

FORMATION OF SCHEELITE (CaWO₄) AND POWELLITE (CaMoO₄) BY
DISPLACEMENT REACTIONS

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ABSTRACT

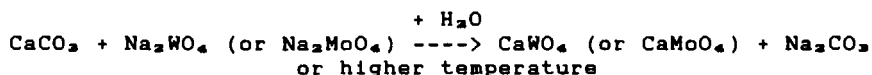
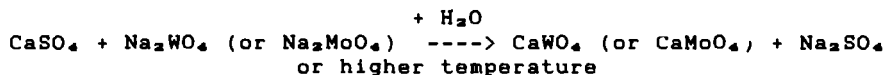
Displacement reactions between Ca-Sulfates or Ca-Carbonates, and Na-Tungstate or Na-Molybdate were investigated by means of TG, DSC, X-Ray and Microscopy. The reaction partners were used in form of single crystals or powders (Ca-compounds), and as solutions, melts or solids (Na-compounds). In some of such reactions the first steps of crystallization are apparently topotactical. As expected there is a pronounced effect of temperature, time and sample configuration on the formation and crystallinity of CaWO₄ and CaMoO₄.

INTRODUCTION

Displacement reactions are characterized by the formation of the reaction products in situ on, or within a solid starting phase. Such reactions are frequently observed between solids, between solids and melts or solutions, or between solids and vapors.

Examples for displacement reactions are the formation of minerals (metamorphic and metasomatic reactions, ore deposits), industrial products (lithopone, silicon carbide), reaction-sintered ceramics, ion-exchanged glasses, corrosion of refractories by melts.

The present paper describes the results of such displacement reactions between calcium sulfates (gypsum, anhydrite) or calcium carbonates (calcite, aragonite), and sodium tungstate or sodium molybdate respectively. The calcium compounds were used either in form of single crystal plates or powders, the sodium salts as aqueous solutions or as solids and melts in the high temperature experiments. The corresponding displacement reactions may be written as follows:



The degree of reaction could be determined from X-ray powder photographs, or from the amount of unreacted gypsum and from the melting peak of Na₂SO₄ by means of DSC/TG-analysis. Of main interest in the present investigations was at first the formation of scheelite.

EXPERIMENTAL

Materials: Well-crystallized mineral samples were either cleaved into 0.5 mm thick plates (gypsum, anhydrite, calcite) or cut with a diamond blade (aragonite). The same minerals were also used in form of fine powders (<60 μm). $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ were of analytical grade (Merck). The aqueous solutions prepared with these salts had a concentration of 1 and 6 WT% respectively. The various displacement reactions were carried out with single crystal plates and powders which were reacted at different temperatures (20-100 $^\circ\text{C}$) with an excess of the aqueous Na-Tungstate or Na-Molybdate solutions for different times.

Instrumental: Microscopic investigations were carried out using a polarizing microscope with a hot stage FP 84, and a camera. The single crystal 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. Thermomicroscopic/DSC-measurements were carried out with the microscope hot stage FP 84 and the Mettler Thermosystem FP 800. The TG and DTG curves were recorded with the Mettler Thermo-analyzer 1 and with the Mettler Thermosystem 3000 & 4000 / TG 50 in air. The heating rates were 2 $^\circ\text{C}/\text{Min.}$, 6 $^\circ\text{C}/\text{Min.}$ and 8 $^\circ\text{C}/\text{Min.}$ respectively. The starting and the reaction products were analyzed by X-ray powder techniques (Guinier, de-Wolff camera with CuK - radiation). The SEM pictures were taken with a Cambridge electron microscope.

RESULTS AND DISCUSSION

Single crystal plates of the Ca-sulfates and Ca-carbonates were immersed in the sodium salt solutions for 0.5 hour at room temperature. In accordance with the different solubility of these minerals in the aqueous solutions, the reactivity increased in the same order, that means from the least soluble Ca-carbonates to the slightly soluble anhydrite and gypsum. Gypsum was the most reactive mineral with Na-tungstate and also with Na-molybdate solutions. The cleavage face was covered completely after 0.5 hour with scheelite or powellite respectively. Fig. 1 shows the differences in reaction of the four Ca-minerals with the Na-tungstate solution. The reaction product CaWO_4 is formed as rounded spherulites and not as well-shaped crystals. Lowering the concentration of the Na-tungstate solution to 1% and increase of the reaction time to 48 hours showed a positive effect on the morphology of scheelite.

The EDAX-analysis of the reaction layer formed on gypsum cleavage plates after immersion in 1%-Na-salt solutions is shown in Figure 2.

Besides the different solubility of the Ca-minerals also their structure has some effect on the reaction behavior. One may assume that during the displacement reaction only the SO_4^{2-} and the CO_3^{2-} groups of the minerals are replaced by the WO_4^{2-} and MoO_4^{2-} groups from the solution. If the coordination of the Ca-ions in the mineral is close to that in scheelite or powellite, the reaction may proceed faster. This is true in the case of the Ca-sulfates which have 8-fold oxygen coordination, similar to

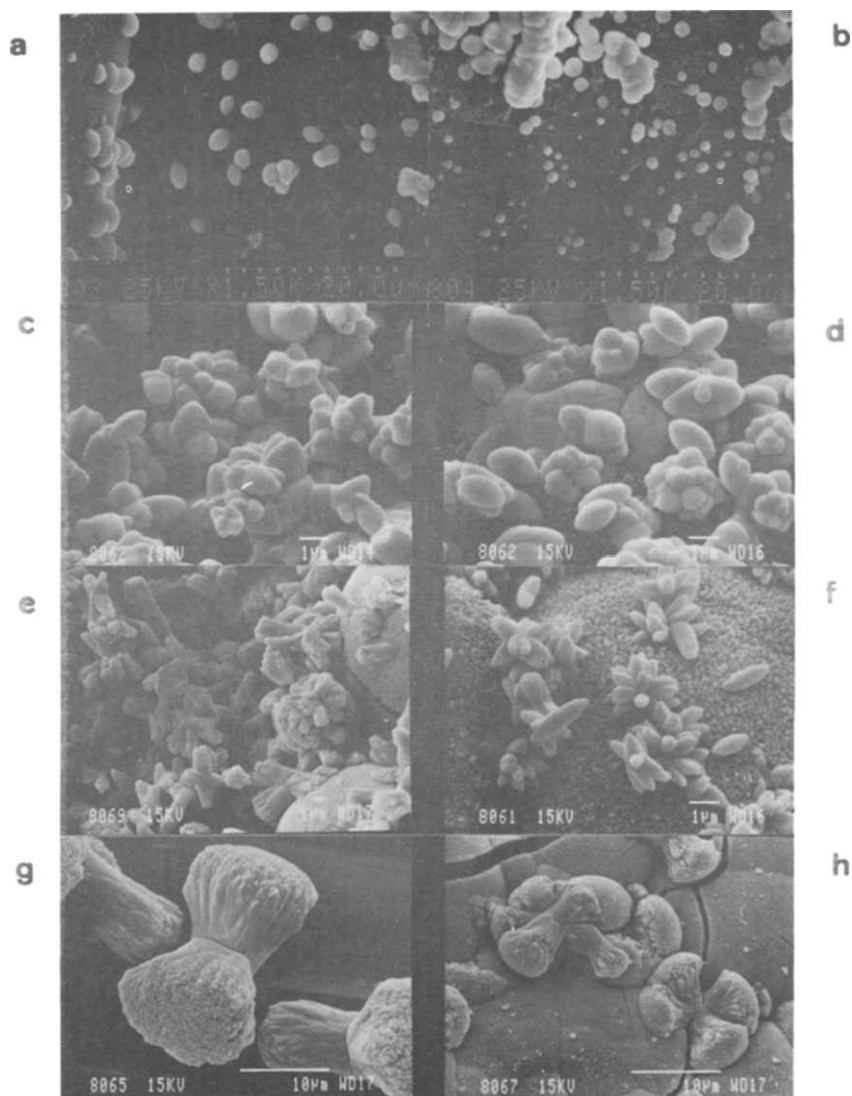


Fig. 1: SEM-photographs of aragonite- and calcite crystal faces after 30 minutes immersion in 6% Na_2WO_4 (a,b) at RT (1500x). Reaction layer after immersion for 48 hours in 1% Na_2WO_4 -solution at RT (c=aragonite (10'000x), d=calcite (10'000x), e=anhydrite (9'500x), f=gypsum (5'000x)). Morphology of scheelite crystals formed on calcite (g) 3'000x and on gypsum (h) 1'500x.

that of the Ca-ions in scheelite and powellite. On the other hand the much less reactive carbonates calcite and aragonite have coordination numbers 6 and 9 respectively.

Powder reactions of the same minerals were also carried out in the Na-salt solutions. The pronounced effect of time and temperature on the formation of scheelite and powellite is obvious from Figure 3.

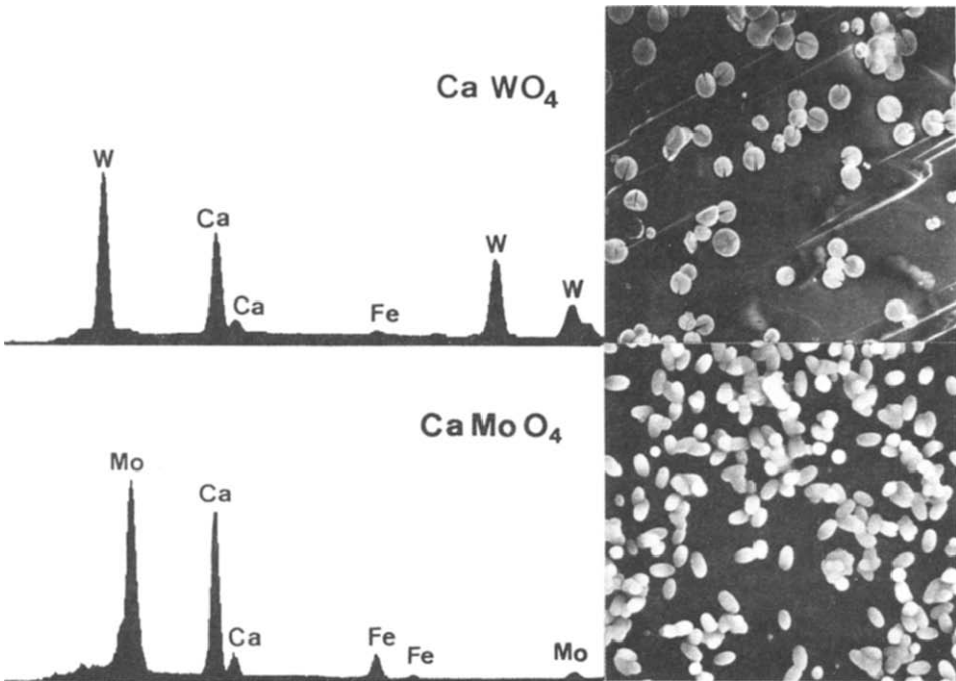


Fig. 2: EDAX-analysis and SEM-photographs of the reaction layers formed on gypsum cleavage plates after 30 Min. in 1% Na-tungstate and Na-molybdate solutions respectively. (SEM magnification Ca-tungstate 200x Ca-molybdate 2000x)

Some interesting observations may be summarized as follows: The reaction rate is increased when raising the temperature (RT to 50 °C). The reaction product scheelite shows improved crystallinity after longer times and especially on calcite as compared to the other minerals. Gypsum and anhydrite powders react rather rapidly with the tungstate - or molybdate solutions. In the case of the carbonates, calcite reacts much faster than aragonite.

For a presentation of the reaction kinetics in the system gypsum (cleavage plates) - Na_2WO_4 (aqueous solution), the amount of unreacted gypsum was determined from TG in function of time and temperature. Figure 4 shows that the reaction rate increases slightly with temperature, but that it is not completed after the rather short reaction times (4 hours). Especially at the lower temperatures pronounced effects of the surface morphology of the cleavage faces on the rate of reaction were observed.

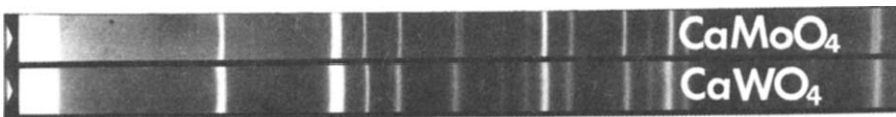


Fig.3: X-ray powder patterns of reaction products formed after immersion of Ca-mineral powders in Na-tungstate and Na-molybdate solution (6%, different times and temperatures).

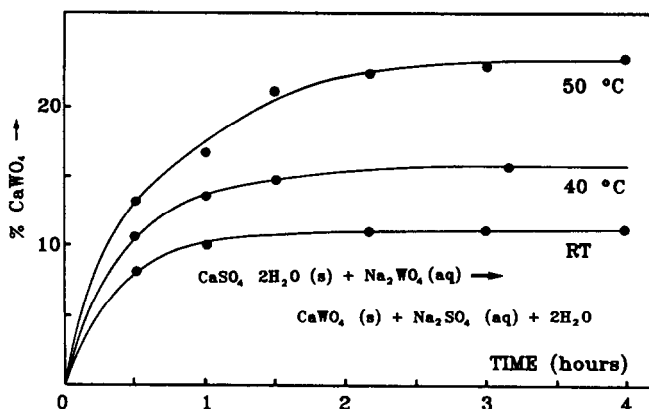


Fig.4: Effect of temperature and time on the formation of scheelite on gypsum cleavage plates immersed in 6% Na_2WO_4 -solution.

Further experiments were carried out on equimolar mixtures between gypsum or anhydrite and $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ with a METTLER TA 4000/DSC 25. They proved that the reaction proceeds already in the solid state at about 680 °C, if slow heating rates (1 °C/Min) are used. With faster heating rates (8 °C/Min.) the formation of scheelite and Na_2SO_4 was not complete even at 750 °C, which is well above the melting temperature of Na_2WO_4 (695.5 °C). Some unreacted Na_2WO_4 still remains which solidifies during cooling down. Fig. 5 shows the DSC-curves of the reaction mixture, as compared to pure $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$. After dehydration of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ from 100 to 600 °C the transformation peak of Na_2WO_4 can be seen at 588 °C, and the melting point at 695.5 °C. Samples heat treated isothermally at 680 °C, 750 °C, 850 °C for 10 hours each did not show any transformation or melting peak or Na_2WO_4 but only the melting peak of Na_2SO_4 (884 °C), which is formed as reaction product in addition to CaWO_4 .

DSC Curves

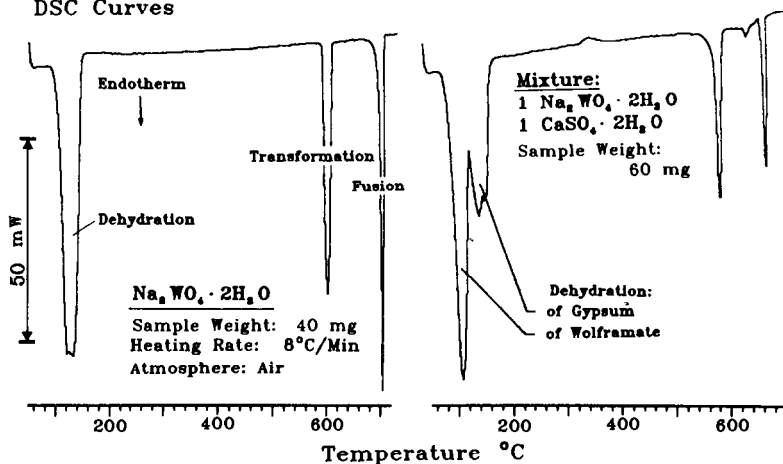


Fig.5: DSC-curves of the reaction mixture 1 $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ / 1 $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ as compared to pure $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$.

CONCLUSIONS

Displacement reactions between Ca-minerals and Na-tungstate or Na-Molybdate were found to occur in solutions at room temperature but also in the solid state at higher temperatures. Besides temperature, time and concentration of the Na-salt solutions also the kind of Ca-mineral and its morphology (single crystal plate, powder) have a pronounced effect on the reaction rate. As expected the high surface area of the powders increases the reaction rate drastically. Generally the slightly more soluble Ca-sulfates (gypsum, anhydrite) react much faster than the Ca-carbonates (calcite, aragonite). There is also a closer structural relation between the sulfates and the reaction products scheelite and powellite. Calcite reacted much faster than aragonite. Fairly well-crystallized scheelite and powellite were formed on single crystal-plates of gypsum, anhydrite and also calcite in dilute Na-salt solutions (1%).

REFERENCES

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