

Are the “Three Ts” of Ammonia Destruction Meaningful?

Amine Best Practices Group Presentation for Virtual Vail

Presented by Al Keller

Background

- Recent member posting:
 - [SRU-396]: This was covered years ago in SRU-093, but I was wondering if there have been any updated best practices – particularly in view of ASRL's conclusion that NH_3 oxidation by SO_2 is the predominant pathway. What do you use for minimum $\text{H}_2\text{S}:\text{NH}_3$ ratio for SRU feed to the burner – co-firing and otherwise? I have been using 2:1 $\text{H}_2\text{S}:\text{NH}_3$.
- The presentation was inspired following remarks from other group members

We All Know The “Three Ts” of Ammonia Destruction...

- **Time**

- 0.8-2 seconds of residence in the thermal reactor

- **Temperature**

- 1200-1250 C (2192-2282 F) as measured by thermocouple or pyrometer

- **Turbulence**

- Sufficient mixing to get air and acid components together for combustion

- *Are these “Rules of Thumb” still meaningful with improved understanding of thermal reactor operation?*

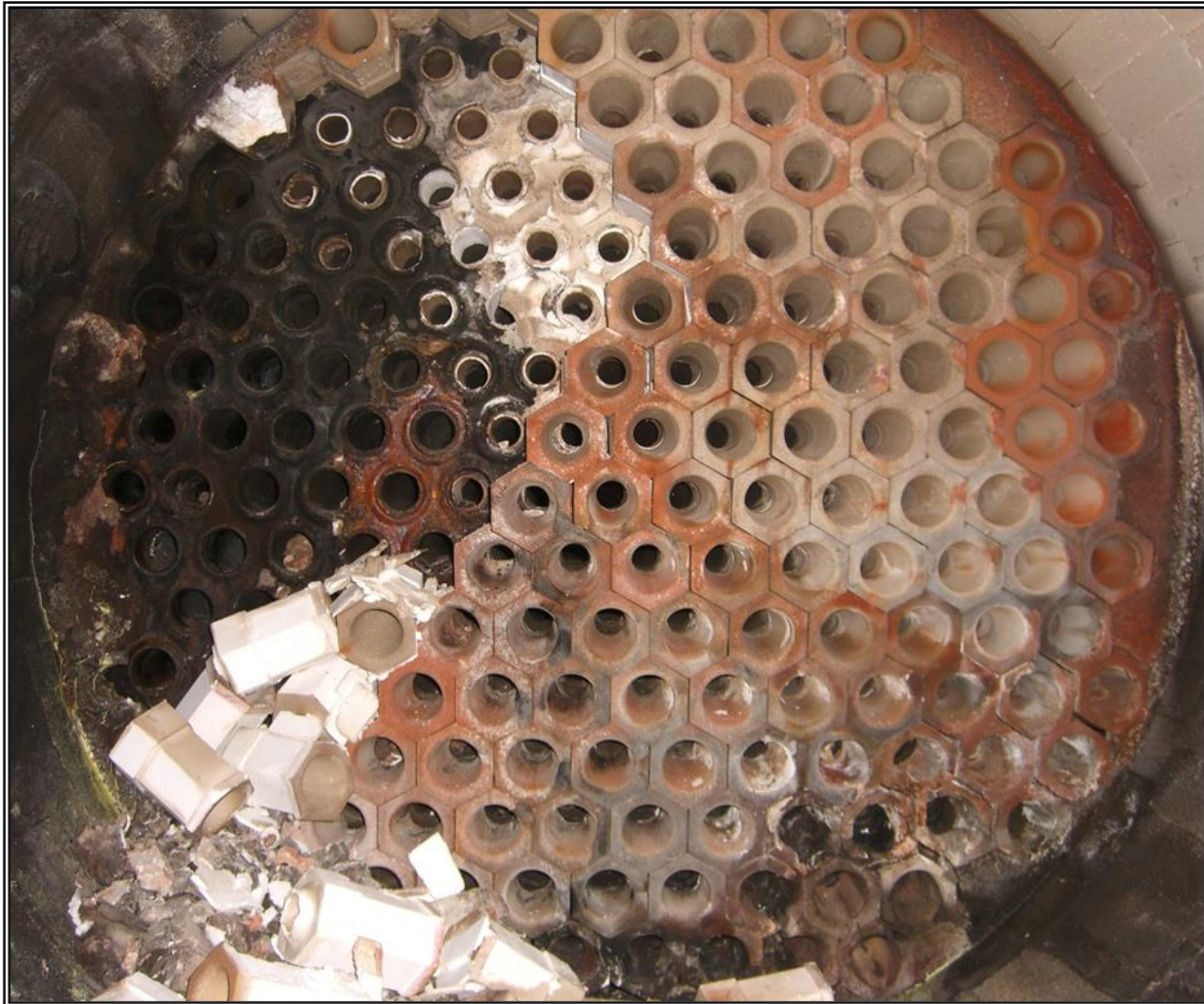
What has changed since the 1970s to 1990s?

- **Computational Fluid Dynamics (CFD) modeling**
 - Exponential increases in computer speed and processing architecture
 - Ability to reduce “cell” sizes and add model complexity
 - Field verification of model predictions
- **Alberta Sulphur Research Ltd. Experiments from late 1990s**
 - The importance of SO₂ in ammonia destruction kinetics
- *Combining these two developments will aid in better understanding of the ammonia destruction process in burner-thermal reactor systems*

Supercomputer Models Don't Lie, Do They?

- **Recent modeling examples with problems**
 - **COVID-19 Spread**-Model predictions 10 times greater than actual fatalities
 - **Global Warming**-CFD type model predictions of rapid temperature rise have not occurred for 20+ years according to satellite measurements
- *With this track record, can we trust CFD for burner-thermal reactor modeling?*
- Let's examine a burner-thermal reactor failure situation to test CFD modeling capability.

What happened?



Me: Why are **all** the ferrule necks broken?

Plant: Blame the ferrules!

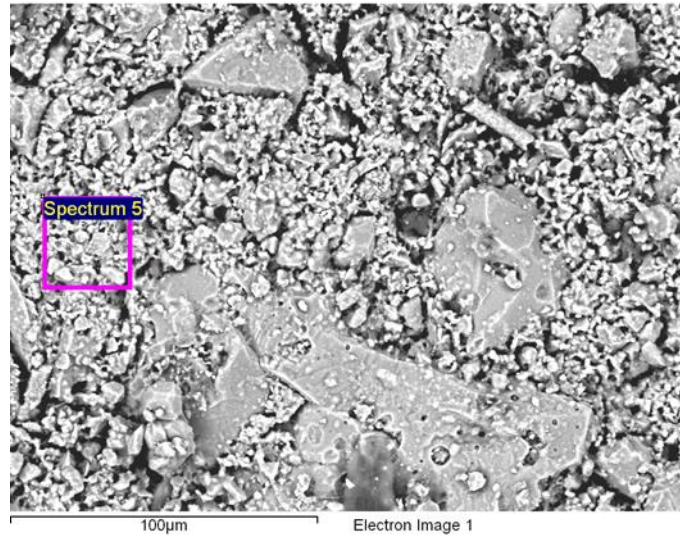
Me: What physical and chemical evidence did we gather?

Plant: Blame pressure swings!

Me: Do a CFD model

Physical and Chemical Evidence

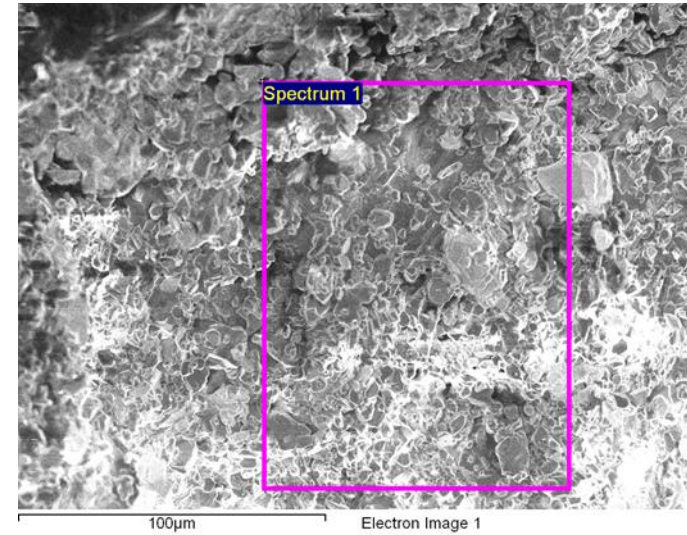
Before



Before-glued grains structure

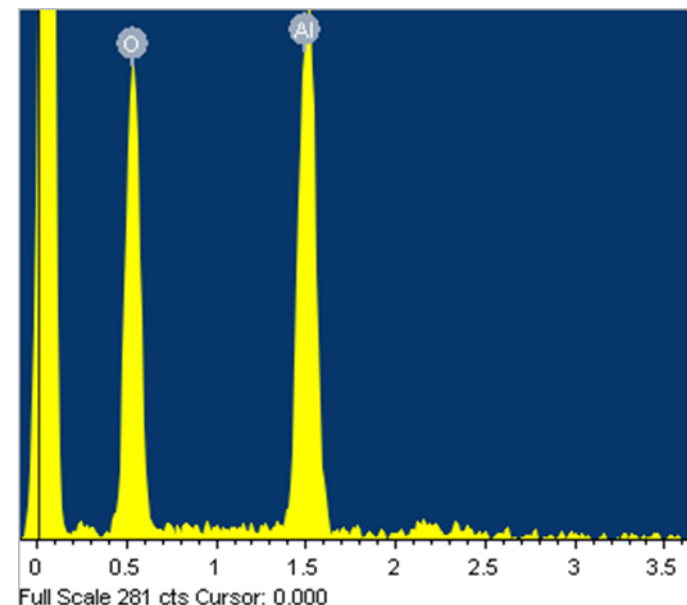
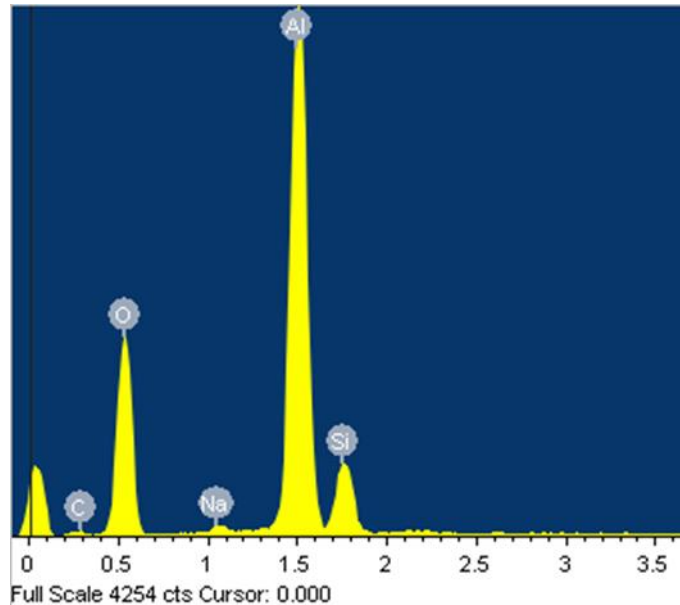
After-vitreous blob structure

After



Before-both silica and alumina present

After-only alumina present



High Temperature Caused Phase Changes

Operating Company XRD Analyses of Ceramic Ferrules

Sample	Al ₂ O ₃	Mullite	SiO ₂ Cristobalite	SiO ₂ Quartz	SiO ₂ Glass	Others (Remarks)
#1 Control	87%	2.4%	5.0%	-	1.7%	
#2 and #3 Stem (average)						
Inside core material	83%	17%	-	-	-	
Surface deposit material	96%	1%	-	0.35%	3%	
#4 Ferrule Head						
Inside core material	82%	18%	-	-	-	
Surface deposit material	96%	0.5%	-	0.3%	3.2%	
#5 Charred Material						
Inside core material	82%	18%	-	-	-	
Surface deposit material	94%	2.6%	-	0.5%	3%	

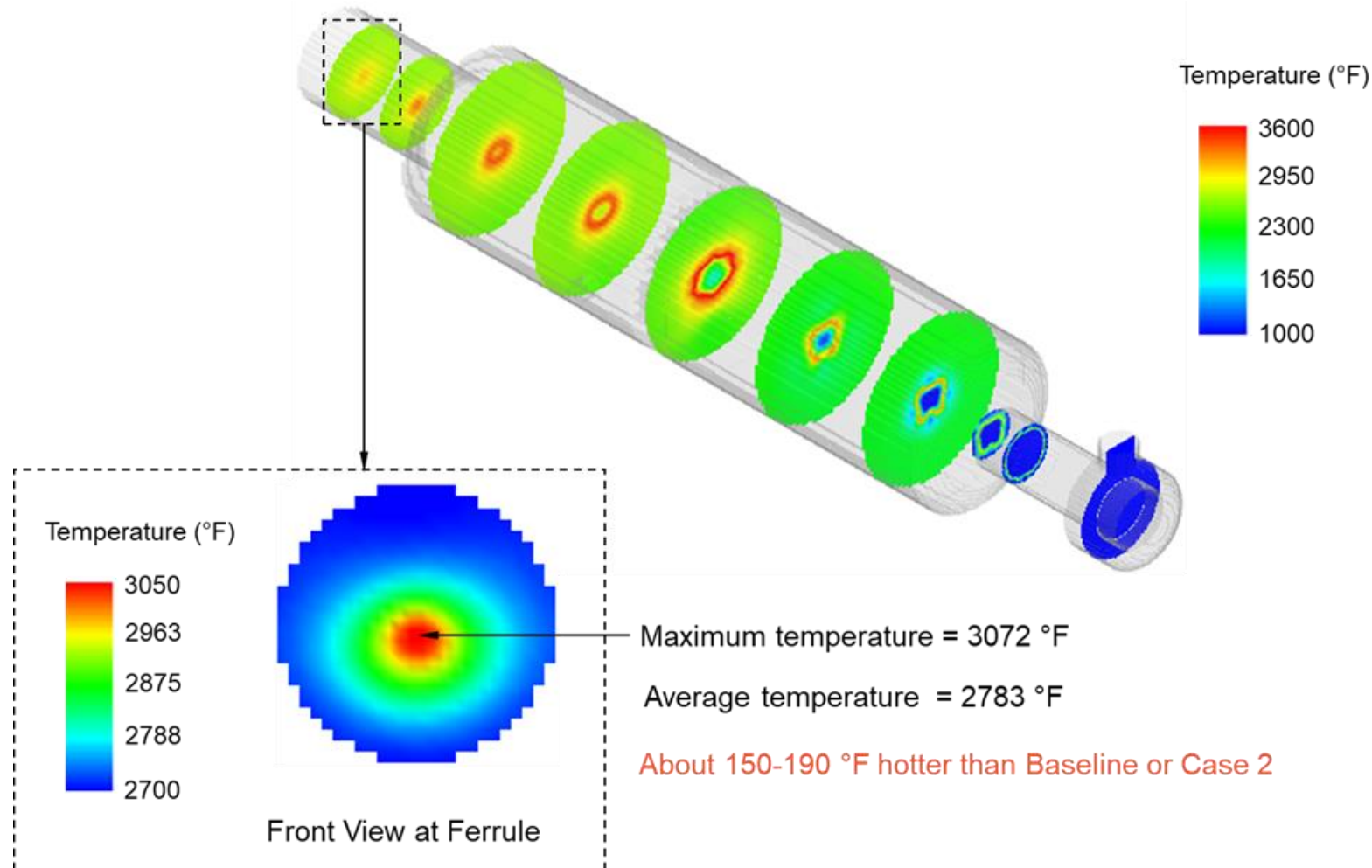
Conclusions:

- Core material of all samples had increased amount of mullite formed at the expense of free SiO₂ mostly present as cristobalite.

There was a constant increase of amorphous SiO₂ glass phase on the outside surface of all samples.

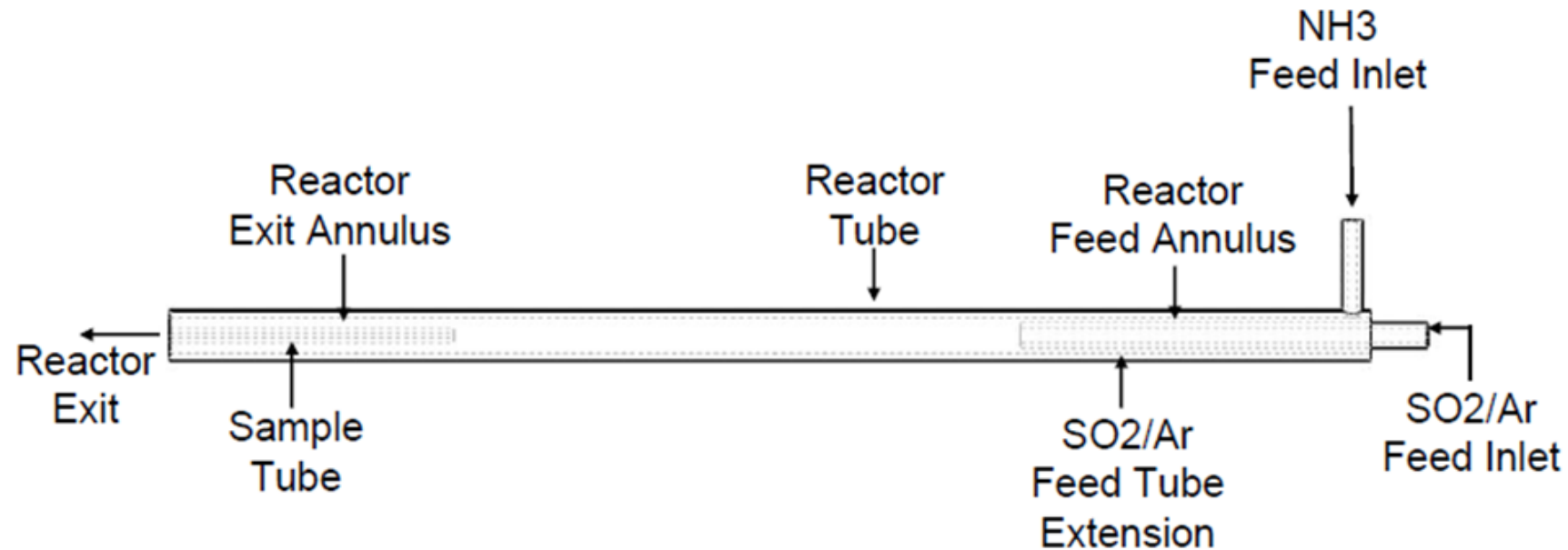
Control sample shows 3 separate phases. Damaged ferrules showed mullite (alumina-silicate) and glass formed at higher temperatures (>2900 F).

CFD Temperatures Consistent with Phase Changes; Builds High Model Confidence



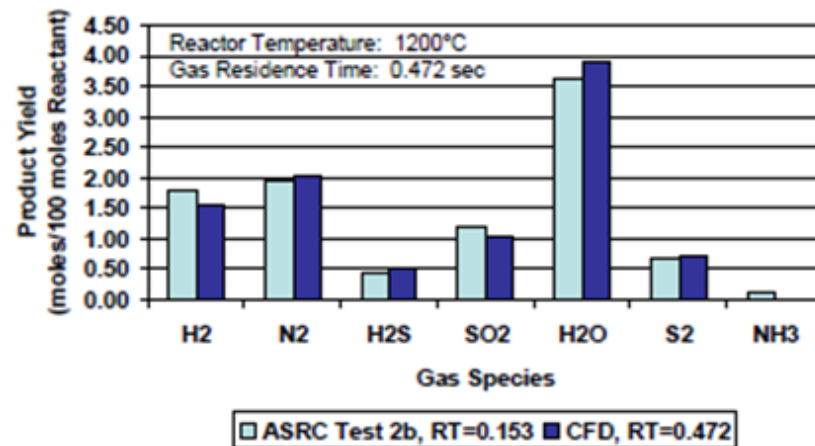
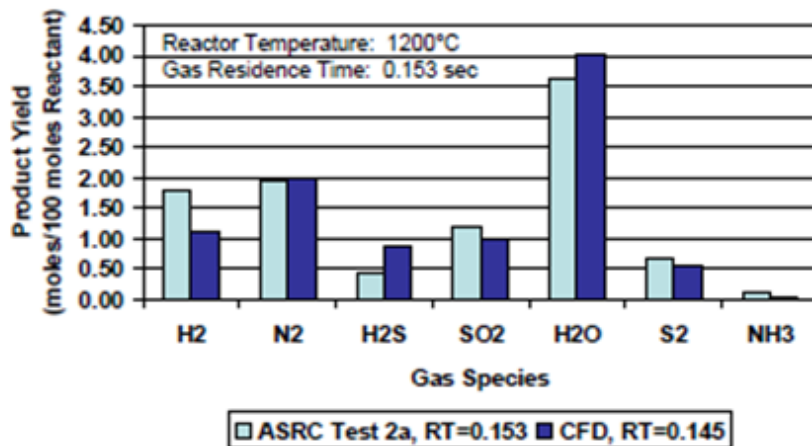
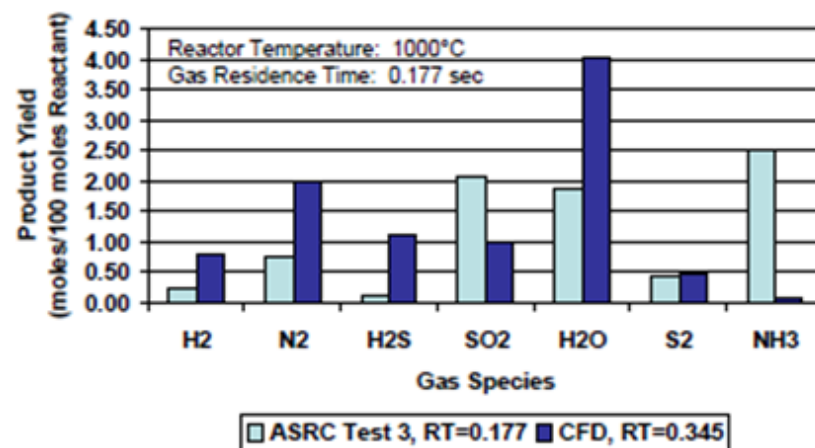
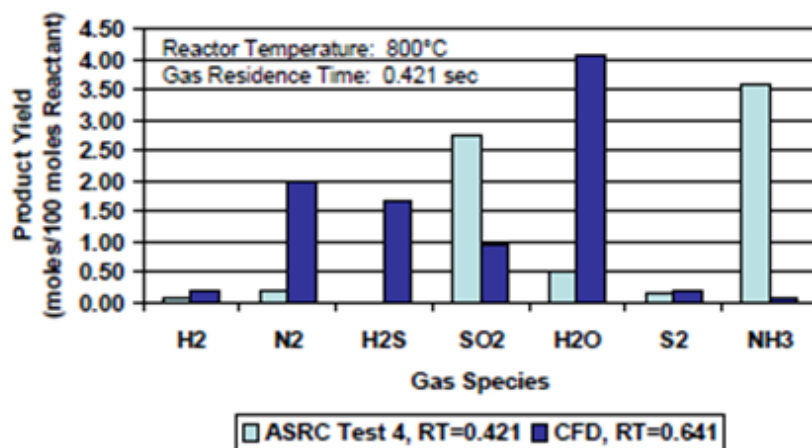
Is CFD Consistent With Laboratory Work?

ASRL Reactor Schematic

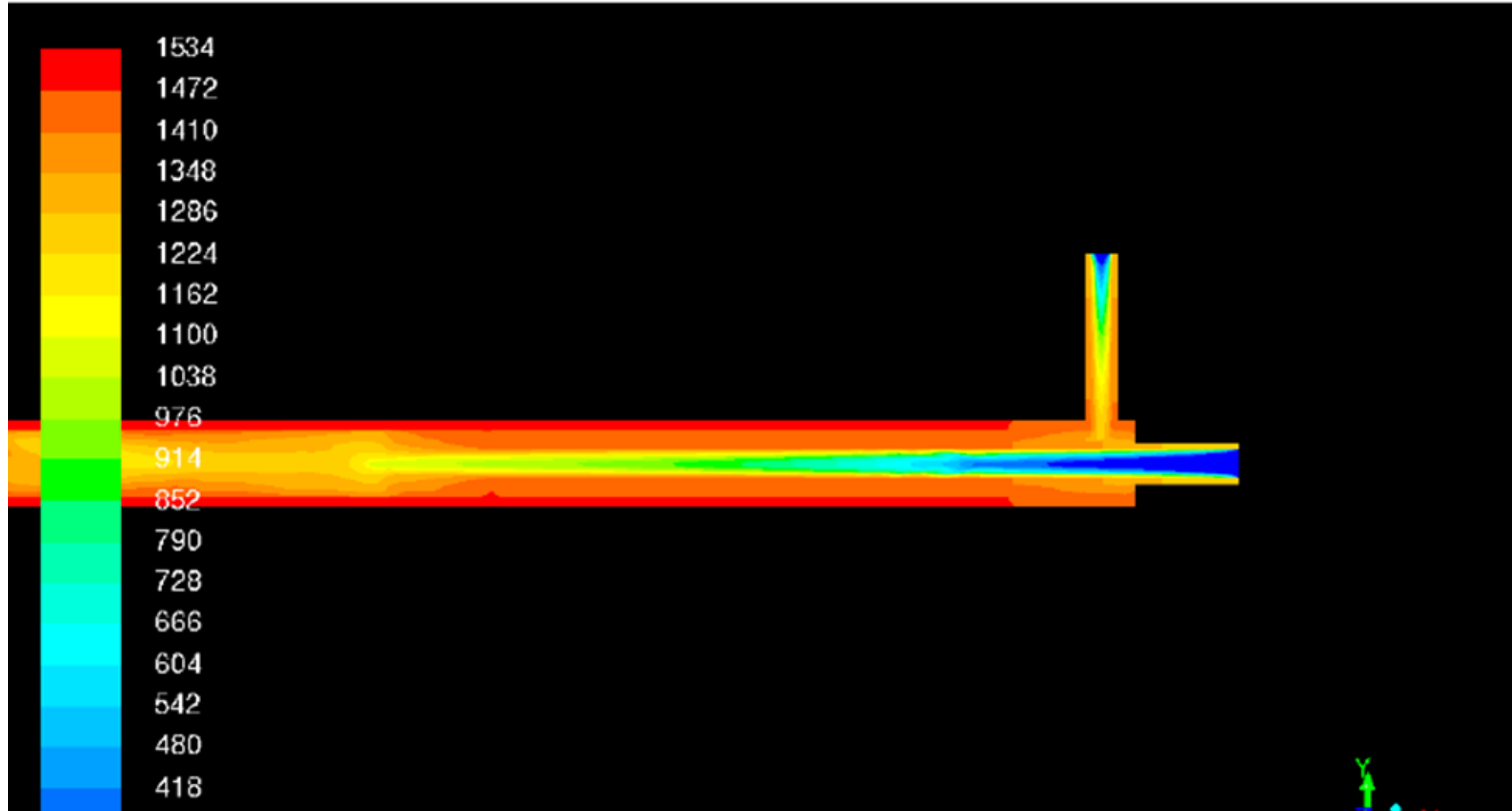


ASRL Tests 2a, 2b, 3, and 4

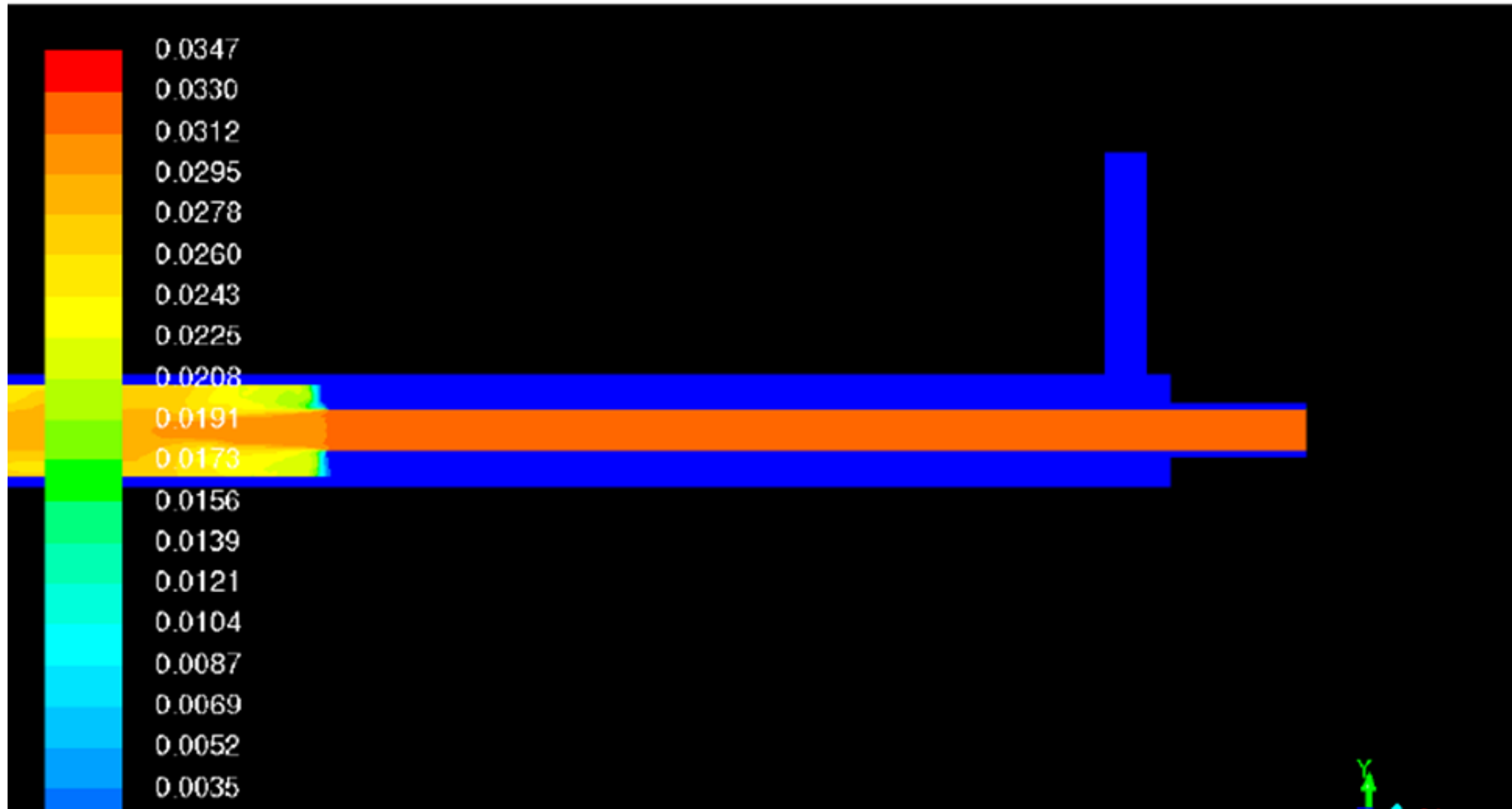
Product Yield Comparison



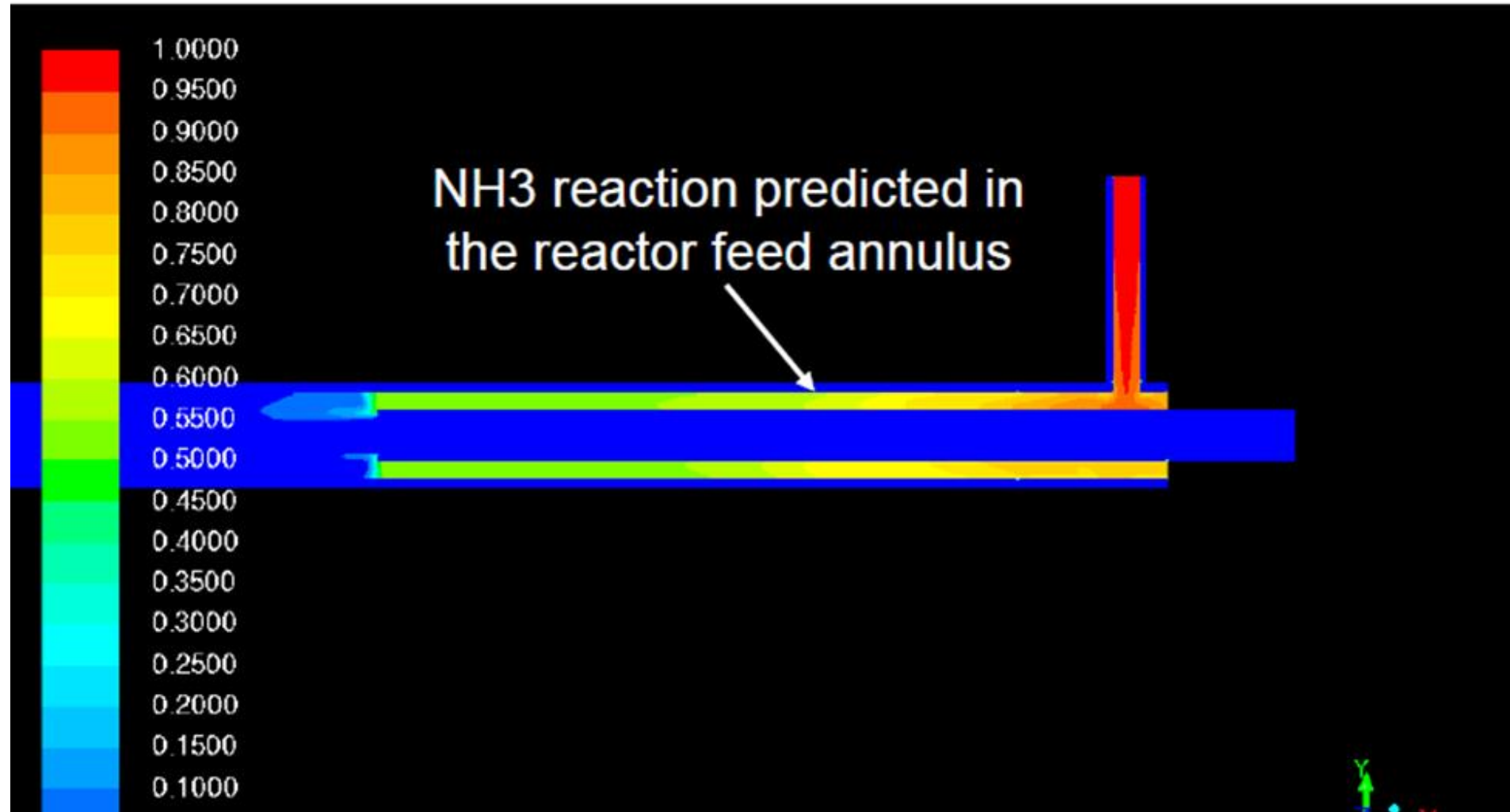
Case 2a Temperature Profile (Reactor Entrance)



Case 2a SO₂ Concentration Profile (Reactor Entrance)



Case 2a NH₃ Concentration Profile (Reactor Entrance)

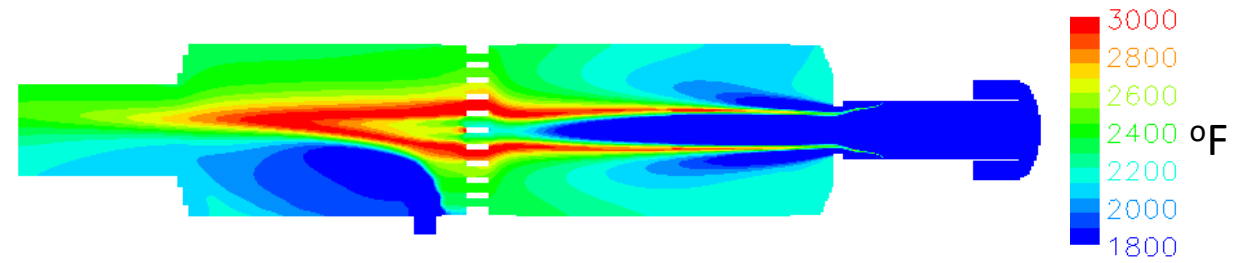
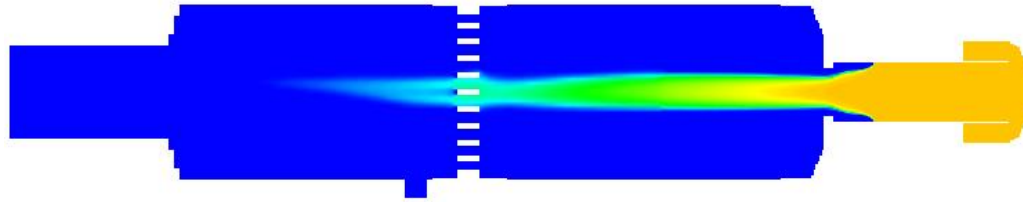


Laboratory/CFD Model Comparison

- Equilibrium CFD assumption inadequate for kinetically limited temperature range (Test 3&4 at 1000 C and 800 C)
- Equilibrium CFD assumption closely matches data at 1200 C. Plug flow residence time does not appear to impact ammonia destruction.
- Laboratory configuration allows ammonia to be heated faster than SO₂. Equilibrium CFD predicts some thermal decomposition, consistent with anhydrous ammonia decomposition in lab work
- *It appears that equilibrium CFD predictions are adequate at temperatures exceeding 1200 C (2192 F).*

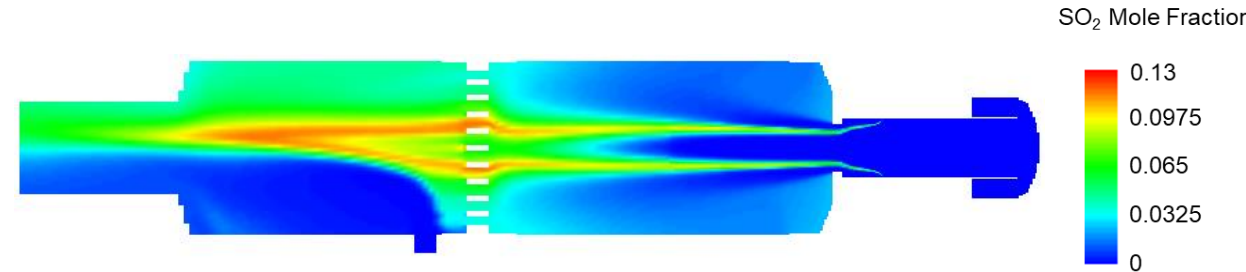
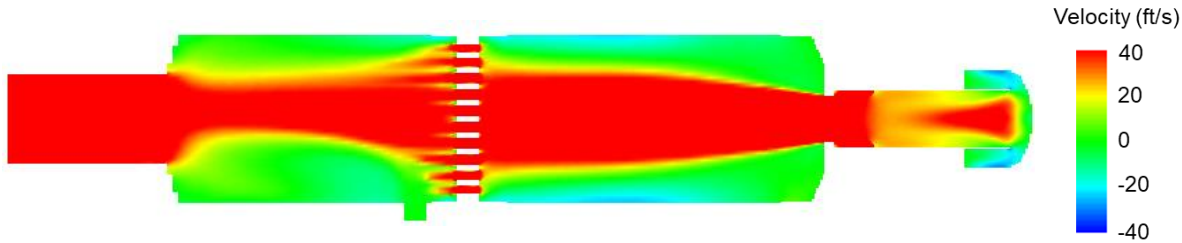
Two-Zone Thermal Reactor with Checker Wall.

Definitely not “plug flow”. Second “colder” zone actually hotter than first “hot” zone. Pyrometers and thermocouples in agreement with CFD where measured.



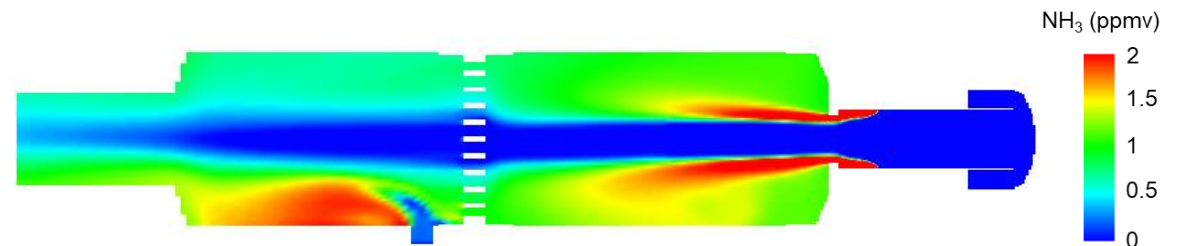
Technically, first zone is oxidizing environment. Unused oxygen in an unmixed zone. Bulk of oxygen consumed after checker wall.

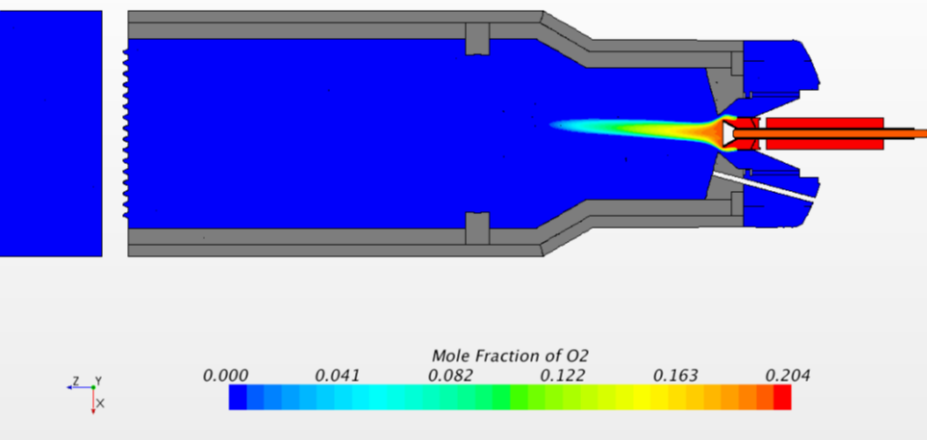
SO₂ rapidly consumed in first zone close to mix point. Most consumed to make sulfur. SO₂ formed in second zone makes up bulk of SO₂ leaving.



Hot gas from combustion zone recirculates to acid gas injection point helping to preheat cold acid gas.

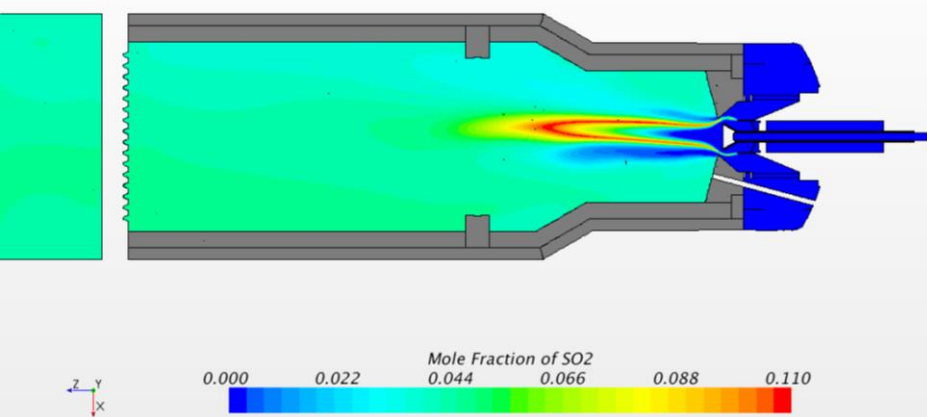
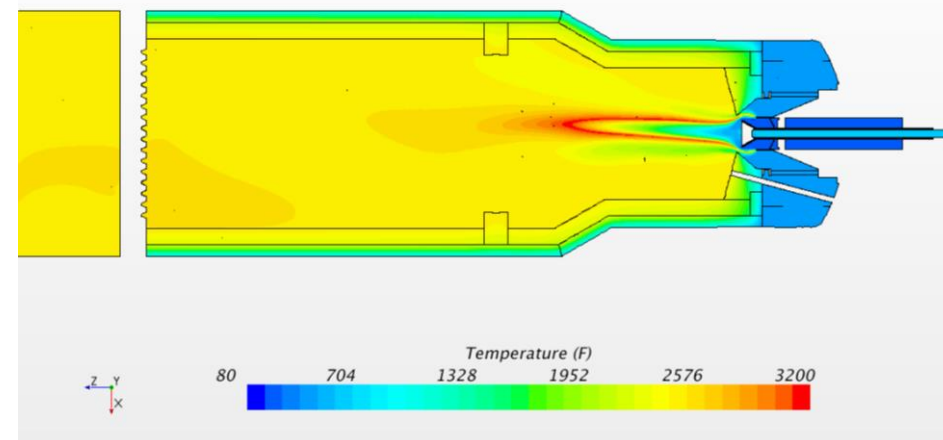
Red is where higher concentration of ammonia enters. The ammonia quickly drops to ppmv levels where SO₂ concentration increases.



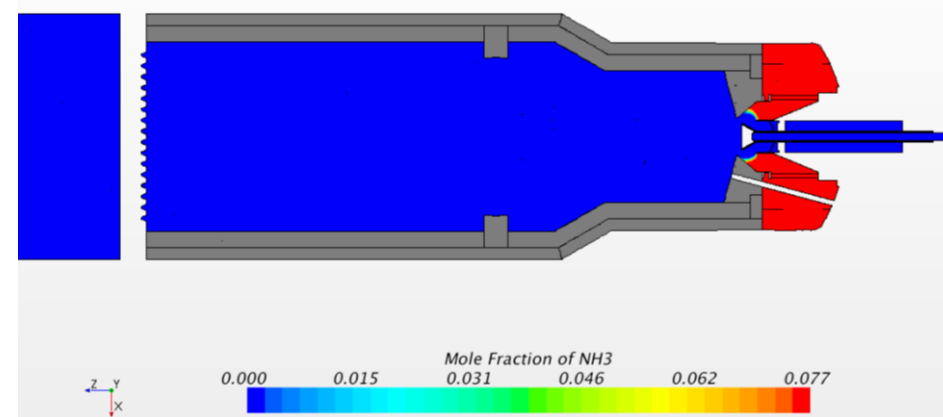


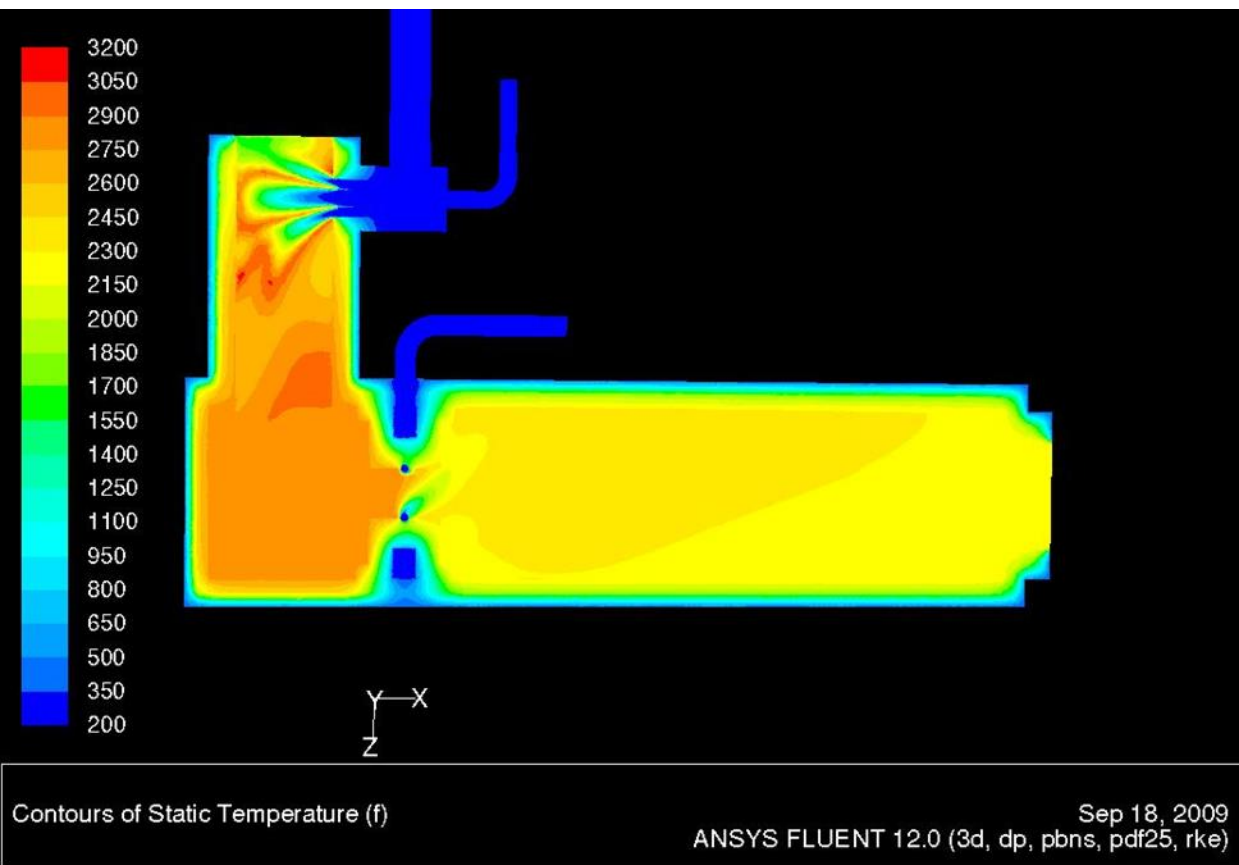
High Intensity Burner with Choke Ring

Left: Rapid oxygen consumption
Right: High temperature zone immediately outside combustion zone. Hot recirculating gases rapidly heat incoming annular acid gas flow.



Left: Highest SO₂ concentration in hottest area.
Right: Ammonia in acid gas is quickly reacted



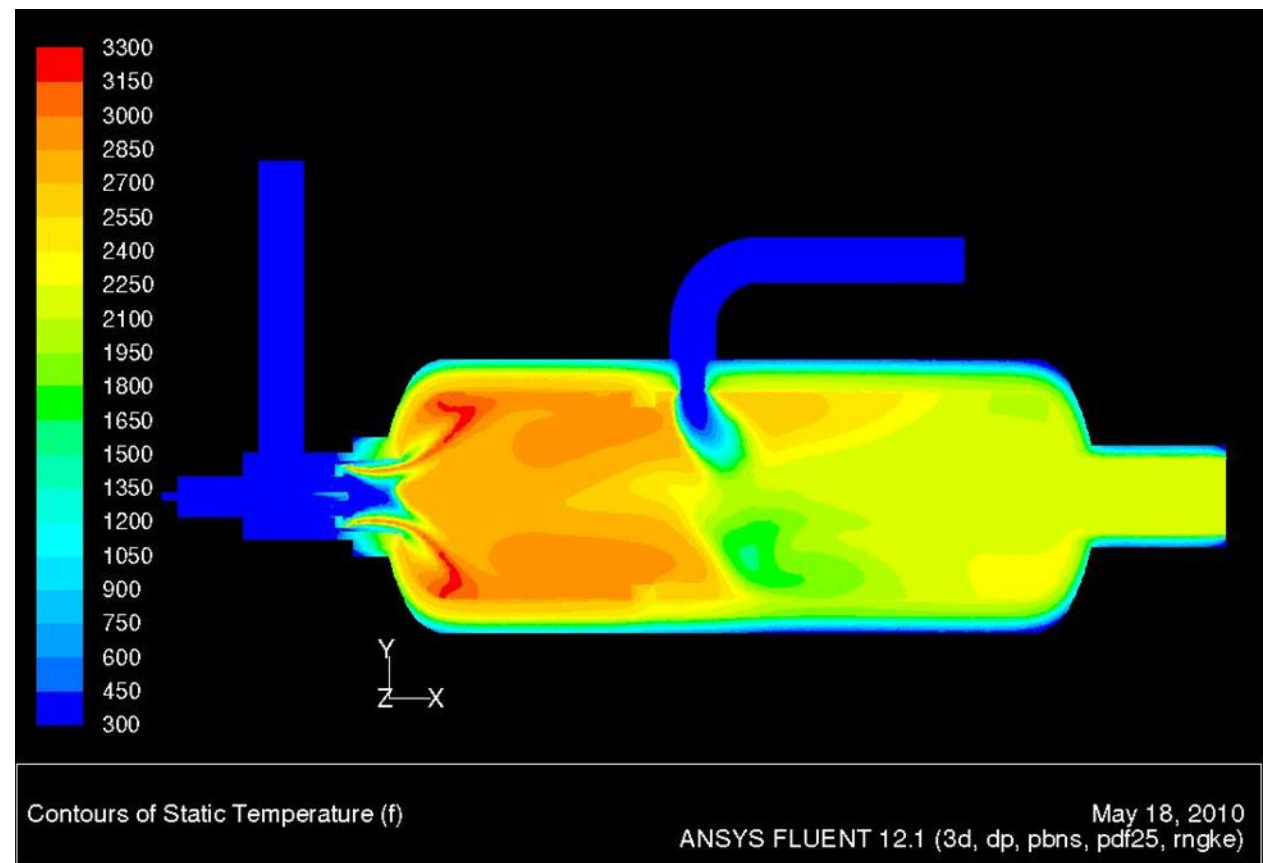


Above: Two-Zone thermal Reactor with Tangential Entry Low Intensity Burner. Air Envelops Incoming Acid Gas

Front zone in this instance is much higher than second zone. Oxygen is rapidly consumed near entry unlike ring/hole acid gas injection

Below: Two-Zone Thermal Reactor with High Intensity Burner. Air Envelops Incoming Acid Gas

Note same high temperature combustion zone in close proximity to acid gas inlet. Hot recirculating gases come back to middle to preheat acid gases.



Reconciling Experience, Lab, and CFD

This study¹ has, however, shown that SO_2 reacts quite readily with ammonia forming N_2 , water or H_2 , and sulfur or H_2S , displaying reaction rates which exceed those of either dissociation or oxidation. Also, it was shown that the ammonia/ SO_2 reaction is able to proceed in the presence of water. These observations and others described in the main text suggest the following protocol for ammonia destruction in the Claus furnace.

¹ *Mechanisms of Ammonia Destruction in the Claus Front End Furnace*, ASRL QB 104, Vol 34, No. 4, pp 1-50

1. Utilize a burner/furnace configuration which allows the SWSG to impinge on a hot, SO_2 -rich flame. **Actual equipment modeled by CFD show this is how they all appear to work! Isn't that amazing?**
2. This could be accomplished by feeding all the oxygen required for ammonia and H_2S conversion with the AG through a main burner with the SWSG impinging on the flame.

Well said Peter, Norm, and Ming.

Concluding Remarks

- The “Three Ts” were once common sense ideas that gained life as scientific absolutes
- The foundation assumptions for the “Three Ts” have been “busted” by CFD. They are still common sense, but not absolutes.
- Ammonia destruction technology works in both the lab and in the field by two mechanisms
 - Rapid preheat of the ammonia in acid gas component by furnace (lab) or by hot recirculating gases (field)
 - Hot SO₂ addition into ammonia (lab) or rapid SO₂ formation and heat release in combustion zone (field) accelerating SO₂ oxidation and thermal destruction of ammonia