Reformate Desulfurization for Logistic SOFC Power Systems

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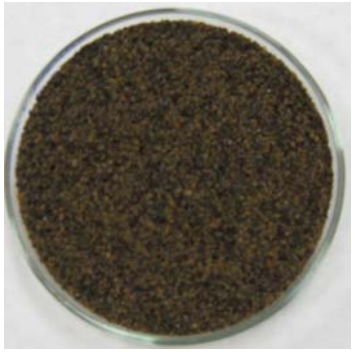
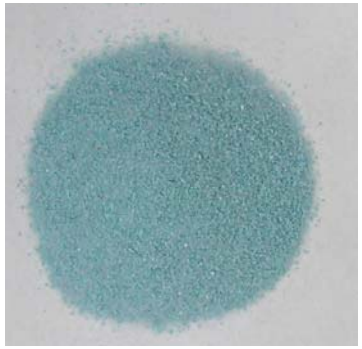
IntraMicron Inc.

IntraMicron Inc is a small business company located at Auburn, AL. Its R&D covers:(1) Filtration; (2) Desulfurization; (3) Fischer Tropsch Synthesis; (4) CO oxidation.

Microfibrous Entrapped Catalyst Particles





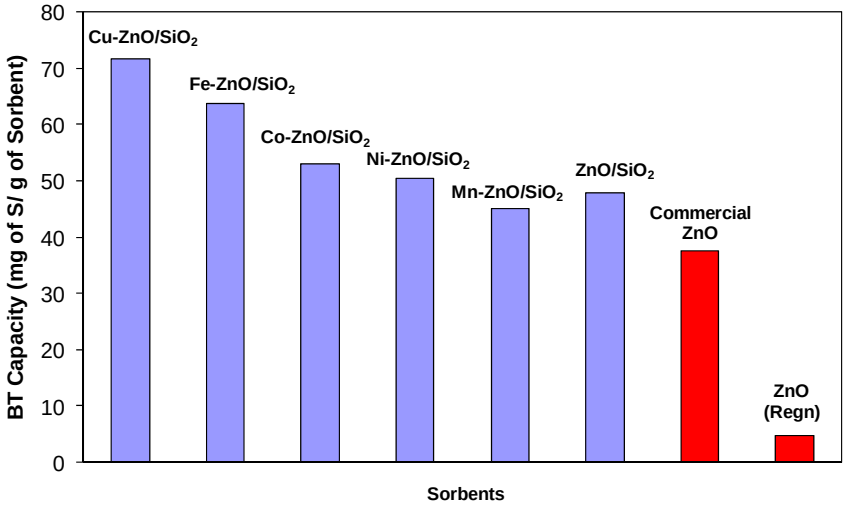
Polishing sorbents for gas phase desulfurization

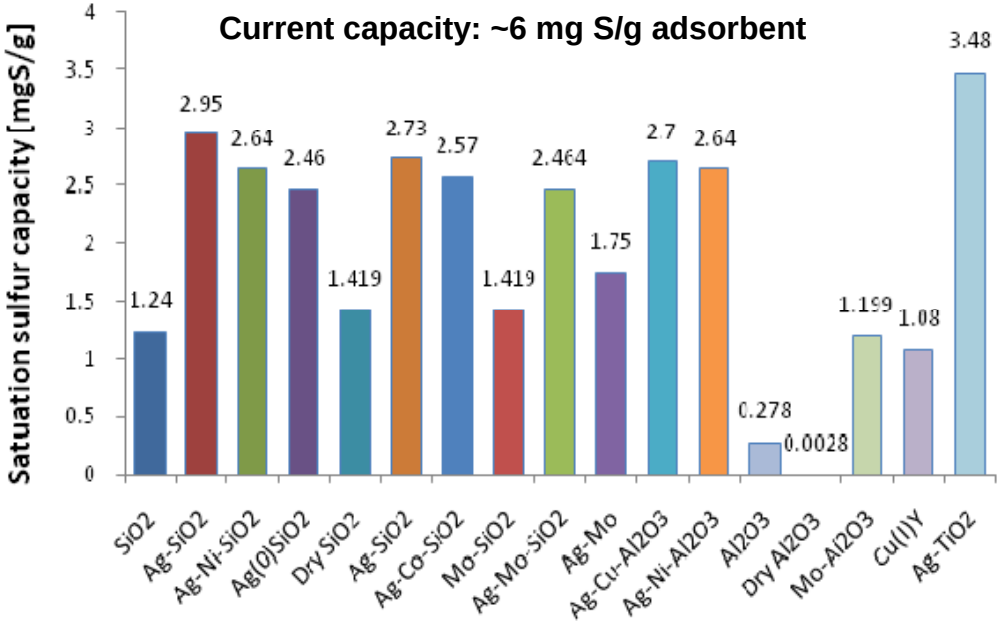
Adsorbent for liquid phase desulfurization

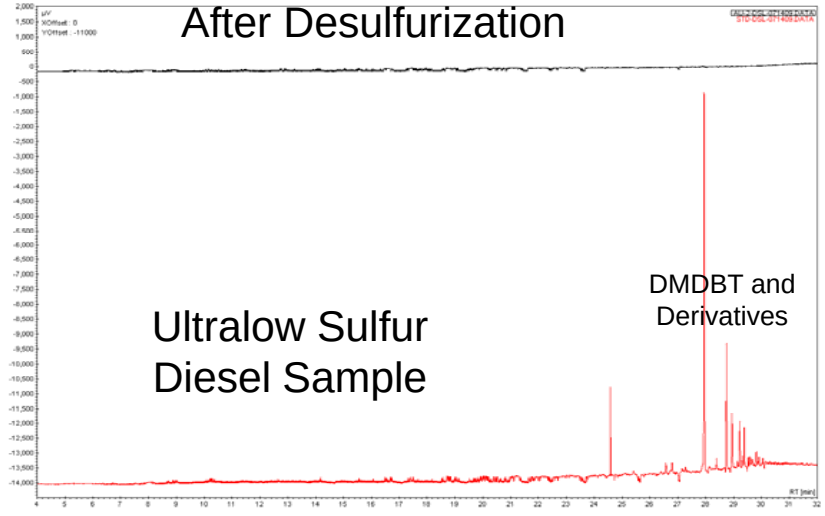
Desulfurization Sorbents/Adsorbents

Low Temperature Gas Phase Desulfurization Sorbent: Cu-ZnO/SiO_2, (Patent Applied for)

Liquid Phase Desulfurization Adsorbents: Ag_2O/TiO_2 for JP-5







Outline

- Sulfur Issue
- Reactor Design and Bed Configuration
- Desulfurization & Regeneration Performance
- Desulfurizer Construction
- Conclusion
- Acknowledgements

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Sulfur Issue

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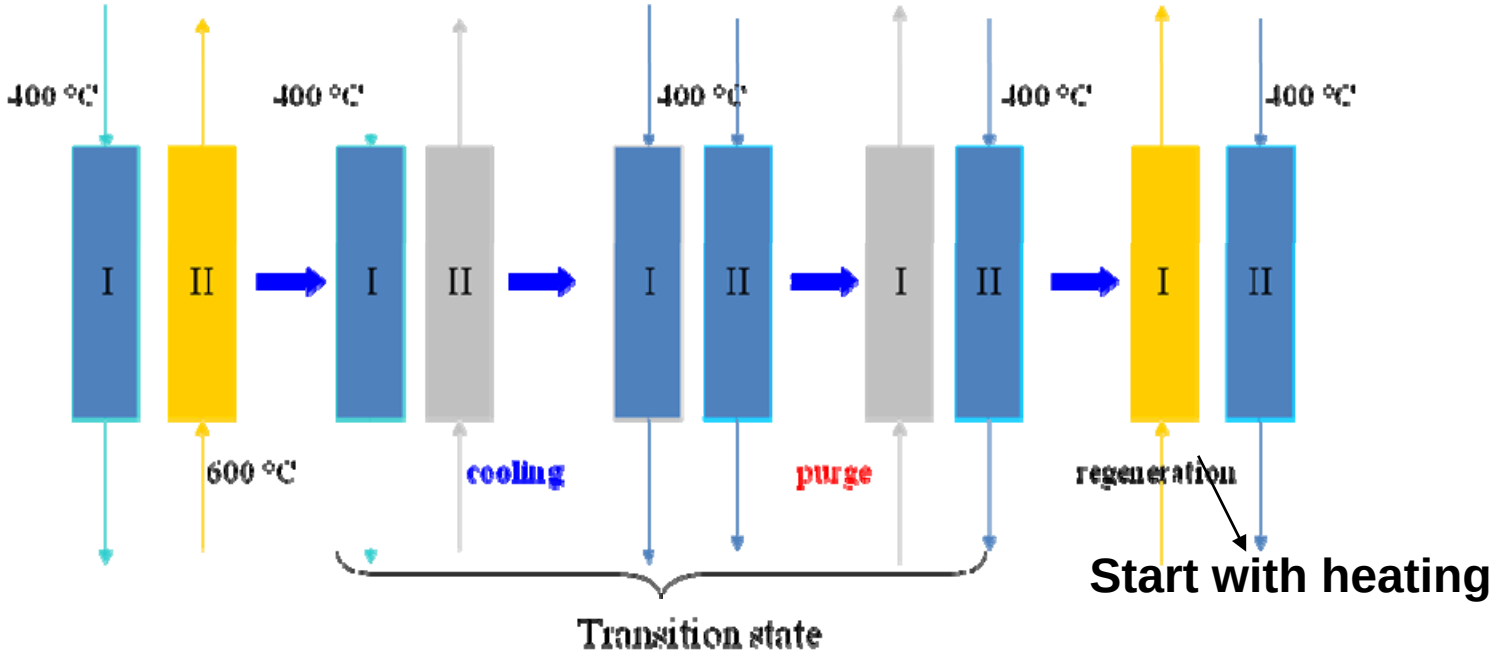
- Typical Fuel Cells Have Low Sulfur Threshold:
  - 0.1 ppmv most for PEM Fuel Cells
  - 2~3 ppmv for typical Solid Oxide Fuel Cells
- Sulfur Content in Logistic Fuels (ca. JP-5, JP-8)
  - i.e. 500~3000ppmw, equivalent to 50~300 ppmv after converted to reformates in reformers.
- Sulfur Removal Techniques
  - Pre Reformer Desulfurization
  - Post Reformer Desulfurization
- Post Reformer Desulfurization Using Reactive Sorbents
  - ZnO, CuO, Fe_2O_3 etc.
  - High sulfur capacity (i.e. 392 mg S/g ZnO), compared to adsorbents for liquid phase desulfurization.

Objectives

- To build a desulfurizer able to
  - Reduce total sulfur concentration to less than 3 ppmv
  - Provide a continuous run of 200 hours
  - Have a good low temperature performance for cold startup and transient operations
  - Small bed size: ~1 foot long
  - Low pressure drop ca. 1-2 psi

Cyclic Arrangement and Transition Operation



Time balance

5hours	=	4hours	1hour Transition

Reactor/Valve Sizes

Preferred desulfurization temperature: 400 C

Preferred regeneration temperature: 600 C

Parameter	Value	Result
Particle size	0.8~1.4 mm	Regn <5 hour
Reactor diameter	6”	60 cm/s ΔP=1.4 psi
Bed length	12”	L/D=2
Pipe /valve size	2”	6 m/s

Note:

The system works at 400 C during desulfurization and 600 C during regeneration. Therefore the valves are required to work at high temperature in the presence of oxygen during regeneration.

Sulfur input: 300 ppmv

Design Challenges

Reformates:

Flow rate: 17 kg/hr .
Temperature from reformer: 850 C
Reformate Composition:

Component	Concentration
CO	**24.9%**
CO_2	**10.2%**
WATER	**6.9%**
H_2	25.0%
N_2	33.0%
H_2S	300 ppmv

High flow rate: Pressure Drop
High Temperature: Need heat exchanger

High CO and CO_2 concentration,
COS formation.
$CO_2+H_2S=COS+H_2O$
$CO+H_2S=COS+H_2$

Breakthrough Concentration: 2~3 ppmv Run time: 200 hours Regenerable

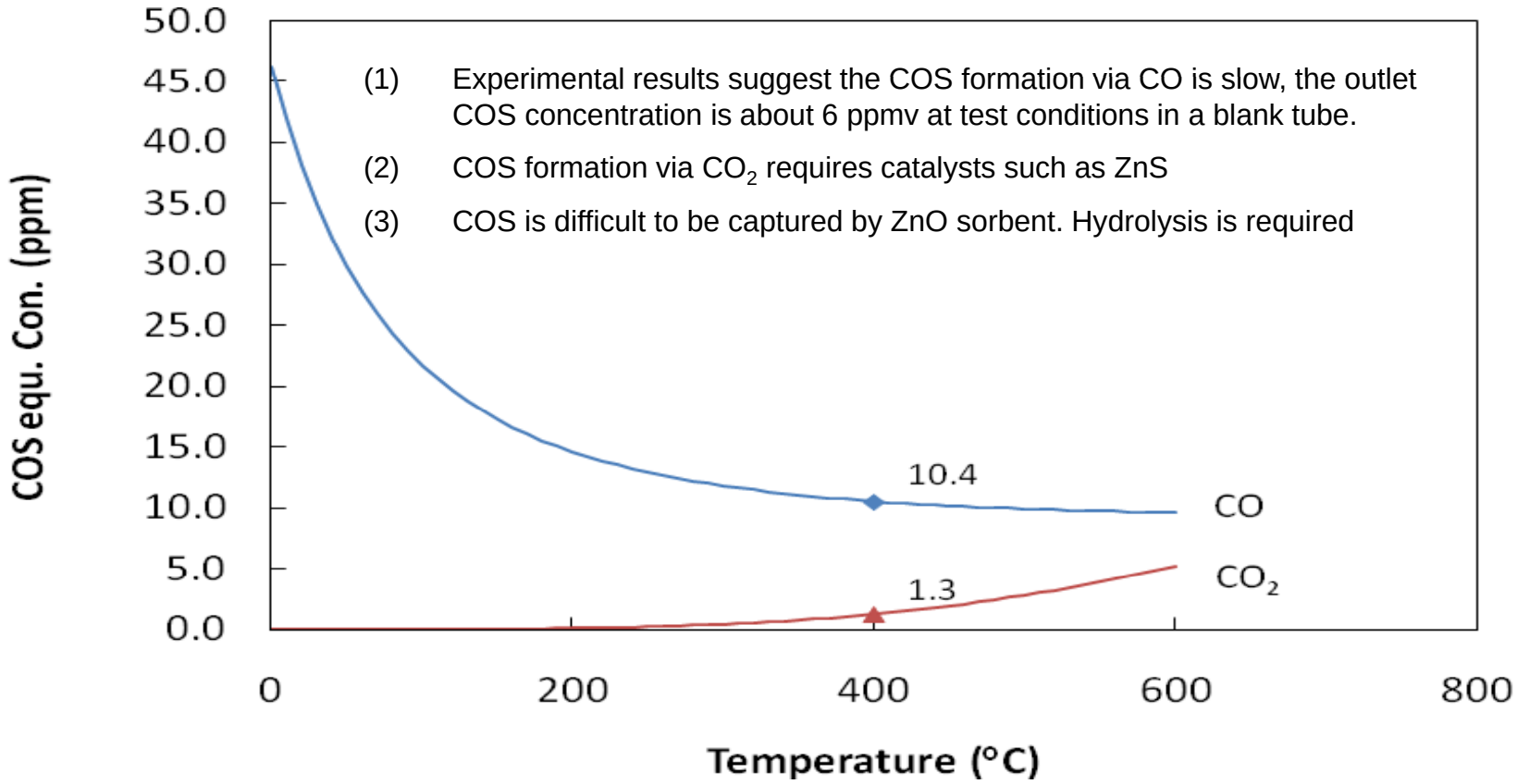
Small Reactor Good Low Temperature Performance for Cold Startup and Transient Operations.

Pressure Drop: < 2 psi

Desulfurization Performance
COS Equilibrium Analyses

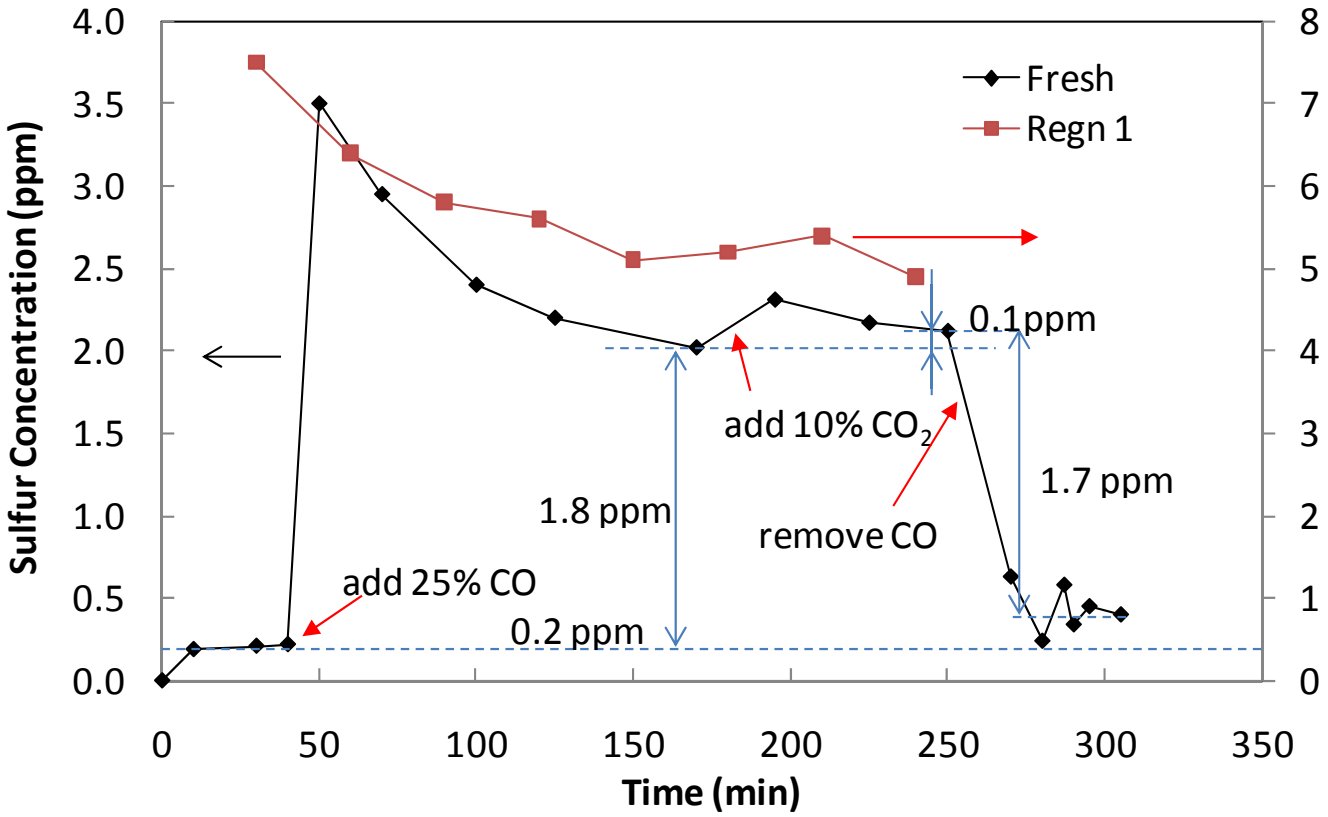
$CO(g)+H_2S(g)=COS(g)+H_2(g)$ (slow homogeneous reaction)

$CO_2(g)+H_2S(g)=COS(g)+H_2O(g)$ (fast heterogeneous reaction)



reformate composition: 25% CO, 25%H_2, 10% CO_2, 7% H_2O and 33% N_2.

Effects of CO and CO_2



Need sorbents for COS removal or conversion

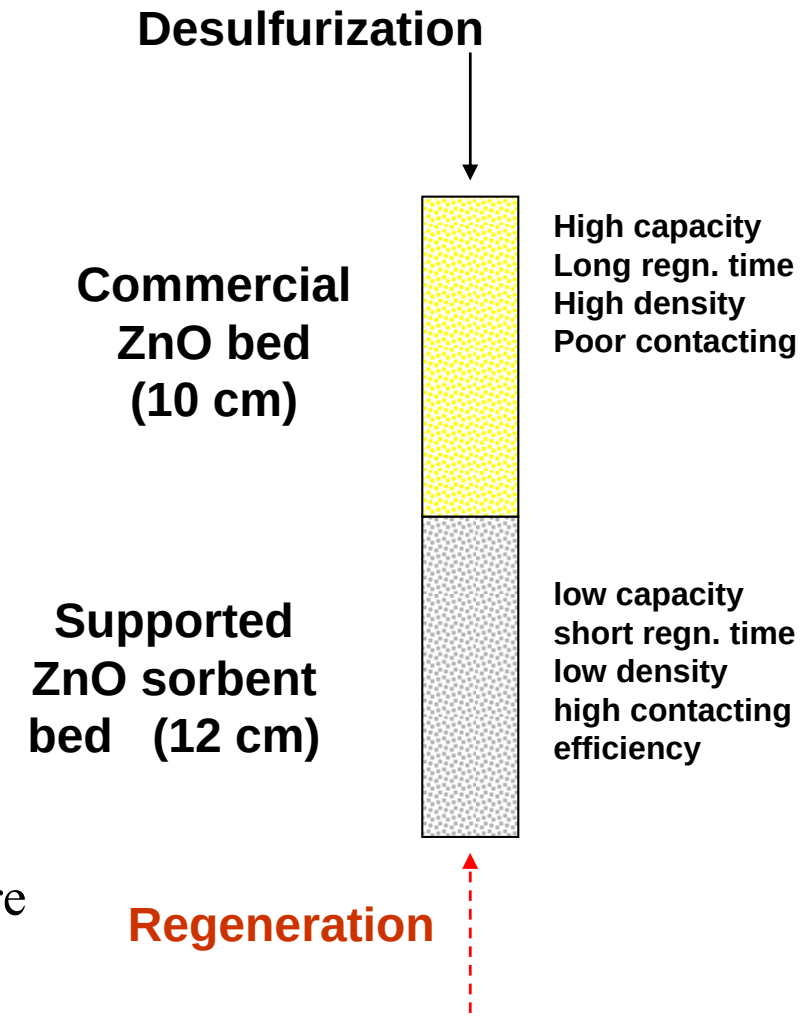
$CO+H_2S=COS+H_2$ K=0.0363 C_e=10.4 ppmv;

$CO_2+H_2S=COS+H_2O$ K= 0.0029 C_e=1.2 ppmv

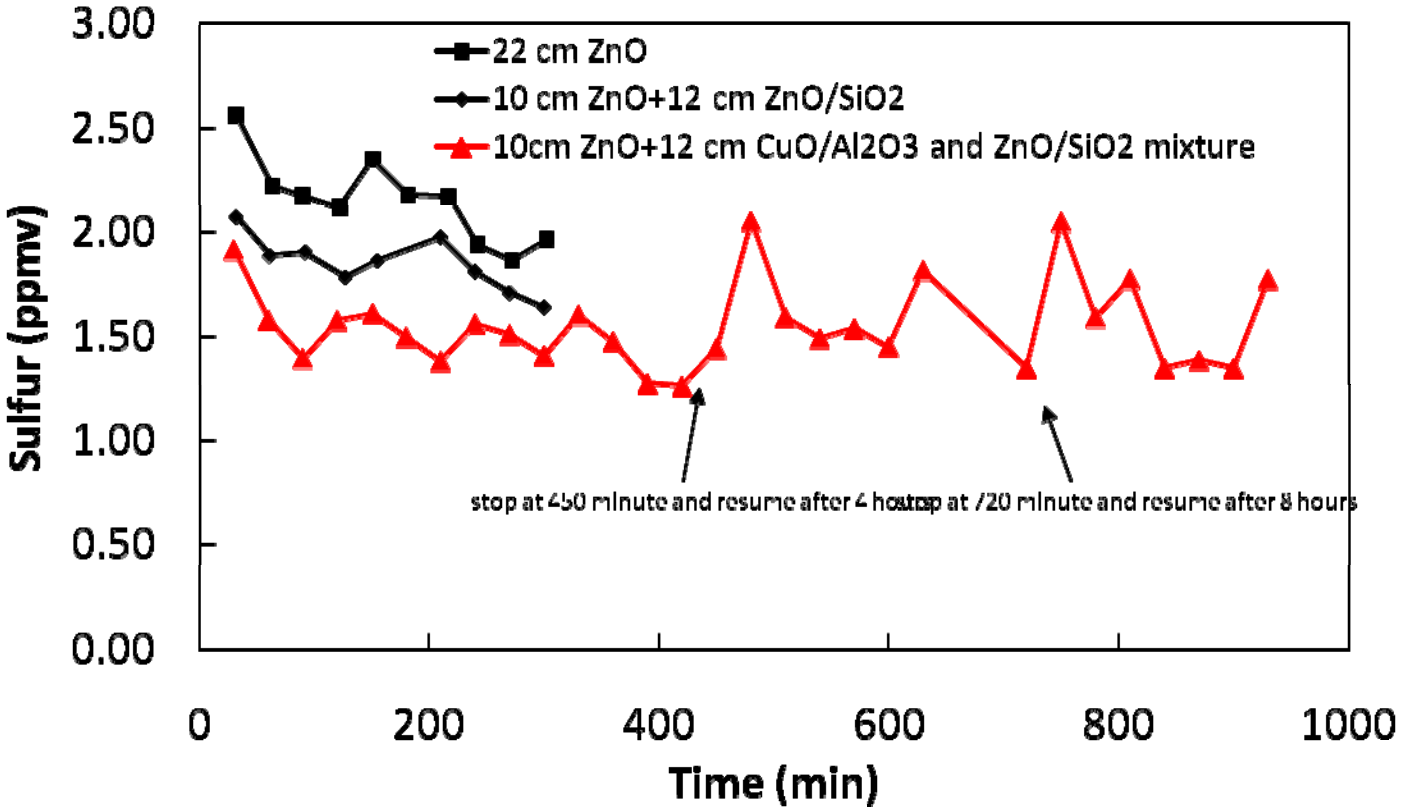
Breakthrough curves of layered beds tested with 300 ppmv H_2S-25% H_2-25% CO-10% CO_2-7% H_2O-33% N_2 at a face velocity=100 cm/s at 400 C. Bed length: 22 cm

Bed Configuration
Layered Bed Design

- Low outlet sulfur concentration (as low as 0.3 ppmv)
- Less weight
- Short regeneration time
- Low temperature function
- Bed Configuration
  - Down flow direction
  - (in desulfurization)
  - Diameter: 2.14 cm
  - Particle size: 0.8~1.4 mm
  - Supported sorbent:
    ZnO/SiO_2 and supported Cu doped ZnO sorbent which has a better low temperature performance.



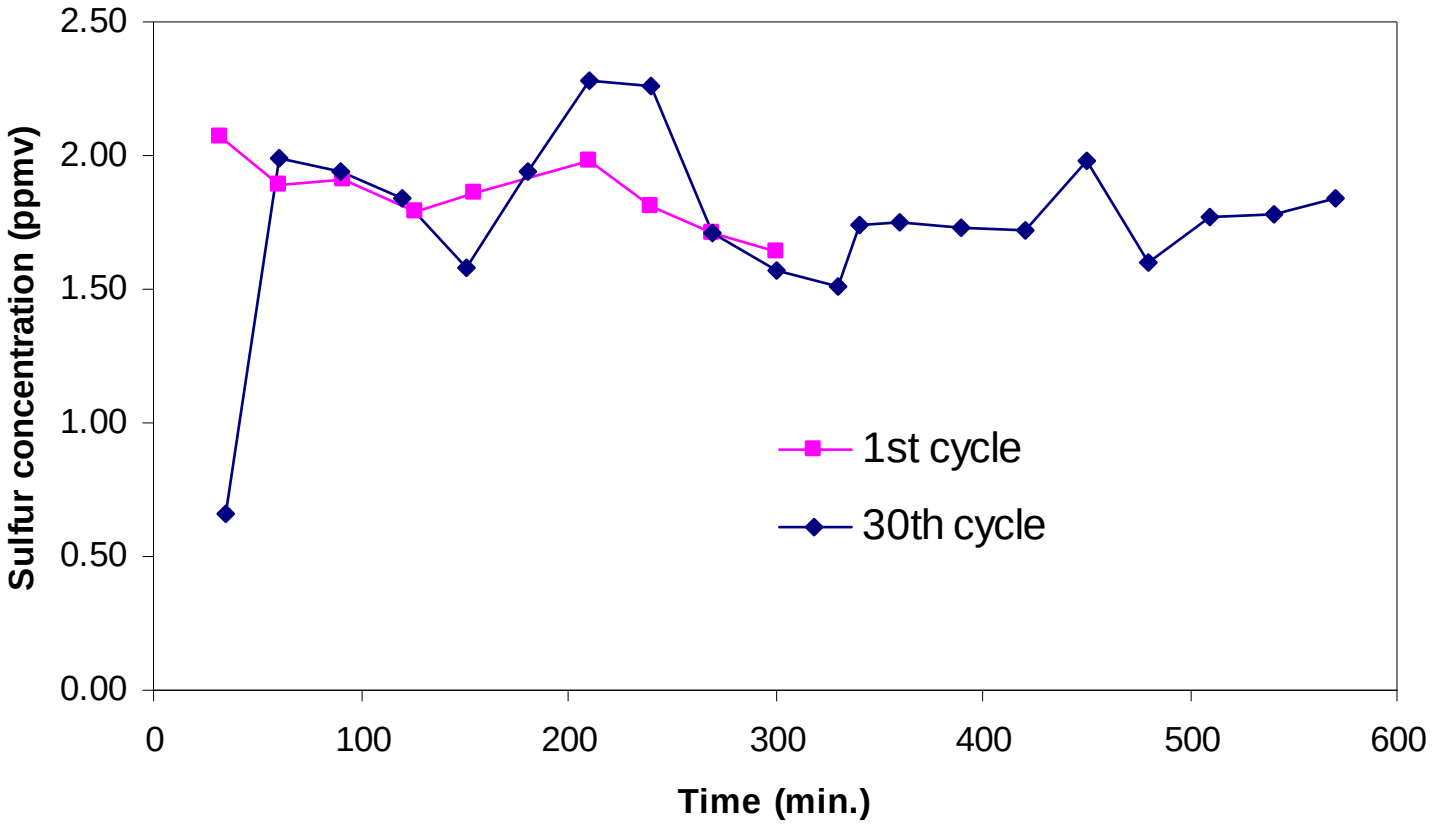
Layered- Bed Performance



(1) Allow multiple stop and resume
(2) Run time can be extended if necessary.

Desulfurization was carried out at 400 C in the presence of reformates containing 300ppmv H_2S-25% H_2- 25% CO-10% CO_2-7%H_2O-33% N_2 at a face velocity of 60 cm/s.

Cyclic Test (Layered Bed of ZnO-ZnO/SiO_2)



2 beds

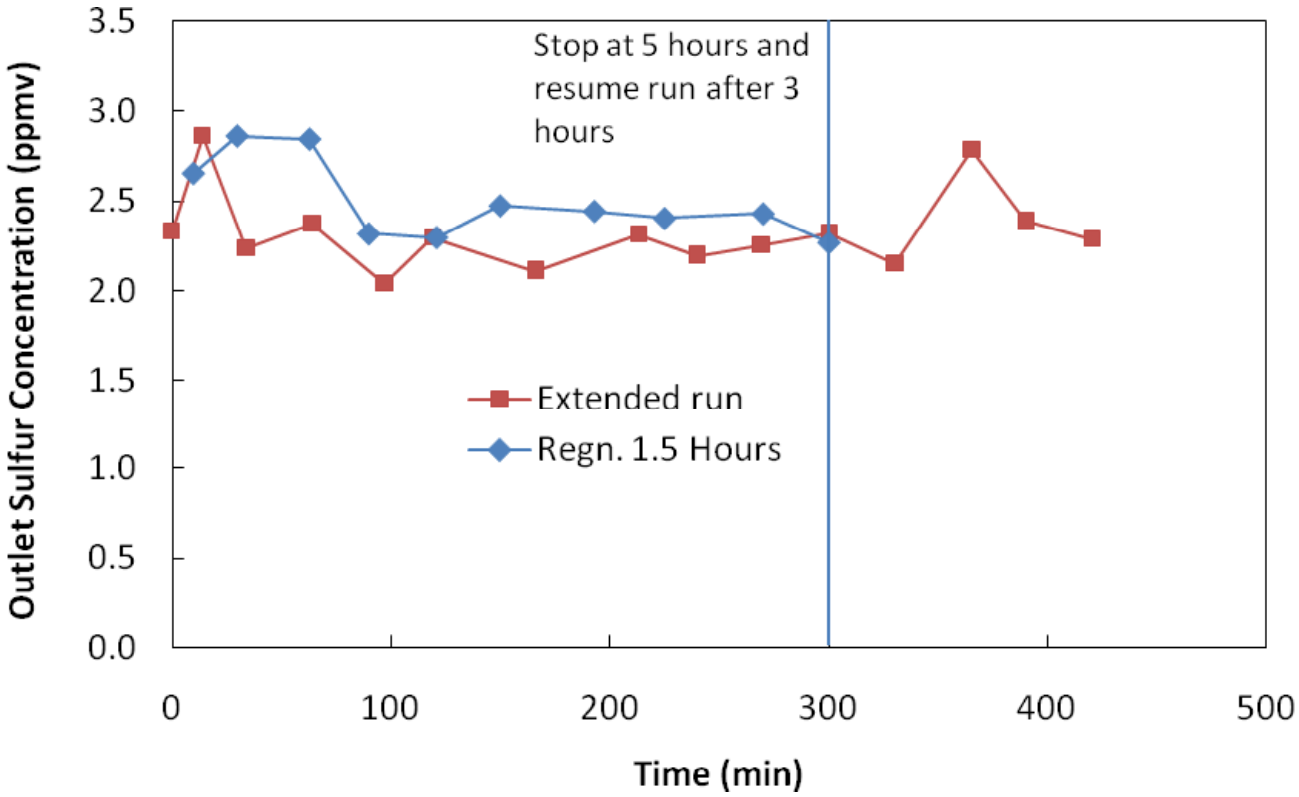
30 cycles/bed

5 hrs/cycle

Total is 300 hours.

Desulfurization was carried out at 400 C in the presence of reformates containing 300 ppmv H_2S-25% H_2- 25% CO-10% CO_2-7%H_2O-33% N_2.

Reduced Regeneration Time



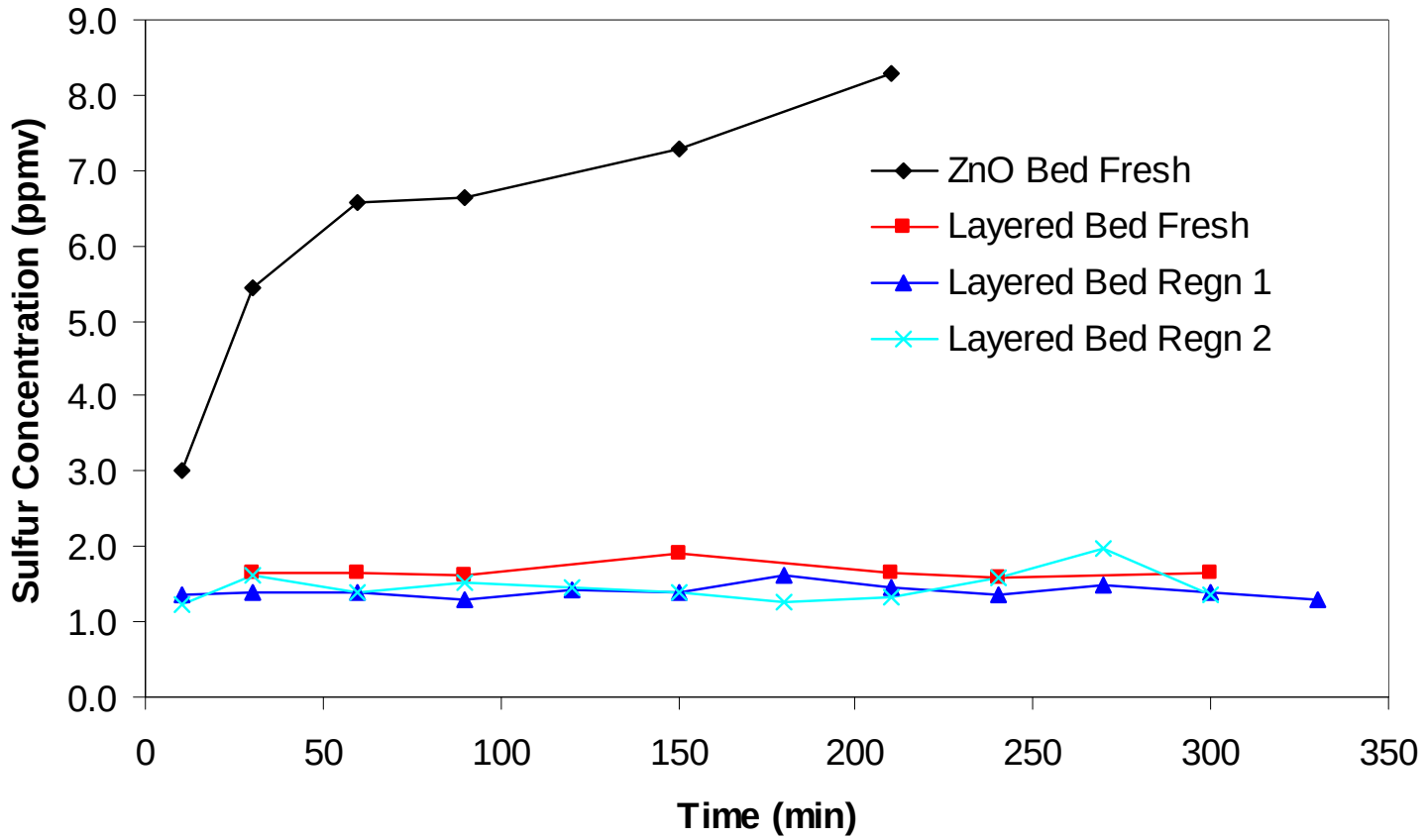
Sorbent can be regenerated in a shorter time;

Sorbent bed can be stop and resume multiple times during the run.

Sorbent bed can provide a longer service time.

Tested with challenge gas containing 300 ppmv, 30% CO, 32% H_2, 30% N_2 and 8% H_2O at a face velocity of 1.0 m/s at 400 C. The sorbent bed contains 56 g of 1.2 mm ZnO particles with a bed length of 10 cm, and ZnO/SiO_2 of 12 cm. Spent sorbent was regenerated in air-steam mixture containing ~14% O_2 for 4 hours.

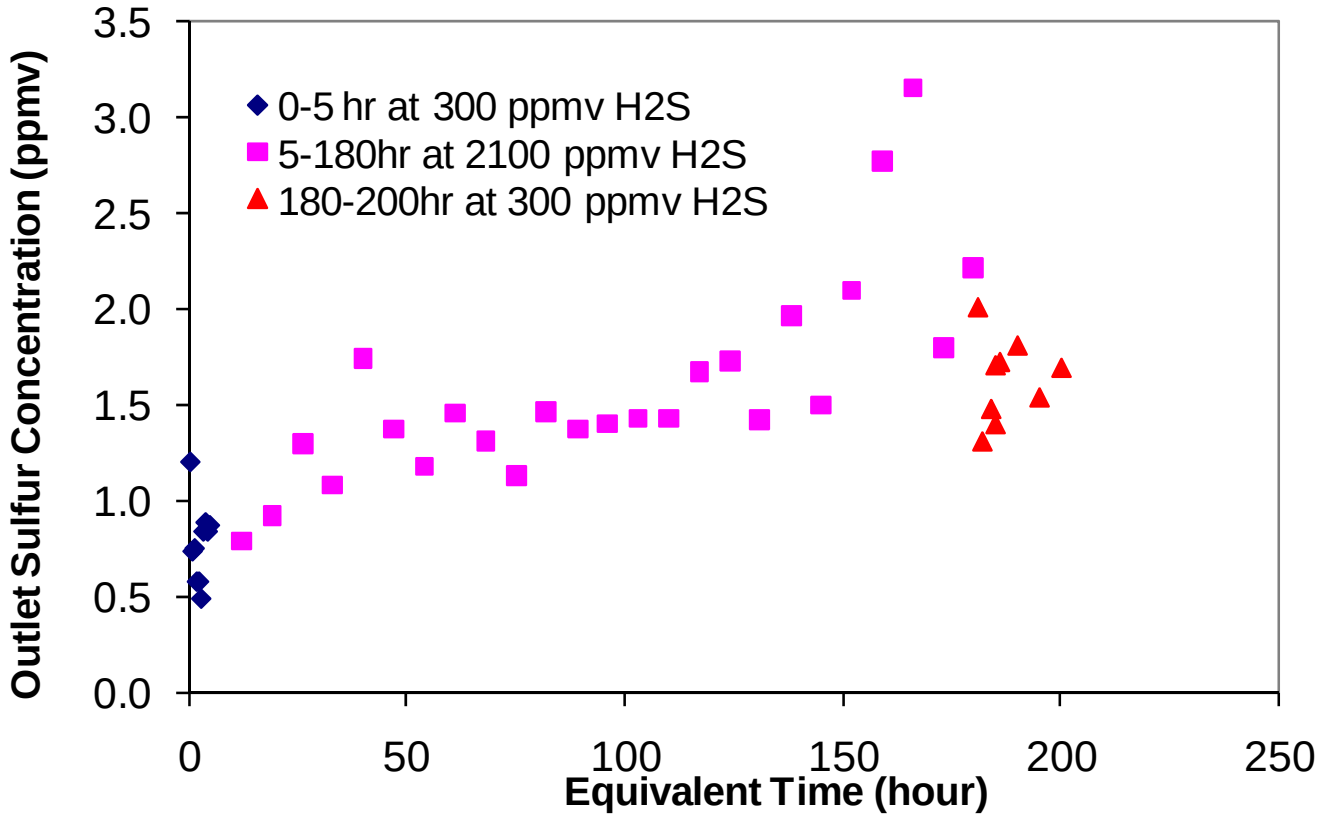
Low Temperature Performance



Desulfurization was carried out at 150 C in the presence of reformates containing 300 ppmv H_2S-25% H_2- 25% CO-10% CO_2-7%H_2O-33% N_2.

Off-Site Regenerable Desulfurizer (Sulfur Cartridge)

- Single reactor provides a run time of 200 hours.



Desulfurization was carried out at 400 C in the presence of reformates containing 300ppmv H2S-25% H2- 25% CO-10% CO2-7%H2O-33% N2 at a face velocity of 60 cm/s.

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Desulfurizer Construction
Sorbent Loaded for Desulfurizer

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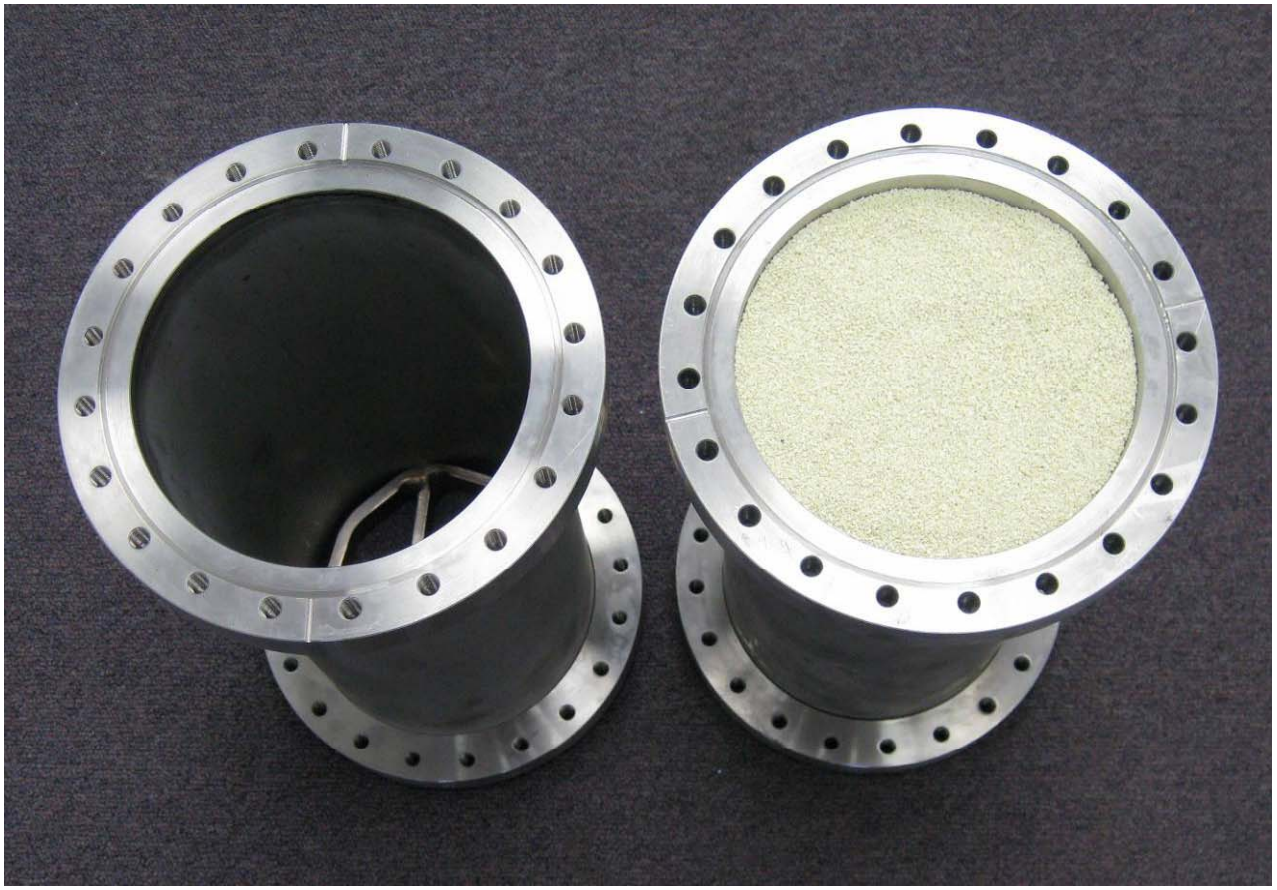

Conclusion

- The layered bed made of commercial ZnO and supported ZnO based sorbent demonstrated a wide operational temperature window (150~400 C).
- The layered bed are highly regenerable. It can be regenerated for 30 cycle without significant changes in desulfurization performance.
- The designed desulfurizer can provide a continuous run with regeneration or 200 hours run as a sulfur cartridge.

Acknowledgements

Award #: W56HZV-07-C-0577

Thank you for your attention

Questions?