Removal of H$_2$S and SO$_2$ by CaCO$_3$-Based Sorbents at High Pressures

Semiannual Report


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August 1998

Work Performed under Grant No.: DE-FG22-95PC95217

Performed for:

U.S. Dept. of Energy
University Coal Research Program
Pittsburgh Energy Technology Center
Pittsburgh, Pennsylvania

Performed at:

University of Rochester
Dept. of Chemical Engineering
Rochester, NY 14627
EXECUTIVE SUMMARY

The theoretical and experimental investigation of the mechanism of SO₂ and H₂S removal by CaCO₃-based sorbents (limestones and dolomites) in pressurized fluidized-bed coal combustors (PFBC) and high pressure gasifiers, respectively, is the main objective of this study. It is planned to carry out reactivity evolution experiments under simulated high pressure conditions or in high pressure thermogravimetric and, if needed, fluidized-bed reactor (high pressure) arrangements. The pore structure of fresh, heat-treated, and half-calcined solids (dolomites) will be analyzed using a variety of methods. Our work will focus on limestones and dolomites whose reaction with SO₂ or H₂S under atmospheric conditions has been studied by us or other research groups in past studies. Several theoretical tools will be employed to analyze the obtained experimental data including a variable diffusivity shrinking-core model and models for diffusion, reaction, and structure evolution in chemically reacting porous solids.

During the six months of this reporting period, more work was done on the study of the behavior of the sulfidation of calcined limestones in the presence of small amounts of oxygen. As it was mentioned in the previous report, the incentive for carrying out sulfidation experiments in the presence of oxygen was provided by the observation that some sulfidation experiments that were conducted as oxygen was accidentally leaking into the feed mixture of the reactor showed completely different behavior from that obtained in the absence of oxygen. Experiments were carried out in the thermogravimetric analysis system that we developed for studying gas-solid reactions at atmospheric or subambient pressures using the two CaCO₃ solids (Greer limestone and Iceland spar) that we employed in our previous experiments. It was decided to conduct more experiments on the sulfidation of calcined limestones in the presence of small amounts of oxygen because the experimental curves that were obtained in our past experiments not only exhibited unsatisfactory quantitative reproducibility, but also in a few cases, the solid material that was placed on the pan (initially CaCO₃) was completely converted to gaseous products during exposure to a N₂-H₂S atmosphere containing small amounts of oxygen (below 0.2-0.3%). The new results led to conclusions that were in agreements with those reached in our
previous studies. For small oxygen concentrations, the weight gained by small particles of the calcined sample during sulfidation went through a maximum, whereas for oxygen concentrations above 0.5-0.8%, it increased continuously and could reach values corresponding to complete conversion of CaO to CaSO$_4$.

The above behavior was more pronounced for the Greer Limestone sample, which past studies had shown that it exhibited much lower resistance to intraparticle mass transport than the other sample (Iceland Spar). The large particles (297-350 µm) of Greer Limestone and Iceland Spar we used in the experiments did not show a maximum in the variation of their weight with time during sulfidation in the presence of oxygen. The conversions and the ultimate weight gain they exhibited in the presence of high concentrations of oxygen were above those for sulfation under the same conditions but lower than the value corresponding to complete sulfation. Some experiments on the effects of the presence of oxygen on sulfidation were also carried out using CaO samples obtained through decomposition of calcium-enriched bio-oil, a material obtained by reacting bio-oil, the product of the flash pyrolysis of wood, with calcium hydroxide. Behavior similar to that exhibited by the small Greer Limestone particles was observed. In some cases, the reduction of the weight corresponded to complete disappearance of the sample from the pan, and this was verified by visual examination of the pan at the end of the experiment. A possible explanation for this behavior is that the CaS-CaSO$_4$ reaction, the most probable cause of the reduction of the weight after some reaction time, proceeds through a volatile intermediate at the temperature of the reaction (possible Ca) which manages to escape from the interior of the reacting particles, if the intraparticle diffusional limitations are not very high, before it is converted to a nonvolatile species (e.g., CaO). This behavior has not been reported in any past study and should be the subject of further investigations.
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1. BACKGROUND INFORMATION

In a fluidized-bed combustor, a bed of combustible (coal) and noncombustible material is fluidized using air blown upward. Using dolomite or limestone as the noncombustible material, it is possible to have fuel combustion and flue gas desulfurization taking place simultaneously in the combustion vessel. If operation occurs under atmospheric pressure, the average partial pressure of carbon dioxide in the combustor (typically, 10-15% of the total pressure) is considerably lower than the equilibrium CO$_2$ pressure for decomposition of limestone (CaCO$_3$) or dolomite (CaCO$_3$MgCO$_3$) at the temperatures usually encountered in FBC units (800-950 °C). In the high temperature environment of the AFBC unit, the limestone or dolomite particles undergo calcination, yielding a highly porous product (CaO or MgO), which reacts with the sulfur dioxide produced during coal combustion forming, mainly, calcium or magnesium sulfate. The sulfates occupy more space than the oxides they replace, and as a result, the pores of the calcine are completely plugged with solid product before complete conversion takes place. (The conversion for complete pore plugging is about 50% for the calcine of a stone consisting of CaCO$_3$ only.) Pores of different size are plugged at different conversion levels, and it is thus possible to have formation of inaccessible pore space in the interior of the particles when the small feeder pores of clusters of large pore are filled with solid product (Zarkanitis and Sotirchos, 1989). Moreover, under conditions of strong internal diffusional limitations, complete pore closure may first take place at the external surface of the particles while there is still open pore space left in the interior. For these reasons, ultimate conversions much lower than those predicted by the stoichiometry of the reaction for complete plugging of the internal pore space (less than 30-40%) are seen in AFBC units.

The reaction of calcined limestones (primarily) and dolomites with SO$_2$ has been the subject of extensive investigation. In accordance with the above remarks, the experimental evidence in most of the studies of the literature indicates strong effects of the pore size distribution on the overall reactivity of the calcined solids (Borgwardt and Harvey, 1972; Wen and Ishida, 1973; Hartman and Coughlin, 1974, 1976; Ulerich et al., 1977; Vogel et al., 1977; Hasler et al., 1984; Simons and Garman, 1986; Yu, 1987; Gullett and Bruce, 1987; Zarkanitis and
Sotirchos, 1989; Zarkanitis, 1991). Unfortunately, the immense volume of information that has been accumulated over the years on the reaction of calcined limestones and dolomites with SO\textsubscript{2} is not applicable to SO\textsubscript{2} emissions control by limestones and dolomites under PFBC conditions. PFBC units normally operate under a pressure of 16 atmospheres, and for an average CO\textsubscript{2} content of 15%, this implies that the partial pressure of CO\textsubscript{2} in the reactor is 2.4 atm. Thermodynamic calculations show that the temperature for CaCO\textsubscript{3} calcination in the presence of 2.4 atm of CO\textsubscript{2} must be larger than 980 °C, that is, well above the temperature range (750-950 °C) encountered in a PFBC unit. Nevertheless, even though formation of a highly porous material with a high specific surface area cannot take place under PFBC conditions, favorable desulfurization is known to occur in PFBC units (Bulewicz and Kandefer, 1986; Murthy et al., 1979). For dolomites, the situation is somewhat different since half-calcination (formation of an MgO-CaCO\textsubscript{3} product) is possible under 2.4 atm of CO\textsubscript{2}. Even in this case, however, if the absorption of SO\textsubscript{2} occurred only in the pore space of the half-calcined solid, the utilization of the calcium content of dolomites should be much smaller than what is seen in practice under PFBC conditions.

The reaction of CaCO\textsubscript{3} with SO\textsubscript{2} may involve various reaction steps (Van Houte et al., 1981):

\[
\text{CaCO}_3 + \text{SO}_2 \rightarrow \text{CaSO}_3 + \text{CO}_2 \quad (1)
\]

\[
\text{CaSO}_3 + \frac{1}{2} \text{O}_2 \rightarrow \text{CaSO}_4 \quad (2)
\]

\[
\text{CaSO}_3 + \frac{1}{2} \text{SO}_2 \rightarrow \text{CaSO}_4 + \frac{1}{2} \text{S} \quad (3)
\]

CaSO\textsubscript{3} decomposes at temperatures higher than 650 °C, and therefore, under typical operating conditions in a PFBC unit, the overall reaction may be written as:

\[
\text{CaCO}_3 + \text{SO}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{CaSO}_4 + \text{CO}_2 \quad (4)
\]
For dolomites, one should also address the question of the reaction of MgO with SO$_2$. If the partial pressure of CO$_2$ within the bed varies, calcination of CaCO$_3$ may take place in regions where CO$_2$ pressures lower than the equilibrium pressure are prevailing. The calcination of CaCO$_3$ will yield a partially calcined product, the extent of calcination depending on the residence time of the solid in the low CO$_2$ concentration region. CaO formed in the solid will react with the SO$_2$ present in the bed in the same fashion as in the case of AFBC units:

$$\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2 \quad (5)$$

$$\text{CaO} + \text{SO}_2 + 1/2 \text{O}_2 \rightarrow \text{CaSO}_4 \quad (6)$$

If the partially calcined solid moves into regions rich in CO$_2$, where reaction (5) is favored to proceed from right to left, carbonation, i.e., recovery of CaCO$_3$, will take place, with reaction (4) competing with reaction (5) for CaO. Decomposition of CaCO$_3$ may also take place even if there is no variation of the CO$_2$ pressure in the reactor. Large variations in the temperature profile (100-140 °C) within the combustor unit have been reported by Smith et al. (1982). Therefore, if the solid particles move into regions where the temperature of the reactor is above the temperature at which CaCO$_3$ is stable, at the average partial pressure of CO$_2$ in the reactor, decomposition of CaCO$_3$ will occur. However, only small amounts of CaO have been found in the reactor by Ljungstrom and Lindqvist (1982), suggesting that direct sulfation of limestones (eq. (4)) is the main reaction occurring in the combustor. Similarly, PFBC data from Exxon (Hoke et al., 1977) with uncalcined Grove limestone showed that most of the unreacted Ca in the bed for CO$_2$ partial pressures above the equilibrium value existed in the form of CaCO$_3$.

Studies of SO$_2$ removal at high pressures have been carried out both with carbonates and precalcined solids (Newby et al., 1980; Ulerich et al., 1982; Dennis and Hayhurst, 1984, 1987; Bulewicz et al., 1986). However, because of the aforementioned complexities, with the exception of the general conclusion that favorable desulfurization is possible under PFBC conditions, there is not much agreement in the literature on the effects of the various parameters
on the process. Dennis and Hayhurst (1984, 1987), for example, found that the reaction rate of precalcined limestones in a fluidized-bed reactor decreases with an increase in the operating pressure, both in the absence and presence of CO₂. Working with a laboratory-size PFBC, Bulewicz et al. (1986) observed an increase in the sorption capacity of Ca-based sorbents (chalk, limestone, and dolomite) with an increase in pressure up to 2 atm, but further increase in pressure caused a reduction in the sorption capacity of all samples. Similar observations were made by Jansson et al. (1982). PFBC studies at Exxon (Hoke et al., 1977) showed better sulfur retention for precalcined limestones, but Stantan et al. (1982) observed no improvement in sorbent utilization by precalcination. Stantan et al. also reported that under weakly noncalcining conditions, a feed of uncalcined limestone gave better sulfur retention than what kinetic studies performed in a thermogravimetric apparatus predicted.

A situation similar to that prevailing in PFBC units is encountered in desulfurization in gasifier at high pressures. Fixed-bed and fluidized-bed gasifiers typically operate around 850 °C with a temperature at the exit of around 500-800 °C. The pressure of operation is in most cases in the 200-300 psi range, and at an average pressure of 250 psi, it turns out that the CO₂ partial pressure in the reactor is about 1.8 and 4.3 atm for air blown and oxygen blown gasifiers, respectively (based on a typical CO₂ content (mole/mole) of 11% and 26%, respectively (Grindley et al., 1985). Almost all observations made for SO₂ removal in PFBC reactors apply to H₂S removal in high pressure gasifiers but with reactions (7) and (8) taking place (primarily) in a gasifier instead of (4) and (6):

\[
\text{CaCO}_3 + \text{H}_2\text{S} \rightarrow \text{CaS} + \text{CO}_2 + \text{H}_2\text{O} \quad (7)
\]

\[
\text{CaO} + \text{H}_2\text{S} \rightarrow \text{CaS} + \text{H}_2\text{O} \quad (8)
\]

Like in the case of sulfation, the main difference between the direct and indirect reactions is that a highly porous solid is involved in the indirect process while that participating in the direct reaction is essentially nonporous. In view of this difference, the information that is presently available on the sulfidation of limestone-derived calcines (e.g., see Borgwardt et al. (1984) and
Efthimiadis and Sotirchos (1992) and sulfidation of half-calcined dolomites (e.g., see Ruth et al. (1972) and Yen et al. (1981)) from studies in thermogravimetric analysis (TGA) systems and other types of reactors is inapplicable to the direct reaction of limestones with H$_2$S. Few fundamental studies have been presented in the literature on the direct reaction of limestones with H$_2$S, and most of those have been carried out under low pressures (Borgwardt and Roache, 1984) or under conditions where both sulfidation reactions ((7) and (8)) could take place (Attar and Dupuis, 1979).

The direct sulfation or sulfidation of calcium carbonate-containing sorbents can be studied under atmospheric pressure provided that there is enough CO$_2$ in the reactor to prevent decomposition of the carbonate (simulated PFBC or high pressure gasification conditions). Tullin and Ljungstrom (1989) performed sulfation experiments in a thermogravimetric analyzer (TGA) under conditions inhibiting calcination of CaCO$_3$ and found that the sulfation rate of uncalcined CaCO$_3$ was comparable with the sulfation rate of calcined material; they thus concluded that desulfurization in PFBC's is achieved by direct sulfation of limestones. Large amounts of sample and small particles (around 150 mg and 10-90 µm) were used by those authors in their experiments, and thus extracting any quantitative information is practically impossible (because of strong interparticle diffusional limitations). A similar procedure was employed by Snow et al. (1988) and Hajaligol et al. (1988), who also observed that the direct sulfation of CaCO$_3$ can reach for some precursors higher conversions than the sulfation of the calcines (CaO). High concentrations of CO$_2$ (70% CO2 by volume) were also used by Borgwardt and Roache (1984) to study the direct reaction of limestone particles with H$_2$S at atmospheric pressure in a differential reactor. They employed a limestone precursor (Fredonia limestone) of relatively high porosity (about 8%), and thus, they were able to explain the behavior of the conversion-time trajectories for large particles (diameter greater than 15 µm) along the lines of the overall mechanism for the sulfidation of limestone-derived calcines (reaction (8)).
A detailed investigation of the direct sulfation of limestones with SO$_2$ and H$_2$S under simulated high pressure conditions was carried out by our research group (Krishnan and Sotirchos, 1993a,b,1994) using three limestone specimens of high CaCO$_3$ content. In accordance with the observations of Tullin and Ljungstrom (1989), Snow et al. (1988), and Hajaligol et al. (1988), our sulfation results (Krishnan and Sotirchos, 1993a,1994) showed that the direct reaction of calcium carbonate with SO$_2$, believed to be the dominant reaction in a PFBC, is qualitatively different from the reaction of limestone calcines. A similar conclusion was reached for the limestone-H$_2$S reaction (Krishnan and Sotirchos, 1994). These results reinforced our early conclusion that the accumulated knowledge in the literature from the extensive study of the reaction of calcined limestones and dolomites with SO$_2$ or H$_2$S cannot be used to derive any reliable conclusions for flue or coal gas desulfurization under high pressure conditions. Nevertheless, with the exception of the studies conducted under simulated high pressure conditions on a few limestones, no fundamental studies have been carried out in the literature on the reaction of limestones and dolomites with SO$_2$ or H$_2$S under true high pressure conditions (i.e., at high pressures and in the presence of CO$_2$). Moreover, even though the experimental data under simulated high pressure conditions have been extremely helpful in elucidating some of the phenomena encountered in the direct sulfation or sulfidation of limestones, it is questionable whether these results are directly applicable to reaction under true PFBC or high pressure gasification conditions, especially for solids with significant dolomitic content.

Based on the above observations, a research program has been proposed for the investigation of the mechanism of SO$_2$ and H$_2$S removal by limestones and dolomites at high pressures. Reactivity evolution experiments will be carried out using thermogravimetric and, if needed, fixed-bed and fluidized-bed reactor (high pressure) arrangements. Thermogravimetric experiments will be carried out under simulated high pressure conditions at atmospheric pressure using a unit currently available in our lab and at high pressures using a high pressure TGA proposed to be set up under this project. The pore structure of fresh, heat-treated, and half-calcined solids (dolomites) will be analyzed using a variety of methods. Our work will focus on limestones and dolomites whose reaction with SO$_2$ or H$_2$S under atmospheric conditions has
been in detail investigated by either us or other research groups. The obtained experimental data will be analyzed using various theoretical tools developed by my research group for studying gas-solid reactions, and will be used as basis for the development of predictive single particle models for use in design models of combustors or gasifiers.

2. WORK DONE AND DISCUSSION

During the six months of this reporting period, more work was done on the study of the behavior of the sulfidation of calcined limestones in the presence of small amounts of oxygen. The incentive for carrying out sulfidation experiments in the presence of oxygen was provided by the observation that some sulfidation experiments that were conducted as oxygen was accidentally leaking into the feed mixture of the reactor showed completely different behavior from that obtained in the absence of oxygen. Experiments were carried out in the thermogravimetric analysis system that we developed for studying gas-solid reactions at atmospheric or subambient pressures using the two CaCO$_3$ solids (Greer limestone and Iceland spar) that we employed in our previous experiments. We employed two particle size ranges (53-62 and 297-350 µm), two temperatures (750 and 850 °C), and a stream of 7,000 ppm H$_2$S in N$_2$, in which we added small amounts of O$_2$. Sulfidation was carried out simultaneously or sequentially with calcination.

Results are shown in Figure 1-12 for the Greer Limestone sample and 13-18 for the Iceland Spar sample. To make the graphs directly comparable with those presented in previous reports, the results are presented as the weight gain added to the initial weight of the limestone before calcination, that is, as $1 + \Delta W / W_0$ vs. time, where $W_0$ is the initial weight of the sample (after heat treatment but before calcination).

The results for the large Greer Limestone particles (Figures 1-3) show that as the concentration of oxygen in the reactive mixture increases, the total weight reached by the sample after some reaction time also increases, reaching for 2% concentration of oxygen values that are well above the weight gain for the conversion of CaO to CaS, which for the sulfidation process
corresponds to \((1 + \Delta W / W_0)\) equal to 1.16. The weight gain for large values of time is above this value even for small concentrations of oxygen in the feed. The additional weight is most probably due to the oxidation of CaS to CaSO\(_4\) by the oxygen added to the feed, and the comparison of Figures 2 and 3 suggests that this process reaches higher conversions as the temperature of reaction increases.

For small Greer Limestone particles, a maximum is observed in the variation of the weight of the sample with the extent of sulfidation if the concentration of oxygen is below 0.5-0.8% (Figures 4-6 and 8). When sulfidation is carried out at the same time as calcination, the maximum occurs after the initial drop in the weight that is caused by the occurrence of calcination, a much faster process than sulfidation. For concentrations above 0.5-0.8%, the weight of the sample increases continuously with time, and as in the case of large particles, the weight gain at large values of reaction is above that corresponding to complete conversion of CaO to CaS (Figures 7 and 9-12). However, in the case of the small particles, the observed weight gain is considerably larger, and for relatively large concentrations of oxygen (2%), it corresponds to almost complete conversion of CaO to CaSO\(_4\). The concentration of oxygen above which a maximum is observed in the variation of the weight gain with time increases with increasing temperature of reaction (compare Figures 4 and 6), and this is also the case for the concentration oxygen above which monotonic variation of weight with time is observed – after the initial drop in the weight in the case of simultaneous calcination and sulfidation (compare Figures 7 and 8).

The behavior of the Iceland Spar particles (Figures 13-18) is qualitatively similar to that of the Greer Limestone particles. A maximum in the variation of the weight with time is exhibited only for small particles, but whenever this happens (Figures 17 and 18), it is less pronounced than in the cases with Greer Limestone particles. For concentrations of oxygen above 0.5-0.8%, the weight of the sample increases monotonically and attains values above that for complete conversion of CaO to CaS, but much lower than that for complete conversion to CaSO\(_4\), even for the 53-623 \(\mu\)m particles. Another difference between the Greer limestone and Iceland Spar samples is that at 750 °C, the simultaneous calcination and sulfidation curve differs substantially.
– especially at low reaction times and for the large particle size – from the composite curve for the sequential process. This is caused by the fact that at this temperature, the rate of calcination becomes comparable to that of sulfidation, and thus, there is significant interference between these two reactions.

The weight change of the sample at large reaction times when a maximum is present in the weight gain vs. time curve is in several cases lower than the value that is expected for complete sulfidation of the solid. Complete sulfidation takes place when the reaction is carried in the absence of oxygen. This suggests that part of the sulfide could be converted back to oxide, most probably through the solid-solid reaction of CaS with CaSO$_4$ formed from the oxidation of CaS. Since the solid sample is continuously exposed to H$_2$S, the leveling off of the weight gain to values at which CaO must be present indicates that CaO formed from the solid-solid reaction of CaS and CaSO$_4$ – if this is the reason for the appearance of a maximum – should exhibit very low reactivity with H$_2$S.

For oxygen concentrations above 0.5-0.8%, the rate of CaSO$_4$ formation from the oxidation of CaS is apparently much higher than that of CaO formation from the solid-solid reaction of CaS and CaSO$_4$, and as a result, the weight of the sample increases continuously in the course of the reaction. It was pointed out that for the small Greer Limestone particles, the weight gain reached by the sample for oxygen concentration around 2% corresponds to complete conversion of CaO to CaSO$_4$. This is a surprising result, since if the particle size does not change, the maximum conversion that can be reached for complete pore filling with CaSO$_4$ is about 50%. We are thus led to conclude that when the calcined limestone particles react with H$_2$S in the presence of oxygen, they react as unconsolidated structures, and thus, their size changes (increases) in the course of the reaction.

Experiments with different sample sizes revealed that the maximum in the variation of the weight of the sample with time became more pronounced as the size of the sample was decreased. This observation, in conjunction with the observation that more pronounced maxima are encountered
in the case of Greer limestone, i.e., the material that exhibits much smaller resistance for transport in the pore space of its calcine (Sotirchos and Zarkanitis, 1992), suggests that the decrease in the weight of the sample must be caused by formation of a volatile product that escapes from the pore space of the materials. The formation of a volatile product can also explain why the weight of the sample decreases monotonically after a maximum is formed since, as we mentioned above, if the presence of the maximum were caused by the formation of CaO in the CaS-CaSO₄ solid-solid reaction, one would expect this species to react with the H₂S that is continuously sent through the reactor.

Some experiments on the effects of the presence of oxygen on sulfidation were also carried out using CaO samples with very small effective particle size, and the results obtained from them offered further support to the volatile intermediate explanation that we presented above. Specifically, we conducted experiments using CaO samples obtained through decomposition of calcium-enriched bio-oil, a material obtained by reacting bio-oil, the product of the flash pyrolysis of wood, with calcium hydroxide. The CaO material that results from the decomposition of calcium-enriched bio-oil typically has very high porosity, and as a result, the intraparticle diffusional limitations in the interior of the formed particles – or flakes when the starting material in a thin coating on the pan – are extremely low. Behavior similar to that exhibited by the small Greer Limestone particles was observed, but the maximum in the variation of the weight with time was much more pronounced. Some results are shown in Figures 19 and 20. In some cases (see Figure 20), the reduction of the weight corresponded to complete disappearance of the sample of the pan, and this was verified by visual examination of the pan at the end of the experiment.

The results of Figures 1-18 and those that we presented in our past report are of great importance for the in situ removal of H₂S in gasifiers through limestone injection since they show that even small amounts of oxygen can lead to completely different behavior of the limestone particles from that revealed by simultaneous or sequential calcination and sulfidation experiments.
3. SUMMARY
During the six months of this reporting period, we did more experiments on the study of the behavior of the sulfidation of precalcined limestones in the presence of small amounts of oxygen. Sulfidation experiments in the presence of oxygen were carried out because in past experiments we had observed that leaks of oxygen into the feed mixture led to completely different results from those obtained in the absence of oxygen. The new experiments reaffirmed the observations that we had made in our previous studies. The behavior of the sulfidation of limestone was found to depend strongly, in both a qualitative and a quantitative sense, on the level of the oxygen concentration in the feed. For small concentration of oxygen, the weight gained by the calcined sample during sulfidation in a N_2-H_2S atmosphere presented a maximum, whereas for concentrations above 0.5-0.8%, it increased continuously, reaching in some cases values that corresponded to complete conversion of CaO to CaSO_4. The maximum in the variation of the weight gain with time tended to become more pronounced as the intraparticle diffusional limitations were decreased. The use of different sample sizes showed that the interparticle diffusional limitations had a similar effect, and this led us to the conclusion that the main cause for the presence of a maximum in the variation of the weight of the sample during sulfidation in the presence of oxygen is the formation of a volatile product (possibly Ca) in the CaS-CaSO_4 solid-solid reaction.
BIBLIOGRAPHY


Figure 1. Variation of the conversion of Greer Limestone 297-350 µm particles at 850 °C during sulfidation simultaneously or sequentially with calcination in the presence of 2% oxygen in the N₂-H₂S mixture.
Figure 2. Variation of the conversion of Greer Limestone 297-350 μm particles at 750 °C during sulfidation simultaneously or sequentially with calcination in the presence of 0.2% oxygen in the N₂-H₂S mixture.
Figure 3. Variation of the conversion of Greer Limestone 297-350 µm particles at 850 °C during sulfidation simultaneously or sequentially with calcination in the presence of 0.2% oxygen in the N₂-H₂S mixture.
Figure 4. Variation of the conversion of Greer Limestone 53-62 µm particles at 850 °C during sulfidation simultaneously or sequentially with calcination in the presence of 0.3% oxygen in the N₂-H₂S mixture.
Figure 5. Variation of the conversion of Greer Limestone 53-62 µm particles at 750 °C during sulfidation simultaneously or sequentially with calcination in the presence of 0.3% oxygen in the N₂-H₂S mixture.
Figure 6. Variation of the conversion of Greer Limestone 53–62 µm particles at 750 °C during sulfidation simultaneously or sequentially with calcination in the presence of 0.2% oxygen in the N₂–H₂S mixture.
Figure 7. Variation of the conversion of Greer Limestone 53-62 μm particles at 750 °C during sulfidation simultaneously or sequentially with calcination in the presence of 0.8% oxygen in the N₂-H₂S mixture.
Figure 8. Variation of the conversion of Greer Limestone 53-62 µm particles at 850 °C during sulfidation simultaneously or sequentially with calcination in the presence of 0.8% oxygen in the N₂-H₂S mixture.
Figure 9. Variation of the conversion of Greer Limestone 53-62 μm particles at 750 °C during sulfidation simultaneously or sequentially with calcination in the presence of 1.4% oxygen in the N₂-H₂S mixture.
Figure 10. Variation of the conversion of Greer Limestone 53-62 µm particles at 850 °C during sulfidation simultaneously or sequentially with calcination in the presence of 1.4% oxygen in the N₂-H₂S mixture.
Figure 11. Variation of the conversion of Greer Limestone 53-62 µm particles at 750 °C during sulfidation simultaneously or sequentially with calcination in the presence of 2% oxygen in the N$_2$-H$_2$S mixture.
Figure 12. Variation of the conversion of Greer Limestone 53-62 µm particles at 850 °C during sulfidation simultaneously or sequentially with calcination in the presence of 2% oxygen in the N₂-H₂S mixture.
Figure 13. Variation of the conversion of Iceland Spar 297-350 µm particles at 850 °C during sulfidation sequentially with calcination in the presence of 2% oxygen in the N₂-H₂S mixture.
Figure 14. Variation of the conversion of Iceland Spar 297-350 µm particles at 750 °C during sulfidation sequentially with calcination in the presence of 2% oxygen in the N₂-H₂S mixture.
Figure 15. Variation of the conversion of Iceland Spar 53-62 μm particles at 750 °C during sulfidation simultaneously or sequentially with calcination in the presence of 2% oxygen in the N₂-H₂S mixture.
Figure 16. Variation of the conversion of Iceland Spar 53-62 µm particles at 850 °C during sulfidation simultaneously or sequentially with calcination in the presence of 2% oxygen in the N₂-H₂S mixture.
Figure 17. Variation of the conversion of Iceland Spar 53-62 µm particles at 750 °C during sulfidation simultaneously or sequentially with calcination in the presence of 0.2% oxygen in the N₂-H₂S mixture.
Figure 18. Variation of the conversion of Iceland Spar 53-62 μm particles at 850 °C during sulfidation simultaneously or sequentially with calcination in the presence of 0.4% oxygen in the N₂-H₂S mixture.
Figure 19. Variation of the conversion of calcium carbonate produced through decomposition of calcium-enriched bio-oil at 750 °C during sulfidation simultaneously or sequentially with calcination in the presence of 0.3% oxygen in the N₂-H₂S mixture.
Figure 20. Variation of the conversion of calcium carbonate produced through decomposition of calcium-enriched bio-oil at 850 °C during sulfidation simultaneously or sequentially with calcination in the presence of 0.3% oxygen in the N₂-H₂S mixture.