Determination of TCAP (Thermal Cycling Absorption Process) Raffinate Purity

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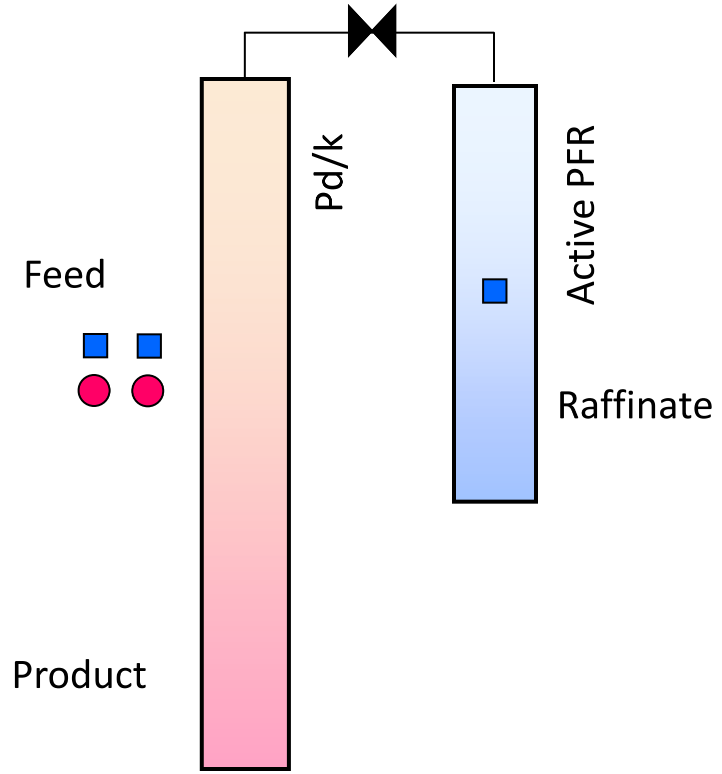
Analytical Issue and Solution in H_2/D_2 R&D

- 99+% D_2 (product) and H_2 (raffinate) from TCAP, better purity than detection limit
- Raffinate has much less D_2 than ultra high purity gas cylinder (natural abundance D/H ratio is 155.78 ppm).
- Raffinate impurity correlates with H_2 stack emission in tritium operation

- ~ 200 sl TCAP raffinate gas was collected in a hydride bed
- The hydride bed was transferred to another room
- The raffinate in hydride bed was oxidized into water in a catalyst evaluation lab reactor
- D/H ratio was analyzed by spectroscopy method

TCAP Working Principle

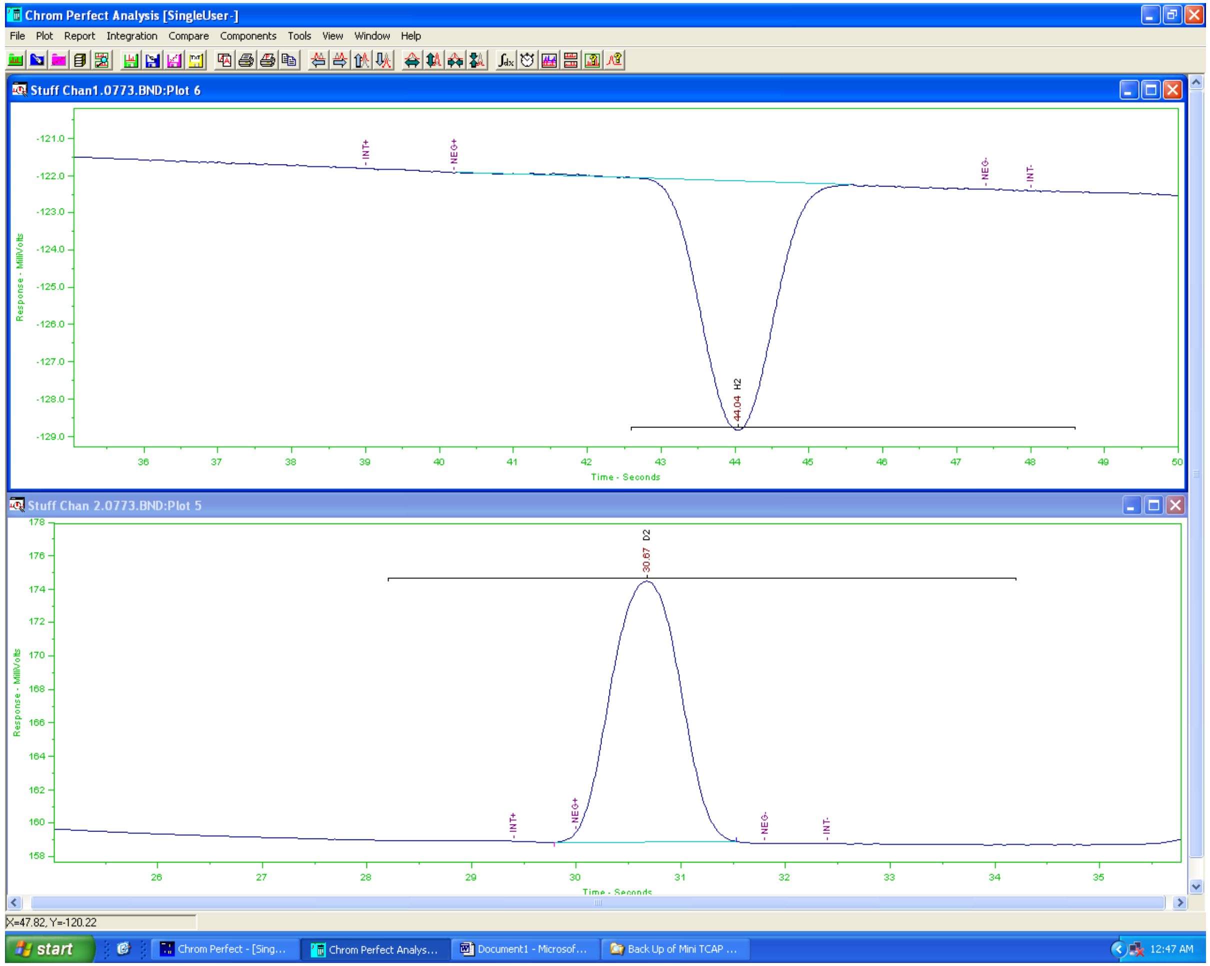


Previous Analysis Using Thermal Conductivity (TCD)

H_2 analysis
using D_2 carrier

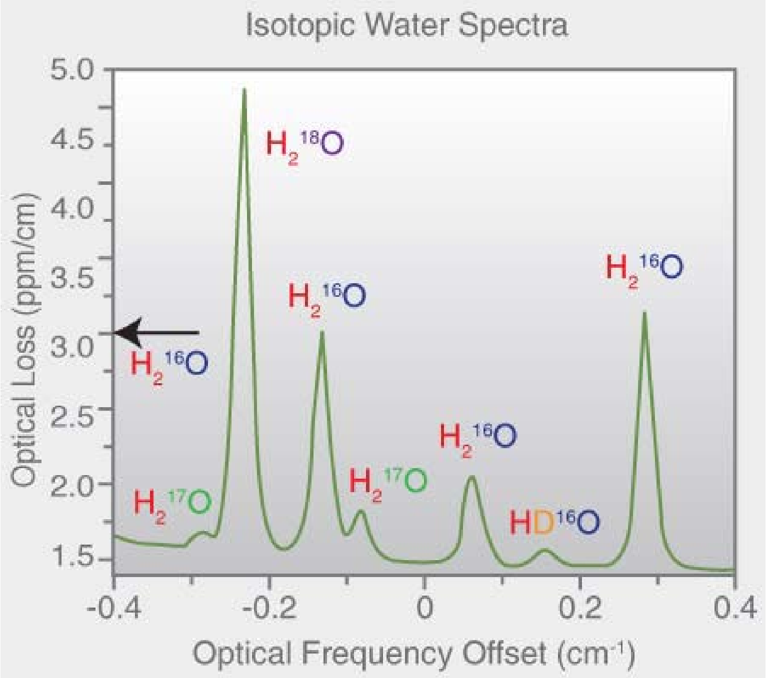
10 ppm resolution
lack of low range
calibration standards

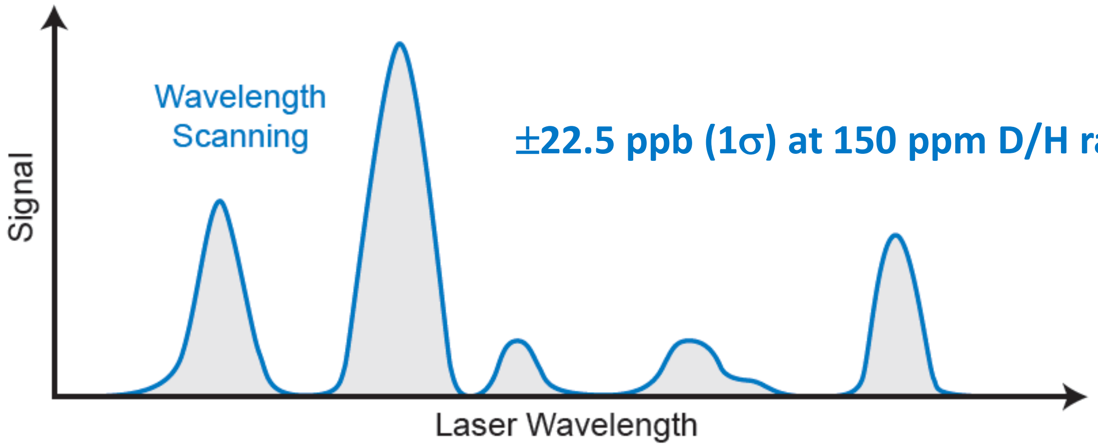
D_2 analysis
using H_2 carrier



H. T. Sessions Jr., "Analytical Method for Measuring Total Protium and Total Deuterium in a Gas Mixture Containing H_2, D_2, and HD via Gas Chromatography", presented at Tririum Conference 2007, Rochester, NY

Tunable Laser for Water Isotope Analysis





±22.5 ppb (1σ) at 150 ppm D/H ratio

Pathways Considered to Oxidize Hydrogen into Water, Safely!

Reaction	Est. Avg. ΔT	T_{Max} (adiabatic)
$H_2 + CuO \xrightarrow[550\ K]{} H_2O + Cu$	20.8°C	1790°C
$Cu + 1/2\ O_2\ (Air) \xrightarrow[550\ K]{} CuO$	15.5°C	1890°C
$H_2 + 1/2\ O_2\ (Air) \xrightarrow[550\ K]{Pt/Al_2O_3} H_2O$	57.8°C	3042°C
$H_2 + 1/2\ O_2\ (Air) \xrightarrow[ambient]{Pt/PSDB} H_2O$	67.6°C	2790°C

Hydrogen autoignition: 565°C

Reactor Design Max Temperature: 538°C

Reduction of Cupric Oxide by Hydrogen

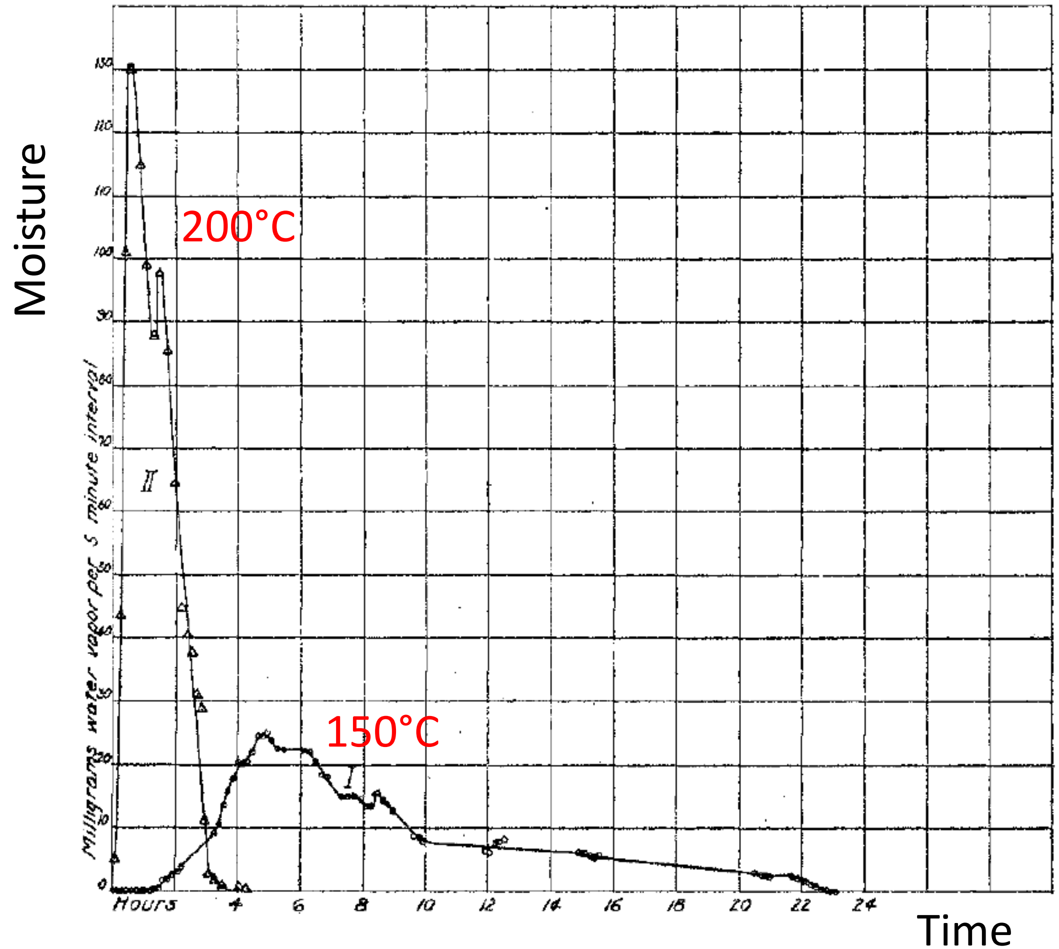
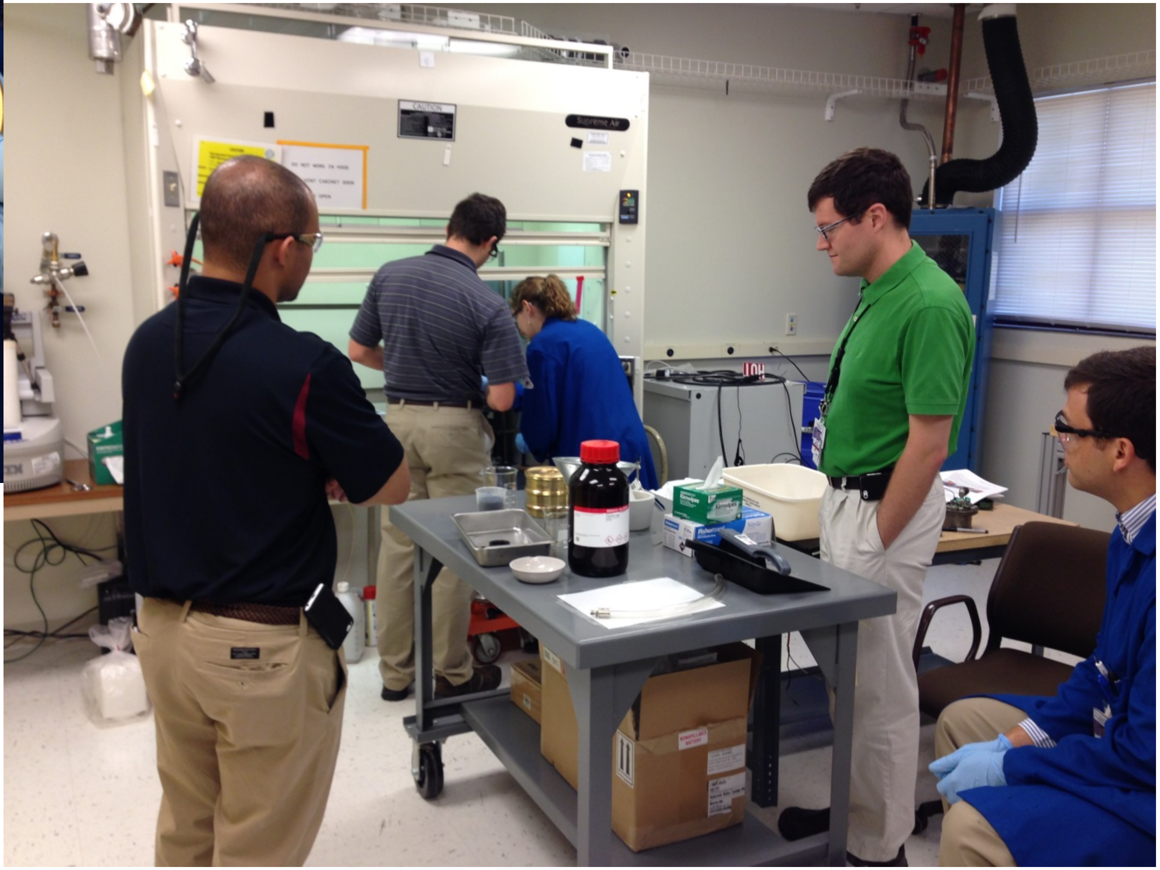


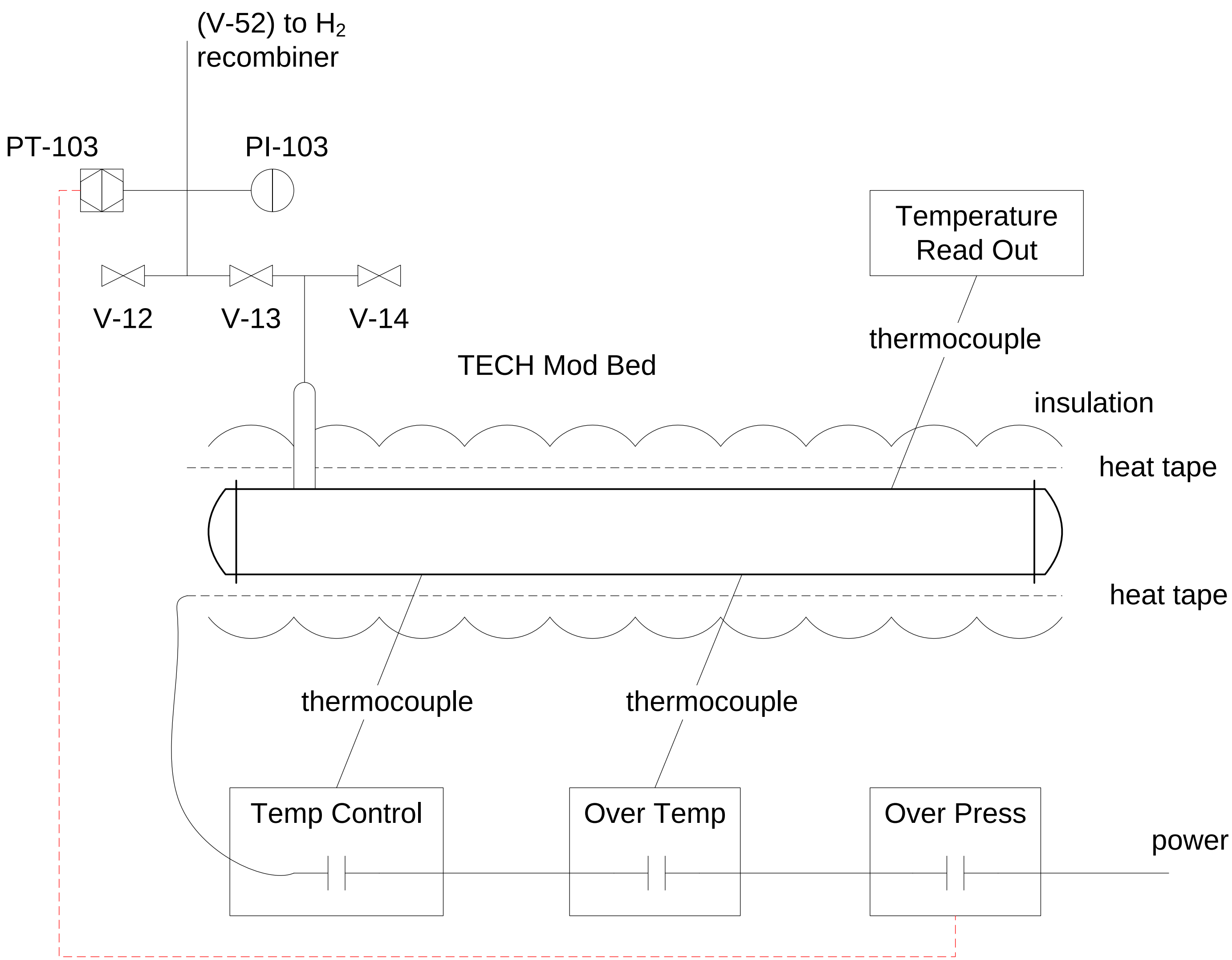
Fig. 2.—Reduction of copper oxide by hydrogen. Curve I, reduction at 150°. Curve II, reduction at 200°.

Robert N. Pgase, H. S. Taylor, "Reduction of Cupric Oxide by Hydrogen", J. Am. Chem. Soc., 1921, 43 (10), pp 2179

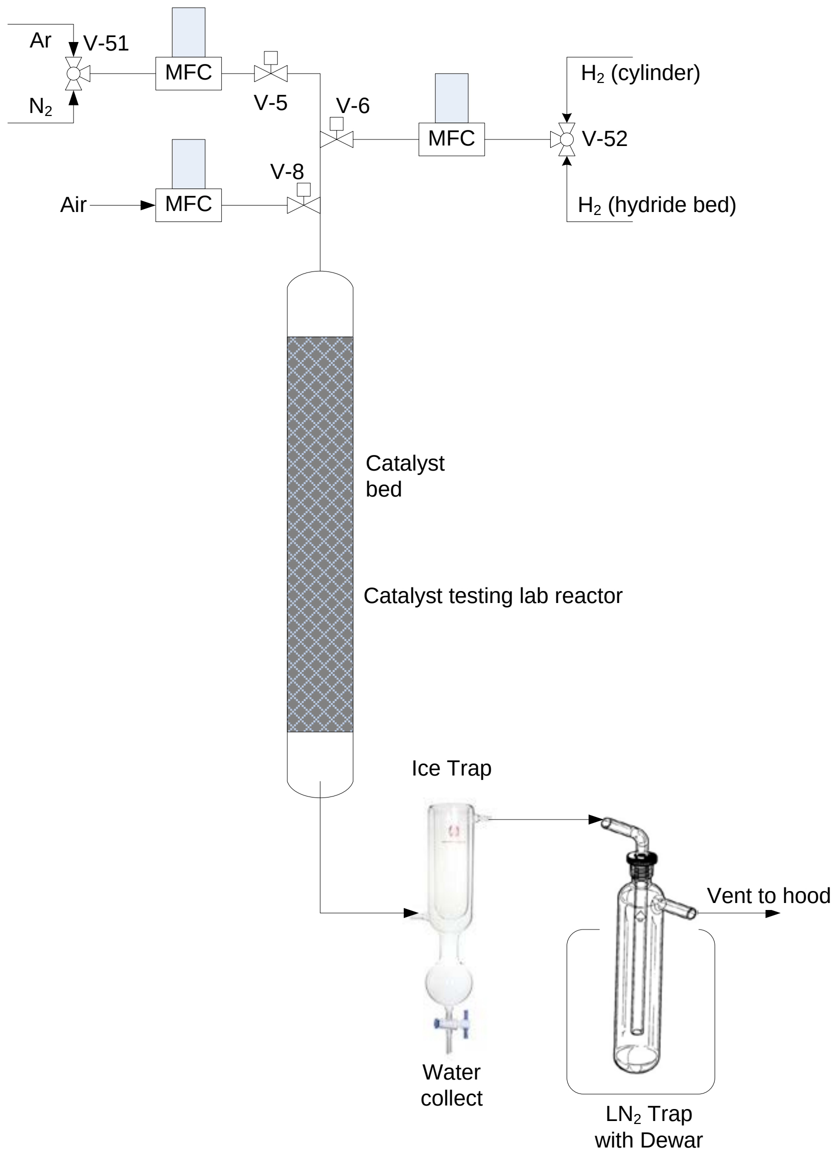
Preparation of Copper Oxide



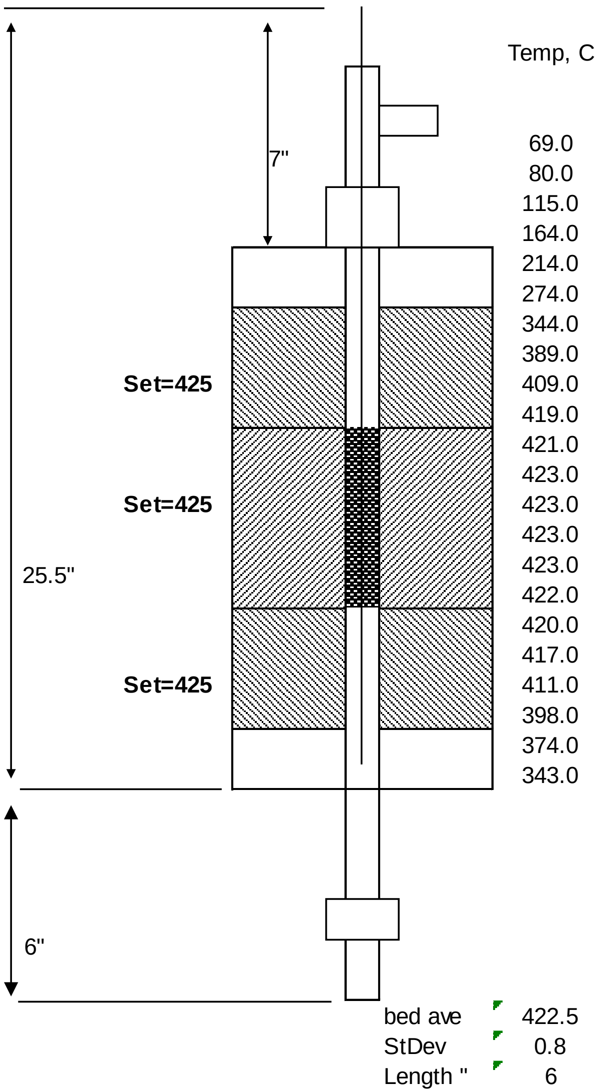
Hydride Bed Setup

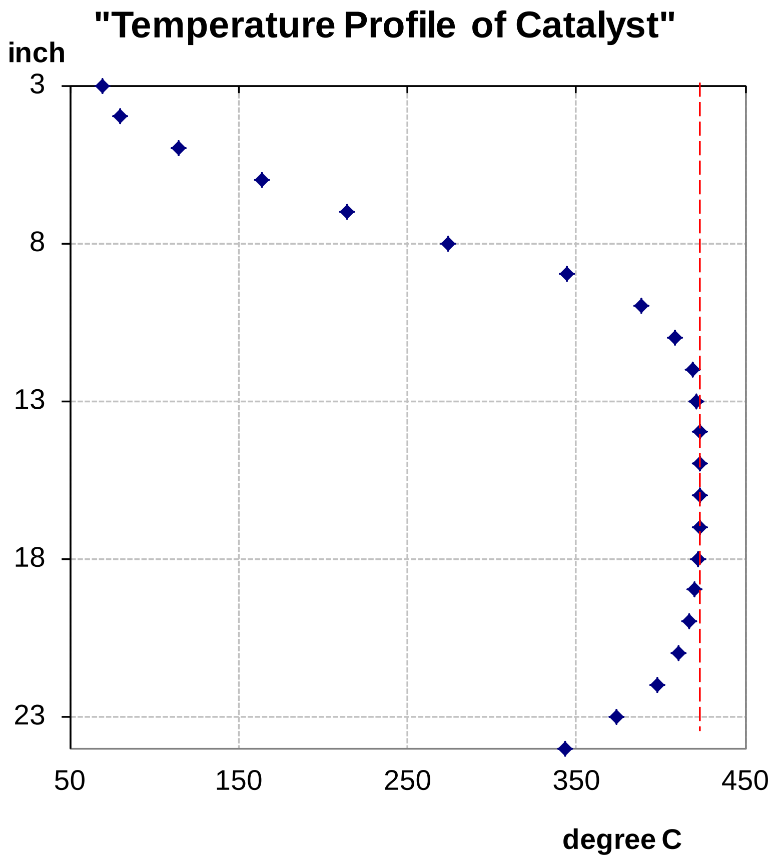


Catalyst Bed Setup

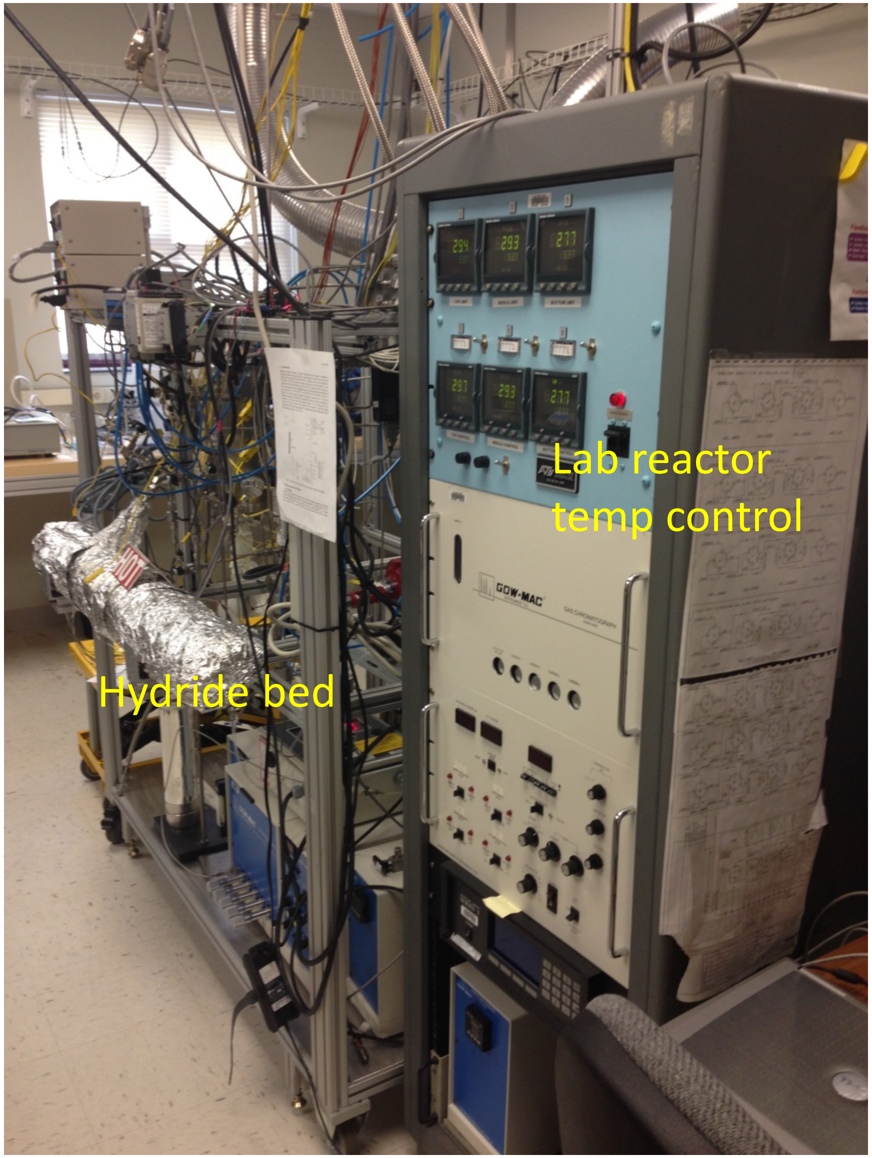


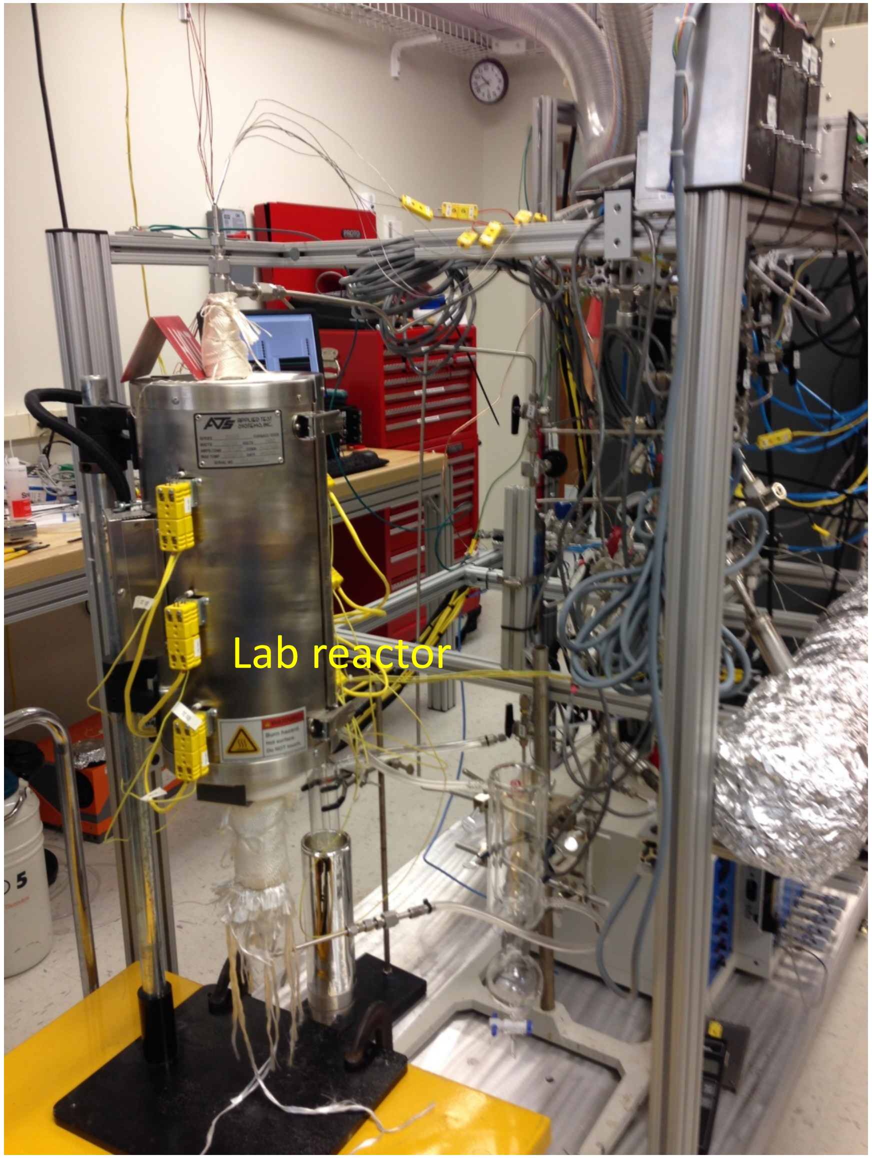
Typical Tube Reactor Temperature Profile



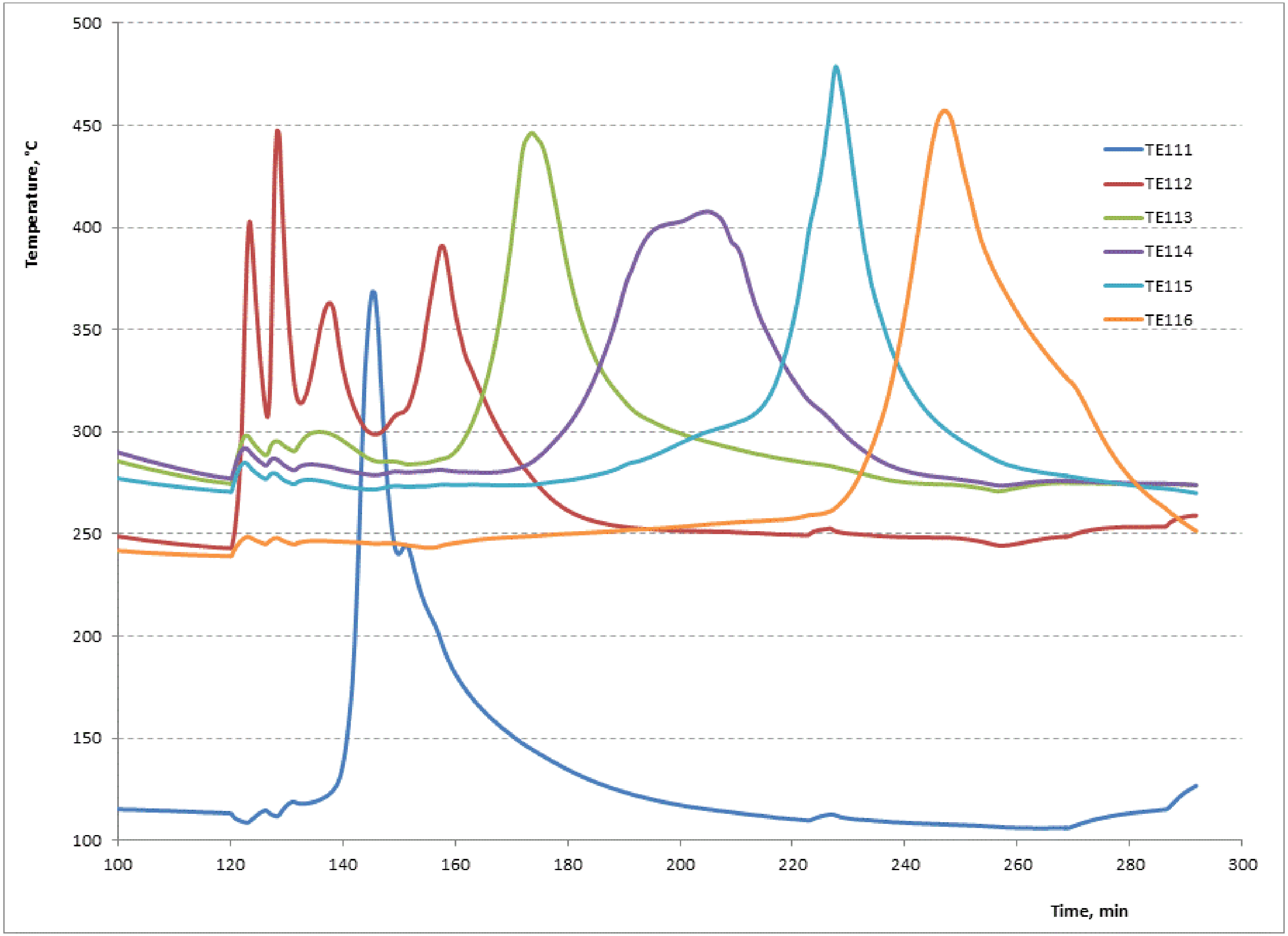


Hydrogen Oxidation in Progress

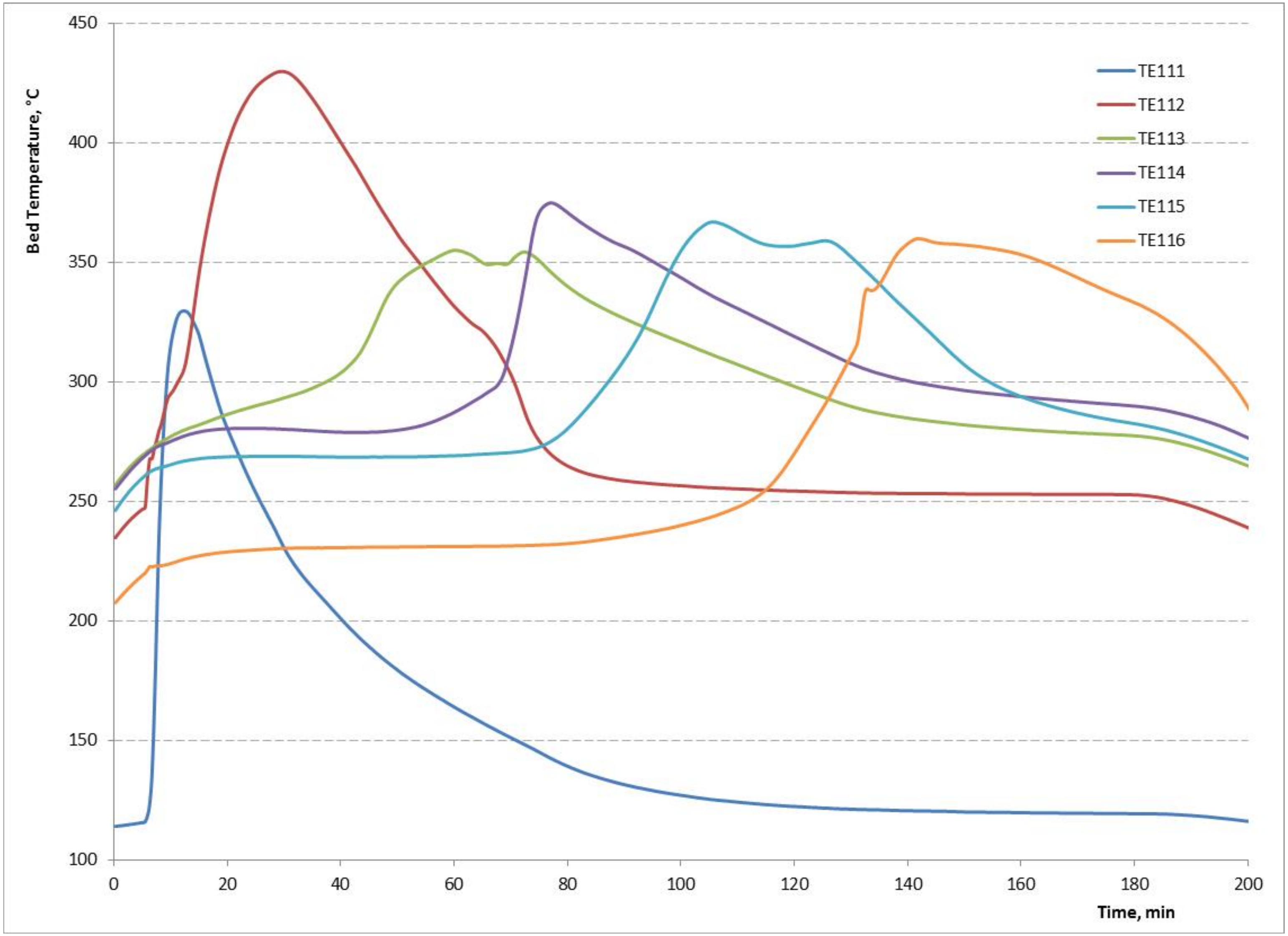




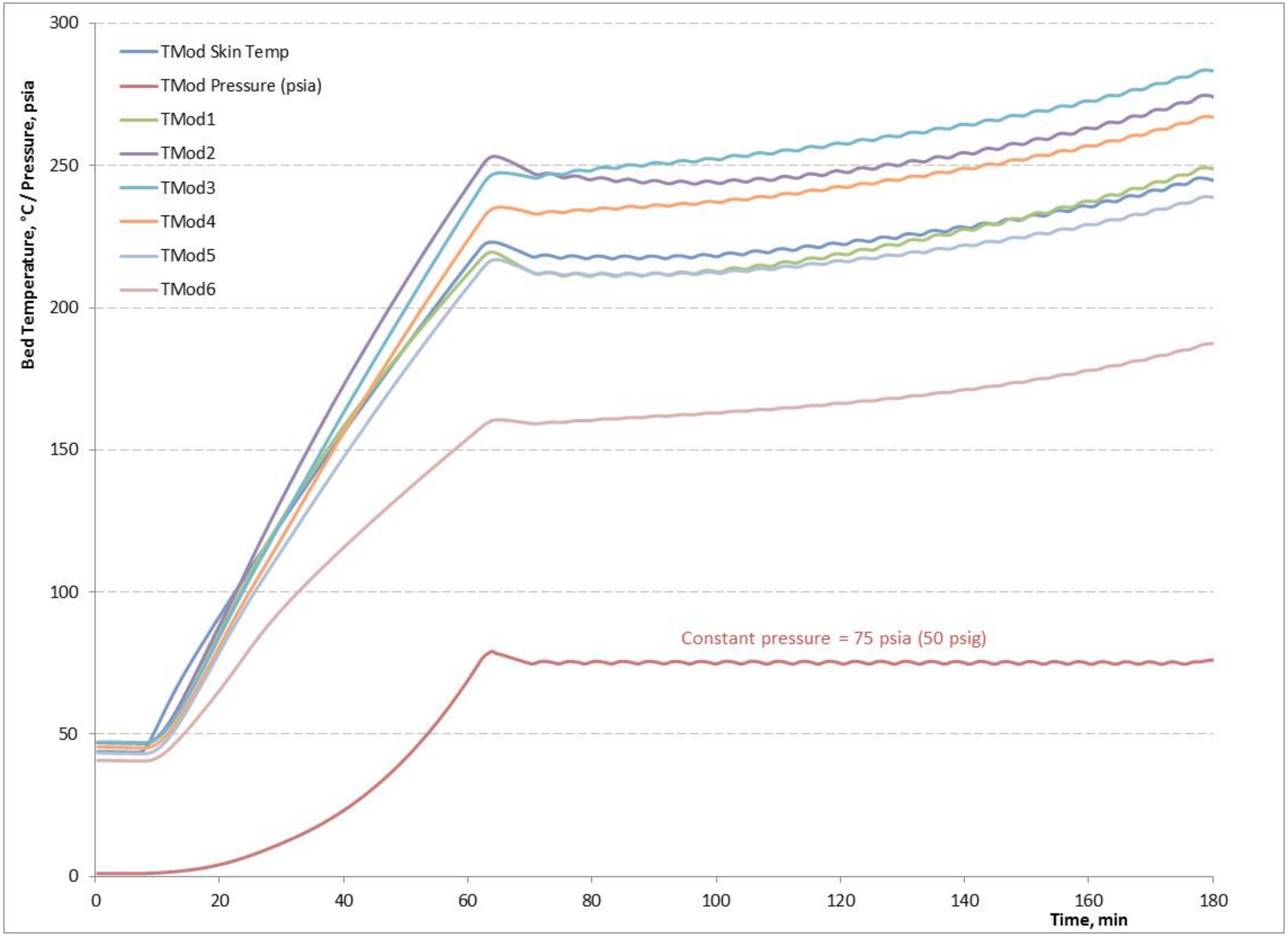
Exothermic Fronts during Hydrogen Oxidation



Exothermic Fronts during Copper Bed Regeneration



Hydride Bed Temperature and Constant Pressure Control



TCAP Raffinate Purity: 99.998% H_2

$H_2 + CuO \rightarrow H_2O + Cu$	Water D/H Ratio, ppm
Test 1	23.2
Test 2	20.3
Test 3	20.5
Test 4	20.1

Single hydride bed supplied gas for 4 tests:

- D_2 reduction ratio: 25000 (50% in feed to 20 ppm)
- Results could be better if residue heel in hydride were purged clean
- Oxidation and bed regeneration can combine with co-feed H_2 and air

Acknowledgements: Jim Klein for suggesting copper oxide for hydrogen oxidation; Katie Heroux for providing TechMod hydride bed; Greg Staack, Ray Battles, Kurt Breitinger, Sherolyn Bishop, Robert Plonski and Joe Wheeler for reviewing safety documentations; Sharon Redd and Donna Allison for lab supports.