

Cyclic Testing of a Long-Life Zinc-Ferrite Sorbent for Moving- Bed Reactors

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Introduction

- **Coal gasifiers coupled with combined cycle power plants (IGCCs) are potentially the lowest cost source of baseload electricity**
- **Coal contains sulfur that is converted to H₂S in the gasifier**
- **The H₂S must be removed before the gases are fed to the gas turbine**

Hot-Gas Cleanup

- It is better to remove the H₂S (as well as COS and CS₂) at high temperatures than to suffer the cost and inefficiencies involved with cooling the gases and removing sulfur at near-ambient temperature

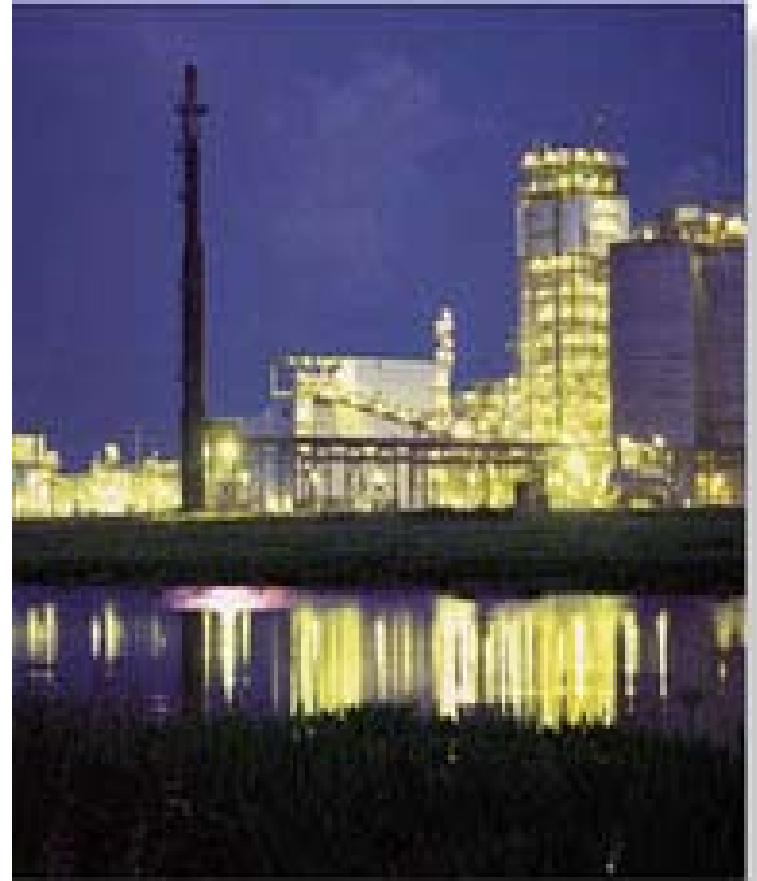
Objective

- **Design a regenerable sorbent that removes H₂S from hot reducing-gases**
- **Suitable for use in a moving-bed hot-gas cleanup system (for example, the G.E. Moving Bed System at the Tampa Electric Polk Power Station)**

Polk County Plant

- **A state-of-the-art integrated coal gasification combined-cycle (IGCC) power plant, Tampa Electric's Polk Power Station produces enough electricity to serve 75,000 homes.**
- **250-megawatt IGCC facility is among the nation's cleanest, most efficient and most economical power generation units. The plant is a first-of-its-kind combination of two leading technologies.**
- **The first technology is called "coal gasification," which uses coal to create a clean-burning gas. The second technology is called "combined-cycle," which is the most efficient method of producing electricity commercially available today.**

The plant combines coal with oxygen in the gasifier to produce the gaseous fuel. After processing, the clean coal gas is used in the combustion turbine to produce electricity.



The TNT- MB Sorbent

- **TDA and NORTON - Moving Bed**
- **Zinc Ferrite + Inert Binders**
- **Absorbs at 600°F - 900°F**
 - Tenth absorption to breakthrough > 1 hour @ 600 °F
 - Tenth absorption to breakthrough > 7 hours @ 900 °F
- **Regenerates at 700°F in 4% O₂**
- **> 13 Lb (Sulfur) Per Ft³ bed at design conditions**

Previous Work On ZnFe_2O_4

- **GE Pilot Plant Run 2B > 1200°F Regeneration = *No Sulfate***
 - Cook et al. (1992) Twelfth Annual Gasification and Gas Stream Cleanup Systems Contractors Review Meeting
- **RTI: “Zinc Ferrite Sorbents Were Found to Be Limited to 550°C” (1022°F)**
 - Gangwal and Gupta (1991) Eleventh Annual Gasification and Gas Stream Cleanup Systems Contractors Review Meeting
- **RTI and SRI International: “Carbon Deposition Rate Exceeds the Rate of Removal by Steam, and Hence Carbon Is Likely to Accumulate on the Sorbent”**
 - Krishnan et al. (1991) *A Preliminary Study of Carbon Deposition on Zinc Ferrite Sorbents*, DOE/MC/25006-3057, contract AC21-88MC25006

Testing of TNT-MB

- **10-Cycle Tests without SO₂ at DOE-FETC-Morgantown (CRADA) completed, (114)**
 - Low Temperature Scoping Tests
 - 10 cycles at 7 atm regeneration
- **3 1/2-Cycle Scoping Tests with SO₂ completed at Institute of Gas Technology (IGT), (114)**
- **10-Cycle Low Temperature Sulfidation Tests without SO₂ at TDA completed, (298)**
 - 10 cycles at 7 atm regeneration
 - 600°F - 700°F Sulfidation Temperatures
- **25-Cycle Test at IGT completed, (298)**

Sulfidation Conditions

Simulated Texaco Gas Stream

- **Carbon Monoxide** : **35.8**
%
- **Hydrogen** : **26.8**
%
- **Carbon Dioxide** : **12.2**
%
- **Hydrogen Sulfide** : **1.2**
%
- **Nitrogen** : **5.9**
%
- **Water** : **18.1** %
- **Space Velocity** : **2000**
 hr^{-1}
- **Pressure** : **20**
atm

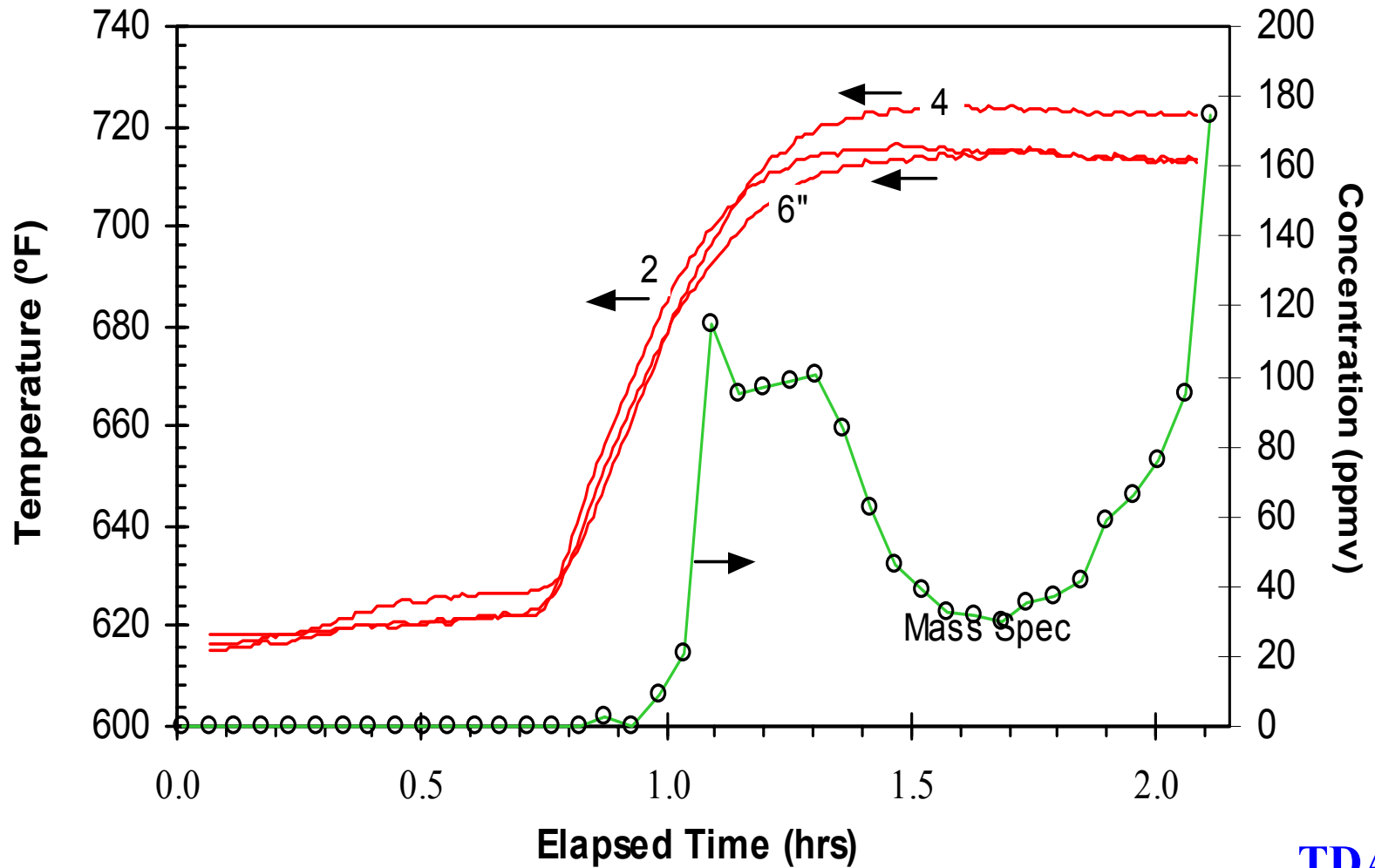
Regeneration Conditions

- **Sulfur Dioxide** : **8%-**
10%
- **Nitrogen** : **87%**
- **Oxygen** : **4.0%**
- **Space Velocity** : **2000** hr
 $^{-1}$
- **Pressure** : **7 atm**
- **Temperature** : **700-**
1300 °F

Oxygen turned off at breakthrough, makeup with Nitrogen.

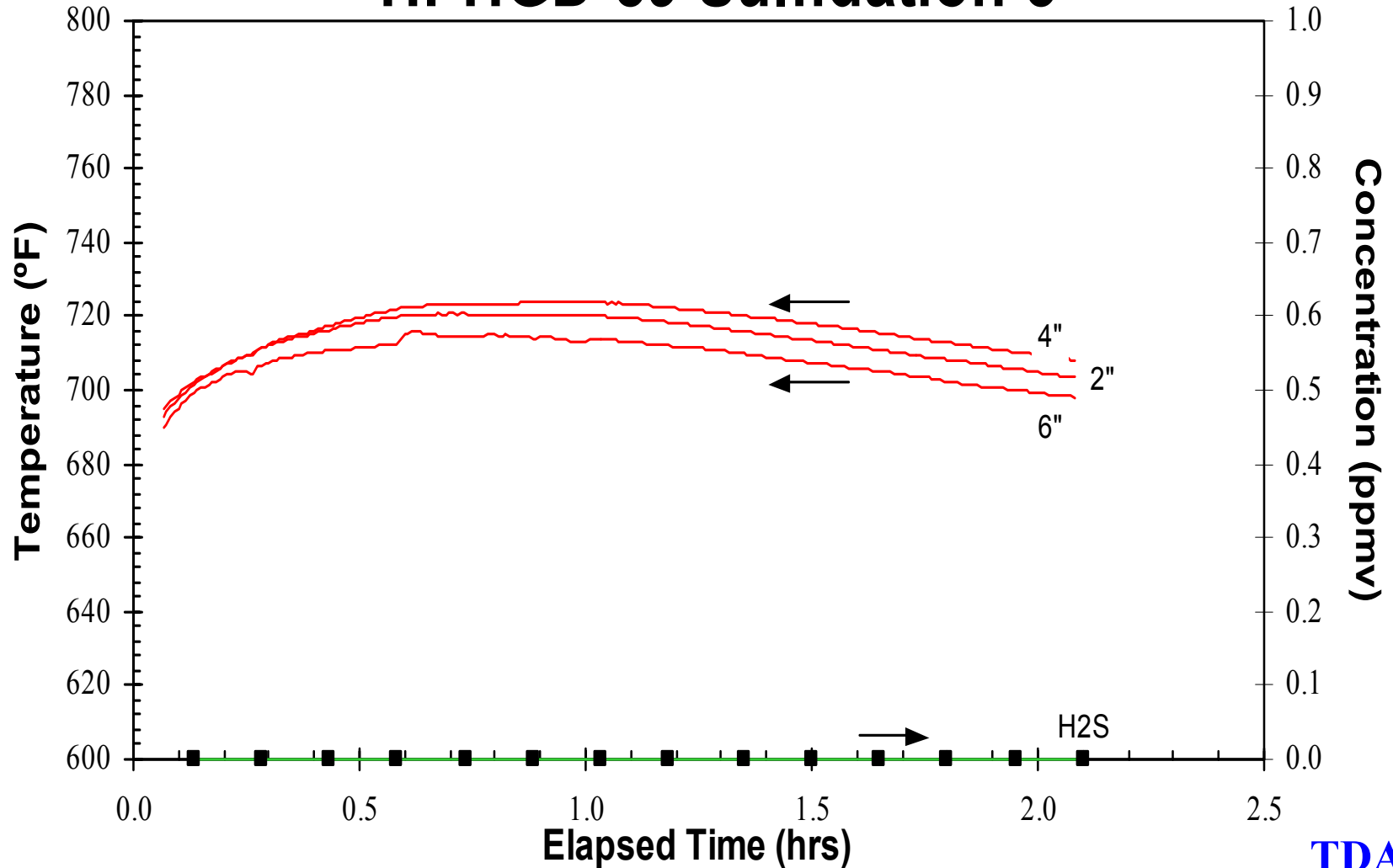
Low Temperature Absorption at 600/700°F at FETC

HPHGD-59 Sulfidation 1

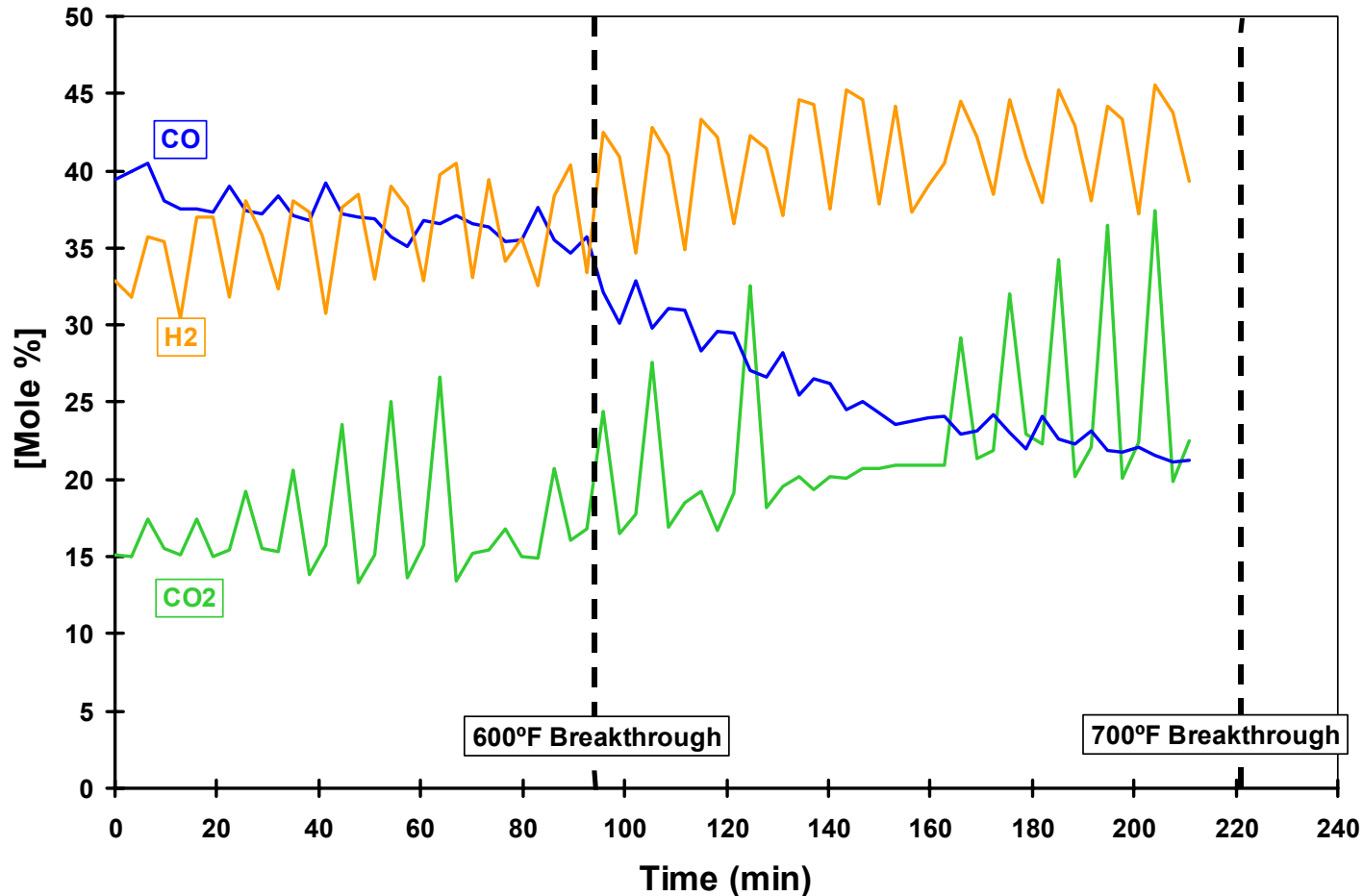


Low Temperature Absorption at 700°F at FETC

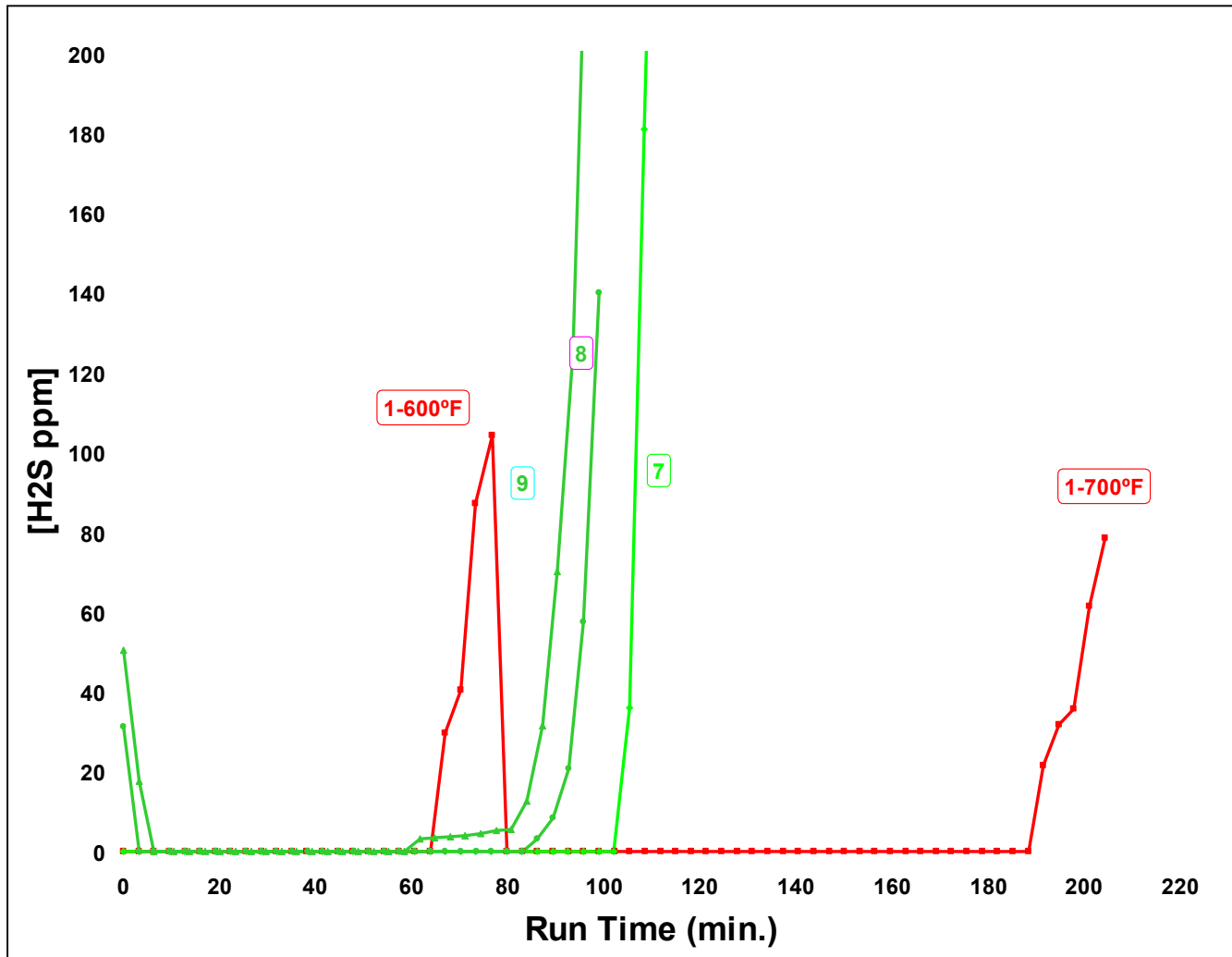
HPHGD-59 Sulfidation 3



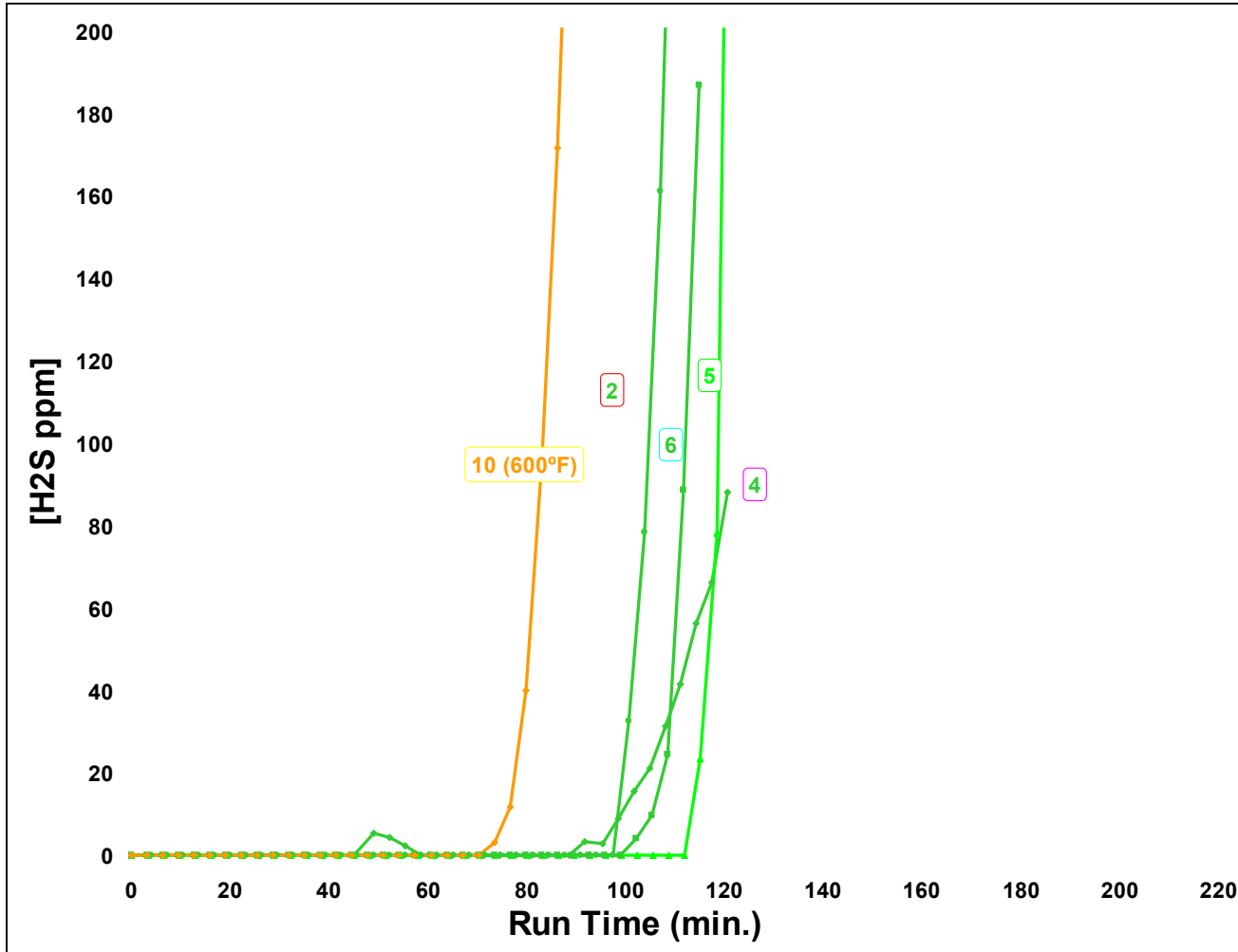
Dry Exit Gas Composition 600-700°F Sulfidation



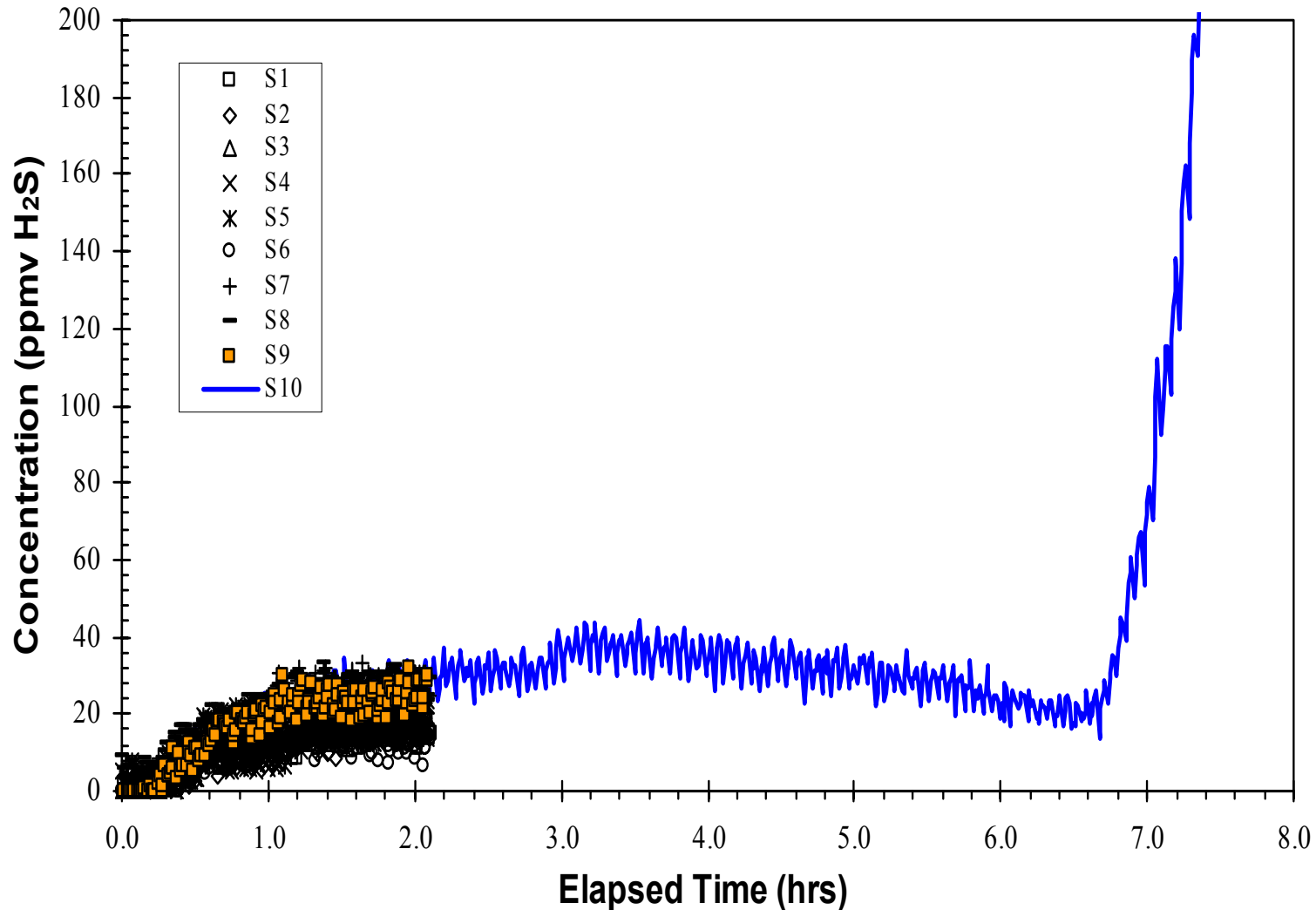
Low Temperature Breakthroughs at 650°F at TDA (17.5-19.5% H₂O)



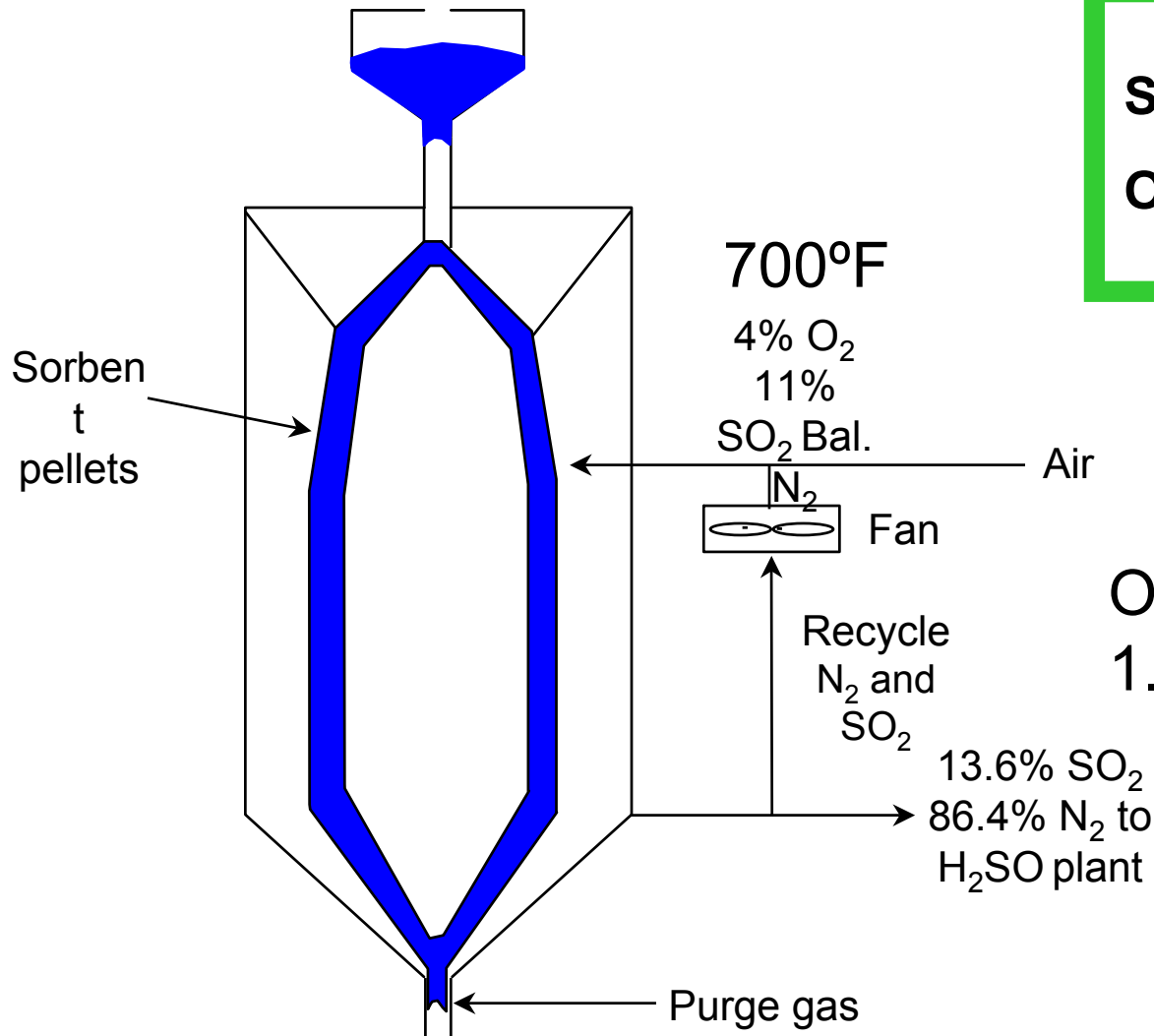
Low Temperature Breakthroughs at 650°F at TDA (10.0-12.0% H₂O)



Breakthroughs at FETC at 900°F (482°C)



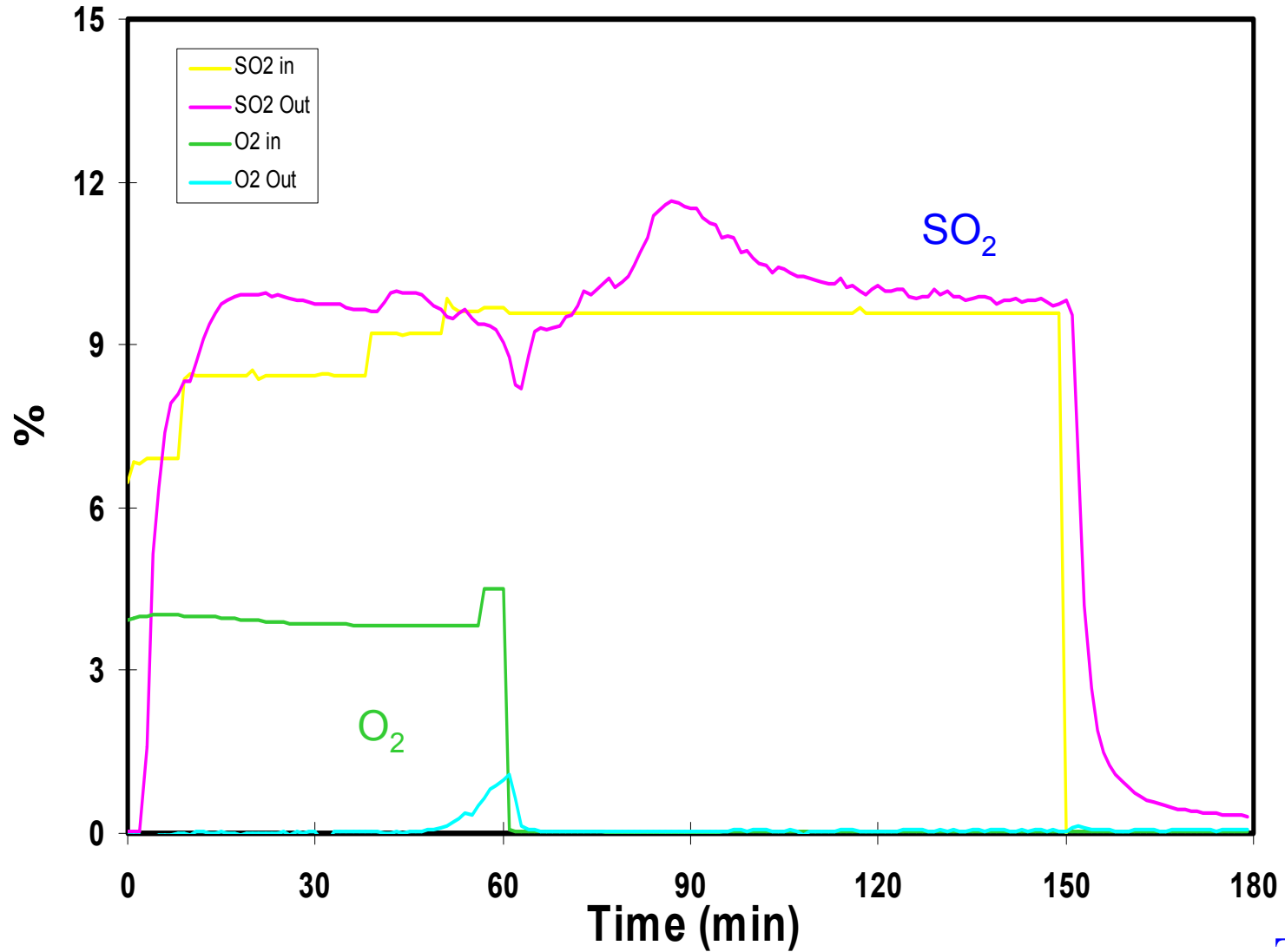
Regeneration of TNT-MB



Simple Co-Flow
One Inlet, One Exit

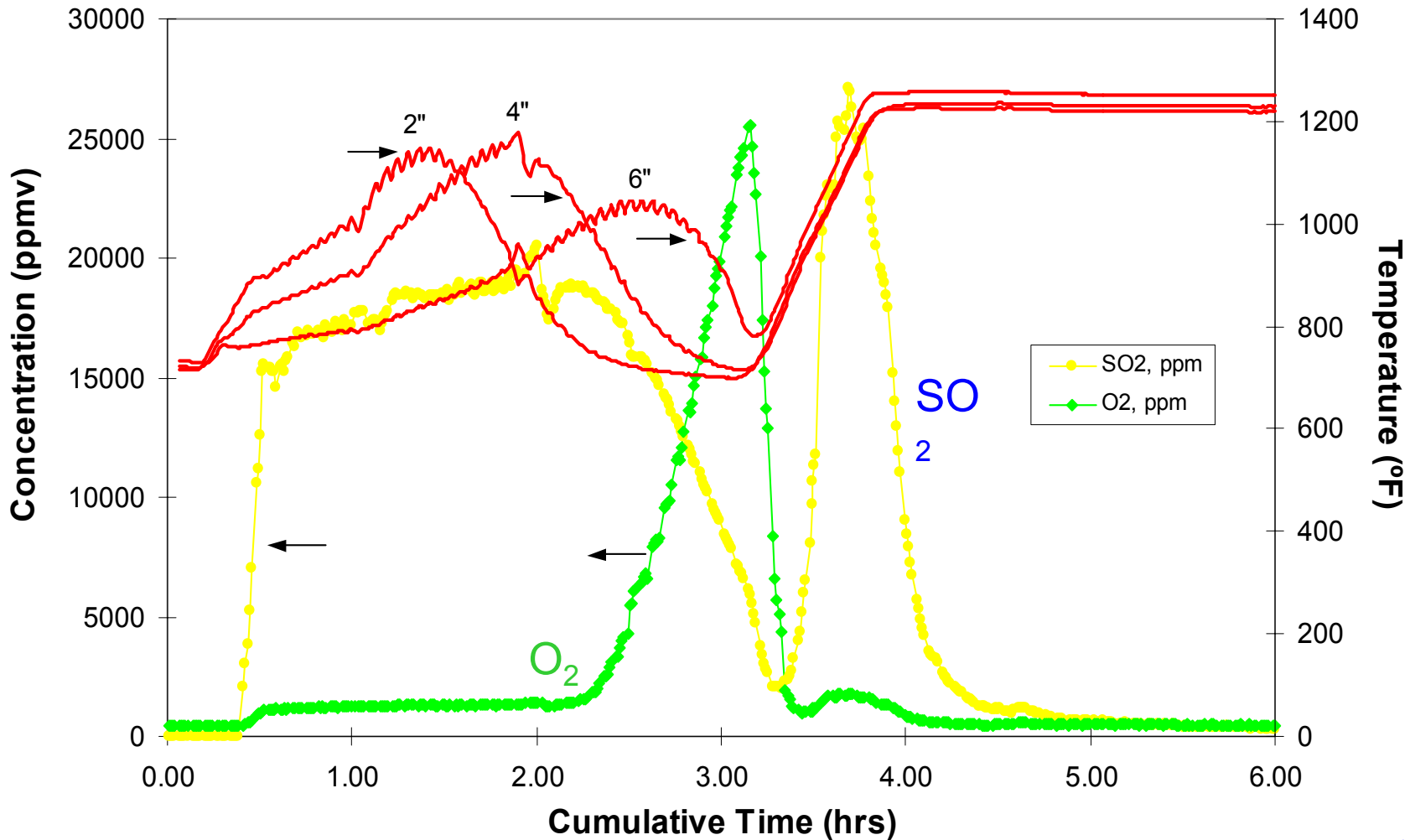
$$\text{O}_2 / \text{H}_2\text{S} = 1.67$$

Regeneration at IGT, 5 atm 8-10% Inlet SO₂

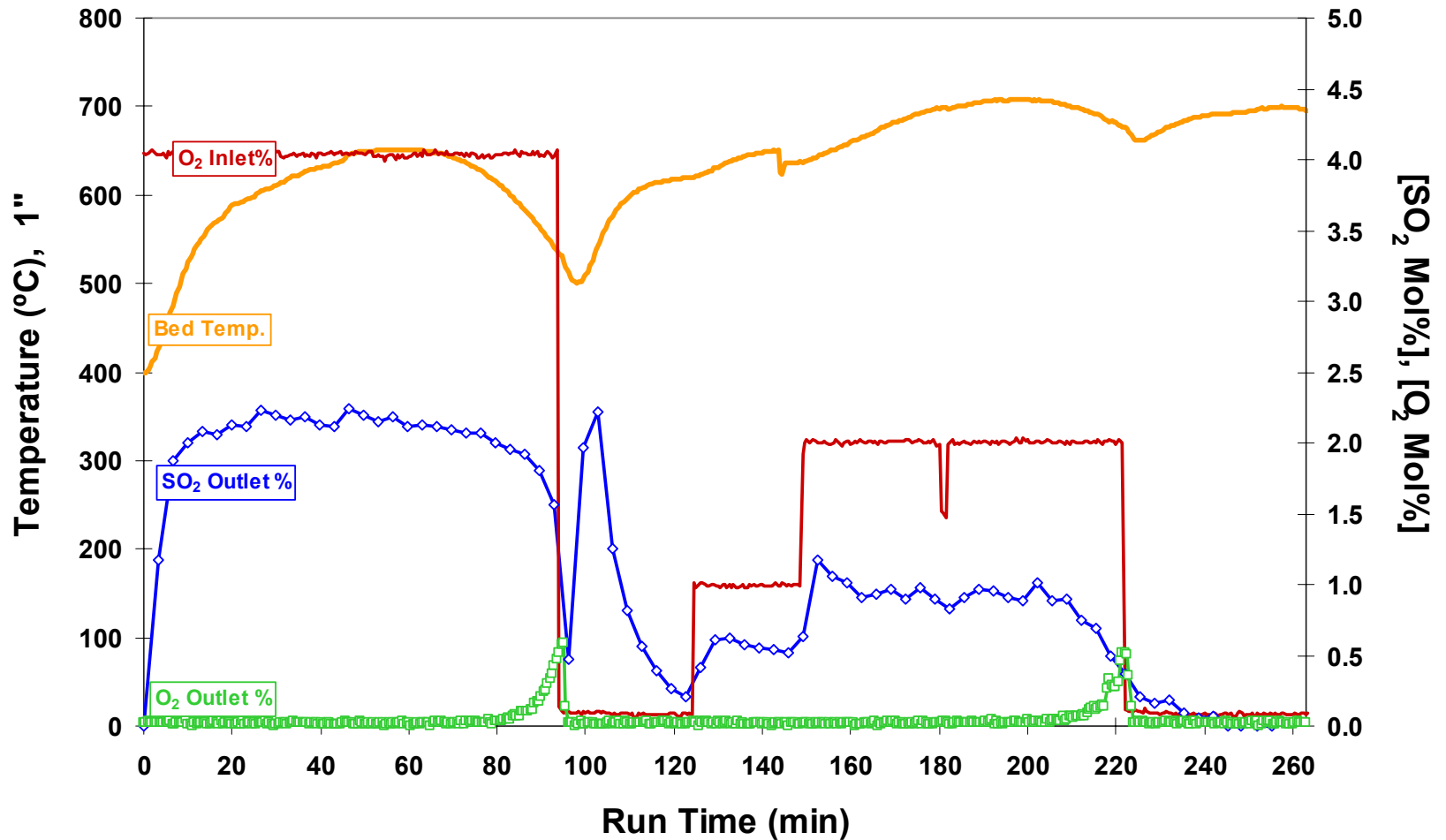


Regeneration at FETC, No Inlet SO₂

HPHGD-60 Regeneration 10



Regeneration at TDA, No Inlet SO₂



Properties of Norton Produced TNT-MB Sorbent (114) 10-Cycle CRADA at FETC

Property	Fresh	4 th Reg	5 th Abs	10 th Abs	10 th Reg
Sulfur (wt%)	0.44	2.0	16.8	14.4	2.8
ASTM Attrition (wt.%)	1.8	1.3	1.1	NA	0.87 inlet 0.64 outlet
Sulfate Sulfur (wt%)	0.42	0.30	NA	0.07	0.27
Carbon (wt%)	NA	< 0.05*	0.05	< 0.5*	NA

900 °F Sulfidations

4th Regeneration with 10% SO₂ at 2 - 3 ATM at TDA

5th Absorption at 20 ATM at TDA

10th Cycle at FETC: NO SO₂ in the inlet during regeneration.

*** Limit of Detection**

Properties of Norton Produced TNT-MB Sorbent (298)

10-Cycle Low Temperature Testing at TDA

	Attrition wt%	Crush Strength lbs.	Surface Area m ² /g	Porosity g/cc	Median Pore Diameter μm	Bulk Density lbs/ft ²	Sulfur wt%	Carbon wt%
As Sintered (TDA)	2.22	31.3	2.55	.2395	.3084	1.35		
As Sintered (Norton)	1.90	31.0	2.76	.2420	.3290	na		
10A - Inlet	1.99	33.4	2.30	.2309	.3093	1.48		
10A-Outlet	1.99	29.9	3.63	.1643	.3544	1.44		
10R - Inlet	1.63	30.4	2.55	.2175	.3296	1.38		
10R - Outlet	1.50	33.3	2.53	.2262	.3184	1.38		

600°F - 700 °F Sulfidations at TDA, No SO₂ in Regenerations

* **Limit of Detection**

Closure

- **TNT-MB is a NON-SPALLING Zinc Ferrite Sorbent**
- **TNT-MB Reduces Regenerator Size & Complexity**
 - Only one inlet
 - Half the current TEGo regenerator used
 - Very high sulfur loadings make reduced sorbent circulation and/or reactor sizes possible in future moving beds
- **The Sorbent Retains Its Activity for Multiple Cycles**
 - 600°F: > 1 hour breakthrough
 - 700°F: > 3 hour breakthrough
 - 900°F: > 7 hour breakthrough
- **Attrition Resistance Improves with Cycling**

Acknowledgments

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 - Tom Feeley, Current Project Manager
 - Dave Berry, CRADA Manager
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