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IGT

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ABSTRACT

The Institute of Gas Technology (IGT) is in the process of developing an advanced coal gasification desulfurization process in which a calcium-based sorbent such as limestone or dolomite is injected into the fluidized-bed gasifier with coal to achieve in-bed desulfurization of coal as it is converted into clean fuel gas. The reactions involving calcium-based sorbents takes place in two steps. In the first step, the desulfurization reaction takes place between hydrogen sulfide and calcium oxide in the reducing zone of the reactor to produce calcium sulfide. The latter subsequently reacts with oxygen in the oxidizing zone of the reactor to produce calcium sulfate which can be safely disposed of along with the coal ash. This process will reduce the capital requirement for coal gasification plants and provide cost effective alternatives to scrubbers for industrial and utility use of high-sulfur coal. This paper addresses the basic research being conducted at IGT to confirm the viability of this process.

INTRODUCTION

The United States has large reserves of high-sulfur, caking, Eastern bituminous coals. The market share of these high-sulfur coals has suffered losses because of the trend toward more stringent government-imposed limitations on sulfur emissions. Thus, there is a real need to develop technologies for utilization of these coals in an environmentally acceptable manner with the minimum gas cleanup cost.

Several gasification process have been developed that can utilize these coals. The Texaco process is fully commercial and is being used with these types of coals for combined-cycle power generation (Cool Water) and production of chemicals (Tennessee Eastman). The Slagging Lurgi under development by British Gas plc should also be able to handle these coals and promises economic improvement over Texaco. There is, nonetheless, opportunity for even further advances in gasification process development.

The Institute of Gas Technology has already developed the U-GAS Process to produce fuel gas from coal with considerable improvement over either the Slagging Lurgi or Texaco. The U-GAS process uses a single-stage fluidized-bed reactor to efficiently convert any type of coal, either run-of-mine or washed, into low- or medium-Btu fuel gas that can be used in industrial plants or utility power plants.[1] The process has been developed during 10 years of testing in a 30 tons of coal per day capacity pilot plant located in Chicago and is currently being commercialized. In a new configuration of the U-GAS process, the U-GAS One-Step Desulfurization Process, limestone or dolomite is fed into the coal gasifier to capture and remove sulfur compounds from the fuel gas within the gasifier. Under the reducing conditions of the gasifier, limestone reacts with sulfur compounds to form calcium sulfide and significantly reduce the sulfur content of the fuel gas. Calcium sulfide is not a stable chemical suitable for disposal. However, some processes such as the U-GAS process may provide an integrated zone for the conversion of calcium sulfide to stable calcium sulfate, which is environmentally acceptable for disposal. The calcium sulfate could then be discharged from the gasifier along with the agglomerated ash. (See Figure 1.)

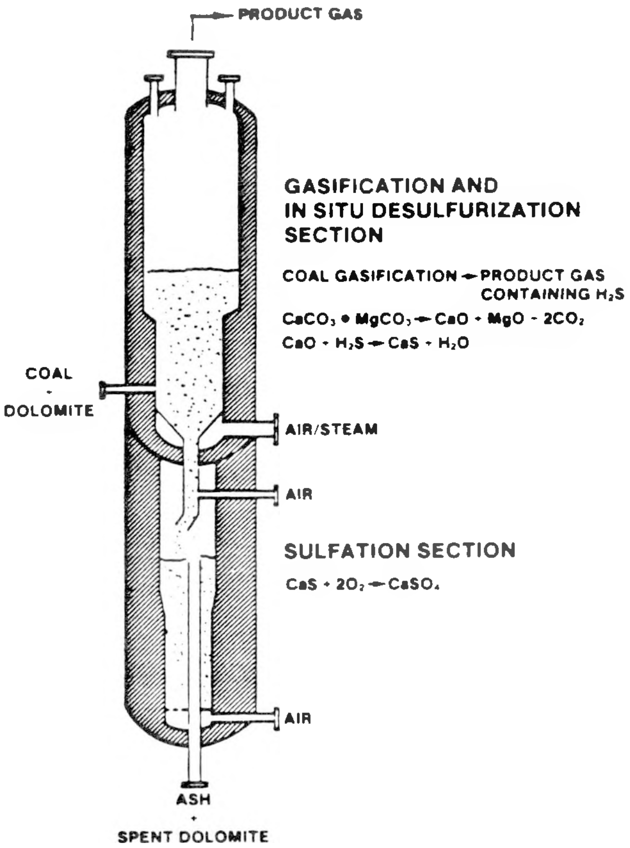

Figure 1: Coal gasification reactor with in-situ sulfur removal.

The Gas Research Institute (GRI) was interested in developing a process whereby in-situ desulfurization was used in a coal gasification process to produce power or synthesis gas (for the production of methane) as co-product.[2] Under the sponsorship of GRI and the Department of Energy, a limited number of tests were conducted at pilot plant facilities that verified the feasibility of in-situ sulfur removing techniques.[1,3] IGT has recently conducted a series of in-situ desulfurization tests with coal and limestone co-feeding to a high-pressure coal gasifier. The purpose of these tests was to determine the effects of pressure and temperature on the extent of in-situ sulfur removal within the gasifier. These tests were conducted at gasification pressures ranging from 1 to 3 MPa in the high-pressure Process Development Unit (PDU), which is based on IGT's U-GAS fluidized-bed coal gasification process. The result of these recent high-pressure tests indicates that the approach to equilibrium usually exceeds 84%.[4]

The work area of desulfurization with limestone and dolomite found in the literature, although confirming the reaction possibilities, is limited in scope and does not extend to the conditions prevailing in the existing coal gasification processes.[5-7] For example, most of the work in sulfidation has been concentrated at temperatures lower than 900°C, whereas the improved process would operate in the range of 980° to 1040°C because it requires ash agglomeration in addition to sulfur capture. Very little work has bee done on the effect of particle size, which is of utmost importance in this new process because the added sorbent must be compatible with char with respect to its fluidization properties. Experimental data on the conversion of calcium sulfide to calcium sulfate within the scope of the proposed process was also lacking in the literature.

This study, which was jointly funded by the Gas Research Institute (GRI) and the State of Illinois Center for Research on Sulfur in Coal (CRSC), was undertaken to obtain engineering data for the development of an advanced coal gasification/desulfurization process.

GAS/SOLID REACTIONS

In the process, the primary sulfidation reactions take place within the fluidized-bed gasifier under the reducing conditions. The limestone is calcined at gasification conditions and sulfur capture occurs through the reaction of calcium oxide with hydrogen sulfide:

$$CaCO_3 \text{ ---> } CaO + CO_2 \qquad (1)$$

$$CaO + H_2S \text{ ---> } CaS + H_2O \qquad (2)$$

The sulfation reactions take place in the ash discharge section under oxidizing conditions to convert the product of sulfidation reaction (CaS) to stable product for disposal ($CaSO_4$).

$$CaS + 2O_2 \text{ ---> } CaSO_4 \qquad (3)$$

When dolomite is introduced into the gasifier, it calcines to produce CaO and MgO. CaO and the resulting CaS react with H_2S and O_2, respectively, according to Reactions 2 and 3, whereas MgO passes through the system as an inert.

FLUIDIZATION

Fluidization tests were conducted on a sample of the coke breeze (dp = 425 μm) and two batches of limestone (dp = 210 μm and 640 μm) and 50:50 mixtures of coke and two sizes of limestone. The tests were conducted in a 10 cm-diameter fluidized-bed column with a flat porous plate gas distributor. The aspect ratio (L/D) was about 1.5. The temperature and pressure were ambient; and the fluidizing gas was nitrogen. Table 1 presents experimental values of the minimum and complete fluidization velocities.

The mixing tests and the fines retention tests were conducted in a 20-cm-diameter fluidization column with an expanded section and sloping grid. To avoid segregation either by size or by density in these tests, they were conducted at a velocity of 0.6 m/s, exceeding the complete fluidization velocity of the coke breeze, which had the highest value.

SOLIDS MIXING

In the mixing tests, 50:50 mixtures of coke/limestone of both sizes [70 mesh (210 μm) and 30 mesh (640 μm)] were fluidized. The fluidized-bed height was maintained at 0.8 m. After 30 minutes of fluidization, the flow of gases was abruptly shut off. Samples were taken in such a way as to be representative of the fluidized-bed material of three sections of equal height (approximately 0.27 m each). The concentrations of limestone in the three sections were determined by measuring the fraction of calcium in the mixture using the atomic absorption technique. The results indicated that the concentration of limestone in all three sections was about 50%, indicating that the velocity of 0.6 m/s is sufficient for either 70 mesh (210 μm) or 30 mesh

Table 1. FLUIDIZATION VELOCITIES

Bed Material	Minimum Fluidization Velocity, (m/s)	Complete Fluidization Velocity, (m/s)
Coke Breeze	0.165	0.56
30 Mesh Limestone	0.315	0.52
70 Mesh Limestone	0.45	0.16
50% Coke-50% 30 Mesh Limestone	0.29	0.52
50% Coke-50% 70 Mesh Limestone	0.15	0.33

(640 μm) limestone to produce a well-mixed bed of char and limestone.

FINES RETENTION

To determine the effect of limestone size and concentration on fines retention, tests were conducted with bed material containing 0%, 25%, 50%, and 75% limestone using both 30 mesh (640 μ) and 70 mesh (210 μ) limestone. In these tests, 2.2 kg of fines were injected into the fluidized bed of char/limestone mixture. The elutriated fines were collected at predetermined periods.

In the test conducted with the various composition of char and limestone, the results indicate that the rate of elutriation of fines from the bed was independent of bed composition. However, the rate of elutriation was a strong function of the bed height. Figure 2 shows that the rate of fines elutriation with a 1.1-meter bed height was 67% of that of a 0.8-meter bed height.

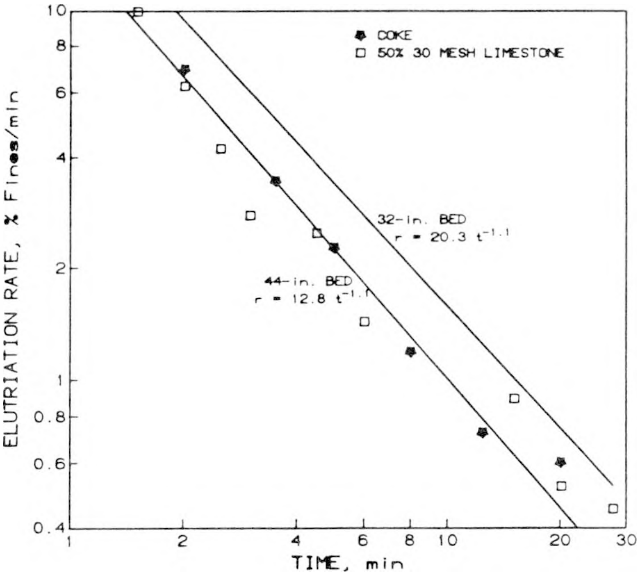

Figure 2: Elutriation rate of coke and coke/limestone mixtures at 0.6 m/s with 1.1 meter and 8 meter.

SULFIDATION REACTION

The sulfidation reaction tests involving the reaction between CaO and H_2S were conducted in an ambient pressure thermogravimetric reactor (TGR). The effects of sample weight, gas flow rate, particle diameter, H_2S concentration, and temperature on the reaction rate were determined.

The sorbent chosen in this study had already been used by IGT and KRW

Energy Systems, Inc. in fluidized-bed gasification tests.

Previous investigation[8] had indicated that the reaction of CaO with H_2S does not depend on the gas composition as long as a constant level of H_2S is maintained. Therefore, in all the tests conducted in this study, the reactant gas consisted of $H_2S/H_2/He$ mixtures. The ratio of hydrogen to hydrogen sulfide was maintained at about 3:1 to prevent dissociation of hydrogen sulfide to elemental sulfur. In these tests the reaction temperature was in the range of 650°-1050°C and particle diameter range from 0.014 to 0.13 cm. The reactant gas contained 0.8% to 3.75% hydrogen sulfide.

Analysis of the experimental data of the sulfidation reaction indicates that the reaction can be described by a shrinking core model for spherical particle of unchanging size. The overall reaction rate can be described by a combination of the chemical reaction rate and the product layer diffusion rate. The extent of CaO conversion can be determined from

$$X_{CaO} = 1 - [1 - \frac{\frac{[H_2S] \cdot t}{\rho_{CaO} \cdot R}}{\frac{R}{2De} + \frac{1}{66.44} \exp [\frac{3889}{T}]}]^3 \qquad (4)$$

In Equation 4, X_{CaO} is the conversion of calcium oxide, $[H_2S]$ is the concentration of H_2S in the gas stream, ρ_{CaO} is the molar density of the calcium oxide, R is the particle radius in meter, T is the reaction temperature in degrees Kelvin, and t is the reaction time in minutes. The effective space diffusivity was calculated by applying the correlation of Fuller[9] to the experimental data of this work. The resulting correlation is --

$$De = 2.6 \times 10^{-6} (T)^{1.75} (P)^{-1} \qquad (5)$$

where De is in cm^2/s, T is in degrees Kelvin, and P is in atmosphere.

SULFATION REACTION

A series of sulfation tests were conducted in a high pressure thermobalance reactor. In these tests, presulfided samples of a limestone and a dolomite were reacted with air in the temperature range of 820° to 1050°C and pressure range of 2 to 3 Mpa. The extent of sulfidation of the starting sulfided samples of limestone and dolomite was 69% and 44%, respectively.

The results of these tests indicated that dolomite could be readily sulfated (greater than 80%) at all operating conditions investigated, whereas, limestone could only be partially (less than 35%) sulfated. A typical sulfation reaction rate curve as a function of time is shown in Figure 3.

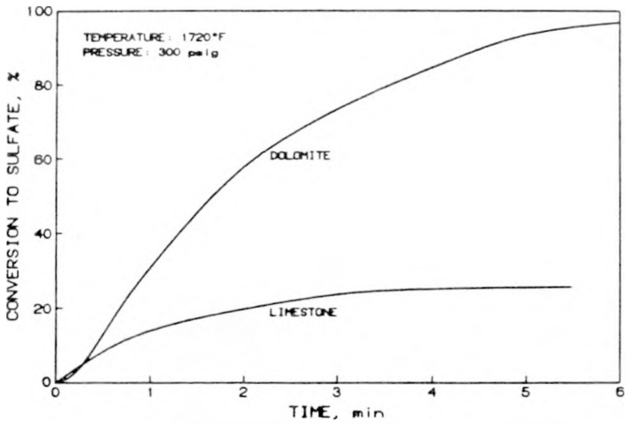

Figure 3: Sulfidation of sulfided sorbents at 938°C.

It is believed that, in the case of dolomite, the MgO matrix provides a more porous structure for oxygen diffusion into the particle, and even though a larger $CaSO_4$ molecule is formed within the outer matrix, there is still sufficient porosity for oxygen to continue to diffuse and complete the sulfation of the inner matrix. In the case of limestone, the outer matrix loses the porosity immediately after the sulfation reaction takes place on the outer surface; hence the sulfation reaction of the inner matrix is paralyzed due to the lack of oxygen transport.

CONCLUSIONS

Within the context of the present gasification technology, the data obtained here indicate that addition of calcium-based sorbents such as limestone or dolomite does not affect the fluidizing characteristic of the gasifier. The rate of sulfidation reaction is high enough to allow desulfurization of the fuel gas to near equilibrium values. Higher levels of conversion of calcium sulfide to calcium sulfate can be achieved with dolomite than limestone.

ACKNOWLEDGEMENT

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