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Sulphate resistance of type V cements with limestone filler and natural pozzolana

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Abstract

Sulphate performance of concrete depends primarily on permeability. Under severe conditions of sulphate exposure, low-permeability concrete is prescribed and it must also be made with high sulphate resisting cement. For portland cement, the sulphate resistance depends on the C_3A content and the amount of CH produced at early stages of hydration. Some parameters that modify the quantity of early CH in the hardened cement paste are investigated in this paper. Two type V cements with quite different C_3S content and blended cements containing natural pozzolana or limestone filler were used. Expansion, flexural and compressive strength of mortar, immersed until 1 yr in sodium sulphate solution, with pH-controlled are presented. Results show that the sulphate performance of portland cement with high C_3S content is very poor compared with low C_3S portland cement. Addition of natural pozzolana provides the maximum sulphate resistance while the addition of 20% limestone filler declining sulphate performance of low C_3A cements. This behaviour can be attributed to the reaction between sulphate ions with CH into the paste that produces an alteration of the predominant mechanism of sulphate attack. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Sulphate attack; C_3S; Blended cement; Natural pozzolana; Limestone filler

1. Introduction

Deterioration of concrete by sulphate attack is commonly observed in structures exposed to soils or groundwater containing a high concentration of sulphate ions. To mitigate this attack, concrete codes [1–4] recommend a concrete mixture with low water/cement ratio and containing a sulphate resistant portland cement.

In the 1930s, sulphate resisting portland cements were developed by Thorvaldson [5] increasing the iron content in raw materials at portland cement's plant. This finding produced a portland cement with a low C_3A content increasing the C_4AF content.

During the last decades, C_3S-content in portland cement has been increased leading to important changes in strength evolution of concrete at early ages. Today, it is possible to obtain an elevated strength level of concrete using a relative high water/cement ratio. Consequently, this practice enlarges the capillary porosity of concrete that also governs the deterioration process in sulphate environment [6]. These changes of C_3S/C_2S ratio in the modern portland cements conduce to a great CH content in the cement paste because the C_3S hydration produces 2.2 times more CH than C_2S hydration. In the sulphate attack, CH plays a decisive role in the reactions that produce gypsum and ettringite [7].

Blended cements containing active mineral admixtures (fly ash, slag, silica fume or natural pozzolana) have demonstrated to be sulphate resistant due to pore size refinement, C_3A dilution, and CH removal by pozzolanic reaction [8–10]. However, filler addition frequently incorporated in modern composite cements does not confer equivalent properties. It stimulates the silicate hydration obtaining a high hydration degree at early ages and consequently an increase of strength [11,12]. For this addition, the CH is not removed from the paste at later ages.

It is commonly assumed that a clinker with a low C_3A content and limited C_4AF content will be used with any mineral additions to obtain a sulphate resistant cement. However, sulphate performance of blended cements depends on the type and replacement level of mineral

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addition and on the clinker composition, especially C_3A and C_3S content.

This paper considers the relative importance on sulphate resistance of low C_3A cements based of C_3S content, the addition of active pozzolana and the addition of limestone filler. The performance of these cements was evaluated using a pH-controlled sulphate environment and the mechanical parameters evaluated were expansion and strength. Finally, the mechanisms of deterioration are discussed to corroborate the changes in mortar composition.

2. Materials and experimental procedures

Two sulphate resisting portland cements with different C_3S content were used in this experimental program. Chemical composition and physical properties of cements are reported in Table 1. Both agree with ASTM C150 requirements for sulphate resistant portland cement (type V). These requirements are related to potential composition (C_3A and $2C_3A + C_4AF$) and to the expansion limit at 14 days when they were testing according to ASTM C452.

For each portland cement, four blended cements were formulated: two containing 20% and 40% of natural pozzolana (P) and two containing 10% and 20% of limestone filler (F). All replacement was made by mass of cement. Natural pozzolana has a good activity index and it has demonstrated to improve the sulphate performance of type I cement in a long time field test [13]. Limestone filler contains 85% of $CaCO_3$ and no clay materials. Table 1 reports the properties of mineral admixtures.

For these 10 studied cements, mortar specimens $25.4 \times 25.4 \times 297$ mm^3 were moulded according ASTM C1012 procedure (sand–binder material ratio 2.75, water–binder ratio 0.485). Specimens were cured in moist cabinet during 24 h and removed from the mould. Then, specimens were cured in lime saturated water until to achieve the compressive strength of 30 ± 3 MPa. At this age, mortar specimens of each cement were stored in individual plastic tanks containing Na_2SO_4 (0.352 M). The pH of solution was periodically adjusted by addition of Na_2SO_4 (0.352 M) plus H_2SO_4 (2 N) solution neutralising the alkalinity and re-establishing the Na^+ and SO_4^{-2} concentration of solution. A few drops of phenolphthalein were used as pH indicator in each plastic tank. Consumption of titration solution was registered and the SO_3 consumption per volume of specimen was calculated.

Expansion and mechanical strength of mortars were measured at 0, 28, 56, 180 and 360 days of sulphate immersion. At each test age, two specimens stored in

Table 1
Chemical composition and physical properties of cements and mineral admixtures

	Low C_3S cement	High C_3S cement	Natural pozzolana	Limestone filler
Chemical composition, % in weight				
SiO_2	23.66	21.00	76.9	10.63
Al_2O_3	3.00	3.29	9.8	1.20
Fe_2O_3	5.41	4.68	3.6	0.78
CaO	62.14	66.00	1.8	47.16
MgO	0.60	0.67	0.5	0.39
SO_3	1.59	2.20	–	0.16
K_2O	–	–	1.4	0.34
Na_2O	–	–	3.7	–
Total alkalis	0.70	0.82	–	–
Loss on ignition	1.61	1.23	2.4	37.50
Composition (Bogue), % in weight				
C_3S	40	74		
C_2S	38	4		
C_3A	0	1		
C_4AF	15	14		
Blaine fineness, m²/kg	313	306	710	698
Compressive strength, MPa				
3 days	11.4	27.3		
7 days	17.6	29.2		
28 days	32.7	32.5		
Expansion (ASTM C452), %				
14 days	0.015	0.012		
360 days	0.030	0.045		

water and two specimens stored in sulphate solution were tested. Flexural strength was obtained in five points of each specimen using a centre-point loading and a span length/deep ratio of 2.5. Then, compressive strength of mortar was determined on four fragments of each specimen broken by flexion using an adapter device for small cubes (25.4 mm). Thereafter, the relative strength was calculated as the ratio between mortar strength in sulphate solution and the mortar strength in water.

For this test method, failure criteria adopted is an expansion value of 0.1%. Blended cements can be considered as sulphate resistant when expansion is lower than 0.1% at 1 yr [14].

To identify the products of sulphate attack, the XRD analysis was performed on mortars pulverised samples in Phillips X'Pert diffractometer equipped with graphite monochromator.

3. Results

3.1. Expansion

Fig. 1 shows the expansion data of mortars with limestone filler and natural pozzolana in sulphate solution for both cements. These curves indicate that high C_3S portland cement is not sulphate resistant, instead of it have a low C_3A content and agrees with standard requirements. For this cement, the expansion value at 360 days was 0.350% whereas the low C_3S portland cement has ten times less expansion (0.035%) at the same test age.

Limestone filler addition to low C_3S portland cement leads to a larger expansion than those of mortar without addition. At 360 days, mortars with 10% and 20% of filler show an expansion of 0.066% and 0.174%, respectively. For mortar with 10% of filler, the final expansion value is lower than the failure criteria for sulphate resistant cement. However, low C_3S cement with 20% of filler may be classified as moderate sulphate resistant according to the limit proposed (0.10% at 180 days) by Patzias [14].

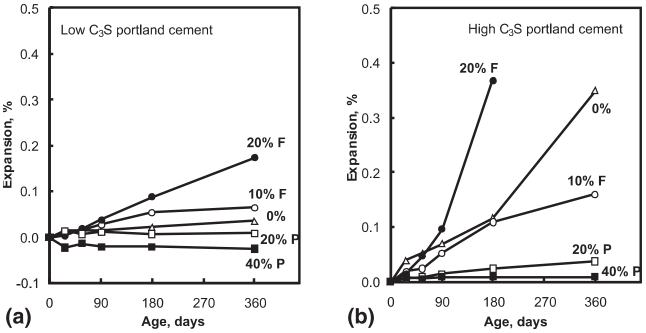

Fig. 1. Expansion of mortars immersed in sodium sulphate solution.

The expansion evolution has a different behaviour according to the filler replacement level in the high C_3S portland cement. Mortars with 20% of filler have a larger expansion than that of plain mortar after 90 days of sulphate immersion. However, expansion was reduced when this cement contains 10% of filler. Both filler cements with high C_3S content cannot be classified as sulphate resistant because they overcome the failure criteria before than 1 yr.

All cements containing natural pozzolana have a notable reduction in expansion at all test ages. Expansion reduction was drastic in mortars with high C_3S portland cement. Mortar containing 20% of natural pozzolana has a similar expansion to low C_3S plain mortar at 360 days, while expansion in mortar with 40% of pozzolana was very little (< 0.010%). Both pozzolanic cements may be classified as sulphate resistant blended cements. For mortars with low C_3S portland cement, the replacement of 20% of pozzolana reduces the expansion while 40% of replacement produces a contraction of 0.020% at the test end.

In summary, 20% of filler addition trends to increase the expansion of low C_3A cements, while natural pozzolana addition reduces drastically the expansion.

3.2. Sulphate demand

Fig. 2 shows the SO_3 consumption per specimen volume during sulphate immersion. This parameter, called sulphate demand by us, indicates the interaction between mortar specimens and sulphate solution.

Sulphate demand of mortars with limestone filler is greater than those of plain mortar for both cements used. For low C_3S cement, the increase of sulphate demand at 360 days was 43% and 62% for 10% and 20% of limestone filler addition, respectively. For high C_3S portland cement, this increment was high (102%) for 20% replacement level and equivalent (38%) for 10% replacement.

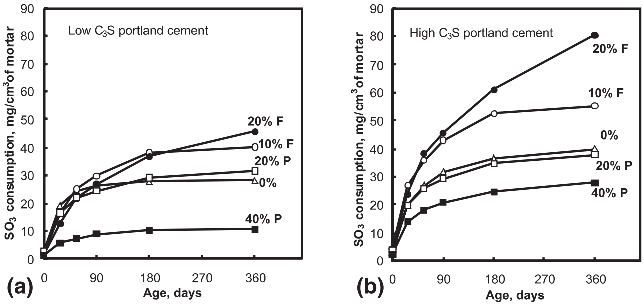

Fig. 2. Specific consumption of titration solution by volume of mortar versus exposure age.

For both portland cements, the addition of 20% of pozzolana caused a slight difference in the sulphate demand (±10%) while replacement of 40% of pozzolana produces a very important reduction in sulphate demand (168% and 30% for low C_3S and high C_3S cement, respectively).

In summary, filler addition increases the sulphate demand and pozzolana addition no changes or reduces this demand.

3.3. Flexural strength

Table 2 reports the flexural strength of mortar immersed in sulphate solution and curing in water and the relative strength calculated as described above. Fig. 3 shows the flexural strength development after sulphate immersion.

Low C_3S portland cement has no reduction of flexural strength at all ages and the final relative strength was 1.18. On the contrary, flexural strength decays in high C_3S portland cement after 180 days. At 1 yr, relative strength was 0.89.

Both cements containing 10% of limestone filler present no significant changes during the test. For mortar with low C_3S and 20% of filler, flexural strength increases until 28 days of exposure and then it decreases slowly. At 1 yr, relative strength was 0.75. For mortar with high C_3S and 20% of filler, flexural strength drops drastically after 28 days, achieving to a relative strength of 0.45 at 360 days.

In mortars containing natural pozzolana, flexural strength increases until 90 days and then it remains without changes. For these mortars, relative flexural strength was ranged from 0.98 to 1.19 at 360 days.

Table 2
Flexural strength, compressive strength and relative strength at selected ages after sulphate immersion

Age, days		Flexural strength, MPa				Compressive strength, MPa			
		0	28	90	360	0	28	90	360
Low C_3S portland cement									
0%	Sulphate	5.70	7.46	8.24	8.09	28.51	29.63	45.00	41.70
	water		6.00	5.67	6.88		32.47	40.80	43.95
	S/W[a]		1.24	1.45	1.18		0.91	1.10	0.95
10% F	Sulphate	5.83	7.33	7.18	7.42	30.12	39.50	35.60	39.43
	water		6.23	6.72	7.17		35.18	39.58	41.17
	S/W		1.18	1.07	1.03		1.12	0.90	0.96
20% F	Sulphate	5.54	7.79	n.d.	4.81	28.36	40.10	40.10	35.47
	water		6.05	6.09	6.44		33.55	35.98	37.26
	S/W		1.29	n.d.	0.75		1.20	1.11	0.95
20% P	Sulphate	5.24	7.76	8.79	9.29	27.52	38.78	43.37	49.25
	water		6.66	6.52	7.78		32.85	36.93	46.67
	S/W		1.16	1.35	1.19		1.18	1.17	1.06
40% P	Sulphate	6.51	7.52	8.11	8.73	27.74	32.82	34.14	43.28
	water		7.30	7.40	7.88		34.88	34.70	42.62
	S/W		1.03	1.10	1.11		0.94	0.98	1.02
High C_3S portland cement									
0%	Sulphate	4.90	5.68	6.38	4.90	28.70	30.69	33.76	n.d.[b]
	water		5.30	5.50	5.49		33.12	36.00	37.10
	S/W		1.07	1.16	0.89		0.93	0.94	n.d.
10% F	Sulphate	5.97	6.44	6.66	6.00	29.91	36.71	36.05	34.17
	water		5.83	6.34	6.57		38.32	39.75	41.40
	S/W		1.10	1.05	0.91		0.96	0.91	0.83
20% F	Sulphate	5.00	5.89	5.06	2.67	29.34	24.20	24.92	16.90
	water		5.26	5.48	5.89		30.10	32.00	32.20
	S/W		1.12	0.92	0.45		0.80	0.78	0.52
20% P	Sulphate	5.23	6.60	7.34	7.43	27.82	31.73	35.20	38.22
	water		6.05	6.41	7.56		31.32	34.59	41.22
	S/W		1.09	1.14	0.98		1.01	1.02	0.93
40% P	Sulphate	5.37	6.91	7.61	7.99	27.95	32.89	32.73	35.68
	water		6.56	6.84	7.27		30.46	35.12	39.80
	S/W		1.05	1.11	1.10		1.08	0.93	0.90

[a] S/W = relative strength.

[b] n.d. = not determined.

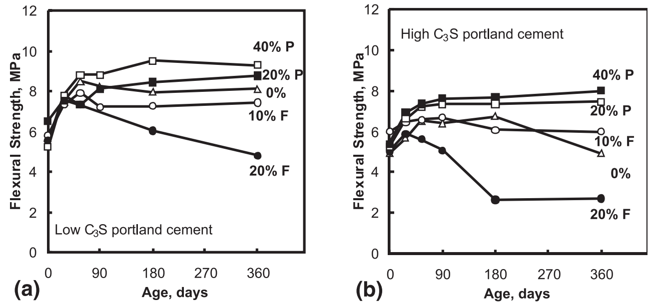

Fig. 3. Flexural strength of mortars immersed in sodium sulphate solution.

3.4. Compressive strength

Results of compressive strength test of mortars are also reported in Table 2. Fig. 4 shows the compressive strength development after sulphate immersion for all cements.

Mortars containing natural pozzolana show a gain or retention of strength during all immersion ages. This behaviour indicates an excellent internal stage of specimens. Relative compressive strength was 0.95 in mortar with low C_3S portland cement, while mortars containing high C_3S portland cement with natural pozzolana have a similar relative strength of 0.93 and 0.90 for 20% and 40% of replacement, respectively.

Evolution of compressive strength of mortar containing limestone filler was quite different. Mortars with low C_3S portland cement show an increase or retention of compressive strength until 90 days, then it declines slowly at the test end. After 360 days, relative strength was 0.95 for both replacement levels.

In mortars with high C_3S portland cement, specimens containing 10% of filler show a strength loss after 56 days of exposure and the relative strength was 0.83 at test end. However, 20% of filler addition shows a decreasing strength after beginning the test and relative strength was 0.52 at 360 days.

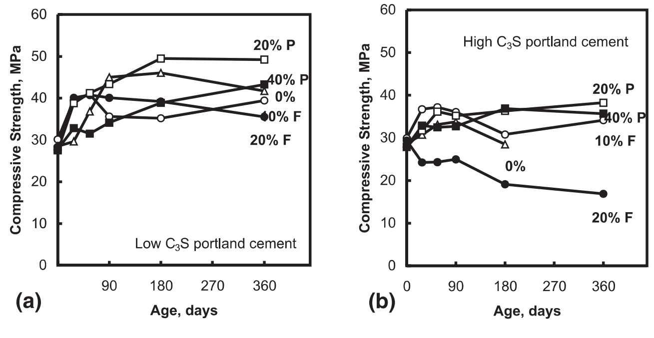

Fig. 4. Compressive strength of mortars immersed in sodium sulphate solution.

3.5. XRD analysis

Fig. 5 shows X-ray diffractograms of mortar samples after 360 days of sulphate immersion. Low C_3S portland cement mortar presents only the gypsum peak ($2\theta = 11.60°$) as reaction compound. A same observation can be made in mortar containing low C_3S portland cement with pozzolana. Both mortars containing low C_3S portland cement and filler exhibit the ettringite peak ($2\theta = 9.08°$) combined with some large intensity gypsum peaks.

In high C_3S portland cement plain mortars, gypsum peaks appear with secondary ettringite. In this cement, ettringite formation is the result of reaction between sulphate ions and ferroaluminate hydrates [15]. When pozzolana is the mineral admixture, ettringite cannot be identified by XRD analysis and gypsum formation decreases. However, high C_3S portland cement with filler reveals the formation of both typical products of

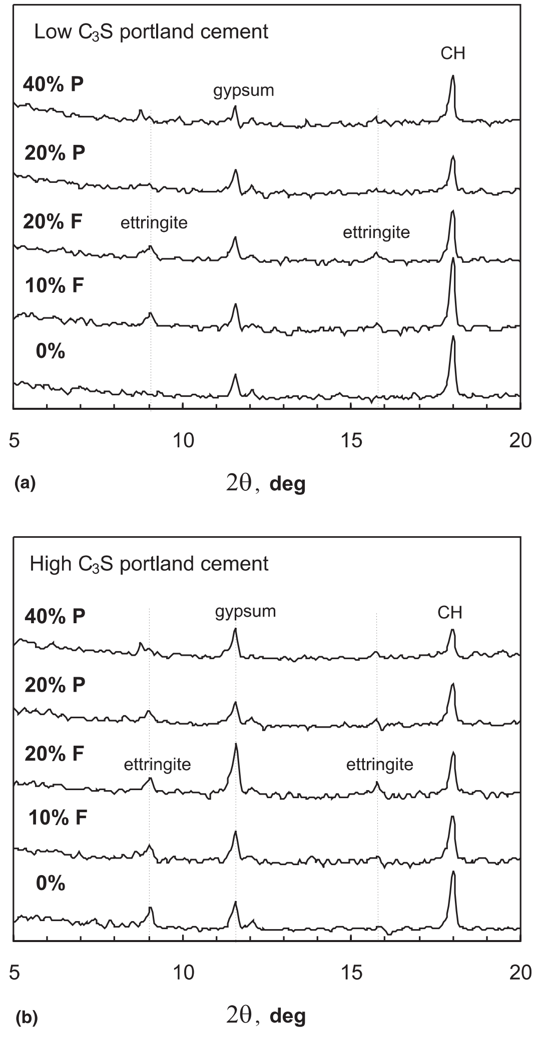

Fig. 5. XRD pattern for mortars exposed in sodium sulphate solution after 360 days of immersion.

sulphate attack. Particularly, gypsum appears with a high intensity in high C_3S portland cement with 20% of limestone filler.

In portland cements with limestone filler mortars, thaumasite ($CaSiO_3 \cdot CaSO_4 \cdot CaCO_3 \cdot 15H_2O$) was not detected as a product of sulphate degradation of mortars containing carbonate additions [16].

4. Discussion

Results show that low C_3S portland cement mortar has an excellent behaviour in sulphate environment according to its low expansion and the high retention of flexural and compressive strength. On the other hand, high C_3S portland cement mortar shows a poor sulphate resistance with expansion and strength loss. This quite different behaviour of both sulphate resistant cements is mainly due to the increase of CH released during silicate hydration when the C_3S/C_2S ratio increases leading to modify the sulphate deterioration mechanism.

First, it is expected that CH leaching increases when cement paste is immersed in water or pH-controlled solution. Fig. 2 shows that the sulphate demand of high C_3S portland cement was 41% higher than that of low C_3S portland cement indicating the extended interaction between mortar and solution at all test ages. Several authors [17,18] have verified the importance of pH control of test solution for ettringite expansion acceleration.

Second, the CH reacts with sulphate ions to form gypsum. Complementary, some authors [19] suggest that the Ca^{2+} consumption produced by this reaction can lead to the decomposition of C–S–H. This type of attack causes the matrix cohesion loss starting the softening of exposed surfaces of mortar or concrete, the mass loss and the strength loss (specially compressive strength) at advanced deterioration degree [17]. Generally, it is assumed that gypsum formation does not produce expansion unless a massive gypsum formation occurs localised at paste–aggregate interface [20]. For low C_3S portland cement mortar, XRD reveals only a little formation of gypsum, then a very low expansion and slight reduction of compressive strength were measured at later ages. For high C_3S portland cement mortar, gypsum was detected by XRD at early immersion ages (90 days). This gypsum formation was predominantly localised at the paste–aggregate interface leading to a large expansion according to data describes in previous paper [15].

Third, gypsum formation into the mortar creates the required environmental conditions to form expansive ettringite derives from aluminate or ferroaluminate hydrates. According to Mehta [7], ettringite formation is expansive when gypsum and CH dominate the paste environment. In ordinary portland cements, secondary ettringite depends principally on C_3A content of cement. But, it depends also on the amount of CH produced during the early stages of hydration, which is closely related to the C_3S content of cement. For high C_3S portland cement mortar, the deterioration mechanism is associated with ettringite formation providing from ferroaluminate hydrates. This ettringite has a similar structure, morphology and properties to the compound formed from C_3A hydrates, where some Al_2O_3 has been partially replaced by Fe_2O_3. Characteristics of this type of sulphate attack are an increase of expansion rate, the microcracking and the drastic drop of flexural strength as can be observed for high C_3S portland cement mortar.

According to the above description, CH plays a decisive role in the performance of low C_3A portland cements exposed to a sulphate environment with pH control. It leads to change the predominant sulphate deterioration mechanism and the performance of sulphate resistant portland cements can vary from excellent to poor.

In mortars containing pozzolana, the CH content in the paste decreases significantly due to the pozzolanic reaction progress reducing the leaching process. This reaction produces a secondary C–S–H that also decreases the capillary porosity of mortars and enhances significantly the paste–aggregate interface. These effects of pozzolanic reaction cause a reduction of sulphate ions diffusion and the transport of sulphate ions from solution to mortar. Then, these processes conduce to a significant decrease of mortar-solution interchange as described the sulphate demand curves (Fig. 2) for all mortars with natural pozzolana, instead of the C_3S content of the portland cement. Reduction in CH always leads to less gypsum formation and then secondary ettringite cannot be detected in mortar at older ages (Fig. 5). Thereafter, mechanical behaviour of pozzolan mortars indicates non-expansion and no reduction of flexural and compressive strength. For high C_3S portland cement mortar, the pozzolana addition reduces drastically the expansion. In this case, transformation of CH crystals located at paste–aggregate interface prevents the massive deposition of gypsum in this location and the generation of gypsum environment needed to expansive ettringite formation. This behaviour corroborates the decisive role played by CH in sulphate attack.

Limestone filler addition results to significant modification of nature of the cement paste [21]. First, filler addition accelerates the cement hydration processes (especially C_3S hydration) increasing the CH formation due to nucleation effect at early ages. This produces a change in the development of mortar capillary porosity [22]. Second, limestone filler produces the dilution of cement components. Third, carbonate ions from limestone filler compete against sulphate ions to react with

C_3A of cement [23]. Products of these reactions are monocarboaluminate (MCA), monosulphoaluminate (MSA), trisulphoaluminate (TSA or ettringite) and tricarboaluminate (TCA). In most experimental works, the formation of TCA cannot be detected in limestone cement paste and the MCA is present at later ages.

In terms of sulphate resistance depending of C_3A content of cement, Vernet and Noworyta [24] demonstrate that the MCA stability is higher than MSA and aluminate-hydrates stability inferring an increase of sulphate resistance of cements with limestone filler as practical consequence. However, these authors omit that ettringite stability is higher than the MCA-stability in sulphate environment [24] causing its transformation. On the other hand, author's opinion is that this situation has a little importance in low C_3A cements used in this experimental study.

For limestone filler mortars, the increase of hydration rate causes a high CH-content at early ages. In mortars, water/cement ratio and the local environment control the CH content. Filler grains provide the nucleation sites for CH crystals modifying the local environment. This increase of CH crystallisation rate conduces inevitably to large oriented crystals in the paste–aggregate zone and then increases the vulnerability of this mortar region. Filler addition fills only the interstices between the cement grains, but it did not produce a cementing compound at later ages. Then, an increase of capillary porosity of paste facilitates the growth of well-defined CH crystals that will be attacked by sulphate ions to form gypsum.

Reasons explained above justify the high sulphate demand of limestone filler mortars at early ages due to the extended calcium leaching process. This behaviour is opposite to mortars with natural pozzolana. On the other hand, the increase of gypsum formation due to the large available space in mortar, the high CH availability and the high mortar-solution exchange lead to an early expansive ettringite formation.

Results presented here suggest that the addition of limestone filler produces a decay in sulphate performance of low C_3S portland cements. For this cement, the hydration process is advantageously accelerated by limestone filler addition. However, the high C_2S content in cement lead to also decrease capillary porosity after sulphate immersion and to reconstitute the microcracks caused by the sulphate attack. For high C_3S portland cement, the hydration process is fully developed during the previous water curing. Then, the benefit computed to limestone filler addition is the C_3S dilution because the capillary porosity increases with the amount of limestone filler added.

Finally, a large capillary porosity at later ages can be computed as a detrimental effect of limestone filler addition. According to Bonavetti [25], when mortar ($w/c + f = 0.485$) attains to hydration degree of 0.8, the porosity capillary calculated using the Powers' model [26] increases 24% and 50% for 10% and 20% of limestone filler, respectively. For this reason, dilution effect of limestone filler is only advantageous when the paste contains unstable compounds (high C_3A cement or high C_3S cement) in sulphate environment and the replacement level did not produce an excessive increase of capillary porosity.

Both portland cements containing 10% of limestone filler have no detrimental effects. But mortars with 20% of limestone filler show the largest expansion and a drop of flexural strength that are associated with the ettringite formation according the mechanism described above.

5. Conclusions

The sulphate resistance of low C_3A portland cements tested in pH-controlled sodium sulphate solution was relatively poor when cement has a high C_3S/C_2S ratio showing a large expansion and a strength retrogression. This behaviour may be attributed to the high amount and localisation of CH in mortar.

Great expansion of high C_3S cement can be attributed to gypsum formation located at the paste–aggregate interface at early stage of attack that produces the environmental conditions needed to expansive ettringite formation from ferroaluminate phases at advanced attack stages.

Natural pozzolana addition improves the sulphate resistance of low C_3A portland cements due principally to the CH reduction in mortars, specially the reduction of CH at paste–aggregate interface that delays and prevents the gypsum formation. Mortars with pozzolans have a very low expansion and a high retention of strength in sulphate environment instead of C_3S content of cement.

Filler addition to low C_3A cements can lead to a worse sulphate performance of composed cements. For replacement of 20%, detrimental effects are mainly attributed to the increase of capillary porosity and the high CH vulnerability in the paste. For 10% of replace level, the sulphate performance has no significant change.

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