Pergamon

Cement and Concrete Research 32 (2002) 707–717

CEMENT AND CONCRETE RESEARCH

Kinetochemical and morphological differentiation of ettringites by the Le Chatelier–Anstett test

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Received 29 November 2000; accepted 26 November 2001

Abstract

In this research, former XRD experiments have been verified by Le Chatelier–Ansttet (L-A) test. For this purpose, 28 cements consisting of 7 Portland cements and 21 blended cements containing 20%, 30% and 40% metakaolin have been submitted to the Le Chatelier–Anstett (L-A) test for 2 years. With all these cements, L-A specimens were manufactured and a direct parameter was measured for these specimens: increase in diameter, $\Delta\emptyset$, or diameter growth. Other complementary determinations were chemical analysis, XDA patterns and SEM of ettringites and specific properties of some cements tested. The experimental results have borne out that the formation rate of the ettringite formed from the reactive alumina, $Al_2O_3^{r-}$, present in pozzolans must be considerably higher than the formation rate of the ettringite from C_3A and much higher than the ettringite from C_4AF, both present in OPC. Owing to this, these ettringites were proposed being named "rapid formation" (ett-rf), "slow formation" (ett-lf) and "very slow formation" (ett-vlf) ettringites, respectively. On the other hand, these experimental results have also shown that the ett-rf has a much smaller size than the ett-lf (this is a direct consequence of the aforementioned conclusion); that almost all the alumina, Al_2O_3, present in M pozzolan must be regarded as being "reactive," $Al_2O_3^{r-}$, or at least, the greatest part; that the detrimental effects derived from gypsum attack are shown much earlier in these POZC than in their plain OPC and, to such an extent, that this aggressive action can be described as rapid gypsum attack; and that none of the 21 POZC tested can be described as high nor moderate sulphate resistant cements according to L-A test.

Keywords: Gypsum attack; Portland cements; Metakaolin; Ettringites; Formation rates; Sizes

1. Introduction

The Le Chatelier–Ansett (L-A) test [1] has been used in some European countries [2–6] as an accelerated test to predict cement behaviour against gypsum attack. However, in this occasion, it was not used mainly for that purpose, but to show some differences between the ettringite formed from reactive alumina (tetra- or penta-coordinated alumina), $Al_2O_3^{r-}$ [7], which is present in pozzolans (from now on "ett-rf"), and the ettringite from C_3A and C_4AF, present in OPC (from now on "ett-lf" and on "ett-vlf," respectively). These differences are related to their formation rates, sizes, their interrelations or interconnection during formation, technological consequences, as well as other effects.

Researchers' disagreement about the effect of pozzolans on ettrigites kinetochemistry have made us use the L-A test in order to bear out phases formation previously obtained [8].

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PII: S0008-8846(01)00749-9

Finally, experimental results obtained have also shown that the L-A specimen's overall dimensions change during water diffusion and chemical reactions [9]. On the other hand, a recent international meeting about sulfate attack [10] have shown other related objectives.

2. Objectives

The main objectives of this research are the following.

(1) To bear out by L-A test that the formation rate of ett-rf (V_f ett-rf) [8] must be higher than the formation rate of ett-lf (V_f ett-lf) [8] and than the V_f ett-vlf (semiquantitative or comparative analysis). That is to say,

$$V_f \text{ ett}-\text{rf must be } > V_f \text{ ett}-\text{lf must be } > V_f \text{ ett}-\text{vlf}$$

(2) To determine if the size of ett-rf crystals is smaller, equal or greater than the size of ett-lf ones.

(3) To study whether all the alumina in M pozzolan is reactive or not.

(4) To determine if the detrimental consequences derived from gypsum attack are shown before in POCZ with M pozzolan than in their plain PC.

(5) To determine the relative extent of gypsum attack to each POZC according to L-A test.

3. Experimental

3.1. Starting materials

The starting materials for this research are shown in Table 1.

In accordance with Eitel's [11] ternary diagram, the following materials were chosen:

1. Four OPC: P-1, P-2, P-31 and P-5 (P-nº), and three SRPC: PY-1, PY-4 and PY-6 (PY-nº).
2. Metakaolin was prepared by kaolin (with ≈50% quartz content) calcination at 750 °C.
3. Gypsum natural stone (with a high $CaSO_4 \cdot 2H_2O$ content) was used as aggressive media.

3.2. Operating procedure

First of all, 21 POZC, with 80%/20%, 70%/30% and 60%/40% (%P-n/%M or %PY-n/%M ratios) were pre-

Table 1
Chemical composition of cementing materials

	Portland cements							
	OPC (P-nº)				SRPC (PY-nº)			Pozzolan
Determinations (%)	P-1 (3,08)[a]	P-2 (3,06)	P-31 (3,06)	P-5 (3,09)	PY-1 (3,12)	PY-4 (3,16)	PY-6 (3,21)	[M (2,55)]
LOI	1,60	2,91	3,45	2,31	2,28	1,64	1,11	0,60
IR	0,70	1,21	0,86	0,62	0,54	0,43	0,15	0,22
SiO_2	19,18	19,36	18,13	21,10	18,75	22,10	21,70	73,53
Al_2O_3	6,44	6,03	5,30	4,30	4,97	1,98	1,52	23,11
Fe_2O_3	1,75	2,89	3,80	2,70	5,52	4,46	4,11	1,19
CaO	63,94	59,49	61,68	64,40	60,82	65,59	67,97	0,63
MgO	1,48	1,21	1,82	1,31	2,59	0,83	0,42	0,03
Na_2O	0,90	1,23	0,76	0,81	0,56	0,15	0,43	0,07
K_2O	0,52	0,69	0,31	0,21	0,23	0,05	0,20	0,70
SO_3	3,50	4,94	3,86	2,30	3,72	2,78	2,34	
Total	100,01	99,96	99,97	100,06	99,98	100,01	99,95	100,08
H_2O (105 °C)	0,24	0,93	0,33	0,42	0,66	0,22	0,22	0,16
CaO free	1,90	0,70	0,63	0,90	0,68	1,20	1,75	
Determinations (%)	Potential calculus bogue (%)							
C_3S	51,05	33,47	58,70	58,84	50,44	58,19	79,43	
C_2S	16,48	30,26	7,70	16,10	15,71	19,46	2,29	
C_3A	14,11	11,09	7,62	6,83	3,83	0,00	0,00	
$C_4AF\ (+C_2F)_{ss}$	5,33	8,79	11,56	8,22	16,80	11,75	10,19	
C_4AF+2C_3A (6)	33,35	30,97	26,80	21,88	24,46	11,75	10,19	
C_4AF+C_3A (1)	19,44	19,88	19,18	15,05	20,63	11,75	10,19	
Spf. Surf. Blaine (cm^2/g)	3192	3015	3248	3100	3811	3233	3287	

Gypsum

Mineralogical composition (%)			
Spf. Surf. Blaine (cm^2/g)		39,81	
H_2O (40 and 217 °C)	20,13	$CaSO_4 \cdot 2H_2O$	95,58
CO_2 (217 and 1000 °C)	0,75	$CaSO_4 \cdot 1/2H_2O$ and/or $CaSO_4$	2,47
IR	0,26	$CaCO_3$	0,75
SiO_2	0,04	$MgCO_3$	0,81
SO_3	45,87	Total	99,61
CaO	32,54		
MgO	0,36		
Na_2O	0,02		
K_2O	0,01		
Total	99,98	H_2O at 40 °C	0,41

[a] Specific weight (g/cm^3).

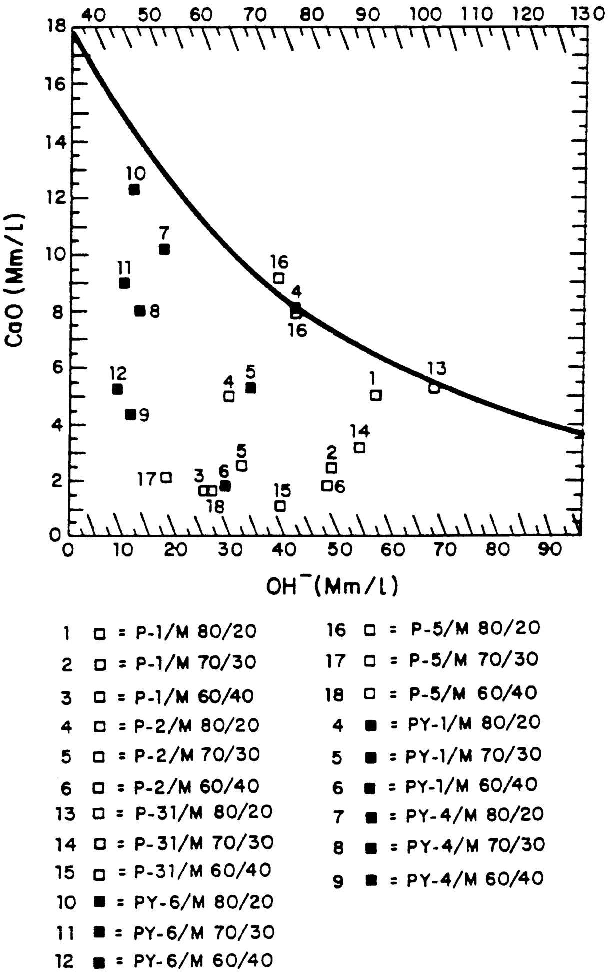


Fig. 1. Fratini test of the 21 POZC.

pared with seven Portland cements — four OPC and three SRPC — and M pozzolan. Secondly, all these POZC were then analyzed by the Frattini [12] test in order to confirm their pozzolanic characteristics at 7 and 28 days (later related to sulfate attack) (Fig. 1). Thirdly, mechanical strengths (flexural and compressive strength) [13] and times of setting [14] were also determined (Table 2). Lastly, each POZC and each PC were submitted to the L-A test [1]. In it, the cement is firstly ground to pass a sieve with approximately an 88-μm opening (a no. 170 sieve) and the grounded cement, 100.0 g, are made into a 0.50 water/cement ratio paste allowed to harden for several weeks (commonly 14 days) and then crushed to 5-mm size and dried at over 40 °C. Gypsum, 50.0 g (as ≃50% of the dried set cement), is added and the mixture is ground to pass a sieve with approximately a 212-μm opening (a no. 70 sieve). Six percent of distilled water by weight of solids is added and the dampened paste is placed in a cylindrical mold, 80 × 30 mm high, and compressed under a pressure of 196 Pa/min. The cylinder is placed on filter paper kept damp by letting the ends be dipped in water and covered with a bell jar to make an airtight joint. The diameter is measured at 24 h, 7 days, 28 days, 90 days or even later, according to the purpose. In this research, the diameter has been measured up to 2 years. The maximum expansion acceptable is 1.25% at 28 days (physical requirement). Direct parameter Δ∅ (%) was measured for L-A specimens from 1 day to 2 years.

Other complementary determinations were chemical analysis of cementing materials used (Table 1), XDA patterns and SEM analysis of ettringites and specific properties [13,14] of some cements tested (Table 2).

4. Results

For the discussion of Δ∅ experimental results, the curves shown in Fig. 2 were divided into groups. Thus, two different kind of curves have been obtained:

(a) Concave curves group with different initial points. This group generallly corresponds to plain OPC and

Table 2
Mechanical strengths and times of setting from OPC, P-1, P-2, SRPC PY-6 and their POZC with M pozzolan

	Mechanical strengths, MS (cement mortar type: EN 196-1) [13]						
	Flexural strength, FS (MPa)		Compressive strength, CS (MPa)		Setting times (h, m) [14]		
Cements	28 days	90 days	28 days	90 days	Initial setting time	Final setting time	Time of setting (TS)
P-1	7.0	7.3	47.7	50.3	2, 00	2, 39	0, 39
P-1/M 80/20	8.2	8.4	54.9	55.9	2, 10	2, 05	0, 40
P-1/M 70/30	8.7	8.9	53.3	54.3	2, 25	3, 10	0, 45
P-1/M 60/40	8.6	8.8	48.3	49.2	2, 15	2, 55	0, 50
P-2	4.0	4.2	27.3	32.4	2, 10	3, 09	0, 59
P-2/M 80/20	8.2	8.4	60.8	61.9	4, 15	6, 55	2, 40
P-2/M 70/30	9.7	9.9	49.7	50.6	4, 55	7, 40	2, 45
P-2/M 60/40	7.7	7.9	45.7	46.5	3, 55	6, 45	2, 50
PY-6	7.8	7.3	54.3	63.0	0, 05	0, 25	0, 20
PY-6/M 80/20	8.8	9.8	59.8	71.6	5, 50	7, 35	1, 45
PY-6/M 70/30	9.5	10.4	57.2	68.4	5, 45	7, 35	1, 50
PY-6/M 60/40	7.3	8.1	54.3	54.6	6, 15	8, 10	1, 55

The rest of the cements (OPC, SRPC and their POZC) reached MS and TS values of similar order.

plain SRPC (Subgroup (a1)), as well as to 80/20 POZC and some 70/30 POZC (Subgroup (a2)).

(b) Convex curves group which tend to be fastly horizontal as M pozzolan and C_3A contents increase and vice versa. This group generally corresponds to 60/40 and 70/30 POZC curves (group (b)).

The explanation of this behaviour can be as follows.

Subgroup (a1): Plain OPC and plain SRPC curves (Fig. 2).

- Their similar concavity,
- their different initial points, and
- the concordance between PCs classifications — according to their C_3A content — and their respective initial points

point out that the formation of ettringite from C_3A should be apparently attributed to topochemical mechanism rather than to through solution mechanism. Therefore, if X g C_3A/50 g gypsum ratio in L-A specimens was as high as possible, higher $\Delta\emptyset$ values would have been achieved at the same age of the test. However, if it was as low as possible, the initial value, $\Delta\emptyset \approx 0.0\%$, would have been maintained for a longer period of time, as it occurred in this research (Fig. 2). Besides, it could be also verified [1,8] that V_f of the ettringite from C_3A must be higher than the V_f of the ettringite from C_4AF (established long time ago). Notice that FFt did not appear (Fig. 3).

Subgroup (a2) (80/20 POZC and some of the 70/30 POZC curves), as well as Group (b) (60/40 POZC curves) (Fig. 2).

(1.1) $\Delta\emptyset$, which was dependent on the amount of M pozzolan added, was achieved for almost all POZC-prepared with OPC (P-n^{o}) or with SRPC (PY-n^{o})-after 1, 7 or 28 days. Thus, it can be told from Fig. 2 that $\Delta\emptyset$ relative values satisfied the following order:

$$< \Delta\emptyset(\%)_{1-7\ \mathrm{days}} <; \mathrm{P-n^{o}/M\ and\ PY-1/M}\ 100/00 < 80/20 < 70/30 < 60/40 \tag{1a}$$

$$< \Delta\emptyset(\%)_{7-28} <; \mathrm{PY-4/M\ and\ PY-6/M}\ 100/00 < 80/20 < 70/30 < 60/40 \tag{1b}$$

(the exception shown by POZC P-2/M 70/30 $\geq$ P-2/M 60/40 does not invalidate the general behaviour (Eq. (1a)) (see Fig. 2b). Besides, $\Delta\emptyset_{1\ \mathrm{day}}$ values for POZC at the age of 1 day could be described as high or very high in most cases.

On the other hand, an opposite classification was obtained at final ages, for those POZC containing mainly C_3A and/or C_4AF. Thus, the following relative values satisfied the following new order at the age of 365 and/or 730 days:

$$> \Delta\emptyset_{365-730\ \mathrm{days}} >; \mathrm{P-n^{o}/M\ or\ PY-n^{o}/M}\ 80/20 > 70/30 > 60/40, \tag{2}$$

some POZC started with this other order (Eq. (2)) at the age of 28 and/or 90 days.

Therefore, relations (1a) and (1b) and the high $\Delta\emptyset(\%)_{1-7\ \mathrm{days}}$ and/or $\Delta\emptyset(\%)_{7/28-730\ \mathrm{days}}$ values achieved were direct consequences derived from the physical substitution of OPC (P-n^{o}) or SRPC (PY-n^{o}) by M pozzolan. That is to say, $Al_2O_3^{r-}$ present in M pozzolan when converted in ett-rf [1,8] (Figs. 4 and 5) prevailed. For this reason, ett-rf [8] must be necessarily the main cause of relations (1a) and (1b) for most POZC families tested. In relation (2), the ett-lf from C_3A and/or ett-vlf from C_4AF present in PC [8] prevailed.

(1.2) Two different matters allow us to conclude that almost all the alumina present in M pozzolan, or at least the greatest part, must be regarded as being "reactive."

(1.2.1) All hydrated calcium aluminates originated from M pozzolan during the 14-day water curing for POZC PY-4/M and PY-6/M are rapidly and totally transformed into "ett-rf" when L-A specimens were exposed to gypsum attack (Figs. 2f and g, 4 and 5).

(1.2.2) Axioms: all the ettringites are expansive despite their possible different origins, among others, from some pozzolanic additions [8]. There is direct relation between expansion and C_3A content present in PCs [4,15–17] and between expansion and $AL_2O_3^{r-}$ content present in pozzolans [16].

Initial data: the alumina, Al_2O_3(%), content present in M pozzolan is 23.11%. However, how many is reactive, $Al_2O_3^{r-}$? There are very much possibilities but they all can be assembled in three groups.

(i) All the Al_2O_3 present in M pozzolan, 23.11%, is regarded as being reactive.

(ii) The reactive alumina, $Al_2O_3^{r-}$, amount present in M pozzolan is <23.11% but this amount would be so small, that being added to OPC P-1, its corresponding ett-rf amount can not change the order to the classification which would be achieved regarding it as being $\mathrm{INERT_{SR}}$, that is:

$$> \Delta\emptyset(\%)_{1-7\ \mathrm{days}} >; \mathrm{P-1/M}\ 100/00 > 80/20 > 70/30 > 60/40 \tag{3}$$

with OPC P-1 and by theoretical stoichiometric calculations [8], this small amount would be 5.25% (amounts smaller than 5.25% would not be able to change such order (Eq. (3)) either, logically).

(iii) The reactive alumina, $Al_2O_3^{r-}$, present in M pozzolan is between 5.25% and 23.11%.

5. Discussion

(i) In the first possibility, all the Al_2O_3 content, 23.11%, present in M pozzolan can not be reactive. Since heating in bulk of caolin to activate it (at 750 °C for 24 h only) gives rise differences between its superficial layers and its internal layers, and as a result, small amounts of γ-Al_2O_3, Al–Si spinel, premullite and mullite phases [7,18] (traces, mainly)

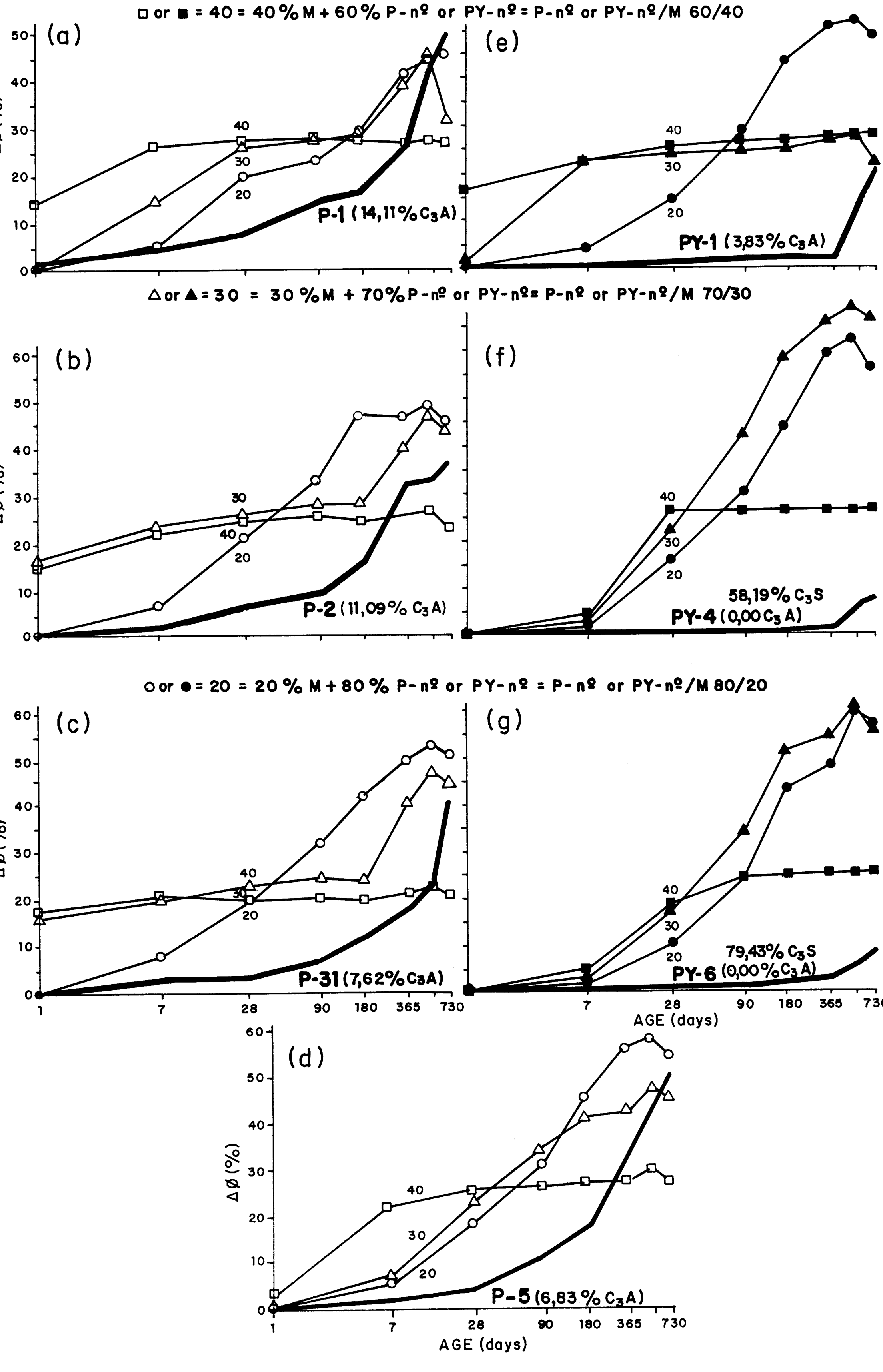


Fig. 2. Specimens: L-A (2) (cement paste). Parameter: increase in diameter, ΔØ (%). Cements: four OPC (P-nº), three SRPC (PY-nº) and 21 POZC. Pozzolan: M.

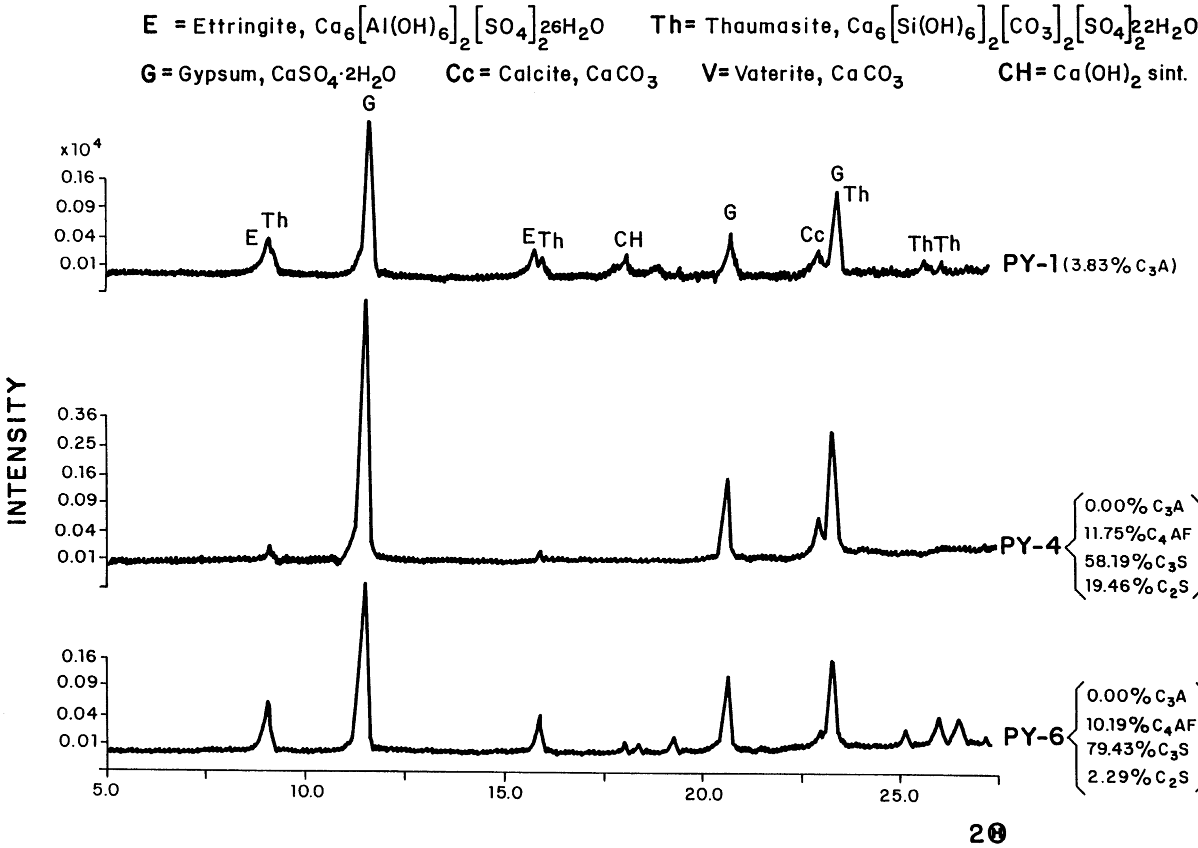


Fig. 3. XRD of the L-A specimens. SRPC: PY-1, PY-4 and PY-6. Age: 2 years.

come out. Even a little original caolin amount remains as well and they all may be also finally present in M pozzolan. These natural and artificial phases have crystalline shape with Al_2O_3 which are not leached by strong acids or bases.

(ii) In this second possibility, firstly, this additional statement must be also taken into account: V_f ett-rf = V_f ett-lf, and their common value would be the V_f ett-lf value. Thus, and despite the fact that the amount of $Al_2O_3^{r-}$ present in M pozzolan is so small, 5.25%, this small amount with SRPC PY-4 and PY-6, would proportionally origin ett-lf which would give rise to a classification that would be opposite to Eq. (3) and similar to the Eqs. (1a) and (1b) classifications. Since both SRPC can not origin ett-lf because their respective C_3A content is 0.00%, although on the other hand, both give rise to ett-vlf, which will finally change the order at latest ages (365, 545 or 730 days)(see Eq. (2) classification).

On the contrary, with OPC P-1, the opposite (Eq. (3)) classification must be achieved by theoretical calculations [8] because greater ett-lf amounts still, from C_3A origin, have been also formed. However, the contrary (Eqs. (1a) and (1b)) classifications have been achieved. Hence, it can be seen once again [8] that there is a great paradox between behaviours ($\Delta\emptyset$ values versus time) and theoretical calculations [8], but taking priority the behaviours. Therefore, the only possible explanation of such notable paradox is that the reactivity of the reactive alumina, $Al_2O_3^{r-}$, of M pozzolan to form ettringite must be notably higher than C_3A from the OPC P-1. For this reason, the M pozzolan would form all the ettringite much more fastly 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. The C_3A would be in opposite case; that is to say, nonideal, 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 also said that the formation rate of its ettringite notably decreases. That is to say, the C_3A will form it more slowly, and consequently, the C_4AF will form it much more slowly yet. This is:

$$V_f \text{ ett} - \text{rf must be} > V_f \text{ ett} - \text{lf must be} > V_f \text{ ett} - \text{vlf}$$

In spite of the this new paradox, the mentioned fact demonstrates that at initial ages specially, the ettringite formed from $Al_2O_3^{r-}$ of the pozzolan M must be greater than the etringite 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) and still greater than ettringite formed from C_4AF of the OPC and/or SRPC.

Consequently, the initial supposition seems not to be right and, on the other hand, the reactive alumina, $Al_2O_3^{r-}$,

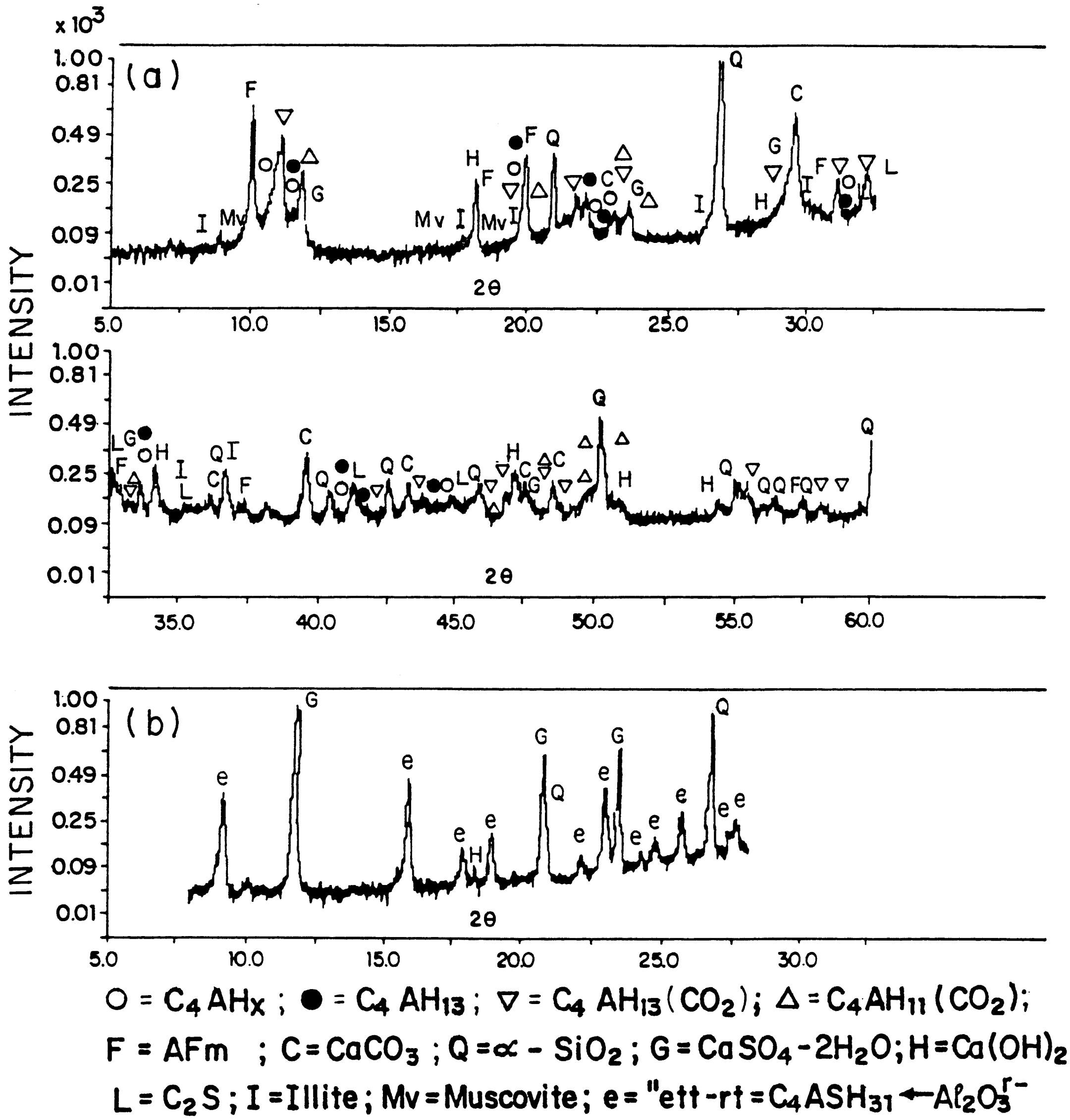


Fig. 4. L-A specimens. XRD of the POZC:PY-6/M 60/40. (a) Partially hydrated according to the L-A test. (b) L-A specimens. Age: 7 days.

content present in M pozzolan may be greater than 5.25% and lesser than 23.11% (see third possibility).

(iii) In this third possibility, at first, the above additional supposition must be also taken into account:

(iiia) Thus, and by theoretical stoichiometric calculations,

–when $Al_2O_3^{r-}$ content in M pozzolan is 21.31% ($\leq$23.11%), all POZC should satisfy this relation: total ett-rf amount is greater than or equal to the total ett-lf amount at the end of the test; but

–when $Al_2O_3^{r-}$ content in M pozzolan is 14.0% ($\leq$23.11%), the same should account, except for POZC P-1/M and P-2/M 80/20, because

$$P-1/M80/20: \text{ Total ett}-\text{rf},\ 33.97\text{ g}$$

$$<\text{ Total ett}-\text{lf},\ 51.68\text{ g},$$

$$P-2/M80/20: \text{ Total ett}-\text{rf},\ 33.97\text{ g}$$

$$<\text{ Total ett}-\text{lf},\ 40.62\text{ g},$$

but in contrast, the greater difference, 17.71>6.65 g, is, the greater $\Delta\emptyset(\%)$ value does not give rise at 1 day because 0.50<0.87%, although it is just to say that both $\Delta\emptyset(\%)$ values practically have the same order. This would mean that 14.0% $Al_2O_3^{r-}$ present in M pozzolan would be the minimum amount that would practically verify classifications (1a) and (1b) by theoretical stoichiometric calculations.

Nevertheless, if the above supposition is not right, the value 14.0% of $Al_2O_3^{r-}$ present in M pozzolan would be possible although lesser values would be it as well. However, now, the above additional supposition must not be taken into account (since behaviours are a contrast to theoretical stoichiometric calculations) but the Fratini [12] test, where

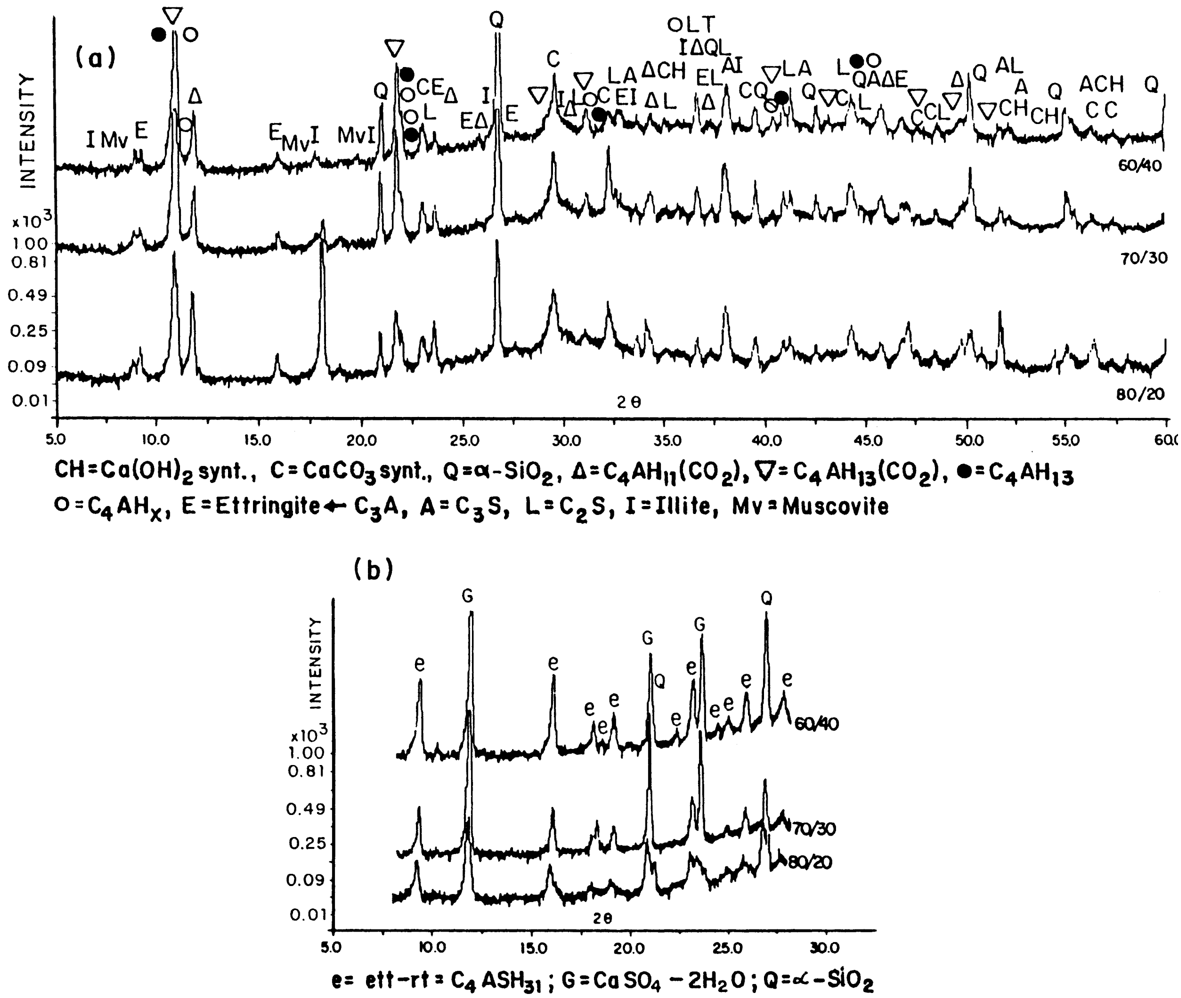


Fig. 5. L-A specimens. XRD of the POZC:PY-4/M 80/20, 70/30 and 60/40. (a) Partially hydrated according to the L-A test. (b) L-A specimens. (a) + Gypsum + H_2O. Age: 7 days.

the greatest part of pozzolanic activity for pozzolans is carried out during the 28 first days of water curing. Thus, and according to this test [12], theoretical stoichiometric calculations must be now made starting from the,

- $\Delta\emptyset_{28\ \mathrm{days}}$ (%) value for OPCs P-1 (for its L-A specimen, Al_2O_3 content from C_3A is 5.33 g) and P-2 (4.19 g Al_2O_3) are, respectively, 8.23% and 7.11%; $\Delta\emptyset_{28\ \mathrm{days}}$ (%) value would be only due to their respective C_3A contents when converted into ett-lf, and
- $\Delta\emptyset_{28\ \mathrm{days}}$ (%) values for 80/20 POZC P-1/M and P-2/M are, respectively, 19.95% and 21.20%; both values would be only due to the reactive alumina, $Al_2O_3^{r-}$, content present in 20 g of M pozzolan when converted into ett-rf and to the Al_2O_3 content from C_3A present in OPCs P-1 and P-2, respectively, when converted into ett-lf.

However, 19.95 − 8.23% = 11.72% and 21.20 − 7.11% = 13.89% would be only the expansion given rise by 20% of M pozzolan and, as a consequence, the reactive alumina, $Al_2O_3^{r-}$, content of the M pozzolan would have to be between 18.96% and 20.73%, or more exactly yet, between 21.62% and 22.82%, if 80% of 8.23% and 7.11%, is only taken into account. However, in any case, both couples of values are greater than 21.33%/2 and than 23.11%/2 as well. Hence, it can be said that almost all alumina present in this M pozzolan, or at least the greatest part, must be regarded as being "reactive."

(iiib) At the beginning of the discussion and interpretation of results, all the curves were divided into two groups: group (a1) or "concave" curves group, and groups (a2) and (b) or "convex" curves group. Both groups are characterized because:

− group (a1) clearly fits all the OPC and SRPC and their respective 80/20 POZC and some 70/30 POZC. That is to say, all cements with greater C_3A and/or C_4AF contents (or with lesser M pozzolan content); whereas

− groups (a2) and (b) clearly fit all the corresponding "brothers" 60/40 POZC and the rest of 70/30 POZC. That is to say, all the cements with greater M pozzolan content (or with lesser C_3A and/or C_4AF contents).

Both groups of curves were achieved by drawing $\Delta\emptyset(\%)$ versus time and all $\Delta\emptyset(\%)$ values were due to the ettringites' expansion. On the other hand, the ettringite formation from C_3A present in OPC was verified by a previous paper [8]. Likewise, it was also shown that pozzolanic additions form ettringite as weel during their exposure to the same sulfate bearing solution (from gypsum) [8].

Therefore, and according to this previous paper [8], it can be rightly said that if the two groups of curves obtained are very different to itself — the first one (group (a1)) is "concave," and the second one (groups (a2) and (b)) is "convex" — the causes that gave rise to them must be necessarily also very different to itself. Thence, all this points out once again that the ettringite from pozzolanic origin or "ett-rf" must be formed faster than ettringite from C_3A, and much faster than ettringite from C_4AF, this is:

$$V_f \text{ ett} - \text{rf must be} > V_f \text{ ett} - \text{lf must be} > V_f \text{ ett} - \text{vlf}$$

In other words, with this supposition (V_f ett-rf = V_f ett-lf), whatever POZC family is considered, their convex curves (see Fig. 2) should be concave and parallel to the concave curve of their respective plain PC, although in any case, the following classification can be obtained

$$> \Delta\emptyset(\%)_{x \text{ days}} >; \text{P} - \text{n}^{\text{o}}/\text{M or PY} - \text{n}^{\text{o}}/\text{M } 80/20$$
$$> 70/30 > 60/40 > 100/00 \quad (4)$$

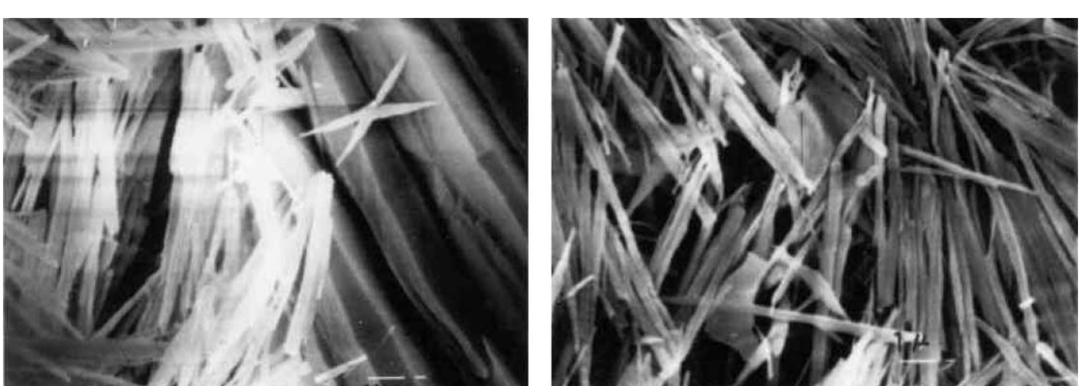
In contrast, this behaviour has not happened but the opposite. Besides, the more contrary POZC curves were to P-1 curve, the most M pozzolan was added to OPC P-1. Then and according to this last behaviour, the V_f of the ett-rf must be also necessarily totally contrary or different to the V_f of the ett-lf (and more yet, to the V_f of the ett-vlf), that is, or V_f ett-rf is much greater than V_f ett-lf, or is much smaller, which once again verify that the above supposition is not right.

However, V_f ett-rf can not be smaller than V_f ett-lf because according to the Von Weimarn's [19] and Garrido's [20] set patterns, their crystals would have to have had greater size than those ones from ett-lf. In addition, they have not been greater but once more again, they have been exactly the contrary, that is, they have been properly smaller because the set patterns of Von Weimarn and Garrido underline that the more insoluble a salt is — and so the ettringite is — the more fastly is formed and the more difficult is to produce a slow precipitation and form great and well formed crystals, as it occurred in this research (see Figs. 6 and 7).

Moreover, the more different the curves have been, the more OPC P-1 was replaced by M pozzolan and vice versa. That is, the greater the quantity of OPC or SRPC containing C_3A was in POZC, the more similar to their plain PC were the creation, evolution and development of $\Delta\emptyset$ values for the corresponding 80/20 specimens (Fig. 2a–e). Nevertheless, for POZC PY-4 and PY-6/M 80/20 and 70/30, the evolution and development of $\Delta\emptyset$ values must be originated by ett-vlf formed from C_4AF present in PY-4 and PY-6 fractions, at intermediate and, mainly, at final ages. Consequently, the only possibility is that the V_f ett-rf must be necessarily greater than the V_f ett-lf and much larger than the V_f ett-vlf.

Therefore, during the first and intermediate ages, $\Delta\emptyset$ values were always reached earlier for all POZC than for their respective plain OPC and/or SRPC. Likewise, the greater the amount of M pozzolan added was, the earlier high $\Delta\emptyset$ values were reached and vice versa.

On the other hand, this last observation also points out that this kind of POZC (with high $Al_2O_3^{r-}$ content in their pozzolan fraction) will be damaged and destroyed by sulfate attack, earlier than its plain OPC and/or SRPC, as it has been shown by this research and some spanish real experience [21]. Thence, the destruction caused by gypsum attack has been able to be accelerated by the presence of M pozzolan, making OPC and/or SRPC life time decrease. This detrimental effect derived from gypsum attack was to such an extent that it could be described as rapid gypsum attack, and



x 10.000 (a) x 10.000 (b)

Fig. 6. Ettringites of rapid formation, ett-rf.

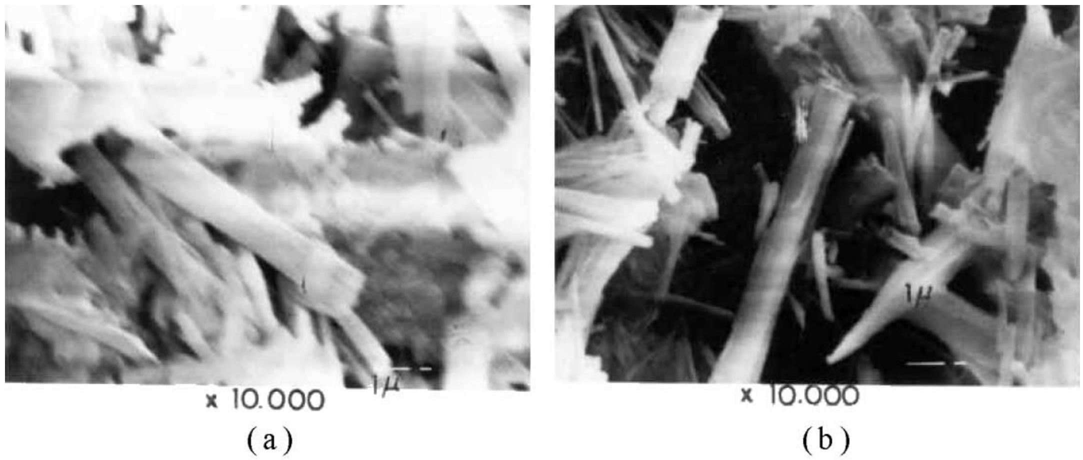


Fig. 7. Ettringites of slow formation, ett-lf.

perhaps, it would also justity some of Mather's [22], Metha's [23] and Tikalsky and Carrasquillo's [24] results.

6. Conclusions

By means of the experimental determination of $\Delta\emptyset$ parameter, the following conclusions were obtained.

(1) L-A test (parameter: $\Delta\emptyset$) has borne out once again [8] that the V_f of the ettringite from the $Al_2O_3^{r-}$ present in M pozzolan must be considerably higher than the V_f of the ettringite from the C_3A present in OPC, and even higher than the ettringite from C_4AF,which is according to conclusions and proposals from Ref. [8].

(2) The ett-rf has a much smaller size than the ett-lf. This is a direct consequence of conclusion 1.

(3) All hydrated calcium aluminates formed from the $Al_2O_3^{r-}$ present in M pozzolan during its storage in water according to L-A test were rapidly and totally transformed into ett-rf when specimens were exposed to gypsum attack.

(4) Almost all the alumina present in this M pozzolan, or at least the greatest part, must be regarded as being "reactive." This conclusion can not be without further applied to neither of the rest of the artifitial pozzolans—mainly, fly ashes—nor of natural pozzolans.

(5) POZC specimens prepared with this M pozzolan were generally damaged by gypsum attack, from 3 to 9 or 12 months earlier than the specimens of their respective plain OPC and/or SRPC.This was promoted by the ett-rf, mainly. Nevertheless, this unsuitable behaviour of this M pozzolan does not allow to say that all fly ashes and natural pozzolans can also promote a detrimental sulfate attack on OPC or on SRPC.

(6) From the point of view of compressive strength, the optimum amoun of M pozzolan is 20%, whereas from the point of view of flexural strength is 30%.

(7) Irrespective of the previous conclusions, according to L-A test (1) and the following specifications: HSR ($=\Delta\emptyset_{28\ \text{days}} \leq 1.25\%$ (1)), MSR ($=\Delta\emptyset_{28\ \text{days}} \leq 4.00\%$ (13)) (15) and LSR ($=\Delta\emptyset_{28\ \text{days}} > 4.00\%$ (13)),

–The seven PC tested had to be qualified as follows.

- SRPC: PY-1 (3.83% C_3A), PY-4 (0.00% C_3A) and PY-6 (0.00% C_3A),
- MSRPC (moderate SRPC): P-31 (7.62% C_3A) and
- LSRPC (low SRPC): P-1 (14.11% C_3A) and P-2 (11.09% C_3A).

Such qualifications fully agree with the ones that would be obtained by considering their C_3A and C_4AF contents.

–The 21 POZC tested by L-A test can be also described as LSR. This LSR is due to the prominent "aluminous" character of M pozzolan, which can not be applied to all the fly ahses and natural pozzolans, mainly, neither "siliceous" nor "aluminic-siliceous" pozzolans because "siliceous" and "aluminic-siliceous" pozzolans cause better behaviours against gypsum attack [8,15] (HSR = high SR; MSR = moderate SR; LSR = low SR).

Finally, it is noted that M pozzolan used in this research was also tested with an OPC = P-32 (9.30% C_3A) and a SRPC = PY-5 (4.50% C_3A). The experimental results confirm the observations, discussions, interpretations and conclusions presented. This other results may be also published in the next future.

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