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## CORRELATION BETWEEN SPECIFIC SURFACE AREA OF ANHYDRITE OBTAINED FROM PHOSPHOGYPSUM AND MECHANICAL PROPERTIES OF ANHYDRITE CEMENT

The study has been conducted in order to determine the influence of specific surface area of anhydrite produced from phosphogypsum by recrystallization in aqueous sulphuric acid as well as conditions of material storage on the mechanical strength of hardened anhydrite cement. Portland cement 35 and potassium sulphate were used as accelerators of setting and hardening process. The research confirmed that the hardening process and mechanical properties of the cement discussed are strongly connected with specific surface area and storage conditions. However the usage of mechanical activation of the anhydrite cement is limited.

### 1. INTRODUCTION

As the production of wet-process phosphoric acid increases, the problem of phosphogypsum utilization becomes increasingly urgent. Jarosiński and Mazanek (1993), and Osiecka (1980) have described practical conditions for application of phosphogypsum and current trends of its utilization in Poland, as well as complex processing of apatite phosphogypsum, including recovery of rare earths, phosphorus compounds and other compounds with simultaneous utilization of anhydrite (Jarosiński et al. 1993). Anhydrite from phosphogypsum does not combine with water similarly to the gypsum anhydrite. The setting and hardening processes of anhydrite are connected with solubility of metastable phase of anhydrite and crystallization of thermodynamically stable phase under process conditions of dihydrate from its supersaturated solution. A small extent of supersaturation of anhydrite towards dihydrate and low rate of dissolving result in the insignificant rate of recrystallization of  $\text{CaSO}_4$  to  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ . Several equations describe the rate of solubility. In general, solubility of anhydrite in water can be expressed by the equation

$$\frac{d\left(\frac{m}{V}\right)}{dt} = \frac{kF}{V}(c_o - c_t)$$

where:  $m$  – weight of anhydrite,  $V$  – make up water volume,  $k$  – rate constant,  $F$  – average surface area of grains,  $c_o$  – concentration of calcium sulphate in the saturated solution,  $c_t$  – concentration of calcium at time  $t$ ,  $t$  – time.

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During the dissolution the diameter of grains, total surface area and driving force of process decrease.

From the above equation it can be supposed that setting and hardening of anhydrite depend on the kind of anhydrite, size distribution (surface area), homogeneity of grains and their surface, amount of make up water, and others.

Apart from mechanical activation, hydration of anhydrite can be accelerated by addition of suitable accelerators, which influence the anhydrite solubility as well as supersaturation degree, which make easier the formation of nuclides of a new phase, decrease the rate of water evaporation, and allow achieving desired properties of anhydrite cement. No sufficient data are available to explain the exact behaviour of accelerators on setting and strength development of anhydrite cement. Therefore, the choice of an accelerator is usually made on the experimental basis. The derivation of anhydrite raw material as well as the way of production of anhydrite cement essentially influence the quality of the final product. Singh et al. (1981), Winkler (1985), Riedel et al. (1989) presented the effect of various accelerators on the course of the hardening process. Moreover, the conditions of material storage (Wagner et al. 1985, Gustaw et al. 1990) as well as the type and amount of impurities included in the anhydrite influence the mechanical properties of anhydrite cement.

A correlation between specific surface area of anhydrite obtained from phosphogypsum by recrystallization in aqueous sulphuric acid and mechanical properties of anhydrite cement have been reported and discussed in this paper.

## 2. EXPERIMENTAL

### 1. Obtaining of anhydrite

To produce anhydrite cement, an apatite phosphogypsum sample was treated twice with sulphuric acid solutions under conditions described earlier (Jarosiński et al. 1989), except that washing was done on a laboratory scale. The chemical analysis of initial material and resultant anhydrite are presented in table 1. X-ray analysis of this sample showed only the anhydrite phase. Content of the impurities in this anhydrite was lower than the standard limits.

### 2. Accelerators

Portland cement 35 and potassium sulphate were used as accelerators. Chemical composition of the cement is given in table 2, while its phase composition is given in table 3. Microscopic examination showed that alite phase was observed mainly in grains of diameter less 90  $\mu\text{m}$ . Belite grains created agglomerates of size from 20 to 50  $\mu\text{m}$ .

Both free lime in the form of individual grains and small agglomerates were identified in the tested sample. The size of lime grains amounted to 30  $\mu\text{m}$ . Filling substance was aluminate and ferrite phase (table 3).

Table 1. Chemical composition of initial apatite phosphogypsum and resultant anhydrite

Component	Phosphogypsum	Anhydrite
	% by weight	
CaO	32.10	37.60
SO <sub>3</sub>	46.20	55.90
SiO <sub>2</sub>	0.70	0.82
Fe <sub>2</sub> O <sub>3</sub>	0.06	0.00
Al <sub>2</sub> O <sub>3</sub>	0.25	0.28
F	0.29	0.01
Na <sub>2</sub> O	0.23	0.00
K <sub>2</sub> O	0.09	0.00
P <sub>2</sub> O <sub>5</sub>	1.60	0.00
Ln <sub>2</sub> O <sub>3</sub>	0.60	0.39
CaSO <sub>4</sub> · 2H <sub>2</sub> O	91.02	0.00
H <sub>2</sub> O	21.41	-

Table 2. Chemical composition of Portland cement 35

Component	Content
CaO	65.5
SiO <sub>2</sub>	22.2
Fe <sub>2</sub> O <sub>3</sub>	3.3
Al <sub>2</sub> O <sub>3</sub>	4.6
MgO	1.7
SO <sub>3</sub>	0.7
Na <sub>2</sub> O	0.13
K <sub>2</sub> O	0.90
Loss by roasting at 1100 °C	0.90

Table 3. Phase composition and modulus of Portland cement 35

Component	Content, %	
	calculated	tested
C <sub>3</sub> S	56.6	69.0
C <sub>2</sub> S	21.0	14.3
C <sub>3</sub> A	6.6	7.0
C <sub>4</sub> AF	10.0	9.0
CaSO <sub>4</sub>	1.2	-
MN = 0.90, MK = 2.81, MG = 1.39		

### 3. Preparing of anhydrite paste

The test samples were prepared with 3% and 5% of Portland cement and with 1% K<sub>2</sub>SO<sub>4</sub>. The anhydrite (from apatite phosphogypsum) was ground in laboratory mill to

specific surface area of  $350 \text{ m}^2 \cdot \text{kg}^{-1}$  according to Blaine. In the final stage of grinding, designed amounts of Portland cement were added and then the mixture was ground down to desired specific surface area. Test were carried out with samples of surface area equal to 390, 400, and  $425 \text{ m}^2 \cdot \text{kg}^{-1}$ . In all experiments the ratio of make up water to anhydrite was equal to 0.23. The beams of anhydrite cement containing various accelerators upon dimensions were cured for different periods in the moisturing chamber or under dry-air conditions at humidity from 50 to 90%. Thereafter, samples were dried at  $42^\circ \text{C}$  and tested for compressive and bending strengths.

### 3. RESULTS AND DISCUSSION

Results of the strength tests of hardened anhydrite cement are given in table 4. Degree of fineness expressed by specific surface area essentially influences the change of strength. Increase in specific surface area to  $425 \text{ m}^2 \cdot \text{kg}^{-1}$  of anhydrite cement obtained from phosphogypsum gives an increase in compressive strength as well as in bending strength.

Table 4. The mechanical properties of the tested anhydrite cement

C. of S.S.	S.S.A. $\text{m}^2 \cdot \text{kg}^{-1}$	Type of A	W/A	$R_c$ after days MPa			$R_z$ MPa
				3	7	28	
P.S.	390	3% cement 35	0.23	1.0	4.5	18.6	4.6
W	390		0.23	3.8	5.8	29.7	12.8
P.S.	400		0.23	1.4	4.6	18.9	6.0
W	400		0.23	3.9	6.3	31.8	14.0
P.S.	425		0.23	3.8	7.6	31.3	5.6
W	425		0.23	7.2	4.8	56.3	16.8
P.S.	390	5% cement 35	0.23	1.1	4.5	19.0	5.8
W	390		0.23	3.9	6.0	30.4	14.1
P.S.	400		0.23	1.6	4.7	20.1	6.4
W	400		0.23	4.0	6.7	33.9	15.6
P.S.	425		0.23	4.1	6.8	32.4	9.4
W	425		0.23	7.5	15.6	58.6	20.6
P.S.	390	1% $\text{K}_2\text{SO}_4$	0.23	5.0		40.5	7.7
P.S.	400		0.23	5.4		43.7	8.1
P.S.	680		0.23	3.3		24.3	7.2

C. of S.S. – conditions of sample storage, S.S.A. – specific surface area, type of A. – type of accelerator, W/A – ratio of water to anhydrite,  $R_c$  – compressive strength of hardened anhydrite cement,  $R_z$  – bending strength of hardened anhydrite cement after 28 days, P.S. – dry-air conditions, W – humidity 98%

Anhydrite cement containing 1%  $\text{K}_2\text{SO}_4$  and of specific surface  $680 \text{ m}^2 \cdot \text{kg}^{-1}$  has lower compressive strength versus the maximum value obtained for  $400 \text{ m}^2 \cdot \text{kg}^{-1}$ . The setting time and hardening process of anhydrite are governed by its hydration and recrystallization. Total hydration rate is limited by the slowest process, namely, the

dissolution of anhydrite. At specific surface area of  $680 \text{ m}^2 \cdot \text{kg}^{-1}$  the rate of dissolution of the anhydrite is certainly higher than the rate of crystallization which influences its mechanical properties. The results indicate that the mechanical activation has a limited practical use. From the above data it is evident that compressive strength of anhydrite after 28 days of curing confirms the minimum specified value of 17.5 MPa given in ASTM designation C 61-50 (1964). Data on the effect of Portland cement addition on the strength indicates that anhydrite cement paste with 5% of this accelerator reaches higher strength than this paste with 3% of Portland cement, regardless of storage conditions.

Hardening of anhydrite cement in the air proceeds slower than in humid conditions, hence the increase in strength of tested material appears after 3, 7 and 28 days of hardening of the anhydrite paste.

## 6. CONCLUSIONS

1. Increase of specific surface area of anhydrite cement obtained from apatite phosphogypsum leads to the increase in the stiffened paste. Distinct effect appears for specific surface area of  $425 \text{ m}^2 \cdot \text{kg}^{-1}$ .

2. Addition of Portland cement to anhydrite brings about an increase in mechanical properties of anhydrite cement not depending on conditions of tested material storage. Maximal compressive strength of anhydrite cement was reached for Portland cement addition equal to 5%.

3. Increasing of specific surface area has a limited practical meaning since the decrease of the strength of tested material is observed for  $680 \text{ m}^2 \cdot \text{kg}^{-1}$  of specific surface area.

4. Tests confirmed the practical usefulness of anhydrite cement obtained from apatite phosphogypsum.

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**Jarosiński A.**, Wpływ powierzchni właściwej anhydrytu otrzymanego z fosfogipsu poapatytowego na właściwości mechaniczne cementu anhydrytowego, *Fizykochemiczne Problemy Mineralurgii*, 153–158 (English text)

Określono wpływ powierzchni właściwej anhydrytu, otrzymanego z fosfogipsu poapatytowego przez jego rekrytalizację w roztworze kwasu siarkowego, oraz warunków sezonowania próbek na wytrzymałość mechaniczną tężącego cementu anhydrytowego. Jako aktywatora użyto cementu portlandzkiego 35 oraz siarczanu potasu. Badania potwierdziły, że proces twardnienia i właściwości mechaniczne omawianego cementu są silnie związane z powierzchnią właściwą i warunkami sezonowania. Stosowanie aktywacji mechanicznej cementu anhydrytowego jest jednak ograniczone.