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THE INFLUENCE OF CALCIUM SULFATE FORM ON THE INITIAL HYDRATION OF CLINKERS CONTAINING DIFFERENT ALKALI COMBINATIONS

Basma Samet
Department of Civil Engineering, Université de Sherbrooke
Sherbrooke, QC J1K 2R1, Canada

Shondeep L. Sarkar
Sarkar & Associates, Inc., 2501 Central Parkway, Suite A-3
Houston, Texas 77092

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ABSTRACT

Three sets of clinkers produced under different pyroprocessing conditions in a commercial dry-process cement kiln yielded alkalis in different combinations: one set was rich in alkali sulfate compounds, alkali-stabilized orthorhombic C_3A was predominant in the second, whereas potassium rich α-C_2S and alkali oxide-aluminate mixture were noted in the third set.

Using different techniques, early hydration analysis was carried out on these clinkers with no addition of calcium sulfate, with a predetermined amount of gypsum, and a corresponding amount of hemihydrate. The results of a study which focused on the identification of the early hydration products, and the interrelationship of calcium sulfate form and different alkali combinations on the hydration kinetics are presented. © *1997 Elsevier Science Ltd*

Introduction

Several important and functional properties of concrete are governed to a great extent by the mineralogy of Portland cement. Not only do the principal phases, but also the minor ones influence the rheolological and mechanical properties of concrete; the form in which alkalis are present in clinker is particularly important [1].

The three clinkers studied were produced in the same cement kiln under different pyroprocessing conditions [2]. This resulted in distinct alkali combinations. For example, the first clinker K_1 was rich in alkali sulfates. Clinker K_2 was rich in orthorhombic C_3A. The third clinker K_3 contained α-C_2S and free alkali oxide mixed with aluminate (potassium aluminate). Since the dissolution rates of gypsum and hemihydrate are known to be different [3], their effects on the initial hydration of these three commercial clinkers with different alkali combinations were analysed. One set of clinkers in which no calcium sulfate was added, was also included in the experimental program.

Experimental

The clinkers were ground to a Blaine fineness of 300 ± 50 m^2/kg. Calcium sulfate in the form of gypsum or hemihydrate was added to two sets to maintain a 2.5% SO_3 level. A water-to-binder ratio (W/B) of 0.50 was used. Hydration was halted at 15, 30, 60 minutes, 2, and 8 hours, and the pastes were separated into two fractions by vacuum filtration in air. The solid fractions were then washed in acetone and dried for 24 hours at 60°C before being subjected to X-ray diffraction (XRD) analysis, differential thermogravimetric analysis (DTG), and differential thermal analysis (DTA) under a nitrogen atmosphere, as well as observation by scanning electron microscopy (SEM) and energy dispersive x-ray analysis (EDXA). The liquid fraction (filtrate) was analyzed by induced coupled plasma scan (ICP).

TABLE 1

Chemical Composition of Clinkers

Oxide (%)/Clinker	**CK_1**	**CK_2**	**CK_3**
SiO_2	22.8	22.8	22.8
Al_2O_3	4.0	4.1	4.3
Fe_2O_3	3.7	3.6	3.1
CaO	64.3	64.4	64.8
MgO	2.4	2.5	2.6
SO_3	0.95	0.64	0.44
Na_2O	0.2	0.2	0.2
K_2O	1.1	1.1	1.1
Free CaO	0.2	0.2	0.3
Na_2O equiv.	0.9	0.9	0.9
Important Moduli			
LSF[1]	90.6	90.7	91.4
SM[2]	3.0	3.0	3.1
AM[3]	1.1	1.1	1.4
Ds[4]	83.8	50.3	33.5
Potential Bogue Composition			
C_3S	56	57	57
C_2S	23	23	22
C_3A	4	5	6
C_4AF	11	11	9

[1] LSF = lime saturation factor [2] SM = silica modulus {SiO_2/ (Al_2O_3 + Fe_2O_3)}

[3] AM = alumina modulus (Al_2O_3/Fe_2O_3)

[4] D_s = degree of sulfatization {SO_3 x 100/(1.292Na_2O + 0.85K_2O)}

Results

The chemical analysis of these clinkers is presented in Table 1. There appears to be very little difference in the chemical composition, except for the degree of sulfatization (D_S).

Hydration of Clinkers without Added Calcium Sulfate. Since the clinkers without added calcium sulfate hydrated very rapidly, our observation on them was limited to two hours after mixing with water.

No significant differences were noted between the X-ray diffractograms of Clinkers K_1 and K_2 up to 2 hours of hydration and that of their unhydrated counterparts. DTA yielded similar results. Clinker K_3 yielded XRD-measurable quantities of portlandite [$Ca(O_2H)$] after 60 minutes of hydration. The three endothermal events noted with Clinker K_3 during hydration are as follows:

1. The first occurred at 240°-260°C. According to Adonyi et al. [4], this peak corresponds to the presence of C_4AH_{13} and C_2AH_8. The height of the peak increased over time.
2. The second which occurred at around 430°C corresponds to the presence of portlandite after 120 minutes of hydration. This result was confirmed from X-ray diffraction.
3. The third appeared at 600-650°C and represents decarbonation of the calcite formed due to $Ca(OH)_2$ exposed to air when the specimens were being prepared and dried for 24 hours.

Observation of the three two hour-hydrated clinkers under SEM revealed that AFt phase in Clinker K_3 was rare with respect to the other two. In general, the AFm phase was greater than the AFt phase (Fig. 1) and followed the pattern: AFm in K_1 > AFm in K_2 > AFm in K_3. These two phases should not occur in hydrated clinkers if there is no sulfate input (gypsum). The alkali sulfates in the clinkers, however, provided SO_4^{2-}, and Ca^{2+} must have originated from calcium silicates or from free lime, resulting in the formation of ettringite and monosulfate (low

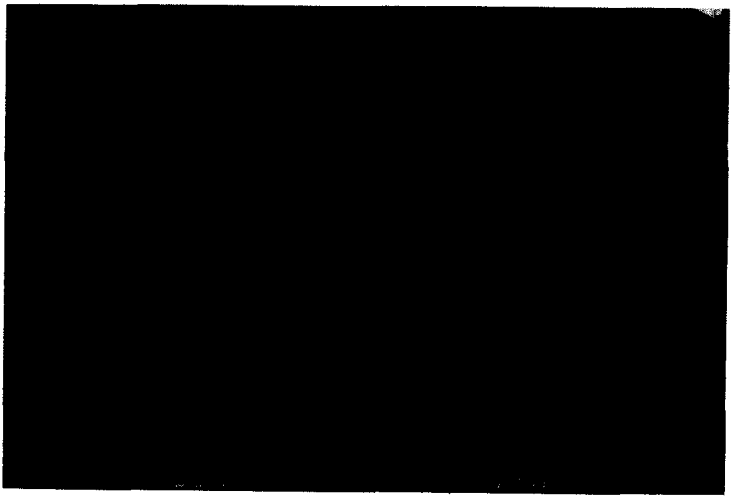

FIG. 1.
AFm crystals in Clinker K_1.

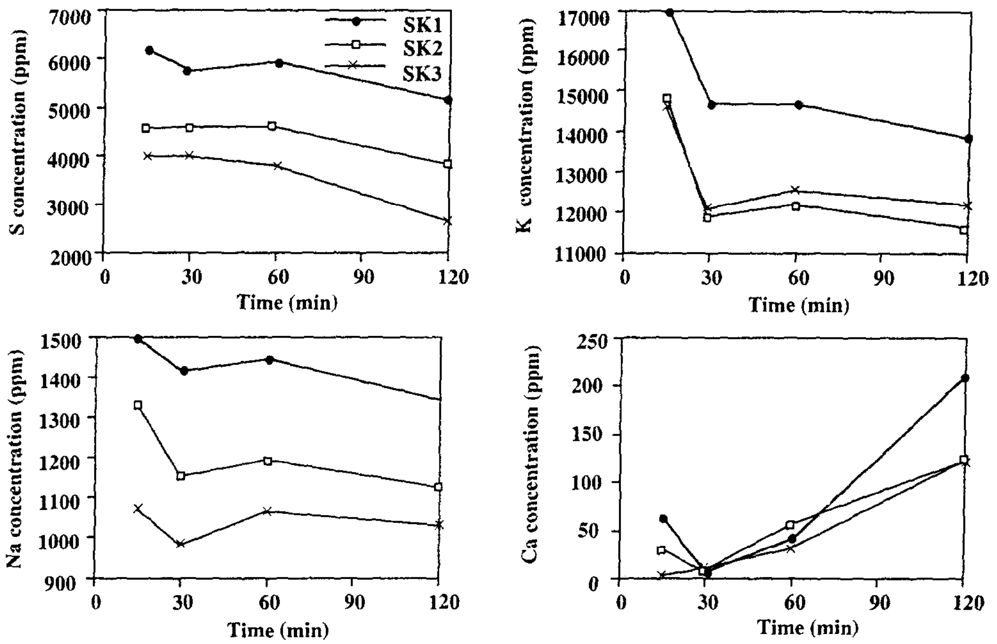

FIG. 2.
Chemical analysis of hydration solutions of clinkers without any added calcium sulfate.

concentration). The abundance of these two phases, observed under SEM, corresponded to the order of sulfur content of the clinkers.

Aluminohydrates and CH were observed in Clinker K_3. The consumption of Ca^{2+} may explain the absence of CH in clinkers K_1 and K_2. Significant quantity of C-S-H was also detected in hydrated Clinker K_3; lesser amounts were noted in the other two. Based on these findings, we can conclude that Clinker K_3 hydrated more rapidly than the other two.

Results of the chemical analysis of hydration solutions SK_1, SK_2, and SK_3 (recovered through filtration) are presented in Figure 2. Four elements were analysed in monitoring clinker hydration. SK_1 has the highest sulfur content, followed by SK_2, then SK_3, which adheres to the same pattern as clinker sulfate content and soluble sulfate concentration. The sulfur concentration tends to decrease over time, which accounts for the formation of AFt and AFm phases in the hydrated pastes. Although SK_1 showed the highest K^+concentration, the potassium contents of SK_2 and SK_3 were fairly close. Since all three clinkers have the same K_2O content (1.1%), the form of the potassium must influence solubility. In fact, most of the alkali content in Clinker K_1 is present as potassium sulfate, which is highly soluble in water [5]. On the other hand, Clinker K_2 has very little alkali compounds containing sulfur—most is combined in C_3A or C_2S. In the third clinker, K_3, the potassium is mainly concentrated in belite [2], which reacts rather slowly, and potassium aluminate.

Moreover, it should be noted that the potassium, sodium and calcium ion concentrations in all three solutions decreases during the first 30 minutes of hydration before stabilizing. It appears that the potassium enters into the composition of the clinker's hydrated phases. Using SEM, we were able to detect the potassium peak in every EDXA of the monosulfate in hydrated Clinker K_3.The sodium content in the solutions is one-tenth that of potassium.

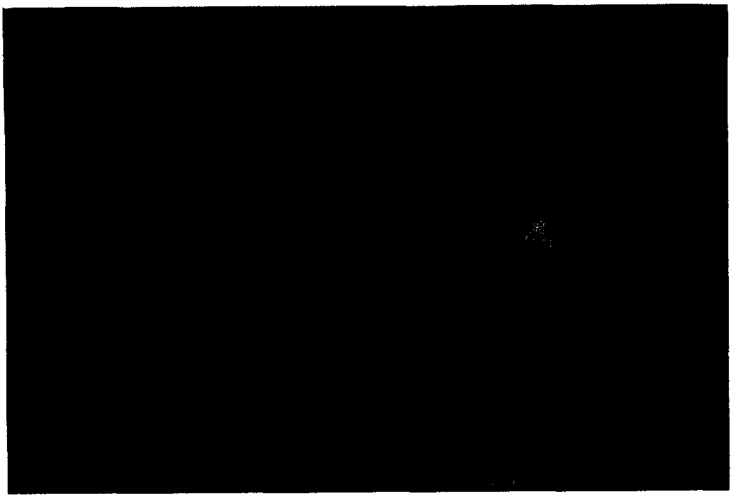

FIG. 3.
Syngenite crystals (sy) in sample GK_3.

The differences in concentration among the three solutions are slight, but the sodium content follows the same pattern as that of potassium and sulfur, that is, decreasing order from the first to the third solution. Although the calcium content is low, its decrease during the first 30 minutes of hydration is due to the precipitation of hydrogarnets [6], and probably AFm and AFt. The Ca^{2+} concentration then increases, which corresponds to the dormant period, characterized by a buildup of calcium ions that precedes the acceleration period.

Hydration of Clinkers with Gypsum (2.5% SO_3). Starting at 8 hours of hydration, portlandite was detected in all three samples; their contents followed the pattern: CH in $GK_2 \leq$ CH in $GK_1 \ll$ CH in GK_3. Thermograms of the three hydrates indicated little ettringite in GK_1, but hydrogarnets in GK_3.

Only those specimens hydrated for 2 and 8 hours were examined under the SEM. Clinkers GK_1 and GK_2 showed abundant amounts of ettringite at 2 and 8 hours; the AFm phase was absent. On the other hand, GK_3 evidenced no ettringite or monosulfate at all, but did contain alumino-hydrates. Its high syngenite content (Fig. 3) indicates that the sulfate liberated from the gypsum reacted with K^+, which went into solution rapidly instead of reacting with the C_3A to form the AFt phase. Hydrated sample GK_3 had the highest C-S-H content.

The curves in Figure 4 depict the variation in concentrations of sulfur, potassium, sodium, and calcium in the three solutions, SG_1, SG_2, and SG_3, collected by filtration. As sulfur is provided by the clinker as well as from the dissolved gypsum, SG_1 was the richest in sulfur, followed by SG_2 and SG_3, as was the case without gypsum. Although the sulfur content tended to decrease over time in SG_1 and SG_2, possibly as a result of ettringite precipitation, as was detected by SEM, it increased after 2 hours of hydration in SG_3. The SO_4^{2-} from gypsum dissolution was consumed by syngenite, and the concentration of SO_4^{2-} increased due to the lack of ettringite. SG_1 exhibited the highest concentration of K^+. The levels of potassium in SG_1 and SG_2 tended to plateau after 60 minutes. In contrast, it increased considerably in SG_3 from 2 to 8 hours. It appears that the potassium bound to the belite and potassium aluminate went into

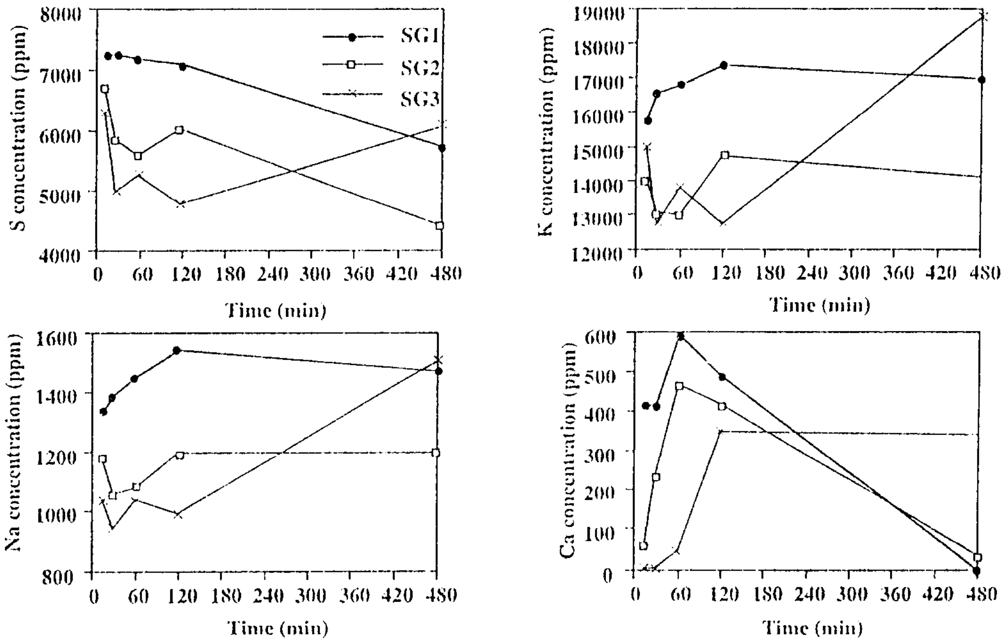

FIG. 4.
Chemical analysis of hydration solutions of clinkers with added gypsum.

solution at this point, and the increase signals the end of the dormant period. The same tendencies noted with potassium also apply to sodium, but sodium is present in much small quantities. The free calcium increased in SG_1 and SG_2 during the first hour of hydration, then decreased sharply as a result of the formation of ettringite, on the one hand, and portlandite and C-S-H, on the other. In contrast, the concentration of Ca^{2+} in SG_3 was practically nil up to 1 hour, which indicates that all the ions in solution were immediately consumed by syngenite and hydrogarnets. From 2 hours, the free calcium in SG_3 increased, then tended to stabilize.

Hydration of Clinkers with Hemihydrate (2.5% SO_3). In order to study the effect of the form of calcium sulfate on hydration, the percentage of hemihydrate was adjusted to ensure that this phase released the same quantity of Ca^{2+} and SO_4^{2-} as the gypsum described above. The quantity of hemihydrate has therefore been expressed as a percentage of SO_3.

By 15 minutes of hydration, most of the hemihydrate in HK_1 and HK_2 had converted into secondary gypsum, as evidenced from XRD patterns and thermal analysis. The evolution of hydration was slow between 15 minutes and 2 hours, since very little syngenite dehydrated around 250°C; the decarbonation of the $CaCO_3$, at about 640°C, evolved slowly during thermal analysis. In HK_3, however, the quantity of hemihydrate decreased considerably and the secondary gypsum content remained fairly low up to 30 minutes. Moreover, it was possible to detect the precipitation of portlandite only after two hours in HK_3.

Sample HK_3 exhibited three additional phenomena of interest. For example, two dehydration peaks for gypsum and hemihydrate were evident at 15 minutes. Dehydration of syngenite and

FIG. 5.
Prismatic crystals of secondary gypsum in sample HK_1.

C_3A hydrates occurred around 270°C. Decarbonation around 630-660°C was relatively stable initially, but increased at 2 hours as hydration evolved.

The calcium sulfate in HK_1 and HK_2 crystallized as rods 10 to 20 μm in length (Fig. 5). This is secondary gypsum [7] which precipitated as a result of the dissolution of hemihydrate and the saturation of the solution with Ca^{2+} and SO_4^{2-}. In contrast, the calcium sulfate in HK_3 appeared as rhombic crystals 5 μm in length (Fig. 6), representing hemihydrate that did not go into solution. Although no syngenite was detected in HK_1, a minor potassium peak in the

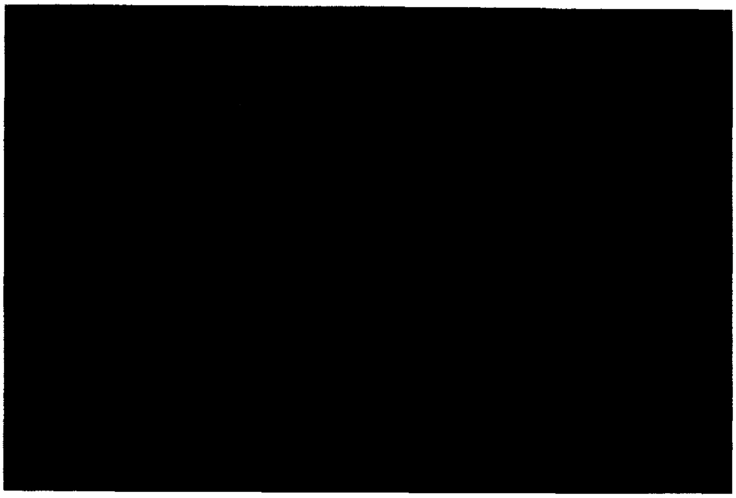

FIG. 6.
Rhombic gypsum crystals in HK_3.

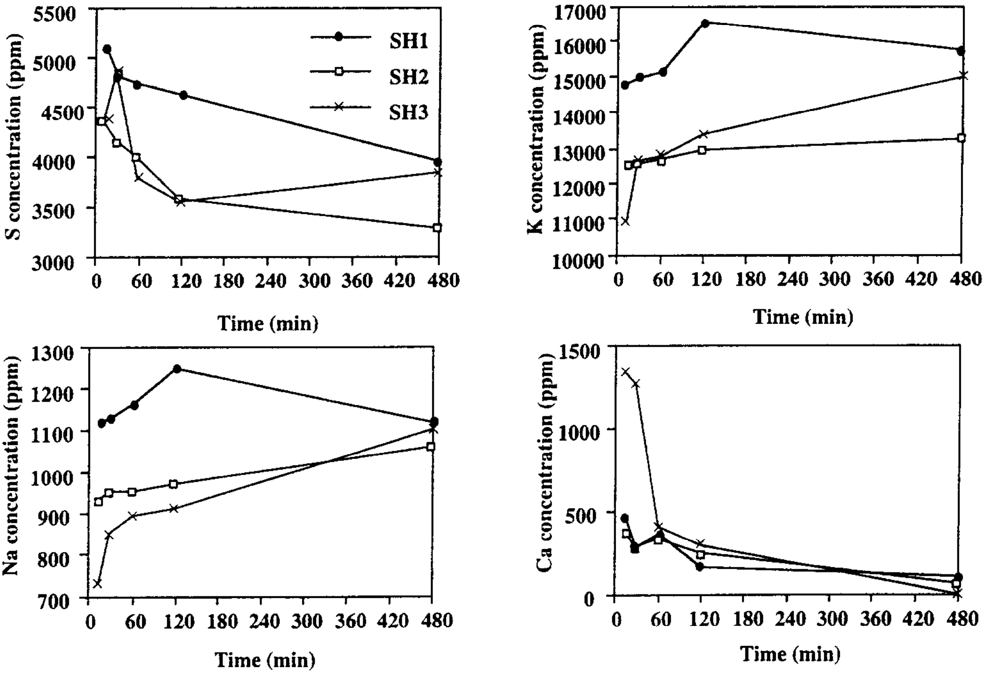

FIG. 7.
Chemical analysis of hydration solutions of clinkers with added hemihydrate.

gypsum crystals was detected by EDXA. Syngenite was relatively rare in HK_3, but quite abundant in HK_2. Finally, C-S-H was more abundant in HK_3 than in the other two samples.

Of interest is the fact that pastes made with Clinkers K_1 and K_2 with added hemihydrate exhibited false set; those made with K_3 were more plastic.

Graphs representing the variations in concentration of sulfur, potassium, sodium, and calcium in the clinker solutions are given in Figure 7. Solution SH_1 followed the pattern seen above in being the highest in sulfur. Solutions SH_1 and SH_2 evidenced sulfur contents that decreased as hydration evolved, while the sulfur content in SH_3 increased from two hours of hydration onwards. SH_1 had the highest concentration of K^+, followed by SH_3 and SH_2. While K^+ concentration tended to stabilize at around 2 hours in SH_1 and SH_2, it continued to increase in SH_3. The much higher concentration of potassium ions (compared to sulfur) suggests that the belite and potassium aluminate had begun liberating its potassium.The same tendencies were noted for sodium. SH_3 recorded a very high concentration of calcium ions from the outset of hydration up to 30 minutes. This suggests that there was a basic variety in solution that considerably accelerated the dissolution of C_3A or hemihydrate. As with hydration with added gypsum, the solutions showed an increase in calcium ions up to 1 hour, followed by a decrease caused by the formation of ettringite, portlandite, and C-S-H.

The pH of the solutions was determined since hydration kinetics is pH-dependent to a considerable extent (Figure 8). SH_3 has the highest pH, followed by SH_1 and SH_2.

Thus, it can be surmised that clinker K_3 contains a chemical compound responsible for the high pH, confirmed as potassium aluminate by SEM [8]. Potassium ions in solution, even in low concentrations, rapidly increase the pH. In K_1, the soluble K^+ tends to increase the pH and

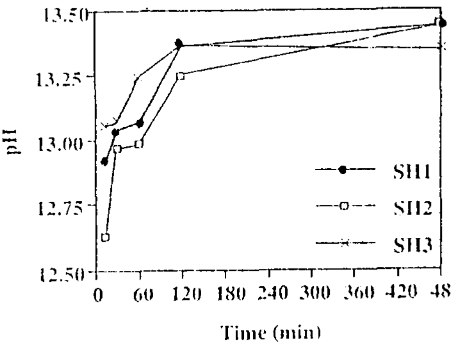

FIG. 8.
Variations in the pH of solutions SH_1, SH_2, and SH_3 over time.

accelerate hydration. This is countered by SO_4^{2-}, which help retard hydration, similar to calcium sulfate. As for K_2, the alkalis contained mainly in C_3A result in a more compact structure [9], which decreases clinker solubility.

Discussion

The main phases that contribute to the initial hydration of cement paste are C_3A, alkali sulfates, calcium sulfate, free lime, and C_3S; belite comes in to play later [10]. The C_3A and free-lime contents of the three clinkers were relatively close; their calcium sulfate content were kept identical in all three cases. The difference between the clinkers can therefore be attributed to the form of alkalis present. Clinker K_1 has a rather high alkali sulfate content (Ds = 84); K_2 has somewhat less (Ds = 50), with a little more orthorhombic C_3A, resulting from inclusion of alkalis in its crystal lattice; and K_3 has the least amount of sulfate (Ds = 33), but contains the same quantity of alkalis. In the latter case, much of it is bound in the belite crystal structure [11] and potassium aluminate.

Scanning electron microscopy, XRD and DTA revealed that hydration had progressed furthest in hydrated Clinker K_3, which had higher portlandite and hydrated calcium aluminate contents. Clinkers K_1 and K_2, somewhat richer in sulfur than K_3, exhibited a slightly developed AFm phase, but the sulfate level was still insufficient to form AFt. In this case, the SO_4^{2-} were provided by the dissolution of alkali sulfates in the clinker and the Ca^{2+} from C_3A and C_3S . Moreover, chemical analysis of the corresponding solutions (SH_1 and SH_2) exhibited a decrease in sulfur and potassium contents until a levelling off at 30 minutes of hydration. Hydration ended in Clinker K_3 with the formation of C_4AH_{13}, which subsequently converted into C_3AH_6 and C_2AH_8, which are the most stable varieties [6].

Solid sample GK_3 (with added gypsum) was richer in portlandite than GK_1 and GK_2 after 8 hours of hydration. Based on the DTA results, GK_3 unlike GK_1 and GK_2, contained no ettringite. GK_3 evidenced formation of syngenite and hydrogarnets, proving that the dissolved gypsum reacted with soluble alkalis to form syngenite instead of combining with the C_3A. This accounts for the low concentration of calcium ions in the solution (SG_3) an hour after the initiation of hydration. The C_3A formed hydrogarnets as if hydration occurred with no gypsum.

Agbodjan [12] used the equation system below to account for the equilibrium between the formation of C_4AH_{13} and ettringite with alkali sulfates:

$$C_3A + CH + 12\ H \rightarrow C_4AH_{13} \qquad (1)$$

$$\begin{array}{ccccc} 3[Al_2O_3.4CaO,13H_2O] & & 3[2Al(OH)_4 + 4Ca^{2+} + 6(OH)^-] & & 2[Al_2O_3,\ 3CaO.\ 3CaSO_4.31\ H_2O] \\ + & \rightleftarrows & + & \rightleftarrows & + \\ 6K_2SO_4 + 32H_2O & & 12K^+ + 6SO^{2-}_4 + 50H_2O & & 2Al(OH)^-_4 + 12K^+ + 10(OH)^- \end{array} \qquad (2)$$

This system shows how the crystallization of ettringite liberates significant quantities of $(OH)^-$ ions, that is, 10 $(OH)^-$ for 6 molecules of K_2O.

Due to the solution product $K = [Ca^{2+}]^4\ [Al(OH)_4^-]^2\ [(OH)^-]^2$ relating to the breakdown of C_4AH_{13}, the concentration of Ca^{2+} is lower, causing the system to reverse (see Equation 2), and limiting the quantity of ettringite. Free alkalis such as potassium break down quite rapidly in contact with water according to Equation (3):

$$K_2O + H_2O \rightarrow 2\ K^+ + 2\ (OH)^- \qquad (3)$$

The free alkalis liberate more $(OH)^-$ ions {2 $(OH)^-$ per molecule of K_2O}. As a result, the $(OH)^-$ concentration in the solution increases, reversing the breakdown of C_4AH_{13} (Equation 2). Consequently, hydrated tricalcium aluminate constitutes the stable phase, to the detriment of ettringite. The K^+ reacts with Ca^{2+} and SO_4^{2-} from the gypsum to form syngenite. After two hours of hydration, the concentrations of potassium, sulfur, sodium increased in SG_3, unlike in SG_1 and SG_2. The ions were contributed by the belite network and the structure of C-S-H. Once all the alkalis have combined, the SO_4^{2-} normally react with the remaining C_3A to form the ettringite detected by DTA in GK_3 after 8 hours of hydration.

Dissolution rate is the main difference with added hemihydrate or gypsum. At ambient temperature, hemihydrate is at least three times more soluble than gypsum [3]. Once the hemihydrate is in solution, and saturation with Ca^{2+} and SO_4^{2-} has been achieved, the secondary gypsum precipitates; resulting in false set. This phenomenon was observed in HK_1 and HK_2 15 minutes after hydration began. In contrast, SEM revealed no secondary gypsum in HK_3 after the start of hydration. This proves that a significant amount of sulfates are immediately consumed when hydration is initiated. As a result, the solution did not contain the critical quantity of sulfates required for the formation of secondary gypsum. In fact, the ions combined with free alkalis to form syngenite.

The comparison of quantitative DTA of hydration products with added gypsum and hemihydrate clearly demonstrate that the presence of hemihydrate yields higher syngenite. This indicates that the free alkalis are much more soluble than calcium sulfates. Consequently, the rate of dissolution of calcium sulfate controls the syngenite precipitation process. Once all the free alkalis have been consumed, the solution saturates in Ca^{2+} and SO_4^{2-}, and the secondary gypsum starts to precipitate.

As in the preceding cases, HK_3 had the highest portlandite and C-S-H contents. Potassium and sulfur peaks showed up in the EDXA of C-S-H, with HK_3 containing more than in HK_1. After two hours of hydration, SH_3 had an increase in potassium, sulfur, and sodium, resulting from the dissolution of belite and potassium aluminate. This increase corresponded to the end of the dormant period.

The high pH level at the start of hydration in SH_3 (resulting from the dissolution of free alkalis) is a good indicator of the hydration kinetics of Clinker K_3, which consistently proceeded at a faster rate than that of K_1 and K_2.

Conclusions

This study clearly demonstrates that the form of alkalis impacts not only on hydration products, but also the kinetics. When the concentration of alkali sulfates was high, as in CK_1, the soluble alkalis tended to accelerate the hydration reactions, while the sulfate counter-ions tended to inhibit them. The lack of calcium sulfate did not prevent the formation of a small amount of monosulfate due to the reaction of inherited clinker alkali sulfates with C_3A. When gypsum or hemihydrate was present (2.5% SO_3 in this study), syngenite formed, thus keeping the pH of the solution low and slightly accelerating their hydration.

When the amount of alkali sulfates was reduced following its inclusion in the orthorhombic C_3A network, the alkalis entered into solution more slowly and the hydration reactions also occurred more slowly. The lack of calcium sulfate led to the formation of small amounts of AFt and AFm that were always the result of SO_4^{2-} combining with the C_3A. With gypsum or hemihydrate, the pH was normal; the initial hydration was somewhat slower, possibly due to the denser crystalline network of the orthorhombic C_3A.

Free alkalis considerably accelerated hydration reactions. In the absence of calcium sulfate, initial clinker hydration led to the formation of hydrogarnets, Even in the presence of gypsum or hemihydrate, hydrogarnets persisted, and at the expense of the ettringite formation syngenite was abundant.

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