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INVESTIGATION OF SELENITE DEHYDRATION IN AQUEOUS SOLUTIONS OF CERTAIN CHLORIDES

The influence of Li^+ , Mg^{+2} and Ca^{2+} ions on selenite hydrothermal dehydration was investigated in this paper. Dehydration reactions were performed in 3 M solutions of the relevant chlorides. The results obtained prove the existence of correlation between ions properties and kinetics reaction as well as the products properties.

Introduction

During dehydration of $\text{CaSO}_4 \times 2\text{H}_2\text{O}$, products, of different properties can be obtained. These products can be composed of smooth, compact, needle-like monocrystals that are well known as high-grade $\alpha\text{-CaSO}_4 \times 0.5 \text{H}_2\text{O}$ crystals on one hand, and on the other, they can be composed of white, soft and porous particles of irregular shape, so called $\beta\text{-CaSO}_4 \times 0.5 \text{H}_2\text{O}$ product. Variation in quality of hemihydrates results from different specific particle surface that absorb different quantities of water. Therefore, mechanical properties of dehydrates obtained by mixing with water are considerably different.

According to the published data, the above mentioned different modifications can be formed in different ways. Namely, β is formed through reactions in a solid phase (so called "dry" methods) while α -modification is formed through reactions in solution (so called "wet" method). Contrary to dehydration of dihydrates through "dry" reactions that have been thoroughly studied and are well known, formation of hemihydrates by "wet" procedures has proved to be very complex and still controversial [1,3]. Some data indicate a "through solution" reaction

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while some other suggest the different mechanism of the same reaction, namely that crystals growth can occur either from the solution or as a supplement to a reaction in a solid phase [2]. A particularly important fact is the lack of data on hydrothermal dehydration reaction that is listed in the most recently established "wet" methods.

In this paper the reaction of hydrothermal dehydration in CaCl_2 , MgCl_2 and LiCl solutions has been investigated under identical experimental conditions. Other alkaline and alkaline-earth metal chlorides prove not to be suitable for such application as their ions form more (Na^+) or less (Sr^{2+}) soluble and complex compounds with Ca^{2+} and SO_4^{2-} ions and due to lower solubility of the same in the latter (BaCl_2) case.

Experimental

All experiments were performed in a charge reactor with perfect mixing (400 rev/min) using 10 g of selenite (purity of 99.87% having granulation of $1.0 + 0.50 \text{ mm}$ in 50 cm^3 of solution. After experiment the product was separated by vacuum filtration and washed with boiling water. Both the composition of products and dehydration time (t_d) were determined by qualitative IR analysis. The α -hemihydrates time formation (t_α) was determined by microscopic analysis while the rate of their formation $V_{\alpha f}$ was estimated on the basis of determined yield for t_α time.

Results and Discussion

The results are presented in Table 1. They show that when

Table 1

The influence of different ions on selenite dehydration

Number of experiment	3 M aqueous solution of	Properties of dehydration reaction			Properties of product	
		t_d (min)	t_α (min)	$V_{\alpha f}$ (g/min)	appear. in t_d	aver. length and width in t_α (μm)
1	CaCl_2	70	80	0.076	α and β	72 ; 6
2	MgCl_2	30	30	0.165	α	144 ; 7
3	LiCl	28	28	0.225	α	45 ; 2.5

salt solutions are used for selenite thermal treatment, the hemihydrate formation rate leads to different properties of obtained products. The α -hemihydrate is produced in either MgCl_2 or LiCl solutions while in the CaCl_2 solution the product is a mixture of both hemihydrates, the complete transformation of which into α form will follow afterwards. Different granulation of the final product was evident, as well. It was also noticed that the hemihydrate was most rapidly formed when using LiCl solution while the opposite effect was observed in the CaCl_2 solution.

The observed differences are caused by presence of various ions in the mentioned solutions as well as by their different influence on the solid phase. These solutions are concentrated electrolyte solutions where extremely strong attaching forces prevail among ions and cause formation of charged and uncharged particles (composed of ions). This phenomenon is somewhat more strongly expressed in those solutions containing ions of greater charges and dimensions which are therefore less "active" (like solution with Ca^{2+}) in comparison with those containing ions of smaller dimensions (Mg^{+}) and particularly of less charge (Li^{+}), where product formation is slower. The evident difference in products granulation results from various number of crystallization centers in given solutions. Namely, the greater the number of particles in electrolyte solution is, the lower is the products granulation and the other way round.

It can be concluded, on the basis of obtained results, that a dependence exists between ions activity and dehydration kinetics, on one side, and products properties on the other side, and perhaps the reaction mechanism (a slower reaction throughout the solid phase or a more rapid reaction in solution in the presence of less or more active ions).

Literature

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Streszczenie

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Przebadano wpływ jonów Li^{+} , Mg^{+2} i Ca^{+2} na hydrotermalną dehydratację selenitu.