Report of Investigations No. 85

THE HIGH-TEMPERATURE PHASE OF CALCIUM SULFATE IN RELATION TO SO_2 REMOVAL BY THE DRY-LIMESTONE INJECTION METHOD

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GEOLOGY SERVES OHIO

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ABSTRACT

Nonstoichiometric removal of SO_2 in stack gases has been observed by the dry-limestone injection system. This has suggested a possible surface sealing effect prohibiting the inner core from reacting with the SO_2. This study investigated the existence of a high-temperature polymorph of $CaSO_4$ by high-temperature X-ray diffraction. The high-temperature phase observed is achievable at temperatures obtained in the stacks and would affect the suggested sealing mechanism.

PREVIOUS INVESTIGATIONS

The existence of a high-temperature polymorphic inversion of calcium sulfate (anhydrite) between 1190°C and 1210°C was suggested originally by Grahmann in 1913 (cited by Gutt and Smith, 1967). Gutt and Smith (1967), in a review of earlier studies based largely on optical investigations, reported the following inversion temperatures: 1232°C (Masuda, 1932); 1230°C (Gruver, 1951); 1214°C (Newman, 1941); 1210±2°C (Dewing and Richardson, 1959); and 1195°C (Rowe, Morey, and Hansen, 1965). Gay (1965), from results of high-temperature X-ray studies, discredited the earlier investigations, claiming that there was inconclusive thermal evidence for the inversion. Gutt and Smith (1967), who made optical and differential thermal analysis studies, found a transformation at 1213°C from low-temperature β-CaSO₄ to high-temperature a-CaSO₄ that could not be preserved to room temperature by quenching.

Studies of SO_2 removal from stack gases by the dry-limestone injection technique have resulted in a practical interest in the high-temperature polymorph of CaSO₄. The SO_2 removal procedure described by Potter, Harrington, and Spaite (1967) and by Coutant, Barrett, and Lougher (1969) is initiated by injecting limestone (CaCO₃) into the base of the stack, where it is calcined. The lime (CaO) absorbs SO_2 to form CaSO₃ and ultimately CaSO₄. The solid particles are carried through the stack and are removed with the flyash at the top. Total retention time in the stack is less than two seconds.

In practice considerably less than stoichiometric removal of SO_2 by CaO absorption has been achieved. Because of the short retention time in the stack the incomplete SO_2 removal was considered to be a problem of kinetics. Additional work has suggested instead that there is within the particle an unreacted core of CaO, sealed by an outer rim of CaSO₄. The calcination reaction results in a porous CaO particle with approximately the same exterior dimensions as the original limestone particle. The sulferization reaction results in the formation of CaSO₄, which has a larger molar volume than the original CaCO₃. This requires a swelling of the particle to achieve stoichiometric absorption. According to the principles of crystal growth the absorption of SO_2 and the resultant growth of CaSO₄ will initially be two-dimensional, with an outer rim of CaSO₄ forming before significant growth toward the center of the particle occurs. The larger molar volume of the CaSO₄ could effectively seal the inner unreacted core from the SO_2 atmosphere, resulting in substoichiometric removal of SO_2. Gutt and Smith (1967) reported that a considerable volume increase accompanied the $\beta \rightarrow a$ inversion of CaSO₄ at 1213°C. This increase in molar volume of the CaSO₄ would enhance its sealing effect and partially explain the incomplete SO_2 absorption. This inversion is critical because it

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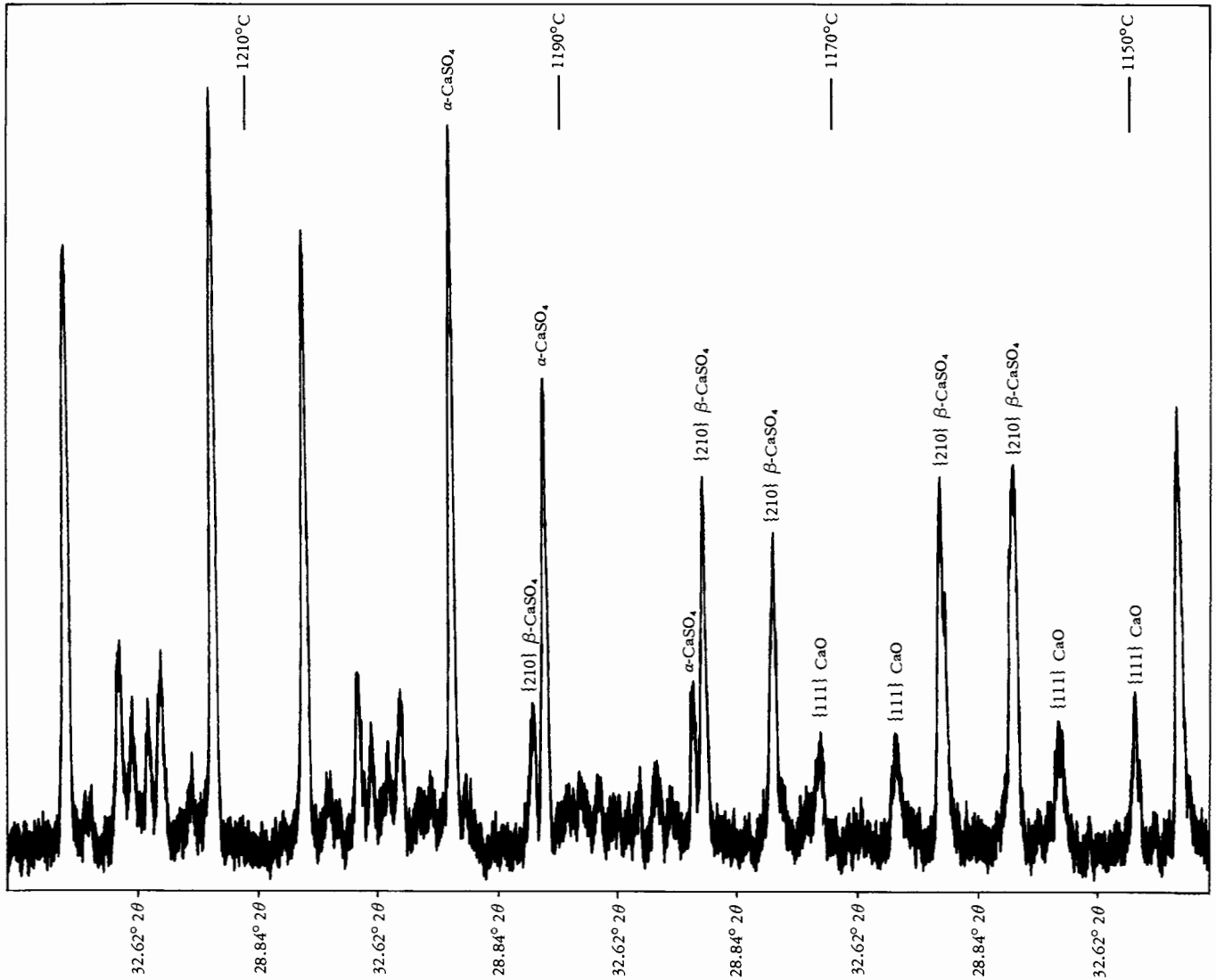
FIGURE 1.—Continuous-oscillation X-ray diffraction pattern over temperature range 1145° to 1225°C and 2θ diffraction-angle range 28.84° to 32.62°.

occurs near the maximum temperature observed in stack gases (1200 to 1600°C); possibly it could be eliminated by operating at slightly lower temperatures.

PROCEDURE AND RESULTS

The author investigated the chemical transformations and the accompanying polymorphic inversion involved in the SO_2 removal procedure by means of high-temperature X-ray diffraction. X-ray oscillations over the $\{10 \cdot 4\}$ $CaCO_3$ diffraction peak at 29.43° 2θ, the $\{111\}$ CaO diffraction peak at 32.2° 2θ, and the $\{210\}$ β-$CaSO_4$ diffraction peak at 31.4° 2θ, from room temperature to 1240°C, were obtained with a Phillips X-ray diffraction unit in conjunction with a Stone high-temperature X-ray furnace. The diffractometer oscil-

lated at $2^\circ 2\theta$ per minute with a heating rate of $5^\circ C$ per minute. The maximum temperature theoretically obtainable with this unit was $1300^\circ C$ and the highest temperature actually achieved was $1240^\circ C$. However, the unit could not be operated for extended periods at temperatures in excess of $1200^\circ C$, resulting in inability to obtain a complete pattern of the high-temperature α-CaSO$_4$ phase.

Two limestone samples, representing two grain sizes, were investigated. One sample, from the Brassfield Formation, was a coarse-grained bioclastic limestone; the second, from the Dundee Limestone, was a very fine-grained lithographic limestone. The samples were fractionated by sieving into four particle size fractions: 60-120 mesh, 120-200 mesh, 200-325 mesh, and <325 mesh. These samples were packed on the thermocouple plate with a spatula and then placed in the X-ray furnace. Each sample was aligned on the {10·4} CaCO$_3$ diffraction peak at $29.43^\circ 2\theta$. After calcination was achieved, SO$_2$ was injected into the furnace, resulting in the immediate formation of CaSO$_4$. After approximately five minutes the furnace was air flushed to remove excess SO$_2$ that otherwise would absorb the X-radiation, decreasing the peak intensities. The CaO peak intensity decreased after SO$_2$ addition, with the new intensity a function of the particle size. The CaO peak intensity decreased with decreasing particle size and the CaSO$_4$ peak intensity increased with decreasing particle size, supporting the theory of an unreacted inner core of CaO. Under the conditions of the present study CaSO$_3$ was not observed as an intermediate product before formation of the CaSO$_4$. The polymorphic inversion from β-CaSO$_4$ to α-CaSO$_4$ occurred near $1200^\circ C$, the exact temperature depending on the particle size. Figure 1 shows a typical inversion as recorded by the X-ray diffraction unit. This sample was less than 325 mesh, resulting in very low oxide peaks and a sharp transformation. At the $5^\circ C$ per minute heating rate there is an observable decrease in the intensity of the {210} CaSO$_4$ diffraction peak and a corresponding shift and increase in intensity of the new phase, presumed to be the previously described α-CaSO$_4$. This inversion was observed in all the runs that attained the prescribed temperatures, with the exception of the run for the 60-120 mesh sample, which behaved erratically. Table 1 contains the observed temperatures of the polymorphic inversion. The temperatures are expressed as a range, with the first temperature corresponding to the initial appearance of α-CaSO$_4$ and the second temperature representing the highest temperature at which β-CaSO$_4$ was observed. There was a general increase in the observed inversion temperature with increasing particle size. The two grain sizes investigated did not show any significant differences in their inversion temperatures. The only difference observed

TABLE 1.—*Observed inversion temperatures of the β- to α-CaSO$_4$ transformation*

Limestone	Particle size (mesh)	Appearance of α-CaSO$_4$ ($^\circ$C)	Disappearance of β-CaSO$_4$ ($^\circ$C)
Dundee	<325	1192	1198
	200-325	1202	1210
	120-200	1188	
	60-120	1215	1232
Brassfield	<325	1182	1192
	<325	1182	1194
	200-325	1200	1210
	120-200	1200	>1215

between the two grain sizes was in decrepitation during the calcination reaction: the Brassfield limestone (coarse-grained) showed considerable decrepitation while the Dundee showed none. Figure 2 illustrates a typical change observed in the d{210} dimension of CaSO$_4$ as a function of temperature. In several deter-

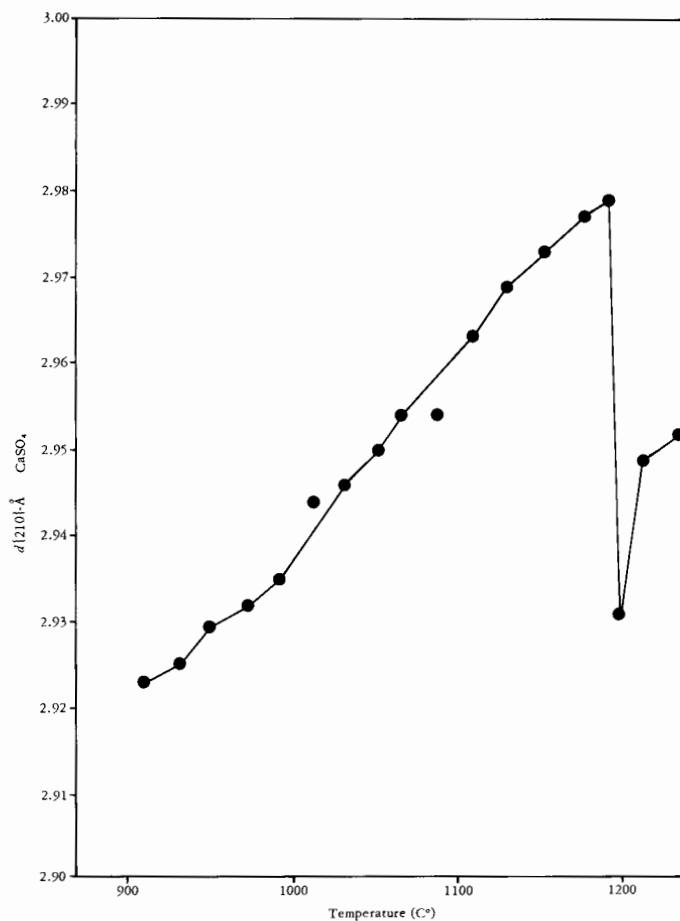FIGURE 2.—Thermal expansion and polymorphic inversion of CaSO$_4$ measured as a function of d{210}.

minations there was a shift and apparent splitting of the {111} CaO diffraction peak. This splitting in conjunction with the polymorphic inversion suggested a differential compression of the CaO inner core, resulting in distortion of the cubic structure. Because complete patterns above 1200°C could not be obtained, no attempt was made to determine the crystallographic structure of the α-CaSO$_4$. Upon cooling, the α-CaSO$_4$ reinverted to β-CaSO$_4$.

SUMMARY

This investigation has supported the existence of a high-temperature phase of calcium sulfate. The polymorphic inversion occurred in the same range reported in earlier studies. Considerable research will be required to understand the implications of the sulferization of calcium oxide. The effect of the outer rim of CaSO$_4$ on the CaO core during the inversion, resulting in the splitting of the oxide diffraction peak, is not completely understood. It is likely that the splitting represents a nonuniform compression of the inner core, but the existence of several particles behaving differently might account for the same effect. The high-temperature polymorph would affect the suggested sealing mechanism, resulting in the nonstoichiometric removal of SO$_2$ by the dry-limestone injection method.

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