High-Temperature H₂S-Removal Processes Using Limestones

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Schedules and Milestones

FY 94 Program Schedule

	O	N	D	J	F	M	A	M	J	J	A	S
Test Plan												
Fabrication												
Testing												
Analysis												

OBJECTIVES

This project is exploring the technical and economic feasibility of using a high-temperature process for cleaning coal gas prior to combustion in a gas turbine. Coal gas would pass through a nearly-isothermal, moving bed of calcium carbonate that would remove particulates (by filtration), hydrogen chloride and hydrogen sulfide

(by chemisorption), and ammonia (by catalysis). The objective of this research is to define the temperature at which these goals can best be realized at a given pressure. Preliminary calculations indicate a probable range for this temperature of 650 ° to 900 °C, about 100 ° to 500 °C below the outlet temperatures of most gasifiers.

A zero-emissions process for converting a mixture of hydrogen sulfide and carbon dioxide to sulfur and synthesis gas has also been under study. In the course of experiments on the sorption of hydrogen sulfide from gases containing carbon dioxide it was discovered that the two can react. The reaction products include elemental sulfur, carbon monoxide and hydrogen. The reaction is favored by high temperature, low pressure and a high $\text{CO}_2/\text{H}_2\text{S}$ ratio. Since unreacted CO_2 and H_2S could be recycled and there would be no tail-gas stream, a process based on this chemistry could lead to an emissions-free alternative to conventional Claus technology. The rate-limiting step in the reaction was shown to be the thermal dissociation of H_2S , for which the kinetics is known. An estimation of the economics (relative to the Claus process) is encouraging; a patent application has been filed and several companies have filed secrecy agreements and are evaluating the process.

Task #1: Sorption of H_2S With Limestone

BACKGROUND INFORMATION

One of the most important advances required in the field of coal gasification is the development of reliable methods of removing solid and gaseous contaminants from the coal gas at high temperatures and pressures. Gaseous contaminants include H_2S , NH_3 and volatilized alkali salts, all formed from trace components of the coal. Suspended solids are mainly gasifier fines formed during the combustion process. It is necessary that all of these be removed prior to combustion of the coal gas to prevent damage to turbine equipment and infringement of emissions legislation. It has been shown by Squires *et al.* (1971) that cleaning the gas at high temperature

and pressure offers numerous advantages over other methods, most notably higher thermal efficiency and reduced volume (hence cost) of processing vessels. Current industrial practice is to add limestone to the gasifier. This achieves a successful removal of H_2S , but requires more than double the stoichiometric quantity of limestone and produces large amounts of mixed limestone-slag solid waste. We hope to improve on this situation.

PROJECT DESCRIPTION

The process under investigation involves removal of H_2S from the coal gas by sorption into a moving bed of limestone (or lime) particles. NH_3 in the coal gas will be broken down by catalysis and gasifier fines will be removed by cycloning and by filtration by the moving granular bed. This project will focus on developing the necessary description of the kinetics of the reaction of H_2S with limestone, and in particular the evolution of the structure of the solid during the course of the reaction. A differential tube quartz reactor system for studying these reactions in the temperature range of interest has been built (Figure 1). Since studies at gasification pressures would require very much more expensive apparatus, this study is confined to atmospheric pressure.

The main reaction of importance in the limestone/ H_2S system is:

which becomes increasingly favorable at temperatures above 1200 °F (650 °C) for the pressures and compositions obtaining in most gasifiers.

Figure 1: Differential Tube Reactor

The external dimensions of the solid are observed to remain constant (Borgwardt *et al.*, 1984) suggesting that the porosity of the solid increases with conversion, which would lead to a fast reaction and high conversion. At a given fugacity of CO_2 , limestone also undergoes calcination if the temperature is high enough:

The lime formed can then react with H_2S :

At the pressure and composition of the effluent from most coal gasifiers, lime sinters relatively rapidly at its calcination temperature. Once sintered (or "dead burned"), lime will sorb H_2S relatively slowly. Below the calcination temperature, the sorption of H_2S by CaO becomes increasingly favored thermodynamically, but H_2S and CO_2 will compete for reaction with the CaO . It is thus of considerable interest to determine the relative rates of Reaction 3 and the reverse of

Reactions 1 and 2 as a function of temperature.

The composition of the gas phase is dictated by the initial C:H:O ratio and the equilibrium of the water-gas-shift reaction (WGS) as a function of temperature:

Failure to account for calcination and WGS equilibration has cast doubt on the validity of most previous studies in this system, therefore a fresh evaluation of the kinetics is being made.

RESULTS

Sintering phenomena

Limestone. Under one atmosphere of CO_2 the calcination temperature is 890° to 900°C . In contrast to CaO (lime) pellets, millimeter-sized limestone grains do not sinter at a significant rate at temperatures below the calcination temperature.

Calcium sulfide. There is a significant drop in the rate of limestone sulfidation after only 10 to 15% conversion of the CaCO_3 to CaS , and the sulfided particles were found to be much smoother than the original limestone. When reagent-grade CaS powder (average grain size about $1.7 \mu\text{m}$) is heated under an atmosphere of either N_2 or H_2 at 850°C for 40 minutes there is no appreciable loss of BET surface area. However, addition of as little as 4% CO_2 to N_2 leads to significant sintering under the same conditions. In an atmosphere of 96% CO_2 , 4% H_2 , the CaS loses about 25% of its initial BET surface area (1.2 to $1.3 \text{ m}^2/\text{g}$) in 80 minutes at 1033 K , more than 50% in the same time at 1181 K . The data for the rate of loss of surface area in this temperature range are fit reasonably well by the model of German and Munir (1976).

Limestone Sulfidation.

1) Extent of sulfidation

About 70 experiments on limestone sulfidation were performed to determine the extent of the reaction as a function of temperature and time for a given concentration of H_2S (nominally 2%, the rest of the gas phase being essentially CO_2), for temperatures ranging from 710°C to 860°C . Up to the calcination temperature (about 890°C), the conversion of CaCO_3 to CaS stays below 10% when the stones are exposed to about 2% H_2S for up to four hours. This confirms the results obtained by Borgwardt (1984). There is an unusual transition in rate behavior that signals a change in the reaction mechanism as discussed below.

2) Kinetics of limestone sulfidation

Experiments to determine the kinetics of the

conversion of limestone to CaS in the 560°C to 880°C range reveal that the rate of the sulfidation reaction is roughly constant for the first 30 minutes of the reaction. Figure 2 displays the initial reaction rate as a function of the inverse of the absolute temperature in an Arrhenius plot. It can be observed that this initial rate first increases as the temperature is increased up to 670°C , then decreases as the temperature increases from 670°C to 710°C before finally increasing again up to the calcination temperature of CaCO_3 (890°C).

3) Apparent reaction order with respect to H_2S .

Figure 3 displays the limestone conversion after 30 minutes at 665°C under several different partial pressures of H_2S , the rest of the gas being mainly composed of CO_2 (about 88.5%), H_2O (about 5.5%), CO (about 5.5%) and H_2 (about 0.5%). Since in this time range the conversion is still proportional to the exposure time, the limestone conversion is proportional to the reaction rate. Thus, the initial reaction rate is proportional to the H_2S partial pressure and the apparent order of the reaction with respect to H_2S is one. The apparent activation energy of 39 kcal/mol is very similar to previous values published by Squire *et al* (1971) and Borgwardt *et al* (1984) for the activation energy of the sulfidation reaction in the absence of diffusion limitations. Figure 4 is similar to Figure 3 except that these data were obtained at 870°C instead of 665°C . At the higher temperature the limestone conversion is proportional to the square root of the partial pressure of H_2S . So, the apparent order of the reaction with respect to H_2S is 0.5. At higher temperatures, the sharp decrease in reaction rate indicates the appearance of a new limiting step in the limestone sulfidation kinetics. In the 820° to 880°C temperature range we found that the reaction was half-order with

Figure 2: Variation of sulfidation rate with 1/T

respect to H_2S , which is characteristic of diffusion-limited kinetics. Moreover, the apparent behavior of the reaction rate indicates that the diffusion follows an activated process, which is characteristic of solid-state diffusion. These two observations, combined with the fact that CaS sinters quickly at these temperatures, leads to the conclusion that the reaction is now limited by the solid-state diffusion of the reacting gas (H_2S) through the sintered product layer of CaS.

4) Kinetic model

Using the shrinking-core model (Levenspiel, 1972), or the more sophisticated grain model (Szekely *et al*, 1976), and postulating that the two possible limiting steps in the kinetics are the (first-order) chemical reaction and the diffusion through the (planar) reaction-product layer, one readily obtains:

$$t = \tau_R X + \tau_D X^2 \quad (5)$$

with:

$$\tau_R = \frac{\rho L}{Ck} \quad \tau_D = \frac{\rho L^2}{2CD} \quad (6)$$

where:

t = time (s)

X = conversion of the solid reactant

ρ = molar density of solid (mol/m³)

C = concentration of gaseous reactant (mol/m³)

k = reaction rate constant

= $k_0 \exp(-E_{act}/RT)$ (m/s)

D = diffusion coefficient (m²/s)

L = characteristic length of reacting solid (m)

**Figure 3: Influence of H₂S partial pressure on limestone conversion at 665 °C
(P_{tot} = 1 bar)**

At this point it is important to note that our experimental data correspond to conversions below 5%. Thus, any effect of the geometry of the solid can be neglected and the conversion expression derived for diffusion through an ideal, planar product layer can be used without any loss of generality. It is also worthwhile to note that the simple relation between time and conversion given above is possible because the chemical reaction happens to be first-order with respect to the gaseous reactant, H₂S.

Parameters for Equation (2) were obtained by methods that have been described in detail in the progress report for the month of April, 1993. Using these parameters, the model describes the

experimental data relatively well (Figure 5). However, the model is still considered quite preliminary. More experimental data (X-ray sulfur mapping, BET surface area analysis...) will be required to confirm the key hypotheses and to evaluate the parameters more thoroughly.

FUTURE WORK

Work will continue to determine the influence of limestone structure and composition on the kinetics and extent of sulfidation. Preliminary experiments show that when limestone is sulfided above the calcination temperature (at 920 ° to 950 °C), a very high conversion to CaS (> 90%)

Figure 4: Influence of H₂S partial pressure on limestone conversion at 870°C ($P_{\text{tot}} = 1$ bar)

is achieved, in contrast to the 10 to 15% conversions found at temperatures only about 50 °C lower. Calcination at these temperatures takes about 15 minutes whereas the sulfidation requires about one hour. Freshly calcined lime has been found to recarbonate rapidly; it is of interest to determine the relative kinetics of CaO sulfidation and recarbonation, and how rapidly CaS reacts with CO₂ at temperatures below calcination.

The use of dolomitic limestones will also be explored. The presence of magnesia in the calcium carbonate structure may hinder the sintering of CaS and promote the diffusion of H₂S to the sorption sites. Finally, since limestone is frequently mixed with the coal fed to a gasifier, it may prove advantageous to use the limestone first to remove particulates and residual H₂S from the coal gas before it is fed to the gasifier.

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Figure 5: Comparison between experimental data and model

Task #2: Development of a Zero-Emissions Sulfur-Recovery Process

OBJECTIVE

The goal of this research is to develop an emissions-free process for the recovery of sulfur from acid gas streams.

BACKGROUND INFORMATION

This project evolved from the experimental observation that when mixtures of CO_2 and H_2S are allowed to equilibrate at high temperatures a substantial fraction of the H_2S is converted to elemental sulfur. A process has been developed

based on this chemistry, and is described below. This process is suitable for recovery of hydrogen sulfide from any acid gas stream, *e.g.*, coal gas, refinery gases or natural gas, and will provide an emissions-free alternative to the Claus Process.

PROJECT DESCRIPTION

The U.C. Berkeley Zero-Emissions Sulfur Process is shown in Fig. 6. Hydrogen sulfide and an equimolar amount of carbon dioxide are removed from the acid gas in the first absorber/stripper loop. If the acid gas contains insufficient carbon dioxide then a make-up stream may be introduced. The mixture of CO_2 and H_2S is heated and enters the high-temperature furnace,

$$H_2S \rightleftharpoons H_2 + 1/2 S_2 \quad (7)$$

The gases leaving the furnace are cooled in a series of heat exchangers that allow for recovery of heat from the hot gas: this heat is used to raise steam for the stripper and hydrolyzer reboilers. The sulfur is separated by condensation and COS is hydrolyzed to H_2S and CO_2 via:

This hydrolysis is accomplished in a separate vessel (labeled "hydrolyzer" in Figure 6), the exact conditions of which are yet to be determined, but which will probably contain a hot, recirculating solution of potassium carbonate. Hydrogen sulfide and carbon dioxide are then absorbed in the second absorber, leaving a stream consisting of carbon monoxide and hydrogen,

Figure 7: The Distribution of Sulfur-Containing Species vs. Temperature, at 1 atm, for a 50:50 CO₂/H₂S feed, sat. with H₂O at 40 °C

saturated with water vapor, that is essentially sulfur-free. The hydrogen sulfide and carbon dioxide removed from the solvent in the second stripper are recycled to the reactor, therefore

emissions of sulfur-containing gases to the environment are determined by the operating conditions of the second absorber, and may be kept as low as is economic for the absorber design.

RESULTS

Thermodynamic Evaluation

A thermodynamic analysis of the behavior of mixtures of $\text{H}_2\text{S}/\text{CO}_2$ at high temperatures has shown that the formation of elemental sulfur is favored by high temperature, low pressure and low amounts of water in the reactor feed (some water vapor is necessarily carried over from the first stripper). The highest fraction of elemental sulfur is formed when the reactor feed contains roughly 7% H_2S in CO_2 ; however, the yield-per-reactor-pass is the product of the conversion and the feed fraction, and the optimum feed ratio for the process is therefore found to be roughly 50:50 $\text{CO}_2/\text{H}_2\text{S}$, since this minimizes the amount of material that must be recycled.

Reaction Kinetics

An investigation of the reaction kinetics of mixtures of hydrogen sulfide and carbon dioxide at high temperatures showed the rate-limiting step to be the thermal dissociation of H_2S . The role of CO_2 is to serve as a hydrogen sink via the water-gas-shift reaction. It has been found that although substantial amounts of COS would be formed as a reaction byproduct if the gas were cooled slowly, COS formation can be minimized by rapid cooling. The experimental data were modeled successfully using kinetic constants taken from the literature (Kaloidas and Papayannakos, 1989). In addition, MoS_2 appears to be a satisfactory catalyst for the rate-limiting step, a discovery that is important for minimizing the size of the high-temperature reactor required for the process.

Process Evaluation

The capital and operating costs of the process described above have been estimated to allow a rough optimization of the process flowsheet, and to permit a comparison with conventional Claus technology. The estimated costs, while quite preliminary, were sufficiently lower to be encouraging. A patent application has been filed and several companies have filed secrecy agreements and are evaluating the process.

FUTURE WORK

The laboratory work on this project has been completed. The information collected will allow design of a pilot plant, the operation of which will be necessary to determine suitable materials of construction as well as demonstrate the proof-of-concept.

REFERENCES

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END

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