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Discussion

A discussion of the paper "Redefining cement characteristics for sulphate-resistant Portland cement" by P.J. Tikalsky, D. Roy, B. Scheetz, T. Krize☆

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The authors [1] have carried out some noteworthy investigations for relating specific characteristics to expansion due to sulphate attack by utilising ASTM 1012, a standard method for length change of hydraulic mortars exposed to sulphate solutions. These mortars had been prepared under similar conditions so as to compare the behaviour of 21 North American cements of statistically broad chemical and physical characteristics. The results obtained revealed that whilst C_3A had typically been targeted as the chief contributor to sulphate attack, Fe_2O_3 as C_4AF combined with the total equivalent alkalis showed a much stronger negative correlation with the measured expansions at all ages. This was in agreement with a broad spectrum of sulphate expansion theories and could provide a better means of specifying sulphate-resistant cement [1].

In sulphate attack, although surface layers can be particularly affected and may be subject to a high level of spalling, depending upon the severity of the attack, the spalling does not necessarily increase the exposure conditions for interior concrete. Sometimes spalling does indeed lead to increased exposure conditions for the internal concrete, but also at times this is not the case since when the unsightly spalling takes place, surface carbonation is likely to ensue. This can effectively clog up the pores and obstruct ingress of sulphate and other extraneous ions into the interior of the concrete. In other words, concrete distress is not by itself a sign of concrete failure. If in doubt about any particular situation, core samples can be taken and checked for their engineering properties like compressive strength. In this way, the likelihood of whether distress may be leading to failure or not can be more reliably ascertained. Unsightliness per se is not a reliable indication of likely concrete failure from phenomena such as sulphate attack.

Also, permeability and porosity should not instinctively be regarded as manifestations of the same phenomenon. As a general rule, when permeability increases, porosity does so as well. However, this is not necessarily the case because of the importance of connectivity and other aspects of microstructure. Permeability may rise whilst porosity falls, or vice versa. Each situation needs to be treated on its own merits.

In their paper, Tikalsky et al. [1] refer to the work of Blaine and Arni [2], who showed that several trace elements appeared to have minor effects on sulphate attack. Strontium, chromium, nickel, phosphorus, vanadium and zinc had a slight positive correlation with sulphate expansion, whereas copper showed a slight negative correlation. Reasons for these particular trends do not appear to have been investigated in any real depth.

The American standards ASTM C150 and AASHTO M85, which have become increasingly aligned over the years, use C_3A as a predictive measure, which has not been observed in any scientific study, but rather a convenient manner of specifying cement with a single variable [1]. I would also endorse this straightforward view of the testing procedure.

C_3A alone showed no significant correlation with sulphate expansion at any age, and also Fe_2O_3 was clearly the most predictable variable in sulphate resistance [1]. Substitution of C_4AF for C_3A has been shown to reduce susceptibility to sulphate attack, although too much C_4AF can decrease the resistance of low C_3A cement [3]. Very high negative correlations between both Fe_2O_3 and C_4AF towards sulphate attack expansions reveal that the cements with high iron contents are the most beneficial in controlling sulphate attack. Iron-rich ettringite (AFt) formed from sulphate attack upon the high iron-containing cements is not as expansive as ettringite produced from the low-iron-containing cements. The roles of alkalis and Al_2O_3 are clearly part of the sulphate attack mechanism, but iron has a strong mitigating effect [1]. The nature of these correlations is discussed below.

It needs to be remembered that Portland cement phases are not pure but are solid solutions containing up to ca. 15

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wt.% of extraneous ions, which can affect both the crystallinity and hydraulic reactivity of these phases [4,5]. The compositions and subsequent reactivities of all these clinker phases in given Portland cements worldwide are in effect unique at each individual cement manufacturing plant due to differences in raw materials, manufacturing processes, kiln fuels, burning conditions, etc. The impurities in solid solution influence the hydraulic activity of the clinker phases. Within each cement, the hydraulicity of each one of the clinker phases is influenced by the presence of the other clinker phases. As a result, each clinker phase in a particular Portland cement from a given cement works is unique.

Therefore, it is not surprising that the authors' results [1] showed that C_3A alone gave no significant correlation with sulphate expansion at any age. Each of the 21 cements and thus their C_3A phases was significantly different from the others in terms of reactivity of the clinker phases and not the same in this respect. Hence, good correlations should not ordinarily be expected when unlike is being compared with unlike in this kind of instance.

Earlier work has shown that ettringite formation is relatively lower in a sulphate-resisting Portland cement (like ASTM type V) than in an ordinary Portland cement (like ASTM type I) because of the slower hydration of the ferrite phase C_4AF compared with the aluminate phase C_3A [6]. Furthermore, ettringite appears to be formed at a relatively faster rate from the ferrite phase when the C_3A content of the cement is low than when it is high due to interactive effects such as competition for space for hydration products to move into during early hydration in particular.

The benefits of increasing the ferrite phase at the expense of the aluminate phase for improved sulphate resistance can be explained from the basic mechanism of sulphate attack [7]. It is well known that the main causes of normal sulphate attack when ingress of sulphate ions come into contact with hardened Portland cements are as follows:

- Calcium hydroxide reacting to form gypsum.
- The "monosulphate"-$C_4(A,F)H_{13}$ solid solution (AFm phase) reacting to form ettringite (AFt phase).

As already mentioned, a higher Fe_2O_3 content in the cement causes more ferrite phase to be produced at the expense of the aluminate phase. Calcium hydroxide produced from alite C_3S and belite C_2S hydration is effectively diminished by at least some of it reacting with ferrite to form ettringite (AFt phase) with more iron (III) in solid solution (than that obtained from aluminate hydration) during normal hydration. This is subsequently followed by reaction of some at least of this ettringite forming monosulphate (AFm phase), which again contains more iron (III) in solid solution than the product obtained from aluminate hydration.

In the hydrating cement pastes, ettringite from aluminate and from ferrite forms an overall solid solution in which it is not possible to ascertain precisely what has derived from aluminate or ferrite. Similar comments apply to the $C_4(A,F)H_{13}$-monosulphate derived from both aluminate and ferrite. Importantly, when containing relatively higher amounts of iron (III) in solid solution, the AFm to AFt reaction is slowed down considerably in the hardened cement. This considerable slowing down thereby allows the hardened cement structure to withstand better the occurrence and extent of this potentially expansive reaction.

The suggestion of changing specification requirements to allow more C_4AF (greater than 7%) to increase the reliability of cement specifications for providing sulphate resistance [1] would need to be carefully thought out since there is no suggested upper limit. With the different grades of class G and class H oil well cements (coarse-ground sulphate-resistant Portland cements [8]) for instance, the moderate sulphate-resistant (MSR) types have a C_3A limit of 8% but no C_4AF limit. The high sulphate-resistant (HSR) types not only have a C_3A limit of 3%, but also a C_4AF limit governed by $2 \times C_3A + C_4AF$ not exceeding 24% [9]. This ferrite limit was a recognition that at higher levels than ordinarily found in sulphate-resistant Portland cements, increases in ferrite phase content can adversely affect the overall sulphate resistance of the cement.

It is, of course, well known that Bogue calculations are only approximate and that representing the ferrite phase as C_4AF for convenience obscures the fact that the actual compositions for ferrite, particularly in sulphate-resistant Portland cements, tend to lie away from the C_4AF composition towards C_6AF_2, unlike for ordinary Portland cements where ferrite compositions conversely tend to lie closer to C_4AF. Consequently, it would be more advisable to seek an acceptable upper limit for ferrite (expressed as C_4AF for convenience). This would need to take into account performance variations in different Portland cements caused by variable reactivities towards water of all the clinker phases present in cements from different origins.

Furthermore, the long-term effect of C_3S content upon sulphate resistance has not been taken into account for optimum sulphate resistance. Such a situation will at some time need to be addressed. Dimic and Droljc [10] showed that above 60 wt.% C_3S, the cement increasingly showed diminished sulphate resistance. They recommended that an upper limit of 60% for C_3S in sulphate-resistant Portland cements be introduced.

A fall off in sulphate resistance with increased C_3S is not altogether surprising because the more C_3S there is, then more calcium hydroxide along with C-S-H is produced upon hydration, along with the same products from C_2S over a longer time period. The extra calcium hydroxide produced will be unable to be largely "accommodated" by effectively reacting with the ferrite during hydration to produce more AFt phase (ettringite). The "loose" calcium hydroxide present in the hardened cement, unable to react with the ferrite, is therefore increasingly vulnerable to longer term external sulphate attack where there is exposure to sulphated environments. There is also likely to be increased shrinkage as the C-S-H levels also rise, which can cause cracking and in consequence facilitate the ingress of external ions including sulphate, and thereby augment any sulphate attack that might be occurring.

The aforementioned comments apply to normal sulphate attack. Where thaumasite sulphate attack arises [11,12], as experienced in numerous countries below 15 °C when conditions are favourable for its formation, sulphate-resistant Portland cements can be equally as vulnerable to this form of sulphate attack as ordinary Portland cements are. Hence, cements with higher C_3S contents can be more susceptible to thaumasite sulphate attack than lower C_3S-containing cements when the potential for this form of sulphate attack appears.

With normal sulphate attack, differences in crystal morphology between ettringite ex C_3A and ettringite ex C_4AF might be detected in some isolated instances. However, these were reported as having been detected by SEM. For cement hydration examinations, SEM (both alone and with EDS analysis) cannot be regarded as a confirmatory technique for sound technical reasons [13,14], bearing in mind the substantial heterogeneities in the crystalline structure and the inherent distortions away from pure octahedral symmetry in the basic $[Al,Fe(OH)_6]^{3-}$ units of ettringite.

These heterogeneities are due to solid solution effects within the crystal lattices of the ettringite phases derived from both C_3A and C_4AF, plus the solid solution effects of both with each other, to form what appears to be a continuous mass. Such differences reported cannot therefore be confirmed as real effects able to differentiate on an absolute basis between ettringite deposits from C_3A and those from C_4AF since the solid solution effects are well known. It is possible that the extent of ettringite solid solution might not be total, but to establish the actual situation convincingly would require the employment of more fundamental techniques like optical microscopy and other methods like X-ray diffraction in a comprehensive diagnostic examination of the system [14].

Despite the difficulties discussed above, the work undertaken by Tikalsky et al. [1] is valuable in highlighting what happens to Portland cements covering a wide range of compositions under controlled conditions of sulphate attack. This work has provided an important impetus for consideration of some of the implications and problems of sulphate attack in more detail. As a result, the actuality of sulphate attack can increasingly become better understood and hopefully prevented from taking place, or at least minimised, in many more instances.

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