

## HIGH TEMPERATURE DESULFURIZATION OF SYNTHESIS GAS WITH IRON COMPOUNDS

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### INTRODUCTION

Generally, coal conversion and sulfur removal are performed in separate processing units. A combination of these two key steps within a single reaction vessel may lead to a more efficient overall process. As part of our efforts to explore this concept, the feasibility of adding iron compounds with the coal feed was examined as a means to capture sulfur in-situ during the partial oxidation of coal in a Texaco gasifier operating in the slagging mode. Iron-based compounds have been previously used as sorbents for sulfur removal but most studies have been done at lower temperatures in external desulfurization beds or with fluidized bed coal gasifiers. Relatively little work has been done to study high temperature desulfurization in conjunction with an entrained flow gasifier.

To rapidly screen iron oxide as a potential sorbent for sulfur capture, we performed theoretical studies and bench-scale testing to study the behavior of coal ash/sorbent systems under slagging gasifier conditions. Our theoretical studies included literature searches, thermodynamic equilibrium calculations, and predictions of ash/sorbent interactions utilizing published phase diagrams. Bench scale tests primarily consisted of mixing the sorbent with coal ash and exposing the mixture to synthetic Texaco coal gasification syngas mixtures at various temperatures to determine sulfur pick up and coal ash-sorbent-sulfur phase equilibria.

### METHODS

Calculations Equilibrium calculations were performed for the iron sulfide/oxide interchange reaction under Texaco coal gasification conditions using either oxygen or air as the oxidant feed. Tables 1 and 2 respectively list the syngas compositions for oxygen and air gasification of Pittsburgh #8 coal at two slag (ash + additive) levels. The compositions shown under the heading "Less Reducing" are typical of normal operating conditions. The "More Reducing" conditions may be more difficult to achieve in practice because of possible slag flow problems at the lower operating temperatures. The corresponding partial pressures of oxygen and sulfur were computed using SOLGASMIX<sup>1</sup>. These computations were performed by keeping the moles of oxygen, carbon, hydrogen, nitrogen and sulfur constant for each case to study the effects of temperature independently.

Experiments To validate these equilibrium predictions, bench scale drop tube furnace equilibrium experiments were performed for selected coal ash-additive systems. The apparatus and experimental procedures have been previously described in our related work<sup>2</sup> evaluating calcium compounds as potential in-situ sulfur capture agents. Coal ash samples mixed with the sorbent are suspended in a crucible exposed to a continuous flow of CO/CO<sub>2</sub>/Ar/SO<sub>2</sub> gas mixtures that match the computed oxygen and sulfur partial pressures

in Texaco coal gasifiers. After equilibration over at least 18 hours, the slag sample was rapidly quenched by dropping the filled crucible into a pool of water or cool syngas. The quenched slag sample was then recovered and characterized by optical microscopic examination as well as electron microprobe EDX analysis of representative grains to measure phase compositions.

## RESULTS

The results of the equilibrium calculations for the iron sulfide/oxide interchange reactions with our various syngas compositions are listed in Table 3. Three major trends were observed. The ratio of iron sulfide to oxide activities increases at lower temperatures and/or more reducing conditions. Also, if one compares the ratio of iron sulfide to oxide activities at the same temperature, one observes that this ratio is higher for the oxygen gasification cases relative to the corresponding air gasification case. This suggests that oxygen gasification appears to be more favorable than air gasification for in-situ sulfur capture with iron as sorbent. Hence, the most favorable case for the iron sulfide/oxide interchange reaction involves oxygen gasification at the lowest temperature and the most reducing condition.

SOLGASMIX was also used to estimate the maximum theoretical level of sulfur capture in the iron oxysulfide phase assuming two different levels of sulfur in the coal: 2.14 wt%, and 4.0 wt%. These calculations assume no loss of iron to the silicate phase and hence represent maximum availability of iron for sulfur capture. The results shown in Figure 1 indicate that a higher percentage sulfur reduction can be achieved as the sulfur content of the coal increases.

In addition to the above equilibrium calculations, published literature data<sup>3-7</sup> were used to predict the partitioning of iron among the metal, oxide and oxysulfide phases. The estimated results at 2200 F are listed in Table 4. The Fe/S atomic ratio increases from 1.33 for the "More Reducing, 12% slag" case to 1.43 for the "Less Reducing, 20% slag" case. Again, these calculations indicate that iron utilization for sulfur capture is more efficient under more reducing conditions. However, the predicted amount of metallic iron is also higher at the more reducing conditions. In addition, the activity of iron oxide in the oxysulfide phase is lower for the more reducing case. Hence, it is expected that the amount of iron that can possibly associate with the silicate phase will be lower for the more reducing case since only iron oxide interacts significantly with the silicate phases.

Based on these calculations, in-situ sulfur capture due to the possible formation of a separate oxysulfide phase appears promising but experimental confirmation is needed. To check these calculations, atmospheric bench scale drop tube equilibrium tests were conducted using coal ash and iron oxide sorbents exposed to simulated syngas that match the computed oxygen and sulfur partial pressures. The results from several bench scale equilibrium tests indicate that when iron oxide was added to Pittsburgh #8 coal ash, a separate major oxysulfide phase formed in addition to the silicate phase. Typical EDX analysis for these two phases from a bench scale test are shown in Table 5. The effect of temperature on the atomic ratio of iron to sulfur in the oxysulfide phase for FeO/Pittsburgh #8 slag mixtures is shown in Figure 2. The Fe/S atomic ratio in the oxysulfide phase decreases from about 1.7 at 2500 F to about 1.15 at 1800 F.

## CONCLUSIONS

The feasibility of adding iron-based compounds as potential sulfur capturing sorbents during coal gasification was examined using theoretical equilibrium calculations as well as

bench scale equilibrium droptube furnace experiments. It is predicted that iron based compounds introduced with the coal-water slurry feed can be effective agents for in-situ desulfurization under simulated syngas conditions commonly encountered in Texaco coal gasifiers operating in a slagging mode. Sulfur capture is enhanced by operating at more reducing conditions, lower temperatures and using oxygen as oxidant. Bench scale drop tube furnace tests indicate that sulfur capture is significantly increased when iron compounds were added to coal ash due to the formation of a new (major) oxysulfide phase in addition to the silicate phase. Experimental data support the predicted trend of increasing sulfur capture with decreasing temperature.

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**TABLE 1:** Syngas composition for Texaco gasification of coal with oxygen oxidant

Case Number	More Reducing		Less Reducing	
	I	II	III	IV
wt% slag (ash+additive)	12	20	12	20
Syngas Composition, vol%				
CO	43.44	41.66	39.09	36.52
H <sub>2</sub>	32.91	32.04	30.12	28.94
CO <sub>2</sub>	9.32	10.35	12.20	13.53
H <sub>2</sub> O	13.11	14.76	17.46	19.91
CH <sub>4</sub>	0.03	0.03	0.02	0.02
Ar	0.06	0.06	0.06	0.06
N <sub>2</sub>	0.45	0.44	0.42	0.41
H <sub>2</sub> S	0.64	0.62	0.60	0.58
COS	0.04	0.04	0.03	0.03

**TABLE 2:** Syngas composition for Texaco gasification of coal with air oxidant

Case Number	More Reducing		Less Reducing	
	I	II	III	IV
wt% slag (ash+additive)	12	20	12	20
Syngas Composition, vol%				
CO	20.14	19.53	15.25	13.89
H <sub>2</sub>	14.58	14.73	10.79	10.14
CO <sub>2</sub>	6.09	6.38	8.28	8.85
H <sub>2</sub> O	8.18	8.93	10.87	12.00
CH <sub>4</sub>	0.05	0.05	0.02	0.02
Ar	0.61	0.60	0.65	0.66
N <sub>2</sub>	50.06	49.50	53.80	54.11
H <sub>2</sub> S	0.27	0.26	0.32	0.31
COS	0.02	0.02	0.02	0.02

**TABLE 3:** Computed equilibrium ratio of activities of iron sulfide to iron oxide ( $a_{\text{FeS}}/a_{\text{FeO}}$ ) for the iron oxide/sulfide reaction  $\text{FeO} + \frac{1}{2}\text{S}_2 = \text{FeS} + \frac{1}{2}\text{S}_2$ 

Case Number	I		II		III		IV	
	Oxygen	Air	Oxygen	Air	Oxygen	Air	Oxygen	Air
Temp., °F								
1800	10.70	8.23	9.48	7.64	7.69	5.15	6.20	4.48
2200	5.09	3.93	4.49	3.66	3.66	2.51	2.96	2.20
2500	3.23	2.59	2.86	2.41	2.33	1.65	1.88	1.45

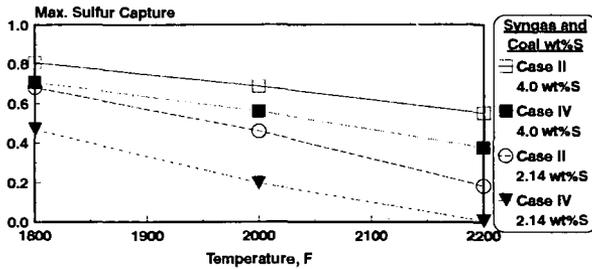
**TABLE 4:** Predicted equilibrium partitioning of iron among oxysulfide and metal phases at 2200°F based on literature data

Case Number	I	II	III	IV
log <sub>10</sub> {Partial pressures}				
S <sub>2</sub>	-4.59	-4.60	-4.57	-4.52
O <sub>2</sub>	-12.40	-12.30	-12.10	-11.90
Elemental, wt%				
Fe	67.70	67.70	67.70	67.70
S	29.00	28.30	27.70	27.00
O	3.30	4.00	4.60	5.30
Fe/S wt ratio	2.33	2.39	2.44	2.51
Fe/S atom ratio	1.33	1.37	1.40	1.43
lbmole/100 lb mix				
FeS	0.91	0.88	0.87	0.84
FeO	0.21	0.25	0.29	0.33
Fe	0.10	0.07	0.05	0.04
$a_{\text{FeO}}$	0.19	0.21	0.24	0.26

**TABLE 5:** Selected EDX analysis results from bench scale testing

Particles	EDX Microanalysis				Calculated Ratios	
	Fe	S	Na	Si	(Fe/S) <sub>Atom</sub>	(Fe/Si) <sub>wt</sub>
Oxysulfide phase	67.53	25.59	2.15		1.51	
	69.68	24.28	2.06		1.64	
	69.67	24.10	2.02		1.65	
	67.86	25.95	2.02		1.49	
Silicate phase	50.28	1.48	1.48	25.64		1.96
	43.63	1.42	1.42	34.62		1.26
	49.63	1.55	1.47	30.34		1.64
	50.98	1.52	1.38	28.65		1.78
	46.57	1.31	1.40	33.40		1.39

**Figure 1:** Estimated maximum theoretical sulfur capture as a function of temperature, syngas composition and wt% sulfur in coal



**Figure 2:** Effect of temperature on oxysulfide phase composition for FeO sorbent and Pittsburgh #8 coal ash slag mixtures

