Minerals of expansive and non-shrinkage sulfomineral cements

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Abstract. Usually to obtain expansive cements sulfoaluminate clinker or mix aluminate clinker with calcium sulfates (gypsum, hemihydrate, anhydrate) are used. For these cements ettringite is an important hydration product and kinetic reaction of this phase plays an important role in determinating performance. The alternative aluminate phases may be ferrite containing ones. This article deals with the composition and properties of solid solution of calcium sulfoaluminate, sulfoferrite and sulfoaluminoferrite cements. It was studied an influence of calcium sulfate on structure and properties of calcium aluminate and ferrite phases, and their stability under high temperatures. Beside that the properties of cements containing these phases were studied. The investigation of hydration and properties of sulfomineral cements shows that ettringite and its analogies are formed in such way to provide expansion and compression of cement stone. Degree of expansion and self-stressing of cement stone depends not only on composition of sulfated minerals but on ratio and types of clinkers. The higher expansion is reached by the use of high alite containing Portland cement clinker together with sulfoaluminate or sulfoalumoferrite one, the lower expansion is reached by addition of sulfoalumoferrite and sulfoferrite clinkers. These cements are classified as self-stressing, expansive or shrinkage-compensating ones depend on the degree of their expansion after 28 days of curing.

1 Introduction

The chemistry of expansive cements was comprehensively discussed on the previous congresses and in many research publications [1,2]. A majority of practical expansive cements have depended on the modification of a Portland cement in such a way as to increase the formation of ettringite. Single expansive cement clinkers are made and they are blended or interground with a normal Portland cement or clinker. In a widely used terminology, expansive cements based on Portland cement and calcium sulfate are categorized as types K, M or S, according to the source of additional Al_2O_3 that is required. Usually cement K is produced by intergrinding Portland cement clinker, gypsum and clinker consisting of $C_4A_3\overline{S}$. Type M cements contain Portland cement, a high alumina (CA) cement and additional cal-

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cium sulfate. Type S cements are Portland cements high in C_3A and with suitable contents of calcium sulfate.

The proportions of expansive clinker and of gypsum are added to the Portland cement depend on composition of the expansive clinker and the degree of expansion required. Depend on the degree of expansion all these cements can be made as shrinkage-compensated, expansive or self-stressing cements [3,4]. It should be noted that there are some problems in the wide production and application of the above mentioned cements. For example, Type S cements are found little favour as they too difficult to control. To produce cement of Type M it is need the calcium aluminate cements, but it too costly to the wide application. The composition of expansive clinker can be varied considerably by the use of raw materials most economically available.

2 Materials and methods

Calcium sulfoaluminate (CSA) and calcium sulfoferrite (CSF) were sinthesized previously. To examine the solubility of ferric oxides in CSA ferric oxides in amount of 1 to 15 % by mass was added. The mix of CSA and ferrite oxide had been held for 20 minutes at 1350^0C and the following time the samples were analyzed by XRA and optical microscopy.
To investigate solid solution of CSA and CSF minerals were blended. The ratio in all the experience being from 25 to 75 %. The prepared mixes were pressured in form of briquettes and fired at temperatures of 1050 - 1300^0C for 20 minutes each. The obtained cakes were subjected by XRA and the optical microscopic analyses.

Calcium sulfoferrites were obtained by the burning of raw mixes intended for the production of calcium alum ferrates with composition of C_6AF_2, C_4AF, C_6A_2F with the addition of calcium sulfate and a blend of calcium alum ferrites having synsthesized beforehand with anhydrite, as well as by the crystallization of sulfated alum ferrite melts.

The obtained expansive clinkers were used to produce expansive cements by intergrinding with Portland cement and gypsum. Cements were tested according to Standard methods.

3 Results of experiments

To study the solubility of ferrite oxides in CSA the samples were analyzed after their sintering at 1350^0C. XR-analysis has revealed that the addition of Fe_2O_3 caused a shift in the major diffraction peaks of $C_4A_3\overline{S}$, this being the more manifest the more Fe_2O_3 added to the mineral (Table 1). The IRE-spectra data show a shift and spreading of the band referring to the various oscillations of the SO_4^{2-} group in the original $C_4A_3\overline{S}$ (absorption bands 1093 and 1180 cm^{-1}) which is due to a change in the coordination environment of that group as a result of the incorporation of ferrite oxides whose presence is evidenced by the emergence of absorption bands in the region of 400 to 500 cm^{-1}.

Such changes in spectra of calcium sulfoaluminate occur when up to 9% ferrite oxides are added, but when the iron content is greater than 9% the formation of aluminoferrite phase was observed. Structure of calcium sulfoaluminate can comprise up to 9% Fe_2O_3, the principal pattern of its crystal lattice remaining unchanged.

The study of the hydration of modified $C_4A_3\overline{S}$ in micro preparations has demonstrated that the oxides available in calcium sulfoaluminate structure retards the reaction of mineral and water. $C_4A_3\overline{S}$ reacts with water during the first minutes of being mixed with water,ettringite is equal to its amount at hydration of initial calcium sulfoaluminate.

Table 1.XRD of calcium sulfoaluminate with addition of Fe_2O_3

Sample	Position of the major diffraction peaks (hkl)		
	422	444	822
Without addition	3.750	2.650	2.166
1% Fe_2O_3	3.748	2.644	2.163
3% Fe_2O_3	3.745	2.641	2.161
5% Fe_2O_3	3.740	2.636	2.158
7% Fe_2O_3	3.733	2.630	2.156
9% Fe_2O_3	3.729	2.575	2.138

The study of powders, consisting of preliminary synthesized minerals (C_4A_3S, C_2F and $CaSO_4$) shows that there is an exchange of aluminate and ferrite oxides between minerals and they are stable under heating up to 1350^0C. The following increase of temperature causes the decomposition of calcium sulfoaluminate find melt appearance which solves the formed earlier phases. During melt cooling calcium aluminoferrites with varying composition are formed. They consist of sulfates. It has been founded that minerals burned together changed their colour, while XR-spectra feature a shift of major diffraction peaks of the minerals are compared with their initial matrixes, i.e. an exchange of aluminum and iron ions takes place between the minerals.

XR-spectra microanalysis of the samples shows that calcium sulfoaluminate has Fe_2O_3 in its structure and calcium ferrite has aluminium oxide (Table 2).

Table 2. Composition of calcium sulfoaluminate and sulfoferrite

Compound	Content of oxides, % by mass			
	CaO	Al_2O_3	Fe_2O_3	SO_3
$C_4A_3\overline{S}$	35.69	47.69	3.12	13.76
$C_4A_3\overline{S}$	34.26	46.28	5.24	12.20
$C_4A_3\overline{S}$	36.39	43.15	7.28	13.45
$C_2FC\overline{S}$	44.82	3.76	46.09	4.98
$C_2FC\overline{S}$	43.58	1.89	48.67	6.01
$C_2FC\overline{S}$	42.42	4.41	47.42	5.94

The results of burning calcium aluminoferrites C_6A_2F, C_4AF, C_6AF_2 together with calcium sulfate testify to the fact that there occurs a location of the latter with aluminoferrite, for the XRD analysis does not indicated the formation of the other compounds.

The general aspect of the radiographs of calcium aluminoferrites and sulfoferrites remains almost unchanged. It indicates the fact that the major pattern of the crystalline structure is preserved. In all cases, however, calcium sulfoaluminoferrites differ from calcium aluminoferrites in the intensity of the characteristic diffraction pears and the shift of interplanarspasings which is caused by a distortion of the crystal lattice of calcium aluminoferrites by calcium sulfates (Table 3).

The investigation of calcium sulfoalumoferrite crystallization from the melt shows that the composition of crystals emerging depends on the cooling rate. It has been established that in the case of a rapid cooling of the melt the crystal are enriched in aluminium to a greater extent that is the case solidified melt. In the case of slow cooling the composition of the crystalising phase is indentical with that of the melt.

Calcium aluminoferrites modified by calcium sulfate have both the difference in the composition and hydraulic activity. It is to be noted that the degree of hydration growed with the increase of the A\F ratio in calcium sulfoaluminoferrite.

Using these data, three clinkers were produced on an experimental plant. Chemical composition of these clinkers is given in Table 4.

Backscattered electron (BE) imaging and X-ray microanalysis are very useful in examining the microstructure of polished clinker sections. Clinker phase identification from SEM images is made on the basis of phase brightness, grain morfology, and grain association via the BE image, and chemical composition by qualitative and quantitative EDS analysis.

Table 3.XRD characteristics of aluminoferrites and sulfoaluminoferrites

Compounds	Position of the major diffraction peaks (hkl)		
	200	141	202
$6CaOAl_2O_32Fe_2O$	2.7914	2.6395	1.9285
$6.3CaOAl_2O_32Fe_2O_3\ 0.3SO_3$	2.7805	2.6485	1.9318
$4CaOAl_2O_3Fe_2O_3$	2.7830	2.6335	1.9212
$4.4CaOAl_2O_3Fe_2O_3\ 0.4SO_3$	2.7733	2.6401	1.9245
$6CaO2Al_2O_3Fe_2O_3$	2.7701	2.6230	1.9151
$6.5CaO2Al_2O_3Fe_2O_3\ 0.5SO_3$	2.7681	2.6395	1.9228

Table 4. Chemical composition of clinkers, in weight percent

Clinker Index	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	R_2O
CSF	11.14	3.93	32.64	41.70	2.08	7.53	0.13
CSAF	16.60	9.88	13.02	53.15	1.61	4.27	0.16
CSA	10.36	28.6	3.46	43.75	2.03	6.94	0.30

CSF is sulfoferrite clinker, CSAF - sulfoaluminoferrite clinker, CSA - sulfoaluminate clinker.

All clinkers were used as an addition to Portland cement clinker. All components were ground to a fineness of 4000 cm^2/g.

The investigation of hydration and properties of sulfomineral cements shows that ettringite and its analogies are formed thus providing expansion and compression of cement stone. Degree of expansion and self-stressing of cement stone depends not only on composition of sulfated minerals but on ratio and types of clinkers. The higher expansion is reached by usage of high-alite Portland cement clinker together with sulfoaluminate clinker (Table 5), the lower expansion is reached by addition of sulfoalumoferrite and sulfoferrite clinkers. Thus cements are classified as expansive with the expansive of 0.1 to 0.4% and strength of 57 to 62 MPa after 28 days of curing.

Table 5. Results of tests of expansive cements

Type of clinker as additive to OPC	Strength, MPa		Expansion, %		Self-stressing, Mpa	
	1 day	28 days	2 days	28 days	1 day	28 days
CSF	15	57	0.04	0.1	0.5	1.5
CASF	16.2	58	0.1	0.2	0.6	2.1
CSA	18	62	0.1	0.4	1.0	3.2

Corrosion resistance is of inverse relationship: sulfoferrite cements are more resistant to attack of aggressive media. These cements are used for obtaining of water-proof, crack-resistant and corrosion-resistant concretes.

4 Conclusion

A new type of clinker was obtained consisting of sulfoferrite, sulfoaluminoferrite phases and dicalcium silicate. These clinkers are used for the production of expansive cements.

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