Surface Cracking of Hydrated Cement Pastes: An Interpretation

J. C. CALLEJA and F. V. TRIVINO, Instituto Eduardo Torroja de la Construccion y del Cemento, Madrid

We tried to determine the possible and probable causes of surface cracking of hydrated cement pastes by chemical and X-ray diffraction techniques. We found differences between the composition and constitution of the cracked surface zones of the pastes and the rest of the mass. There is good correlation between certain chemical constituents, calculated from chemical analysis, and those deduced from X-ray diffraction results.

The differences are thought to be due to bleeding of the aqueous solution in the cement paste together with extraction of soluble alkalies and calcium sulfate. Consequently, the bleeding enables a greater carbonation, a greater shrinkage and, possibly, a faster set of the surface zone, as compared with the internal mass of the paste.

We surmised that the bleeding is caused by an abnormal particle size distribution of the cement, involving an excess of finer or coarser particles resulting from deficiencies in the grinding process caused by mechanical failures.

•THE CHEMICAL Department of the I.E.T.C.C. was requested to investigate an occurrence that took place at different times, apparently independently, in the laboratories of two plants located in the same zone belonging to the same cement manufacturing company.

In the standard Spanish test for volume changes of cement, neat cement paste cakes are made. In two cases, the cakes showed cracking on their surface, with the cracks penetrating into the cakes to a depth of about 1 mm (Fig. 1). Such cracks were observed both on baked cakes and on cakes moist cured at ordinary temperature.

In neither case was there initially any correlation between the observed cracking and any unusual situation or change in normal operating conditions. The behavior of the cement at the dates on which the cracking took place was considered to be normal as regards setting, strength, soundness, etc. It was assumed that each plant works with practically constant quality raw materials and under almost uniform processing conditions. The isolated and transitory character of the abnormal behavior of the cakes indicated that the causes were accidental and not systematic. The problem was, therefore, to establish the possible and most probable causes of the cracking.

PRELIMINARY CONSIDERATIONS

The appearance of the cakes (Fig. 1) was reminiscent of the cracking observed in specimens of expansive cements submitted to the Anstett test; it was also similar to the cracking of plastic clays on drying. The appearance could suggest differential shrinkage phenomena between two apparently similar layers of a hypothetically homogeneous mass of paste which really is neither equal nor homogeneous. This seems to apply, at least, to the cake in the foreground of Figure 1. Consequently, it was necessary to establish initially whether we were dealing with an expansive or with a shrinkage phenomenon.

Figure 1. Cement paste cakes showing surface cracks.

POSSIBLE CAUSES OF CRACKING

Cracking, considered as a mass phenomenon, has been related to drying shrinkage, and mainly observed initially in too wet cement pastes (1, 2).

Carbonation.—Surface cracking has been related to atmospheric carbonation, since the depth of the cracks corresponds to the thickness of the carbonated layer. The fact that the conversion of calcium hydroxide to calcium carbonate, taking into account the densities of both, takes place with a volume gain of 0.05 percent (expansion) does not invalidate the hypothesis that cracking is connected with a shrinkage process. In fact, carbon dioxide action is not limited to its combination with calcium hydroxide; it is more complex, as CO_2 also reacts with silicates and aluminates, destroying them and forming silica and alumina gels. As a whole, all these actions correspond to a shrinkage process.

Carbon dioxide action depends on water, in a quantitative aspect. Carbon dioxide absorption by cement pastes saturated with water, or immersed, is slow, owing to the low water solubility of CO_2. Absorption is also slow in very dry pastes, so that there is an optimum value of water content for which the rate of absorption is a maximum. In general, absorption of CO_2 is more rapid in pastes with an almost dry consistency.

When water is being lost through evaporation, the external parts of a cement paste absorb CO_2 with increasing speed until a maximum absorption is reached, so that shrinkage takes place. To this shrinkage due to absorption of CO_2 the drying shrinkage must be added, which is also greater in the external parts of the cement pastes. On the other hand, this drying shrinkage begins to take place before the CO_2-absorption shrinkage.

Bleeding.—Regardless of how bleeding of a cement paste is produced, water tends to flow back into the upper part of the mass to produce a much more fluid cement paste (with a greater water/cement ratio) than the whole. On setting and hardening, this forms a film or crust different in nature from the rest of the hardening mass. This crust has a greater drying shrinkage than that of the internal mass, so that a differential behavior may be established between them, both with respect to the drying as well as to carbon dioxide absorption phenomena.

Bleeding may be produced by an excess of water in the paste or by excessive working of the paste, particularly if attempts are made to smooth the paste surface. On the other hand, applying concepts of concrete technology to the case of cement paste, bleeding is a particular case of segregation, considered as a general phenomenon. This, when referring to the aggregate, is an index of deficiencies in its particle size distribution.

Consequently, in the case of cement pastes, bleeding may be due to insufficiently fine grinding and milling of the cement clinker, which leads to easier sedimentation of the larger particles.

Furthermore, if the remaining conditions are constant, shrinkage becomes more marked with increasing amount of cement, with the fineness of the cement, and with increasing amount of water in the paste, so that it will be greater in the external upper part of the mass subjected to bleeding, as a fluid cement paste richer in the finer particles of the cement accumulates in that part.

Alkalies.—Cement alkalies derived from raw materials may be found in a water-soluble form, or they combine with silicates and aluminates to form phases such as $KC_{23}S_{12}$ and NC_8A_3, or they form vitreous compounds, if the clinker has been rapidly cooled (3).

The easily and rapidly soluble alkalies form sulfates—mainly a double sulfate, $3\,K_2SO_4 \cdot Na_2SO_4$—in cements from raw materials containing sulfates. Hence, when such cements are mixed with water, a great portion of alkalies immediately disolves, particularly more potassium oxide than sodium oxide (approximately one-half of the total content of the former and one-fourth of the total content of the latter). In cements with low content of sulfates the rapid solution of alkalies affects only ten percent of these.

Cement alkalies usually hasten the setting process, for in alkaline solutions with a great concentration of hydroxyl ions, calcium oxide is scarcely soluble. It does not form saturated or supersaturated solutions of $Ca(OH)_2$ unless the presence of calcium sulfate counterbalances the inhibiting action of alkalies in the solution of calcium oxide, eliminating them according to the process

$$CaSO_4 + 2\,KOH \rightarrow Ca(OH)_2 + K_2SO_4$$

In such cases, when there is either a small amount of alkali or no alkali, $C_4A \cdot aq$ is formed instantaneously. This covers and protects the anhydrous phase retarding their hydration. Exactly the same happens when, in the presence of calcium sulfate, calcium sulphoaluminate is formed as follows:

$$3\,CaSO_4 + C_4A \cdot aq \rightleftarrows C_3A \cdot 3\,CaSO_4 \cdot aq + Ca(OH)_2$$

In this case $Ca(OH)_2$ in excess displaces the above equilibrium towards the left, favoring the formation of $C_4A \cdot aq$. In addition, $C_3A \cdot 3\,CaSO_4 \cdot aq$ also forms enveloping films, which protect anhydrous aluminates from hydration.

Furthermore, alkalies may facilitate carbonation in humid atmosphere, fixing $Ca(OH)_2$ in the form of $CaCO_3$ and inducing false set.

Finally, cements, particularly those with a high C_3A content, require an optimum amount of gypsum to reduce their shrinkage to a minimum. This optimum amount of gypsum is greater when the content of alkalies is high. For Spanish cements, for instance, the optimum is, on the average, about 3.5 to 4 percent, expressed as SO_3.

EXPERIMENTAL WORK

The available material was very limited—only the four cakes for the volume change test, shown in Figure 1. Samples of the cements employed to make the cakes were not available, so it was not possible to repeat the expansion test under favorable and unfavorable conditions.

In view of the different appearance of the cracked surface layers of the cement paste as compared with the rest of the mass, an attempt was made to remove these layers by mechanical means. This was not easy, as the layers were firmly attached to the underlying mass.

Once the surface layers were removed, the two resulting samples of paste were ground and mixed separately, sample A corresponding to the surface layers, i.e., the

external upper part of the cement paste, and sample B corresponding to the rest of the mass of paste. A complete chemical analysis of both samples was carried out, including gravimetric CO_2 determinations and flame-photometric Na_2O and K_2O determinations (4, 5). Combined water was calculated as a difference between total ignition loss and CO_2 content. Analytical results were referred to the respective ignited samples, and with the new data the potential compositions of the corresponding anhydrous cements were estimated.

RESULTS

Results of the chemical analyses are given in Table 1.

X-ray diffraction diagrams of the samples were also obtained using standard techniques (6). Results are presented graphically in Figures 2 and 3 where the diagrams corresponding to both samples are shown together for comparison. Operating conditions are shown in Figure 2.

Discussion of Results

From Table 1 the following main differences between the analytical and calculated results for samples A and B may be considered:

(i) a greater ignition loss in sample A;
(ii) a greater CO_2 content in sample A;
(iii) as a result of (i) and (ii), a lower content of combined water in sample A;
(iv) a somewhat higher content of SO_3 in sample A;
(v) as a consequence of (iv), a higher content of gypsum (calculated and expressed as $CaSO_4$) in sample A;
(vi) a lower content of total lime in sample A;
(vii) because of (vi), a lower content of calculated C_3S and a higher content of calculated C_2S in sample A;
(viii) a higher content of total and individual alkalies in sample A;
(ix) a lower $SO_3/K_2O + Na_2O$ ratio (about one half) in sample A.

Calculated total amounts of silicates, aluminates, and ferrites, as well as the rest of the analytical items, do not differ substantially from one sample to the other.

A careful analysis of the X-ray diffraction diagrams (Figs. 2 and 3) discloses the following:

(1) peak heights of lines identified as corresponding to $Ca(OH)_2$ are much smaller in the case of sample A;

(2) consequently, peak heights of lines identified as corresponding to $CaCO_3$ are much greater in the case of sample A;

(3) in accordance with (1) and (2), peak heights of lines identified as corresponding to C_3S are smaller in the case of sample A;

(4) peak heights of lines identified as corresponding to $C_3A \cdot 3\overline{S} \cdot aq$ ($3\,CaO \cdot Al_2O_3 \cdot 3\,CaSO_4 \cdot 30\,H_2O$—ettringite) are greater in the case of sample A;

(5) conversely, peak heights of lines identified as corresponding to $C_3A \cdot \overline{S} \cdot aq$ ($3\,CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 12\,H_2O$) are smaller in the case of sample A;

(6) amounts of $Ca(OH)_2$ and $CaCO_3$ are in general noticeable, whereas $C_3A \cdot 6\,H_2O$ and ettringite are scarce; amount of $C_3A \cdot \overline{S} \cdot aq$ is intermediate.

A comparison between analytical and calculated chemical results and those of X-ray diffraction establishes the following facts:

(a) points (i), (ii), (iii), (vi) and (vii) on the one hand, and (1), (2) and (3) on the other, corroborate each other; they demonstrate the validity of the corresponding calculated values given in Table 1;

(b) points (iv) and (v) on the one hand, and (5) on the other, also corroborate each other and show the validity of the corresponding calculated values given in Table 1;

(c) point (4) is a consequence of (b).

TABLE 1

CHEMICAL ANALYSIS OF PASTE CAKES

Analytical or Calculated Items (%)	Upper External Zone A (surface layer)						Lower Internal Zone B (mass)					
	Sample			Ignited Sample			Sample			Ignited Sample		
Ignition loss	19.25	19.25	19.25	—	—	—	13.20	13.20	13.20	—	—	—
Insol. residue	0.92	18.84	27.12	1.14	23.31	33.56	0.79	19.47	28.20	0.91	22.43	32.49
SiO_2	17.92			22.17			18.68			21.52		
Al_2O_3	5.75	8.28		7.12	10.25		6.10	8.73		7.03	10.06	
Fe_2O_3	2.53			3.13			2.63			3.03		
CaO	49.27	49.27	50.46	61.02	61.02	62.49	54.64	54.64	55.87	62.94	62.94	64.36
MgO	1.19	1.19		1.47	1.47		1.23	1.23		1.42	1.42	
SO_3	2.50	2.50	2.50	3.09	3.09	3.09	2.36	2.36	2.36	2.72	2.72	2.72
K_2O	0.60	0.73	0.73	0.74	0.90	0.90	0.28	0.33	0.33	0.32	0.38	0.38
Na_2O	0.13			0.16			0.05			0.06		
Total	100.06	100.06	100.06	100.04	100.04	100.04	99.96	99.96	99.96	99.95	99.95	99.95
CO_2	12.55	19.25					3.25	13.20				
H_2O	6.70						9.95					
$SO_3/K_2O + Na_2O$				3.43						7.15		
C_3S				18.73	68.23					33.33	69.96	
C_2S				49.50						36.63		
C_3A				13.58	23.09					13.51	22.72	
C_4AF				9.51						9.21		
$CaSO_4$				5.25	5.25					4.62	4.62	
Rest				3.51	3.51					2.71	2.71	
Total				100.08	100.08					100.01	100.01	

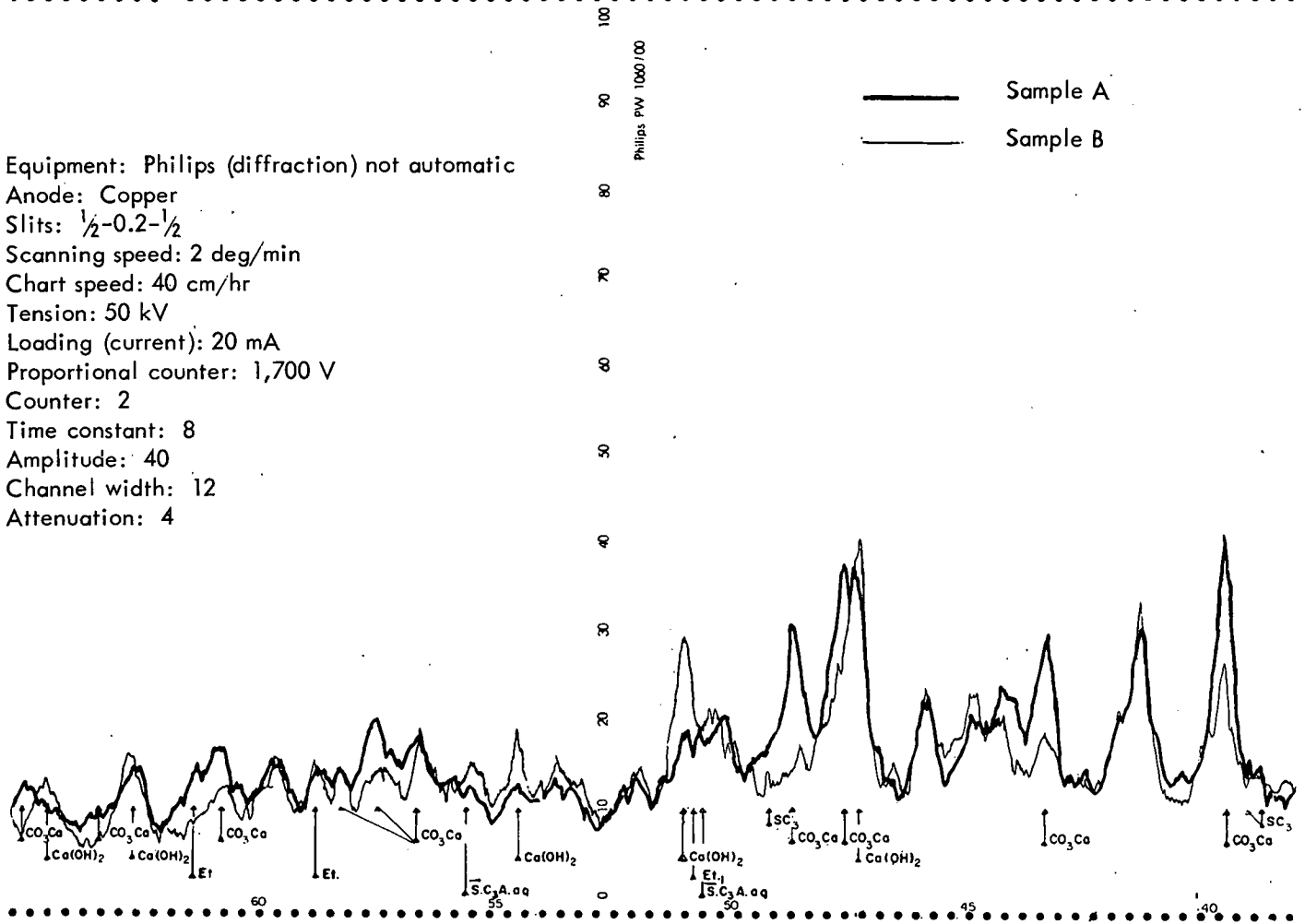

Figure 2. X-ray diffraction diagrams of cement paste samples.

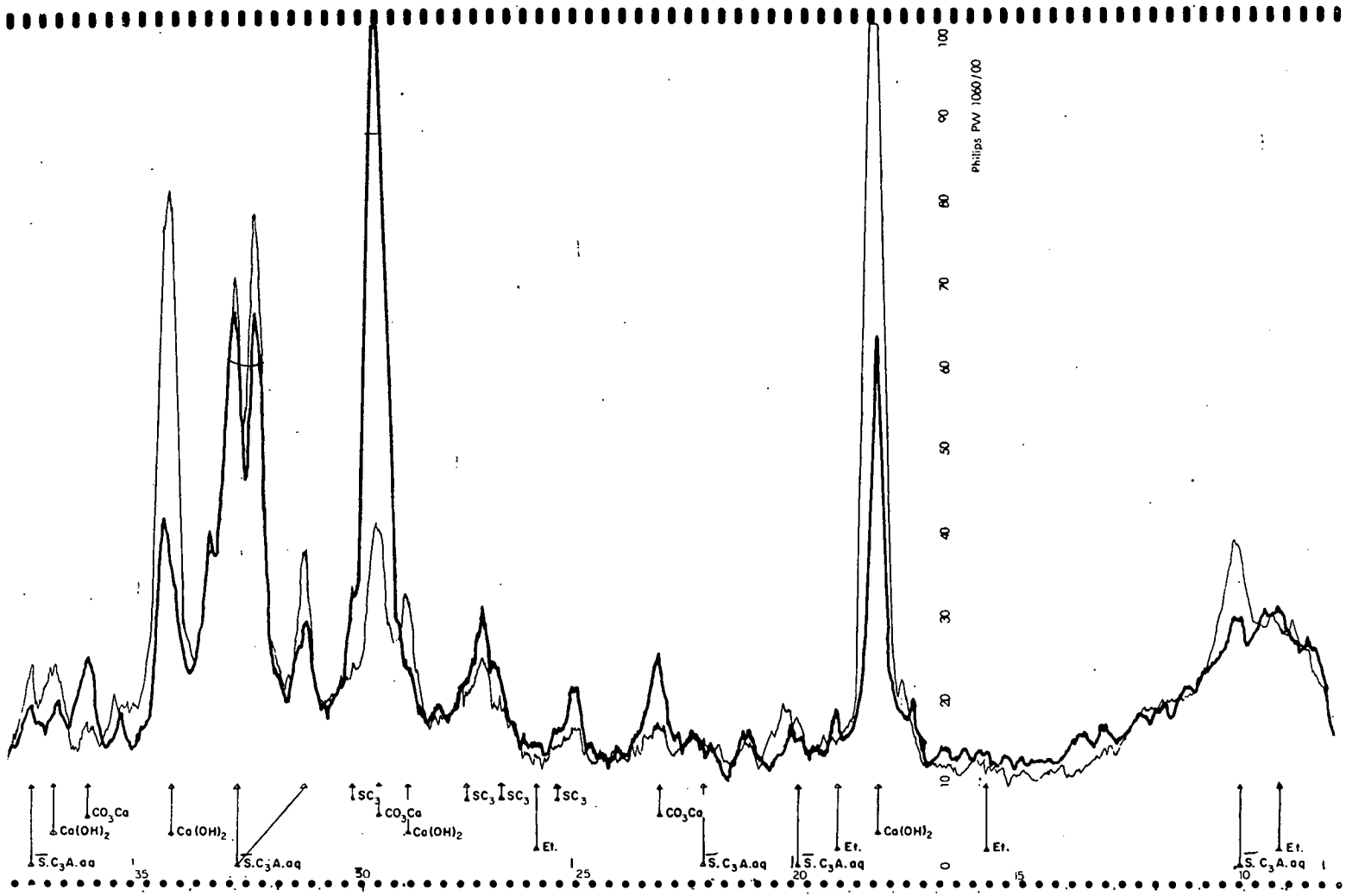

Figure 3. X-ray diffraction diagrams of cement paste samples.

Interpretation of Results

External cracking of cakes forming surface layers about 1 mm thick, partially detached from the main cement-paste mass (Fig. 1), is interpreted as a cracking phenomenon produced by shrinkage. It is considered that this shrinkage is much greater in the outer part of the paste than within the rest of it, so that it has a differential character.

The behavior of the paste in the internal and in the external parts of the cake is different, as if these parts were formed with cements of different properties. Differences found in the chemical analysis and in the calculated values, confirmed by X-ray diffraction results, support this explanation.

Concerning the mechanism by which the cracking was produced, the following hypothesis was formulated: whatever the cause, a bleeding of the paste was produced during the making of the cakes, causing a much more fluid paste to come to the surface. This fluid cement paste contained in solution a good proportion of the total alkalies of the cement, as well as a slight excess of SO_3 (gypsum) over the mean content of this component. Thus the SO_3/alkalies ratio was considerably lower (about one half) in the external than in the internal part of the paste. Alkalinity in turn was noticeably higher.

In addition, the surface layer was richer in the finest particles of the cement, including those of gypsum (which in the grinding and milling process with the clinker becomes finer). This helps to explain the greater content of SO_3 in the surface of the paste.

The higher alkalinity of the surface of the paste and its direct exposure to the atmosphere make this surface paste more subject to carbonation, precisely to a given depth, namely that of the more fluid cement paste. This carbonation transforms the $Ca(OH)_2$ derived from the hydrolysis of silicates into $CaCO_3$, during which water is liberated. This water and the excess water of the more fluid layer evaporate easier and faster, so that in the external parts of the cakes the content of calculated combined water is lower.

The more rapid and complete carbonation of the more fluid layer, due to its strongly alkaline character, produces a shrinkage cracking. In addition to this, if carbonation of the alkalies occurs, it may induce false set or, alternatively, setting conditions different from those which apply in the internal part of the cement mass.

The alkalies themselves may accelerate the setting process, an action that supplements the preceding one, with increased results. This could be counteracted by a higher content of SO_3 (gypsum) in the external part of the paste, but the fact that precisely in this part the ratio SO_3/alkalies is lower seems to show that the action of alkalies is more decisive than the opposite action of gypsum.

Finally, the higher content of $C_3A \cdot \overline{S}_3 \cdot aq$ (the sulphoaluminate richer in sulfate) found in the external zone by X-ray diffraction methods seems to show that the equilibrium

$$3\,CaSO_4 + C_4A \cdot aq \rightleftarrows C_3A \cdot 3\,CaSO_4 \cdot aq + Ca(OH)_2 \qquad (1)$$

is shifted to the right. This displacement may be favored, at least in a given proportion, by the removal of calcium hydroxide owing to a carbonation reaction, aided in turn by alkalies according to the processes

$$Ca(OH)_2 \rightleftarrows Ca^{2+} + 2\,OH$$

and

$$CO_2 + 2\,OH^- + Ca^{2+} \longrightarrow CaCO_3 + 2\,H_2O$$

or otherwise

$$(Na, K)_2CO_3 + Ca(OH)_2 \rightarrow CaCO_3 + 2\ (Na, K)OH$$

so that alkalies remain once more free to repeat the cycle.

The removal of $Ca(OH)_2$ in Eq. 1 causes the consumption of $C_4A \cdot aq$ and, in turn, the consumption of $CaSO_4$ in its reaction with $C_4A \cdot aq$ makes the redeposition of $Ca(OH)_2$ more difficult as in the process

$$CaSO_4 + 2\ KOH \rightarrow Ca(OH)_2 + K_2SO_4$$

Summarizing, the greater amount of alkalies and $CaSO_4$ in the external parts of the cement paste, together with a greater and more rapid carbonation, may produce a shrinkage cracking and a faster process of setting. Shrinkage probably is not counteracted by a greater formation of $C_3A \cdot \bar{S}_3 \cdot aq$, for this complex compound has an expansive character only when its formation takes place by a topochemical process (7, 8) instead of crystallization from solution. Neither is the shrinkage compensated by the greater content of SO_3, for the SO_3/alkalies ratio is not favorable in the external part of the paste.

These conclusions are the result of chemical actions. In addition, the more fluid surface layer is richer in water and finer cement particles, and this in turn contributes to a greater shrinkage. Thus, by a combination of chemical and physical processes, the shrinkage cracking may be explained as a consequence of bleeding and settlement of the cement paste.

As to the direct cause of this bleeding, it is suggested that there was an abnormal and even discontinuous grading of the cement, probably due to a deficiency in the grinding process of the clinker or in grinding equipment.

CONCLUSIONS

Chemical analysis, flame photometric analytical techniques, calculated potential composition, and X-ray diffraction results reveal important composition and constitution differences between the internal and external zones of neat cement paste cakes which developed surface cracking. These differences, considered from chemical and physical points of view, indicate the existence of a much greater shrinkage in the external zones of the cakes.

The shrinkage may be attributed to bleeding of the paste accompanied by a segregation of the finest particles of the cement, mainly alkalies and gypsum, to the external upper part of the cakes. As a probable cause of such bleeding, an abnormal particle size distribution in the cement may be assumed, due to a deficiency in the grinding equipment or process.

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