

**EVALUATION OF CALCIUM COMPOUNDS AS SORBENTS FOR IN-SITU  
DESULFURIZATION WITH TEXACO COAL GASIFICATION PROCESS**

Mitri S. Najjar and Dick Y. Jung

Texaco Inc.  
P. O. Box 509  
Beacon, NY 12508

Keywords: in-situ desulfurization; coal gasification; calcium

**SUMMARY**

The feasibility of using calcium-based compounds as potential sulfur-capturing sorbents for in-situ desulfurization in combination with partial oxidation of coal in a slagging mode was examined using thermodynamic calculations and bench-scale experimental tests. Although pure calcium compounds are excellent sorbents for capturing sulfur, problems may be encountered when other compounds which are commonly found in coal slags are present. Under the simulated reaction conditions used in Texaco coal gasifiers, calcium compounds were found to preferentially react with the silicates commonly found in coal slags rather than capture sulfur.

**INTRODUCTION**

To utilize coal in an environmentally safe manner, it is necessary to remove the gas phase sulfur compounds released during the combustion and/or gasification of coal. In recent years, integrated gasification-combined cycle (IGCC) processes have been demonstrated which gasify coal to produce synthesis gas (syngas) which is fired in a turbine to generate electrical power. Typically, these processes separate the reaction step (where coal is converted to raw syngas under reducing conditions at high temperatures) from the acid gas removal step (where physical solvents are generally used to scrub hydrogen sulfide and carbonyl sulfide from the crude syngas). This approach requires significant capital investments as well as operating utility costs since the hot syngas must be cooled to the low temperatures commonly needed for physical solvents and subsequent reheated prior to its introduction into the gas turbine.

A potentially more efficient alternative is to combine coal combustion with the sulfur removal step in the same vessel. However, the solubility of sulfur in coal slags is quite low (typically between 0.01 and 0.5 weight percent). One possible approach to enhance sulfur solubility in coal slags is the addition of sulfur-capturing sorbents along with the coal feed to the gasifier. The ideal sorbent should be an inexpensive additive that chemically reacts with the sulfur compounds in the gas (primarily hydrogen sulfide with smaller amounts of carbonyl sulfide) to form a disposable sulfide that is encapsulated in the resultant slag but this additive should not cause any complications for slag flow from the gasifier.

Although calcium-based compounds have been commercially used in fluidized bed combustion to perform in-situ desulfurization,

only bench scale work has been reported using these potential sorbents to study high temperature desulfurization in conjunction with an entrained bed coal gasifier. It was hoped that the sulfur from the gas phase would be captured in the slag as calcium sulfide under the reducing atmosphere commonly found in these coal gasifiers. Whitney, et al.<sup>1</sup> have suggested that the use of concentrated coal-water slurries mixed with finely divided lime (CaO) or limestone (CaCO<sub>3</sub>) represents a promising avenue for coal conversion with simultaneous sulfur capture but they reported evidence of mass transfer limitations. Freund and Lyon<sup>2</sup> performed thermodynamic calculations that indicate a range of attainable conditions where high levels of sulfur capture could be achieved for fuel-rich combustion of coals containing calcium-based sorbents. However, they also point out that even though the thermodynamics of sulfur sorption may be favorable, there are no assurances that the kinetics will be fast enough for practical use. In addition, neither group of researchers consider the interactions among calcium compounds and other components in the coal slag (such as aluminosilicates) or the effect of these additives on slag removal from the gasifier. To explore the possibility of using calcium-based compounds to capture sulfur in the more reducing atmosphere typically found in Texaco coal gasifiers with coal-water slurry feeds operating in a slagging mode, theoretical thermodynamic calculations as well as bench scale drop tube furnace equilibrium experimental runs were performed.

## METHODS

### Calculations

Thermodynamic equilibrium calculations were performed using a multiphase free energy minimization computer program by an in-house version of SOLGASMIX<sup>3</sup> augmented with additional thermodynamic data<sup>4</sup>. The systems considered in this study include calcium compounds alone as well as with inorganic species (e. g. silicon-, iron- and aluminum-based compounds) commonly found in coal slags under simulated syngas compositions expected in Texaco coal gasifiers with coal-water slurry feeds operating in a slagging mode.

### Experiments

To validate these equilibrium predictions, bench scale drop tube furnace equilibrium experiments were performed for selected coal slag-additive systems. These tests were conducted at atmospheric pressure using temperatures and gas compositions selected to simulate gasifier conditions using the apparatus shown schematically in Figure 1. The principal units for high temperature testing are two identical LeMont Scientific quench furnaces capable of reaching 3000°F. Samples of the slag and sorbent (50-100 mg) were placed in a crucible that is suspended in the furnace by a thin platinum wire which is then equilibrated by exposure to a flowing gas mixture for at least 18 hours. Gaseous mixtures of CO, CO<sub>2</sub> and 1 vol %SO<sub>2</sub> in Argon were selected to simulate the S<sub>2</sub> and O<sub>2</sub> partial pressures at the desired temperatures and ambient pressure based on the thermodynamic equilibrium calculations using an in-house version of SOLGASMIX<sup>3</sup>. The suspended slag-sorbent sample was then rapidly quenched by dropping the crucible into a pool of water or simulated syngas. This was

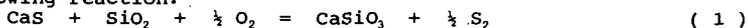
accomplished by passing an electrical current through the suspending platinum wire which causes the wire to break.

The quenched sample was recovered and characterized by petrographic examination using a Leitz Orthoplan microscope and electron microprobe analysis. An Amray 1645 scanning electron microscope equipped with secondary and backscattered electron detectors for imaging as well as a Tracor Northern TN-5500 energy dispersive X-ray microanalysis system with 40 MByte data storage capacity and color display were used to obtain SEM photomicrographs to show phase morphologies as well as EDX multielement semiquant chemical analysis to confirm phase identifications.

## RESULTS

Equilibrium calculations based on the calcium oxide/calcium sulfide system with simulated syngas from a Texaco coal gasifier initially looked quite promising for sulfur capture. Phase diagrams indicate that calcium sulfide (in the absence of other coal slag compounds) is stable over the temperature range as well as oxygen and sulfur partial pressures commonly expected in Texaco coal gasifiers. The calculations suggest that in-situ sulfur capture with calcium (when there is no interactions with the coal slag) is favored by lower temperatures and/or more reducing conditions.

However, when other compounds from the coal slag are incorporated into these calculations, the situation is now altered. For example, if silica ( $\text{SiO}_2$ ) is added to this calcium oxide/sulfide system, new phases must now be taken into account which form via chemical reactions. Consider  $\text{CaSiO}_3$  which is formed by the following reaction:



Note CaS is now stable only below the CaS-SiO<sub>2</sub>-CaSiO<sub>3</sub> region shown in Figure 2. The now smaller CaS stability region would translate into a reduced sulfur capture for this system in comparison to the system without silica added. Note that a much lower oxygen partial pressure is now needed for a stable CaS phase which may not be possible for a Texaco coal gasifier with a coal-water slurry feed operating in a slagging mode. If one now further considers the addition of iron and aluminum compounds (which are commonly found in most coal slags) to this system, the situation becomes even more complex with a plethora of new phases that must now be considered. A sample calculation result is shown in Table 1 which indicates that with even a relatively high calcium additive loading, most of the calcium is predicted to appear in various aluminosilicate compounds rather than the desired CaS under oxygen and sulfur partial pressures expected in Texaco coal gasifiers. Hence, calcium would be a less effective sorbent for sulfur capture under these conditions.

To qualitatively confirm these predictions, bench scale equilibrium drop tube furnace runs were performed using simulated oxygen and sulfur partial pressures selected to match those expected in Texaco coal gasifiers. The EDX semiquant chemical analyses for several silicate phase grains from these experimental runs are listed in Table 2. Note that the sulfur content for these silicate particles is relatively low even though the calcium and silicon content were relatively high. No calcium sulfide grains were identified. Hence, these experimental data support the

prediction that under the simulated syngas conditions for a Texaco coal gasifier with a coal-water slurry feed operating in a slagging mode, calcium compounds preferentially react with the silicate compounds in the coal slag rather than the sulfur compounds in the gas phase.

#### CONCLUSIONS

The feasibility of adding calcium-based compounds as potential sulfur capturing sorbents during coal gasification is being examined using theoretical equilibrium calculations as well as bench scale equilibrium drop tube furnace experiments. Although it is predicted that calcium-based compounds can be effective agents for desulfurization when used alone under simulated syngas conditions commonly encountered in Texaco coal gasifiers with a coal-water slurry feed operating in a slagging mode, thermodynamic calculations suggest calcium compounds can preferentially interact with other common coal slag components, especially the silicates, which limit their usefulness as in-situ sulfur sorbents during coal gasification. EDX semiquant chemical analyses for silicate phase grains obtained from experimental bench scale equilibrium drop tube furnace runs are presented which are consistent with these predictions.

#### ACKNOWLEDGEMENTS

The authors gratefully acknowledge financial support for this work under the five year Texaco/Department of Energy Cooperative Program (Contract No. DE-FC21-87MC23277) on "Integration and Testing of Hot Desulfurization and Entrained Flow Gasification for Power Generation Systems" with METC's Dr. J. Beeson as Contract Manager. Uygur Kokturk assisted in designing and troubleshooting the bench scale drop tube furnace units. Ron McKeon performed most of the experimental runs while Tris Laurion provided EDX analyses of the slag samples.

#### REFERENCES

1. G. M. Whitney, Z. Yunming, M. M. Denn and E. E. Petersen, "Sulfur Capture during Partial Coal Combustion", Chem. Engineering Comm., **55** (1987) 83-93.
2. H. Freund and R. K. Lyon, "The Sulfur Retention of Calcium-Containing Coal during Fuel-Rich Combustion", Combustion and Flame, **45** (1982) 191-203.
3. G. Eriksson, Acta Chem. Scand., **25** (1971) 2651.
4. R. A. Robie, B. S. Hemingway and J. R. Fisher, "Thermodynamic Properties of Minerals and Related Substances at 298.15 K and 1 Bar ( $10^5$  Pascals) Pressure and at Higher Temperatures", U. S. Geological Survey Bulletin 1452, U. S. Government Printing Office, Washington (1979).
5. J. W. Larimer, "An experimental investigation of oldhamite, CaS; and the petrologic significance of oldhamite in meteorites", Geochimica et Cosmochimica Acta, **32** (1968) 965-82.

**TABLE 1**

Calculated equilibrium compositions at 1600 K (2420 F) and 38 atm. to check for stable phases in a system with coal slag and calcium additive under simulated Texaco coal gasifier syngas conditions

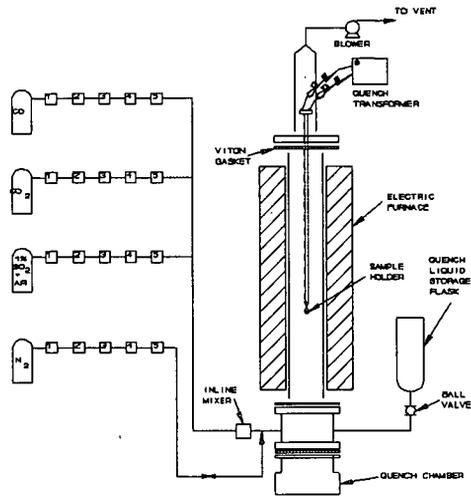
<u>GAS PHASE COMPOSITION</u>			
<u>Gases</u>	<u>Mole Fraction</u>	<u>Mole</u>	<u>Partial Pressure (atm)</u>
CO	0.410	0.687	15.6
CO <sub>2</sub>	0.0987	0.165	3.75
H <sub>2</sub>	0.278	0.466	10.6
H <sub>2</sub> O	0.199	0.334	7.58
COS	1.38E-04	2.32E-04	5.26E-03
H <sub>2</sub> S	2.79E-03	4.67E-03	0.106
O <sub>2</sub>	5.98E-13	1.00E-12	2.27E-11
N <sub>2</sub>	0.0102	0.0170	0.386
SO <sub>2</sub>	2.52E-07	4.21E-07	9.56E-06

<u>EQUILIBRIUM SOLID PHASES</u>					
<u>Solid</u>	<u>Mole</u>	<u>Solid</u>	<u>Mole</u>	<u>Solid</u>	<u>Mole</u>
FeO	0.00400	CaS	0.00270	Ca <sub>3</sub> Al <sub>2</sub> Si <sub>3</sub> O <sub>12</sub>	0.0
FeS	0.0	CaSiO <sub>3</sub>	0.0	Fe <sub>2</sub> SiO <sub>4</sub>	0.0
Fe	0.0	Ca <sub>2</sub> Al <sub>2</sub> SiO <sub>7</sub>	0.00180	Al <sub>2</sub> SiO <sub>5</sub>	0.0
CaO	0.0161	Ca <sub>2</sub> SiO <sub>4</sub>	0.00490	CaAl <sub>2</sub> Si <sub>2</sub> O <sub>8</sub>	0.0
SiO <sub>2</sub>	0.0	Al <sub>2</sub> O <sub>3</sub>	0.0	Ca <sub>2</sub> Fe <sub>2</sub> O <sub>5</sub>	0.0

**TABLE 2**

EDX chemical analysis for particles from bench scale drop tube furnace runs at 2200°F with calcium added to Pittsburgh #8 slag

<u>Grain</u>	<u>Na</u>	<u>Al</u>	<u>Si</u>	<u>S</u>	<u>Ca</u>	<u>Fe</u>
1	1.40	21.02	43.97	0.32	19.23	11.91
2	3.14	12.87	54.01	0.34	12.13	14.50
3	3.23	13.34	53.39	0.25	12.84	13.50
4			40.93		58.87	
5	0.64	12.15	34.86		43.80	4.28



1. FRONT PRESSURE REGULATOR
2. SHUT-OFF VALVE
3. ROTAMETER
4. FILTER
5. MASS FLOW CONTROLLER

FIGURE 1 Schematic for Equilibrium Furnace

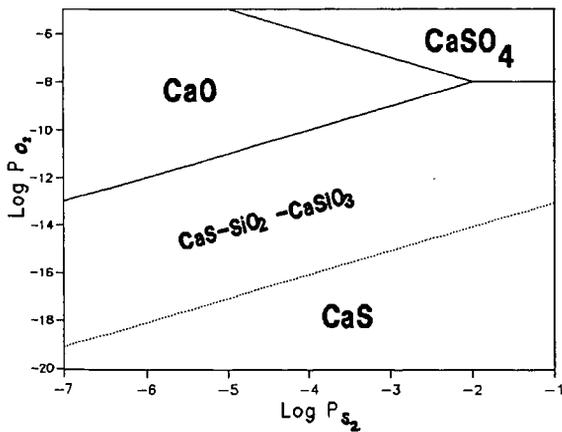


FIGURE 2 Silicate-sulfide-oxide equilibrium for Calcium at 2200°F