

TRANSFORMATION OF CALCIUM SULPHATE HEMIHYDRATE TO INSOLUBLE ANHYDRITE*

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The transformation of calcium sulphate hemihydrate through soluble anhydrite to insoluble anhydrite‡ is of considerable practical importance. The first stage involving the removal of approximately half a molecule of water occurs readily with very little change of structure. But the removal of the last trace of water is difficult (Kelley, Southard, and Anderson 1941) and the conversion to insoluble anhydrite occurs much more slowly and requires a complete reorganization of the lattice.

One of us (Powell 1958) has already reported that in the early stages of heating at 200 °C the rate of transformation of macrocrystalline samples of α -hemihydrate to insoluble anhydrite is very much greater than that of samples of β -hemihydrate prepared by dry calcination. Mitsuki and Kita (1959) have more recently shown that a reduction of particle size of α -hemihydrate decreases the rate of transformation.

In the present communication the results of a further study of the transformation to insoluble anhydrite are presented.

Transformation of the α - and β -Hemihydrates to Insoluble Anhydrite at Various Temperatures

Samples were prepared by autoclaving calcium sulphate dihydrate in saturated steam (α), by digestion in concentrated nitric acid at 60 °C (α), and by calcination at 120 °C and 10 mmHg absolute pressure (β). Portions (2 g) of each were placed in open crucibles and heated continuously for appropriate periods in air ovens maintained at temperatures between 120 and 200 °C. The amount of insoluble anhydrite was estimated from the water content after the sample had rehydrated at 21 °C and 55% relative humidity and then dried at 40 °C for 1 hr. The presence of insoluble anhydrite in samples was also confirmed by X-ray powder patterns, the amount in samples containing more than about 5% being determined by comparison with powder patterns of known mixtures.

The percentage of α -(autoclaved) and β -hemihydrate transformed to insoluble anhydrite is plotted against time of heating in Figures 1 and 2. The initial change of β -hemihydrate to insoluble anhydrite was not confirmed by X-ray methods but indirect evidence from cyclic experiments described later suggests that it is at least partly real.

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‡ The term "insoluble anhydrite" refers in this paper to the anhydrous calcium sulphate which is crystallographically identical with natural anhydrite.

Different rates of transformation were noted for α -hemihydrate prepared by different methods (Table 1). The transformation of material prepared by the nitric acid method was much slower at temperatures below 200 °C than that of the autoclaved material, but the position was reversed at 200 °C. This preparation contained about 0.1% nitrate ion which could not be removed by washing.

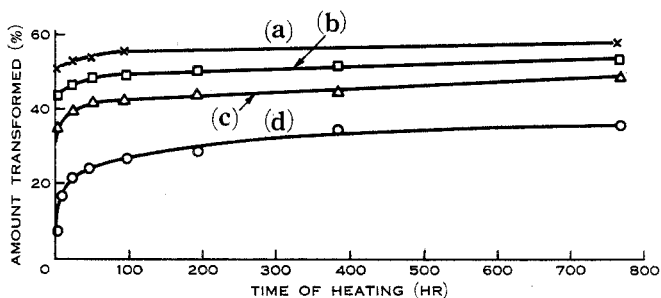


Fig. 1.—Transformation of α -hemihydrate to insoluble anhydrite. (a) Continuous heating at 200 °C; (b) continuous heating at 160 °C; (c) continuous heating at 140 °C; (d) continuous heating at 120 °C.

The rapid partial conversion to insoluble anhydrite suggests that the original hemihydrates (or the soluble anhydrites produced from them) contain active sites about which insoluble anhydrite can form rapidly, though to a limited extent under the experimental conditions, and that further stable nuclei are not readily formed. The observed slower initial rate of the nitric acid preparation

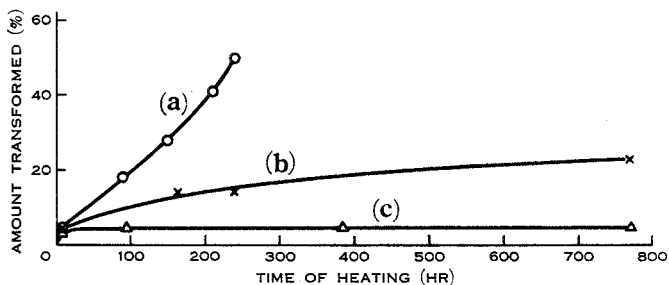


Fig. 2.—Transformation of β -hemihydrate to insoluble anhydrite. (a) Cyclic heating and rehydration, 16 hr heating at 200 °C, 8 hr rehydration; (b) continuous heating at 200 °C; (c) continuous heating at 120–160 °C.

below 200 °C may be due to a hindering of nuclei formation as a result of accumulation of nitrate ions at sites where nuclei would otherwise form (Gregg and Pope 1961). The different initial rates of transformation shown by samples may be attributed to differences in density of active sites, the presence of impurities, and to differences in crystal size and perfection.

Acceleration of the Transformation by Water Vapour

Both α - and β -hemihydrates transformed to insoluble anhydrite much more rapidly when cycles of heating and rehydration were used. For example, a sample of β -hemihydrate heated at 200 °C for 16 hr and then allowed to rehydrate in air for 8 hr transformed to the extent of 50% after 15 such cycles (240 hr heating time) compared with 16% transformation in a control sample heated continuously for the same time (Fig. 2, curve (a)). Continuous but small increases were also noted for cyclic runs at 120, 140, and 160 °C. Similar cyclic treatment of a sample of α -hemihydrate resulted in the transformation of 69% after 16 cycles (256 hr heating) compared with 50% transformation after continuous heating at 160 °C for the same period.

TABLE 1
TRANSFORMATION OF α -HEMIHYDRATE PREPARED BY AUTOCLAVING AND BY
REACTION WITH NITRIC ACID

Temperature (°C)	Sample Transformed (%)			
	Autoclaved		Nitric Acid	
	1 Day	4 Days	1 Day	4 Days
120	21	26	3.6	11
160	46	49	31	43
200	53	56	61	65

It is unlikely that the bulk of the escaping water has a mild hydrothermal effect since much the same accelerated rates were obtained in cyclic runs when most of the intracrystalline water was pumped off prior to reheating.

Acceleration of the transformation of samples by cycles of heating and rehydration may be due to water vapour catalysing the growth of a new phase (e.g. Garner 1955, p. 222) or to the rehydration process producing further effective potential sites about which insoluble anhydrite can form when the sample is again heated.

Transformation of α -Hemihydrate to Insoluble Anhydrite at Room Temperature

It was found possible to transform α -hemihydrate to insoluble anhydrite at room temperature by prolonged outgassing over P_2O_5 . Thus in one experiment three samples of α (autoclaved)-hemihydrate after evacuation at 10^{-2} mm Hg absolute pressure for periods of 4, 96, and 288 hr contained 0, 16, and 18% insoluble anhydrite. The water contents after evacuation were 0.46% for the first and about 0.1% for the other two samples. To decide whether failure of the first of these samples to transform was due to the presence of water in excess of about 0.1% in the lattice or to a slow rate of transformation, this sample was again dehydrated at 10^{-2} mmHg for 4 hr and then stood over P_2O_5 in a desiccator for 96 hr, reweighed to ensure that the sample had not taken up water on standing (the water content actually fell to 0.3%), and then rehydrated in

air. No measurable transformation occurred in this time, suggesting that the water content has to be reduced at least below 0.3% before insoluble anhydrite can form at room temperature. No significant conversion occurred in samples of β -hemihydrate evacuated for prolonged periods under similar conditions.

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