# *Sulfur removal from reformate*

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# Introduction

- Hydrogen can be produced by reforming fuels such as gasoline, natural gas, and diesel.

- These fuels contain sulfur compounds that can poison catalysts in the fuel processor and fuel cells.

| | |
|---|---|
| – natural gas | 20 ppm S by volume |
| – gasoline/diesel (future) | 30 ppm S by weight |

- Corresponding $H_2S$ content of reformate (by volume)

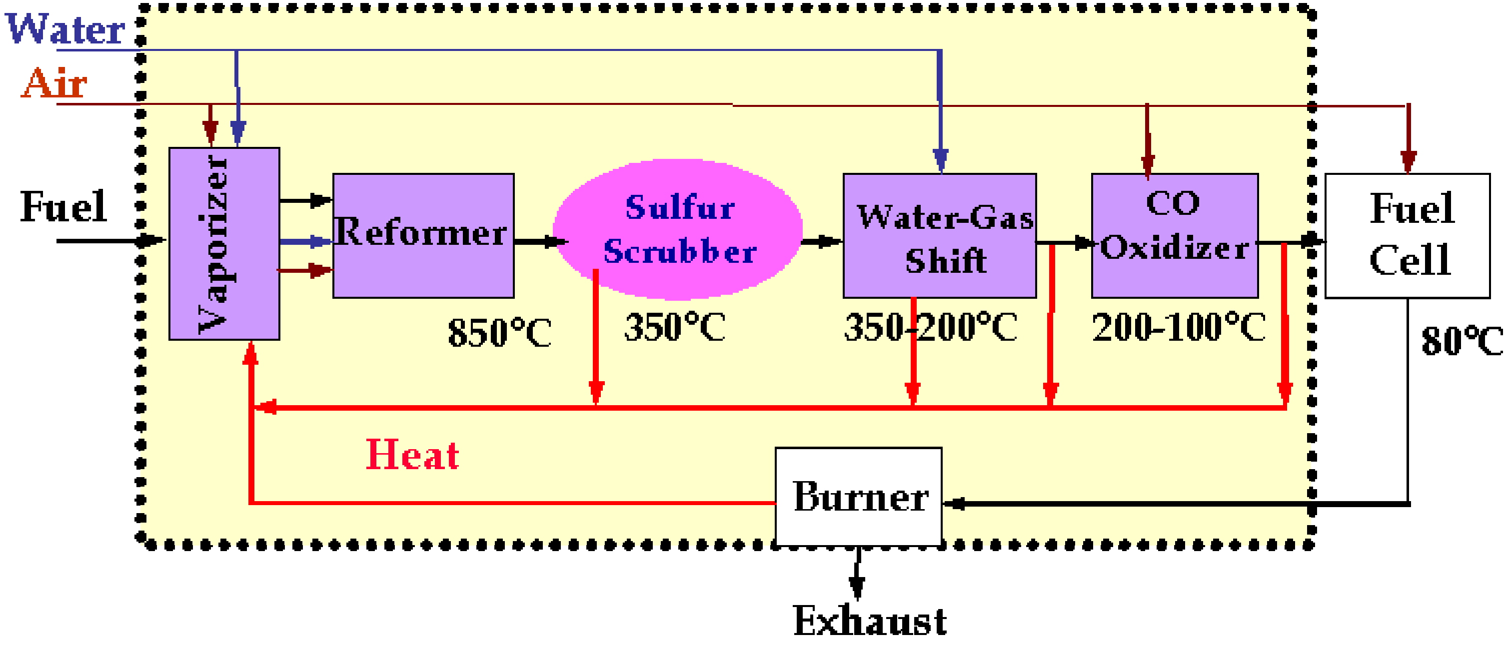
| | |
|---|---|
| – natural gas | 10-14 ppm |
| – gasoline/diesel | 3-5 ppm |

# *Objective: develop a sulfur removal process for use in on-board fuel processor*

- $H_2S$ concentration in reformate (dry basis)
  - < 50 ppb (2005)
  - < 10 ppb (2010)
- Reactor size and cost
  - <0.06 L/kWe (<0.06 kg/kWe)
  - ≥ 50,000 $h^{-1}$ gas hourly space velocity
  - ≤ \$1/kWe

This work addresses technical barriers J and L.

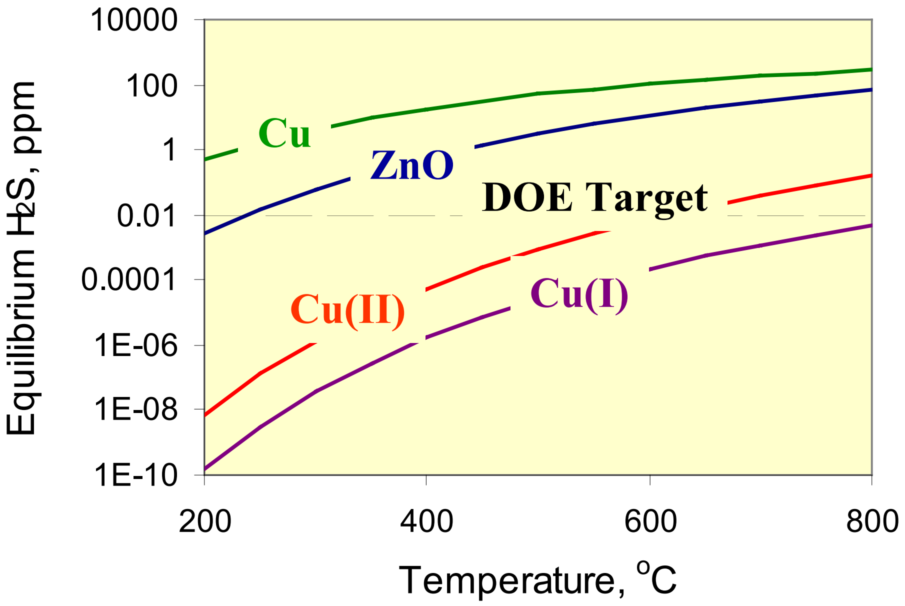
# Our strategy is to remove $H_2S$ from reformate within the fuel processor



- Requires that the reforming catalyst be sulfur-tolerant.
- The catalyst that is least tolerant defines the concentration to which $H_2S$ must be reduced.

# Copper oxide is our choice for $H_2S$ removal

- Benefits
  - among the lowest $H_2S$ equilibrium concentration of metal oxides
  - lower vapor pressure than ZnO allows for higher operating temperatures
  - low cost
- Challenges
  - Cu oxides reduce to metallic Cu under fuel processing conditions
  - metallic Cu has less favorable $H_2S$ equilibrium than ZnO



# *Approach*

- Synthesize mixed metal oxides to stabilize Cu in the oxide form
  - non-Cu transition metal oxide is resistant to reduction to metallic form under fuel processing conditions
  - mixed metal oxide is dispersed on a high surface area support, such as $\gamma$-$Al_2O_3$
- Determine the extent of desulfurization of a $H_2S$-containing simulated reformate as a function of operating parameters including
  - mixed metal oxide composition
  - temperature
  - gas-hourly space velocity
  - reformate composition

# *Reviewers' comments from FY02 Annual Review*

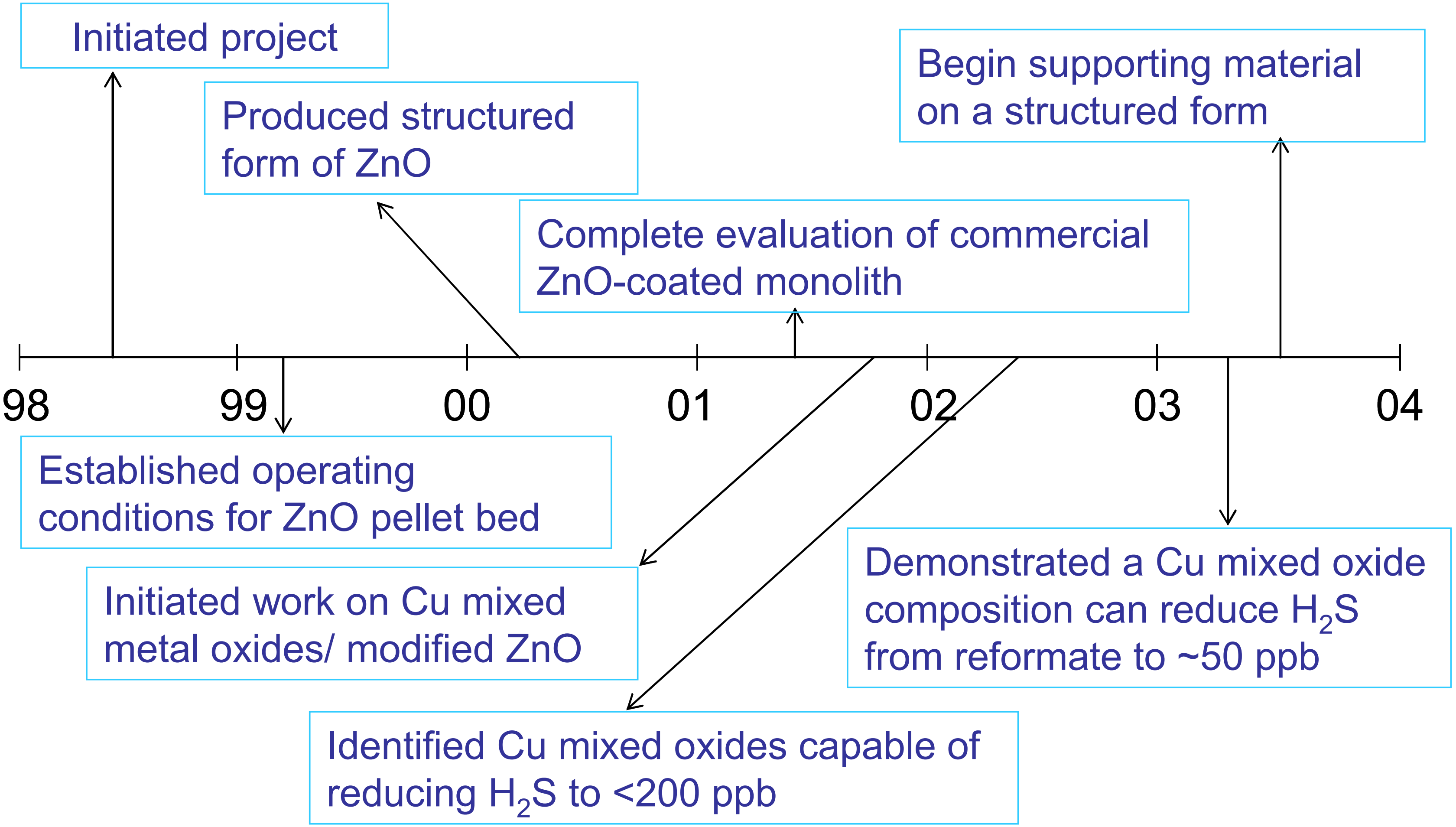
- Scope of work is too limited; expand to include liquid-phase desulfurization

  We believe that on-board liquid-phase desulfurization processes will not meet the DOE targets for size and weight for sulfur removal unit. Residual sulfur may be present in fuels that have been desulfurized off-board and will have to be removed on-board.

- Need for more surface characterization to better understand competitive adsorption

  Our main focus has been to identify a Cu-containing mixed oxide that can reduce the $H_2S$ concentration in reformate to <100 ppb under fuel processing conditions. We plan to do characterization studies (SEM/TEM and EXAFS/XANES) to further improve the performance of this material.

# *Project timeline*



Initiated project

Produced structured form of ZnO

Complete evaluation of commercial ZnO-coated monolith

Begin supporting material on a structured form

Established operating conditions for ZnO pellet bed

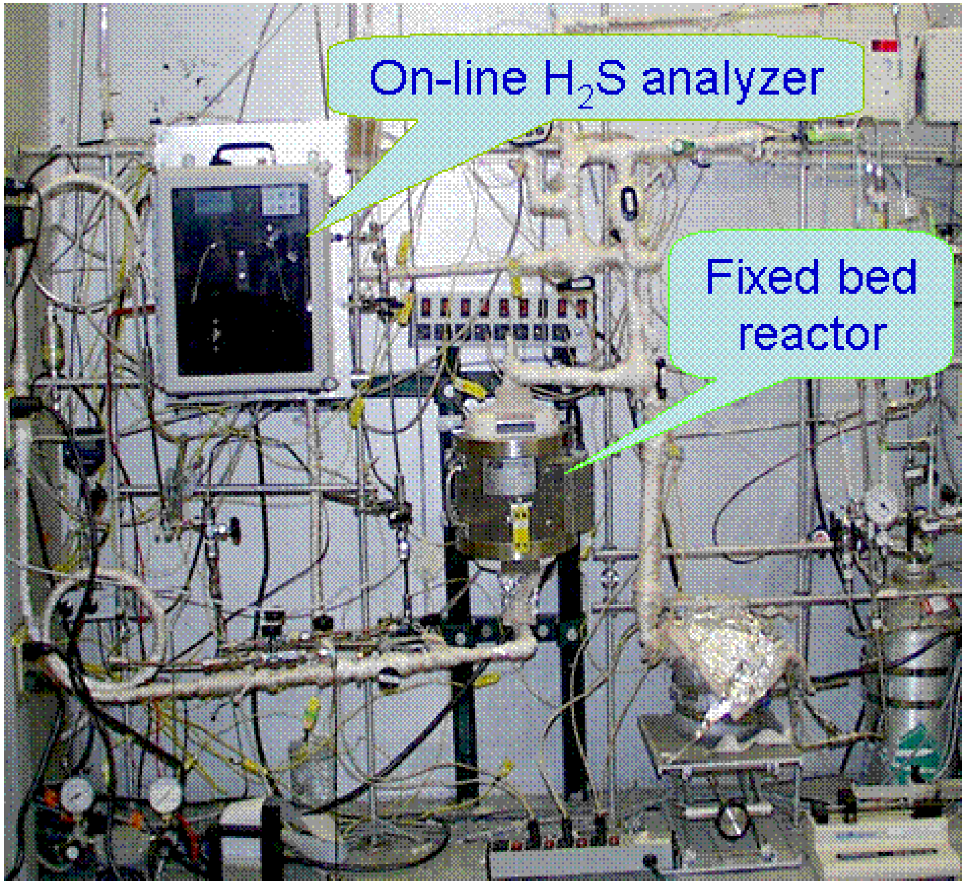
Initiated work on Cu mixed metal oxides/ modified ZnO

Identified Cu mixed oxides capable of reducing $H_2S$ to <200 ppb

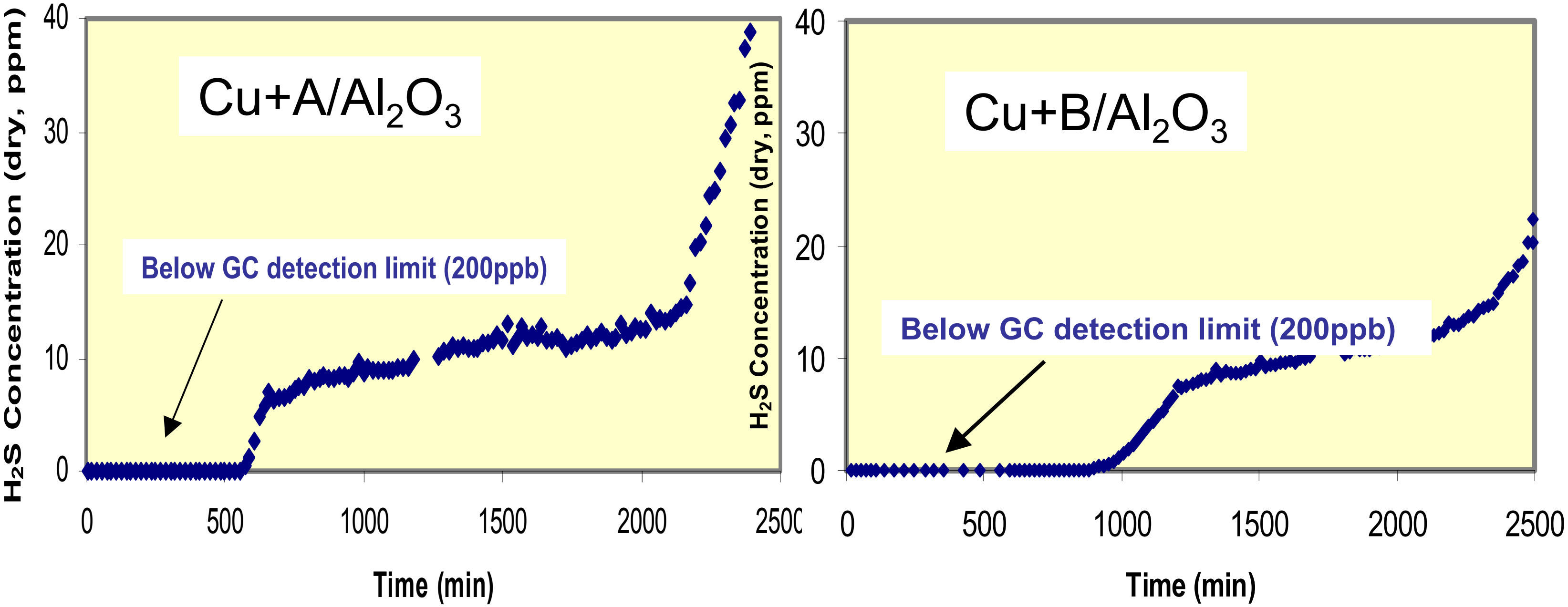
Demonstrated a Cu mixed oxide composition can reduce $H_2S$ from reformate to ~50 ppb

# *Microreactor system for evaluating the $H_2S$ removal performance of candidate sorbents*

- Fixed bed microreactor
- All fittings, tubing, and valves treated with Sulfinert® to minimize $H_2S$ uptake by system hardware
- Flame photometric detector (FPD) for $H_2S$ and COS (detection limit is 200 ppb)
- On-line $H_2S$ analyzer for $H_2S$ (detection limit is 20 ppb)



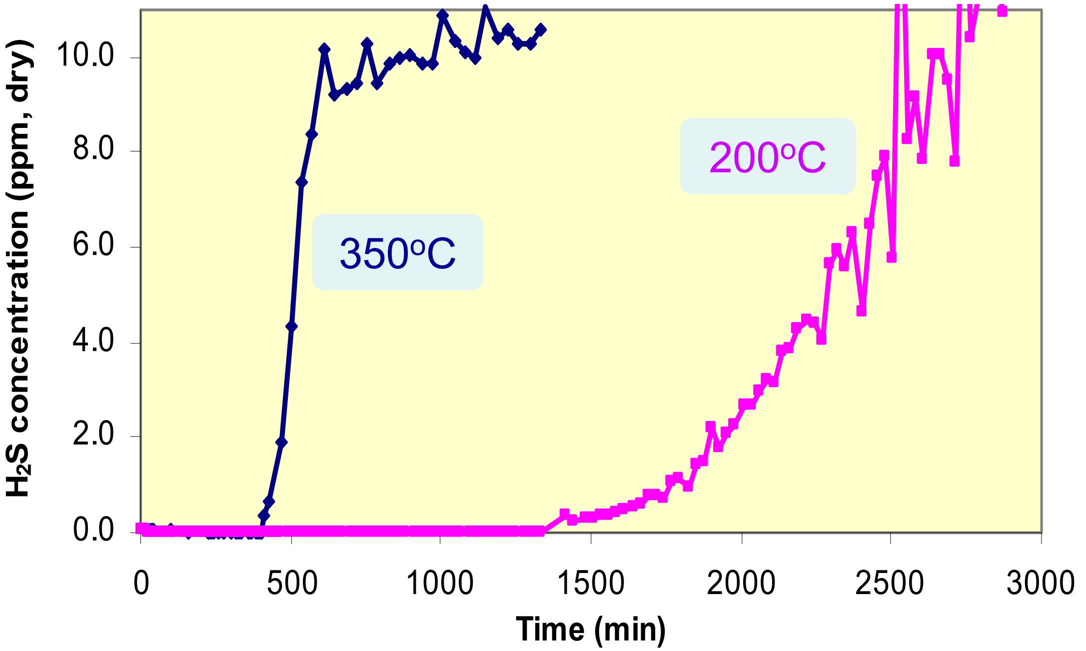
# Cu+A and Cu+B were able to reduce the $H_2S$ concentration to less than 200 ppb



Test conditions: T = 350°C, GHSV = 2000 $h^{-1}$, sorbent volume is 2 ml.

Inlet gas composition: 40 ppm $H_2S$, 19% $H_2$, 20% $H_2O$, 4% CO, 4.1% $CO_2$, 0.4% $CH_4$, balance $N_2$

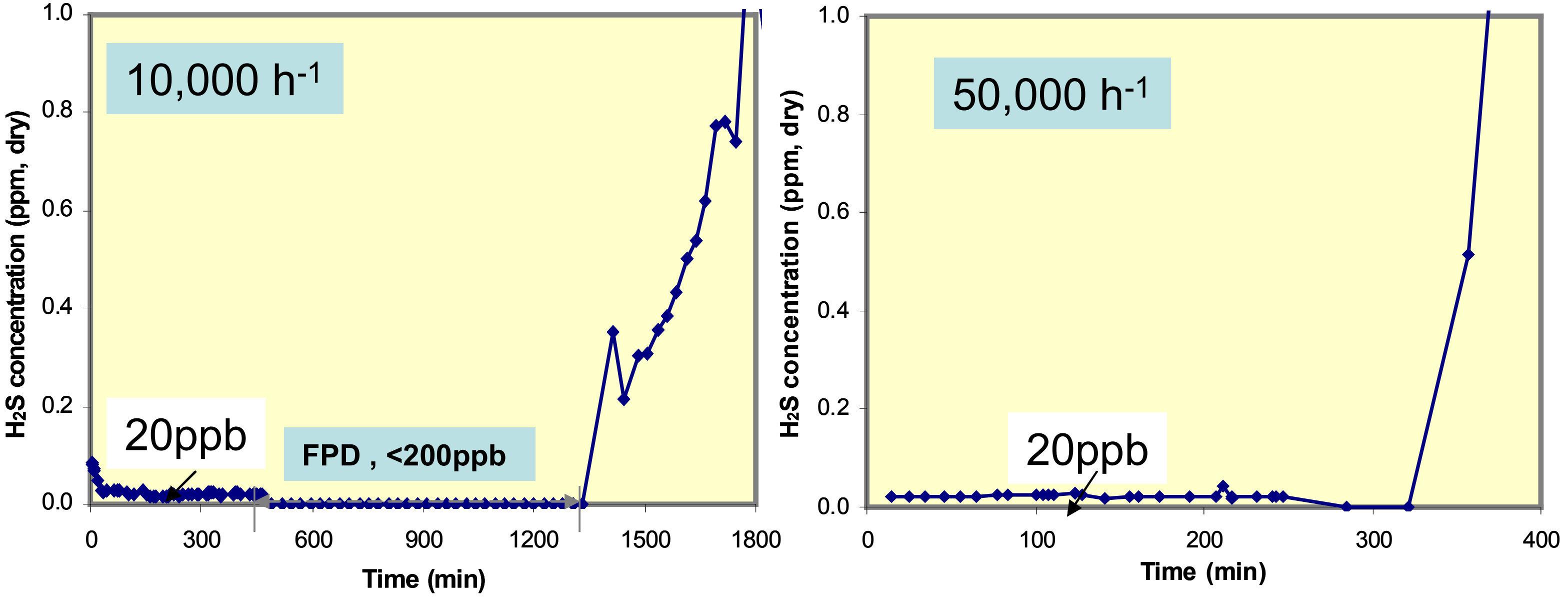
# *Longer breakthrough time observed at lower temperature for $Cu+C/Al_2O_3$*



Test conditions: GHSV = 10,000 $h^{-1}$, sorbent volume is 1 ml, diluted to 2 ml with $Al_2O_3$.

Inlet gas composition: 10 ppm $H_2S$, 29% $H_2$, 20% $H_2O$, 6% CO, 6.1% $CO_2$, 0.2% $CH_4$, balance $N_2$

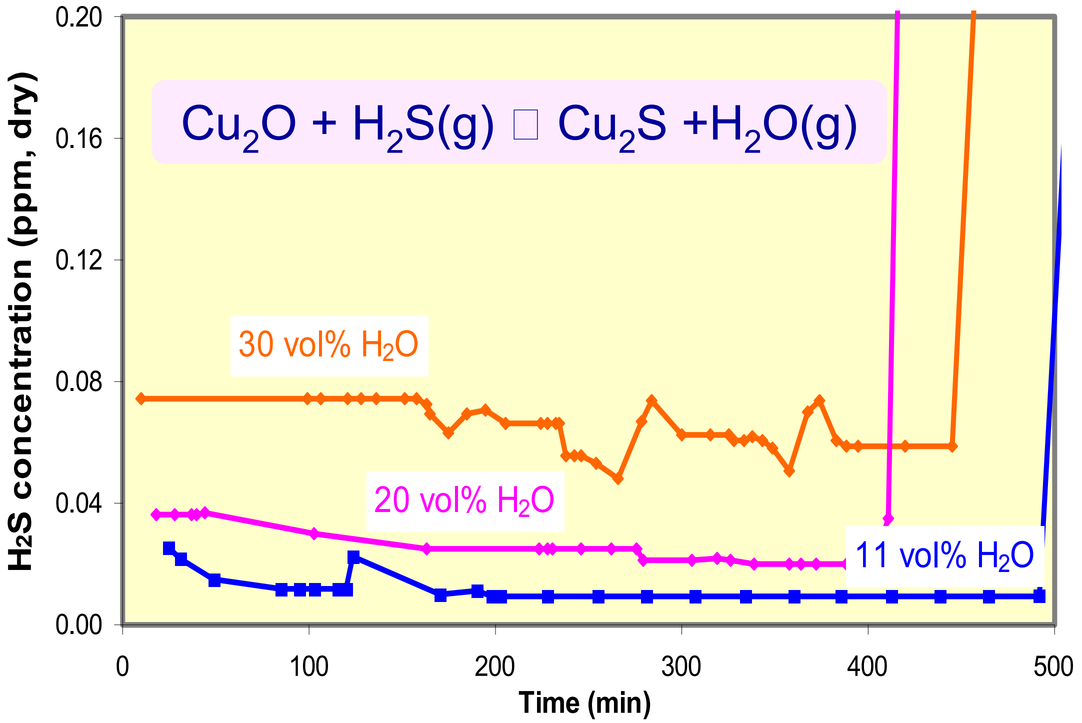
# *Shorter breakthrough time with increasing flowrate for Cu+C/$Al_2O_3$*



Test conditions: T = 200°C, sorbent volume varied, diluted to 2 mL with $Al_2O_3$.

Inlet gas composition: 10 ppm $H_2S$, 29% $H_2$, 20% $H_2O$, 6% CO, 6.1% $CO_2$, 0.2% $CH_4$, balance $N_2$

# *Higher water content yields higher $H_2S$ concentrations for $Cu+C/Al_2O_3$*



Test conditions: T = 350°C, GHSV = 10,000 $h^{-1}$, sorbent volume is 1 ml, diluted to 2 ml with $Al_2O_3$

Inlet gas composition: 10 ppm $H_2S$, 29% $H_2$, varied $H_2O$, 6% CO, 6.1% $CO_2$, 0.2% $CH_4$, balance $N_2$

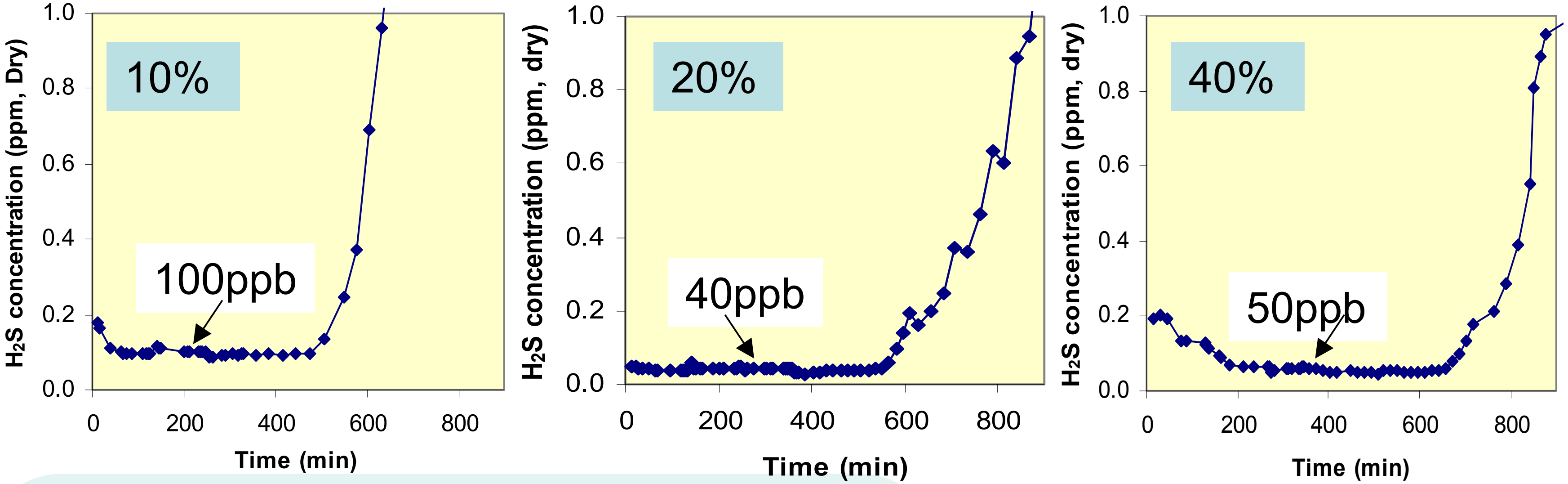
# *Copper utilization ranged from 32.8 to 57.9% for Cu oxides tested*

| Sorbent formulation | Surface area ($m^2/g$) | Sulfur uptake (%, based on Cu content)[a] |
|---|---|---|
| $Cu+A/Al_2O_3$ | 197.9 | 37.3 |
| $Cu+B/Al_2O_3$ | 199.5 | 57.9 |
| $Cu+C/Al_2O_3$ | 211.3 | 53.9 |
| $Cu+D/Al_2O_3$ | 201.5 | 44.0 |
| $Cu+E/Al_2O_3$ | 202.3 | 32.8 |
| $Cu/Al_2O_3$ | 258.8 | 36.3 |

[a] Calculated based on $H_2S$ uptake until breakthrough occurs (1 ppm $H_2S$).

Test conditions: T = 350°C, GHSV = 2000 $h^{-1}$, sorbent volume is 2 ml.
Inlet gas composition: 40 ppm $H_2S$, 19% $H_2$, 20% $H_2O$, 4% CO, 4.1% $CO_2$, 0.4% $CH_4$, balance $N_2$

# *Varied loading of Cu+C on $Al_2O_3$ affected both $H_2S$ removal efficiency and capacity*

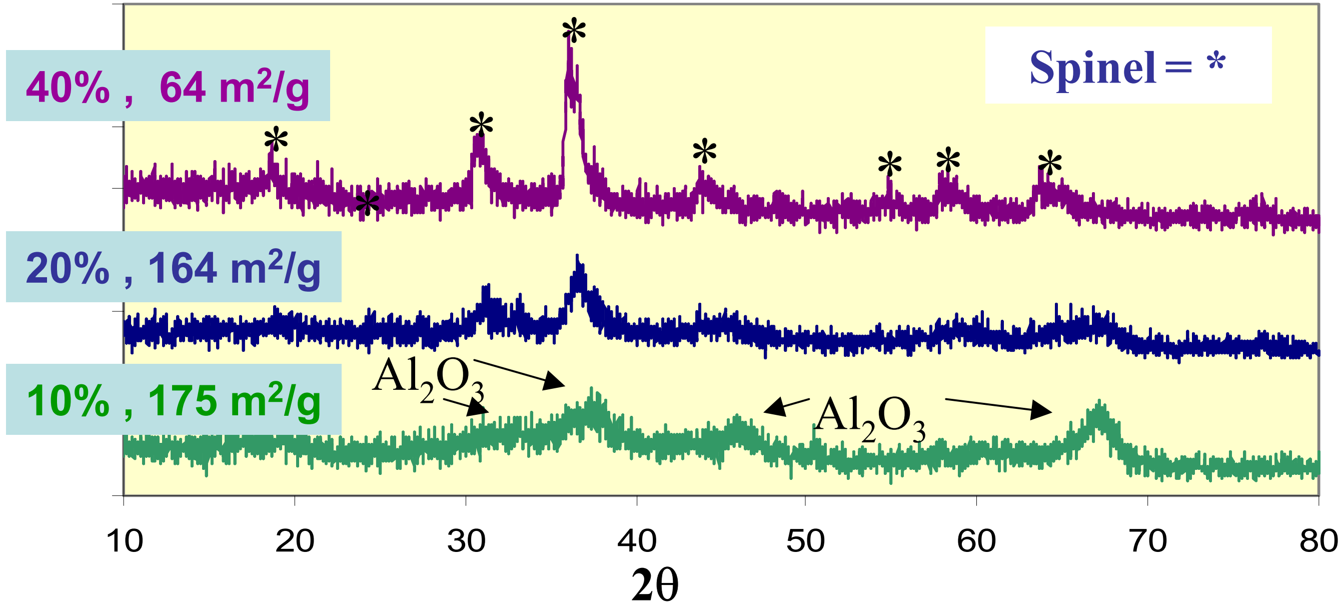


- Breakthrough time increased as the Cu loading was increased.
- The breakthrough time increased by ~200 minutes when the loading was increased from 10 to 20%.
- Only a slight increase in breakthrough time was observed when the loading was increased from 20 to 40%.
- An optimal loading (20%) gives best efficiency

Test conditions: T = 350°C, GHSV = 15,600 $h^{-1}$, sorbent volume is 1 ml, diluted to 2 ml with $Al_2O_3$

Inlet gas composition: 11 ppm $H_2S$, 31% $H_2$, 20% $H_2O$, 7% CO, 8% $CO_2$, 0.1% $CH_4$, balance $N_2$

# *XRD shows loss of surface at high Cu+C loading on $Al_2O_3$*



- Surface area decreases as the loading is increased. The surface area decreased by ~60% when the loading was increased from 20 to 40%.
- Spinel formation at higher loadings may make the material less active which leads to a higher $H_2S$ concentration.

# Summary

- A Cu-based mixed oxide has been identified that can reduce the concentration of $H_2S$ in a synthetic reformate from 10 ppm to <50 ppb at 200-350°C.
- Initial rate studies show that <20 ppb $H_2S$ can be achieved at a GHSV of 50,000 $h^{-1}$ at 200°C.
- Based on sulfur uptake and Cu loading, more than 50% of the Cu was utilized.

# *Technical Challenges/Issues*

- Processing rates (GHSV) are still low.
  - 10,000-50,000 $h^{-1}$ for powders
  - DOE target is 50,000 $h^{-1}$ for supported material
- Long-term stability of Cu-based adsorbents under fuel processing conditions has not been determined.
  - Cu sintering at high temperatures may be problemetic
  - effect of air exposure needs to be explored
  - stability of the Cu-sulfur complexes during startup needs to be addressed

# *FY 2003 milestone*

| Milestone | Date |
|---|---|
| Demonstrate a sulfur "getter“ capable of reducing the $H_2S$ concentration in a synthetic reformate to <50 ppb. (DOE FY2005 target for on-board reforming). | 06/03 |

*Showed that a Cu oxide-based composition reduced $H_2S$ concentration from 10 ppm in reformate to <50 ppb.*

# *Future work*

- Optimize the composition and materials processing to achieve DOE targets for extent of sulfur removal, GHSV, and durability.
- Determine the stability of Cu-containing mixed oxides/sulfides during startup and air exposure at reaction temperatures.
- Determine the optimal structured form (monolith or foam).
- Long-term testing operating on reformate produced from a sulfur-containing fuel.
- Conduct characterization studies to improve the performance and address stability issues.
- Establish industrial collaboration. Several companies have requested samples for testing.