Fizykochemiczne Problemy Mineralurgii, 31 (1997), 137–143

Andrzej JAROSIÑSKI[*], Czes³aw OSTROWSKI*

EFFECT OF PORTLAND CEMENT ON STRENGTH DEVELOPMENT OF PHOSPHOANHYDRITE-POZZOLANA CEMENT

The paper is a part of the research on a complex alternative technology of apatite phosphogypsum (PG) obtained during the production of phosphoric acid from Kola apatite, on rare earth concentrate and phosphoanhydrite cement with the recovery of phosphate compounds. The effect of Portland cement on mechanical properties of phosphoanhydrite-pozzolana cement has been determined. The samples of binder were prepared with phosphoanhydrite and a constant amount of fly ash while the content of Portland cement amounted from 5 to 20%. Maximum strength of the discussed cement was reached for Portland cement addition in the amount of 20 wt. %, after 90 days. The presence of ettringite in the tested samples was confirmed by means of chemical and X-ray analysis. The change of mechanical properties of the above cements is connected with the formation of ettringite and its decomposition during the hydration process of binder. It was found that the change of linear expansion is also connected with the content of the ettringite phase in binders.

INTRODUCTION

With regard to hydration, anhydrite differs from semihydrate, ($CaSO_4 \cdot 0,5H_2O$) essentially in the degree of supersaturation and the rate of hydration. The hydration activity of anhydrite can be increased by increasing its degree of fineness or by the addition of suitable accelerators, which influence the anhydrite solubility as well as supersaturation degree, which make easier the formation of nuclei of a new phase. The effect of various accelerators on the course of the hardening process was presented in many papers, e.g. (Skalmowski 1964, Riedel et al. 1989). Hitherto, the mechanism of the Portland cement as an accelerator in the hardening process of anhydrite paste has not been completely explained. Calcium hydroxide forming during the Portland cement hydration brings about the increase of solution supersaturation of Ca^{2+} towards dehydration, which allows achieving the desired properties of anhydrite cement. But increase of anhydrite activation by means of this substance can be only partially explained by a common ion effect, because the solubility of $Ca(OH)_2$ is lower than both sulphate phases.

---

[*] Instytut Chemii i Technologii Nieorganicznej Politechniki Krakowskiej, 31-155 Kraków, ul. Warszawska 24.

Phosphogypsum (PG) can usually be used as a substitute for natural gypsum or anhydrite after suitable treatment. The choice of the employed treatment of PG influences the habit, size distribution and surface area, homogeneity of grains. The effect of various accelerators and specific surface area on the properties of PG anhydrite cement are presented for example in (Singh et al.,1989; Gustaw et al. 1991; Jarosiñski 1994, 1994a).

On the other hand, research on the development of a new type binder based on industrial wastes containing reactive silica, alumina, for example fly ash has been carried out (Bereteka et al. 1991, Bereteka et al.1994). These materials so-called pozzolanes and reactions between these compounds and water to form stable products which characterised hydraulic properties, are named pozzolana reactions. Crystalline components of fly ash are very suitable for pozzolana reactions, which are being activated by adding water and calcium compounds. Moreover, the addition of fly ash influences favourably the activation properties of phosphoanhydrite cement, at the same time brings about a colour change of the binder (Jarosiñski 1994 b). Cementous mineral phases with undecomposed fly ash particles formed during the hardening process fill all the spaces between the different particles in the mortar of anhydrite, conferring suitable mechanical properties of the materials.

The aim of the present work is to determine the effect of Portland cement on mechanical properties of mortars containing fly ash and phosphoanhydrite obtained from apatite PG by recrystallization in aqueous sulphuric acid.

EXPERIMENTAL

Material

In order to obtain anhydrite, an apatite PG was treated twice with sulphuric acid solutions as it was described elsewhere (Jarosiñski 1994). Instead of exactly rinsing phosphoanhydrite to eliminate the absorbed sulphuric acid on the surface, the material was neutralised with caustic soda. The amount of neutralising agent corresponded to a stoichiometric amount. The degree of reduction of rare earths amounted to 52% while fluorine as well as phosphorus compounds reached 100%.

X-ray analysis of this product showed only the anhydrite phase (*d* – 0.389; 0.350; 0.312; 0.286; 0.280; 0.248; 0.233; 0.221; 0.218; 0.2101 nm).The content of impurities in the tested anhydrite was lower than the standard limits.

Portland cement 35 and fly ash were used as accelerators of the hardening process. Chemical composition of these materials is given in Table 1.

Phase composition and moduli of the discussed cement are presented in Table 2. The results of the X-ray examination of fly ash indicated that the main phase of this material was mullite (*d* – 0.540; 0.343; 0.338; 0.288; 0.269; 0.253; 0.245; 0.212;

0.189; 0.182; 0.169 nm). Other phases were quartz, hematite, and magnetite. Because of the high temperature of the combustion process in which the ash formed, quartz partly transformed to pyrogenetic silica. For this reason pozzolana activity of fly ash was determined according to ASTM-C-379-65 T. This value amounted to 15,6%

Table 1. Chemical composition of materials used in the tests (% weight)

Component	Portland cement 35	Fly ash	Phosphoanhydrite
SiO_2	22.6	50.9	0.80
Fe_2O_3	2.8	4.9	0.00
Al_2O_3	4.8	33.0	0.28
MgO	1.5	1.1	–
SO_3	0.80	0.50	55.90
Na_2O	0.10	0.60	0.24
K_2O	0.95	1.91	–
CaO	65.7	1.12	0.10
CaO_F	1.0	–	37.60
F	–	–	0.01
Ln_2O_3	–	–	0.39
P_2O_5	–	–	0.00
Loss by rosting	0, 8	6,5	

CaO_F – free lime, Ln_2O_3 – rare earth oxides.

Table 2. Potential phase composition according to Bogue and modulus of Portland cement 35

Component	C_3S	C_2S	C_3A	C_4AF	$CaSO_4$
% weight MN = 0.88; MK = 2.97; MG = 1.71	53.0	24.8	8	8.5	1.36

Preparing of paste

The samples were prepared with a constant content of fly ash with 5–20% of Portland cement 35. The phosphoanhydrite with the above agents were ground in a laboratory mill. In all cases weight ratio of the fraction above 0.2 mm in the tested materials amounted to 1% whereas the weight ratio of the fraction below 0.08 mm amounted to 2%.

The tests were carried out for water requirement $W/(A + F) = 0.28$; 0.30; 0.32. Beams of phosphoanhydrite pozzolana cement containing different accelerators were cured for different period in the moisturising chamber. Next, they were dried at 40 °C and tested for the mechanical strength according to Polish standard PN-73/B-04300. A Graf–Kaufman apparatus was used to determine the change of linear expansion of the tested cements after appropriate time of hardening.

RESULTS AND DISCUSSION

The results of the tests into the effect of Portland cement 35 on the strength development of the phosphoanhydrite-pozzolana cement are given in table 3 and 4. These results indicated that the discussed cement with 20 per cent Portland cement reached the highest strength value after 90 days for water requirement 0.28. Increase of the ratio of the make-up water to the binder brought about a decrease of the mortar strength of the tested material.

The effect of hardening time on the flexural strength development of the phosphoanhydrite pozzolana cement at $W/(A + F) = 0.28$ is shown in Table 5.

Table 3. Effect of various amounts of Portland cement on the compressive strength of phosphoanhydrite-pozzolana cement for water requirement 0.28

No. of sample	Amount of addition, %	Compressive strengths R_S				
		3	7	28	90	180
1	P – 5 F – 25	9.8	13.0	25.6	35.8	32.9
2	P – 8 F – 25	11.0	13.4	27.5	38.8	34.0
3	P – 10 F – 25	11.3	16.9	28	38.8	34.8
4	P – 12.5 F – 25	12.0	17.9	28.9	40.4	36.3
5	P – 15 F – 25	12.6	18.1	30.1	43.9	38.9
6	P – 20 F – 25	13.2	19.8	33.7	48.8	42.7

P – Portland cement, F – fly ash

Table 4. Effect of water requirement $W/(A+F)$ on the compressive strength of phosphoanhydrite-pozzolana cement

No. of sample	$W/(A+F)$	Compressive strength R_s, MPa after day		
		3	7	28
7*	0.3	10.6	15.7	28.8
	0.32	9.8	15.2	27.6
8*	0.3	12.0	18.0	32.1
	0.32	10.9	16.9	30.2

*Composition of samples 7 and 8 corresponded to the composition of samples 5 and 6 but the tests were carried out for different water requirement.

Table 5. Change of bending strength and of linear expansion, % as a function of hardening time (sample No. 6)

	Hardening time days			
	7	28	90	180
Bending strength, MPa	6.9	10.3	11.6	7.8
Linear change	0.11	0.3	0.4	0.45

The results indicate that up to 90 days of storage the flexural strength increased but after 180 days decreased and reached 7.8 MPa. For the tested material a change of linear expansion in dependence on hardening time was observed.

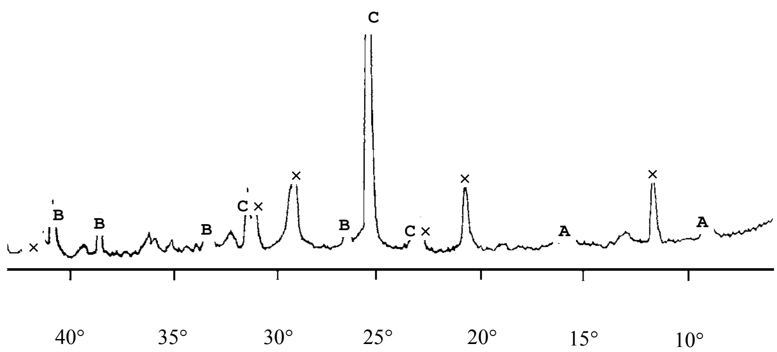

Fig.1. X-ray diffraction pattern for sample No. 6;
B – mullite, C – anhydrite, × – gypsum, A – ettringite

An example of the results of X-ray analysis for the tested samples is presented in Fig. 1. All the samples after 28 days of the hardening process contained the same phases – anhydrite, gypsum and ettringite. In the case of sample storage for time shorter than 28 days in the tested samples by means of X-ray analysis the presence of ettringite was not detected. The presence of this phase was confirmed by means of chemical analysis according to data (Uchikawa et al.1974). The content of ettringite was also determined by the above method in sample 6, with phosphoanhydrite-pozzolana cement after 7, 28 and 90 days, and it was increased to 1.23; 3.35 and 3.94% $C_3A \cdot 3CaSO_4 \cdot 32H_2O$, respectively., The content of ettringite in the samples after 7 days of hardening was small and this phase was not revealed by means of X-ray examination. The increase of ettringite phase in the tested materials brought about a rise in the linear expansion. After 180 days the content of ettringite was lower and amounted to 3, 5%. Probably, ettringite underwent carbonation due to the reaction with carbon dioxide from air which is caused by decreasing strength as well as by increasing porosity. The product of this reaction causes destructive expansion in cement.

4. CONCLUSION

- Addition of Portland cement to phosphoanhydrite-pozzolana cement brings about an increase of its mechanical properties. Maximum compressive strength of the tested materials was reached for Portland cement addition equal to 20% after 90 days.
- Hardening process of the discussed mortar is connected with the ettringite formation and its decompositions.
- After 6 months of storage the compressive strength for all the tested phosphoanhydrite-pozzolana cement decreased.
- Change of linear expansion depends on the hardening time as well as on the content of the ettringite phase.

REFERENCES

GUSTAW K., BIENIAS Z., IWANCIW I., 1991, *Hydratacja i w³aœciwoœci spoiw anhydrytowo-klinkierowo-popio³owych*, Cement Wapno Gips, 6, 160–162.

JAROSIÑSKI A., 1994, *Properties of anhydrite cement obtained from apatite phosphogypsum*, Cem. Concr. Rec., 22, 99–108.

JAROSIÑSKI A., 1994, (a) Correlation *between specific surface area of anhydrite obtained from phosphogypsum and mechanical properties of anhydrite cement*, Fizykochem. Probl. Mineralogii, 28, 153–158.

JAROSIÑSKI A., 1994, (b) *Effect of fly ash on the properties of anhydrite cement obtained from apatite phosphogypsum*, International Conference Environment and Mineral Processing, Part II, Ostrava, 307–312.

MAHADEW D., 1991, *Synthetic gravel derived from ash on the basis of pozzolana reactions*, Environment Technology, November 1991, 3–6.

RIEDEL W., BLOMBERG R., GOHLING, 1989, *Baustoffindustrie, Einfluss von Anregen auf die Eigenschaften eines synthetischen Anhydritebinders aus Fluoranhydrit*, 2, pp. 62–66.

SKALMOWSKI W., 1964, *Teoria wi¹zania i tworzenia spoiw gipsowych i anhydrytowych wg opracowañ polskich, materia³y i studia*, Warszawa, PWN.

SINGH M., REHSI S.S., TANEJA C.A., 1981, *Entwicklung eines Phosphatgips–Anhydrits*, Zement–Kalk–Gips, 11, 595–598.

UCHIKAWA H., UCHIDA S., 1974, *The analysis of ettringite in hardened cement paste*, Cem. Concr. Res., 4, 821–826.

Jarosiñski A., Ostrowski Cz., Wp³yw cementu portlandzkiego na wytrzyma³oœæ cementu fosfoanhydrytowo-pucolanowego. *Fizykochemiczne Problemy Mineralurgii*, 30, 137–143 (w jêz. angielskim)

Praca stanowi wycinek badań nad kompleksową przeróbką fosfogipsu poapatytowego, otrzymanego w procesie wytwarzania ekstrakcyjnego kwasu fosforowego na koncentrat ziem rzadkich, cement anhydrytowy z jednoczesnym odzyskiem związków fosforu. Określono wpływ cementu portlandzkiego na właściwości mechaniczne cementu fosfoanhydrytowo-pucolanowego. Próbki spoiwa przygotowywano z fosfoanhydrytu i stałej zawartości popiołu lotnego, a zawartość cementu portlandzkiego wynosiła 5–20%. Maksymalną wytrzymałość omawianego cementu uzyskano po 90 dniach hydratacji przy zawartości cementu portlandzkiego 20% wag. Obecność etringitu w badanych próbkach została potwierdzono na drodze analizy chemicznej i rentgenograficznej. Zmiana właściwości mechanicznych badanych cementów związana jest z tworzeniem się fazy etryngitowej oraz z jej rozkładem podczas procesu hydratacji spoiwa. Stwierdzono, że zmiany liniowe również są związane z zawartością fazy etryngitowej w spoiwie.