Recovery of lime from coal gasifier waste containing calcium sulfide

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INTRODUCTION

Calcium-based materials hold great promise as sorbents for reduced sulfur compounds at high temperature. Such materials are needed for hot gas clean up or for direct addition to coal gasifiers in several types of integrated coal gasification, combined-cycle (IGCC) power generation systems under development. Calcium-based materials are suitable for this application because they are inexpensive, readily available, and effective at high temperature because very stable CaS is formed [1,2]. However, their use has been hindered by the lack of a suitable regeneration process for converting CaS back to CaO. In principle, the regeneration of CaO could be accomplished by oxidation of CaS particles with air at high temperature. Indeed, previous work had shown that CaS particles can be converted to CaO by oxidation at 1450 to 1550°C [3,4]. Unfortunately, such temperatures are not achieved easily and the CaO would probably be dead burned and unreactive so that it could not be reused. Attempts to oxidize CaS at lower temperature produced particles containing both CaO and CaSO₄ [3,5,6]. But the formation of CaSO₄, which occupies a larger volume than CaS, led to plugging of particle pores and incomplete conversion of CaS.

Recently it was discovered in our laboratory that CaS particles can be converted rapidly and almost completely to CaO by a cyclic process which exposes the material alternately and repeatedly to oxidation and reduction at 900 to 1100°C. During oxidation with air a small portion of CaS is converted to CaSO₄, which upon treatment with a reducing gas is converted to CaO. By repeating the cycle numerous times, individual particles are converted completely to CaO. Such a process can be carried out in a fluidized bed reactor which either has both oxidizing and reducing zones or is supplied with gas that is alternately oxidizing and reducing [7].

The cyclic oxidation/reduction process for converting CaS to CaO has been demonstrated with a thermogravimetric analysis (TGA) systems, and the results are reported below. The effects of temperature and gas composition on the overall rate of conversion are indicated as well as the effect of subjecting typical sorbent materials to repeated sulfidation and regeneration.

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EXPERIMENTAL METHODS

Calcium sulfide powder (99% pure from Cerac, Inc.) and reagent grade CaCO_3 powder were utilized as well as two samples of crushed limestone having the following compositions: Sample A, 52.0% CaO , 2.8% MgO , 1.1% SiO_2 ; Sample B, 49.3% CaO , 1.0% MgO , 2.9% SiO_2 . The powdered materials were briquetted with a hydraulic press which produced flat discs having a diameter of 6.35 mm and thickness of 1-2 mm. For some experiments the discs were used directly, whereas for other experiments the discs were crushed first, and the particles were sized by screening.

For demonstrating the cyclic oxidation/reduction process, a single disc of pure CaS was placed in a quartz basket which was suspended inside of a 25 mm diameter tubular quartz reactor from a calibrated electrobalance. As the reactor was heated by a temperature-controlled electric furnace, nitrogen was passed through the reactor at a flow rate of 1.0 liter/min. measured at room temperature and pressure. When the sample reached the required temperature, the gas composition was changed at 1.0 min. intervals in order to subject the material to the cyclic treatment. As a run progressed at a constant temperature, the weight of the sample was recorded continuously, and when the sample approached a constant weight, the run was discontinued.

For demonstrating repeated sulfidation and regeneration of typical sorbents, a number of crushed and sized particles of either pure calcium carbonate or limestone were placed on a quartz pan which was suspended inside of the tubular reactor. The sample was heated and calcined in a stream of nitrogen to decompose carbonate minerals, and the material was sulfided by treatment with the following mixture: 10% SO_2 , 15% CO , and 75% N_2 . Sulfidation was followed by regeneration using the oxidation/reduction treatment described above.

EXPERIMENTAL RESULTS AND DISCUSSION

A preliminary series of experiments was conducted with the TGA apparatus to determine the effects of gas composition and temperature on the overall rate of conversion of CaS to CaO by the cyclic oxidation and reduction process. Single discs of pure CaS were treated alternately and repeatedly to oxidizing and reducing gas mixtures at constant temperature, and the progress of the reactions was observed by recording the weight of each disc continuously. A 2 min. cycle time was used with 1 min. devoted to oxidation and 1 min. to reduction. Temperature, oxygen concentration, and the type of reducing gas and its concentration were varied among different runs. The conversion of CaS to CaO was determined throughout each run from the loss in weight of the reacting disc.

By conducting a number of runs at 1050°C in which either the O_2 concentration or the type and concentration of reducing gas were varied among runs, it was established that an O_2 concentration of 20% in conjunction with one of the following reducing gas concentrations gave the highest overall rate of reaction: 2% propane, 5% natural gas (principally CH_4), or 30% CO . Small deviations from these concentrations did not have a large effect on the rate of conversion.

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The optimum reducing gas concentration seemed to be related to the stoichiometric quantity of reducing gas required to convert CaSO_4 to CaO and SO_2 . The stoichiometric conversion of one mole of CaSO_4 requires either 0.1 mole propane, 0.25 mole methane, or 1.0 mole CO . With less than the optimum concentration of reducing gas, the rate of conversion of CaSO_4 to CaO increased with an increase in reducing gas concentration which was to be expected. For concentrations greater than the optimum value, the rate of conversion of CaSO_4 to CaO was probably depressed by the simultaneous conversion of part of the CaSO_4 to CaS .

After establishing the optimum gas composition, additional runs were conducted to establish the optimum temperature. In one set of runs, 20% O_2 was used for oxidation and 5% natural gas for reduction while the temperature was varied from 960 to 1100°C among runs. During each of the runs, the overall rate of conversion was nearly constant until the material was almost completely converted. The rate of conversion was observed to increase with each increase in temperature so that the maximum rate was observed at 1100°C. At this temperature a disc of CaS was completely converted to CaO in 40 min. which corresponded to an overall average rate of conversion of 2.5%/min. This rate was three times that observed at 960°C.

The temperature was also varied during another set of runs which was similar to the preceding set except that 30% CO was used in place of 5% natural gas. In this set the maximum rate of conversion was also observed at 1100°C, but it was slightly lower than that observed with 5% natural gas.

Since the preliminary experiments were highly encouraging, further experiments were conducted to see whether or not various sulfur adsorbents would retain their reactivity when subjected to repeated sulfidation and regeneration. The adsorbents were derived from pure calcium carbonate and two different limestones. Since the pure calcium carbonate was obtained as a fine powder, it was first pelletized and crushed to prepare particles in the range of 0.83 to 1.17 mm. Limestone particles of a similar size were prepared by screening the as received materials which had been crushed previously. The materials were calcined to decompose the carbonate minerals. In each experiment a number of particles were subjected to a series of sulfidation and regeneration cycles at 1100°C. During the sulfidation phase of each cycle, CaO was converted to CaS by passing a gas mixture containing 10% SO_2 and 15% CO over the particles until the material approached a constant weight. Then the sorbent was regenerated by subjecting the particles to the oxidation/reduction cyclic treatment to convert CaS back to CaO . For the regeneration step 10% O_2 was used for oxidation and 30% CO for reduction, and the treatment was continued until the material approached a constant weight.

In one run the sorbent derived from pure CaCO_3 was subjected to four sulfidation and regeneration cycles. During the first part of each cycle CaO seemed to be converted completely to CaS , and during the second part CaS seemed to be completely converted back to CaO . The time required for sulfidation was 18 min. for each of the first three cycles and 14 min. for the fourth cycle, whereas the time required for regeneration was 20 min. for the first cycle, and it decreased to 14 min. for the fourth cycle.

In a second run in this series the sorbent derived from limestone A was subjected to five sulfidation and regeneration cycles. Again during each cycle the conversion of CaO to CaS and the regeneration of CaO appeared complete. For the first three cycles the time required for sulfidation was 14 min., and for the last two cycles it was 12 min. For the first cycle the regeneration time was 36 min. and for most of the remaining cycles it was 34 min.

In a third run in this series the sorbent derived from limestone B was subjected to seven sulfidation and regeneration cycles. With this less pure material the conversion of CaO to CaS was 85-86% during each cycle while the regeneration of CaS was complete. For the first four cycles the time required for sulfidation was 24 min., and for the last three cycles it was 20 min. Interestingly, the time required for regeneration was 20 min. for the first cycle, and it decreased steadily from one cycle to the next until only 10 min. was required for regeneration in the final two cycles.

In all three of the preceding experiments the maximum levels of sulfidation and regeneration remained constant from one cycle of sulfidation and regeneration to the next. Furthermore, the cycle time decreased between the first and last cycles of each run. Therefore, the reactivity of the materials appeared to increase with repeated sulfidation and regeneration.

CONCLUSIONS

The experimental results showed that CaS can be converted to CaO by a cyclic oxidation/reduction process. The overall rate of conversion depends on reaction temperature and the concentration of oxygen during the oxidizing phase and the type and concentration of reducing gas during the reducing phase. The repeated sulfidation and regeneration of typical calcium-based sorbents seems to enhance the reactivity of the materials.

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