Pergamon

Cement and Concrete Research, Vol. 25, No. 1, pp. 63-70, 1995
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0008-8846/95 $9.50+.00

0008-8846(94)00113-8

A KINETIC STUDY OF DELAYED ETTRINGITE FORMATION IN HYDRATED PORTLAND CEMENT PASTE

Yan FU*, Ping GU*, Ping XIE*, J. J. BEAUDOIN**

** Dept. of Civil Eng., University of Ottawa,*
Ottawa, Ontario, Canada, K1N 6N5
*** Materials Laboratory, Institute for Research in Construction,*
National Research Council, Ottawa, Ontario, Canada, K1A 0R6

(Communicated by I. Odler)
(Received December 1, 1993; in final form April 20, 1994)

ABSTRACT

Results of a kinetic study of delayed ettringite formation in hydrated Portland cement paste by XRD analysis over the temperature range 5 to 85 °C are reported. Two competitive reactions in terms of gypsum consumption are discussed. These involve both C-S-H gel and the hydrated calcium aluminates. An increase in temperature apparently accelerates sulphate absorption rate by C-S-H gel. Ettringite formation is relatively temperature independent during the first day of hydration in the range 65 to 85 °C. A mechanism for secondary ettringite formation in high temperature steam cured Portland cement material is advanced.

INTRODUCTION

The potential for deterioration of Portland cement concrete due to secondary ettringite formation has been recognized in the precast concrete industry since Heinz et al reported cases related to high temperature (>75 °C) steam cured concrete [1,2]. They argued that delayed expansion in the concrete was due to the transformation of metastable monosulphate to ettringite when steam curing was followed by normal temperature moist curing at later ages. The chemical composition of the cement, especially the SO_3/Al_2O_3 molar ratio, was considered a critical parameter. It has been recently reported however [3] that ettringite is still formed at elevated temperatures (80°C); monosulphate was not observed by XRD. It would appear that another mechanism of supplying sulphate for secondary ettringite formation may exist. Some insight into this apparent controversy is provided by early research by Lerch et al [4,5]. They found that some sulphate added to Portland cement in the form of gypsum could not be accounted for subsequent to hydration. They postulated that the sulphate could be bound into the C-S-H gel structure to form a new phase called "phase X". Kalousek and Adams [6] believed that "phase X" was a gel containing all oxide constituents of cement.

It was transformed from the solid solution of sulphoaluminates in the temperature range 25 to 100 °C. The transformation rate clearly increased with the increase of temperature. Copeland et al [7] reported that sulphate combined with C-S-H gel at early ages and was then released at later ages. Odler [8] also reported similar results from his more recent work in 1980. He found that ettringite apparently formed without any external additions of sulphate indicating that the sulphate for secondary ettringite formation must come from somewhere inside the hydrated Portland cement itself. Taylor concluded that, although C-S-H gel was not directly involved in reactions leading to ettringite formation, it did affect the stability of ettringite through its ability to take up both sulphate and aluminate [9].

The research reported here focuses on the kinetic characteristics of delayed ettringite formation in hydrated Portland cement paste. The competitive consumption of gypsum between C-S-H gel and hydrated calcium aluminates was studied by XRD analysis in the temperature range, 5 to 85 °C.

EXPERIMENTAL

Materials include Type 10 Portland cement (chemical composition (wt.%): SiO_2=19.83; CaO=61.21; Fe_2O_3=3.20; Al_2O_3=4.18; MgO=4.09; SO_3=3.93; Na_2O=0.45 and K_2O=0.82.; the Bogue compound composition (wt.%) is: C_2S=15.8; C_3S=54.6; C_3A=5.7; C_4AF=9.7) and reagent grade gypsum. Two hundred grams of cement were mixed with 400 ml distilled water in a sealed plastic bottle. The sample was rotated on a roller for 6 months; XRD analysis indicated that the cement paste was well hydrated. The hydrated OPC was filtered and washed with acetone. Then the paste was dried at 65 °C in the oven for 24 hours. No carbonate was detected by XRD after the treatment. Two grams of hydrated OPC were weighed and placed into sample bottles. Gypsum was added into each sample bottle. The amount of gypsum (weight percentage of hydrated OPC) was 5, 10, 15, and 20%. Distilled water (5 ml) was added into each bottle. The sample bottles were rotated on rollers. Four temperatures, 5, 25, 65 and 85 °C, were used in the rehydration treatment of the above mixtures. XRD analysis for initial mineral content was carried out two hours after the sample was fully mixed. The wet sample was used immediately after removal from the sample bottle. Special effort was made to prepare consistently uniform sample coating to optimize repeatability of results.

TEST RESULTS

The XRD intensities of characteristic peaks for gypsum and ettringite in hydrated Portland cement during rehydration at 5 °C are shown in Fig. 1. The d-spacings, 0.756 nm and 0.973 nm were used for following the development of gypsum and ettringite. In general, the peak intensities of both gypsum and ettringite for all the samples were very small. Ettringite could be detected in hydrated Portland cement paste without the addition of extra gypsum. Further ettringite formation after the addition of extra gypsum was not clear.

The XRD peak intensities of gypsum and ettringite in hydrated Portland cement during rehydration at 25 °C are shown in Fig. 2. The reduction of the gypsum peak intensity occurred mainly in the first 24 hours for the samples with added gypsum content above 15%. Further ettringite formation after the addition of gypsum was still not readily apparent.

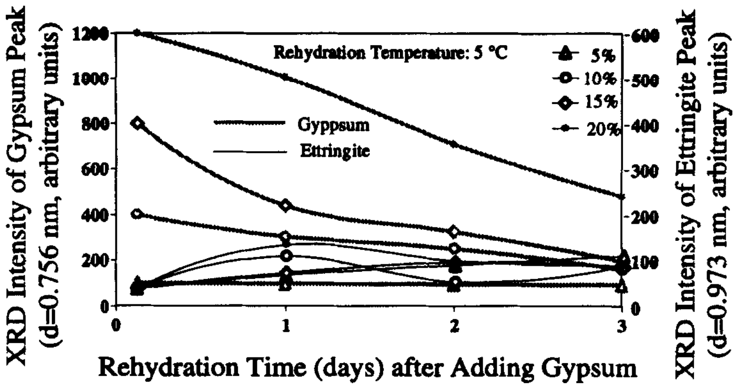

Fig. 1. Gypsum consumption and delayed ettringite formation in the hydrated Portland cement - gypsum - water system at 5 °C and varying gypsum content.

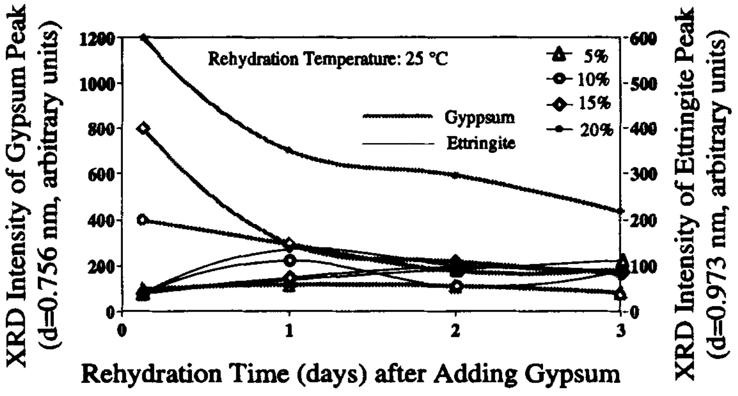

Fig. 2. Gypsum consumption and delayed ettringite formation in the hydrated Portland cement - gypsum - water system at 25 °C and varying gypsum content.

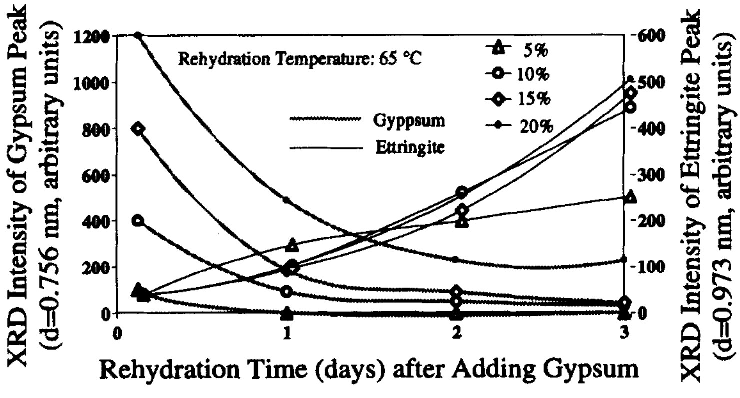

Fig. 3. Gypsum consumption and delayed ettringite formation in the hydrated Portland cement - gypsum - water system at 65 °C and varying gypsum content.

The XRD peak intensities of gypsum and ettringite in hydrated Portland cement during rehydration at 65 °C are shown in Fig. 3. The decrease of the gypsum peak intensity with hydration time was much more rapid than those at 5 and 25 °C. The gypsum was mainly consumed in the first day of hydration. Ettringite formation was clearly observed at 65 °C. A large amount of ettringite was formed between one and three days. The ettringite peak intensity at the first day was only 1/5 of that of the third day. Minor differences only were detected for the ettringite peak intensity between the samples containing additional gypsum 10, 15 and 20%.

The XRD peak intensities of gypsum and ettringite development in hydrated Portland cement during rehydration at 85 °C are shown in Fig. 4. A greater decrease of the gypsum peak intensity in the first day of rehydration was observed at 85 °C. Ettringite apparently formed after one day for samples with added gypsum content above 10%. The ettringite peak intensities of the samples containing 10% and 15% additional gypsum were almost similar. The ettringite peak intensities of the samples containing 20% added gypsum were the highest of all at three-days rehydration.

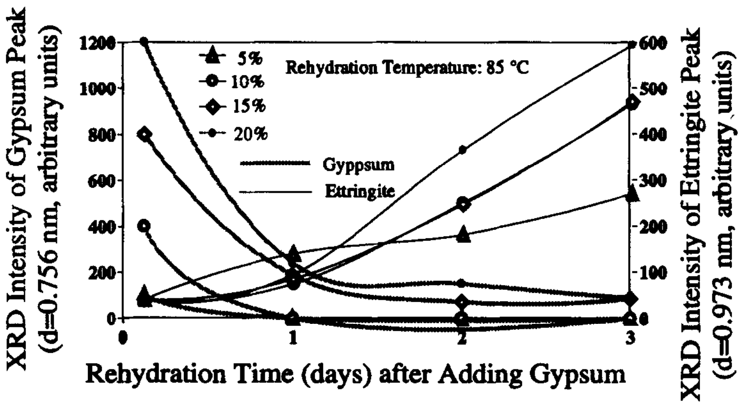

Fig. 4. Gypsum consumption and delayed ettringite formation in the hydrated Portland cement - gypsum - water system at 85 °C and varying gypsum content.

The effect of temperature on gypsum and ettringite XRD peak intensities in hydrated Portland cement paste containing 5% added gypsum is shown in Fig. 5. For the samples rehydrated at 65 and 85 °C, the gypsum peak was not detected after one-day. For the samples at 5 and 25 °C, very little change in the gypsum peak was observed after extra gypsum was added. The ettringite formation became obvious when the hydration temperature was higher than 65 °C. Ettringite peak intensity values generally increased with temperature and hydration time.

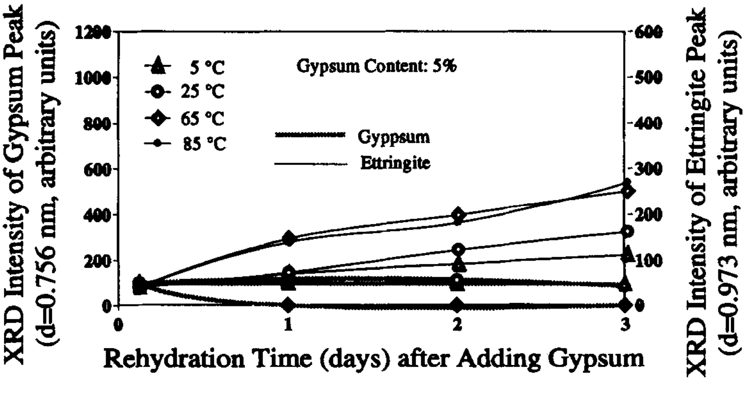

Fig. 5. Effect of temperature on gypsum consumption and delayed ettringite formation in the hydrated Portland cement - gypsum - water system containing 5% added gypsum.

The effect of temperature on gypsum and ettringite XRD peak intensities in hydrated Portland cement paste containing 10% added gypsum is shown in Fig. 6. Gypsum content reduced slowly and only a small amount of ettringite formed at 5 and 25 °C. Gypsum peak intensities decreased rapidly at one day for samples rehydrated at 65 and 85 °C. Ettringite formation occurred mainly after one day.

Temperature played an important role in the reduction of the gypsum peak intensity for the samples containing 15% added gypsum (Fig. 7). The gypsum peak

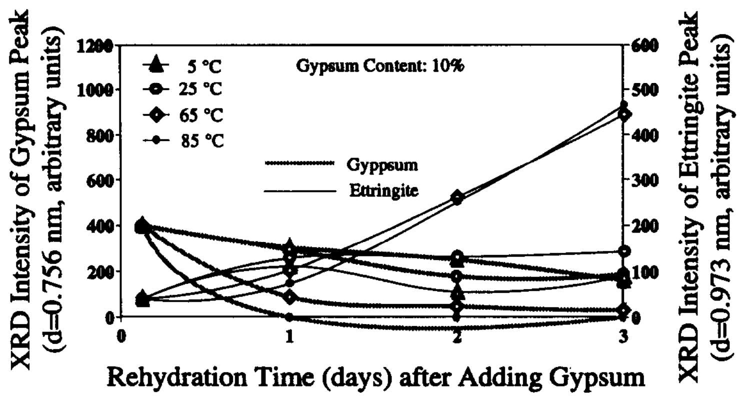

Fig. 6. Effect of temperature on gypsum consumption and delayed ettringite formation in the hydrated Portland cement - gypsum - water system containing 10% added gypsum.

intensity decreased more rapidly with the increase of rehydration temperature from 5 to 85 °C. The consumption of gypsum mainly occurred in the first day of rehydration at 65 and 85 °C. Ettringite formation was accelerated after one-day. Ettringite formed very slowly in samples cured at 5 and 25 °C. The amounts were similar. The amount of ettringite formation was also similar at 65 and 85 °C. A critical change in amount of ettringite formation occurred between 25 and 65 °C.

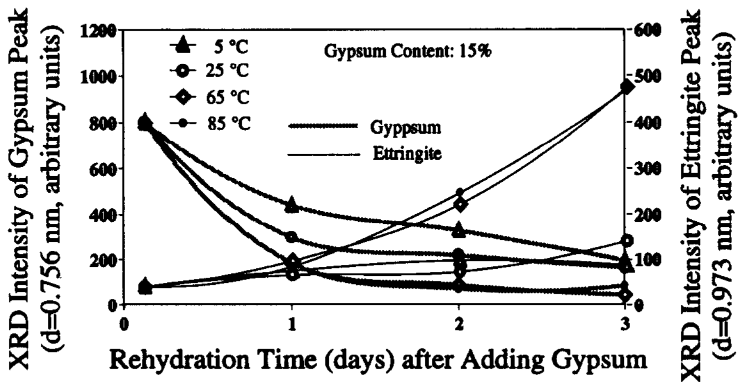

Fig. 7. Effect of temperature on gypsum consumption and delayed ettringite formation in the hydrated Portland cement - gypsum - water system containing 15% added gypsum.

The amount of ettringite formation for the samples containing 20% added gypsum (Fig. 8) was similar to those described in Fig. 7. The effect of temperature on gypsum reduction was more pronounced. The gypsum peak intensity greatly decreased

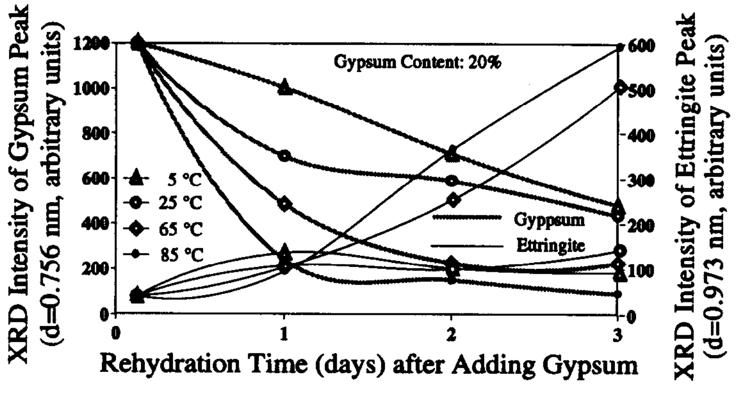

Fig. 8. Effect of temperature on gypsum consumption and delayed ettringite formation in the hydrated Portland cement - gypsum - water system containing 20% added gypsum.

during the first day of hydration. The gypsum peak intensity reduced from 1000 units to 200 units as the temperature increased from 5 ° to 85 °C. Little difference in ettringite peak intensity was found after one-day hydration at 5 and 25 °C. However, ettringite formation was clearly accelerated after one-day at temperature increased to above 65 °C.

DISCUSSION

It appears that it can be inferred from this study that there is a correspondence between gypsum depletion and ettringite formation in the hydrated cement - gypsum - water system particularly at high temperatures (65-85 °C). Gypsum is mainly consumed in the first day after which ettringite formation accelerates. Two competitive reactions appear to influence the rate of gypsum consumption and ettringite formation. Assessment of the kinetics of these reactions should provide some insight as to the mechanisms controlling delayed ettringite formation in high temperature steam cured Portland cement paste.

Gypsum depletion

Mechanisms of gypsum depletion detected by XRD analysis of the hydrated cement - gypsum - water system are considered as follows:

(1) Dissolution in hydrated Portland cement paste solution

The solubility of gypsum is in the range of 0.00222-0.00272 gram/ml water. Supersaturation of gypsum in the Portland cement paste system can occur after a few minutes of hydration [10]. In this study gypsum was added to hydrated Portland cement paste prepared with water/cement ratio of 2.5. The gypsum/water ratios are correspondingly 0.02 - 0.08 gram/ml. The gypsum content in the water is so high that only a small amount of the gypsum (less than 10%) will dissolve in the water even at 85 °C. The solubility of gypsum will be less than in pure water as hydrated Portland cement paste is rich in calcium hydroxide. Therefore dissolution of gypsum in the paste is negligible and cannot account for the gypsum depletion.

(2) Reaction to form ettringite

Test results indicate that only a limited amount of ettringite is formed during the period of major gypsum consumption.

(3) Consumption by C-S-H gel

Odler reported that, 100 g of C_3S can incorporate 9.8 g SO_3 [8]. Similar results were also obtained by Copeland et al [7], Bentur [11] and Mehta and coworkers [12]. Theoretically two grams of hydrated Portland cement (containing about 1.1 gram C_3S) can combine with about 0.25 gram gypsum (12%). Test results are in very close agreement. It would appear then that the sulphate adsorption by C-S-H gel is a strong possibility. The surface chemistry of C-S-H gel has been extensively studied. The large surface area of C-S-H gel makes it possible to adsorb sulphate ions. This adsorption reduces the sulphate ion concentration in cement paste. Gypsum then dissolves until C-S-H is saturated with sulphate. The adsorption process can occur very rapidly at early ages and then slow down. The adsorption rate is strongly enhanced by increasing temperature.

Competitive reactions involving gypsum, hydrated calcium aluminates and C-S-H gel

Ettringite formation in the hydrated cement - gypsum - water system is clearly delayed in contrast to the rapid depletion of gypsum. It generally occurs after 24 hours at 65 to 85 °C when most of the gypsum has been consumed. Two competitive reactions involving sulphate consumption are postulated:

(1) Sulphate consumption by C-S-H gel

$$CaSO_4{\cdot}2H_2O \rightleftharpoons Ca^{2+} + SO_4{}^{2-} + 2H_2O \tag{1}$$

$$nSO_4{}^{2-} + mC\text{-}S\text{-}H \rightleftharpoons \text{Phase X} \tag{2}$$

where "phase X" is a phase containing C-S-H and sulphate as defined by Lerch [4,5]

(2) Sulphate -aluminate reaction to form ettringite

$$C_4AH_{13} + 3SO_4{}^{2-} + 2CH + 17H \Longrightarrow C_3A{\cdot}3C\bar{S}{\cdot}H_{32} \tag{3}$$

It appears that on the basis of test results the first reaction is faster than the second one, and greatly accelerated by increasing temperature at very early ages. In this stage, C-S-H gel consumes sulphate to form phase X at high temperature (above 65 °C), and ettringite formation is limited. The first reaction reaches dynamic equilibrium after one day and the sulphate concentration in C-S-H gel approaches saturation; the formation of ettringite then becomes controlling. Sulphate can be continuously supplied by release from phase X during the process of ettringite formation. Ettringite growth with hydration time is almost linear as indicated by the test results. The rate of ettringite formation is probably controlled by the diffusion rate of sulphate from C-S-H gel. This process and the inherent dynamic equilibrium is maintained until the sulphate is completely released and reacted. The reaction process may last for long periods depending on the diffusion rate and microstructural characteristics of the hardened Portland cement paste.

Delayed ettringite formation

Grusczscinski et al [13] reported that ettringite formation from pure aluminates (C_3A, HAC and C_4A_3S) and gypsum generally occurred within 40 minutes at 50 to 70 °C. Ettringite formation is clearly delayed for about 24 hours in the studied system. Two reasons are suggested:

(1) Ettringite formation rate from hydrated calcium aluminates is apparently lower than from anhydrous calcium aluminates [14].

(2) Sulphate adsorption by C-S-H gel reduces the degree of supersaturation and reduces the rate of ettringite formation. The release of sulphate ions from C-S-H gel is diffusionally controlled. In hardened cement paste, the release rate of sulphate should be much slower than presented in this study. A large amount of ettringite is produced in the sample with 20% gypsum (Fig. 4) during three days rehydration at 85 °C indicating that there is an appreciable amount of calcium aluminate phase available in hydrated Portland cement. These aluminates are a source for ettringite formation at later ages. Delayed ettringite formation can result from release of sulphate from the C-S-H gel.

High potentials for delayed ettringite formation in high temperature steam cured Portland cement paste

Elevated temperature enhances the rate of gypsum consumption. It does not however appear to affect the manner of ettringite formation during the first day of hydration. No monosulphate was detected by XRD even at 85 °C hydration. This has also been confirmed by Brown and co-workers [3,13]. In high temperature steam cured Portland cement paste, the hydration rate of C_3S is highly increased. More C-S-H gel forms and correspondingly more sulphate is consumed by the C-S-H phase. This consumption reduces sulphate concentration in the paste and limits ettringite formation. Hydrated calcium aluminates remaining in the cement paste matrix react further with the sulphate released from C-S-H gel at later ages. Rate of delayed ettringite formation may depend on the diffusion rate of sulphate from hardened C-S-H gel. Any measure to reduce the sulphate consumption by C-S-H gel should be helpful to prevent deterioration from delayed ettringite formation.

CONCLUSIONS

It appears that two competitive reactions in terms of gypsum consumption exist between C-S-H gel and hydrated calcium aluminates in the hydrated cement - gypsum - water system. The increase of temperature apparently accelerates sulphate adsorption by C-S-H gel. Ettringite formation is relatively temperature independent in the range 65 to 85 °C during the first day of hydration. This would appear to account for delayed ettringite formation in high temperature steam cured Portland cement based materials.

ACKNOWLEDGMENT

Financial support from NSERC and the Network of Centers of Excellence on High Performance Concrete is gratefully acknowledged.

REFERENCES

1. Heinz, D. and Ludwig, U., Amer. Concr. Inst., SP 100-105, pp 2059, (1987).
2. Heinz, D., Ludwig, U., and Rudiger, I., Concrete Precasting Plant and Technology, Issue 11/1989, pp.56-61, (1989).
3. Brown, P. W. and Bothe, J. V., Advances in Cem. Res., No. 18, pp.47-63, (1993).
4. Lerch, W., Res. Lab. of Portland Cem. Assoc., Bulletin 12, (1946).
5. Lerch, W., Ashton, F. W. and Bogue, R. H., J. of Res. of Nati. Bureau of Standards, V 2, No. 4, pp.715, (1929).

6 Kalousek, G. L. and Adams, M., J. of ACI, Title No. 48-7, pp.77-90, Sept. (1951).

7. Copeland, L. E., Bodor, E., Chang, T. N. and Weise, C. H., J. Portland Cem. Assoc. Res. Dev. Lab., V 9(1). pp.61-74, (1967).
8. Odler, I., "Interaction between gypsum and the C-S-H phase formed in C_3S hydration", 7th Intnl. Cong. Chem. Cem., Paris, Vol IV, pp.493-495, (1980).
9. Taylor, H. F. W., "Sulfate reaction in concrete", Reseau de centres d'excellence sur les betons a haute performance, Centre de recherche interuniversitaire sur le beton, Universite de Sherbrooke, (1993).
10. Taylor, H. F. W., "Cement Chemistry", Academic Press, p. 118, (1990).
11. Bentur, A., J. Amer. Ceram. Soc. V 59, pp.210-213, (1976).
12. Mehta, P. K., Pirtz, D. and Polivka, M., Cem. Concr. Res., V 9, pp.439-450, (1979)
13. Grusczscinski, E., Brown, P. W. and Bothe, Jr., J. V., Cem. and Concr. Res., Vol. 23, pp.981-987, (1993).
14. Fu, Y., Sheikh, S. A. and Hooton, R. D., Accepted for publication, ACI Mater.Jour., (1993).