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Role of Cement in Sulphate Attack of Reactive Aggregate Mortars

Rôle du ciment dans l'attaque de mortiers à aggrégats réactifs par les sulfates

Rolle des Zementes beim Sulfatangriff auf reaktive Mörtel

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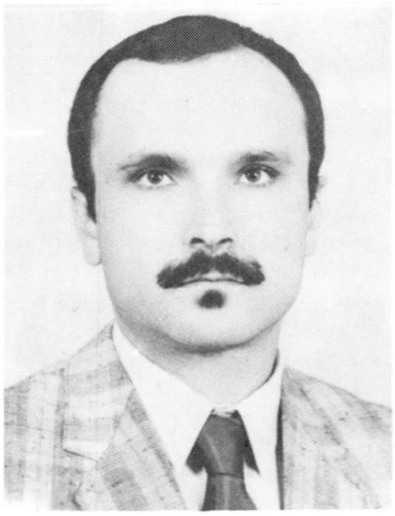

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SUMMARY

This paper presents results of the influence of cement type on the durability of mortars made with sulphate reactive aggregates in a calcium hydroxide saturated medium, and kept under sea water after different curing periods. The observations, some of them over a period up to 20 years have enabled the authors to classify the resistance of the different cement types to sea water attack, when reactive aggregates are used.

RÉSUMÉ

On présente des résultats concernant l'influence du type de ciment sur la durabilité des mortiers préparés avec des agrégats réactifs aux sulfates dans un milieu saturé d'hydroxyde de calcium, et maintenus immergés dans l'eau de mer après différents temps de cure. L'observation, qui en quelques cas s'est prolongée pendant 20 ans a permis de classer la résistance des différents types de ciment à l'attaque de l'eau de mer lorsqu'on utilise des agrégats réactifs.

ZUSAMMENFASSUNG

Dieser Beitrag behandelt den Einfluss der Zementart auf die Beständigkeit des Mörtels mit sulfatreaktiven Zuschlagstoffen in einem mit Kalkhydroxid gesättigten Medium. Die untersuchten Bauelemente wurden dem Meerwasser ausgesetzt. Es wurden verschiedene Behandlunsperioden mit Beobachtungszeiten bis zu über 20 Jahren durchgeführt. Es war möglich, die verschiedenen Widerstände der untersuchten Zemente und der reaktiven Zuschlagstoffe bezüglich der Angriffigkeit des Meerwassers festzustellen.

1. INTRODUCTION

All research in the area of sulphate attack is based on formation of ettringite as a result of reaction between sulphates and C_3A present in portland cements. The ettringite formation can, however, take place without the presence of C_3A, if the reactive alumina for the formation of ettringite is provided by the aggregate [1]. When an aggregate contains kaolinized feldspar, the alumina from the aggregate reacts with sulphates, forming ettringite. The ettringite formed will be expansive as long as the reaction of alumina with sulphate takes place in a medium oversaturated with calcium hydroxide [2].

A concrete dock structure of Leixões Harbour, in the north of Portugal, built in 1940, suffered large expansions and cracking 6 months after the original installation. It was not until 15 years later that a proper explanation for the failure could be found in reactions involving sea water and the weathered feldspar of the aggregate.

With the same aggregates used in that structure, a study was undertaken to compare the resistance of different types of cements to the formation of expansive ettringite, on mortar prisms maintained under sea water in laboratory, after previous curing which varied from 2 days to 1 year. The specimens were subjected to visual inspection for detecting fissures and to length change measurements. The correlation between the Fratini test results and the behaviour of the mixes of portland cement and pozzolan are also discussed.

2. EXPERIMENTAL

The chemical analysis and some physical characteristics of cements and pozzolanas used are described in tables 1 and 2. There are no elements about the portland cement type V, according to ASTM, with exception to C_3A content that was 4.5%. The pozzolanic cement used was a ferric-pozzlanic one, from Italy. The compressive and flexural strengths were determined using prisms with 4 cm x 4 cm x 16 cm; the strength of pozzolanas was measured in pastes of standard consistency with 1 part of lime and 3 parts of pozzolan, by mass.

The pozzolana named Cape Verde is a natural one, existing in the Republic of Cape Verde. Kaoline and diatomite were activated by calcination at 850°C.

The granite, composition of which is presented in table 3, was sieved between 0.8 and 0.4 mm, the grading that has already shown to produce the most rapid alteration of the mortars.

The mortars consisted of 1 part of cementious material, 5 parts of crushed weathered granite sand and 1 part of water, by mass. When using pozzolanas, the cementious material was composed of portland cement and different percentages of pozzolana, varying from 0% to 50%. The mortars were hand mixed and the prisms with 4 cm x 4 cm x 16 cm were also hand consolidated. For each condition, 2 prisms were molded.

The prisms were kept in the molds, in a fog room, for 48 h, and then were either immediately immersed in small plastic tanks filled with sea water, or they were air-cured in the laboratory for 7 d, 28 d, 90 d and 360 d, before immersion. As sea water was encrusting, the protective layer of calcium carbonate was frequently removed. In the same way, as the pH of the water went up quickly after the contact with the prisms, specially when the prisms were not air-cured, the sea water was also replaced. All the procedures are fully described in an earlier publication [3].

The Fratini test [4] was carried out on pozzolanic cement and on mixes of portland cement and pozzolana.

Cements	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	Na_2O	I.loss
Portland	20.0	6.9	3.5	62.9	2.4	2.1	0.7	0.0	1.5
High alumina	5.5	40.4	16.0	36.6	0.6	Vest.	---	---	0.9
Pozzolanic	29.2	17.0		44.1	2.0	1.1	0.9		5.0
Natural	22.2	6.0	2.6	53.3	3.2	3.6	---	----	7.5
Slag	28.1	7.3	2.1	52.0	4.1	2.3	0.8	0.2	1.6

Pozzolanas	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	Na_2O	I.loss
Cape Verde	49.5	20.2	2.3	1.9	1.7	0.3	5.2	6.2	12.8
Kaoline	52.3	33.2	1.3	0.0	Vest.	0.0	3.6	1.1	8.2
Diatomite	81.0	3.1	4.8	0.5	0.0	0.9	0.4	0.8	10.0

Table 1 Chemical analyses of cements and pozzolanas

Cements and Pozzolanas	45 µm sieve residue %	Surface area Blaine cm^2/g	Mortar or paste strength, MPa			
			Compressive 7 d	Compressive 28 d	Flexural 7 d	Flexural 28 d
Portland	----	4270	25.2	35.4	5.3	6.9
High alumina	----	3250	65.5	69.6	6.7	7.4
Pozzolanic	21.1	4430	6.7	19.5	2.0	4.4
Natural	----	4930	4.1	7.5	1.3	2.3
Slag		3800	20.7	33.8	5.2	7.9
Cape Verde	48.0	4270	4.6	10.3	2.0	3.8
Kaoline	15.3	10472	0.6	7.7	0.3	3.6
Diatomite	10.1	23100	2.5	12.6	1.0	3.0

Table 2 Physical characteristics of cements and pozzolanas

Constituents (% by mass)				
Plagioclase	Alkaline feldspar	Quartz	Muscovite	Other minerals
36.6	20.4	31.5	13.0	0.7

Table 3 Composition of weathered granite

3. RESULTS AND DISCUSSION

Results and their discussion will be mainly based on the number of prisms not disrupted, once it was observed that the measured expansion was not a good reference: some prisms cracked under little expansion, others did not crack under high expansion levels.

3.1 Cements

Table 4 presents, for each cement, the number of prisms not disrupted, as a function of the curing time, as well as the time of disruption of the others, that is, the time when a visible crack was recorded.

As shown, the best performance was achieved with natural cement, followed by the pozzolanic one from Italy. According to the theory set out in an earlier publication [2], expansive sulphoaluminate forms only in the presence of calcium hydroxide oversaturated solutions. Therefore, natural cement, with a composition close to that of hydraulic lime, without C_3S and C_3A, does not originate that kind of solutions and so expansive ettringite. The pozzolanic reaction explains the performance of the pozzolanic cement.

The most surprising results were obtained with high alumina cement, usually considered as resistant to sulphate attack. The results are yet more surprising, because other prisms made with not weathered granite evidenced fissuration earlier. It is difficult to find an explanation; maybe this cement does not work well with aggregates of acid nature. Curing time did not change the performance of the cement owing to absence of lime to be hydrated.

Slag cement seems to have excellent performance, on account of results until 7 years, which are compared in fig. 1 with those of a mix of portland cement and 50% of pozzolana, by mass, which showed very good behaviour, as will be seen later. In the two cases the prisms were immersed in sea water 48 h after casting.

3.2 Mixes of portland cement and pozzolana

Table 5 shows, in the same way, the number of prisms disrupted and time until disruption, depending on time of curing and percentage of pozzolana added to cement.

Increasing the percentage of pozzolana, the durability of mortars is also increased: with 40% or 50% of pozzolana, total protection from sulphate attack is obtained, even with 48 h curing. Nevertheless, with other less reactive pozzolanas, the curing time may have to be increased in order to get similar results.

Diatomite was the best pozzolana used, maybe owing to its great surface area. One of the prisms made with the pozzolana of Cape Verde, cured for 7 d, cracked after 6 years approximately, which is thought to be an exceptional result.

3.3 Curing time

The idea behind the consideration of different times of curing was determining the minimum period of cement hydration or pozzolanic reaction to obtain the necessary chemical resistance. As shown in tables 4 and 5, this period depends on the type of cement or on the percentage of pozzolana: it is possible to get good results with only 48 h curing, though increase to 7 or 28 d is always beneficial.

The most salient aspect was total protection obtained when the cure had a duration of 1 year, even for portland cement. As a matter of fact, after 6 months all prisms were completely carbonated, without free calcium hydroxide, which avoided the formation of expansive ettringite. At 7 d, 28 d and 90 d, the depth of carbonation was 2 mm, 7 mm and 14 mm, respectively.

Cements	Prisms not disrupted					Time of disruption, years				
	48 h	7 d	28 d	90 d	360 d	48 h	7 d	28 d	90 d	360 d
Portland	0	0	0	0	2	0.4	2.2	1.2	6.0	>22
High alumina	0	0	0	0	0	4.4	4.3	4.0	2.1	3.1
Pozzolanic	0	0	2	2	2	5.7	6.2	>22	>22	>21
Natural	0	0	2	2	2	12.4	16.3	>22	>22	>21
Slag	2*	-	-	-	-	>7.0	---	---	---	---
Type V	0	-	-	-	-	0.8	---	---	---	---

Table 4 Behaviour of cement mortar prisms as a function of curing time

Pozzolanas	Time of curing	Prisms not disrupted					Time of disruption, years				
		10%	20%	30%	40%	50%	10%	20%	30%	40%	50%
Cape Verde	48 h	0	0	0	1	2	0.9	2.9	5.9	8.9	>23
	7 d	0	0	2	2	1*	3.8	5.2	>23	>23	6.6*
	28 d	0	0	0	2	2	4.0	5.2	5.9	>23	>23
	90 d	0	2	2	2	2	7.2	>23	>23	>23	>23
	360 d	2	2	2	2	2	>22	>22	>22	>22	>22
Kaoline	48 h	0	0	0	2	2	0.5	0.5	13.2	>18	>18
Diatomite	48 h	0	0	2	2	2	1.5	4.2	>17	>17	>18

Table 5 Behaviour of cement and pozzolana mortar prisms as a function of the percentage of pozzolan

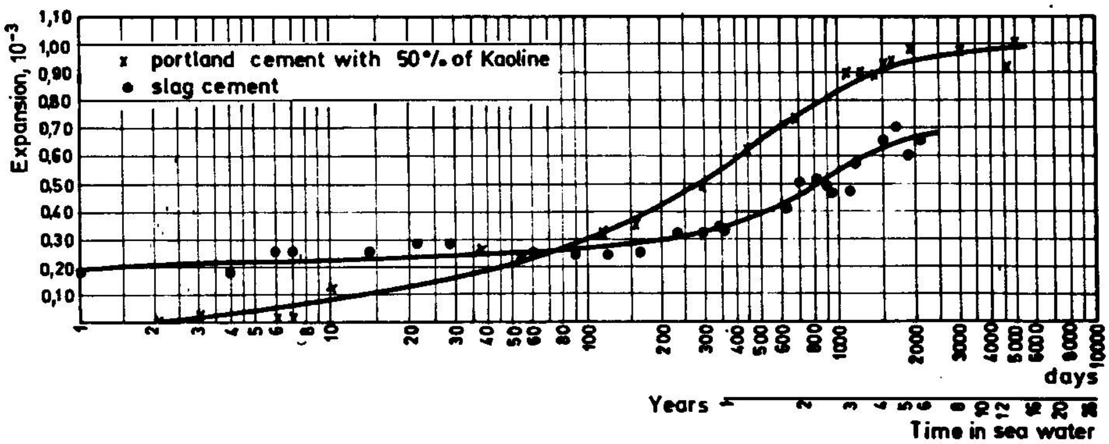

Fig. 1 Expansion of prisms made of two cementious materials

3.4 Fratini test

The Fratini test results were not conclusive to foresee the behaviour of the mixes of cement and pozzolana. Clearly pozzolanic mixes, according to this test, did not show good performance with short curing time. It is believed that the pastes for test should be kept at the same temperature of mortars and tested at the age of their contact with the aggressive medium, so that correlation can be possible. In the standard test the pastes are kept at 40°C for 7 d, which gave rise to an acceleration of the pozzolanic reaction.

4. CONCLUSIONS

The cement that exhibited better performance was the natural one, followed by the ferric-pozzolanic cement: a curing period of 28 d gives total protection against sulphate attack, with this kind of aggregates. With a short cure, 48 h, only slag cement seems to give this protection. High alumina and type V cements did not show good performance.

With an adequate percentage of pozzolan in the mix with portland cement, it is possible to get total protection, even with only 48 h of cure. In the pozzolanas tested, this percentage varied from 30% to 50%.

A curing period of 48 h may be enough for total protection, but increasing it is always advantageous.

The Fratini test does not give information about the behaviour of mixes of portland cement and pozzolana: clearly pozzolanic mixes did not provide total protection with the shorter curing period.

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