

A SETTING PROBLEM INVOLVING WHITE CEMENT AND ADMIXTURE

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Quick setting was experienced when a particular water-reducing admixture was used with certain white cements containing less than 1.6 percent SO_3 . These cements set normally at normal temperature without the admixture but set rapidly in the presence of the admixture, both at normal and at high concreting temperatures. Other cements from the same mill with higher SO_3 contents gave normal setting times, both with and without the admixture and irrespective of temperature. Investigation revealed that, in the presence of the admixture, consumption of SO_3 was accelerated in the case of the problem cements and that insufficient SO_3 remained in solution in the period immediately following mixing to properly control the hydration reactions of C_3A . Other factors also were involved, such as inherent clinker reactivity and the state of dehydration of the gypsum.

●SEVERAL instances of quick setting of type 1 cements were encountered, and these all involved either use of a water-reducing admixture or high concreting temperatures, or both. At normal temperatures of 70 to 75 F (21.1 to 23.9 C) and in the absence of admixture, the cements set normally. Without exception the quick-setting cements all had rather low SO_3 contents (about 1.50 to 1.60 percent). However, the SO_3 deficiency was not so great as it seemed at first glance, since drying shrinkage and 24-hour strength tests had indicated an optimum SO_3 content of only about 1.8 to 2.0 percent. Other cements from the same mill with higher SO_3 contents gave normal setting times, both with and without admixture, and even at the high concreting temperatures. Addition to the quick-setting cements of gypsum equivalent to 0.3 or 0.4 percent SO_3 caused them to set normally.

Although the low SO_3 content of the cements was clearly a critical factor in their quick-setting tendencies, other cements with equal or only slightly higher SO_3 contents set normally. An attempt was made to find reasons for this anomaly in chemical differences between the cements, but there was no obvious correlation. The only explanation appeared to be that there were minor differences in the clinkers or in the ground cements that made them slightly more or less reactive on hydration.

This paper describes a specific setting problem experienced with a particular admixture. It is not intended to imply that the type of quick setting described has not been observed before; however, that it is not mentioned in a recent review of the causes of abnormal setting of portland cements (1) suggests that it is not a frequent occurrence. Because of the practical importance of the problem to the field use of white cement, a laboratory study of the factors involved was undertaken. Since the work was originally done to gain information as quickly as possible, the data are not so complete as they would have been had the project been planned from the beginning as a research study.

MATERIALS AND METHODS OF STUDY

Three cements (A, B, and C) were selected for this investigation, the chemical analyses of which are given in Table 1. One of these, cement A, set rapidly in the field when used at temperatures of about 90 F (32.2 C) with a particular water-reducing admixture and also at normal temperatures in the laboratory. This admixture is reported

to be of the carbohydrate type and is probably based on corn syrup. The second cement, B, set rapidly in the absence of admixture when the temperatures of concreting were between 90 and 102 F (32.2 and 38.9 C). Cement B was not used with admixture in the field. Cement A contained 1.55 percent and cement B contained 1.54 percent SO_3 . Cement C contained 1.85 percent SO_3 and behaved satisfactorily with and without admixture. Cements B and C contained approximately 2.5 percent $\text{Ca}(\text{OH})_2$ by differential thermal analysis (DTA), presumably resulting from hydration of free CaO .

The hydration experiments were performed on small paste samples that were hydrated at normal laboratory temperature [approximately 73 F (23 C)] for periods of 5 min, 15 min, 1 hour, and either 3 or 4 hours. The water-cement ratio was 0.50 in all cases. When the admixture was used, it was incorporated in the mixing water at a rate equivalent to 3 oz (8.87 ml) per sack of cement. The admixture was the same as that used with cement A in the field. In some experiments, additional SO_3 was added to the cement in the form of reagent-quality gypsum.

The unhydrated cements and the pastes hydrated for different periods of time were analyzed by DTA. The hydrated samples were vacuum dried before analysis. The quantity of sample was the same in all DTA experiments, and the relative amounts of hydration products were estimated semiquantitatively from thermal peak intensities. The particles were essentially all small enough to pass the No. 200 sieve, and the rate of heating was 50 F (10 C) per min. In a few instances, X-ray diffraction (XRD) patterns were obtained as confirmation of the DTA results. The DTA data were correlated with setting-time tests.

EXPERIMENTAL RESULTS

Cement A

Cement A was hydrated both with and without the admixture. The DTA curves are shown in Figure 1. Calcium sulfate, mostly in the form of gypsum, is indicated on the curve of the unhydrated cement by the double endotherm between 212 and 392 F (100 and 200 C). The curves of the hydrated pastes show that the reaction of C_3A with calcium sulfate to produce ettringite is rapid in the absence of admixture and is accelerated even further in the presence of the admixture. Ettringite is indicated by the deep endotherm between 212 and 392 F (100 and 200 C). Without admixture, a little calcium sulfate remains unreacted after 15 min of hydration but appears to be completely consumed at 3 hours of hydration. In the presence of admixture, the calcium sulfate appears to be completely reacted after 15 min. After 3 hours of hydration with the admixture (bottom curve in Figure 1), a new complex endotherm appears, and the ettringite endotherm is reduced in size. The new endotherm, appearing in the region of 302 to 662 F (150 to 350 C), represents calcium aluminate monosulfate hydrate (or monosulfoaluminate) formed after depletion of the calcium sulfate (2). XRD was used to confirm the presence of monosulfoaluminate in hydrated pastes after occurrence of quick setting. The 8.9 Å line was considered to be characteristic of this compound (3). The monosulfoaluminate was already identifiable in a sample of paste hydrated for 1 hour (not shown in Figure 1). The endotherm at about 932 F (500 C) in the 3-hour samples is due to $\text{Ca}(\text{OH})_2$.

It was noted that the formation of monosulfoaluminate corresponded to a marked drying and stiffening of the pastes at about $\frac{1}{2}$ hour after mixing. This observation correlated with the mortar laboratory tests, in which quick setting was observed about 35 min after mixing when the admixture was used at 73 F (22.8 C). Addition of 0.3 percent SO_3 as gypsum lengthened the setting time of this cement in the presence of admixture to about 3 hours, even at 90 F (32.2 C).

Cements B and C

Cements B and C were both hydrated without the admixture, and cement B was also hydrated with the admixture, even though the field problem of quick setting with cement

Table 1. Chemical composition and fineness of cements A, B, and C.

| Component | Cement A (percent) | Cement B (percent) | Cement C (percent) |
|--------------------------------|--------------------|--------------------|--------------------|
| SiO ₂ | 23.2 | 22.3 | 22.7 |
| Al ₂ O ₃ | 5.1 | 5.5 | 5.0 |
| Fe ₂ O ₃ | 0.3 | 0.3 | 0.3 |
| CaO | 67.9 | 68.5 | 67.8 |
| MgO | 0.8 | 0.7 | 0.7 |
| SO ₃ | 1.55 | 1.54 | 1.85 |
| Na ₂ O | 0.19 | 0.19 | 0.15 |
| K ₂ O | 0.01 | 0.01 | 0.00 |
| Loss ^a | 1.16 | 1.28 | 1.25 |
| Free CaO ^b | 0.6 | 0.4 | 0.5 |
| C ₃ S | 61.3 | 69.2 | 63.7 |
| C ₂ S | 20.2 | 11.8 | 17.1 |
| C ₃ A | 13.1 | 14.0 | 12.8 |
| C ₄ AF | 0.9 | 0.9 | 0.9 |
| CaSO ₄ | 2.64 | 2.62 | 3.15 |

Note: Blaine's surface area measurements are 3470 cm²/g for cement A; 3720 cm²/g for cement B; and 4010 cm²/g for cement C.

^aOn ignition.

^bNot determined at time cements were studied; values obtained about 2 years later.

Figure 1. DTA curves of cement A unhydrated and hydrated for different times with and without water-reducing admixture.

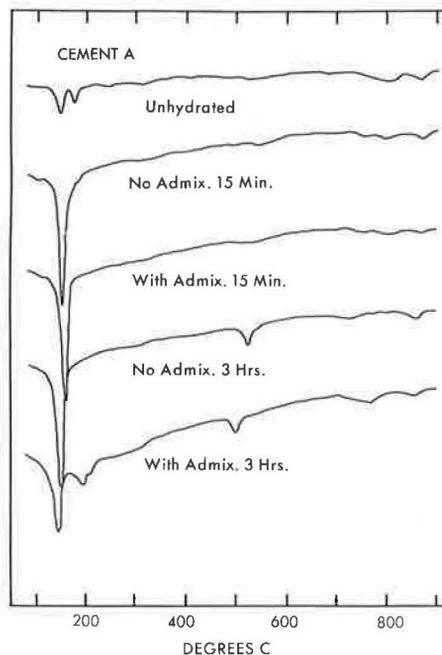


Figure 2. DTA curves of cement B unhydrated and hydrated for different times with and without water-reducing admixture.

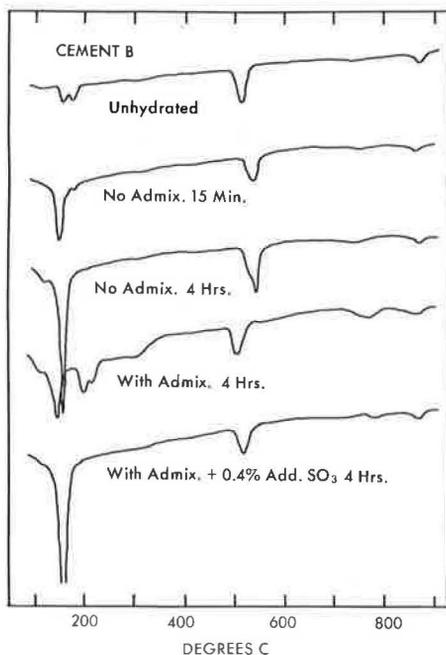
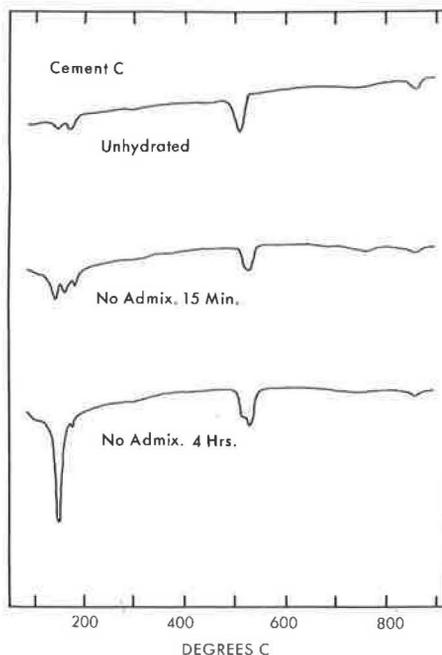


Figure 3. DTA curves of cement C unhydrated and hydrated for different times.



B had not involved an admixture addition. Both with and without the admixture, cement B behaved much like cement A. The DTA curves are shown in Figure 2. At normal laboratory temperature and in the absence of admixture, the calcium sulfate is essentially completely reacted after 4 hours of hydration, but there was no evidence of monosulfoaluminate formation or of quick setting at this length of time. Since this cement gave quick-setting problems in the field, it is probable that a few degrees of increase in temperature would have triggered the conversion to monosulfoaluminate and given the accompanying quick setting at some time earlier than 4 hours. Unfortunately, no DTA hydration experiments were conducted at temperatures in the range of 90 to 102 F (32.2 to 38.9 C). However, such data would be valuable as supporting evidence for the conclusions of the study. However, since cement B stiffened rapidly in the field at a high concreting temperature without admixture, it seems reasonable to assume that a higher laboratory temperature would also have induced quick setting in the absence of admixture.

When cement B was hydrated in the presence of the admixture, the early reactions were accelerated. Calcium sulfate was depleted and monosulfoaluminate began to form in less than 1 hour (not shown in Figure 2), and quick setting was evident. Figure 2 shows the considerable amount of monosulfoaluminate formed after 4 hours of hydration, compared with the absence of this compound in the paste with no admixture hydrated for the same length of time. The bottom curve of Figure 2 shows that, with the addition of 0.4 percent SO_3 as gypsum, no monosulfoaluminate was detectable after 4 hours. This confirms the conclusion that additional SO_3 is needed to properly control the setting of cement B when used with admixture.

Cement C, which contained 1.85 percent SO_3 , behaved normally in the field and had calcium sulfate remaining unreacted at 4 hours as shown in Figure 3. Cement C contained less ettringite than cement B at 4 hours; this suggests that the C_3A -calcium sulfate reactions were basically slower in this cement. This led to the suspicion that the sensitivity to quick setting of cement B was due to a combination of a deficiency in SO_3 and a somewhat greater inherent reactivity on hydration. No DTA tests were made with cement C in the presence of the admixture; therefore, no direct comparison with cement B is available under these conditions.

Mortar laboratory tests correlated well with the hydration experiments. Both cements B and C gave setting times at normal temperatures of about 3 hours. At 94 F (34.4 C), cement C gave a setting time of 165 min; cement B set at 81 min. Addition of the admixture to cement C actually prolonged its setting time at 94 F (34.4 C) to greater than 225 min; however, the setting time of cement B was shortened to 23 min under these conditions.

To confirm the suspicion (previously mentioned) that cement B was inherently more reactive than cement C, the two were hydrated with 0.31 percent SO_3 as gypsum added to cement B so that the total SO_3 contents would be equal. DTA of the original unhydrated cements had shown that, although cement B had a lower total SO_3 content, it actually contained more gypsum than cement C. This is seen by comparing the upper curves of Figures 2 and 3. Hydration of the two cements with SO_3 adjusted to the same level showed quite convincingly that cement B did indeed react more rapidly, as shown in Figure 4. At both 1 and 3 hours not only was more ettringite produced in cement B but also less gypsum was left unreacted, even though the original amount before hydration was considerably more in cement.

Description of other experiments made with cement B follows because they are of considerable technical interest and because they may be of some practical importance. A portion of the cement was heated overnight at 230 F (110 C) to convert the gypsum completely to hemihydrate. The heated cement was hydrated for periods of time up to 3 hours with and without addition of the admixture. The DTA results are shown in Figure 5. Surprisingly, the reactions were found to be much slower than before heating. In fact, the admixture appeared to have less of an accelerating effect on the heated than on the unheated cement. Both with and without admixture, the paste contained considerable unreacted calcium sulfate (gypsum and hemihydrate) after 3 hours of hydration. This was in sharp contrast to the pastes made with unheated cement.

Mortar laboratory results again paralleled the DTA data. At 94 F (34.4 C), the

Figure 4. DTA curves of cement C and cement B with added gypsum to give equal total SO_3 content, hydrated for different times.

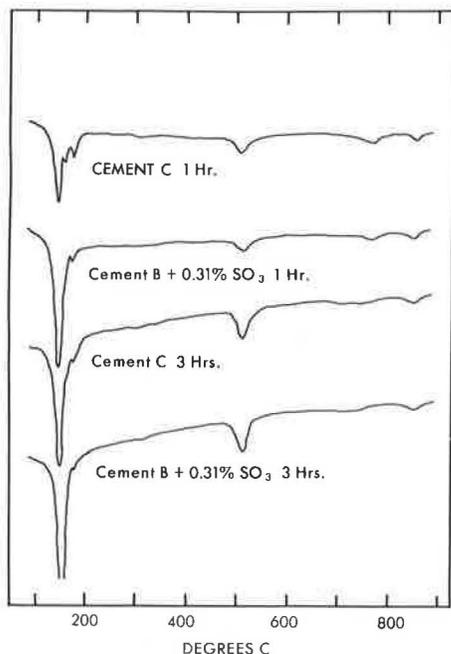
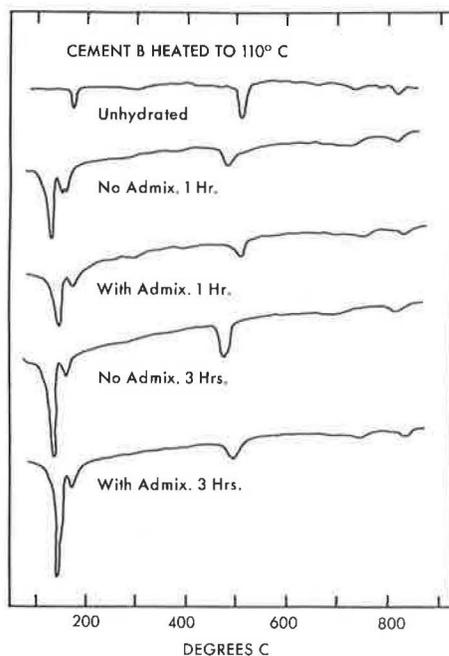


Figure 5. DTA curves of cement B after heating to 230 F (110 C), unhydrated and hydrated for different times with and without water-reducing admixture.



heated sample of cement B gave setting times of 190 min without the admixture and 330 min with the admixture, compared with 81 and 23 min respectively for the unheated sample. The reason for this behavior is not known, but one may theorize that the higher concentration of sulfate in solution resulting from the presence of hemihydrate in the heated cement produced a more impermeable or durable protective coating on the C_3A grains, thereby retarding their reaction. Schwiete and Niel (4) have observed that the ettringite layer on C_3A is stabilized by hemihydrate.

These results suggest the possibility of lengthening the setting time of these sensitive cements by increasing the proportion of hemihydrate through higher grinding temperatures without recourse to an increase in total SO_3 . It is recognized, however, that this procedure might induce false setting because of gypsum crystallization and thereby cause more problems than it solves. In any case, the practical feasibility of this approach would have to be thoroughly tested.

DISCUSSION AND CONCLUSIONS

From these experiments it was concluded that the quick-setting problem resulted from insufficient sulfate being available in solution in the period immediately following mixing to properly control the hydration reactions of C_3A when accelerated by temperature or the admixture or a combination of the two. The admixture effect appears to be the same type of acceleration of stage 1 hydration described by Seligmann and Greening (5) when sucrose was used. However, the fact that normal or near-normal setting behavior was observed with other cements having comparable or even lower SO_3 contents makes it clear that other factors are involved as well. Most important of these is probably the inherent reactivity of the clinker. Later production of white cement from this same mill, containing 1.56 percent SO_3 , which is in the same range as the quick-setting cements, showed no adverse setting behavior, even with the water-reducing admixture and

and at 95 F (35 C). This proves that factors other than SO_3 content are involved. The gypsum in this cement had been essentially completely converted to hemihydrate during grinding; therefore, in view of the heating experiment with cement B previously described, it appears that the hydration state of the calcium sulfate may also affect the setting behavior of some cements when used with admixtures.

The most practical and obvious solution to this type of problem is to make sure that there is adequate SO_3 in the cement for all expected conditions of use. Now the SO_3 content of type 1 white cement is specified at between 1.8 and 2.2 percent. Further setting problems have not been experienced since this level of SO_3 has been maintained.

In addition, the problem of insufficient, readily soluble SO_3 in the presence of admixtures is not restricted to white cement. It can occur and has occurred with gray cements.

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