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COMPARATIVE XRD ANALYSIS ETTRINGITE ORIGINATING FROM POZZOLAN AND FROM PORTLAND CEMENT

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ABSTRACT

The ettringite is often formed when concrete is attacked by sulphatic waters. In this investigation, a semi-quantitative analysis and study of the ettringite (2Θ = 9.08°) in the solid phase of the Fratini test was made by XRD. The cements P-1 (14.11% C_3A) P-31 (7.6% C_3A) and PY-6 (0.00% C_3A), five pozzolans, D,O,A,C and M and five mixed cements PUZC 70/30, PY-6/D, O, A, C or M, respectively, were used. These PUZC were mixed with gypsum in proportions to give 7.0% or 21.0% SO_3. Identical analysis and study was made of the corresponding mixtures of each pozzolan plus $Ca(OH)_2$ and gypsum.

The experimental results have demonstrated that 1. The formation rate of ettringite from pozzolan, is notably higher than the formation rate of ettringite from OPC. 2. The topochemical mechanism of the etrringite formation can proceed when ALL the necessary reactive materials, including the "reactive alumina," $Al_2O_{3r^-}$ [or better perhaps, "aluminate anion" or "amorphous alumina" (tetra- or penta-coordinated alumina)], are in the solution.

Introduction

The sulphate attack on portland cements, involves the formation of expansive ettringite from C_3A. A substantial bibliography exits about pozzolanic cements and pozzolans.

The question would be whether portland cements with pozzolan form ettringite when they are attacked by sulphate ions, or whether these cements resist the attack.

It is a widespread belief that: One of the causes for not forming ettringite, is the low concentration of $Ca(OH)_2$ in the liquid phase due to their reaction with the pozzolan. The first part of the theory of Lafuma (1) is in harmony with this hypothesis. Another cause may be the formation of C-S-H type products from the pozzolan. A third cause may be that the high specific surface of the pozzolans plugs the pores of the paste impeding the access of the aggressive solutions.

But these suppositions are still debated. For this reason this debate is being cleared by means of this paper. Shortly, other papers will be published with the same purpose.

For that and in accordance with the ternary diagram of Eitel (2) and the chemistry requirement that the standard ASTM C618-85 (3) imposes on the pozzolanic additions, the five pozzolans (4) in Table 1 have been chosen to demonstrate that the pozzolans can form ettringite

TABLE 1

DETERMINATIONS (%)	CEMENTS			POZZOLANS				
	P-1	P-31	PY-6	D	O	A	C	M
	(3,08)*	(3,06)	(3,21)	(2,59)	(3,08)	(2,41)	(2,68)	(2,55)
LOI	1,60	3,45	1,11	0,23	0,40	3,92	6,92	0,60
I.R.	0,70	0,86	0,15	0,42	1,10	–	0,43	0,22
SiO_2	19,18	18,13	21,70	91,81	45,12	41,38	54,18	73,53
Al_2O_3	6,44	5,30	1,52	1,91	13,84	19,36	20,10	23,11
Fe_2O_3	1,75	3,80	4,11	2,39	13,82	12,05	3,12	1,19
CaO	63,94	61,68	67,97	1,23	10,48	11,11	2,38	0,63
MgO	1,48	1,82	0,42	0,38	9,54	10,58	2,04	0,03
Na_2O	0,90	0,76	0,43	1,50	3,18	1,24	5,64	0,07
K_2O	0,52	0,31	0,20	0,12	2,40	0,44	5,17	0,70
SO_3	3,50	3,86	2,34	–	0,46	–	–	–
TOTAL	100,01	99,97	99,95	99,99	99,94	100,08	99,98	100,05
H_2O(105°C)	0,24	0,33	0,22	0,07	0,55	4,02	4,03	0,16
CaO free	1,90	0,63	1,75					

DETERMINATION(%)	POTENTIAL CALCULUS BOGUE(%)		
C_3S	51,05	58,70	79,43
C_2S	16,48	7,70	2,29
C_3A	14,11	7,62	0,00
$C_4AF(+C_2F)_{ss}$ 9*	5,33	11,56	9* 10,19
C_4AF+2C_3A (6)	33,55	26,80	10,19
C_4AF+C_3A (1)	19,44	19,18	10,19
Spf. Surf. 2*	3192	3248	3287

*.- Spf. Weight (g/cm^2)
2*-Spf. Surface (cm^2/g)

CHEMICAL ANALYSIS OF THE GYPSUM

DETERMINAT. (%)	MINERALOGICAL COMPOSIT. (%)
H_2O (40°C a 217°C) – 20,13	$CaSO_4 \cdot 2H_2O$ - 95,58
CO_2 (217°C a 1000°C – 0,75	$CaSO_4 \cdot \frac{1}{2}H_2O$ y/o
R.I. – 0,26	
SiO_2 – 0,04	$CaSO_4$ — 2,47
SO_3 – 45,87	
CaO – 32,54	$CaCO_3$ — 0,75
MgO – 0,36	$MgCO_3$ — 0,81
Na_2O – 0,02	TOTAL 99,61
K_2O – 0,01	
TOTAL 99,98	H_2O a 40°C - 0,41

and also, the possible differences between this type of ettringite and the ettringite from C_3A origin of a OPC.

Objectives

Confirm or disprove the formation of ettringite from portland cement and pozzolan origin. Establish differences between the ettringites of such origins. Establish relations between the quantity of ettringite formed and/or some chemical parameters related to its reagent origin.

Experimental Procedure

The Fratini test is based on the experiments of N. Fratini (5), regarding the saturation of calcium hydroxide in a solution, in the presence of alkalis in variable ratios. Several european countries—Italy, Portugal, France and Spain—presently use this pozzolanity test (5) as an evaluation of the lime in the over-floating liquid (100 cm^3) in contact with the possible pozzolanic cement paste (20g) at a given age, according to certain defined specifications. For our research the solid phase of this test (5) was used and it was analyzed by XRD. Previously such solid phase had

TABLE 2
Materials Dosage

Materials	CEMENTS:																POZZOLANS	
	PORTLANDS						POZZOLANICS 70/30										D,O,A,C ó M	
	P-1		P-31		PY-6		PY-6/D		PY-6/O		PY-6/A		PY-6/C		PY-6/M		4,78 (g)	3,25 (g)
	% SO_3 OF THE CONGLOMERANT-MIXTURE CEMENT PLUS GYPSUM																	
	7,0	21,0	7,0	21,0	7,0	21,0	7,0	21,0	7,0	21,0	7,0	21,0	7,0	21,0	7,0	21,0	7,0	21,0
Cement (g)							PY-6+D 12,32+5,28	(PY-6+D) 7,88+3,38	PY-6+O 12,33+5,29	(PY-6+O) 7,89+3,38	PY-6+A 12,34+5,29	(PY-6+A) 7,90+3,36	PY-6+C 12,32+5,28	(PY-6+C) 7,88+3,38	PY-6+M 12,30+5,27	(PY-6+M) 7,37+3,37		
	18,35	11,74	18,51	11,84	17,66	11,43	17,60	11,26	17,62	11,27	17,63	11,28	17,60	11,26	17,57	11,24	---	---
Gypsum (g)	1,65	8,26	1,49	8,16	2,14	8,57	2,40	8,74	2,38	8,73	2,37	8,72	2,40	8,74	2,43	8,76	3,01	9,03
$Ca(OH)_2$ R.A. (g)																	12,21	7,88

been prepared with gypsum using two OPC - P-1(14,11%C_3A) and P-31(7,62%C_3A), one SRPC PY-6(0,00%C_3A) and ten pozzolanic cements PUZC 70/30. These had been prepared from SRPC PY-6, pozzolans, $Ca(OH)_2$ Ch.R. and gypsum to give 7,0% SO_3 and 21,0%SO_3, see Tables 1 and 2. Once such plasterbearing mixture was prepared and adequately mixed, 20g. of this was mixed with 100 ml distilled water and stored at 40°C.

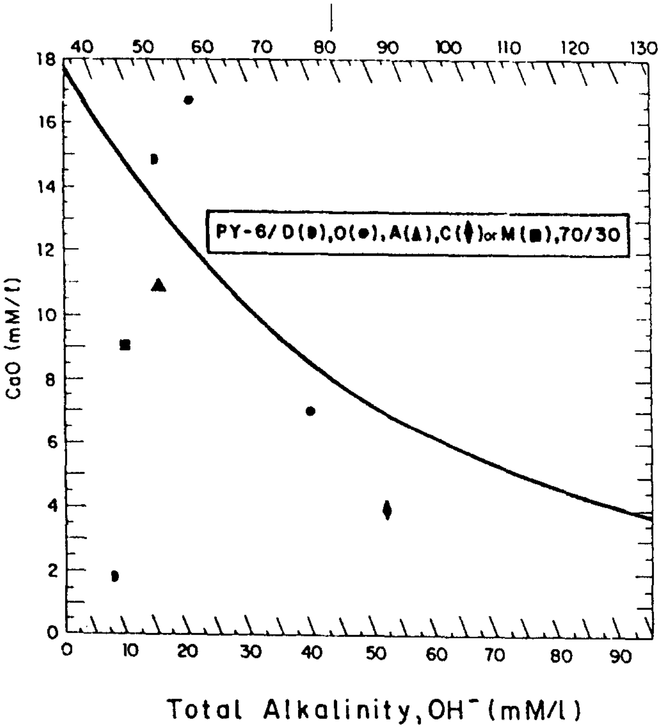

FIG. 1.
Fratini test of the pozzolanic cements PY-6/D, O, A, C or M 70/30.

After 1, 7, 14, 21, 28, 60, 90, 275 and 730 days, the solid phase of each plasterbearing mixture (a sample) was subjected to XRD having been previously taken at nitrogen atmosphere. The analysis was carried out choosing selected ettringite peaks such as 2Θ = 9.08° and 2Θ = 15.788°.

Results and Discussion

Firstly, the original Fratini test (5) showed the pozzolanic activity at 7 or at 28 days, from all pozzolans which had been chosen obligatorily for this research,see Fig.1. On the other hand, the graphic representation of the remaining experimental results, was semilogarithmic on the "x" axis, Figs. 2 a),b),c),d),e) and f).

In both cases, 7.0% SO_3 or 21.0 % SO_3, all pozzolans tested carried out a faster ettringite formation (7 to 14 days before), except D. In addition, the first great peak of ettringite formation (and commonly the greatest of them all) from pozzolan origin, has usually surpassed in almost all cases—except the pozzolan A in some occasions—in at least 7 days to the corresponding greatest peak of ettringite formation from OPC origin (from its C_3A), in spite of the fact that by stechiometry and according to Murat (6)(7)(8)(9), the opposite fact should have occured.

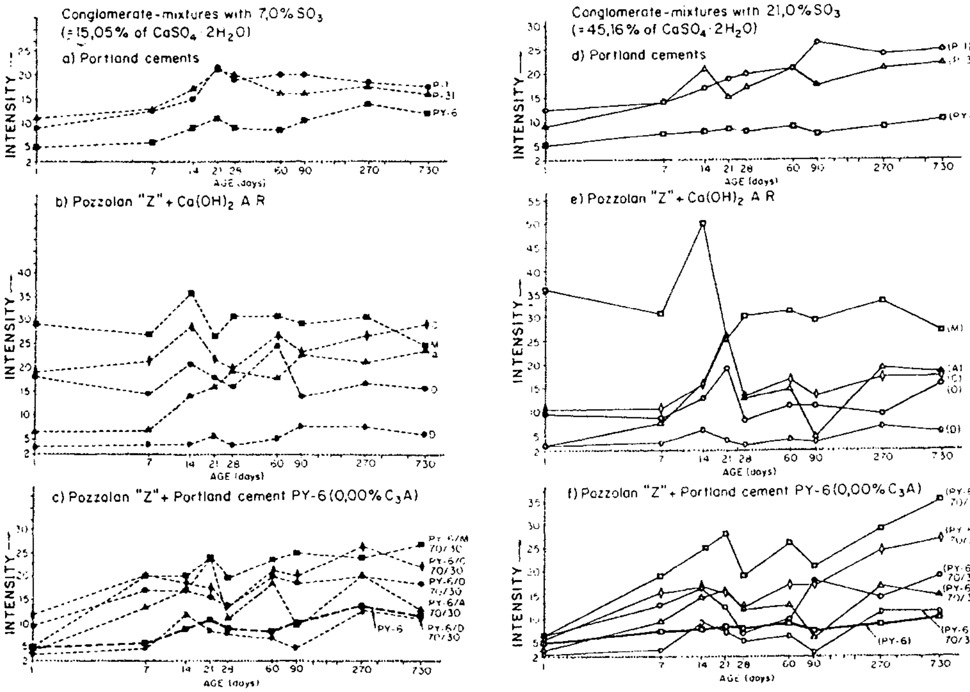

FIG. 2.

Semi-quantitative analysis of ettringite in different conglomerate-mixtures with gypsum.

On the other hand, the greatest part of the total ettringite formed by the pozzolans in the case of 7,0% SO_3, either mixed separately with hydrated lime or with the SRPC PY-6, was originated during the first 21-28 days of the test. Moreover, the pozzolan M has originated greater quantity of ettringite than the other ones and than either OPC,P-1 or P-31, alone. This fact has no coincidence with what should be hoped from the theoretical stechimetric calculations carried out of their respective dosages, Table 2. According to such dosages, the quantity of ettringite that should have been formed in each case, is listed in the Appendix.

As can be seen, there is a great disparity between the real and the theoretical calculations, according to Murat (6)(7)(8)(9). The only possible explanation of such notable differences is that the reactivity of the reactive alumina, $Al_2O_3^{r-}$, of the pozzolan(s), must be notably higher than the C_3A^* from the OPC. For this reason, the M pozzolan would form ALL the ettringite, MUCH MORE RAPIDLY than that of the C_3A from OPC, and in addition it is formed a greater quantity in the first case than in the second. For this, it can be rightly said that such a notable reactivity of the $Al_2O_3^{r-}$ could be found in the IDEAL physical-chemical state for this process (reactive alumine or perhaps better, tetra or penta-coordinated alumine (10) in solid state). The C_3A would be found in the opposite case, that is to say, the NON IDEAL, or at least, less ideal form of the same results, up to the point that, as a consequence of the obtained results, it can be said that the formation rate of its ettringite notably decreases, that is to say, the C_3A will be formed more slowly.

For which and in spite of the paradox, the mentioned fact demonstrates that at initial ages specially, the ettringite formed from $Al_2O_3^{r-}$ of the pozzolan M, in both cases—with hydrated lime and with SRPC PY-6—must be greater than the ettringite formed from C_3A of the OPC P-1 (12,13 g.ett/g $Al_2O_3^{r-} >$ 4,58 g.ett/g C_3A at the end of the test). Therefore it is possible to say that the formation rate of the ettringite from $Al_2O_3^{r-}$ origin of the pozzolans must be notably higher than the formation rate of the ettringite from C_3A of the OPC.

Also noteworthy is that the quantity of ettringite formed-depending on its intensity of peak (2Θ=9,08°)-from pozzolan origin, with hydrated lime or with the SRPC PY-6, has supported a direct relationship with its Al_2O_3 contents. For this reason the classifications which have been obtained in terms of this parameter, have been practically concurrent, especially at those main ages of the test: 1,7,14,28 and 730 days, [see Table 1 and Figs. 2 b),c),e) and f)]. Nevertheless, it cannot be deduced that all Al_2O_3 content of a natural and artificial pozzolanic additon will always form ettringite; for instance, if such Al_2O_3 (%) content were as mullite, it would not be formed.

Finally, in the individual and comparative analysis carried out among the M,C and D pozzolans, it has also been observed that the $Al_2O_3^{r-}$ of the C and D pozzolans is similar to that of M, although notable lower quantity, especially the D, whose quantity must be very small.

Conclusions

ALL pozzolans tested in this work have fixed sulphate ions in order to form ettringite. This fact does not allow to say that ALL pozzolans can provoke a noxious sulphate attack on OPC or on SRPC. For this reason, it is necessary to make additional tests with specimens from different PUZC, to show all the possibilities.

Nevertheless it is necessary to highlight the fact that the ettringite from pozzolans versus the ettringite from OPC are formed at different rates and that the formation rate of the ettringite from $Al_2O_3^{r-}$ origin of pozzolans turns out to be notably higher. Moreover, the topochemical mechanism of the formation must be carried out with previous solution in water of all the necessary reactive materials which are involved, including the $Al_2O_3^{r-}$ of the pozzolan.

On the other hand the quantity of ettringite formed from pozzolan alone or along with that from SRPC PY-6, has maintained a direct relationship with their respective contents of Al_2O_3 (%). This fact do not allow to deduce that the total content of Al_2O_3(%) of natural or artificial pozzolanic additions will always form ettringite; for instance, if such Al_2O_3 (%) content were as mullite it would not be formed.

The pozzolanic activity of a given pozzolan—higher or lesser Fratini test (5)—would be able to support a certain relationship with its higher or lesser attack by the gypsum. The silica fume would not be included in that relationship.

On the whole, all the plaster-bearing mixtures with the 21,0% of SO_3, have potentially originated a greater quantity of ettringite than their corresponding of the 7,0 SO_3; this behaviour allows to say that the first ones have been nearer to the stechiometry than the second ones. This fact may be a real possibility for that the 21,O SO_3 content, could be perhaps more suitable for an accelerated test.

Proposals

As a consequence of the main conclusions derived, we propose that, henceforth:

- the ettringite formed from $Al_2O_3^{r-}$ of the pozzolan can be called **"ETTRINGITE OF RAPID FORMATION"** or **"ett-rf"**,
- the ettringite formed from C_3A of the portland cement can be called **"ETTRINGITE OF SLOW FORMATION"** or **"ett-lf"**, and
- the **"TOTAL ETTRINGITE"** = **"ett-rf"** + **"ett-lf"**—which could be different in absolute value and size from one age to another —could be symbolized by **"ett-T"**.

Appendix

a) Ettringite formed from C_3A of the portland cements P-1, P-31 and PY-6, respectively, see Tables 1 and 2 and to calculate:

Reaction: $C_3A + 3(CaSO_4 2H_2O) + nH_2o \rightarrow 3CAO.Al_2O_3.3CaSO_4.31H_2O$

18.35 g of portland cement P-1 (14.11% C_3A) + 1.65 g Gypsum + $nH_2O \rightarrow$ 7.26 g ettringite

11.74 g " " P-1 (14.11% C_3A) + 8.26 g Gypsum + $nH_2O \rightarrow$ 7.58 g "

18.51 g " " P-31 (7.62% C_3A) + 1.49 g Gypsum + $nH_2O \rightarrow$ 6.46 g "

11.81 g " " P-31 (7.62% C_3A) + 8.16 g Gypsum + $nH_2O \rightarrow$ 4.13 g "

17.86 g " " PY-6 (1.0 % C_3A) + 2.14 g Gypsum + $nH_2O \rightarrow$ 0.82 g "

11.43 g " " PY-6 (1.0 % C_3A) + 8.57 g Gypsum + $nH_2O \rightarrow$ 0.52 g "

b) Ettringite formed from $Al_2O_3^{r-}$

–of the pozzolan M + $Ca(OH)_2$ + Gypsum + H_2O, and

–of the pozzolan M (30%) + portland cement PY-6 (7%) + Gypsum+H_2O

see Tables 1 and 2 to calculate, also taking into account these previous considerations:

1st. – A pure metakaolin normally has around 2.08% of $Al_2O_3^{r-}$, which would originate with $Ca(OH)_2$ "... small quantities of C_4AH_{13}" according to Murat (6) (7) (8) (9)

2nd.– Pozzolan M employed in this work contains at least 50.35% metakaolin (rest quarz)

3rd.– The quantity of pozzolan M employed in preparing the Gypsum—bearing Fratini of the 7.0% SO_3 or 21.0% SO_3 with the mixture, cement PY-6/M 70/30 plus plaster, has been respectively 17.57 × 0.3 = 5.271 g and 11.24 × 0.3 = 3.372 g.

Reaction: $Al_2O_3^{r-} + 3\ CaO + 3(CaSO_4{\cdot}2H_2O) + nH_2O \rightarrow C_3A.3CaSO_4.31H_2O$

17.57 g cement PY-6/M 70/30 + 2.43 g Gypsum + $nH_2O \rightarrow$ 1.23 g ettringite
11.24 g " PY-6/M 70/30 + 8.76 g Gypsum + $nH_2O \rightarrow$ 0.79 g ettringite
4.78 g of pozz. M + 3.01 g Gypsum + $nH_2O \rightarrow$ 0.61 g ettringite
3.09 g of " M + 7.88 g Gypsum + $nH_2O \rightarrow$ 0.39 g ettringite

Nevertheless and if we consider that all the Al_2O_3 content of the pozzolan M (23.11%), was reactive, the formed quantities of ettringite would be as following 15.34 g, 9.82 g, 13.41 g and 8.66 g, respectively.

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