from Grace Davison, in a 6.375" WR284 Waveguide (2.84" x 1.34") with Quartz Windows on Both Sides of the Assembly, Progressing from

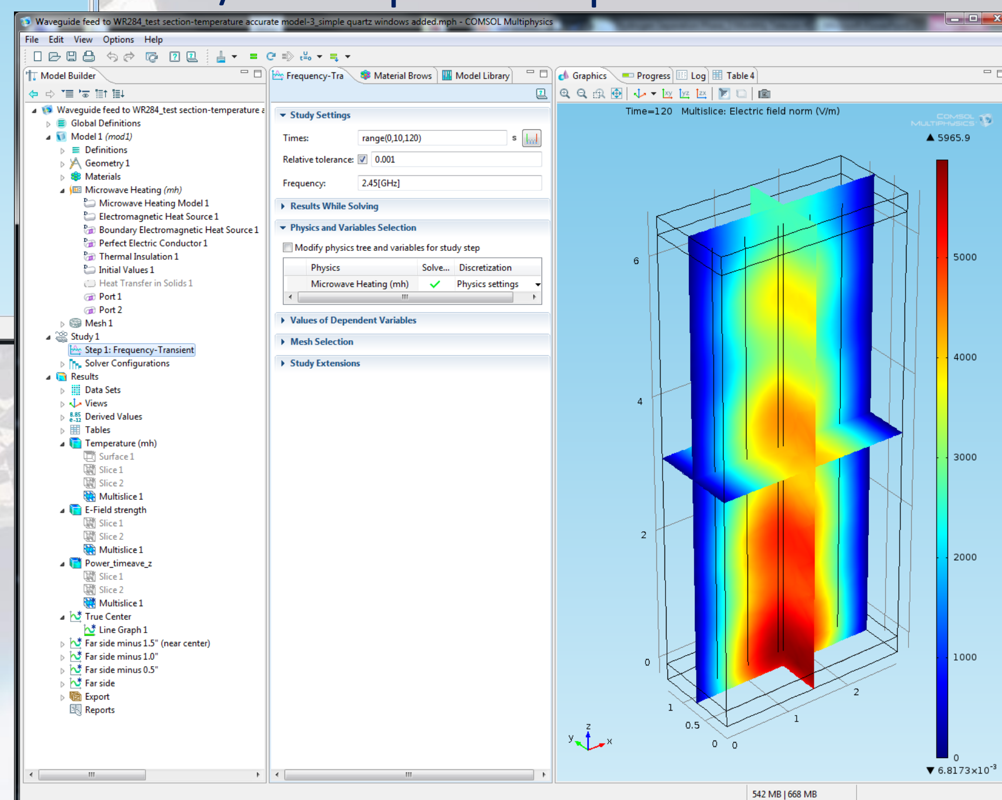


Profile Readings for the Microwave Test Assembly (2nd Test on 4/7/15)
60 sec @ 100 W with 20-30% Reflected Power Using 13x from Grace Davison, in a 6.375" WR284 Waveguide (2.84" x 1.34") with Quartz Windows on Both Sides of the Assembly, Progressing from

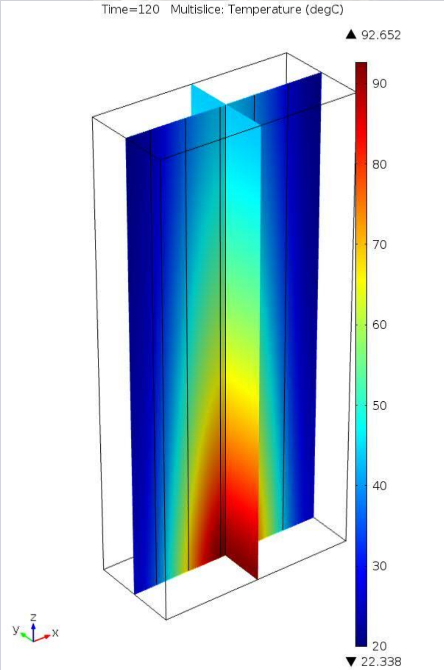
Computer Model Preparation

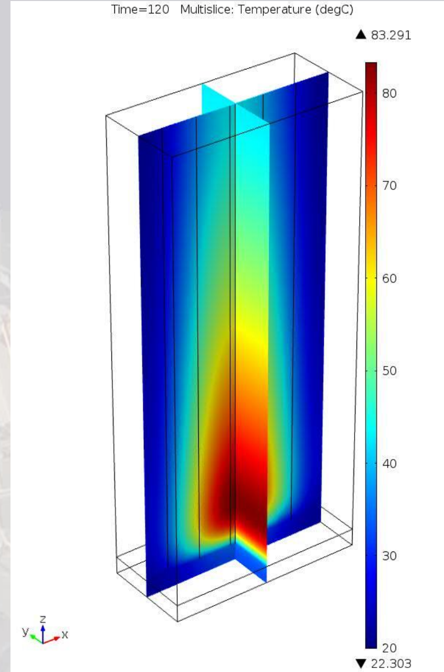
- Comsol Multiphysics Microwave Heating module
- WR284 waveguide test section at 6.375” length filled with 13x
- 0.25” microwave transparent quartz windows confine media
- 1/8” temperature probes

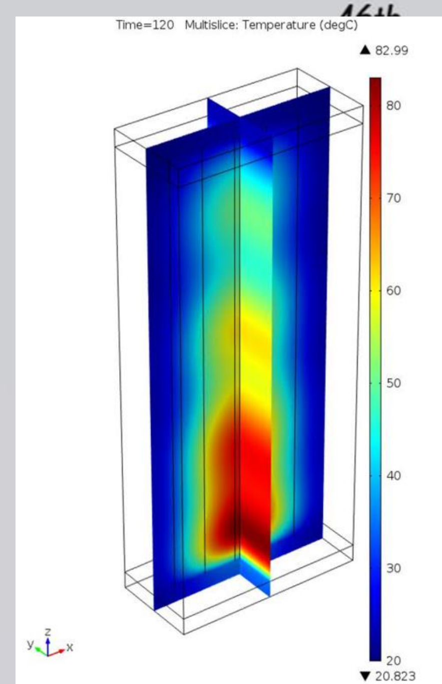




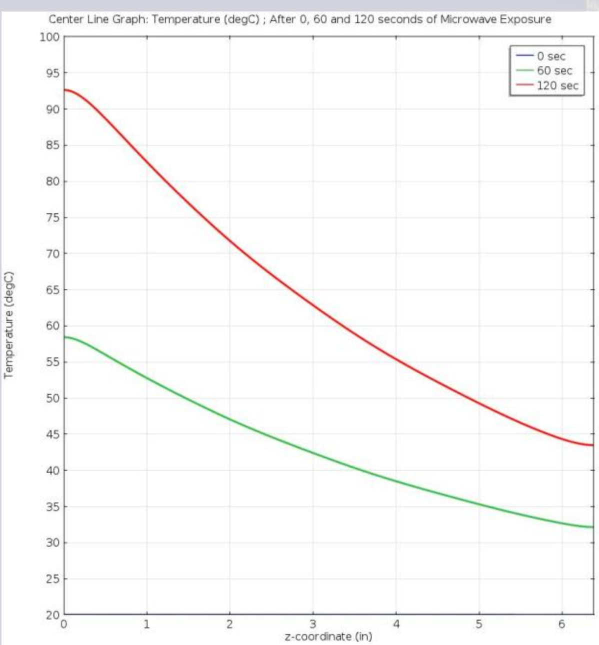
Model Predictions Compared to Measured Values



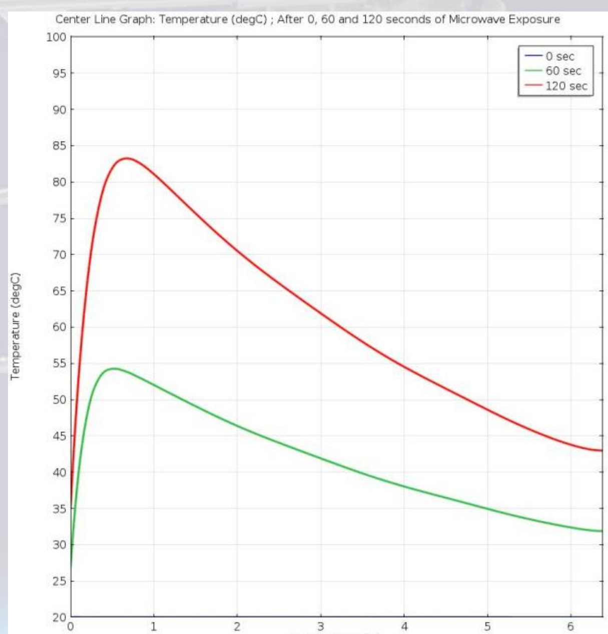




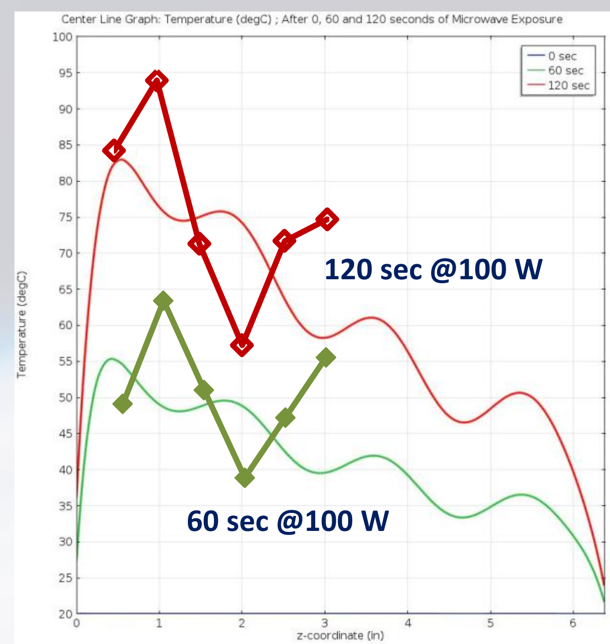
No quartz windows:



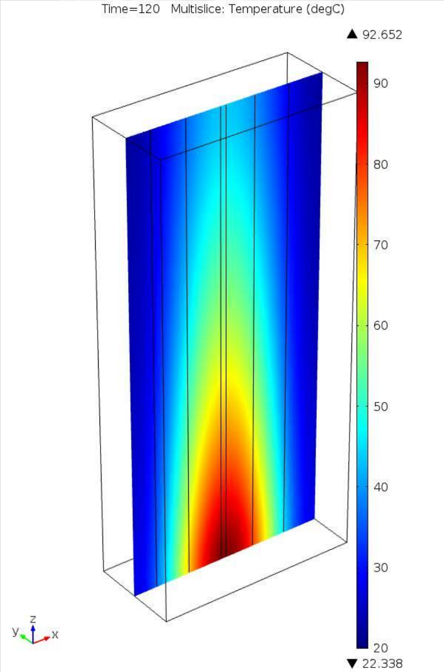
With inlet window only:

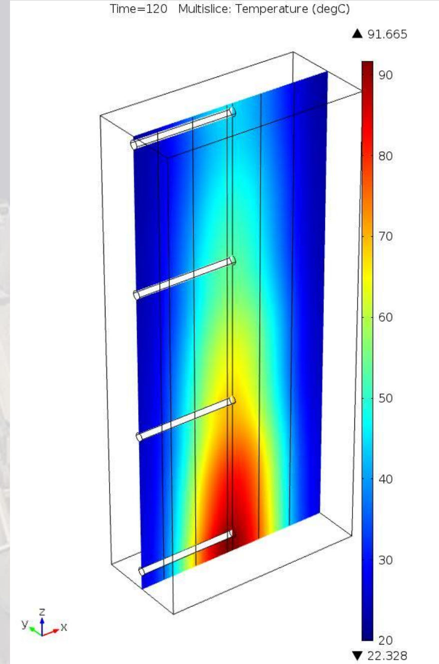


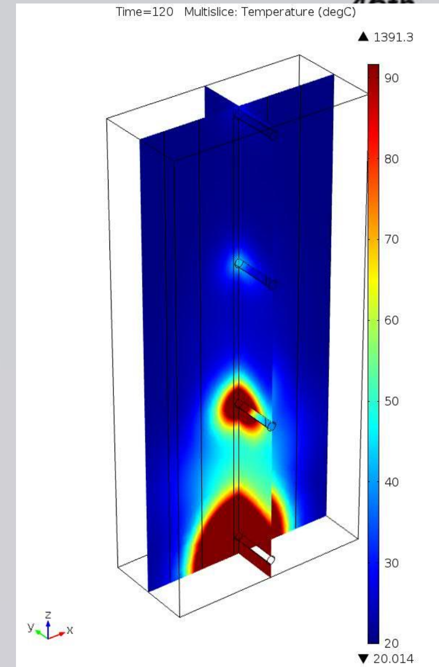
With both windows:



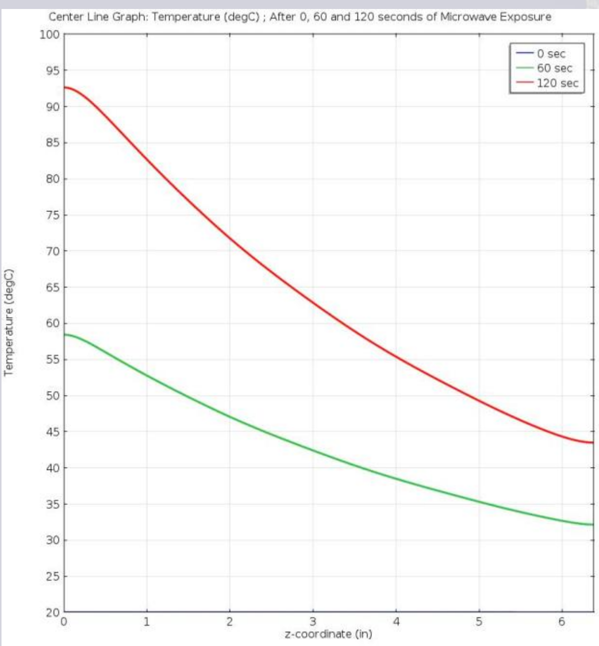
Model With 1/8 inch Probes Inserted



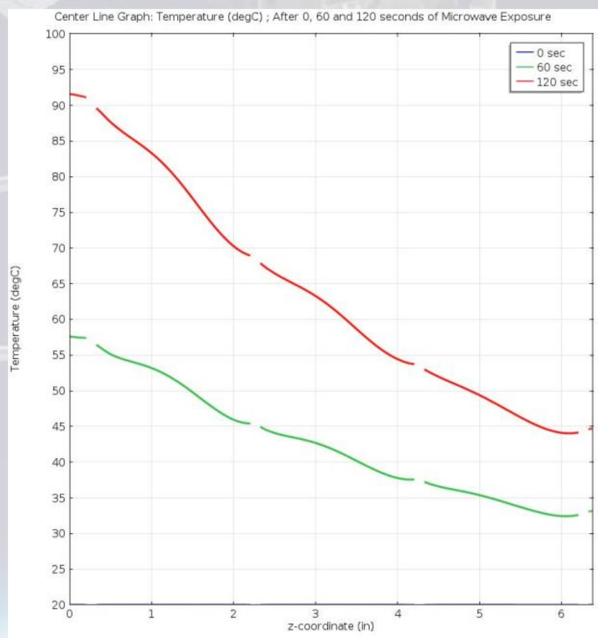




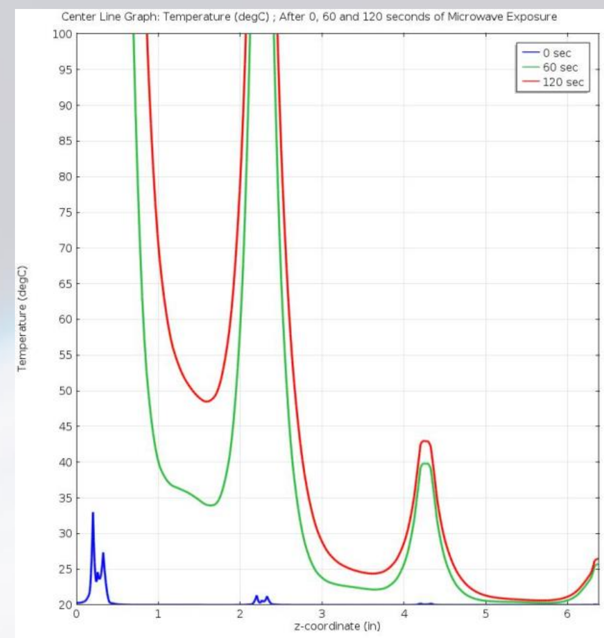
No quartz windows:



Multiple Narrow-Wall Probes:



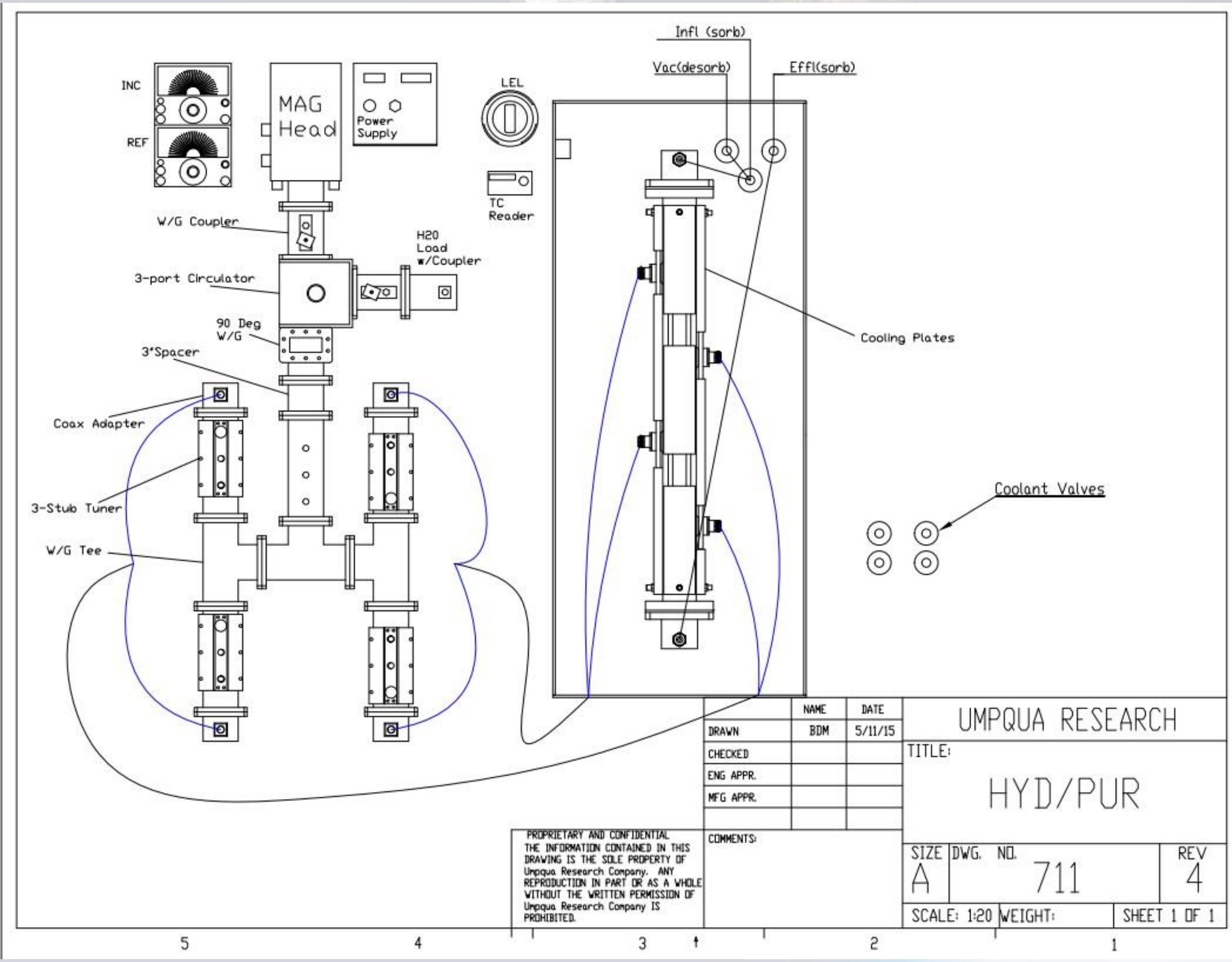
Multiple Broad-Wall Probes:



Conclusions From Testing / Modeling and Comparisons

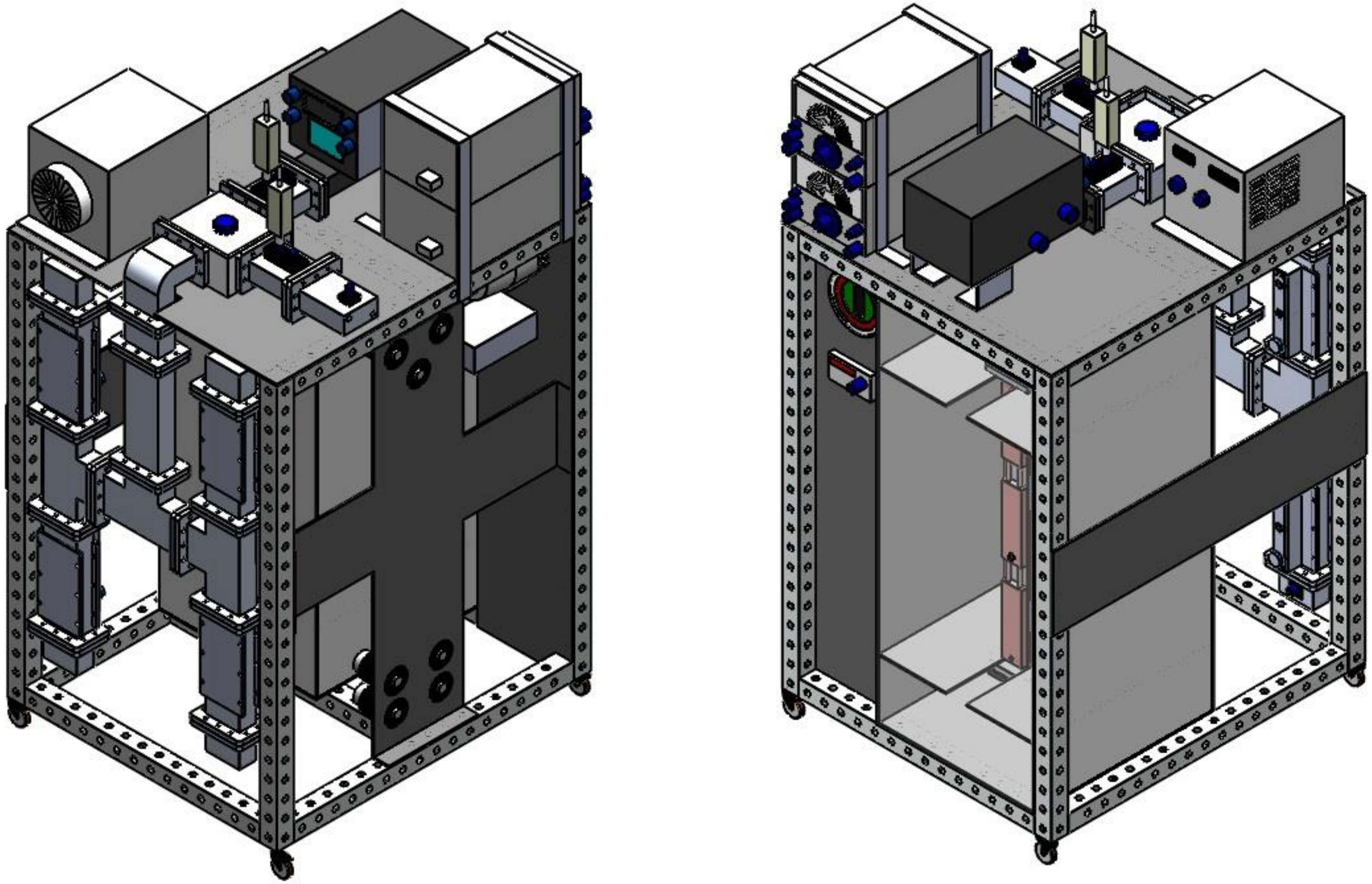
- Dielectric properties used appear to be accurate.
- Modeling results match observed effects in real device.
- Thermocouple probes can be inserted orthogonally to electric field with minimal impact on operation.
- Significant microwave heating occurs for 13x and regeneration temperatures over 400 °C are attainable.
- Single-ended waveguide power feed yields poor media coverage due to rapid attenuation (the flip side of good heating).

Evolved Prototype Process/Hardware Design (Month 2)



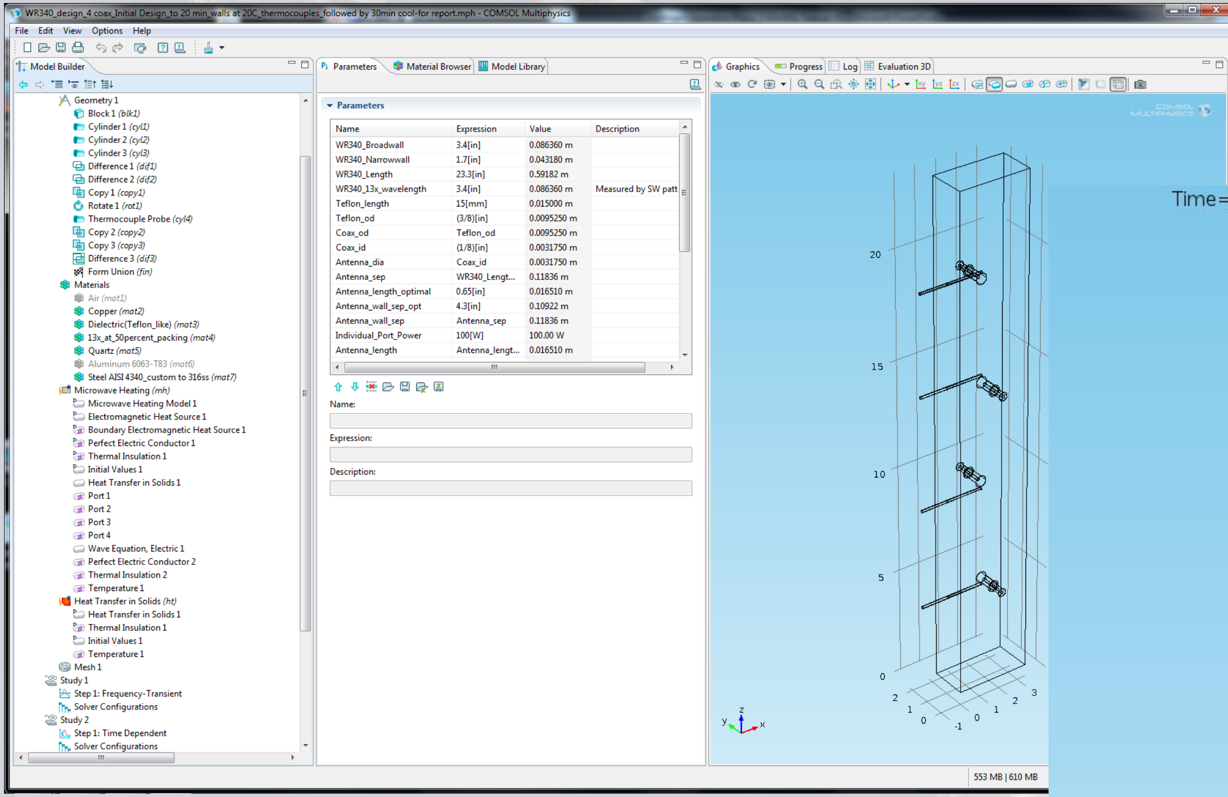
- **Minimal hardware necessary to demonstrate technology**
  - **Manual push button controls**
  - **Microwave components and meters**
  - **Waveguide sorbent bed**
  - **Temperature probes and reader**
  - **Plumbing and solenoid valves as necessary for basic operation**
  - **External vacuum source, cooling loop and gas flow control required**
- **Microwave power distributed along length of sorbent bed**
- **Coaxial cable feeds to antennae inserted in media**
- **Surface cooling plates used for rapid cool down**
- **LEL monitors all connections and gas components within a hazardous gas enclosure and removes gas flow on alarm**

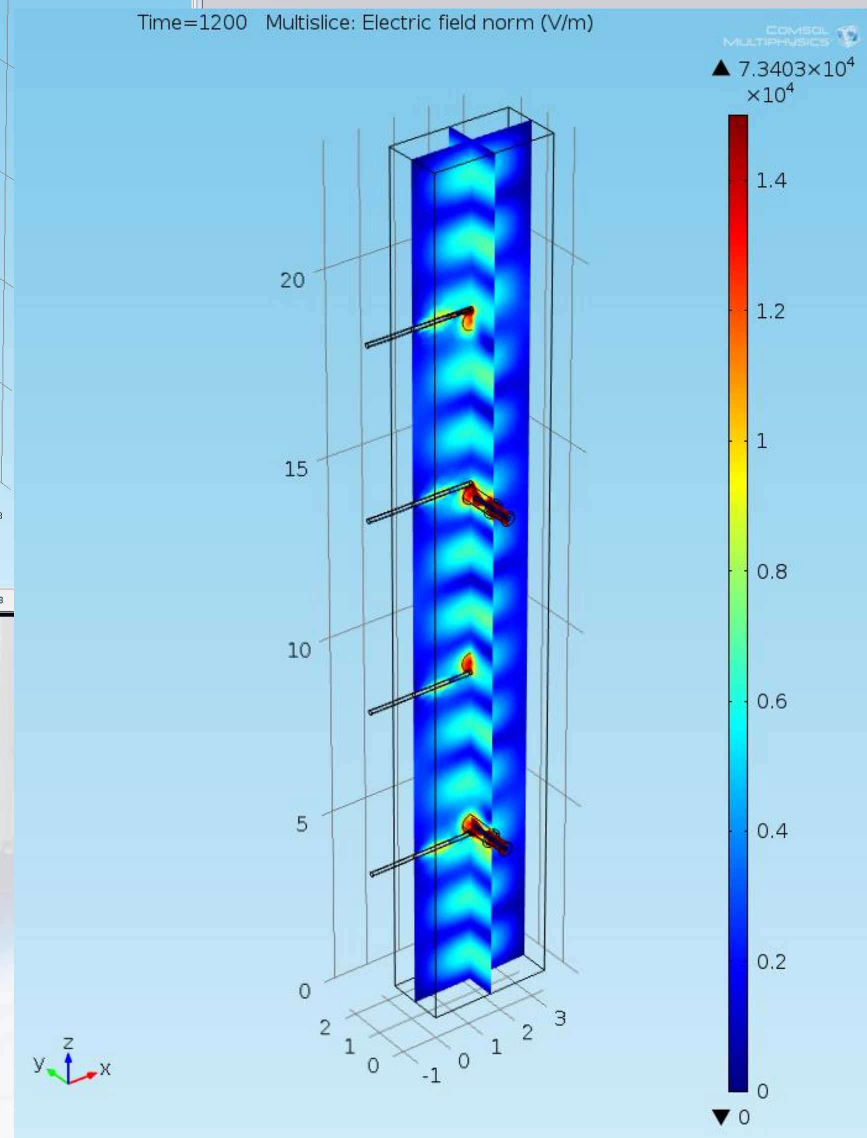
Prototype Hardware Rack Layout Design



Quantity		UNLESS OTHERWISE SPECIFIED:		NAME	DATE	UMPQUA RESEARCH
		DIMENSIONS ARE IN INCHES TOLERANCES: FRACTIONAL ± ANGULAR: MACH ± BEND ± TWO PLACE DECIMAL ±.010 THREE PLACE DECIMAL ±.005	DRAWN	BDM	5/12/15	TITLE:
			CHECKED			HYD-PUR
			ENG APPR.			
			MFG APPR.			
		INTERPRET GEOMETRIC TOLERANCING PER:	Q.A.			
		MATERIAL	COMMENTS:			SIZE DWG. NO. REV

Computer Model Preparation

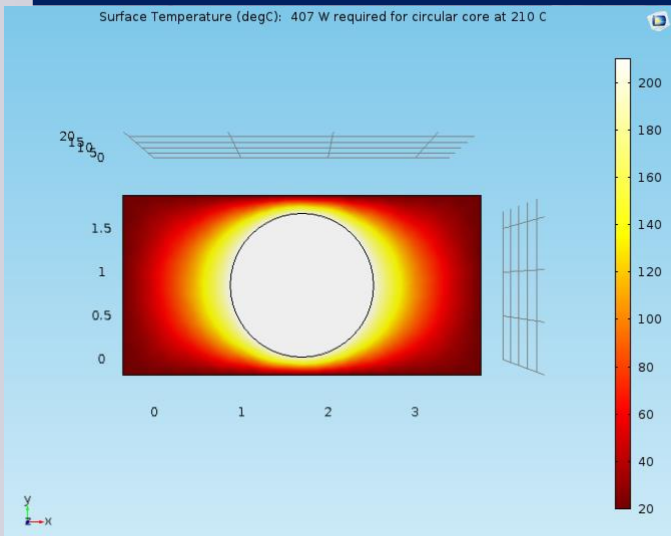




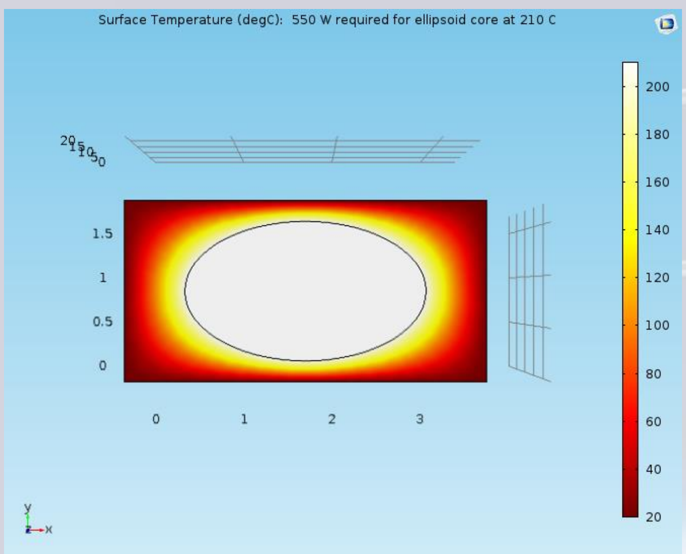
- Construct model closely resembling targeted design
- Build upon successful simple models to become more elaborate (complete) prototype design

Thermal Power Analysis (Feasibility Study for Required Heating Rate)

- WR340 waveguide cross section
- Solid quartz block used as crude, easily modeled representation of media
- Conductive heat transfer
- Core volume representative of microwave power distribution held at 210 °C regeneration temperature
- Walls at 20 °C
- Steady-state heat flow integrated over outer walls



Circular Core:
407 W thermal output

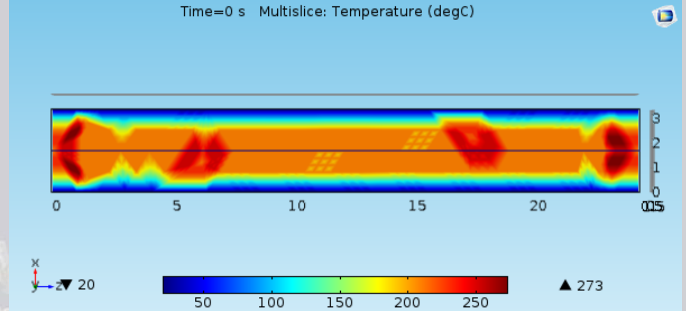


∴ 400-500 W of microwave heating should be sufficient!

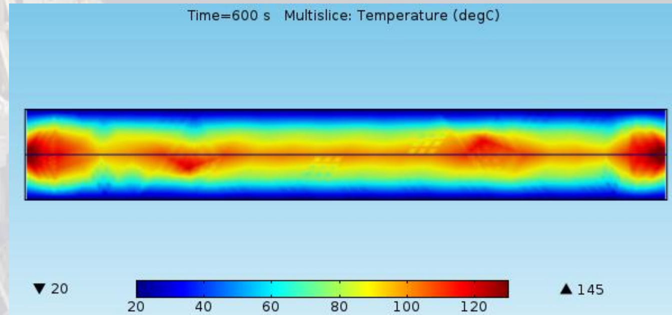
Elliptical Core:
550 W thermal output

Post regeneration cooling time evaluation

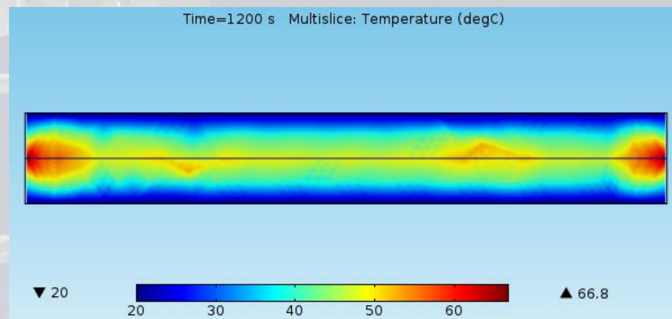
- WR340 waveguide 23.3” long
- 13x media at 50% packing density
- Mixed media approximation of material properties
- Model initial temperature set to 210 °C uniformly throughout bed
- Walls at 20 °C and ends insulated
- Temperature distribution progression over time
- Temperature below 40 °C in 30 minutes (bulk of core ~30 °C)



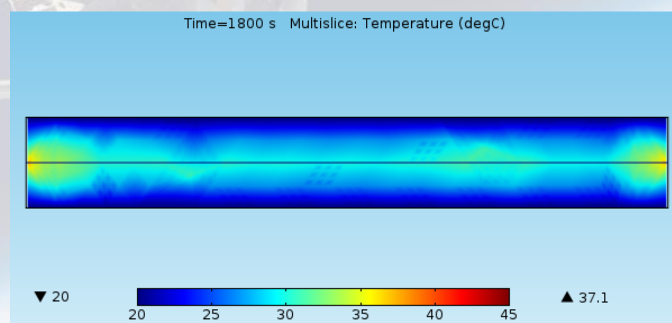
t=0 minutes



t=10 minutes



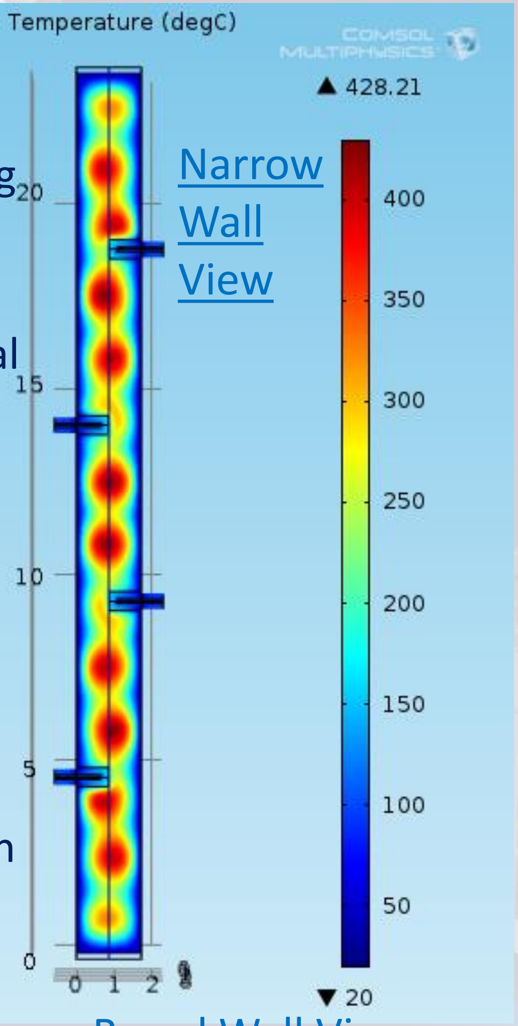
t=20 minutes



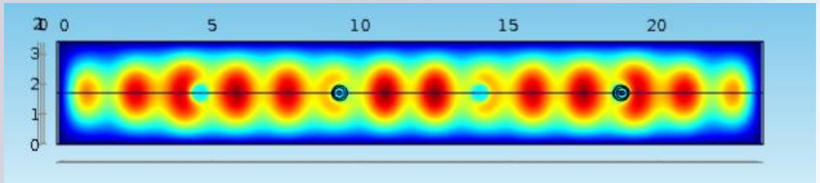
t= 30 minutes

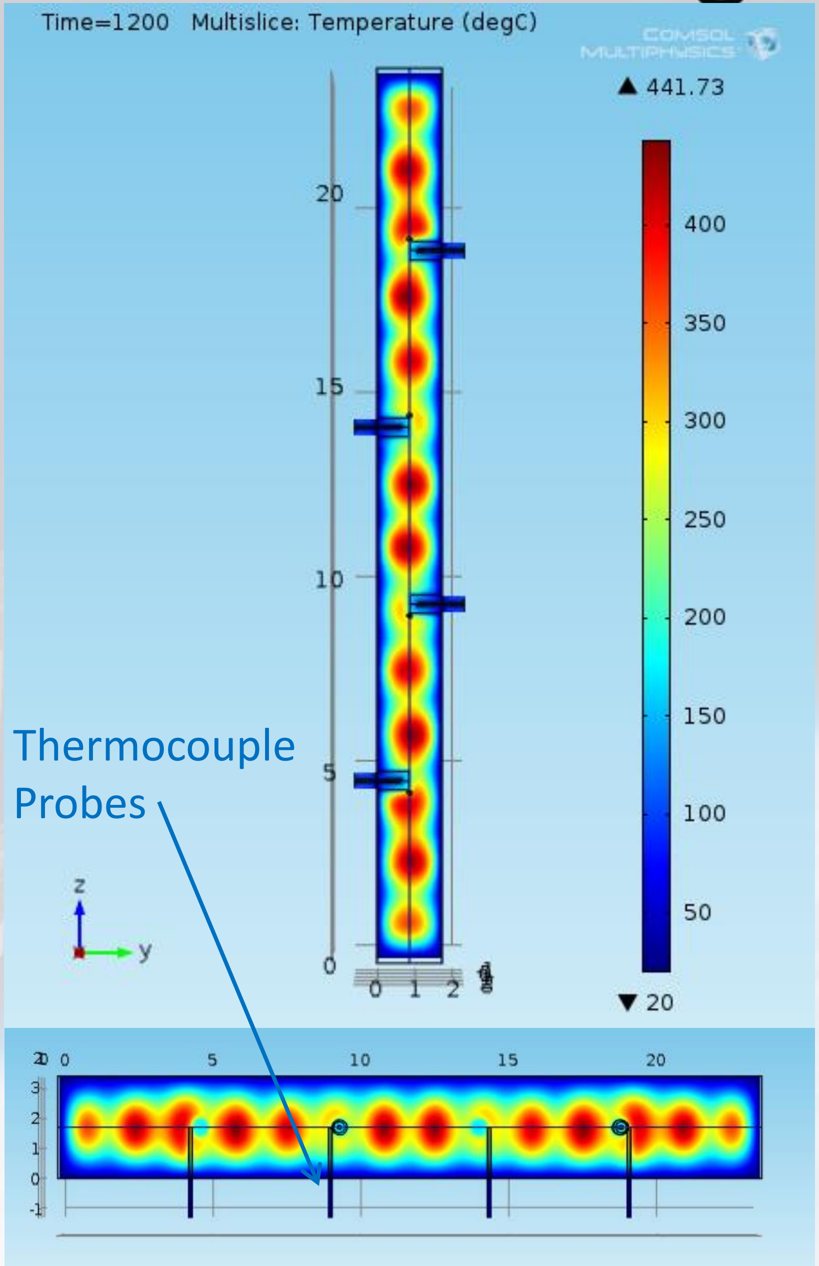
Microwave Regeneration Temperature Distribution

- WR340 waveguide 23.3” long
- 13x media at 50% packing density
- Mixed media approximation of material properties
- Walls at 20 °C and ends insulated
- 4 coax antennae
- Quartz sleeves evaluated as antennae media buffers
- Temperature profiles with (left) and without (right) thermocouple probes
- 20 minutes at 400 W

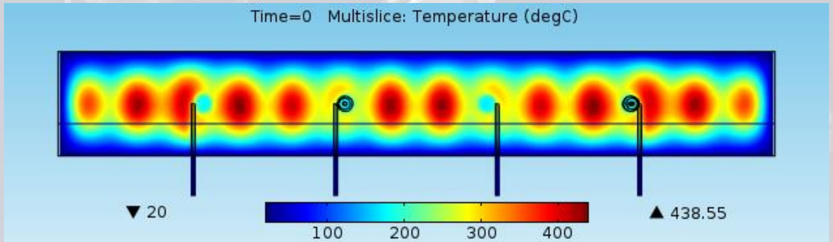


Broad Wall View

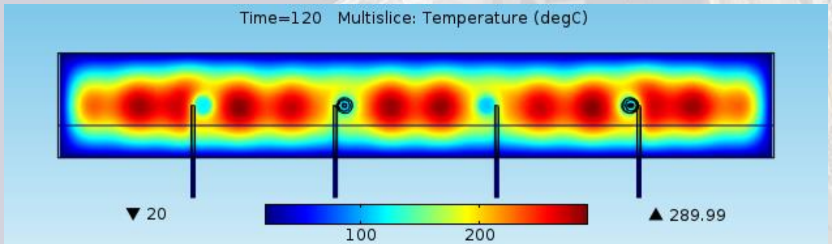




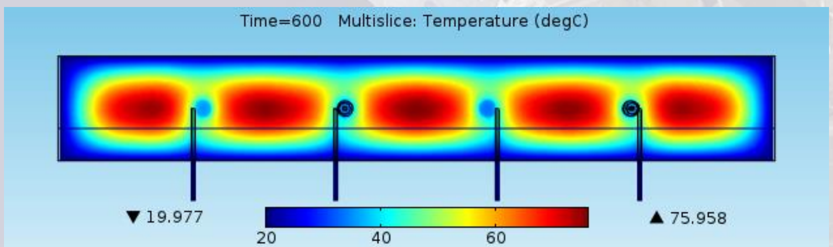
Post Regeneration Cooling Time Evaluation



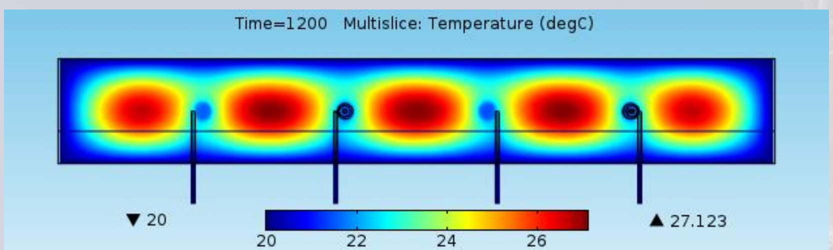
t=0 minutes



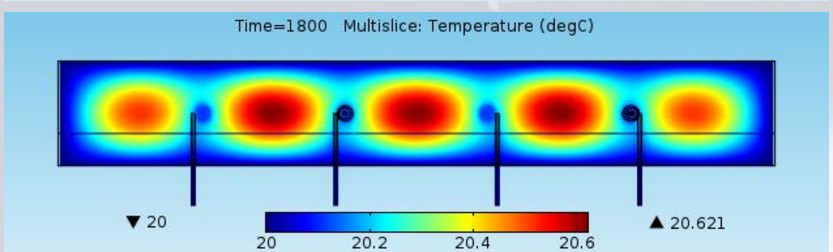
t=2 minutes



t=10 minutes



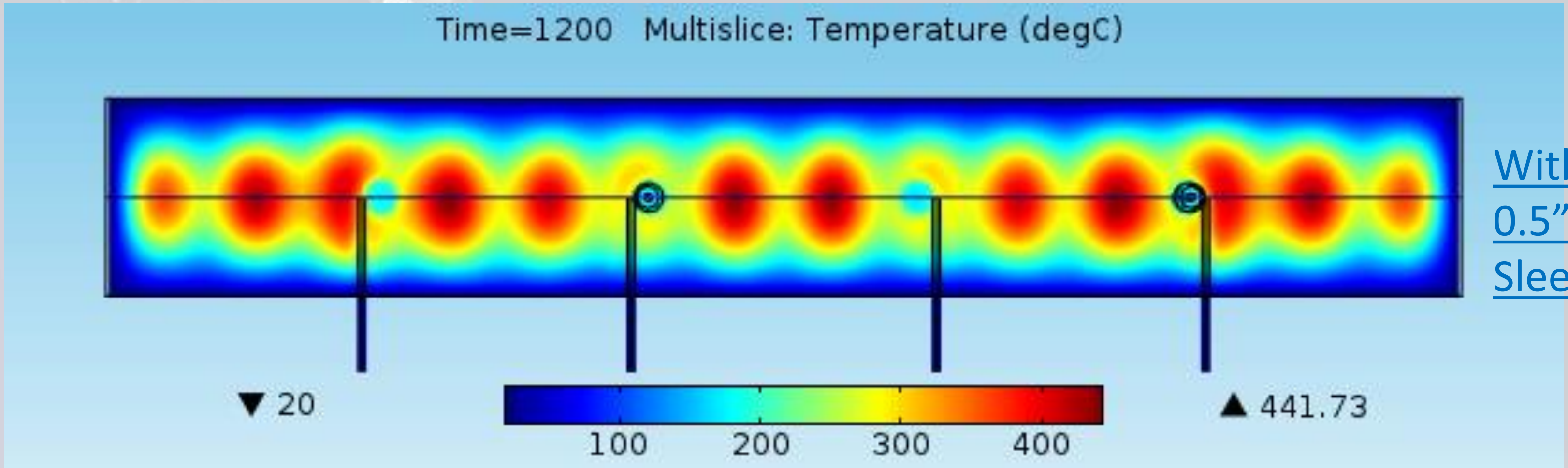
t=20 minutes



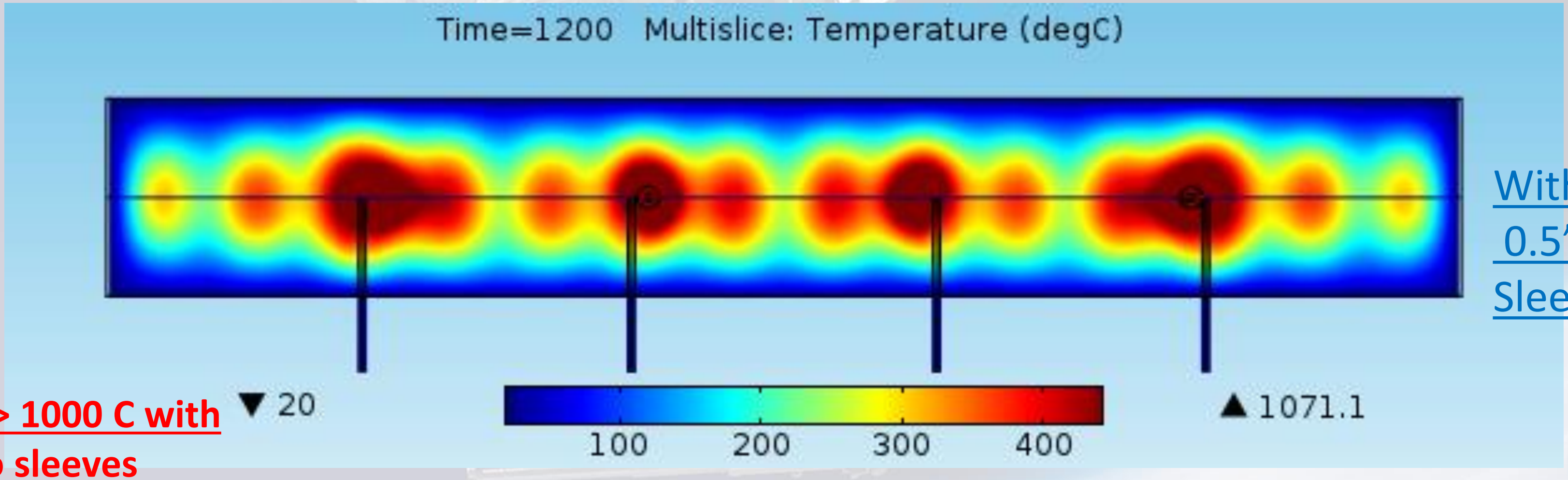
t=30 minutes

- Full thermal model of proposed design
- 20 minutes at 400 W initial state
- Walls at 20 °C and ends insulated
- Cools to under 30 °C in 20 minutes (even faster than predicted in earlier crude evaluation)

Impact of Quartz Sleeves



With 0.5” Sleeves



Without 0.5” Sleeves

T > 1000 C with no sleeves

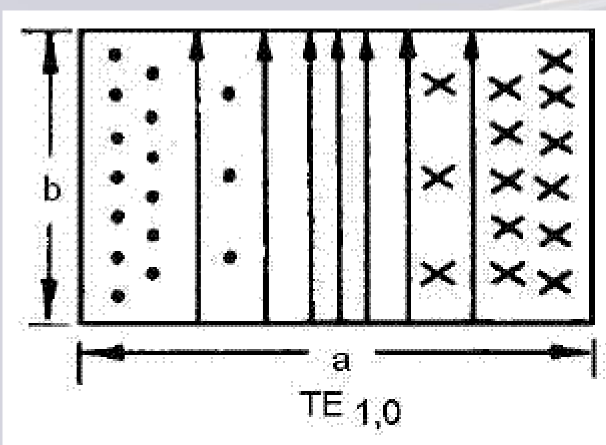
- Field intensity drops off as 1/d^2
- Quartz is both thermally stable and microwave transparent

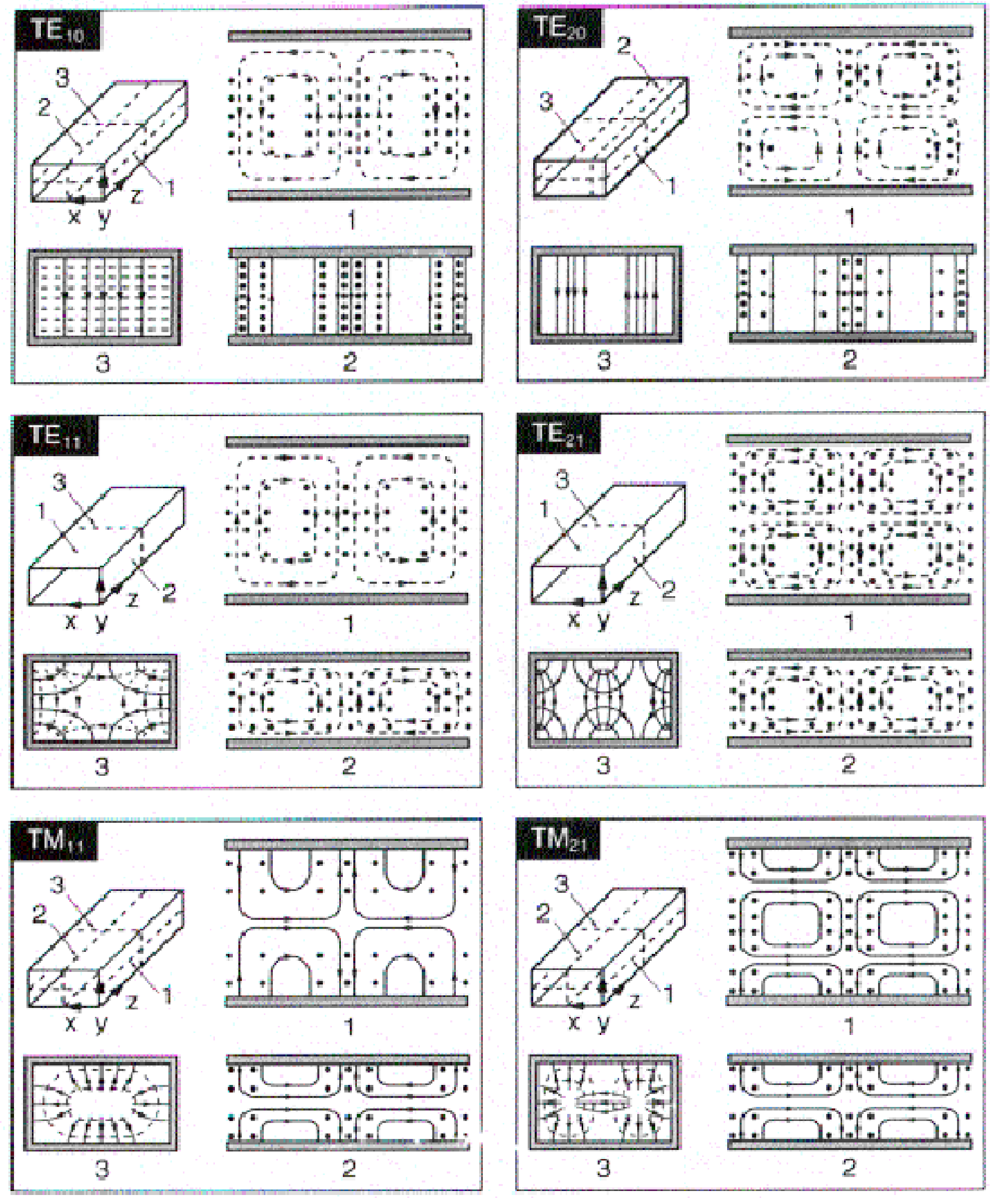
Key Decisions / Direction

- Proceed with overall prototype fabrication
- Identify and order balance of prototype hardware except for bed
- Grace Davison 13x sorbent media to be provided by Marshall.
- Develop computer model for a second (cylindrical) candidate microwave desorbable H_2 purification bed design
- Compare each bed design's strengths and weaknesses and select best design for prototype
- Begin fabrication of selected bed ASAP

Waveguide mode analysis

- Solutions to Maxwell's equations
- TEM wave solutions in free space
- TE and TM modes in waveguides
- Dielectric materials in waveguides can increase possible number/types of modes
- Higher order modes have not been observed in modeling with 13x in WR340 even though they can exist





Modes in Rectangular Waveguide

Evaluation of custom 3-stub tuner design

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- Expected tuner operation confirmed by modeling
- Tuning to greater than 99% power transfer can be achieved
- If no specific stub tuning combination works then turn asymmetrical tuner 180 degrees and retry
- Works just like tuners used in lab

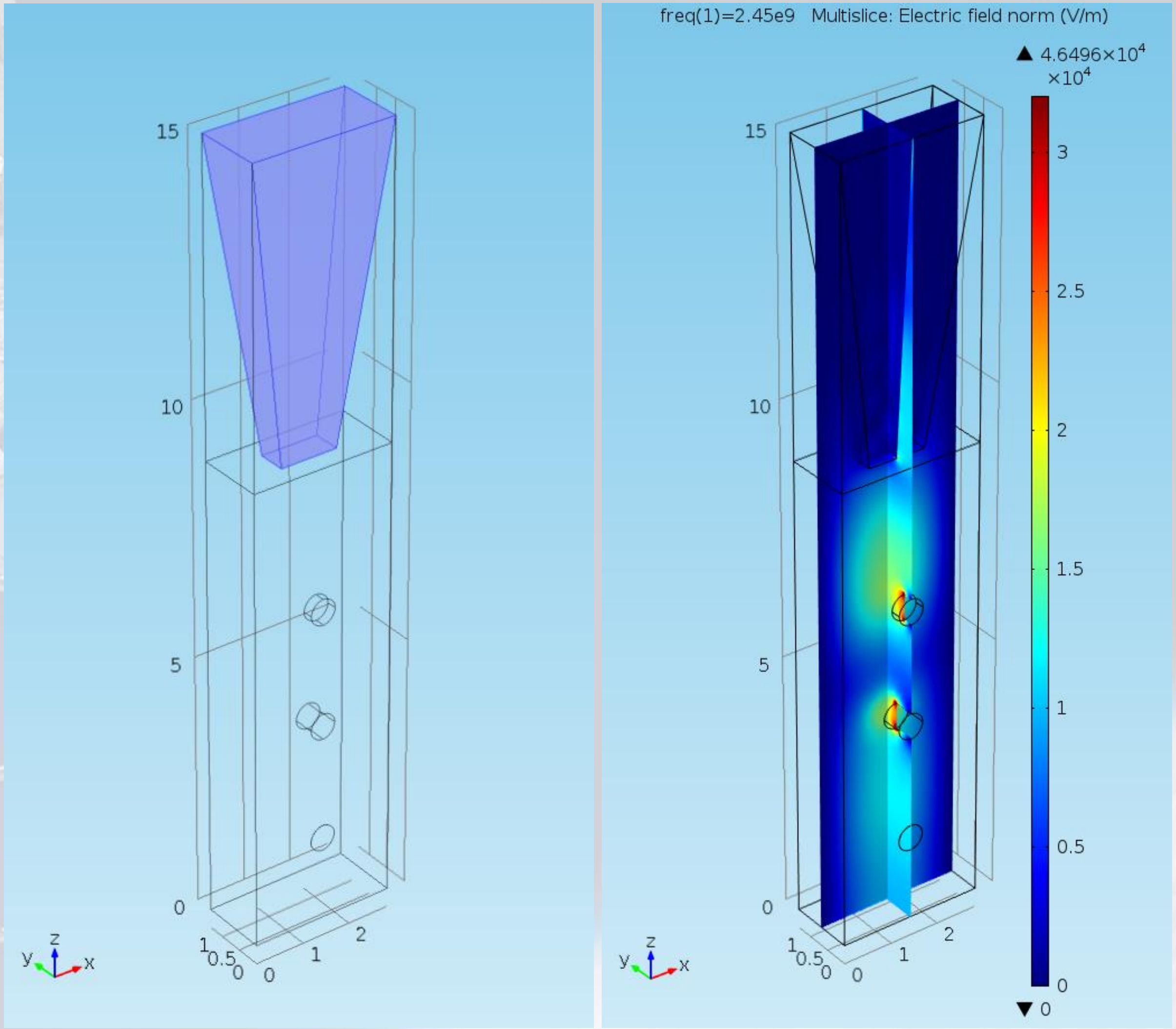
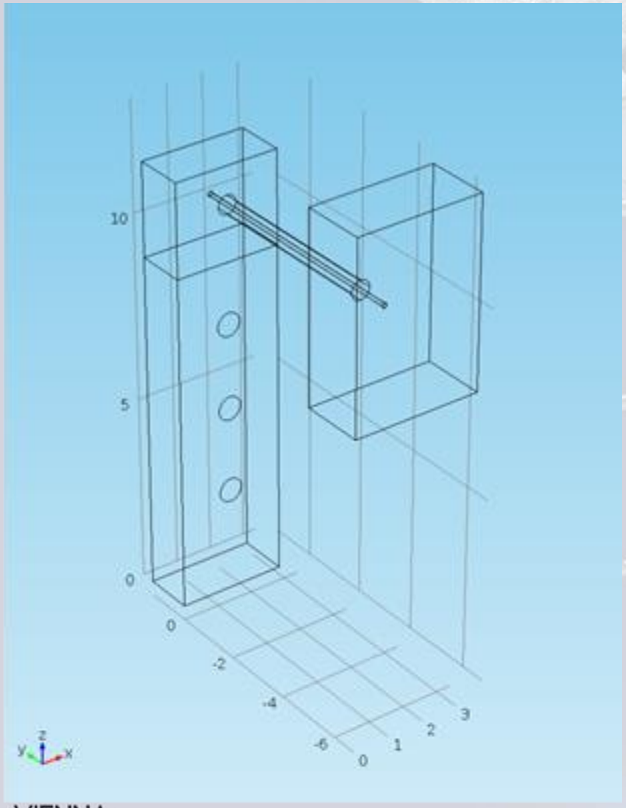
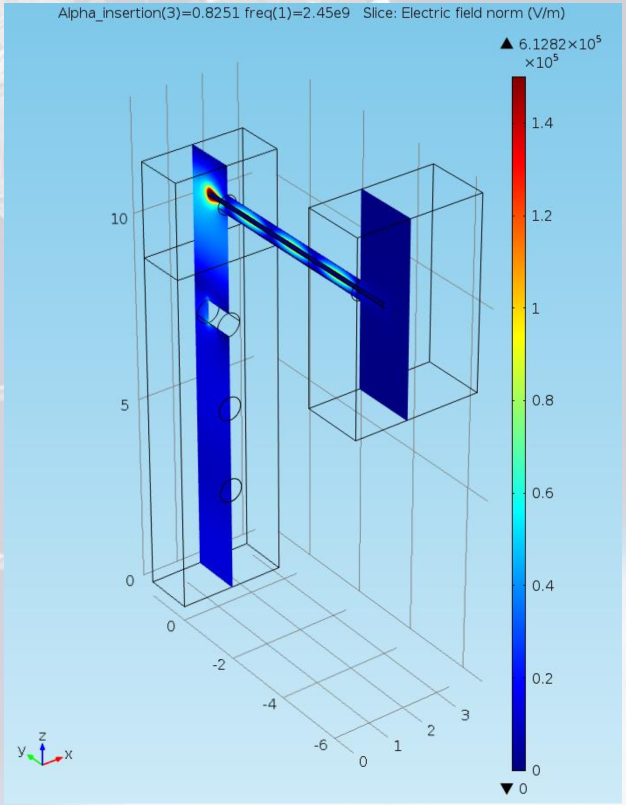


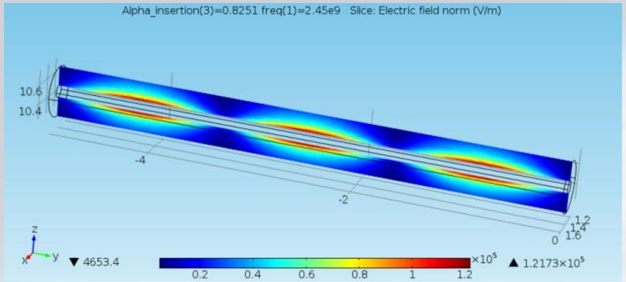
Figure 1. WR284 waveguide based 3-Stub Tuner Evaluation. (Left-) Tuner attached to a pyramid shaped water load. (Right-) Resulting electric field intensity profile.

Feasibility analysis of 3-stub tuning approach for a typical coax to sorbent bed interface

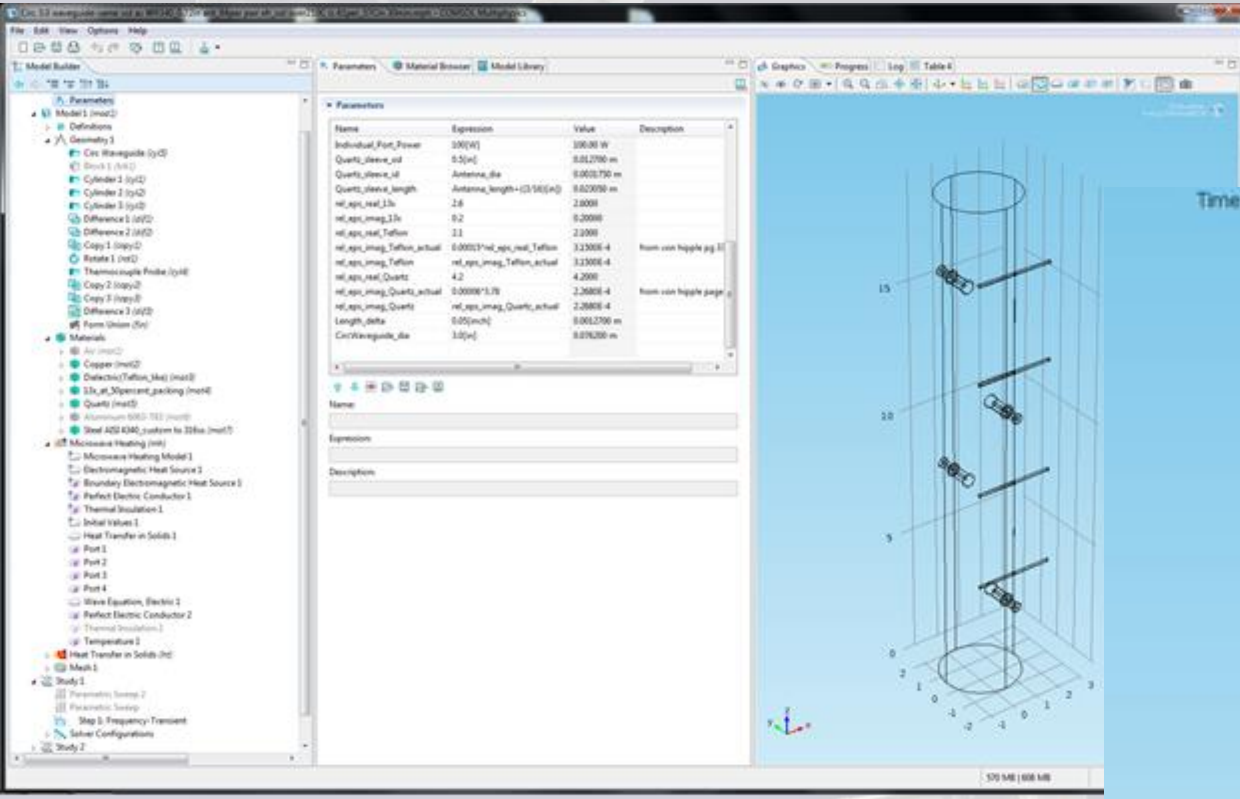
- Simple model prepared: tuner->coax transition->coax cable->load.
- Will hot spots degrade cable power handling?
- Reflection coefficient determined by measuring peaks and valleys.
- When tuned to 97% power transfer to load, VSWR =1.25 which is less than maximum value of 1.35 specified for PE345 cable.

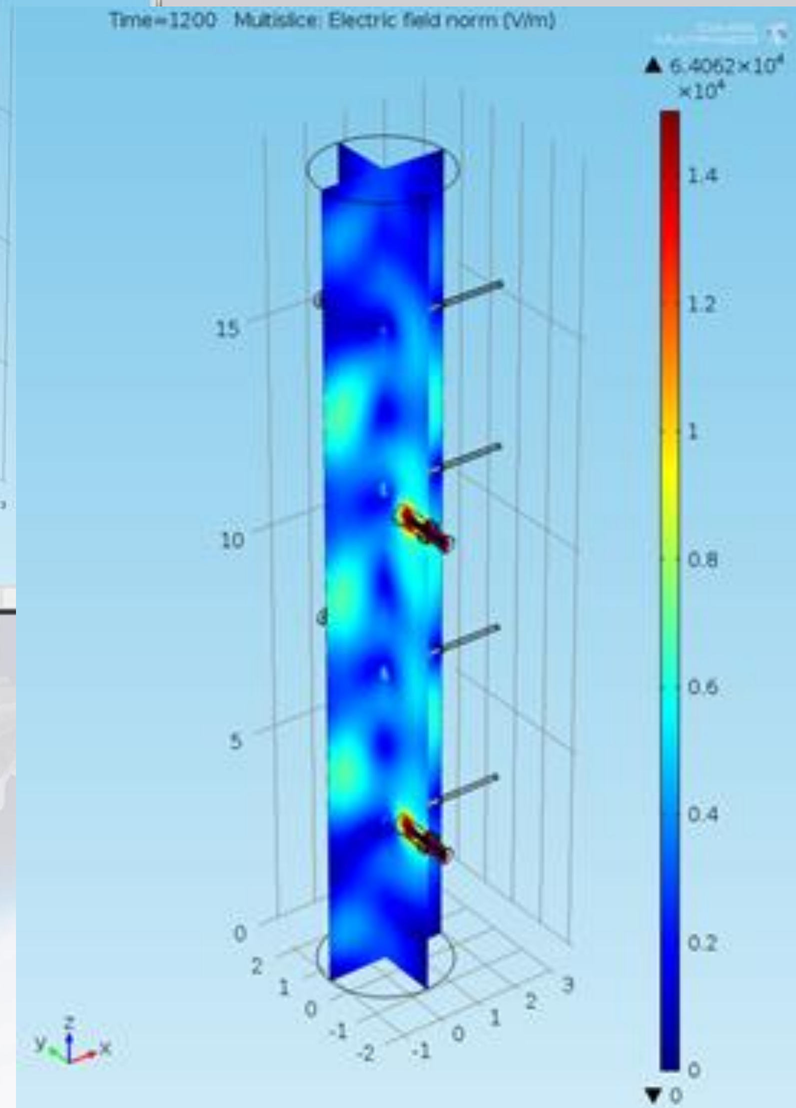






Computer model preparation of circular waveguide sorbent bed

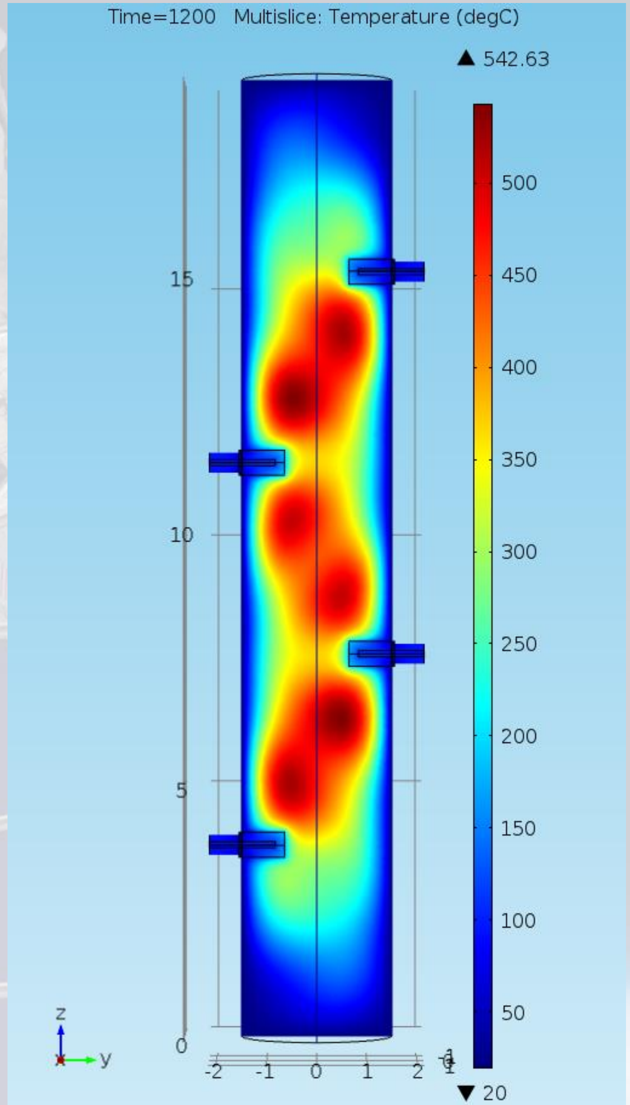


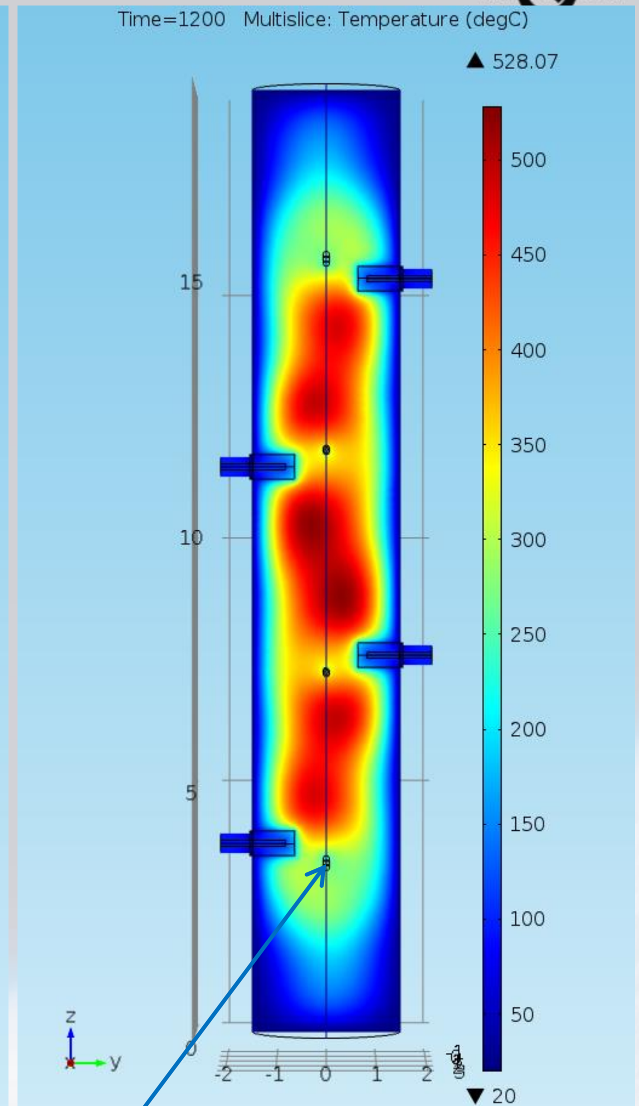


- Clear advantage to starting from a working rectangular model (short model development time)
- WR340 rectangular model modified for a 3.0 inch circular waveguide

Microwave Regeneration Temperature Distribution

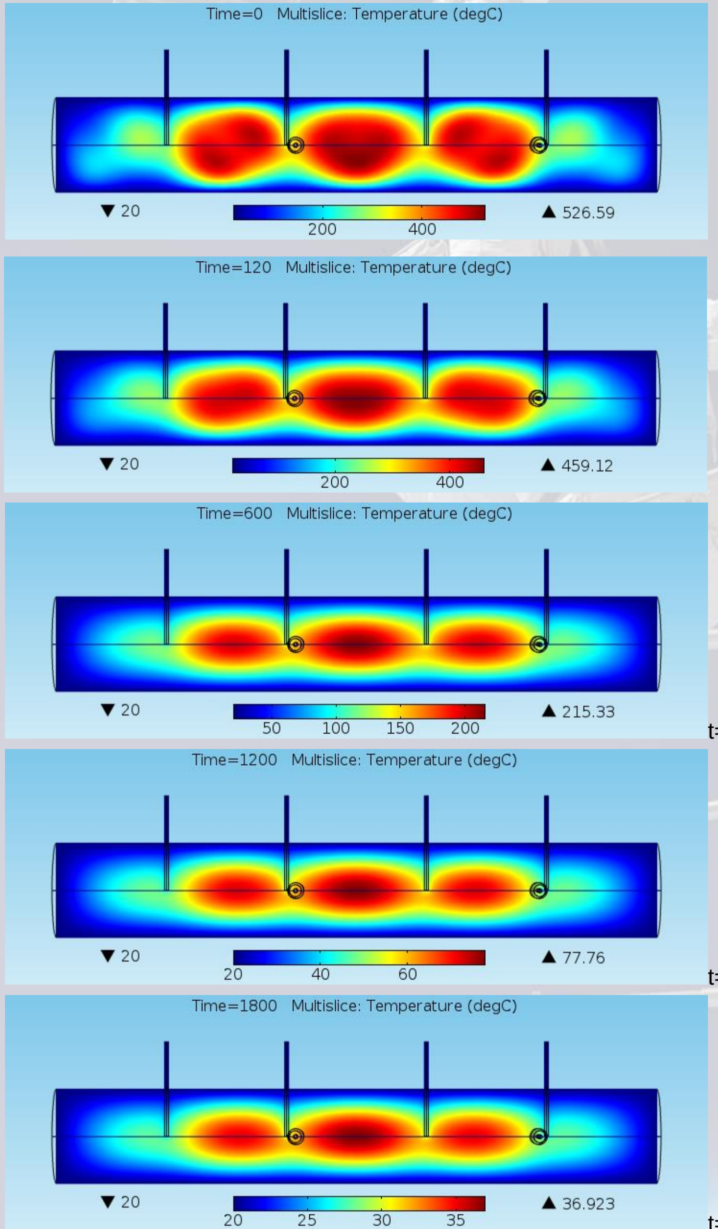
- 3.0 inch i.d. circular waveguide 19” long
- Same volume as WR340 rectangular waveguide
- 13x media at 50% packing density
- Mixed media approximation of material dielectric properties
- Walls at 20 °C and ends insulated
- 4 coax antennae
- 0.5 inch o.d. quartz sleeves on each
- Temperature profiles with and without thermocouple probes
- 20 minutes at 400 W
- Higher peak temperature than rectangular design





Thermocouple Probes

Post Regeneration Cooling Time Evaluation



t=0 minutes

t=2 minutes

t=10 minutes

t=20 minutes

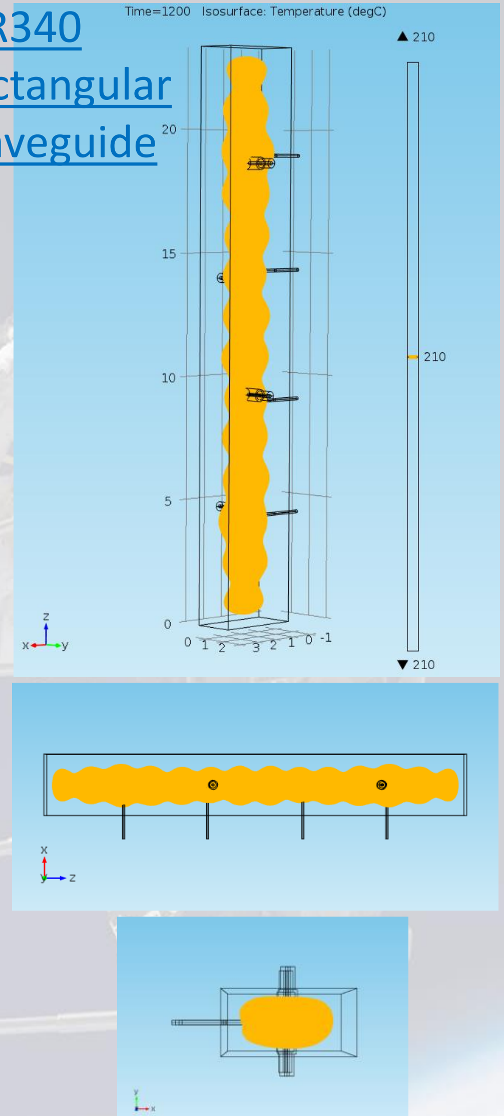
t=30 minutes

- Full thermal model of proposed design
- 20 minutes at 400 W initial state
- Walls at 20 °C and ends insulated
- Snapshots taken of temperature distribution over time
- Cools to 37 °C in 30 minutes (similar to rectangular design)

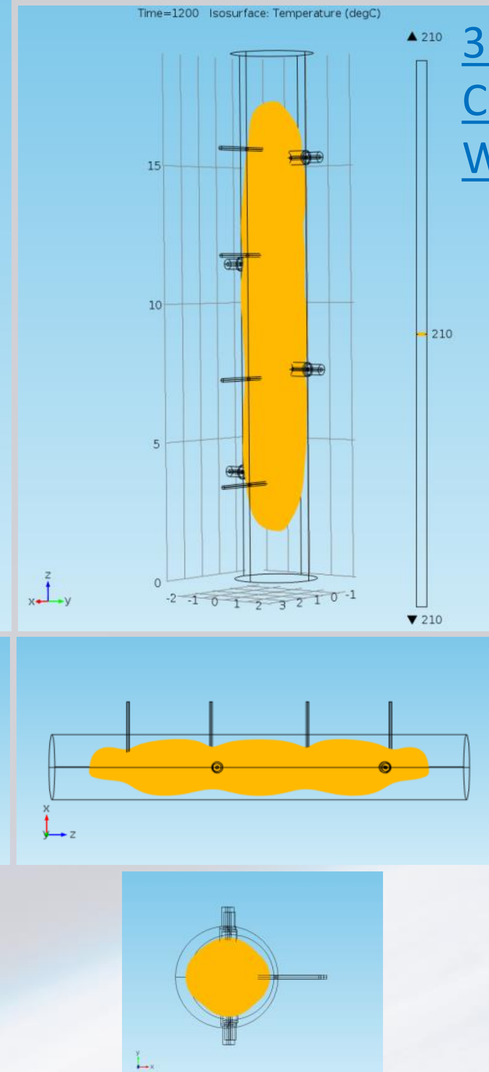
Isothermal surface profiles at 210 °C after 20 min. at 400 W

- Equal volume rectangular and circular cross-section beds compared
- Targeted minimum regeneration temperature envelope of 210 °C develops down the center of each bed design
- ~30% of WR340 bed volume above 210 °C vs. ~50% of 3.0 in circular bed (however, ends are under utilized)
- Despite better regeneration coverage, fabrication of a circular bed that incorporates cooling is costly and much more complicated
- Therefore rectangular design selected for fabrication

WR340 Rectangular Waveguide



3.0 inch Circular Waveguide



Photos 6-25-15 (Month 3)

Photos 7-21-15 (Month 4)

Figure 1. MRSHP prototype assembly. (Top Left-) Empty rack with door closed; (Top Center-) Empty rack with door open; (Top Right-) Rack with microwave hardware on top; (Middle Left-) Rack with waveguide H-mount; (Middle Center-) Waveguide H-assembly; (Middle Right-) Rack with waveguide H-assembly mounted; (Bottom Left-) Custom tuner, coax transition, coaxial cable and antenna; (Bottom Center-) Coaxial panel mount antenna; (Bottom Right-) Copper cooling plate assemblies.

Photos 7-21-15 (cont.)

Figure 2. MRSHP waveguide bed. (Upper-) WR340 Bed; (Lower-) Bed and narrow side cooling plates.

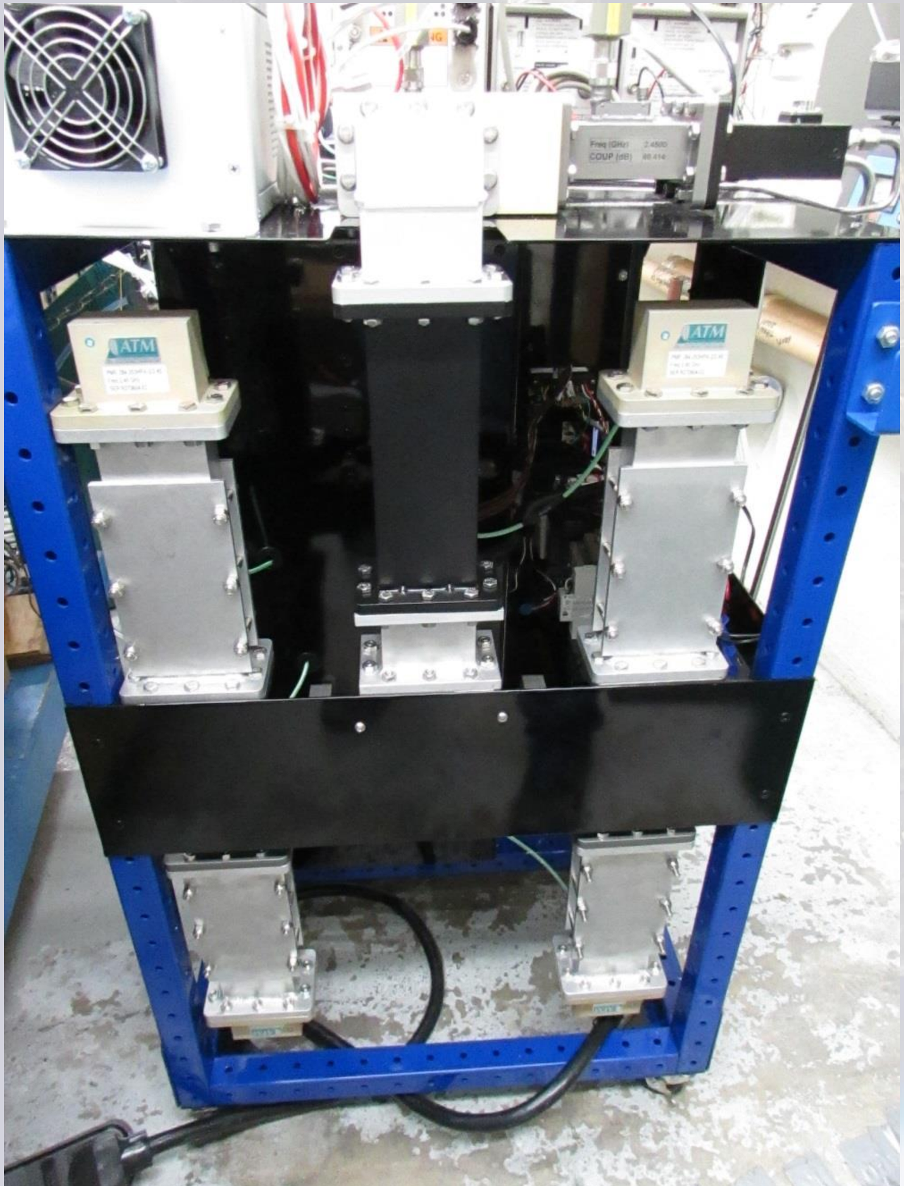
Photos 8-19-15 (Month 5)

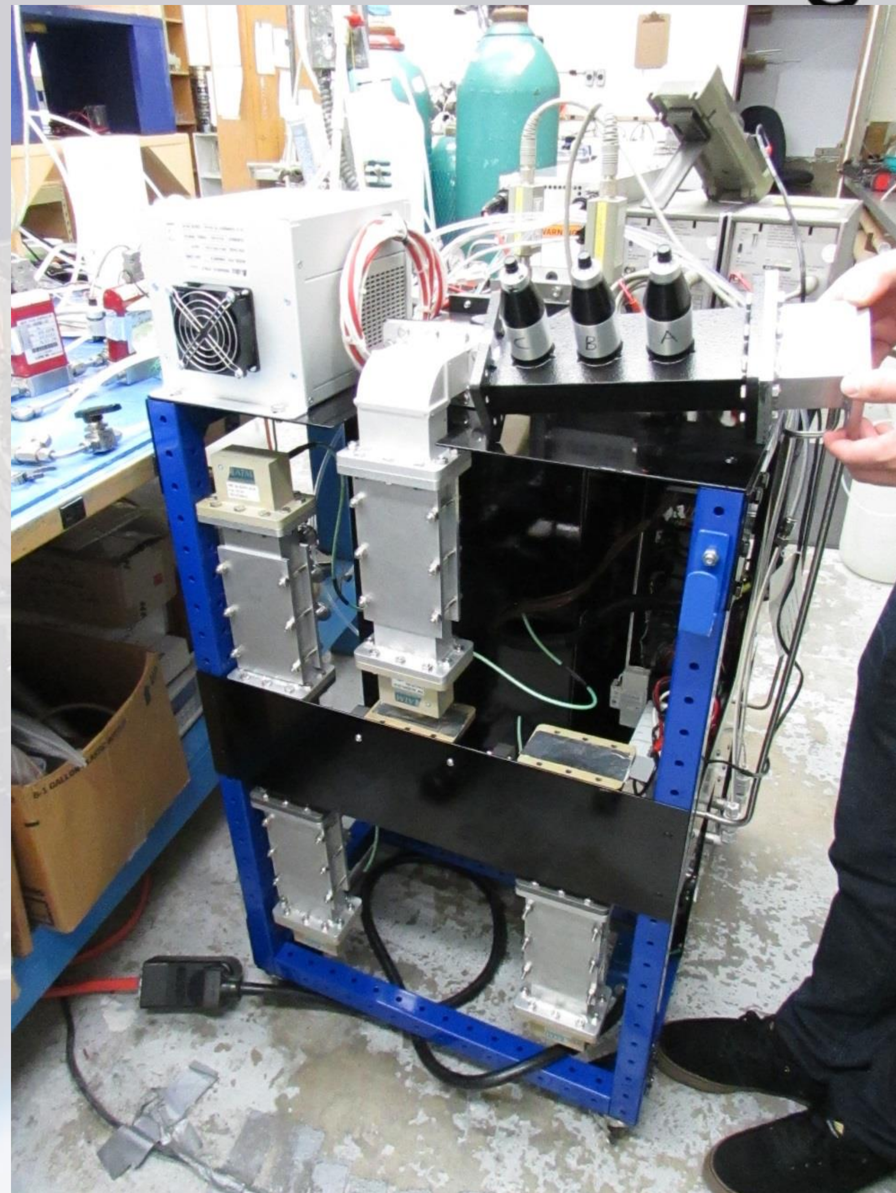
Figure 1. Loading of the WR340 rectangular waveguide based sorbent bed. Top to Bottom: (1st Row, Left-) Empty bed; (1st Row, Middle-) bed with quartz wool at bottom; (1st Row, Right-) First layer of 13x added; (2nd Row, Left-) Second layer added; (2nd Row, Middle-) Third layer added; (2nd Row, Right-) Final layer of 13x added; (3rd Row, Left-) Top layer of quartz wool added; (3rd Row, Middle-) Perforated plate added; (3rd Row, Right-) Gas inlet/distributer end piece added; (4th Row) Fully assembled bed.

Photos 8-19-15 (cont.)

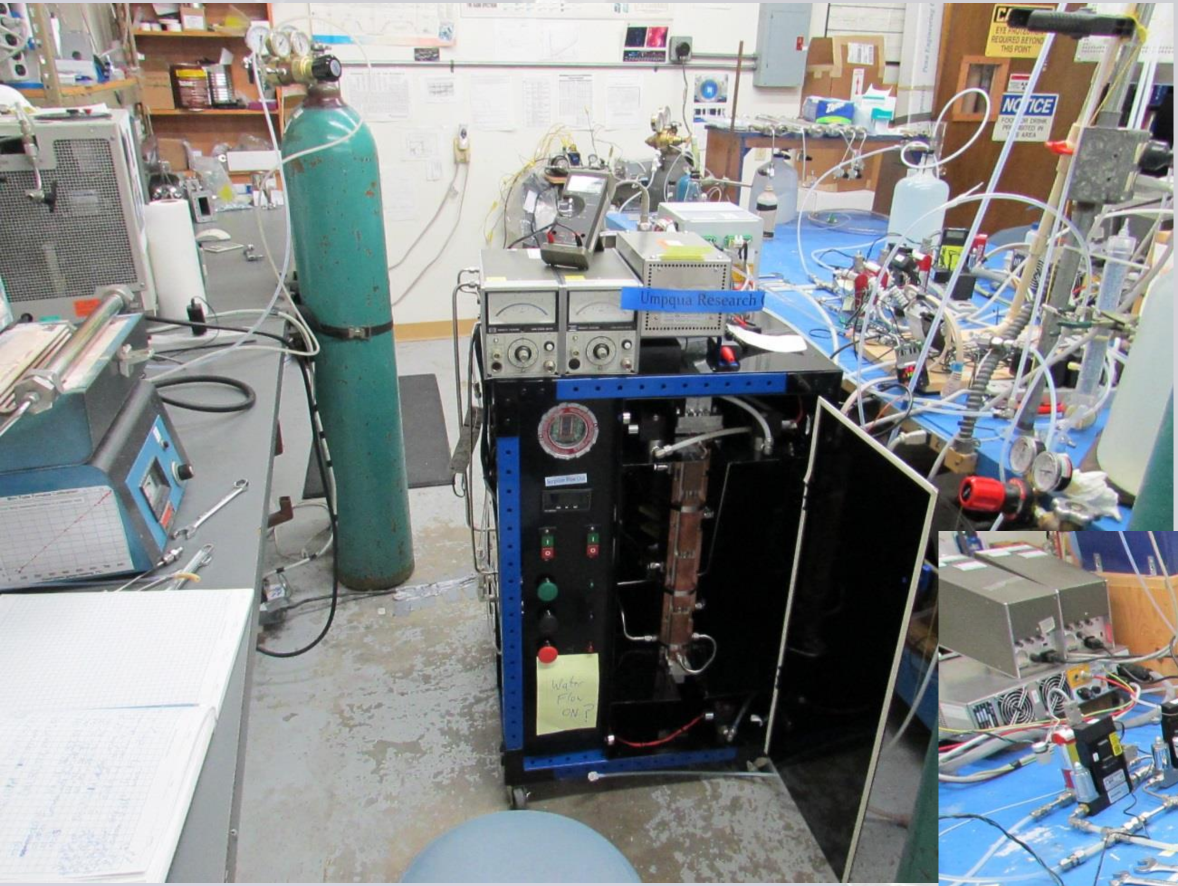
Figure 2. Final assembly of the MRSHP prototype. Top to Bottom: (1st Row, Left-) Front view; (1st Row, Middle-) Front view with door open; (1st Row, Right-) Close up view of bed and control panel; (2nd Row, Left-) Left side view; (2nd Row, Middle-) Right side view; (2nd Row, Right-) Rear view.

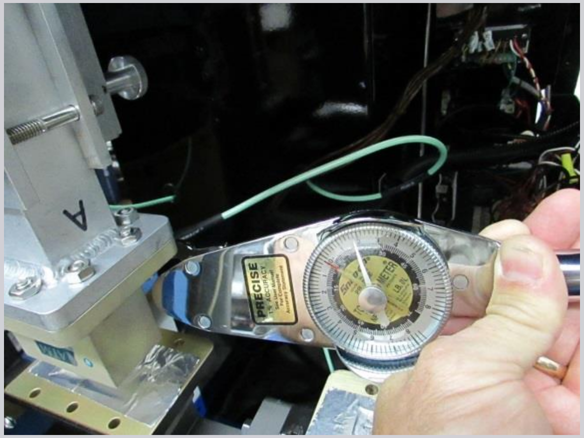
Individual Port Tuning

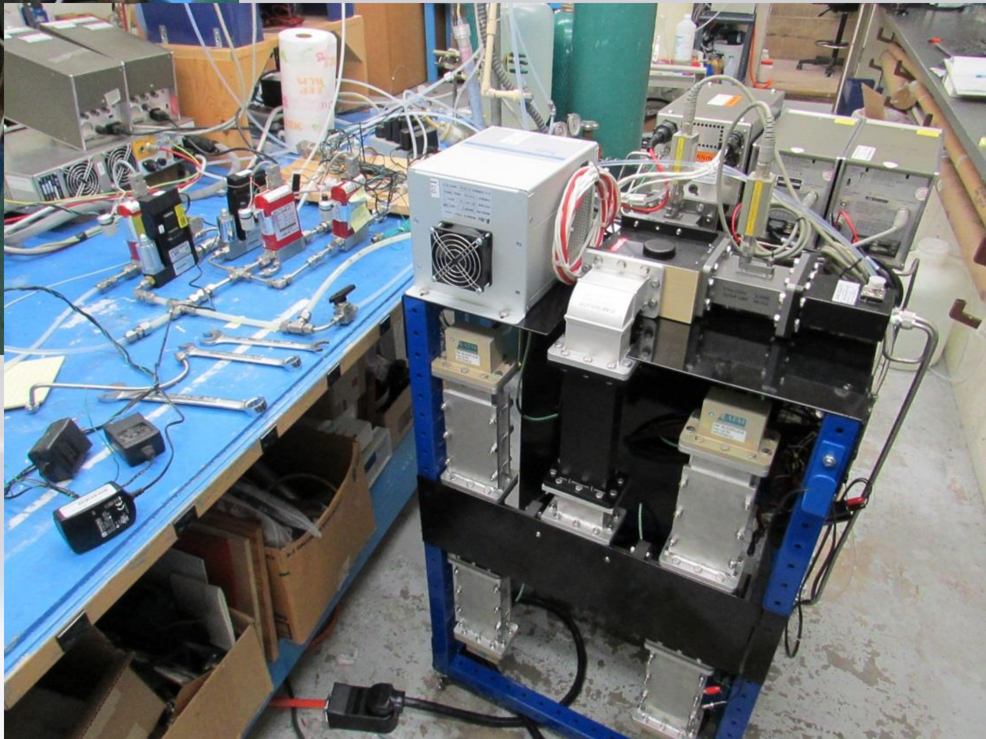




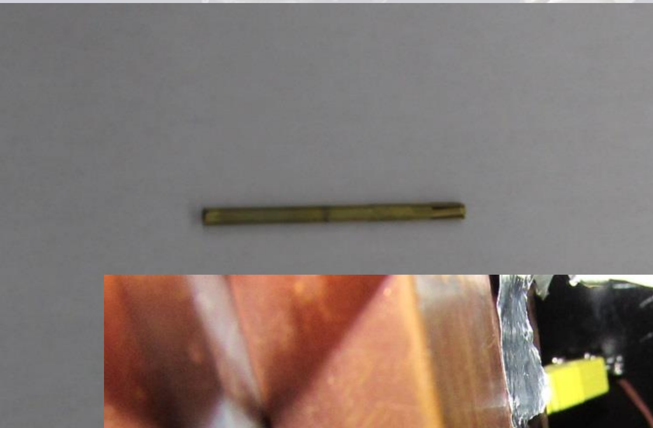
Prototype Testing (Month 6)

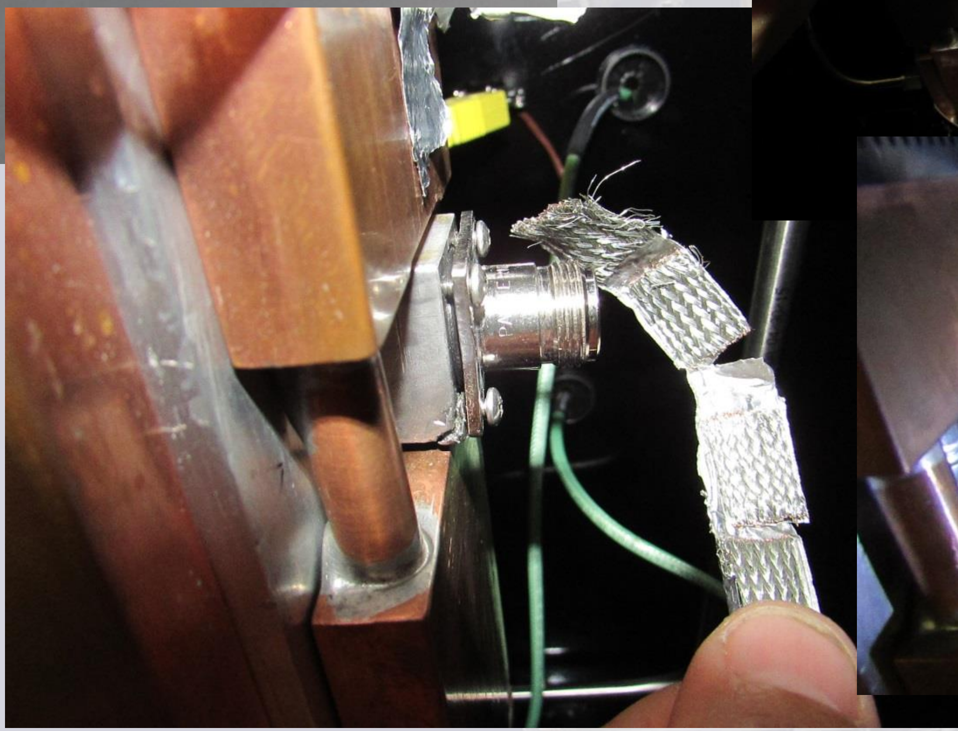


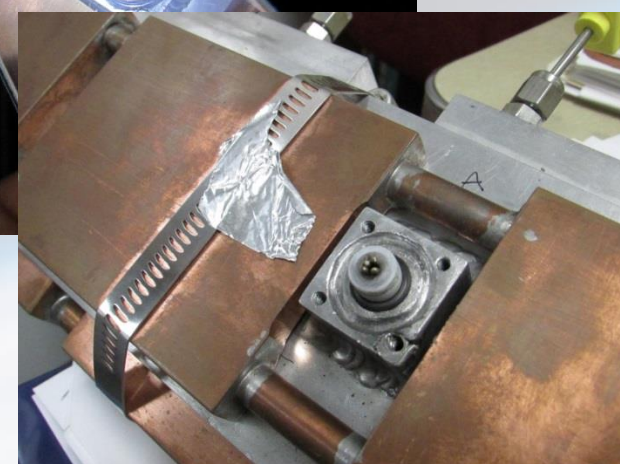




Performance Testing /Defining Upper Limits :/

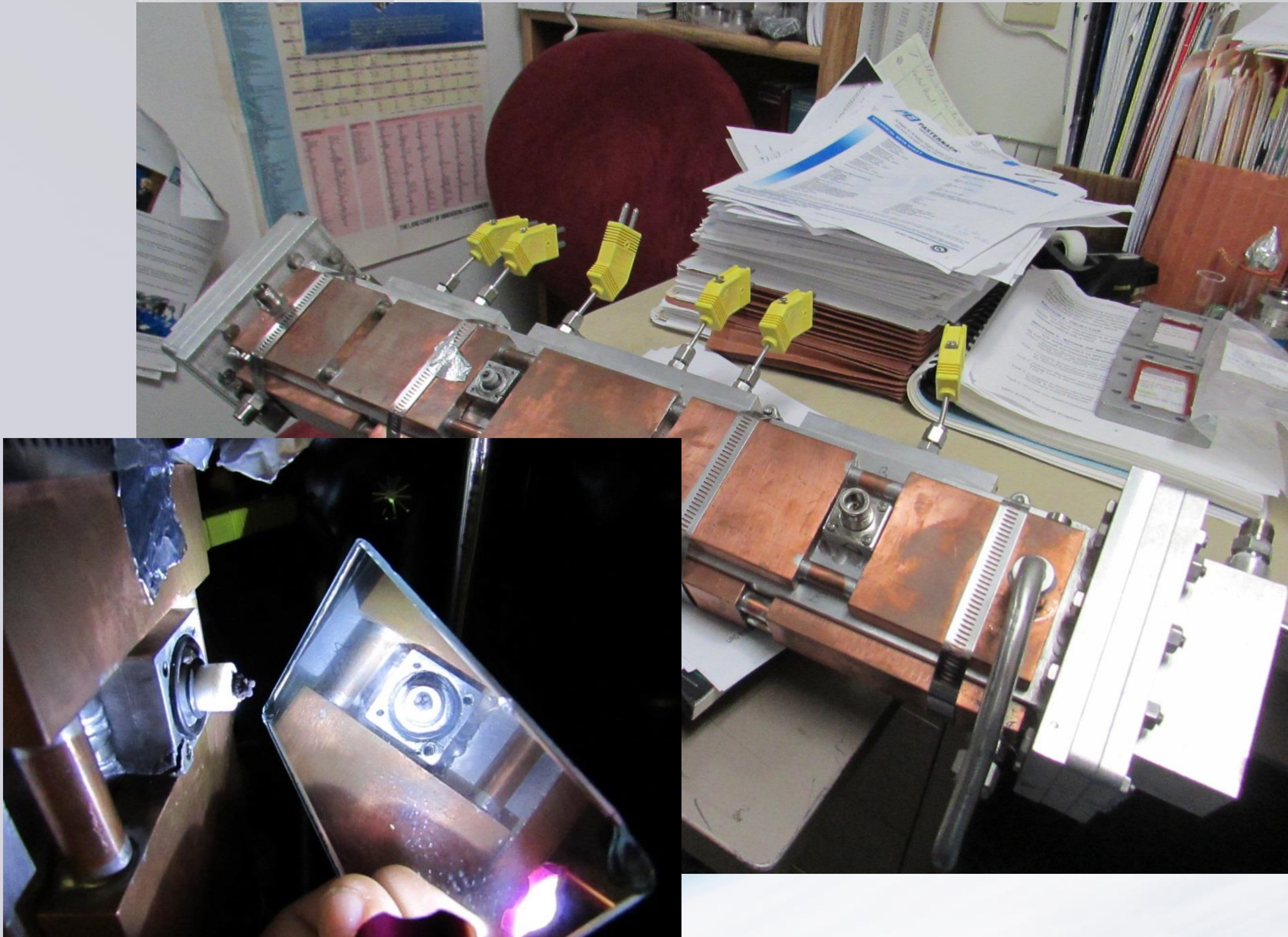






- Not much time for this activity in a 6 mo. project
- Cables and connectors destroyed
- Bottom Line → 300 °C and/or 400 W too extreme
- Note that this is discovered in the last two weeks of the project…

Cont.



Outline of Rebuild and Re-test Progression in Final Week of Contract

- Improved connector design
- Plugs in holes at end of quartz sleeves to keep media away from antennae
- Sorbent bed reassembled
- Poor performance was observed when retested?? Why?? What changed??
- Oops, wrong Teflon used (not specified for electrical applications)
- Rapid rebuild and refurbishment for delivery, with new cables and original connector design and original Teflon
- Last minute evaluation tests confirm that original performance restored
- 200 W and 210 °C limits used for large safety margin (compared to 400 W and 300 °C)
- Connector and cable temperatures stay well below rated levels

Evaluation Testing

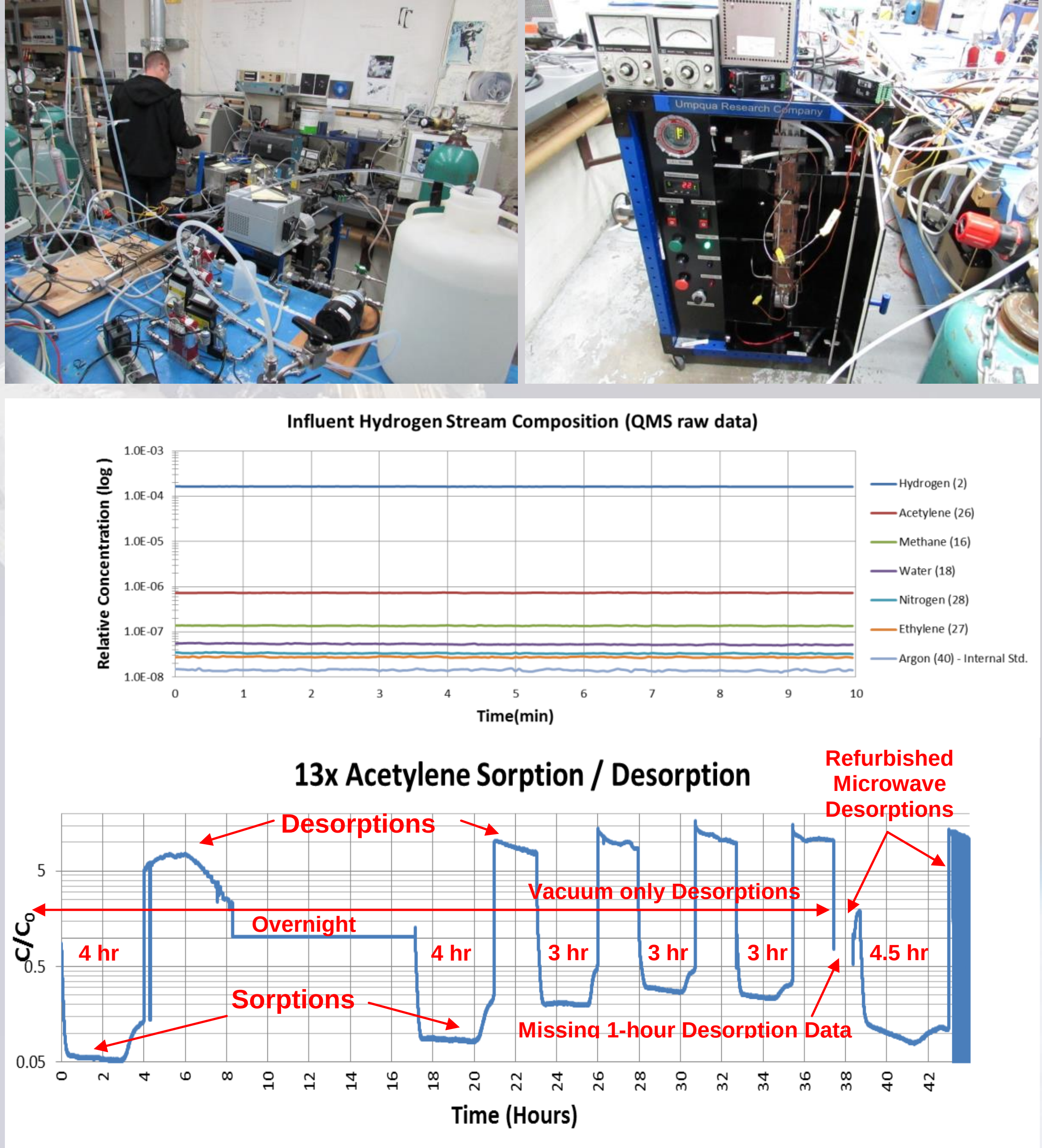


Figure 2. Evaluation testing of the MRSHP prototype. (Upper) Prototype under test; (Middle) Sorption influent composition at 2-CM PPA effluent levels; (Lower) Acetylene Sorption / Desorption profiles.

Performance Summary

- Assuming a 2 hour vacuum/microwave heated desorption (regeneration) in each case :
  1) Steady-state regenerated bed capacity, while operating at 2-CM equivalent PPA effluent levels, was observed to be at least 4 hours.
  2) Predicted steady-state regenerated bed capacity, while operating at 1-CM equivalent PPA effluent levels, should be 8 hours.
  3) Predicted steady-state regenerated bed capacity, while operating at 0.5-CM equivalent PPA effluent levels, should be 16 hours.
- These compared to the design target of 0.5-CM capacity with 0.5 hour regeneration after 8 hours.
- Note that shorter regeneration times were not tested. Therefore a 1 hour regeneration may restore adequate capacity. Further testing required…

Refurbishment and Final Preparations

Figure 3. Preparation of the MRSHP prototype for delivery. Left to Right: (Upper Photos) Refurbishment- empty HGE, new cables w/ disassembled bed, media removed and saved; (Middle Photos) Reassembly- quartz sleeves affixed inside bed and shielding placed on thermocouple probes; (Lower Photos) Tuning, labeling, photos and shipping.

Delivered MRSHP

Further Development

- Integrated performance testing is required using sub-scale Microwave Regenerative Sorbent-based Hydrogen Purifier
- Results will provide important guidance to advanced designs
- Scale-up to full 4-CM capacity requires a significant level of effort such as a 2-year SBIR Phase II
  - Optimize power utilization and distribution for heating media
  - Minimize system volume and complexity
  - Investigate cylindrical design with possible 2-fold regenerated capacity improvement over rectangular waveguide
  - Full-scale prototype would be designed to demonstrate continuous long-term operation as integrated to the advanced PPA located at MSFC

Acknowledgement:

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