

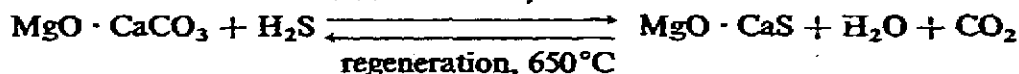
THE SULFIDATION AND REGENERATION OF HALF-CALCINED DOLOMITE*

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ABSTRACT

High-temperature sulfur removal from fuel gas, such as in the Westinghouse fluidized bed coal gasification process, may be achieved using dolomite in the reaction desulfurization, 870°C



Although the regeneration process reduces the sorbent requirement and solid waste handling, a major problem has been the difficulty in completing regeneration and the decrease in regenerability with sulfidation/regeneration cycles. Reactions were carried out in a pressurized TG system and structural information of the solid products was obtained employing scanning electron microscopy, energy dispersive analysis by X-ray, electron microprobe analysis, and X-ray diffraction. The morphological changes during half-calcination, sulfidation, regeneration and cyclic sulfidation/regeneration reactions were correlated with chemical kinetic measurements obtained from TGA. A reaction mechanism which postulates the migration and crystallite growth of MgO onto CaS crystals explains the deterioration in dolomite regenerability, and is supported by the kinetic TG measurements. Time at temperature, and desulfurization temperature are the significant variables which control the regenerability of the product calcium sulfide.

INTRODUCTION

The desulfurization of fuel gas generated at ~1.5 MPa from high-sulfur coals for power generation such as the Westinghouse coal gasification system requires a high-temperature process for energy recovery efficiency. Calcium carbonate is an excellent sorbent for H₂S provided it is used in the form of half-calcined dolomite MgO · CaCO₃, and the rates of reaction are such that virtually all the calcium is utilized and the sulfur is fixed in a dry solid form. This solid must be disposed of in a once-through system, or regenerated by the reaction

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such that sulfur may be recovered and the sorbent re-used to trap more fuel sulfur. While operating a once-through system is simpler, regenerative operation reduces the sorbent requirement as well as waste handling.

Extensive thermogravimetric experiments were carried out to study the sulfidation/regeneration reaction cycle up to 30 cycles. Results indicated that dolomite can be fully sulfided after each regeneration, but the extent of regeneration decreases rapidly as a function of sample cycling^{1, 2}. These results agreed with those reported by Conoco Coal Development Co.³ for the decline in regenerability of calcium sulfide. Although the extent of regeneration increases with increasing temperature, regeneration temperature lower than 700°C is defined by the equilibrium H₂S concentration required for recovery¹. The poor regenerability of CaS in dolomite is also a concern for the two-step regeneration of the fluidized-bed coal combustion process where CaSO₄ is first reduced to CaS which is converted to CaCO₃ with CO₂ and steam in the second step².

A study of morphological changes in dolomite samples which have undergone half-calcination, sulfidation, regeneration and sample cycling has been carried out to probe the decline in calcium sulfide recarbonation. Microstructural changes found at various stages of the cyclic sulfidation/regeneration reactions were correlated with the chemical kinetic measurements obtained from TGA. A reaction mechanism is postulated to explain the decrease in regenerability of dolomite samples.

EXPERIMENTAL

Apparatus

Samples used for the morphological studies were produced by TG runs designed to produce dolomite at various stages of the desulfurization reactions: half-calcination, sulfidation, regeneration and cyclic sulfidation/regeneration.

The thermogravimetric analyzer used was a DuPont 951 thermogravimetric balance controlled by a DuPont 990 console. The system, which is shown in Fig. 1 and described elsewhere in detail⁴⁻⁶, is capable of handling corrosive gas-solid reactions at pressure up to 30 atm and at temperature up to 1200°C. In addition to the analog recorder, the weight and temperature signals are fed to a Fluidyne multi-channel interface. The signals are digitized and input to a Wang 2200 calculator with a 8 K memory, and cassette tape recorders. The data may be conditioned, or reduced, before recording. After a run, the data is reduced and analyzed through the Wang calculator and graphically output on a typewriter plotter.

Methods explored for structure investigation included optical and scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDAX), electron microprobe analysis (EMA), and X-ray diffraction (XRD). A Cambridge Model 2A SEM was used in conjunction with an International 502/504 EDAX which was capable of chemical identification of various phases observed on SEM of half-calcined,

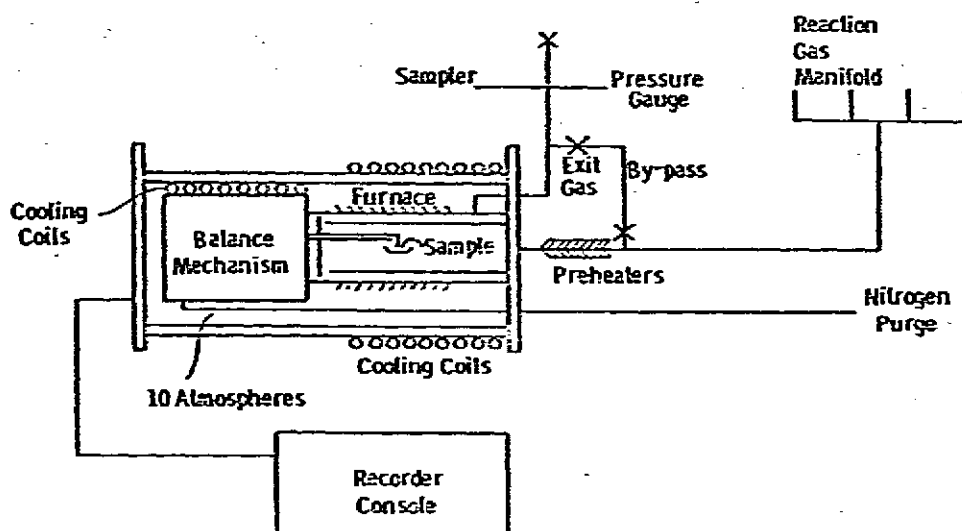


Fig. 1. Schematic diagram of the TG system.

sulfided, regenerated and cycled dolomite samples. A MAC 400 electron microprobe analyzer was employed to obtain elemental profiles on polished cross-sections of reacted dolomite samples. Both a Norelco X-ray diffractometer and camera (2 Radians Debye-Scherrer) were used for chemical identification of the reaction products

TABLE 1

SAMPLES USED FOR SULFIDATION/REGENERATION STUDY

Sample	Particle size (μm)	Ca (wt. %)	Mg (wt. %)	Loss on ignition (wt. %)
Glasshouse dolomite (dolomite 1337)	1000-1200	21.5	12.5	47.7
Tymochtee dolomite	1000-1200	20.5	11.9	44.4
Salamonie Dolomite	1000-1200	21.6	13.0	47.8

TABLE 2

TYPICAL REACTION CONDITIONS

Reaction	Gas Mixture	Temperature ($^{\circ}\text{C}$)	Pressure (MPa)
Half-calcination	10% CO_2 in N_2	870	1.01
Sulfidation	0.5% H_2S , 10% CO_2 in N_2	870	1.01
Regeneration (recarbonation)	50% CO_2 , 10% H_2O in N_2	650	1.01

and the former was also used for crystallite size determination by line breadth broadening method. Cu K α radiation with Ni filter was used. Optical microscopic examination by Leitz NM5 metallograph was attempted to determine grain size of reaction products. Unlike the larger-grained initial dolomites, crystallites of reacted samples were below the microscopic resolution, even with the assistance of polarized light and acid etching.

Material

Three natural dolomites (Glasshouse, Tymochtee and Salamonie) were selected as dictated by their extensive use as desulfurization sorbents in the fluidized bed gasification and combustion studies. Table 1 summarizes the chemical composition. Samples were ground and sieved and the 1000–1200 μm fraction appropriate to the fluidized bed process was used in this study. The solid sample was contained in a platinum gauze basket in the TG apparatus.

Hydrogen sulfide, carbon dioxide, and nitrogen were used as supplied from cylinders. Steam was supplied by injection and evaporation of water. The rotameters were calibrated for pressurized operation using a back pressure regulator and a Brooks flowmeter calibrator. Typical reaction conditions are summarized in Table 2.

Initial structural study

For the initial structural study, TG experiments were designed to provide samples of three dolomites (Glasshouse, Tymochtee, and Salamonie) at various stages of the reaction sequence under conditions representative of process applications (Table 2).

Figure 2 shows the effect of sulfidation/regeneration cycles on regeneration, i.e. molar percent of CaS regenerated, for a 30-cycle TG run. Two points should be noted. First, the regeneration was incomplete even for the first cycle despite the

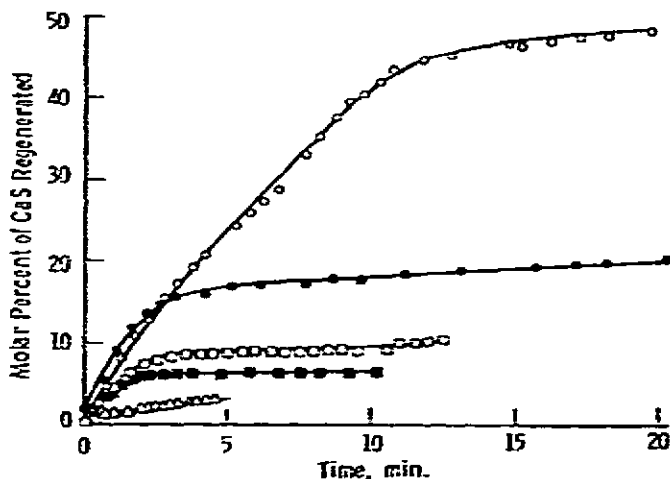


Fig. 2. Regenerability of sulfided dolomite as a function of number of sulfidation/regeneration cycles. ○, 1st cycle; ●, 4th cycle; □, 7th cycle; ■, 11th cycle; △, 30th cycle.

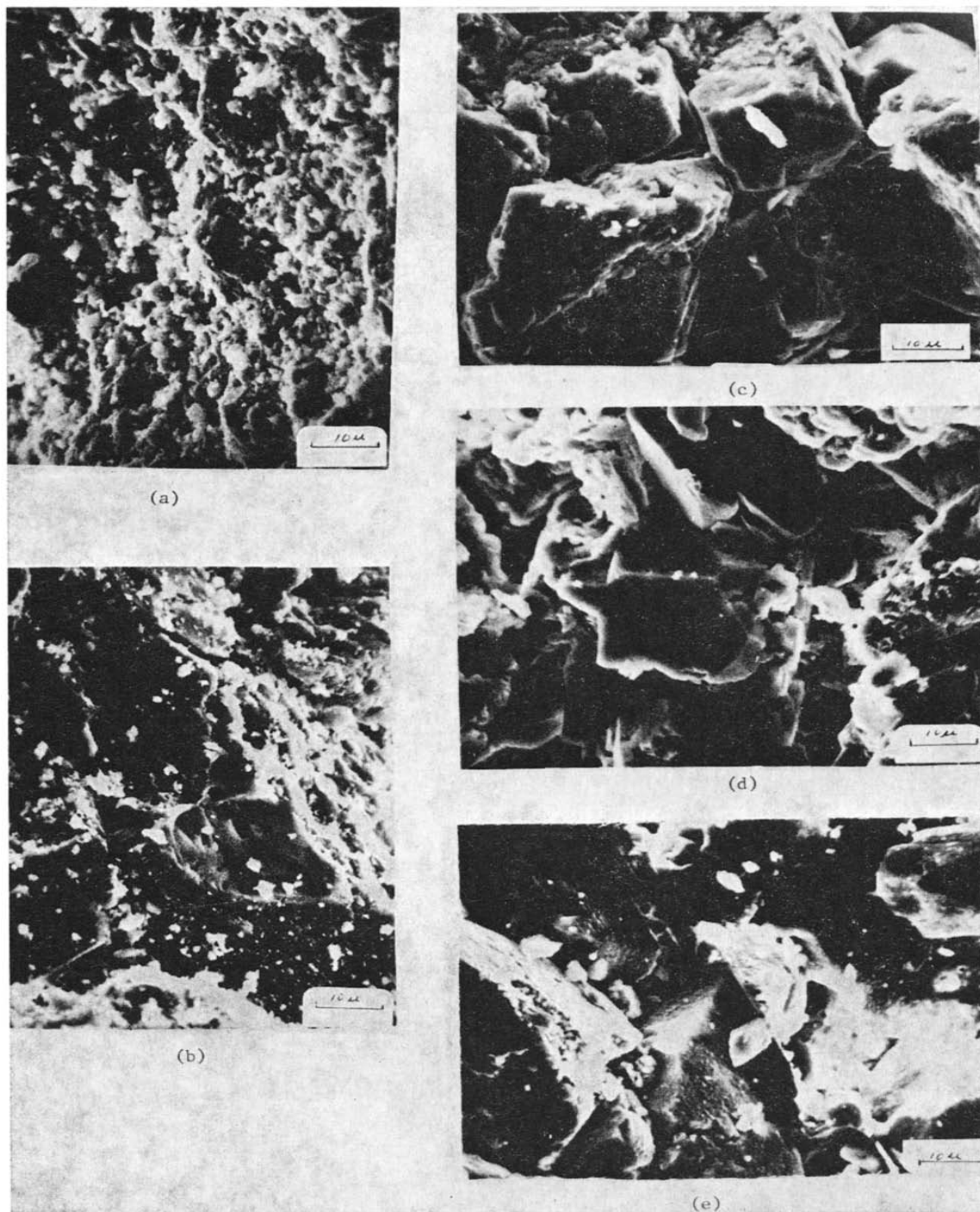


Fig. 3. SEM photomicrographs of (a) Glasshouse dolomite 1337; (b) half-calcined; (c) sulfided; (d) regenerated; (e) sample after five sulfidation/regeneration cycles.

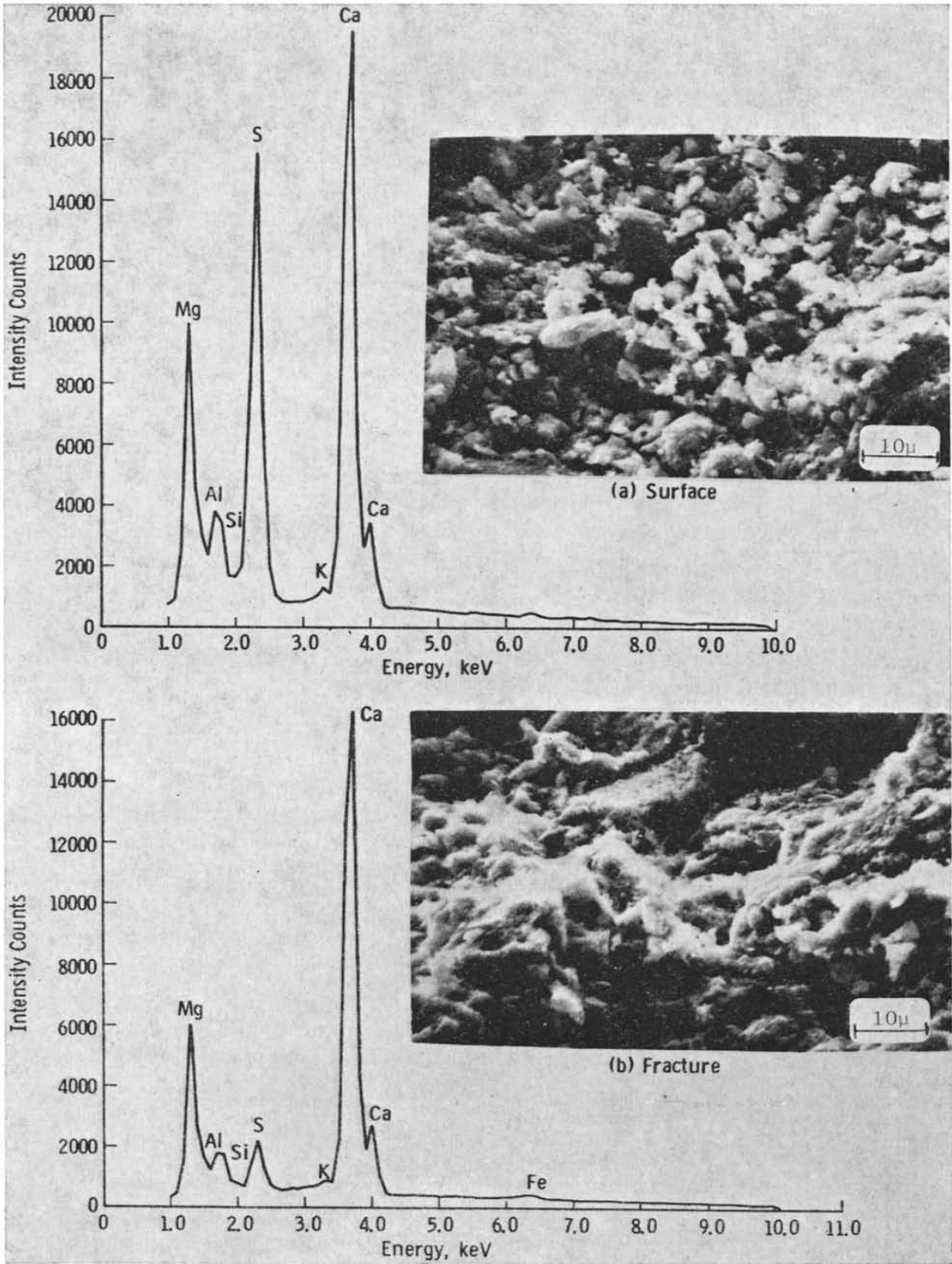


Fig. 4. SEM photomicrographs and EDAX spectra of a partially sulfided dolomite particle.

favorable thermodynamics. Secondly, the extent of CaS regenerability decreased with increasing number of sulfidation/regeneration cycles.

Initially SEM was employed with the intention of correlating morphological changes with chemical reactions. Figure 3 shows typical scanning electron microphotographs of Glasshouse dolomite at different stages in the reaction sequence: half-calcination, sulfidation, regeneration and five sulfidation/regeneration cycles. Although the general shape of the crystal aggregate of the half-calcined dolomite remained largely unchanged throughout the sulfidation/regeneration cycles, the

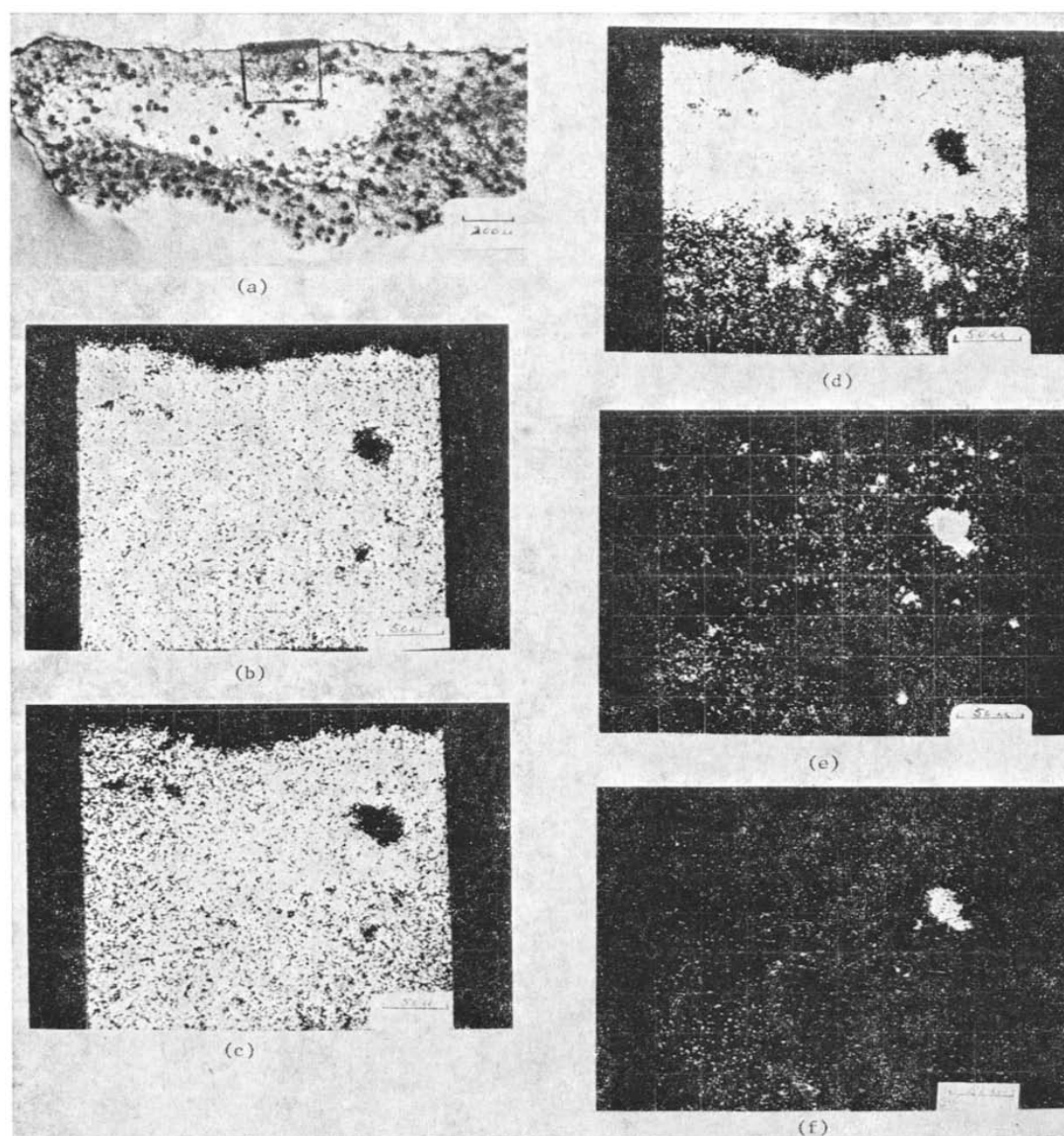


Fig. 5. Microprobe photomicrographs of a partially sulfided Tymochtee dolomite. (a) Particle cross-section marking the area scanned by EMA; (b) EMA area scan for Ca; (c) Mg; (d) S; (e) Si; (f) Al.

crystallite surface became more rough, pebbly and styrofoam-like with sample history. The styrofoam-like surface was particularly typical for the cyclic samples. The small pebbly elevations covering the surface were suspected to be minute MgO crystallites, as reported in the literature⁷. Very little concrete information emerged from the SEM study and it proved necessary to rely on elemental scans from EDAX and EMA to determine the nature of the products.

EDAX analysis showed that although some larger CaCO_3 and CaS were present occasionally, the majority of scans ($1\ \mu\text{m}$ diameter) displayed intimate intermingling of small MgO with CaCO_3 and CaS . This was in agreement with the report by Argonne that much of the MgO might be distributed within the CaCO_3 crystals themselves for half-calcined dolomites⁸. Figure 4 (a) and (b) show typical SEM and EDAX spectra for area scans of a partially sulfided dolomite particle surface and fractured surface, respectively. The sulfur concentration was higher on the surface suggesting that the sulfidation reaction took place from the exterior of the particle and was controlled by gas diffusion into the solid. Small amounts of aluminum, silicon and

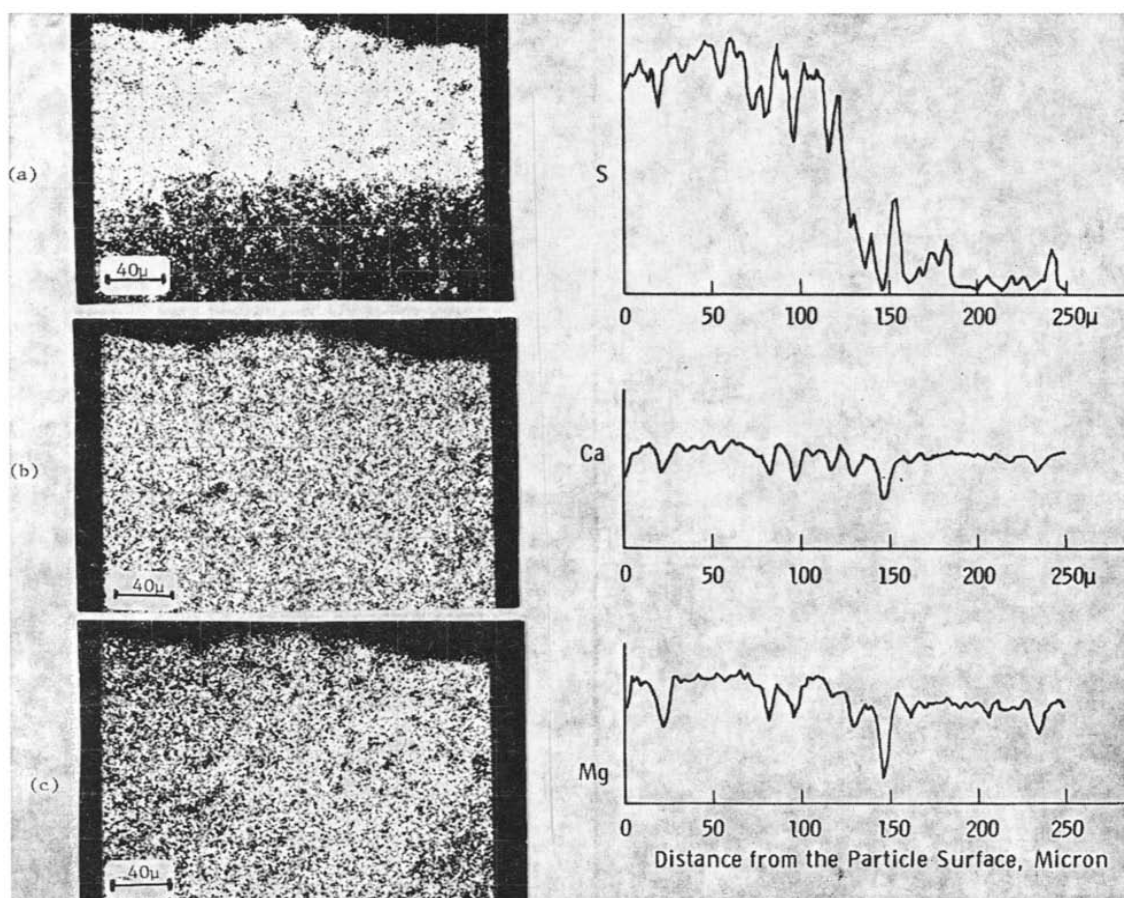


Fig. 6. EMA of a partially sulfided dolomite particle. Area scan and line trace for (a) S, (b) Ca, (c) Mg.

trace amounts of potassium and iron were also detected. Closer examination revealed that the Mg/Ca ratio was also greater at the surface where there was higher CaS concentration. The same phenomena were also observed by electron microprobe analysis (EMA).

Figure 5 shows typical EMA area-scan photomicrographs of a partially sulfided dolomite. A cross-section of a particle is shown in Fig. 5(a) in which the darker periphery is the sulfided area. The square block indicates the area scanned for calcium magnesium, sulfur, silicon and aluminum which are shown in Fig. 5(b)–(f). The quantity of an element present is reflected by the intensity of the white dotted characteristic X-ray counts on the photos. It is obvious from Fig. 5(d) that sulfur was richer near the particle surface. It can also be seen that silicon and aluminum were present in clusters where calcium, magnesium and sulfur were deficient. This suggests that silicon and aluminum do not form migrating liquid phase with calcium and magnesium under the reaction conditions. Thus we can safely rule out the formation of glass phases in grain boundaries (so as to block gas–solid contact) as the cause of decrease in regenerability. In addition, partially sulfided dolomite displayed a magnesium-rich layer in the sulfur-rich area, shown in Fig. 6. Magnesium gradient was not obvious from the area scan photo, but was seen more clearly from the line-trace profile for magnesium on the same sample from the particle surface to 250 μm inward. It can be seen that the sulfur-rich layer was approximately 130 μm thick, where the magnesium concentration was approximately 20% higher than the unsulfided area, whereas calcium intensity stayed constant throughout. The fact that magnesium was more concentrated where the dolomite was sulfided suggested that MgO migrated toward CaS. There are two reasons why this would tend to take place. First, as CaS has a smaller molar volume than CaCO_3 , which it replaces, the small MgO crystals which were scattered among the CaCO_3 crystallites would have a tendency to move toward the less crowded region where CaS is newly formed. Secondly, let us consider the crystal structures of the three compounds involved: CaCO_3 is rhombohedral, while both CaS and MgO are cubic and would be expected to be more compatible with each other^{9, 16}. Therefore, as the rhombohedral CaCO_3 reacts with H_2S to form cubic CaS, there could be a tendency for the cubic MgO to migrate toward it or grow around it.

Completely sulfided dolomite displayed uniform distribution of calcium, magnesium and sulfur as expected. Partially regenerated samples following complete sulfidation did not exhibit a sulfur gradient indicating that the regeneration reaction took place uniformly (on a macroscale) within the particles. This means that the incomplete regeneration of the sulfided dolomite sorbents was not limited by gas ($\text{CO}_2/\text{H}_2\text{O}$) diffusion into the macropores of the solid particles and the barrier for the regeneration reaction existed within the individual crystallites or crystallite aggregates. Dolomite sorbents after several cycles of sulfidation and regeneration reactions also showed uniform calcium, magnesium and sulfur within the particles. The source of the regenerability problem appears to lie in the individual crystallites

of which the solid is composed, and attention was, therefore, subsequently focused on X-ray examination of these individual crystallite sizes.

X-Ray line broadening study

Since preliminary investigation of crystallite size by the X-ray diffraction line-broadening method revealed that the crystallites in the dolomite desulfurization system fell within the measurable range using the line breadth broadening method, a series of TG runs was carried out to provide samples for investigating the sintering effect of dolomite samples at various stages of sulfur removal processes. In addition to sample cycling up to 30 cycles, other parameters explored for their effects on crystallite size and regeneration included sulfidation temperature from 650 to 950°C, total sample exposure time under half-calcination conditions and under sulfidation conditions.

The mean crystallite dimension of each compound was determined from a number of X-ray diffraction peaks for MgO, CaCO₃, CaO and CaMg(CO₃)₂ in selected dolomite samples at various stages using Sherrer's line breadth broadening method and Jones' correction procedures for instrumental broadening and K₂ doublet¹²⁻¹⁴. Broadening of diffraction lines increases as the average crystallite size decreases. Relatively large crystallites (1000–4000 Å) were found in all three (Glass-house, Tymochtee, and Salamonie) dolomites. Small CaCO₃ (~200 Å) was found in all samples (calcined, sulfided, regenerated and cycled dolomites) regardless of processing conditions. However, formation of larger crystallite aggregates (pseudo-crystals) was observed under SEM. Small MgO crystallites were formed during half-calcination, but sintering of MgO crystallites took place during sulfidation. Crystallite size of CaS also increased with increasing sulfidation time and temperature but decreased after regeneration.

Table 3 shows the effect of sulfidation temperature on crystallite size. Larger MgO and CaS were found in samples sulfided at higher temperature. Similarly, small CaCO₃ crystallites were found in all cases. Figure 7 illustrates the effect of sulfidation temperature on regeneration. The extent of CaS regenerability increased with decreasing sulfidation temperature.

TABLE 3

EFFECT OF SULFIDATION TEMPERATURE ON MEAN CRYSTALLITE SIZE

Temperature of sulfidation/regeneration (°C)	Mean crystallite size (Å)		
	MgO	CaS	CaCO ₃
650/650	322	279	282
700/650	367	261	277
870/650	454	381	260
950/650	457	612	284

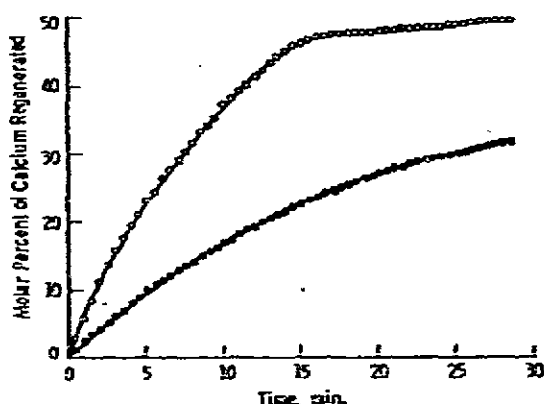
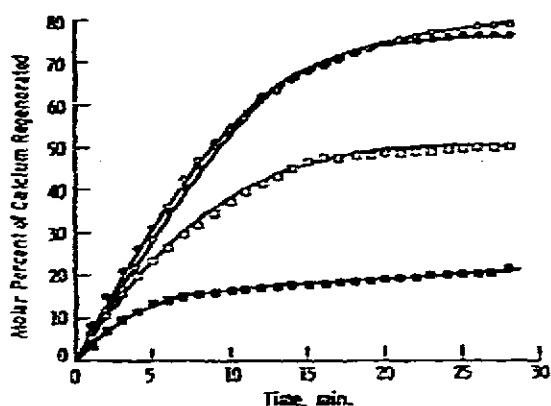


Fig. 7. Effect of sulfidation temperature on regeneration. ○, 650°C; ●, 700°C; □, 870°C; ■, 950°C.

Fig. 8. Effect of sulfidation time on regeneration. ○, 25 min; ●, 192 min.

Table 4 shows the effect of sample exposure time under sulfidation conditions on the average crystallite size. Sintering of MgO and CaS was observed with sulfidation time. CaCO_3 remained unchanged. Figure 8 shows the effect of sulfidation time on CaS regenerability. Longer sample exposure under sulfidation conditions lowered both the regeneration rate and the extent of regenerability of CaS.

TABLE 4

EFFECT OF SULFIDATION TIME ON MEAN CRYSTALLITE SIZE

Sample history	Sulfidation time (min)	Mean crystallite size (\AA)		
		MgO	CaS	CaCO_3
Sulfided at 950°C	10	530	883	229
Sulfided at 950°C	120	797	1020	
Sulfided at 950°C	210	859	1000	
Sulfided at 870°C, regenerated at 650°C	25	454	381	260
Sulfided at 870°C, regenerated at 650°C	192	612	463	223

TABLE 5

EFFECT OF REGENERATION ON THE AVERAGE SIZE OF CaS CRYSTALLITES

Sulfidation	Regeneration	Size of CaS crystallites (\AA)
Yes, 870°C	No	505 \AA
Yes, 870°C	Yes, 650°C	381 \AA
Yes, 950°C	No	883 \AA
Yes, 950°C	Yes, 650°C	457 \AA

TABLE 6

EFFECT OF SULFIDATION/REGENERATION CYCLES ON MEAN CRYSTALLITE SIZE

Sample history	No. of cycles	Mean crystallite size (\AA)			
		$\text{CaMg}(\text{CO}_3)_2$	MgO	CaS	CaCO_3
Original dolomite	0	2112			
Half-calcined	0		255		164
Sulfided/regenerated	1		454	381	260
Sulfided/regenerated	11		935	378	203
Sulfided/regenerated	30		1168	594	

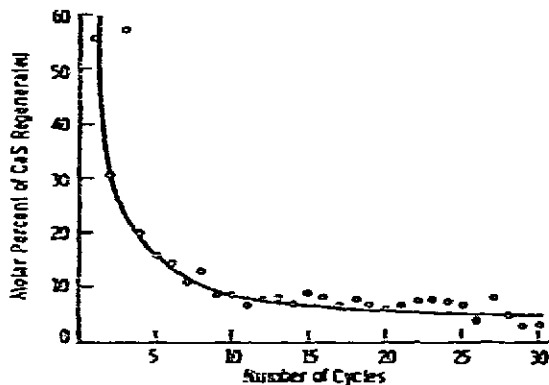


Fig. 9. Effect of sulfidation/regeneration cycles on dolomite regenerability.

Table 5 shows the effect of regeneration on average size for CaS crystallites. A decrease in CaS size always occurred during the regeneration reaction.

Table 6 shows the effect of the number of sulfidation/regeneration cycles on crystallite size. As the model predicted, MgO sintering took place with sample cycling, and there was a small increase in CaS crystallite size. Again, CaCO_3 crystallite size remained unaffected. Figure 9 summarizes the TG results for a 30-cycle run. The decrease in dolomite regenerability was obvious.

SUMMARY

The experiments demonstrate that structural changes occur in the dolomite sorbent which parallel the decline in its regenerability. Migration and sintering of magnesium oxide occur in regions which are rich in calcium sulfide, and reduce accessibility of reactant gases at the reaction sites, and escape paths for the product. The migration and sintering of MgO is accelerated by higher sulfidation temperature, and longer residence time at higher temperature. The occurrence of these internal changes explains the relatively good correspondence between our TG data and data of Curran^{3, 11} et al. from fluidized bed studies, since the internal kinetically limiting mechanism can reasonably be assumed to be the same in both environments.

It appears that time at temperature is the important process variable which leads to deactivation of the calcium sulfide. In most process schemes, the solids residence times at high temperature will be much longer than in the TG apparatus. This finding is in agreement with studies on the regenerability of calcium sulfide produced by reduction from calcium sulfate. In those experiments, residence times greater than one hour at 870°C were required to reduce the sulfate, and less than 25% of the product calcium sulfide was regenerable.

Clearly, if the sulfidation temperature and residence times were lowered, as in the case of the CCNY studies^{15, 16} regenerability would be improved. However, for practical applications, lower temperature applications of the dolomite-based process may not be competitive with the regenerable iron oxide system¹⁷. Further studies are required to probe the validity of the mechanism proposed here for sorbents with different grain structures and for sorbents with significant additional impurities which may prevent MgO migration.

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