

Combustion of Coal in a Bed of Fluidized Lime

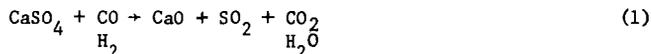
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Under Contract to the Office of Research & Monitoring -
US Environmental Protection Agency

A program is being conducted for the Environmental Protection Agency to develop a regenerative limestone process for fluidized bed coal combustion and desulfurization. The potential of fluidized bed combustor for air pollution control is good because the intimate gas-solid contacting in a fluidized bed promotes high SO₂ removal efficiency on suitable materials such as limestone or dolomite.

A schematic diagram of the process is shown in Figure 1. In the combustor, the sulfur in the coal is burned to SO₂ which then reacts with the lime to form CaSO₄. The system under study involves transferring the partially sulfated lime from the combustor to a separate regeneration vessel where the sulfated lime is regenerated according to the reaction



The regenerated stone (CaO) can then be returned to the combustor for further use, thereby substantially reducing the fresh limestone requirement. The off gas from the regenerator has a high SO₂ concentration and can be used as feed to a by-product sulfur or sulfuric acid plant.

Previous Studies

Various laboratories have studied fluidized bed coal combustion over the past few years. The results of the studies have shown that coal can be burned efficiently with over 90% removal of SO₂ and with reduced NO_x emissions. Regeneration of sulfated limestone has been studied using a number of regeneration methods. The method currently under study has been shown to give 6-10% SO₂ in the product gas when carried out at 1 atm and about 2000 F. The recycled lime was also shown to maintain a reasonably high level of activity after 7 combustion/regeneration cycles.

Economic studies carried out by Westinghouse Research Laboratories under contract to EPA⁽¹⁾ have indicated that operation of the combustor and regenerator at higher pressures, approximately 10 atm, would be significantly more economical than atmospheric pressure operation. As a result, the current studies are being made at higher pressures.

Objectives

Objectives of the current experimental program consist in (1) investigating the factors influencing the reduction of NO_x emissions in fluidized bed combustion, and (2) studying the regeneration of sulfated lime at pressures up to 10 atm.

EXPERIMENTAL RESULTSFactors Affecting NO_x Emissions

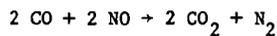
It was determined previously that NO_x emissions measured at the low temperatures occurring in fluidized bed combustion are formed by oxidation of nitrogen compounds in the coal. Oxidation of atmospheric N₂ occurs only at higher temperatures.

In this study, the effect of temperature, excess air and fluidized bed material on NO emissions was measured. The effect of temperature using a bed of CaSO_4 in the combustor is shown in Figure 2. As temperature decreases, NO emissions drop and drop rather sharply below 1500°F. The effect of excess air using a bed of CaSO_4 is shown in Figure 3. Actual NO emissions decreased as excess air (percent O_2) was increased. However, when the emissions were normalized to a constant gas volume (at 3% O_2), the NO emissions increased as the excess air increased. The NO formation rate was thus increased by the higher average oxygen concentration in the bed. The effect of bed material is shown in Figure 4. CaSO_4 gave lower emissions than alundum. With a CaO bed, the emissions were high initially, but as the bed sulfated, the emission level approached that of CaSO_4 .

One consistent explanation for these results is the reaction of NO with CO. CO emissions are higher at the lower temperatures and at lower excess air conditions. The higher CO levels then give lower NO emissions. The effect of bed materials appears to be a catalytic effect.

Reactions of NO and CO

The reaction of CO and NO was studied further in fixed bed units. The effect of bed material, temperature and feed gas composition were studied. In a dry system, CaSO_4 catalyzed the reaction slightly and showed a small effect of temperature, but alumina and an empty bed gave essentially no reaction. However, the addition of water enhanced the reaction and gave the same NO conversion regardless of the presence of the bed material. But when CaO was used as the bed material in a dry system, a very rapid reaction occurred which gave over 90% conversion of the limiting reactant as shown in Table 1. The reaction proceeded in 1/1 molar ratio of CO and NO suggesting the reaction



CO_2 was then added to the feed and reduced the conversion significantly over both calcined limestone and calcined dolomite. This is shown in Table 1.

TABLE 1

<u>BED SOURCE</u>	<u>NO-CO REACTIONS</u>					
	<u>CALCINED LIMESTONE</u>			<u>CALCINED DOLOMITE</u>		
<u>INLET GAS COMP.</u>						
NO ppm	1400	1800	860	1400	1990	840
CO ppm	940	1870	990	900	2080	980
CO_2 %	0	0	17	0	0	16
<u>OUTLET GAS COMP.</u>						
NO ppm	400	20	640	350	240	680
CO ppm	10	160	770	20	100	830
CO_2 %	0	0	17	0	0	17
<u>CONV. (%)</u>	99	99	26	98	95	16

TEMPERATURE: 1600°F

RES. TIME: 0.3 SEC

The most likely explanation for these effects is a kinetic limitation caused by the presence of the CO_2 . Formation of CaCO_3 and inhibition caused by chemical reversibility were considered as possible explanations, but were ruled out after closer examination.

Reactions of NO and SO₂

Studies of the reaction of NO and SO₂ were also made in a fixed bed reactor. The effects of bed material and temperature were studied. The results show that NO and SO₂ do not react in the vapor phase or over alundum or CaSO₄. However, a reaction does occur over partially sulfated lime and appears to be dependent on SO₂ concentration. Further rate studies indicated a 0.5 order dependence on the NO concentration. Temperature had a negative effect on the rate, decreasing the rate with increasing temperature. A proposed mechanism for the reaction involves the reversible formation of CaSO₃ intermediate from CaO and SO₂. The sulfite then reacts with NO to form N₂ and CaSO₄. However, it is known that the sulfite becomes unstable in the temperature range where the SO₂/NO reaction rate drops and this instability is the probable explanation for the negative temperature effect.

Two Stage Combustion

The reactions of NO with CO suggest the possible lowering of NO emissions by operating a staged combustion system. Air would be injected at two points in the combustor giving an O₂ lean section at the bed inlet. This should promote NO reduction because of the relatively high CO levels. The second step would then complete combustion. The fluid bed combustor was then modified to operate in a staged fashion. As the ratio of the amount of air added to the second stage to the amount added to the first stage increased, the NO emissions dropped from 600 to 200 ppm. Although these conditions may not be feasible in commercial operation, the principal of staged combustion appears attractive.

Regeneration of Sulfated Limestone

Regeneration studies were carried out in fixed and fluidized beds using CaSO₄ at pressures up to 10 atm.

Concentrations of SO₂ in the off gas as high as 7.5% have been measured at pressures up to 6 atm. At 10 atm, the highest SO₂ concentration measured to date is 3%. Comparisons were also made with SO₂ levels estimated from equilibrium calculations made by Argonne National Laboratory⁽²⁾. In general, the measured SO₂ concentrations were 40-50% of the equilibrium levels. Further work is planned in the fluidized bed regeneration unit to determine the SO₂ levels attainable at pressures up to 10 atm as a function of temperature, regeneration gas composition and flow rate, particle size and sulfated lime source. Activity maintenance of various stones will also be measured by cycling the stones between a pressurized combustor and the regenerator unit.

BIBLIOGRAPHY

- (1) Archer, D. H., et al., Evaluation of the Fluidized Bed Combustion Process Vol. I, Westinghouse Research Laboratories, Pittsburgh, Pa., Under contract to EPA.
- (2) Jonke, A. A., et al., Reduction of Atmospheric Pollution By the Application of Fluidized-Bed Combustion, Argonne National Laboratory Monthly Progress Report No. 38, December, 1971, Under agreement with EPA.

Fluidized Bed Combustion -
 Lime Regeneration System

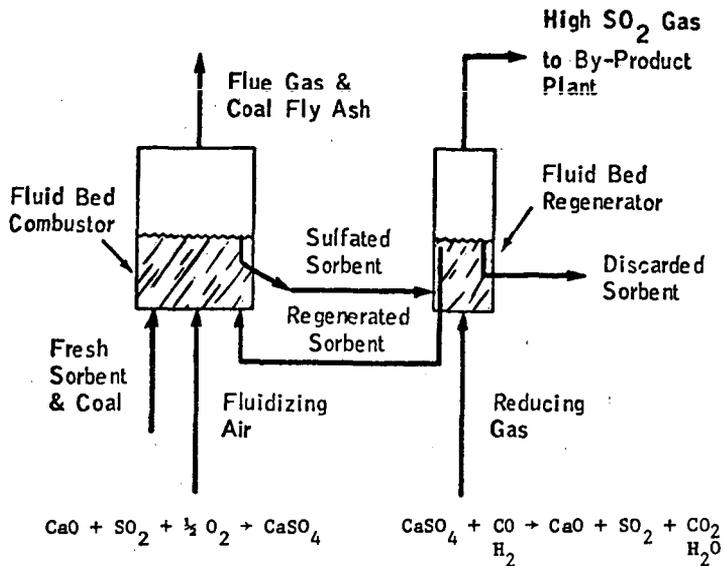


FIGURE 2

NO EMISSIONS AS A FUNCTION OF BED TEMPERATURE

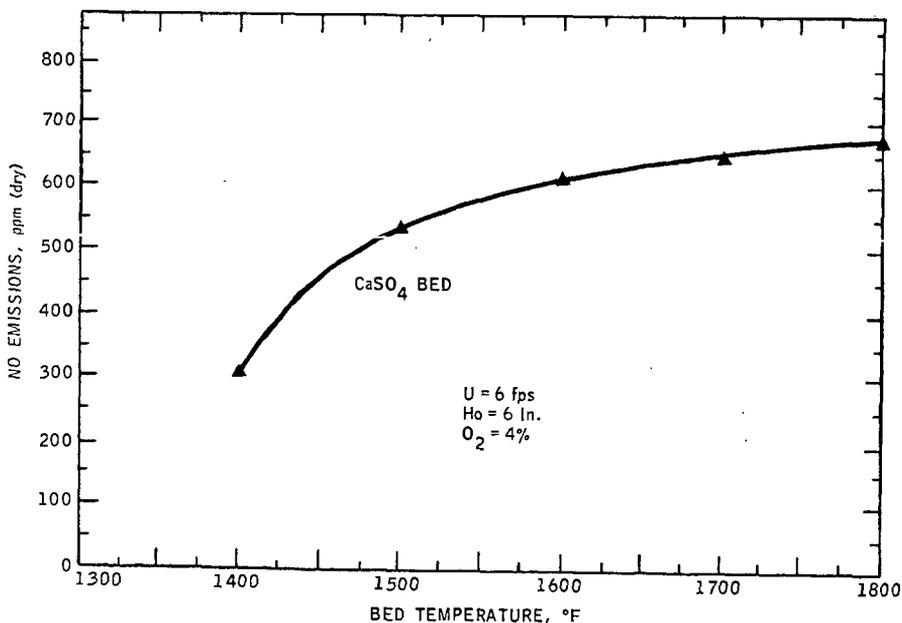


FIGURE 3

EFFECT OF O₂ IN FLUE GAS ON NO EMISSIONS (CaSO₄ BED)

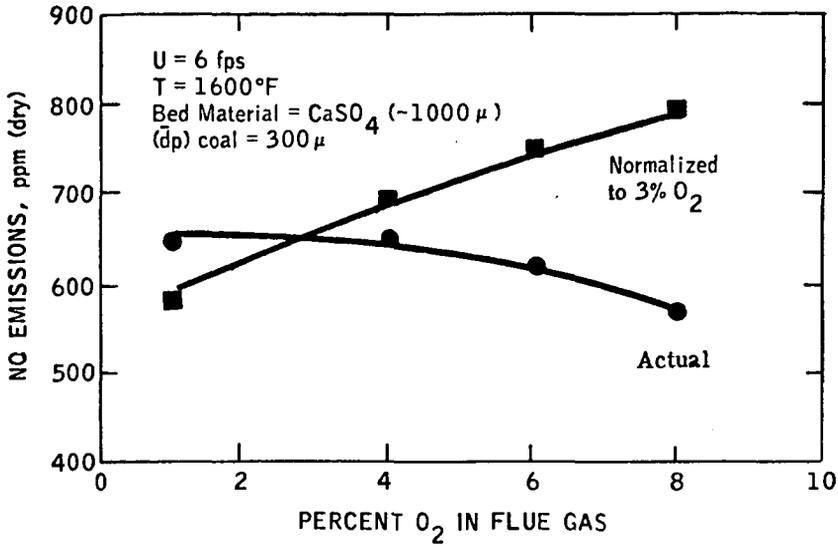


FIGURE 4

NO EMISSIONS USING DIFFERENT BED MATERIALS

