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Discussion

A discussion of the paper "Durability of the hydrated limestone–silica fume Portland cement mortars under sulphate attack" by J. Zelić, R. Krstulović, E. Tkalčec and P. Krolo☆

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A recent paper by Drs. J. Zelic, R. Krstulovic, E Tkalcec, and P. Krolo [1] examines the effects of limestone filler and silica fume on the sulfate resistance of mortar cements. I agree with some parts of the paper, but I have some commentaries that I would like to point out.

Form the experimental procedure, it is understood that the authors have used mortar bars without gypsum added in excess. Then, the test method that was used to determine the potential sulfate resistance could not be the ASTM C 452-68. This test method has been found effective in distinguishing the high C_3A and the low C_3A portland cements. It is obvious that this method is not suitable for application in blended portland cements, such as portland slag cements and portland pozzolan cements [2,3]. For these types of cement, test methods based on the external sulfate attack with pH-controlled environment, such as the ASTM C 1012, are recommended. pH control is a decisive factor in evaluating the attack created by gypsum formation, which causes the reduction of strength and spalling of mortars.

The authors overlooked the important effect produced by the addition of silica fume or limestone on the water/cement ratio. They point out that the water/cement ratio varied from 0.50 to 0.67 to have the same flow consistency of the mortar. However, they did not explain the changes observed in the function of the increase of water/cement ratio.

The cement used is a commercially blended portland cement containing blast furnace slag. However, the authors failed to discuss the influence of slag or the interaction between slag-silica fume and limestone filler. The slag content was 30% in this commercial cement. The European experience shows that, in order to obtain a good sulfate-resistant cement, a minimum of 65% of the mass of slag is needed (independent of Al_2O_3 content) [4]. On the other hand, cements with low slag content (20% or 30%) are not sulfate-resistant and sometimes, a low slag replacement level could induce a reduction of sulfate resistance [5,6]. If the cement used has no slag content, the sulfate resistance was probably even worse due to the high content of C_3S (70%) in the clinker. The influence of C_3S on the sulfate resistance of portland cement has been discussed by several researches [7–9] and the combination of high C_3S, limestone filler and pozzolans has been studied recently in our laboratory [10]. The synergic effect between the additions has been proven, and should be taken into account. The authors cannot ignore the composition of clinker and the addition of slag to judge the effect of limestone filler and silica fume.

The authors also discussed the effect of blended cement with silica fume (series P) and the effect of limestone filler and silica fume (series PK). In the sulfate resistance of mortar, the amount of CH and the location of crystal play a decisive role. The precipitation of CH crystals at very early stages causes massive deposits of oriented crystals on the paste–aggregate interface, which lead to the inevitable increase of porosity in this region. Thereafter, in the sulfate environment, several authors have observed a massive gypsum formation around the aggregates. According to Mehta [11], the presence of CH to form a gypsum environment is also needed for the expansive ettringite formation, too. In this case, limestone filler increases the portland cement hydration rate, leading to the precipitation of CH located around the filler grains and the aggregate surfaces. As the authors point out, the principal contribution of silica fume is the CH consumption, while the limestone filler does not contribute to the CH reduction. From the XRD pattern presented for the PK series, the reduction of CH is the main change when silica fume was added. From XRD in Fig. 5 of Ref. [1], the reduction of the CH peak and the increase of gypsum peak in P-0 mortar is the remarkable difference in comparison to the P-8 mortar—where the CH peak is present, but not the gypsum peaks. The beneficial effect

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of silica fume may be also computed in the pore size refinement, which blocks the sulfate ingress into the mortar structure. The XRD pattern shows the presence of CH, but the sulfate ions after 120 days cannot ingress and convert the CH to gypsum. Some long crystals of ettringite are shown as evidence of sulfate reaction, but they could not induce expansion because crystal growth into the pores was not restricted and the surrounding environments are dominated by CH, as indicated in the XRD analysis. The expansive cracking occurs when the internal stress overcomes the tensile strength and the mortar presents a dominant gypsum environment due to the continuous removal of CH. Under this condition, Mehta [11] suggests that the CSH starts to lose strength and stiffness, and the ettringite crystals become expansive. This is the scene in the P-0 mortar.

The positive effect of the limestone filler addition (PK series) on sulfate resistance is demonstrated by the extended failure time—from 60 (P-0) to 150 days (PK-0). The authors affirm that the sulfate attack is centered on the hydrated calcium aluminate, and its transformation into more stable compounds (such as monocarboaluminate) during the hydration of cement contribute to the better stability of the PK series in sulfate solution. However, for PK-0, a strong peak of ettringite was detected, which confirmed my dissident opinion that monocarboaluminate is an unstable compound in sulfate environment.

For the PK series, the authors omitted to discuss the dilution effect of the harmful compounds of portland clinker in sulfate the environment (C_3A and C_3S), which has been indicated to contribute to the improvement of the sulfate performance of portland cements [12,13]. In this experiment, C_3A dilution has significance because the cement used has a 6% C_3A content. On the other hand, the dilution of C_3S can be analyzed in association with the increase of the C_3S hydration rate induced by the addition of limestone filler [14].

I would agree with the authors that during cement hydration, carbonate ions coming from limestone filler modify the hydration products. Reaction products from C_3A phase of portland cement in the presence of limestone filler include: monocarboaluminate, monosulfoaluminate, and ettringite. Vernet and Noworyta [15] report that monocarboaluminate stability is better than those of the monosulfoaluminate and aluminate hydrates, and these authors also inferred a relative greater resistance of limestone filler cements exposed to sulfate attack. In our experimental studies [14,16], monocarboaluminate formation was detected by XRD after 3 days of water curing, and the transformation of monosulfoaluminate into monocarboaluminate and ettringite was detected in 28 days. But, the XRD results (see Fig. 5 of Ref. [14]) of mortars with limestone filler immersed in sulfate solution denote that the ettringite formation originated by the transformation of monocarboaluminate in the sulfate environment. Their conclusions overlook the fact that ettringite is more stable than monocarboaluminate in the sulfate environment as described in the solubility product and stability study (K_{sp} (monosulfoaluminate) = 1.7×10^{-28}, K_{sp} (monocarboaluminate) = 1.4×10^{-30}, K_{sp} (ettringite) = 1.1×10^{-40} [17]). The only contribution that I can glean from this point of view is related to the part of aluminates that remain as ettringite (a stable compound in sulfate medium) due to the monosulfoaluminate decomposition by carbonate ions in the limestone filler cement. However, monocarboaluminate is an unstable compound in the presence of a new external source of sulfate ions, as shown by the XRD analysis of limestone filler cement studied in this paper and in our previous paper.

References

[1] J. Zelic, R. Krstulovic, E. Tkalcec, P. Krolo, Durability of the hydrated limestone–silica fume Portland cement mortars under sulphate attack, Cem Concr Res 29 (1999) 819–826.

[2] ASTM C 452-68, Standard Method of Test Potential Expansion of Portland Cement Mortars Exposed to Sulfate, Annual Book of Standards, ASTM, Philadelphia, 1971 Part 9.

[3] P.K. Mehta, O.E. Gjorv, A new test for sulfate resistance of cement, J Test Eval 2 (1974) 510–514.

[4] J. Geisler, H. Kollo, E. Lang, Influence of blast furnace cements on the durability of concrete structures, ACI Mater J 92 (1995) 252–257.

[5] ACI Committee, ACI 226.1R-87: Ground granulated blast furnace slag as a cementitious constituent in concrete and mortar, ACI Mater J 92 (1995) 321–322.

[6] J. Frearson, Sulfate resistance of combinations of portland cement and ground granulated blast furnace slag, Fly Ash, Silica Fume, Slag, and Natural Pozzolans in Concrete, SP-91, American Concrete Institute, Detroit, MI, 1986, pp. 1495–1524.

[7] D. Dimic, S. Droljc, The influence of alite contents on the sulfate resistance of portland cement, Porc. 8th. Int. Congress on the Chemistry of Cement, Rio de Janeiro, Brazil, 1986, V, (1986) 195–199.

[8] Rasheeduzzafar, Influence of cement composition on concrete durability, ACI Mater J 89 (1992) 574–586.

[9] M. González, E.F. Irassar, Ettringite formation in low C_3A portland cement exposed to sodium sulfate solution, Cem Concr Res 27 (1997) 1061–1072.

[10] E.F. Irassar, M. González, V. Rahhal, Sulphate resistance of type V cements with limestone filler and natural pozzolan, Cem Concr Comp submitted.

[11] P.K. Mehta, Mechanism of sulfate attack on portland cement concrete — another look, Cem Concr Res 13 (1983) 401–406.

[12] I. Soroka, Effect of calcareous filler on sulfate resistance of portland cement, Ceram Bull 55 (1976) 594–595.

[13] R.D. Hooton, Effects of carbonate additions on heat of hydration and sulfate resistance of portland cements, in: R.D. Hooton (Ed.), Carbonate Additions to Cement, ASTM STP 1064, Philadelphia, 1990, pp. 73–81.

[14] M. González, E.F. Irassar, Effect of limestone filler on the sulfate resistance of low C_3A portland cement, Cem Concr Res 28 (1998) 1655–1667.

[15] C. Vernet, Noworyta, Mechanism of limestone fillers reactions in the system ($C_3A-CSH_2-CH-CC-H$), Proceedings of 9th International Congress on the Chemistry of Cement, New Delhi, India, (1992) 430–436.

[16] V. Bonavetti, V. Rahhall, E.F. Irassar, Studies on the carboaluminate formation in limestone filler blended cements, Cem Concr Res submitted.

[17] F. Zhang, Z. Zhou, Z. Lou, Solubility product and stability of ettringite, Proceedings of 7th International Congress of the Chemistry of Cement, Paris, France II, (1980) 88–93.