

**BENCH-SCALE TEST RESULTS AND CALCULATION PROCEDURE FOR
IN-SITU SULFUR CAPTURE VIA SORBENT ADDITION TO
COAL SLAGS UNDER PARTIAL OXIDATION CONDITIONS**

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SUMMARY

The addition of sorbents with the coal feed is being examined as a means to capture sulfur in-situ during the partial oxidation of coal in a Texaco gasifier operated in the slagging mode. To rapidly screen candidate sorbents for sulfur capture prior to their being tested in an experimental bench scale unit, a calculation scheme based on an extended use of the concept of optical basicity is being tested for estimating the solubility of sulfur in a given coal slag with and without added potential sorbents. This calculation method identified iron, calcium and sodium based compounds as well as combinations of these additives as potentially good sulfur-capturing sorbents for a coal slag. Experimental EDX data from bench-scale drop tube furnace runs with coal slag using these additive packages under simulated Texaco coal gasifier syngas conditions are presented which verify the predicted higher sulfur solubility in the resultant slag-additive mixtures.

INTRODUCTION

One of the most promising approaches for utilizing coal in an environmentally safe manner that has been recently demonstrated is the generation of electric power via partial oxidation of coal in an integrated gasification-combined cycle (IGCC) plant. To minimize emission of sulfur compounds, these processes typically 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). Currently, this approach requires cooling of the hot syngas to the low temperatures commonly needed for physical solvents and subsequent reheating of this cleaned syngas prior to its introduction into the gas turbine. Consequently, these heating and cooling cycles require significant capital investments as well as operating costs.

A potentially more efficient alternative is to combine coal combustion with the sulfur removal step in the same vessel. However, the total solubility of sulfur in coal slags is typically quite low (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 would be an inexpensive additive that chemically reacts with the gas phase sulfur compounds (primarily hydrogen sulfide with smaller amounts of carbonyl sulfide) to form sulfide(s) that are encapsulated in a disposable slag-additive mixture but the addition

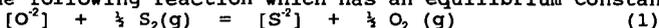
of this additive should not cause any complications for slag flow from the gasifier.

To rapidly screen candidate sorbents, a method to estimate the amount of sulfur captured by the mixture of coal slag with these potential additives would be quite useful to reduce the number of required experimental tests. Consequently, we have been exploring the use of an extended concept of optical basicity to estimate the sulfide capacity for mixtures of coal slag with various additives. This proposed calculation scheme estimates the sulfide capacity at a given temperature based solely on the elemental composition of the slag-additive mixture. With an estimate of the sulfur and oxygen partial pressures as well as the weight percentage of sulfur in the coal, the sulfur content in the slag mixture can then be approximated.

METHODS

Calculations

Slag basicity may be defined as being directly proportional to its free oxygen ion activity. Wagner¹ defined the basicity of a slag with respect to its "capacity" to absorb various constituents. For example, the main reaction that describes the sulfur-oxygen exchange behavior between slag and gas under reducing conditions is represented by the following reaction which has an equilibrium constant K_1 :



where the brackets indicate that ions are present in the slag. Since the oxygen ion activity as well as the sulfide activity coefficient are difficult to measure in ionic melts, Fincham and Richardson² expressed the potential of a silicate slag to absorb sulfur in terms of a measured quantity called the sulfide capacity (C_s) that is related to the oxygen and sulfur partial pressures in the gas phase by:

$$C_s = [\%S] (P_{O_2}/P_{S_2})^{1/2} \quad (2)$$

where $[\%S]$ represents the concentration of sulfur as sulfide (sulfur solubility) in the slag mixture while P_{O_2} and P_{S_2} represent the oxygen and sulfur partial pressures in the gas phase, respectively. Utilizing the equilibrium constant expression for the reaction in Equation (1) and solving for the sulfide capacity:

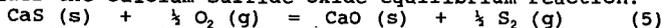
$$C_s = K_1 (a_{O_2}/Y_{S_2})^{1/2} = [\%S] (P_{O_2}/P_{S_2})^{1/2} \quad (3)$$

This equation ties the equilibrium constant and the sulfide capacity with the gas phase oxygen and sulfur partial pressures inside the gasifier. The sulfide capacity for a number of slag compositions has been measured³ by classical physicochemical methods. However, the available literature data on sulfide capacity for slags are insufficient to cover the entire range of compositions that are of interest for in-situ sulfur capture.

An alternative approach is to estimate the slag's sulfide capacity using the concept of "optical basicity". Optical basicity (denoted by Λ) refers to a measure of basicity determined by spectroscopic methods that has been shown to be predictable from Pauling's electronegativity of the individual elements in a slag. For a large number of slag compositions at 1500°C, the relationship⁴ between the optical basicity of a slag and its sulfide capacity is:

$$\log C_s = 12.6 \Lambda - 12.3 \quad (4)$$

To account for the effect of temperature on the equilibrium reaction, consider the calcium sulfide-oxide equilibrium reaction:



Based on this chemical equilibrium, a temperature-dependent correction

term (B) is introduced which gives the following temperature-corrected expression⁵ for the sulfide capacity:

$$\log C_s = \log C_s' + B \quad (6)$$

$$B = -4534 (1773 - T) / (1773 T) \quad (7)$$

where T is the temperature of interest in degrees Kelvin. The advantage of using optical basicity lies in the observation that it is simply extended to multicomponent systems by:

$$\Delta = N_A \Lambda_A + N_B \Lambda_B + \dots + N_Z \Lambda_Z \quad (8)$$

where N_i is the normalized "equivalent cation fraction" of the ith oxide in the solution based on the formula MO_x , i. e. the number of atoms of oxygen per metal in the oxide. Values of optical basicities^{3,4} for several oxides commonly found in coal slags are available in the literature. Hence, it is possible to estimate the optical basicity for a slag-sorbent mixture knowing just its chemical composition.

It should be noted that these correlations were empirically developed based primarily on experimental data for metallurgical slags and have not been tested for coal slag mixtures with sulfur sorbents. Consequently, equilibrium drop tube furnace experiments using coal slags with selected additives were performed to check if the potential sorbent systems identified by this proposed calculation procedure would indeed capture sulfur.

Experiments

Bench scale 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. Slag and sorbent samples (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, CO₂, and 1 vol %SO₂ in Argon were selected to simulate the S₂ and O₂ partial pressures at the desired temperatures and ambient pressure based on equilibrium calculations using a multiphase free energy minimization computer program, an in-house version of SOLGASMIX⁶. 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

Calculations based on this extended use of the concept of optical basicity identified additive systems based on iron, calcium, and sodium compounds along with combinations of these compounds as potential sulfur-capturing sorbent systems under oxygen and sulfur

partial pressures found in Texaco coal gasifiers. For these additive packages, the sulfur solubility in the resultant mixture for these slag-additive systems are estimated to be substantially increased. A summary of several calculation results for Pittsburgh No. 8 coal slag with and without several additive packages are listed in Table 1. Note the increase in the predicted sulfur solubility in the resultant slag-additive mixtures depends on the chemical composition of the additive package.

The effects of gas composition and temperature on equilibrium in-situ sulfur capture were considered. For constant temperatures, calculations predict that a more reducing gas atmosphere (i. e. lower oxygen partial pressure) increases the sulfur solubility in the slag-additive mixture. Also, for constant sorbent composition, the sulfur solubility in the slag-additive mixture increases as the temperature decreases. Hence, the most favorable Texaco coal gasifier conditions for in-situ sulfur capture by these sorbents are expected to be at lower temperatures with a highly reducing gas atmosphere. However, several practical considerations (e.g. coal conversion and slag viscosity) place limits on the achievable operating conditions in Texaco coal gasifiers.

In addition, the effect of sorbent composition was also examined. The calculations indicate that sodium is incrementally more effective than either iron or calcium as a sulfur sorbent. Among the additive mixtures considered, calculations indicate that the iron-sodium package is expected to be the most effective with possible synergistic effects between the two components while the iron-calcium package is expected to be marginally better than a physical mixture of the two components.

To validate these predictions, experimental bench scale data using coal slag equilibrated with several of these proposed sorbent packages under simulated Texaco coal gasifier syngas environments were performed. Experimental sulfur solubilities in the slag's silicate phase as measured by EDX are shown as a function of temperature for bench scale runs for Pittsburgh No. 8 slag with a sodium additive are shown in Fig. 2. These experimental results qualitatively confirm the predicted increase in sulfur solubility for these resultant slag-additive mixtures as a function of temperature under simulated syngas conditions for a Texaco coal gasifier operated in a slagging mode with a coal-water slurry feed. In addition, several sorbent mixtures were tested that qualitatively confirm the estimated greater incremental effect of sodium-based sorbents versus either iron- or calcium-based sorbents as well as the synergistic interactions for a combined iron-sodium sorbent package. Hence, the extended use of the concept of optical basicity shows promise as a means to identify additive packages which can enhance the sulfur solubility in coal slag-additive mixtures under simulated Texaco coal gasifier syngas conditions.

CONCLUSIONS

A proposed calculation scheme based on an extended use of the concept of optical basicity was found to qualitatively identify several possible sorbent packages that could potentially capture sulfur in-situ under simulated Texaco coal gasifier syngas conditions. Experimental bench scale data confirm that addition of several of these additive packages enhance sulfur solubility in the resultant coal slag-additive mixtures. Consequently, this proposed calculation

scheme shows promise as a rapid method to identify potential sorbent packages which can enhance in-situ sulfur capture by the slag.

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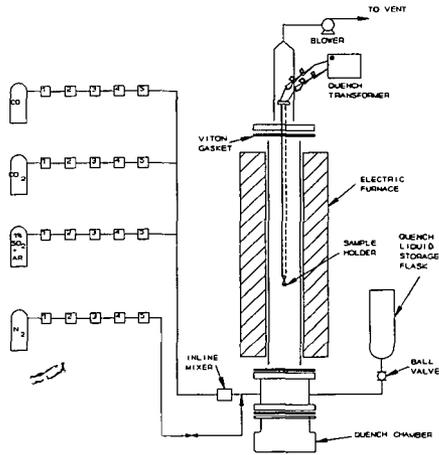
REFERENCES

1. C. Wagner, Met. Trans., **6B** (1975) 405-409.
2. C. J. B. Fincham and F. D. Richardson, "The behavior of sulfur in silicate and aluminate melts", Proc. Roy. Soc. London, **A223** (1954) 40-62.
3. J. A. Duffy and M. D. Ingram, "The Behavior of Optical Basicity Indicator Ions in Relation to the Ideal Optical Basicity of Glasses", Physics and Chemistry of Glasses, **16** (1975) 119-23.
4. I. D. Sommerville and D. J. Sosinski, "The Application of Optical Basicity Concept to Metallurgical Slags", in A. H. Fine and D. R. Gastell (Ed.), Second International Symposium on Metallurgical Slags and Fluxes, The Metallurgical Society, AIME, Warrendale, PA, (1984) 1015.
5. J. F. Elliot, Private communication.
6. G. Eriksson, Acta Chem. Scand., **25** (1971) 2651.

TABLE 1

Calculation results for Pittsburgh No. 8 coal slag with various additive packages based on extended use of optical basicity

Pittsburgh No. 8 slag Chemical Analysis (wt%)		Syngas Conditions			
Na ₂ O	1.42	Temperature = 2200°F			
CaO	5.04	Total Sulfur = 2.14 wt%			
MgO	1.00	P _{S₂} = 4.09 x 10 ⁻⁵ atm			
Al ₂ O ₃	22.33	P _{O₂} = 2.59 x 10 ⁻¹² atm			
SiO ₂	44.57	Coal-water slurry feed			
FeO	24.17	Air Gasification			
TiO ₂	1.05	Slagging Mode			
P ₂ O ₅	0.42				
Additive, wt% slag	Case I None	Case II 22wt% CaO	Case III 12wt% Na ₂ O 10wt% FeO	Case IV 22% Na ₂ O	
Optical basicity	0.61	0.65	0.68	0.71	
log(Sulfide Capacity)	-5.10	-4.47	-4.20	-3.92	
Sulfur Solubility in slag	0.03	0.14	0.25	0.47	



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

FIGURE 1 Schematic for Equilibrium Furnace

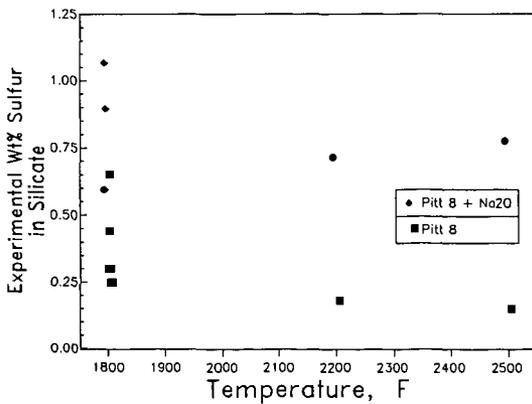


FIGURE 2 Effect of temperature and sodium addition on sulfur capture for Pittsburgh No. 8 slag under simulated Texaco coal gasifier slagging mode conditions