

DISPLACEMENT REACTIONS IN GYPSUM AND IN ANHYDRITE

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SUMMARY

Displacement reactions between calcium sulfates (gypsum and anhydrite) and aqueous solutions of Ba-, Sr- and Pb-salts were investigated by means of TG, DSC, microscopy and x-ray. The reactions can be followed directly by microscopy when cleavage plates of gypsum crystals are used. The first steps of crystallization are in some cases of a topotactical nature. The results presented in this paper deal mainly with the formation of barite, celestite and anglesite by displacement reactions at different temperatures.

INTRODUCTION

Displacement reactions are reactions between two or more components with mutual exchange of atomic constituents. The reaction products are formed in situ on, or within the solid starting phase. This type of reactions may occur generally between solids, between solids and melts or solutions, or between solids and vapors. They are usually favoured by higher temperatures and may proceed at any pressure. Displacement reactions are of importance in minerals formation (pseudomorphs), metasomatic reactions, ore deposits, industrial products (lithopone, silicon carbide), reaction-sintered ceramics, ion exchanged glasses, etc.

In mineralogy generally the term replacement (or metasomatism) is used for the process of simultaneous solution and deposition. During such reactions a new mineral of partly or wholly differing composition may grow in the body of the original mineral. Replacement is governed by the laws of thermodynamics which are complicated however by surface phenomena. It may or may not proceed with changes of volume.

The present paper discusses further results of investigations on displacement reactions between calcium sulfates (gypsum, anhydrite) and aqueous solutions of different salts (1).

Either formation of a Ca-compound or of a sulfate of lower solubility than gypsum may occur. The reaction products are formed in situ on and within the crystals or powders and grow further as long as the salt solution has access to it. They can be observed directly by microscope when cleavage plates $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ are used. Solutions of alkali salts (MeOH , MeF , Me_2CO_3 , $(\text{Me,H})_3\text{PO}_4$, Me_2MoO_4 , Me_2WO_4) reacted with formation of the corresponding Ca-salts: $\text{Ca}(\text{OH})_2$, CaF_2 , CaCO_3 , $\text{Ca}_3(\text{PO}_4)_2$, apatite, CaMOO_4 and CaWO_4 . The reactions between gypsum or anhydrite and chloride- or nitrate-solutions of Sr, Ba and Pb yielded the insoluble sulfates, SrSO_4 , BaSO_4 and PbSO_4 . Further studies are carried out on displacement reactions in anhydrite and alkaline earths carbonates, also in the solid state.

EXPERIMENTAL

Rhombohedral-shaped gypsum cleavage plates of about 0,5 mm thickness were used in most of the experiments. For comparison gypsum and anhydrite were also reacted in form of powders. The salt solutions were prepared with analytical grade chemicals (Merck). The gypsum cleavage plates or the powders were immersed in the various salt solutions from 10 minutes to 20 hours each, at different temperatures up to 100°C . Microscopic investigations were carried out using a polarizing microscope with a hot stage FP 82, and cameras for still or motion pictures (2). The gypsum cleavage plates were placed on microscope slides with a round cavity in the center, the salt solutions were introduced below the plates. Thereby it was possible to follow the displacement reaction on one crystal face only which was essential for reasons of light transmission and focussing. Simultaneous thermo-microscopic/DSC-measurements were carried out with the microscope hot stage FP 84 and the Mettler Thermosystem FP 800 which is connected to a personal computer. For a quantitative evaluation of the reaction kinetics, TG- and DTG-curves were recorded and numerically evaluated using the Mettler TA 3000 system. The reaction products were identified by means of a Nonius X-ray camera, System Guinier, with $\text{CuK}\alpha$ -radiation.

RESULTS AND DISCUSSION

Investigations of displacement reactions between gypsum cleavage plates and alkali carbonate solutions were reported by Flörke (3) and by Bayer and Wiedemann (4). Depending on the kind of alkali carbonate solution, its concentration and temperature either vaterite, calcite or aragonite may be formed on the gypsum crystal surface. Further displacement reaction studies were carried out in the systems gypsum-alkali hydroxide (1). Also here the reactions are favored by higher alkali concentration and by higher temperatures (40°C). Formation of CaCO_3 could be avoided by using CO_2 -free atmosphere. The crystalline $\text{Ca}(\text{OH})_2$ -reaction layer on the gypsum surface consists of well developed, hexagonal plates which show preferential orientation at the beginning. Probably, the first crystallization steps are of a topotactical or epitaxial nature.

In both types of reactions — either in alkali carbonate - or alkali hydroxide solutions — it is possible to follow the reaction rate by TG. Both $\text{Ca}(\text{OH})_2$ and CaCO_3 show a decomposition with a defined weight loss which allows to calculate quantitatively their amounts. These data can be controlled by determination of non-reacted gypsum which again can be derived from TG-measurements. In the case of displacement reactions in gypsum which lead to formation of thermally stable compounds such as CaF_2 , CaMoO_4 , CaWO_4 , BaSO_4 , SrSO_4 or PbSO_4 the degree of reaction can be determined only indirectly from the amount of unreacted gypsum. Such thermo-analytical investigations have been carried out in the case of formation of BaSO_4 . Of course in all such displacement reactions it is always possible to determine the concentrations of the various reaction products by quantitative x-ray analysis.

Following is a brief discussion of experiments with single crystals and powders of both gypsum and anhydrite which were reacted with aqueous solutions of different salts. The starting materials and the reaction products are summarized in Table 1.

The majority of these experiments was concerned with the formation of barite. This sulfate is of special interest both mineralogically and as an industrial mineral.

TABLE 1

Displacement reactions in gypsum and anhydrite

Starting materials	Solutes	Reaction products
Gypsum: cryst.cleavage plate polycryst.powder hardened plaster	$\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$	BaSO_4
	$\text{Ba}(\text{NO}_3)_2$	SrSO_4
	$\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$	PbSO_4
Anhydrite: cryst.cleavage plate polycryst.powder	$\text{Sr}(\text{NO}_3)_2$	
	$\text{Pb}(\text{NO}_3)_2$	

Formation of BaSO_4 from gypsum, plaster and anhydrite

Cleavage plates of gypsum were immersed for different times in aqueous solutions of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ (2,5 and 20%). After rather rapid nucleation and initial crystal growth of BaSO_4 the reaction slowed down and took place mainly in the surface layer (Fig. 1). The same is true for the formation of SrSO_4 and PbSO_4 . This is probably due to the type of reaction with reconstructive changes in oxygen coordination around the large Ba-ion and the decrease in the rate of diffusion. On the other hand, the reaction of gypsum cleavage plates with aqueous solutions of alkali hydroxides, -carbonates, or -fluorides was rather continuous and complete throughout the crystal plates. Cleavage plates of anhydrite showed this type of displacement reactions to a considerably smaller degree and mainly at higher temperatures (100°C). This was also found for samples of hardened plaster (cubes of 10 mm edge length) which reacted much easier with solutions of NaF, Na_2WO_4 , NaOH or Na_2CO_3 as compared with solutions of Ba-, Sr- or Pb -salts.

The effect of time, temperature and concentration was investigated by using powders of gypsum, hemihydrate, and anhydrite which were mixed with different salt solutions. The reaction products (BaSO_4 , SrSO_4 , PbSO_4 , CaF_2 , CaWO_4) and the degree of reaction were checked by means of x-ray, TG and microscopy. In the case of BaSO_4 formation, the following observations were made: The reaction starts immediately and proceeds rather rapidly. Within 10 minutes around 70% of the Ca-sulfate is transformed into BaSO_4 , about 90% after 6 hours and practically 100% after 20 hours. These figures can be derived from the amount of unreacted gypsum by TG, and from the weight gain of the sample (1g gypsum would react to 1,35g BaSO_4).

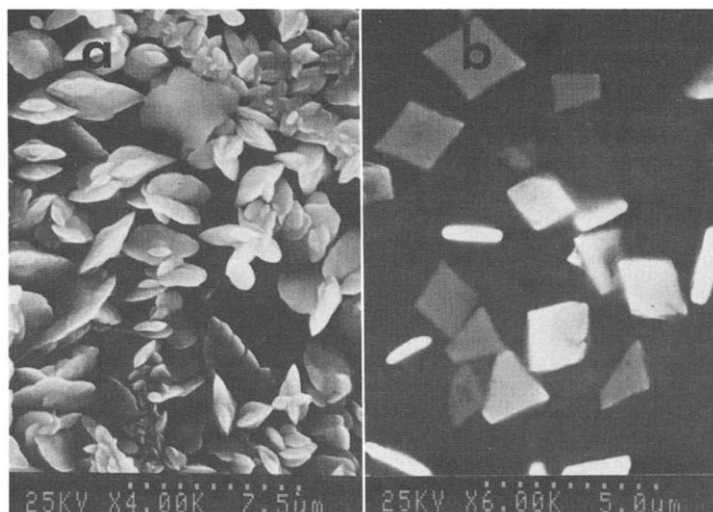


Fig. 1 . SEM photograph of a) BaSO_4 - and b) PbSO_4 - crystals grown on gypsum cleavage plate immersed in corresponding nitrate solutions

Higher temperature increased the reaction rate to some degree. It did not make a big difference whether the calcium sulfate powders were reacted with BaCl_2 -solution at 5° , 20° , 50°C or 100°C for the initial reaction step, only the completion of the reaction was achieved in shorter time at higher temperatures. The size and the form of the BaSO_4 crystals was better developed when less-concentrated Ba-salt solutions were used. Fig. 2 shows TG curves of gypsum powder samples (1g) after reaction with BaCl_2 (2%)-solution. The weight steps correspond to the decomposition of unreacted gypsum. Fig. 3 shows the x-ray powder patterns of the mixture $1 \text{ CaSO}_4 \cdot 2\text{H}_2\text{O} / 1 \text{ BaCl}_2 \cdot 2 \text{H}_2\text{O}$ before and after reaction in water for 10' and for 20 hours. The dry mixtures did not show any displacement reaction when heated in the thermoanalyzer up to 500°C , but immediate reaction at room temperature when water was added. This was accompanied by a temperature increase of about 3°C for a reaction mixture of 10g with 20 cc H_2O added.

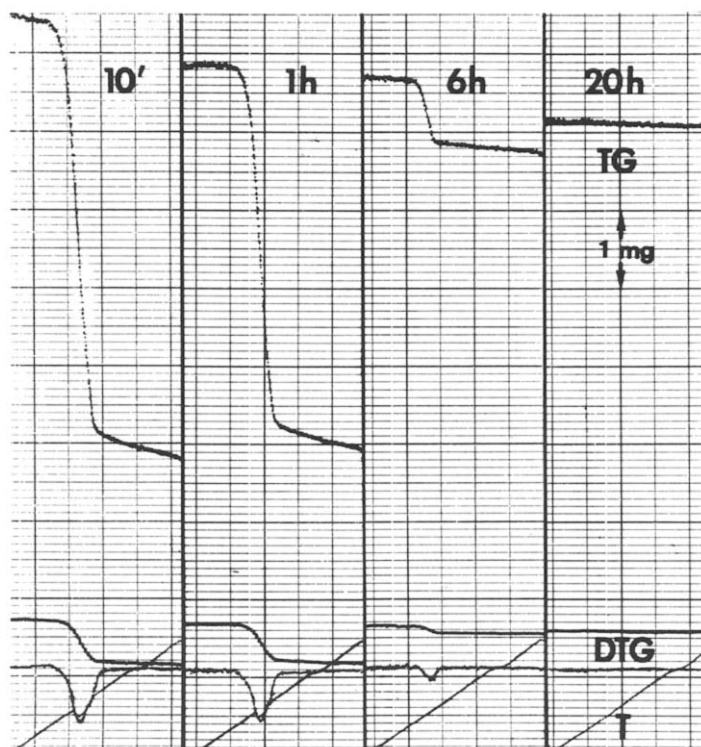


Fig. 2 TG curves of gypsum powder samples after reaction with BaCl₂ (2%) - solution for different times at 50°C

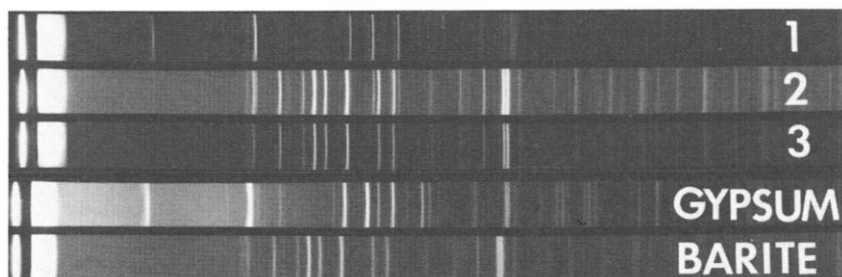


Fig. 3 X-ray powder patterns of mixtures 1 gypsum / 1 BaCl₂ · 2H₂O before and after reaction

Formation of BaSO₄ from BaCO₃

Another possibility for displacement reactions leading to the formation of BaSO₄ is to react BaCO₃ with different sulfate solutions. Corresponding experiments showed that all alkali sulfates reacted with BaCO₃ forming BaSO₄, especially at elevated temperature (80°). The reaction was slowest for (NH₄)₂SO₄ and for CaSO₄, which was also tried.

Besides of such displacement reactions in aqueous solutions also solid state reactions between alkali sulfates and BaCO₃ have been studied in the temperature range 500 to 700°C. Also here complete displacement was observed leading to BaSO₄ and to the corresponding alkali carbonates. The slower reaction rate in mixtures BaCO₃ / Na₂SO₄ could be increased by addition of Li₂SO₄ or NaCl. Mixtures of BaCO₃ and anhydrite did not show any reaction when heated in air up to 500°C, that is below the decomposition of CaCO₃ which would be formed. At higher temperatures e.g. 700°C however reaction took place with formation of BaSO₄ and CaO, in spite of the thermal stability of pure CaSO₄ up to at least 950°C. Such thermal displacement reactions between BaCO₃ and CaSO₄, or BaCO₃ and SrSO₄ respectively were investigated also by Nishino et al (5,6). Even at temperatures up to 900°C and in CO₂-atmosphere the CO₃' ↔ SO₄" exchange was not complete, but rather the formation of solid solution occurred. Furthermore exchange reactions between anhydrite and micas have been studied recently by Aitta et al (7,8). It was found that especially phlogopite reacts easily with CaSO₄ at temperatures above 800°C. Thereby the potassium in the mica is exchanged up to 80% by calcium. This displacement reaction allows to recover potassium from phlogopite in form of a water soluble K-Ca-sulfate.

The solid state exchange reaction between muscovite and CaSO₄ does not occur as easily as with phlogopite although the structures of these micas are very similar. In this case the best potassium recoveries were obtained by using CaCl₂ instead of CaSO₄.

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