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## ISOAMYL ALCOHOL AS A MODIFIER OF THE GROWTH OF CRYSTALS OF $\alpha$ -CaSO<sub>4</sub> · 0.5H<sub>2</sub>O PRODUCED FROM MINERAL SELENITE

A process was developed for obtaining  $\alpha$ -hemihydrate by the "wet" method, i.e., by boiling selenite in a liquid medium at atmospheric pressure. Pure water and aqueous chlorides of Li, Na and K were used as a liquid medium. After the addition of isoamyl alcohol to pure water, no significant differences in the dimensions of crystals of  $\alpha$ -CaSO<sub>4</sub> · 0.5H<sub>2</sub>O were noticed. On the other hand, addition of the same alcohol to a solution of aqueous LiCl resulted in the formation of large aggregates of crystals. And finally, the addition of isoamyl alcohol to aqueous NaCl and KCl, leads to crystals of  $\alpha$ -CaSO<sub>4</sub> · 0.5H<sub>2</sub>O with a larger length-to-width ratio. From these results it follows that isoamyl alcohol, as a surface active agent, plays an important role in the regulation of the growth of  $\alpha$ -hemihydrate crystals.

### Introduction

The utility of  $\alpha$ -hemihydrate of calcium sulphate depends, to a great extent, on the size and appearance of its crystals. When  $\alpha$ -hemihydrate consists of long, smooth needle-or prism-like monocrystals, with a high length-to-width ratio, it exhibits better mechanical characteristics and wider practical significance. The influence of phosphoric acid, magnesium hydroxide and some sulphates and carbonates on the size of  $\alpha$ -hemihydrate crystals produced with appropriate autoclave processes, has been reported in literature [1,2]. Generally, the influence of some substances on the size of hemihydrate crystals, produced during the boiling of an aqueous suspension of CaSO<sub>4</sub> · 2H<sub>2</sub>O, has

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not been fully explained and described. The processes reported in literature consisting of boiling, under atmospheric pressure,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  in aqueous solutions of salts and solutions of salts with surface active agents, with the aim of producing crystalline  $\alpha\text{-CaSO}_4 \cdot 0.5\text{H}_2\text{O}$  of high quality, have been mentioned in literature [3,4], but not studied widely. On the basis of our previous results [4], we concluded that processes involving boiling the mineral in aqueous solutions of appropriate salts have considerable advantage over those involving boiling in pure water only. By using solutions with the same anions, we also confirmed [4,5] that in solutions with smaller cations ( $\text{Mg}^{2+}$ ,  $\text{Li}^+$ ), larger crystals of  $\alpha\text{-CaSO}_4 \cdot 0.5\text{H}_2\text{O}$  were obtained than in solutions with greater cations ( $\text{K}^+$ ,  $\text{Ba}^{2+}$ ,  $\text{Sr}^{2+}$ ). On the other hand, by the use of solutions with the same cations, we found that in solutions with greater anions ( $\text{Br}^-$ ,  $\text{J}^-$ ), larger crystals of  $\alpha\text{-CaSO}_4 \cdot 0.5\text{H}_2\text{O}$  were formed than in solutions containing smaller anions ( $\text{Cl}^-$ ,  $\text{NO}_3^-$ ), [6]. Literature data indicate [7] that there is more expressive tendency of a cation to hydrate if its size is smaller; and of an anion, if its size is greater. Because of this, it can be concluded that the existence of hydrated ions in the solutions facilitate the formation of larger crystals of  $\alpha\text{-CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ . This is in close agreement with literature data [8] indicating that the formation, development and growth of crystals are a "through-solution" process, and the properties of the ions in the solutions is one of the most important factors affecting the size of crystals.

In this work, we investigated the influence of the surface active agent (isoamyl alcohol) on the size of  $\alpha\text{-CaSO}_4 \cdot 0.5\text{H}_2\text{O}$  crystals produced by boiling  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  in water and in the aqueous solutions of chlorides of Li, Na, and K. The tests were analogous to literature studies [9], according to which surface active agents are used to modify the growth of crystals in the process of producing cement.

#### Experimental work

High-purity selenite, containing only 0.11% impurities, was used. The concentration of salts in the solutions was 3 moles of salt in 1000  $\text{cm}^3$  of distilled water. In all the experiments, the same fraction of selenite ( $-1 \pm 0,5$  mm) was used. In the first series of experiments, selenite was treated with boiling distilled water alone, and boiling aqueous LiCl, NaCl, and KCl under atmospheric pressure. In the second series, selenite was boiled in aqueous solutions of the same salts with an added 2  $\text{cm}^3$  of isoamyl alcohol. In all the experiments, the same

sample of mineral (5 g) and the same volume of solution ( $100\text{ cm}^3$ ), was used. The time of boiling was also the same in all the experiments (90 min). The experiments were performed with a charge reactor at a constant mixing rate (600 rpm) of the magnetic stirrer. After each experiment, solid products were separated from the solutions by vacuum filtration, and then washed with boiling distilled water. The drying of solids was performed in a dryer, at  $105^\circ\text{C}$ , for 90 minutes. The products were examined utilizing qualitative IR-analysis (in order to determine their chemical compositions), a binocular microscope (in order to determine the size, shape and other characteristics of the crystals), and qualitative analysis (Perkin-Elmer spectrophotometer, type 397).

### Results and discussion

The infrared spectrum of the product obtained by boiling selenite in an aqueous solution of LiCl is presented in Fig. 1. A comparison of this spectrum with the IR spectrum of  $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$  from literature [10] showed that they were identical. Moreover, the IR spectra of all other products, obtained from both series, were identical with the standard IR spectrum of  $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ . Thus, it may be concluded that  $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$  was produced in all the experiments.

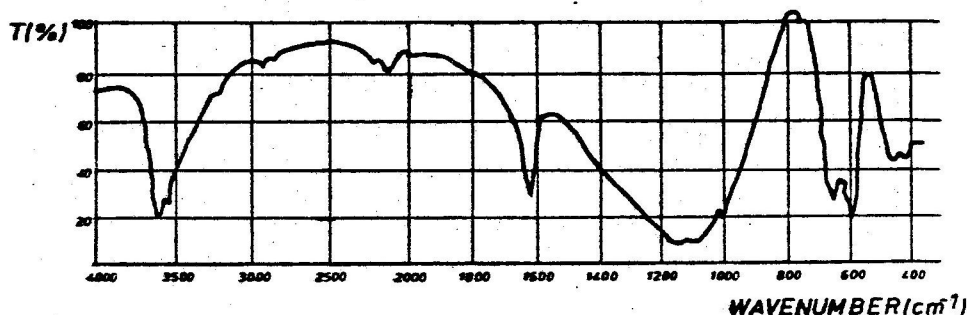


Fig. 1. Infrared spectrum of product formed in solution of LiCl

Results of our investigation of the shape and size of the crystals produced are presented in Table 1. It follows from Table 1 that the attempt to produce  $\alpha\text{-CaSO}_4 \cdot 0.5\text{H}_2\text{O}$  crystals with larger dimensions by adding isoamyl alcohol to water was not successful. In this experiment, crystals similar to the crystals obtained by treating the mineral in pure boiling water were formed. They were very small microcrystals, and they formed very porous aggregates (experiments 1 and 2). By treating selenite in boiling aqueous LiCl containing isoamyl alcohol, very large

Table 1

Characteristics of  $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$  crystals produced by thermal treatment of selenite in an aqueous solutions

N°	Solution	Dimensions of crystals*		Appearance of crystals
		Width (mm)	Length (mm)	
1	$\text{H}_2\text{O}$	-	-	Soft and porous aggregates of needle like microcrystals
2	$\text{H}_2\text{O} + \text{iso-C}_5\text{H}_{11}\text{OH}$	-	-	Soft and porous aggregates of needle - like microcrystals, larger than in experiment N° 1
3	$\text{LiCl}$	0,017	0,150	Needle - like monocrystals
4	$\text{LiCl} + \text{iso-C}_5\text{H}_{11}\text{OH}$	1,200	2,000	Translucent, very hard and compact plate - like aggregates of crystals
5	$\text{NaCl}$	0,016	0,130	Needle - like monocrystals
6	$\text{NaCl} + \text{iso-C}_5\text{H}_{11}\text{OH}$	0,015	0,140	"
7	$\text{KCl}$	0,007	0,050	"
8	$\text{KCl} + \text{iso-C}_5\text{H}_{11}\text{OH}$	0,005	0,060	"

\* Average values. \*\* The values were not measured.

aggregates of crystals of hemihydrate were produced. They were larger than those of the original particles of selenite. The crystals were different from the crystals produced in aqueous  $\text{LiCl}$  without alcohol (experiments 3 and 4). They were also different from all other crystals produced in this work, and from all the crystals produced in our previous works [4,5,6], with respect to both their size and shape (plate-like). These crystals are also very translucent and consequently they are very hard. Finally, from aqueous  $\text{NaCl}$  and  $\text{KCl}$  containing isoamyl alcohol, needle-like monocrystals of  $\alpha\text{-CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ , with a larger length-to-width ratio than those from solutions of the same salts without alcohol were formed (experiments 5,6,7,8).

Surface active agents may be used as modifiers of crystal growth [9]. This is due to their adsorption on the surface of solid particles, thus forming, surface thin layers a thin layer of surface active agent on the particle surface changes the rate of water diffusion, which is very important for the formation and growth of crystals.

From the results of this research, it can be concluded that isoamyl alcohol (a surface active agent) has an active role in the regulation of the crystal growth of  $\alpha\text{-CaSO}_4 \cdot 0.5\text{H}_2\text{O}$  (experiments 3-8).

The addition of isoamyl alcohol to the aqueous chlorides of Li, Na and K permits its adsorption and the formation of a thin layer on the surface of the selenite particles. This thin layer reduces the rate of water diffusion, and in this way, facilitates the formation of larger crystals in aqueous LiCl, and longer crystals in aqueous NaCl and KCl.

#### References

1. C. Genin, P. Blazy, J. Yvon, Congrès de la société de l'industrie minière, Paris 1983, p. 633.
2. C. Genin, J. Yvon, P. Blazy, XVth IMPC, Tome I, Cannes 1985, p. 142.
3. Yu.M. Butt et al., Tekhnologiya toploizolyatsionnykh materialov, Izdatelstvo Vysshaya Shkola, Moskva 1966, p. 95.
4. S. Marinković, A. Kostić-Pulek, S. Popov, Fizykochemiczne problemy mineralurgii, Zeszyt Nr 17, 1985, p. 157.
5. A. Kostić-Pulek, S. Marinković, R. Tomanec, 25th Symposium "Hornicka, Příbram ve Vědě a Technice", 1986, p. 486.
6. S. Marinković, A. Kostić-Pulek, R. Tomanec, XXVIII Savetovanje Hemicara Srbije, Beograd 1986.
7. A.P. Wells, Structural inorganic chemistry, Oxford, 1952, p. 435.
8. J.A. von Fraunhofer, Scientific Aspects of Dental Materials, Butterworth, London and Boston, 1975, p. 63.
9. A.A. Abramzon, Poverkhnostno aktivnye veshchestva, Izdatelstvo Khimiya, Leningrad, 1981, p. 297.
10. R.A. Nyquist, R.O. Kagel, Infrared Spectra of Inorganic Compounds, Academic Press, New York and London, 1971, p. 121.

#### STRESZCZENIE

Marinković S., Kostić-Pulek A., Tomanec R., Popov S., 1987. Alkohol izoamylowy jako modyfikator wzrostu kryształów  $\alpha$ -CaSO<sub>4</sub>·0,5H<sub>2</sub>O produkowanego z naturalnego selenitu. Fizykochemiczne Problemy Mineralurgii 19; 269-274.

Opisano metodę produkcji  $\alpha$ -CaSO<sub>4</sub>·0,5H<sub>2</sub>O z selenitu przez gotowanie w cieczy pod ciśnieniem atmosferycznym. Jako cieczy użyto czystej wody oraz wodnych roztworów chlorków litu, sodu i potasu. Gotowanie w wodzie z dodatkiem alkoholu izoamylowego nie wpływa zasadniczo na wymiary kryształów  $\alpha$ -CaSO<sub>4</sub>·0,5H<sub>2</sub>O. Jednakże dodatek tego alkoholu do wodnego roztworu LiCl prowadzi do tworzenia się dużych krystalicznych agregatów.

Gotowanie w roztworach NaCl i KCl z dodatkiem alkoholu izoamylowego pozwala uzyskać kryształy  $\alpha$ -CaSO<sub>4</sub>·0.5H<sub>2</sub>O z jeszcze większym stosunkiem długości do szerokości. Z opisanych badań wynika, że alkohol izoamylowy, będąc związkami powierzchniowo-czynnym, odgrywa ważną rolę w regulacji wzrostu kryształów  $\alpha$ -półhydratu ( $\alpha$ -CaSO<sub>4</sub>·0.5H<sub>2</sub>O).

#### СОДЕРЖАНИЕ

С.Маринкович, А.Костич-Пулек, Р.Томанец, С.Попов, 1987. Изоамиловый спирт, как модификатор увеличения кристаллов  $\alpha$ -CaSO<sub>4</sub>·0.5H<sub>2</sub>O, производящегося из натурального селенита, Физикохимические вопросы обогащения, I9; 269-274.

Описан метод получения  $\alpha$ -CaSO<sub>4</sub>·0.5H<sub>2</sub>O из селенита в жидкости под атмосферным давлением. В качестве жидкости использована чистая вода, а также водные растворы хлоридов лития, натрия и калия. Варение в воде с добавкой изоамилового спирта принципиально не влияет на размеры кристаллов  $\alpha$ -CaSO<sub>4</sub>·0.5H<sub>2</sub>O. Однако, добавка этого спирта в водный раствор LiCl<sub>2</sub> ведет к образованию больших кристаллических агрегатов. Варение в растворах LiCl<sub>2</sub> и NaCl с добавкой изоамилового спирта позволяет получить кристаллы  $\alpha$ -CaSO<sub>4</sub>·0.5H<sub>2</sub>O с еще большим отношением длины к ширине. Из описанных исследований следует, что изоамиловый спирт, являясь поверхностноактивным соединением, играет важную роль в регуляции увеличения кристаллов