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DISPLACEMENT REACTIONS IN GYPSUM. I. *

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ABSTRACT

Displacement reactions between gypsum cleavage plates and alkali hydroxide solutions were investigated by means of TG, DSC, microscopy and X-ray. The nucleation and crystallization of the reaction products—$Ca(OH)_2$ and $CaCO_3$—were followed in relation to time, temperature and concentration of the MeOH solutions.

INTRODUCTION

The term displacement reaction is generally applied to reactions between two or more components which involve the exchange of atomic constituents. The reaction products are formed in situ on, or within the solid starting phases. This type of reaction may occur between solid reaction partners, between solids and melts or solutions, or between solids and vapors. Displacement reactions are of importance in mineralogy, chemistry and materials science and technology, e.g., minerals formation (pseudomorphs), petrography (metamorphic reactions, pegmatites), industrial products (lithophone, silicon carbide), multiphase ceramics, composites, ion exchanged glasses and ceramics, corrosion of refractories by melts. In certain cases it is possible to predict or to correlate the product morphology and orientation when thermodynamic and structural data are available and when the diffusion and the solubility of the reacting species are known. The growth of the product phases frequently shows parabolic kinetics [1,2].

Displacement reactions where only two reactions partners are involved and where no ternary phases are formed, may be written as follows

(1) $A + BC \rightarrow AC + B(\text{or } AB + C)$

(2) $AB + CD \rightarrow AD + BC(\text{or } AC + BD)$

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Examples of such reactions are

(1) $Al + Fe_2O_3 \rightarrow Al_2O_3 + Fe$; $C + SiO_2 \rightarrow SiC + CO$

(2) $CaSO_4 + Na_2CO_3 \rightarrow CaCO_3 + Na_2SO_4$; $AlN + TiO_2 \rightarrow Al_2O_3 + TiN$

The present paper is concerned with displacement reactions in gypsum, $CaSO_4 \cdot 2H_2O$, which take place in aqueous solutions of different salts.

These reactions are of type 2 and result in the formation either of a Ca-compound or of a sulfate of lower solubility than gypsum. The reaction products are formed in situ within the gypsum crystal surface and grow further as long as the salt solution has access to it; they may show preferential orientation in certain cases [3]. Such displacement reactions in gypsum might be of importance in the formation of minerals. They can be observed and followed directly by microscope when cleavage plates of $CaSO_4 \cdot 2H_2O$ are used. Our present experimental studies deal with reactions between gypsum and solutions of alkali salts (MeOH, MeF, Me_2CO_3, $(Me, H)_3PO_4$, Me_2MoO_4, Me_2WO_4) whereby the corresponding, insoluble Ca salts are formed ($Ca(OH)_2$, CaF_2, $CaCO_3$, $Ca_3(PO_4)_2$, apatite, $CaMoO_4$, $CaWO_4$). Besides, the reactions between gypsum and chloride or nitrate solutions of Sr, Ba and Pb are also being studied, which lead to the formation of the insoluble sulfates, $SrSO_4$, $BaSO_4$ and $PbSO_4$. The nucleation and crystallization of some of these reaction products are followed and recorded in relation to time, temperature and concentration of the salt solutions.

EXPERIMENTAL

Rhombohedral-shaped cleavage plates of about 0.5 mm thickness and 10–12 mm edge length were used in the experiments. They could be prepared by inserting the edge of a razor blade parallel to the (010) plane of natural gypsum crystals (Salzburg, Austria) and applying slight pressure.

The various salt solutions were made with analytical grade chemicals (Merck). The microscopic investigations were carried out using a polarizing microscope (Amplival, C. Zeiss, Jena) equipped with a hot stage FP 82 and cameras for still or motion pictures. The gypsum cleavage plates were placed on microscope slides having a round cavity in the center. By the use of a syringe the salt solutions were introduced into this cavity, below the cleavage plates. Thereby, it was possible to follow the displacement reaction on only one side of the cleavage plate which was essential for reasons of light transmission and focusing (Fig. 1). For the simultaneous thermomicroscopic/DSC measurements the microscope hot stage FP 84 and the Mettler Thermosystem FP 800 were used [4]. The observation and microphotography of changes in the sample which is placed in a sapphire crucible, were carried

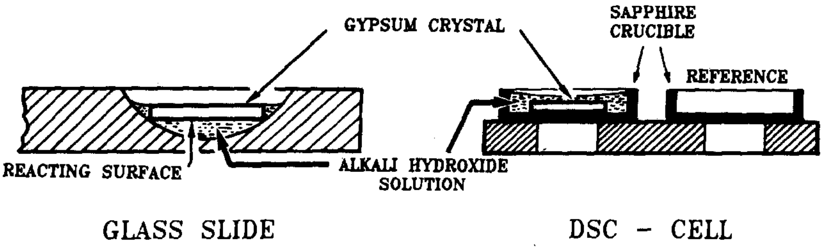

Fig. 1. Experimental set-up for microscopic and DSC investigations of displacement reactions in gypsum cleavage plates.

out in transmitted light. The microscope with the hot stage FP 84 or FP 82 and the control unit FP 80 is connected to a personal computer system with evaluation programs. X-ray investigations for identification of the reaction products were carried out with a Nonius X-ray camera, System Guinier, with Cu K_α-radiation.

RESULTS AND DISCUSSION

Displacement reactions between gypsum cleavage plates and alkali carbonate solutions have been studied first by Flörke [3] and later by Bayer and Wiedemann [5]. It was found that all three modifications of $CaCO_3$ (calcite, aragonite and vaterite) may be formed during such reactions depending on the alkali carbonate, on the concentration and on the temperature. Vaterite is formed preferentially in Na_2CO_3 and K_2CO_3 solutions of higher concentrations (≥ 2 M) and transforms gradually to calcite at room temperature, or to aragonite above 40°C. Figure 2 shows an SEM photograph of the surface of a gypsum cleavage plate after immersion in 2 M Na_2CO_3 at room temperature. Typical are the rather poorly crystallized vaterite spherulites which are partly transformed to calcite.

The present investigations were concentrated first on the reaction behavior of gypsum cleavage plates immersed in alkali hydroxide solutions of different concentrations, in which the time and the temperature were varied. Some of these results are summarized in Table 1. They proved that the rate of the displacement reaction $CaSO_4 \cdot 2H_2O + 2\ MeOH + x\ H_2O \rightarrow Ca(OH)_2 + Me_2SO_4 + (x+2)\ H_2O$ is favored by higher MeOH-concentration and higher temperatures. Since these experimental runs were carried out in air, some carbonate (calcite) was also formed especially in KOH and at lower concentration and after longer reaction time (Fig. 3). This formation of $CaCO_3$ could be avoided by using a CO_2-free gas atmosphere, preferably nitrogen or argon. The X-ray photographs of carefully separated and mounted reaction layers from the cleavage plates indicate a preferential orientation of the crystalline $Ca(OH)_2$ reaction layer. Figure 4 compares the X-ray pattern

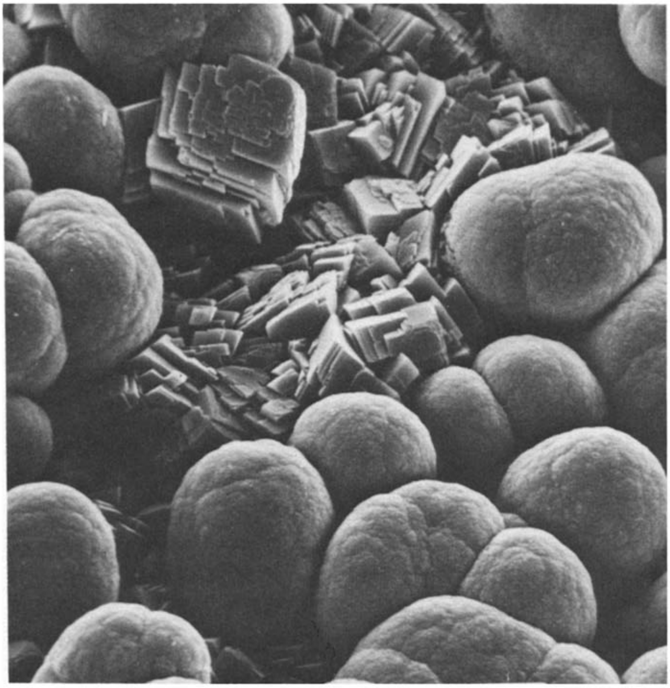

Fig. 2. Formation of vaterite and calcite on a gypsum cleavage plate after immersion in 2 M Na_2CO_3 (SEM photograph, 2000×).

of pure polycrystalline $Ca(OH)_2$ (Merck) to those of the reaction layers. It can be seen that the $Ca(OH)_2$ layer formed on gypsum immersed in 2 N NaOH gives much higher intensities for ($h00$) and ($hk0$)-reflections, especially for (110) and (200), as compared to the much weaker reflections ($h0l$), ($00l$) and (hkl). This is in agreement with the microscopic observations, that

TABLE 1

Reaction products on gypsum cleavage plates immersed in MeOH-solutions (Me = Li, Na, K, NH_4)

MeOH	Concentration (wt%)	8°C (20 h)	20°C (10 h)	60°C (4 h)	100°C (10 min)
NaOH	1	$Ca(OH)_2$	*$CaCO_3$* $Ca(OH)_2$	*$CaCO_3$* $Ca(OH)_2$	$Ca(OH)_2$
	10	*$Ca(OH)_2$* Na_2SO_4	$Ca(OH)_2$	$Ca(OH)_2$	$Ca(OH)_2$
KOH	1	–	$CaCO_3$	$CaCO_3$	$Ca(OH)_2$
	10	$Ca(OH)_2$	$Ca(OH)_2$	*$CaCO_3$* $Ca(OH)_2$	$Ca(OH)_2$
LiOH	1	–	$CaCO_3$	–	–
NH_4OH	25	–	$CaCO_3$	–	–

Fig. 3. Formation of calcite on cleavage steps of a gypsum crystal immersed in 5% KOH (100×).

hexagonal $Ca(OH)_2$ crystals are nucleated on cleavage steps and tend to grow first as thin hexagonal platelets, whereas the bulk of crystallites are oriented afterwards with their *c*-axis parallel to the cleavage plane of the gypsum crystal.

The following microphotographs (Figs. 5a and b) show these displacement reactions on gypsum cleavage plates which were immersed in (a) 2 N NaOH and (b) 25% NH_4OH at room temperature in air. For these microscopic studies the Mettler hot stage FP 82 was used. The experiments in 2 N NaOH showed that the crystallization of hexagonal $Ca(OH)_2$ crystals starts on cleavage steps. It proceeds slowly with the growth of an increasing number of crystals which are no longer oriented with their hexagonal *c*-axis perpendicular to the cleavage plane but rather parallel to it. Obviously the first steps of crystallization are of a topotactical or epitaxial nature. When KOH was used in the same concentration (2 M) the reaction was much too fast, therefore a 1 M solution was used.

Also, in this case, the reaction is still much faster than in NaOH and the $Ca(OH)_2$ crystallites formed are much smaller. However, a preferred growth of rather large calcite crystals was found to occur on the fracture edges of the gypsum cleavage plates (Fig. 3).

Experiments with saturated solutions of ammonia proved that here the reaction rate is very slow. No $Ca(OH)_2$ was formed but only calcite crystals (by CO_2 from the air) which adhered weakly to the cleavage surface Fig. 5b.

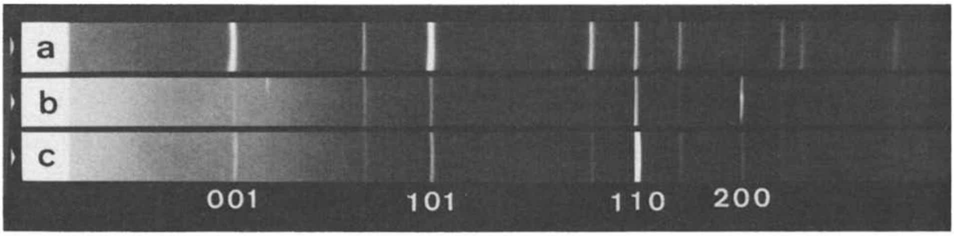

Fig. 4. X-ray powder diffraction photograph (CuK_α radiation) of precipitated $Ca(OH)_2$ (a), of $Ca(OH)_2$ reaction layers formed on gypsum immersed in 2 M KOH (b) and in 2 M NaOH (c).

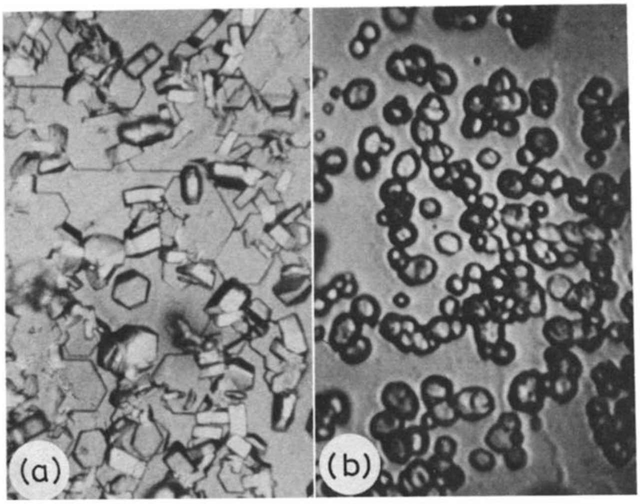

Fig. 5. Reaction layer on gypsum cleavage plates immersed (a), in 2 M NaOH, 1000× (b), 25% NH_4OH, 1860×.

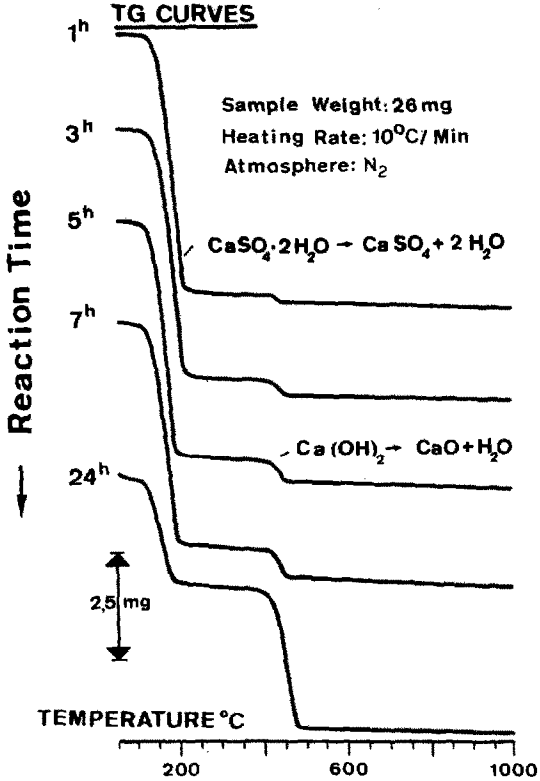

Fig. 6. TG curves of gypsum cleavages plates after reaction with 2 M NaOH in air at 16.5°C for different times (TG in N_2).

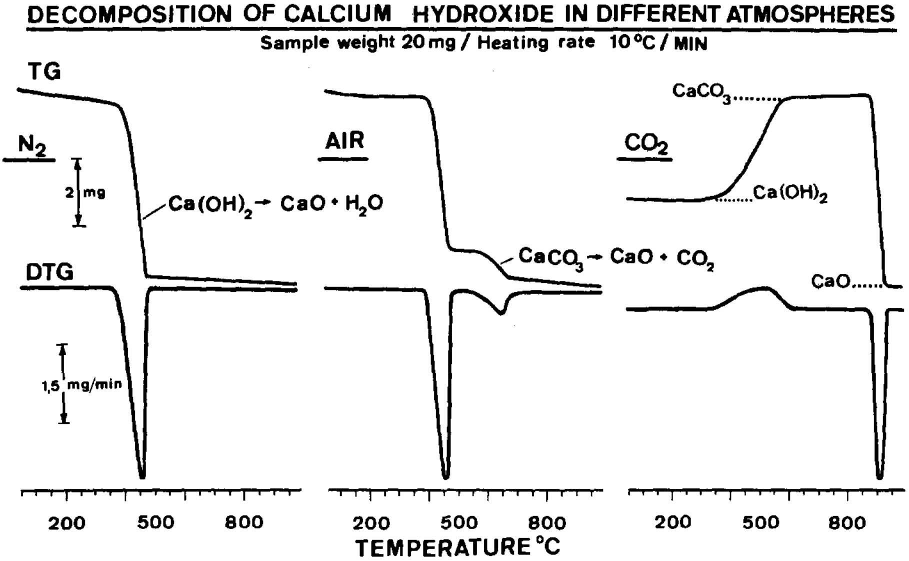

Fig. 7. TG and DTG curves of the decomposition of $Ca(OH)_2$.

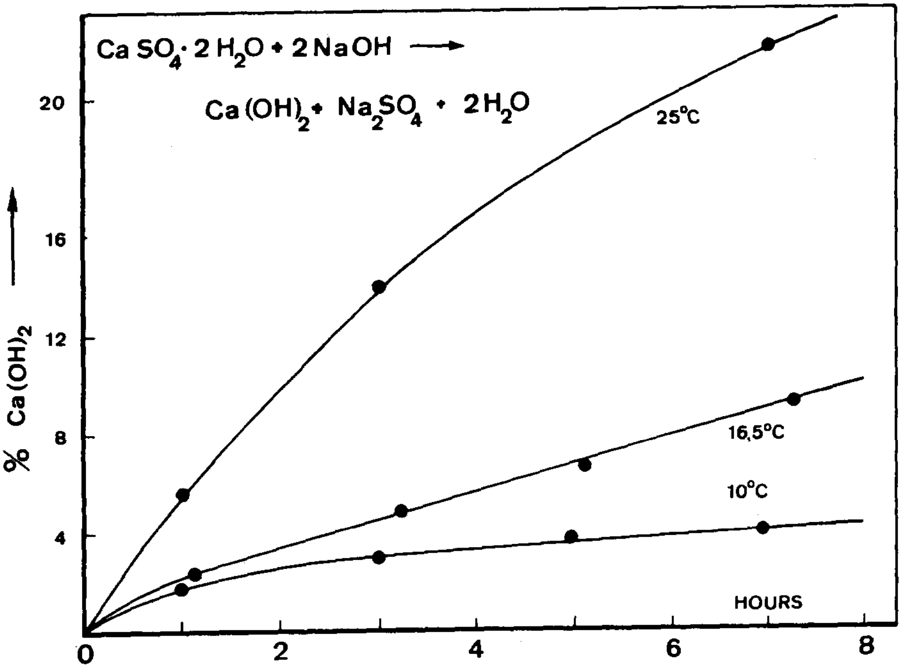

Fig. 8. Effect of temperature and time on the formation of $Ca(OH)_2$ on gypsum cleavage plate immersed in 2 M NaOH.

At the edges of the cleavage plates, preferred growth of spherulites occurs, which have a similar morphology to vaterite.

For a quantitative presentation of the reaction kinetics, TG and DTG curves were recorded and numerically evaluated using the Mettler TA 3000 system. The gypsum cleavage plates were immersed in NaOH, KOH, and 25% NH_4OH from 1–48 h each, carefully washed and dried, and heated in the thermoanalyzer up to 1000°C (N_2 atmosphere). The weight steps correspond to the decomposition of unreacted gypsum (100–200°C), to the decomposition of $Ca(OH)_2$ (400–500°C) and to the decomposition of $CaCO_3$ (550–800°C). Of course, the progress of the formation of $Ca(OH)_2$ is slowed down due to decreasing diffusion of alkali hydroxide through the reaction layer formed on the gypsum cleavage plate.

Figure 6 shows the TG curves of gypsum cleavage plates which were immersed in 2 M NaOH for different times at 16.5°C. The core of the

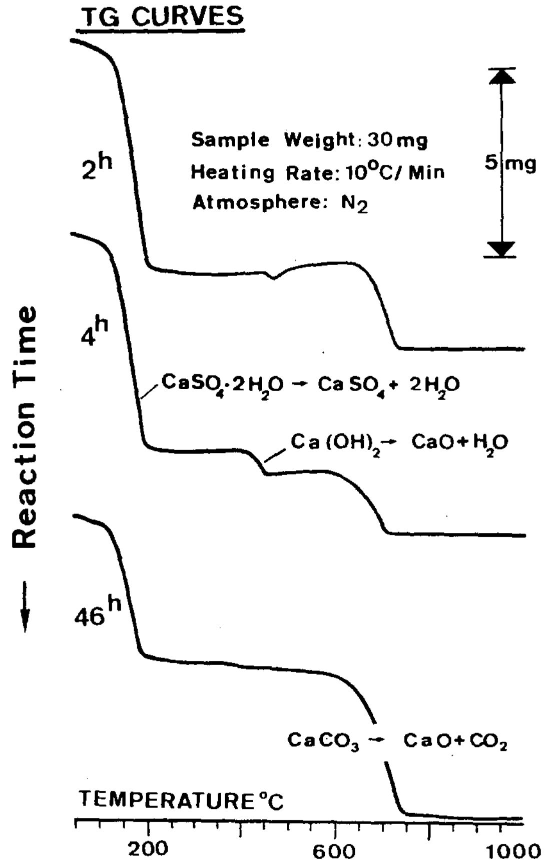

Fig. 9. TG curves of gypsum cleavage plates after reaction with 1 M KOH in air at 10°C for different times (TG in N_2).

sample was still unreacted gypsum, therefore there is a pronounced weight loss at 100–220°C, due to dehydration of gypsum. The curves prove that with increasing time more $Ca(OH)_2$ is formed and no $CaCO_3$ since these experiments were carried out in N_2. In order to clarify the decomposition of $Ca(OH)_2$ and its reaction to $CaCO_3$, pure $Ca(OH)_2$ was heated up in the thermobalance in nitrogen, in air and in pure CO_2. The TG and DTG curves shown in Fig. 7 prove that the formation of $CaCO_3$ from $Ca(OH)_2$ occurs within the decomposition range of $Ca(OH)_2$, e.g., from 350–500°C. Therefore, formation of $CaCO_3$ on gypsum cleavage plates which were immersed in NaOH is probably due to the reaction of the primarily formed $Ca(OH)_2$ with CO_2 from the air. A quantitative evaluation of the kinetics of the reaction between gypsum and NaOH is shown in Fig. 8. It proves that the formation of $Ca(OH)_2$ increases strongly with temperature and with time.

Figure 9 shows the TG curves of gypsum cleavage plates which were immersed in 1 M KOH for different times at 10°C. The first curve (after 2 h) shows very little $Ca(OH)_2$ and much more $CaCO_3$, besides unreacted gypsum. The second curve (after 4 h) shows more $Ca(OH)_2$, but a large amount of $CaCO_3$ and unreacted gypsum was present. Finally the third TG curve from a sample after 46 h KOH treatment, only shows the decomposition steps of gypsum and calcium carbonate. Practically no $Ca(OH)_2$ was present due to

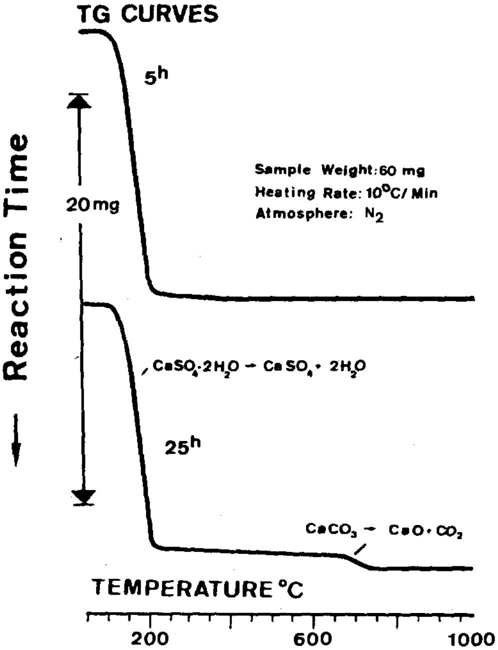

Fig. 10. TG curves of gypsum cleavage plates after reaction with 25% NH_4OH in air at 23°C for different times (TG in N_2).

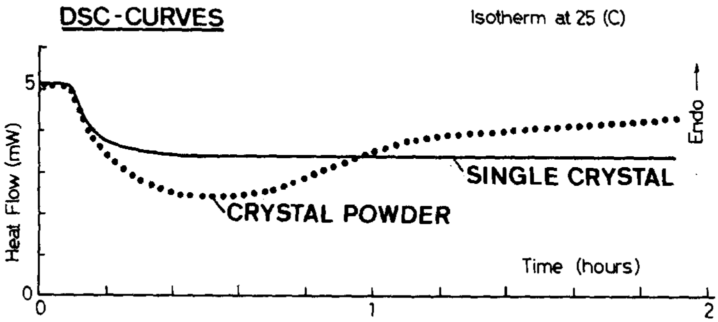

Fig. 11. DSC curves of gypsum powder and single crystal after immersion in 1 M KOH for 2 h at 25°C.

the enhanced reaction with CO_2 from the atmosphere which dissolved in KOH. This is a pronounced difference to the reaction behavior of gypsum cleavage plates in NaOH.

TG curves of gypsum cleavage plates which were immersed in 25% ammonia for different times at 23°C are shown in Fig. 10. The first curve after 5 h proves that the gypsum cleavage plate is still unchanged. Only after 25 h a small quantity of calcite is formed due to reaction with CO_2 from the air.

The DSC curve of a gypsum cleavage plate which was immersed in 1 M KOH is presented in Fig. 11. The deviation in the curve corresponds to the change in C_p due to the formation of $CaCO_3$. The displacement reaction is still not completed during the time of recording (2 h), therefore, the curve does not return to the zero line but rather runs parallel to it. Only when smaller samples are used in the order of 1–2 mg, complete reaction to $CaCO_3$ was observed.

CONCLUSION

Displacement reactions of the type $CaSO_4 \cdot 2H_2O + 2\ MeOH + x\ H_2O \rightarrow Ca(OH)_2 + Me_2SO_4 + (x+2)\ H_2O$, where Me = Na, K, NH_4, are favored by higher MeOH concentration and higher temperatures (40°C). When such reactions are carried out in air, $CaCO_3$ is also formed especially in KOH at lower concentrations and after longer reaction times. This formation of $CaCO_3$ can be avoided by using CO_2-free atmosphere. NH_4OH showed no displacement reaction with gypsum, only a small amount of $CaCO_3$ was formed after prolonged reaction time in air.

X-ray and microscopic studies proved that the crystalline $Ca(OH)_2$ reaction layer shows preferential orientation on the gypsum crystal surface. Obviously, the first steps in crystallization are of a topotactical or epitaxial nature. Quantitative evaluation of the reaction kinetics by means of TG and

DTG proved that the formation of $Ca(OH)_2$ increases strongly with time and temperature.

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