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A STUDY ON THE HYDRATION PRODUCTS OF A NON-EXPANSIVE SULFOALUMINATE CEMENT

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ABSTRACT

In the context of a project aiming at the preparation of an energy-saving cement within the $CaO-SiO_2-Al_2O_3-SO_3$ system having non-expansive properties, clinker was prepared by sintering a mix of industrial raw materials at 1280 °C in a laboratory oven.

The hydration products of the cement cured to 90 days were studied by Scanning Electron Microscopy, X-Ray Diffraction and Thermogravimetric Analysis, and found similar to these of a typical sulfoaluminate cement. The low rate of hydration of the belite phase was attributed to its microcrystalline form.

Introduction

Most of the published research on sulfoaluminate cements refers to types showing expansive behaviour during hydration. Only a limited number of reported works comprise the study of non-expansive sulfoaluminate cements with a good hydraulic behaviour.

Sudoh et al (1) and Deng Jun-an et al (2) proposed the use of cement of the $CaO-Al_2O_3-SiO_2-SO_3$ system for purposes other than these relating only to expansive properties and reported about rapid hardening, high early and final strength, slightly expansive and self stressing properties of these sulfoaluminate cements.

According to Mehta (3) energy-saving cements capable of performing characteristics similar to those of Portland cement may be prepared by modifying the Portland cement composition, such that C_3S and C_3A are replaced by $C_4A_3\bar{S}$ and $C\bar{S}$, and higher proportions of the reactive ferrite phase and β-C_2S are introduced. Cement composition of this concept, containing β-C_2S, C_4AF, $C_4A_3\bar{S}$ and $C\bar{S}$, exhibited both high early strength development as well as exceptionally high strengths at later ages.

Beretka et al (4) synthesized low energy cements based on calcium sulfoaluminate using commercial materials and process wastes, with interest towards a lower firing temperature and grinding energy, as compared to the ordinary Portland cement, as well as a high early strength. They studied their mechanical behaviour up to 28 days and planned further experiments with the purpose of better understanding the long-term behaviour of these cements regarding their resistance to chemical attack.

The hydration of the $C_4A_3\bar{S}$ phase follows a very rapid reaction, leading to the formation of needle-like ettringite, which is responsible for the quick setting of the sulfoaluminate cements (2,3,5,6). The formation of ettringite can be described by the following reactions (2, 7-9) :

$$C_4A_3\bar{S} + 2C\bar{S}H_2 + 34H \longrightarrow C_3A.3C\bar{S}.32H + 2AH_3 \quad \{1\}$$

$$C_4A_3\bar{S} + 6Ca(OH)_2 + 8C\bar{S}H_2 + 74H \longrightarrow 3\,C_3A.3C\bar{S}.32H \quad \{2\}$$

$$AH_3 + 3Ca(OH)_2 + 3C\bar{S}H_2 + 20H \longrightarrow C_3A.3C\bar{S}.32H \quad \{3\}$$

The $Ca(OH)_2$ in the reaction {2} and {3} may be derived either from the hydration of CaO_{free} or C_2S (which could be mineralogical constituents of the sulfoaluminate clinker), or from hydration of Portland cement, if the latter is blended with a sulfoaluminate cement for the production of an expansive mixture (3,7,10).

Most of the published investigations on the expansive properties exhibited during the hydration of $C_4A_3\bar{S}$ phase conclude that the ettringite produced under high lime concentration caused expansion, whereas the ettringite formation in CaO-deficient mixtures did not result in expansion (2,8,11,12). The alkalinity of the hydration environment deriving also from an increased alkali content promote the expansion according to Deng Min et al (13).

The microstructure of the hydration products is referred to as a governing factor. If most of the ettringite is formed before full development of the skeletal structure and hardening of the paste no linear expansion is observed (9,11). Sudoh et al (1) observed in their mixtures that the needle-like ettringite crystals after 1 day of hydration fill the inner vacant spaces of the hardened body without resulting in undesirable expansion. The particle size distribution of the sulfoaluminate cement is another factor related to the expansibility (8,9).

In the present work a sulfoaluminate cement was synthesized in the context of a project aiming at the preparation of an energy-saving cement having expansibility similar to that of Portland cement (OPC). Based on the above mentioned literature the objective of the synthesis was a mineral composition with a moderate $C_4A_3\bar{S}$ content, low alkali content, containing β-C_2S as calcium silicate, free $CaSO_4$ and no CaO_{free}. This synthesis was expected to form the most of ettringite according to reaction {1} without any expansion, since the hydration of β-C_2S produces a lower amount of lime relative to C_3S and at a slower rate relative to CaO_{free}, and forms the CSH structure after the formation of the greatest amount of ettringite.

Experimental

Industrial raw materials, such as limestone, gypsum, bauxite, silica sand and a iron-rich industrial by-product, were used to synthesize the sulfoaluminate clinker.

The raw meal was sintered at 1280°C and the clinker prepared was ground to a fineness of 3700 cm^2/g without any supplementary addition of gypsum (3).

The chemical analysis and the potential mineral composition of the cement produced are given in Table 1. The $C_4A_3\bar{S}$ content was calculated on the basis of SO_3 content in the sulfoaluminate phase (14). The mineral composition was qualitatively identified by X-Ray Diffraction Analysis (Fig.1). The microstructure of the clinker was examined by Optical Microscopy (Fig.2). The sulfoaluminate phase appeared well-formed, distinct among the other clinker phases. The belite phase had very fine crystal form and was dispersed in the ferrite and sulfoaluminate phases.

TABLE 1
Chemical Composition of Sulfoaluminate Cement.

Chemical Analysis (%)		Potential mineral composition (%)	
SiO_2	16.71	$C_4A_3\bar{S}$	20.1
Al_2O_3	13.01	β-C_2S	47.1
Fe_2O_3	4.55	$CaSO_4$	19.8
CaO	51.45	C_4AF	13.8
MgO	0.56		
K_2O	0.17		
Na_2O	0.05		
SO_3	14.28		
CaO_{free}	0.14		

The prepared sulfoaluminate cement was tested for its expansibility according to EN and ASTM standard methods which are applied for ordinary Portland cements (15,16), as its behaviour should be compared ultimately to this cement.

The cement pastes for the study of the hydration products were prepared by using a w/c-ratio 0.40. They were cured in tap water at a temperature 20±2°C. At the ages of 6 and 12 hours and 1,2,7,28 and 90 days the hydration was stopped by means of acetone and ether extraction and the hydration products were studied by X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and Thermogravometric Analysis (TGA).

Results and Discussion

Expansibility.

The volume expansion of the cement paste was measured as indicated by the relative movement of two needles in four Le Chatelier rings (15). The min value was 0.3mm, the max value was 1.5mm and the average was 0.7 mm. These results are similar to typical values for OPC, which are 1-2mm, and conform with the specification (17), which gives an upper limit of 10 mm for each test result.

The autoclave expansion of two standard paste prisms according to ASTM (16) was -0.018%, conformed also with the corresponding specification (18), which gives a max limit 0.8% and was lower than the typical values for OPC (0.02-0.05 %).
The above results characterize the behaviour of the prepared sulfoaluminate cement as non-expansive and similar to Portland cement.

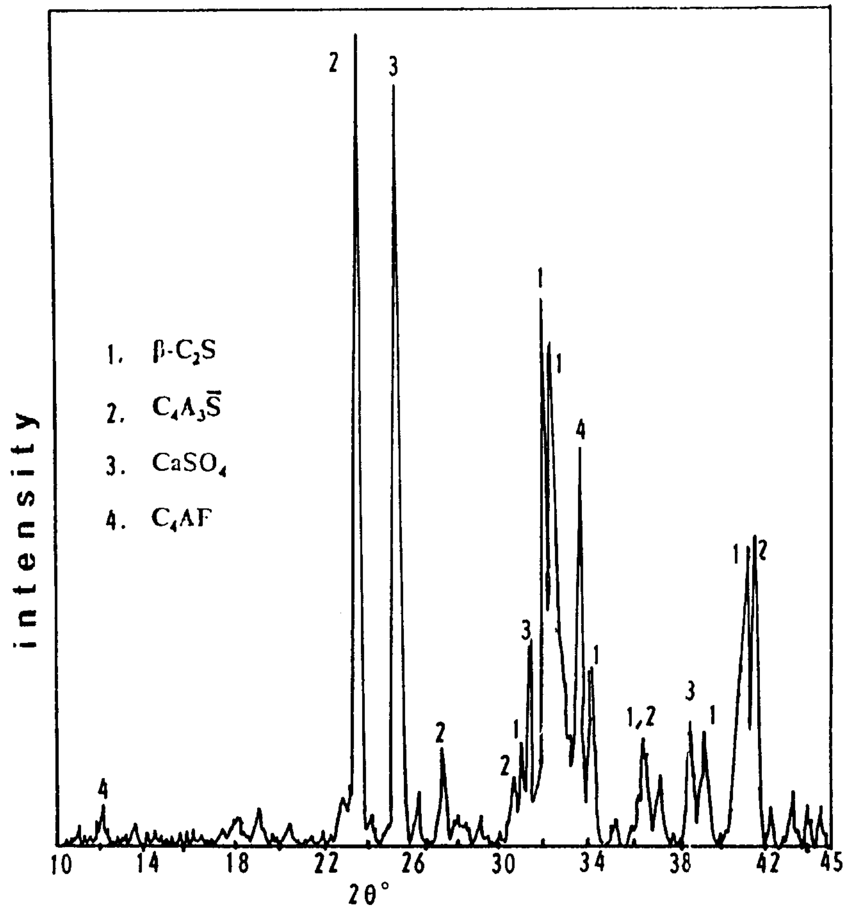


Fig. 1: X-Ray diagram of sulphoaluminate clinker

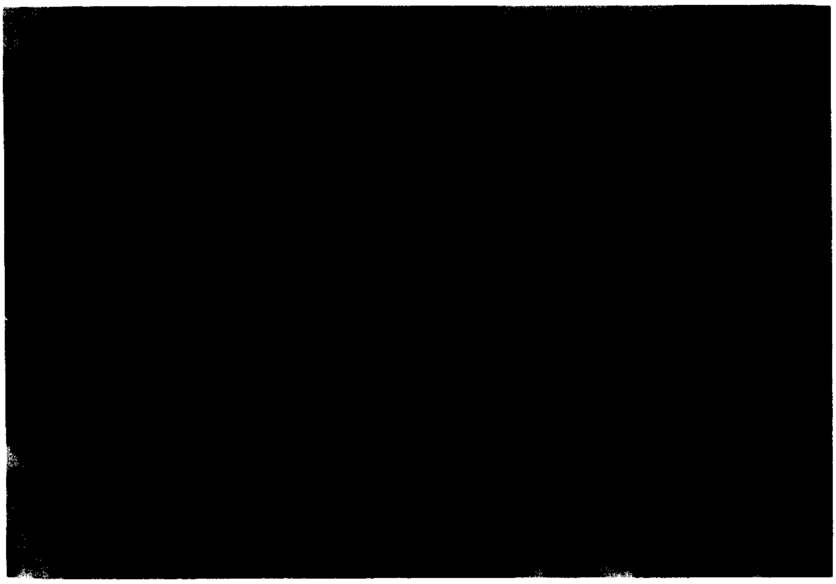


Fig. 2: Microstructure of sulphoaluminate clinker (★ $C_4A_3\bar{S}$ phase)x100.

Similarily the free expansion of the sulfoaluminate prism cured in a water bath for 90 days (Fig.3) is comparable to that of an OPC paste prism. At 90 days it reaches the value 0.015%, while the corresponding value for OPC is 0.033%. This verifies too, that the behaviour of the prepared sulfoaluminate cement is similar to that of Portland cement regarding dimensional stability.

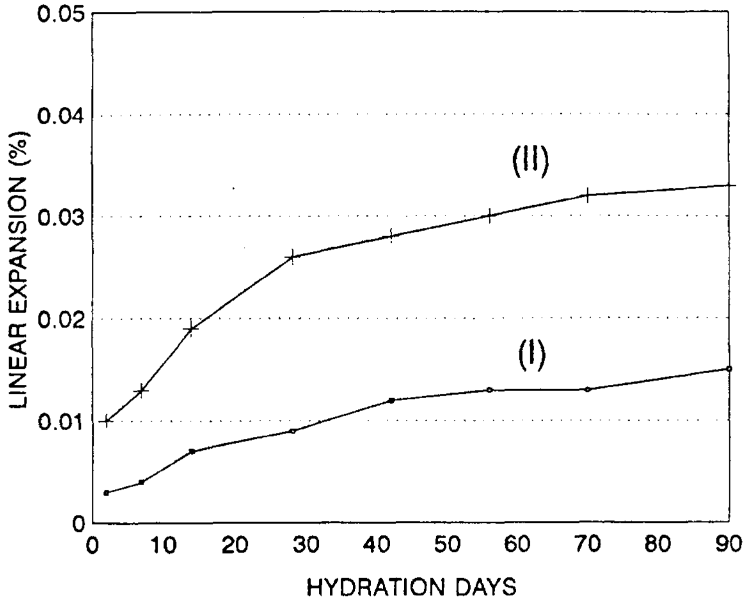


Fig. 3: Linear expansion of sulphoaluminate (I) and OPC (II) paste prisms

XRD Study of the Hydration of the Cement Pastes.

The progress of the hydration process, as derived from the study of the X-Ray diagrams (Fig.4), is presented in the following:

6 hours of hydration : After 6 hours the sulfoaluminate phase has been extensively hydrated. The $CaSO_4$ phase seems also to be slightly reduced as having been consumed in hydration. The hydration of these compounds results in the formation of ettringite. The peak of the ferrite phase was significantly reduced, indicating an almost complete hydration of this phase. The peak of β-C_2S indicates that the hydration of this phase has not yet started.

12 hours and 1 day of hydration : The hydration of $C_4A_3\bar{S}$ and $CaSO_4$ continues forming ettringite, while the β-C_2S remains unhydrated.

2 days of hydration : There are only traces of unhydrated $C_4A_3\bar{S}$ phase.

7 days of hydration : The $C_4A_3\bar{S}$ has been completely hydrated, while the hydration of β-C_2S seems to have commenced. These indicate that all the sulfoaluminate phase has been hydrated according to reaction {1}. A considerable amount of $CaSO_4$ still exists, because the molar ratio $CaSO_4/C_4A_3\bar{S}$ was 4.4 and the reaction {1} consumed a molar ratio $CaSO_4/C_4A_3\bar{S} = 2$.

The above observations regarding the hydration of the sulfoaluminate phase and $CaSO_4$ are in agreement with those of Collepardi et al (7).

After 7 days Ogawa and Roy (11) also found unreacted $CaSO_4$ in CaO-deficient mixture of $C_4A_3\bar{S}$ hydration, which had not the stoichiometric proportions of reaction {2} and resulted in essentially no expansion. The only difference to the present results is that incomplete reaction of $C_4A_3\bar{S}$ took place, as they mention.

28 days of hydration : The hydration of the belite phase still proceeds with an unexpected slow rate. The small amount of $Ca(OH)_2$ formed by this process does not appear in the diagram, but seems to form ettringite (reaction {3}), as its peak still increases.

90 days of hydration : The increase of the ettringite peak is attributed as above to the reaction of small amounts of $Ca(OH)_2$ according to reaction {3}. The belite phase still remains unexpectedly unhydrated in a considerable amount and consequently, CaSO4 remained unconsumed.

It is noted that up to 90 days of hydration no monosulfate was detected due to the presence of $CaSO_4$. This was expected according to Klein and Mehta (19), due to the molar ratio $C/\bar{S}$ and taking into account the CaO of the hydrated components.

SEM Study of the Hydration of Cement Pastes.

The study of the microstructure of hydration products by means of SEM leads to results similar to these derived from the XRD Analysis. The photos in Fig.5,6 present the characteristic structure of the hydration products from 6 hours to 90 days.

Ettringite in fine crystal form is observed at the age of 6 and 12 hours (Fig.5,a,b). As the hydration proceeds, the typical needle-like ettringite structure is observed at 1 and 2 days filling the large pores (Fig.5,d-f). After 7 days these crystals change to a prismatic tile form (Fig.6,a,b,f). The non-expansive behaviour of this cement may be related to the observed development of the greatest amount of ettringite in the inner vacant spaces (1). No ferrite phase is observed after 6 hours of hydration. This fact confirms the results of XRD investigation.

The belite phase is observed to remain unhydrated up to the age of 7 days (Fig.5,c,d,f). After 28 and 90 days, unhydrated β-C_2S crystals are still often found, though small amounts of calcium hydroxide and calcium silicate hydrate are also observed (Fig.6,c,e), indicating that the β-C_2S hydration has commenced and proceeds with a slow rate.

At later ages (28 and 90 days) small amounts of needle-like ettringite crystals appear to be formed again out of the pores on the surface of the grains (Fig.6,d,f), indicating that ettringite continues to be produced. Since the XRD analysis showed that all $C_4A_3\bar{S}$ phase has already been hydrated at these ages, this ettringite should be a product of the reaction {3}.

TGA Study of the Hydration of Cement Pastes.

The results of the thermogravimetric analysis of the hydrated cement pastes are presented in Fig.7. The total hydration water (THW) is the weight loss at the temperature range 20-850°C and hydration water combined in ettringite crystals (EW) is accordingly the one at 20-220°C. These quantities are expressed as percentage of the sample of the hydrated cement paste versus hydration time.

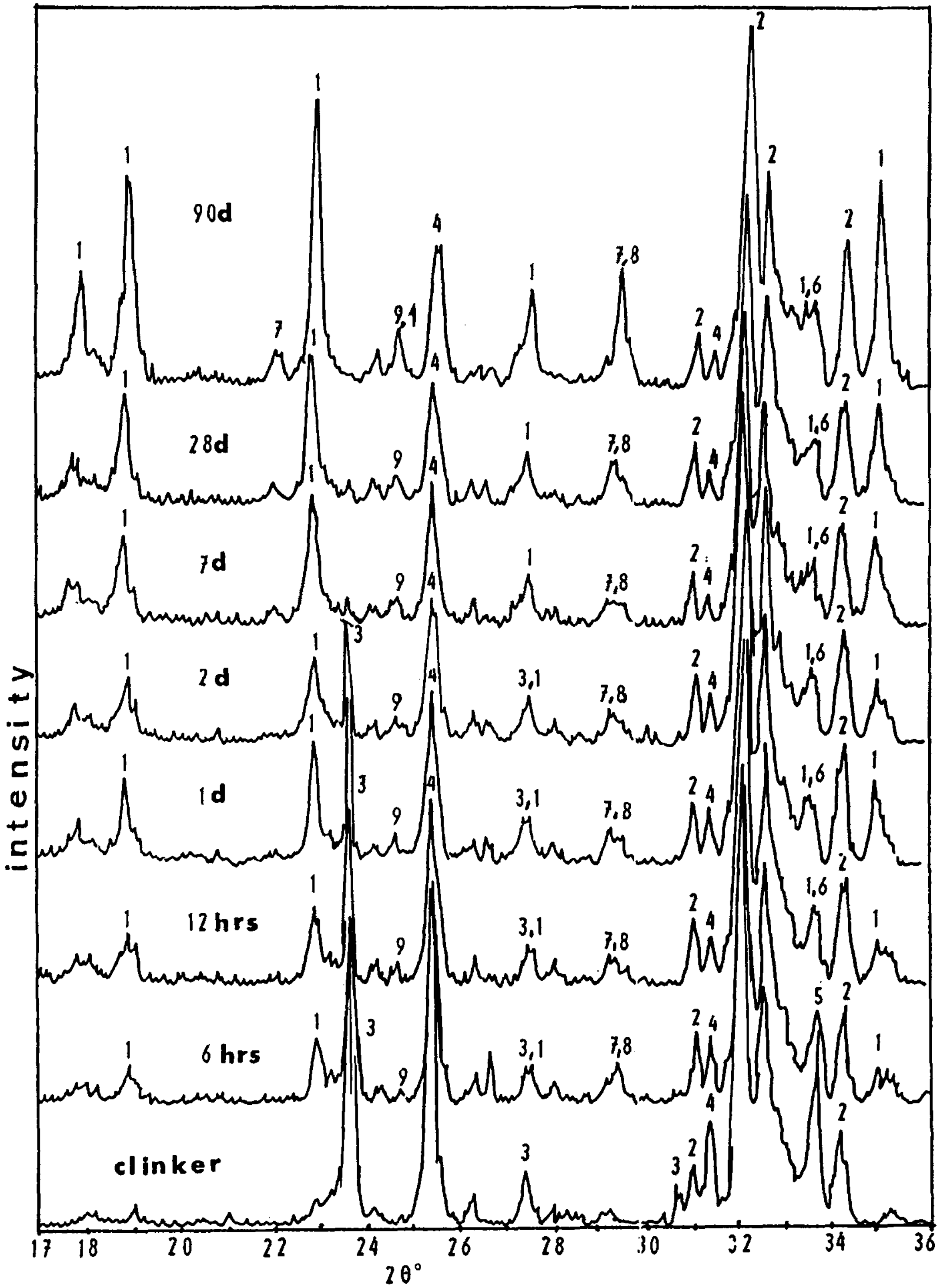
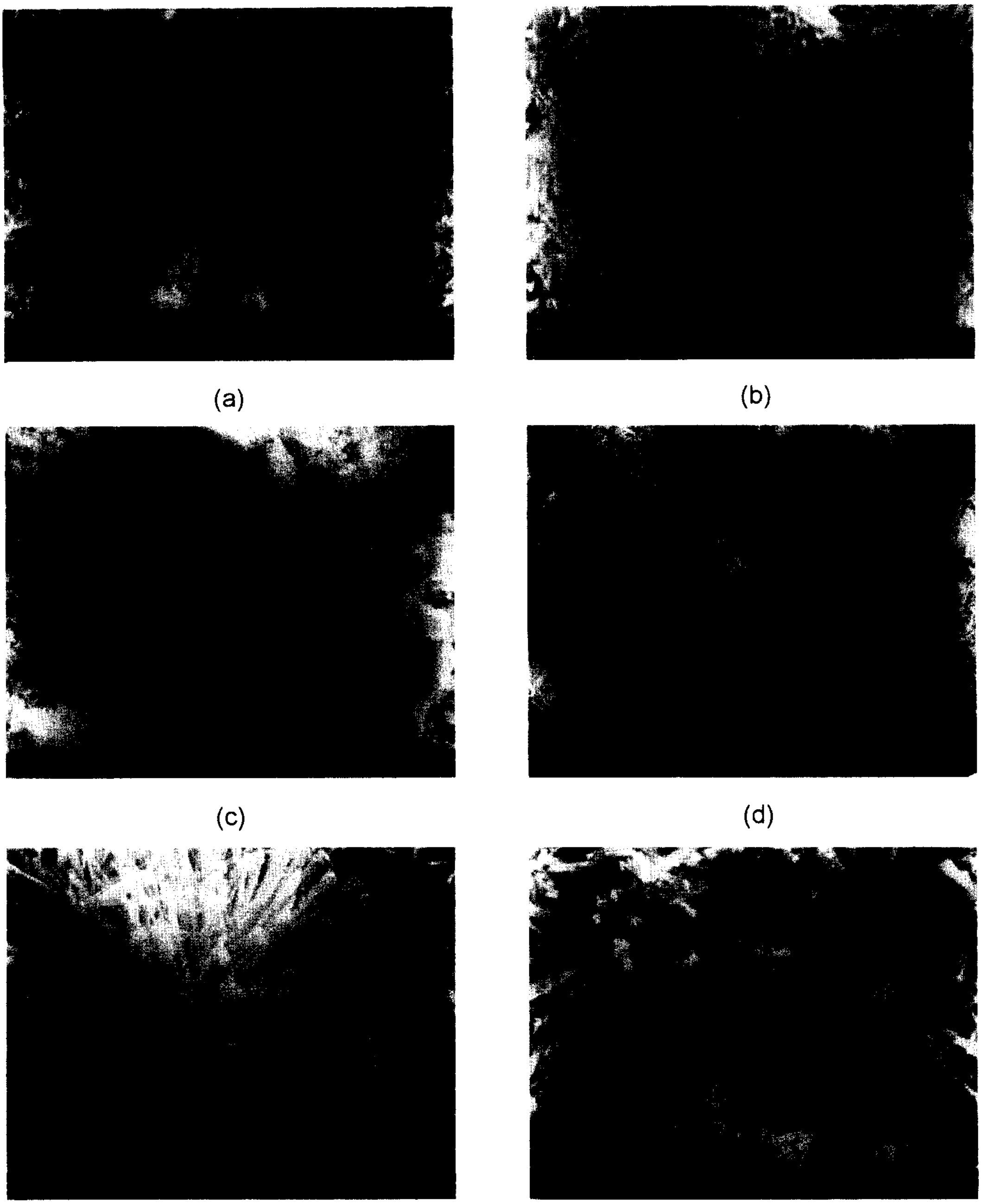


Fig. 4: Multiple plotting of X-Ray diagrams of sulfoaluminate clinker and pastes:
1: Ettringite 2: β-C_2S 3: $C_4A_3\bar{S}$ 4: $CaSO_4$ 5: C_4AF 6: $CaFe_3(SiO_4)_2OH$
7: $Ca_5(SiO_4)_2(OH)_2$ 8: $C_2S.0.3H_2O$ 9: $C_4A_3H_6$ 10: $Ca(OH)_2$.



(a) (b) (c) (d) (e) (f)

Fig. 5: SEM photos showing the development of hydration products: (a)6hrs, (b)12hrs, (c)12hrs, (d)1d, (e)1d, (f)2d.

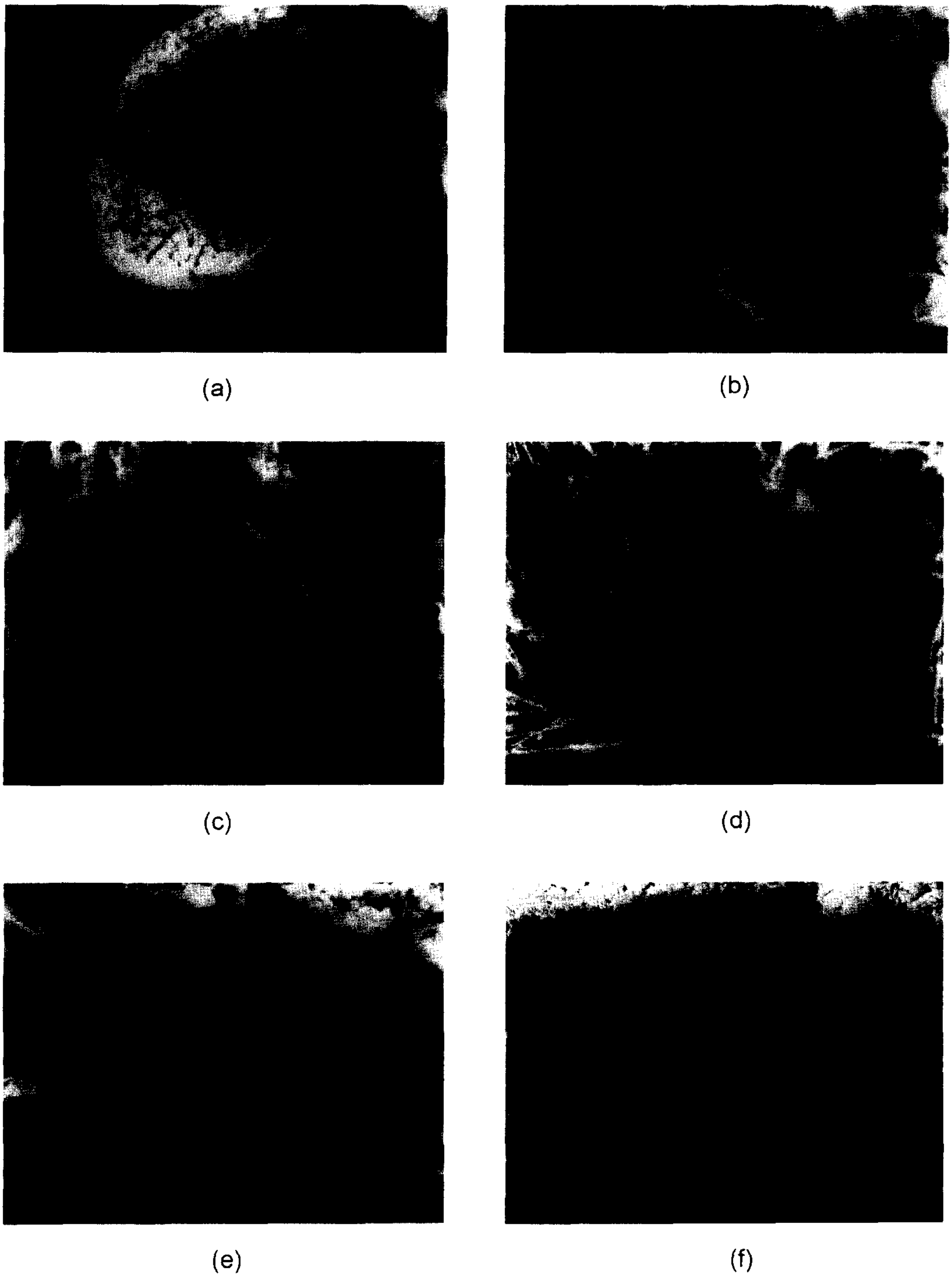


Fig. 6: SEM photos showing the development of hydration products: (a)7d , (b)28d, (c)28d, (d)28d, (e)90d, (f)90d.

The THW increases in a very similar way to the EW. From the early hydration ages a small difference is observed between them, which is attributed to the combined water in other hydrates, and shows that the main hydration compound is ettringite

Most of the ettringite has already been formed in the first day of hydration. The slight increase of both curves up to 90 days indicate that ettringite formation still proceeds with slow rate. The weight loss curves in the individual thermograms did not indicate dehydration of any measurable amount of calcium hydroxide at any age.

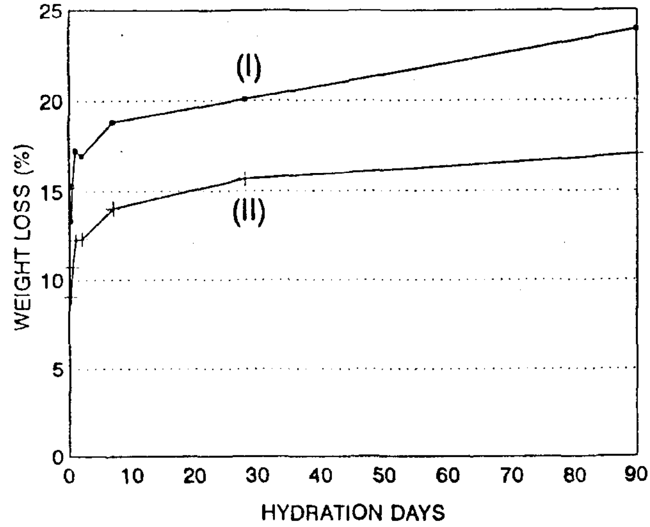


Fig. 7: TGA of hydrated sulfoaluminate cement pastes (I:THW, II:EW).

The results derived by all three methods used for the analysis and study of the hydration products of this cement indicate that the hydration of β-C_2S did not proceed to the expected extent. This can be attributed to the small crystal size (5-10 μm) of this compound. C_2S crystals of this size in an OPC are considered to be of lower reactivity (20) during hydration, which seems to be also the case in this sulfoaluminate cement. The formation of an efficient size of β-C_2S crystals can be achieved by changing properly the burning conditions of the clinker (20) .

Conclusions

A sulfoaluminate cement has been prepared by suitably combining industrial raw materials and by products which were sintered at 1280 °C.

Its linear and volume expansion measured according to standard methods conformed with the specifications for Portland cement.

The study of its hydration products up to 90 days has shown that :

- The hydration of $C_4A_3\bar{S}$ occurs rapidly at the first hours resulting in the formation of remarkable amounts of ettringite, which fill the inner vacant spaces. The typical needle-like ettringite crystals, which are well-formed in the first two days, change to a prismatic tile form after about seven days of hydration.

- The hydration of the sulfoaluminate phase has been completed in the first two days of hydration.

- The formation of needle-like ettringite continues up to later ages as a product of reaction of $Ca(OH)_2$, derived from the hydration of β-C_2S with $CaSO_4$ and calcium aluminate hydrates.
- No monosulfate was formed and a considerable amount of $CaSO_4$ existed after 90 days.
- The low hydration of the β-C_2S phase of this cement was attributed to its microcrystalline form.

References

1. G.Sudoh, T.Ohta and H.Harada, Proc. 7th Int.Con.Cem.Chem., Paris 1980, Vol.III, p.V-152.
2. Deng Jun-An, Ge Wen-Min, Su Mu-Zehn and Li Xiu-Ying, Proc. 7th Int.Con. Cem.Chem., Paris 1980, Vol.IV, p.V-381.
3. P.K.Mehta, World Cem.Techn., 11(4), 166 (1980).
4. J.Beretka, B.de Vito, L.Santoro, N.Sherman and G.L.Valenti, Cem. Conc. Res. 23, 1205 (1993).
5. K.Ikeda, Proc. 7th Int.Con.Cem.Chem., Paris 1980, Vol.II, p.III-31.
6. Wei Jin-Zhao and Wang Yue-E, Silicates Industriels, 1983/4-5, 93 (1983).
7. M. Collepardi, R.Turriziani and A.Marcialis, Cem.Concr.Res.2 , 213 (1972)
8. T.Nakamura, G.Sudih and S.Akaiwa, Proc. 5th Int.Symp.Cem.Chem., Tokyo 1968, Vol.IV, p.351.
9. M.D.Cohen and C.W.Richards, Cem.Conc.Res.12, 717 (1982).
10. H.El-Didamony, N.Mostafa and M.Z.Mostafa, Cem.Concr.Res.6, 707 (1976).
11. K.Ogawa and D.M.Roy, CemConc.Res.12, 247 (1982).
12. W.Kurdowski and A.Thiel, Cem.Conc.Res.11, 29 (1981).
13. Deng Min and Tang Minshu, Cem.Conc.Res.24, 119 (1994).
14. L.D.Adams and E.E.Larkin, Cem.Concr.Res.8, 539 (1978).
15. prEN 196-3 : Methods of thesting cement - Part 3 : Determination of setting time and soundness, Final Draft, Sept.1992.
16. ASTM C151-93a, Standard Test Method for Autoclave Expansion of Portland Cement, Vol.04.01, 1994.
17. prENV 197-1 : Cement composition, specifications and conformity criteria , Part 1 : Common Cements, First Draft, Sept.1992.
18. ASTM C150-94, Standard Specification for Portland Cement, Vol.04.01, 1994.
19. A.Klein and P.K.Mehta, Proc. 5th Int.Symp.Cem.Chem., Tokyo 1968, Vol.IV, p.336.
20. Y.Ono, Proc. Holderbank Microscopy Workshop, Ch.16, 1989.