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Performance of metakaolin and Portland cements in ettringite formation as determined by ASTM C 452-68: kinetic and morphological differences

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Abstract

In this study, the results of prior XRD and Le Chatelier–Ansttet test experiments were re-verified in terms of a relative parameter, the Length Growth Rate, Vcl(=ΔL (%)/day). For this purpose ASTM C 452-68 testing was conducted for 2 years on 40 cements, 10 Portland cements–6 OPCs and 4 SRPCs–and 30 blended cements containing 20%, 30% and 40% metakaolin (M pozzolan). ASTM C 452-68 specimens were manufactured with all cements and their daily *length growth rate* was calculated by dividing the measured increase in length, ΔL (%), by the number of days lapsing since the preceding measurement. Additional experiments were also run: chemical analysis, XRD and SEM analysis of ettringites and tests to determine specific properties of some cements tested. The results have once again borne out that:

(a_1) The formation rate of the ettringite deriving from the reactive alumina, $Al_2O_3^{r-}$, present in pozzolans is considerably higher than the rate for ettringite forming from the C_3A (and, logically, much higher than for C_4AF ettringite) present in OPC. Owing to this, these ettringites were termed: "rapid formation" (**ett-rf**), "slow formation" (**ett-lf**) and "very slow formation" (**ett-vlf′**) ettringites, respectively.
(b_1) The foregoing directly affects the size of the respective crystals, which are much smaller in **ett-rf** than in **ett-lf**.

These results have also shown that:

(a_2) In a gypsum and water environment (ASTM C 452-68 specimens), the pozzolanic reactions involving the reactive alumina, $Al_2O_3^{r-}$, present in pozzolans take place during the first 28 days of age–and, sometimes, even during the first 7 days (this occurred for most POZCs prepared with this M pozzolan and PC)–, and ettringite from both, $Al_2O_3^{r-}$ and C_3A, origin, are the reaction products in all cases.
(b_2) **Ett-rf** and **ett-lf** formation does not take place independently from one another, but inter-dependently or in a joint way or interactive way. Consequently, both ettringites appear, to a greater or lesser extent, when dealing with gypsum and water environments. Nevertheless, the reaction products are closer to **ett-rf** than to **ett-lf**, when more M pozzolan is added (40%) and vice versa (20%), and in any case, topochemical mechanism with prior dissolution must be preponderant over through-solution mechanism.
(b_3) According to ASTM C 150-95 standard, the optional physical requirement to characterize SRPCs is $\Delta L_{14\ \mathrm{days}} \leq 0.040\%$. Unlike the requirement formerly used, i.e., $\Delta L_{28\ \mathrm{days}} \leq 0.054\%$, this requirement "predicts" rather than "assures" the most probable behaviour of a PC under gypsum attack. Moreover, if the results of the tests set out in standards EN 196-1, EN 196-3, EN 196-5 and EN 450 and/or ASTM C 311-94b, mainly, are positive, the ASTM C 452-68 test can be validly used to characterize and differentiate at 28 days, POZCs prepared with M pozzolan–or any other natural or artificial (fly ash) pozzolan–, which would give rise to low, moderate or high sulfate resistance. The only requisite in this regard would be to establish suitable standard and chemical–physical requirements and specifications.

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

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1. Introduction

The ASTM C 452-68 test [1] has been used as an accelerated method for predicting the potential behaviour of plain Portland cements under gypsum attack, but not the behaviour of Portland cement blended with pozzolans and/or blast furnace slags. In the present study, however, it was not used primarily for that purpose, but to reveal certain differences between the ettringite formed from the reactive alumina (tetra- or penta-coordinated alumina), $Al_2O_3^{r-}$ [2], present in pozzolans (hereafter "**ett-rf**" [3–6]), and the ettringite deriving from the C_3A present in OPCs (hereafter "**ett-lf**" [3–6]). These differences are related to their formation rates, sizes, inter-relations or inter-connections during formation, technological consequences in terms of the properties of the paste, mortar and concrete made from these blended cements and other possible aspects.

Previous studies [3–6] have shown that ettringite can form from the C_3A present in OPCs and that pozzolanic additions also form ettringites when exposed to the same sulfate bearing solutions (gypsum in distilled water) [3–6].

In light of the lack of consensus among researchers about the influence of pozzolans on ettringites kinetochemistry and morphology, the ASTM C 452-68 test was used in the present study, but in conjunction not with the direct increase in length (%), ΔL (%), but with an indirect or relative parameter, the *Length Growth Rate*, Vcl(=ΔL (%)/day), in order to verify previous conclusions about phase formation [3,5,6].

Moreover, experimental results have shown that the overall dimensions of ASTM C 452-68 specimens change during water diffusion and chemical reactions [7], and attention was drawn to other related effects in a recent international meeting on sulfate attack [8]. A few years ago, Santhanam et al. [9] expressed their disappointment over the loss of interest in sulfate attack, an area to which so much importance had been attached in the past, and advocated the resumption of research to determine the service life of concrete foundations subject to sulfate attack. This would call, firstly, for an understanding of the reagent substances involved and reaction products formed and possibly also involved when pozzolanic additions come into contact with Portland cements attacked by gypsum, as well as their respective morphologies, sizes, formation rates, inter-reaction or inter-connection during formation, technological consequences and other possible aspects.

In short, both past and present research [10–32] shows that sulfate attack has not withered [9].

For all these reasons, a series of experiments were conducted a new and a hitherto little used indirect parameter, Vcl, and a new line of reasoning was deployed not to confirm or verify, but to actually prove with this approach that the formation rate in the rapid formation of ettringites (from reactive alumina, $Al_2O_3^{r-}$, present in M pozzolan), is greater than the rate in the slow formation of ettringites (from C_3A present in OPC) this fact, and its corollary, the smaller size of the **ett-rf** crystals. Information was also sought on how long the reactive alumina, $Al_2O_3^{r-}$, sustained pozzolanic reactions, primarily in a gypsum and water environment–ASTM C 452-68 specimens–, as well as on the identity of the new phases or reaction products originated in all cases. Finally, the respective inter-relation or inter-connection during formation was also the object of analysis.

With these aims in mind, 30 POZC were prepared with 10 Portland cements, PCs–6 OPCs and 4 SRPCs–, blended with M pozzolan (metakaolin) in the following (P-n° or PY-n°/M) ratios: 80%/20%, 70%/30% and 60%/40%, and subsequently tested using the ASTM C 452-68 method. The indirect parameter used this purpose was the aforementioned Vcl, which was not measured directly day by day, but mathematically calculated by dividing the measured ΔL (%) by the time lapsing between any two successive measurements.

2. Objectives

The objectives sought in this research were primarily:

1. To prove with the ASTM C 452-68 test, via the parameter: Vcl(=ΔL (%)/day), that the formation rate of **ett-rf(**$\mathbf{V_f}$ **ett-rf)** is higher than the formation rate of **ett-lf(**$\mathbf{V_f}$ **ett-lf)** (semiquantitative or comparative analysis only), i.e., $\mathbf{V_f}$ **ett-rf>**$\mathbf{V_f}$ **ett-lf**.
2. To bear out that the **ett-rf** crystals are smaller than **ett-lf** crystals and to find a conclusive explanation for both.
3. To bear out that, for ettringites formation, the topochemical mechanism, TPQ, with previous dissolution, must be preponderant over the through-solution mechanism, **TS**.
4. To determine whether all or the greatest amount of pozzolanic reactions involving $Al_2O_3^{r-}$ present in M pozzolan takes place in ASTM C 452-68 specimens during the first 28 days, or even much earlier–7 days–for most of the POZCs tested.
5. To determine whether or not there is any relationship between **ett-rf** and **ett-lf** during their formation in a common gypsum and water environment (ASTM C 452-68 specimens).
6. To determine the "predictive" value of $\Delta L_{4\ \mathrm{days}}$ (%)≤0.040% and $\Delta L_{28\ \mathrm{days}}$ (%)≤0.054% with respect to the potential behaviour of a given PC under gypsum attack.

3. Experimental

3.1. The starting materials for this study are shown in Table 1

Pursuant to Eitel's ternary diagram [33], the following materials were chosen Table 1:

1. Six OPCs–P-1, P-2, P-4, P-32, P-31 and P-5 (=P-n°)–and four SRPCs–PY-5, PY-1, PY-4 and PY-6 (=PY-n°).

Table 1
Chemical–physical determinations

Chemical parameters (%)	**Portland cements**										**Pozzolan**
	OPCs						**SRPCs**				
	P-1 (3.08)	**P-2** (3.06)	**P-4** (3.12)	**P-32** (3.06)	**P-31** (3.06)	**P-5** (3.09)	**PY-5** (3.17)	**PY-1** (3.12)	**PY-4** (3.16)	**PY-6** (3.21)	**M** (2.55)[a]
L.O.I.	1.60	2.91	1.28	2.47	3.45	2.31	0.80	2.28	1.64	1.11	0.60
I.R.[b]	0.70	1.21	0.97	1.57	0.86	0.62	0.40	0.54	0.43	0.15	0.22
SiO_2	19.18	19.36	19.70	18.53	18.13	21.10	19.00	18.75	22.10	21.70	73.53
Al_2O_3	6.44	6.03	5.70	5.54	5.30	4.30	4.70	4.97	1.98	1.52	23.11
Fe_2O_3	1.75	2.89	2.60	3.18	3.80	2.70	4.70	5.52	4.46	4.11	1.19
CaO	63.94	59.49	64.00	62.39	61.68	64.40	65.11	60.82	65.59	67.97	0.63
MgO	1.48	1.21	1.77	1.31	1.82	1.31	1.59	2.59	0.83	0.42	0.03
Na_2O	0.90	1.23	0.21	1.11	0.76	0.81	0.43	0.56	0.15	0.43	0.07
K_2O	0.52	0.69	1.00	0.28	0.31	0.21	0.06	0.23	0.05	0.20	0.70
SO_3	3.50	4.94	2.80	3.66	3.86	2.30	3.30	3.72	2.78	2.34	-
Total	100.01	99.96	100.03	99.94	99.97	100.06	100.09	99.98	100.01	99.95	100.05
H_2O(105°C)	0.24	0.93	0.61	0.04	0.33	0.42	0.20	0.66	0.22	0.22	0.16
CaO free	1.90	0.70	0.90	1.20	0.63	0.90	1.44	0.68	1.20	1.75	
Mineralogical composition (%)	**Potential Calculus Bogue**										
C_3S	51.05	33.47	57.45	55.67	58.70	58.84	68.07	50.44	58.19	79.43	
C_2S	16.48	30.26	13.14	11.13	7.70	16.10	3.12	15.71	19.46	2.29	
C_3A	14.11	11.09	10.71	9.30	7.62	6.83	4.50	3.83	0.00	0.00	
$C_4AF(+C_2F)ss$	5.33	8.79	7.91	9.68	11.56	8.22	14.30	16.80	11.75	10.19	
C_4AF+2C_3A	33.55	30.97	29.33	28.28	26.80	21.88	23.30	24.46	11.75	10.19	
C_4AF+C_3A	19.44	19.88	18.62	18.98	19.18	15.05	18.80	20.63	11.75	10.19	**M**
BSS[c] **(cm^2/g)**	3192	3015	3059	3062	3248	3100	3088	3811	3233	3287	3937

Gypsum			
Chemical parameters (%)		**Mineralogical composition (%)**	
H_2O(40°C a 217°C)	20.13	$CaSO_4$ $2H_2O$	95.58
CO_2 (217°C a 1000°C)	0.75	$CaSO_4$ $1/2H_2O$ and/or	
I.R.	0.26	$CaSO_4$	2.47
SiO_2	0.04	$CaCO_3$	0.75
SO_3	45.87	$MgCO_3$	0.81
CaO	32.54		
MgO	0.36		
Na_2O	0.02		
K_2O	0.01		
		Total	99.61
Total	99..98	H_2O at 40°C	-0.41

b = insoluble residue
a = Specific gravity (g/cm^3)
c = Blaine Specific Surface

2. Metakaolin (M pozzolan) was prepared by kaolin (with ≈50% quartz content) calcination at 750°C, being its granular composition in accordance with ASTM C 595M-95 standard [34] (amount retained when wet-sieved on no. 325 (45 μm) sieve, max=20%).
3. Gypsum, natural stone (with a high Ca $SO_4 \cdot 2H_2O$ content) was used as aggressive media.

Although metakaolin has been extensively studied in the literature in light of the value of this artificial pozzolan as a building material, particular attention is drawn here to the papers [35–52] that are related in one way or another to this study.

3.2. The operating procedure consisted of

Thirty POZCs, with ratios of 80%/20%, 70%/30% and 60%/40% (%P-n°/%M or PY-n°/%M) were first prepared with 10 PCs–6 OPCs and 4 SRPCs–and M pozzolan. A ratio of 100%/00% (=100/00) is indicative of the plain OPCs or SRPCs used in this study.

The Frattini test [53] was then conducted on all these POZCs to determine their pozzolanic properties (later related to sulfate attack) at 28 and/or 7 days (Fig. 1 and Table 2). The Frattini test compares the amount of calcium hydroxide in the aqueous solution in contact with the sample (20 g of anhydrous POZC) hydrated (with 100 cm^3 of distilled water at 40 °C) at 40 °C, at 28 and/or 7 days only (ages formerly specified and now replaced by 15 and/or 8 days only) to the isotherm of calcium hydroxide solubility in an alkaline solution also at 40 °C. This test is considered to be positive for a natural or artificial pozzolanic addition (metakaolin in this study), when the calcium hydroxide concentration in the POZC P-n°/M and/or PY-n°/M solution is below the solubility isotherm (positive for pozzolanicity, or simply, +).

Mechanical strengths (flexural, FS, and compressive, CS, strength) [54], volume stabilities and times of setting [55] were also determined(Tables 3 and 4) for some of the cements tested.

Lastly, each POZC and PC were tested with the ASTM C 452-68 method. Only four specimens (1″ ×1″ ×11 1/4″)

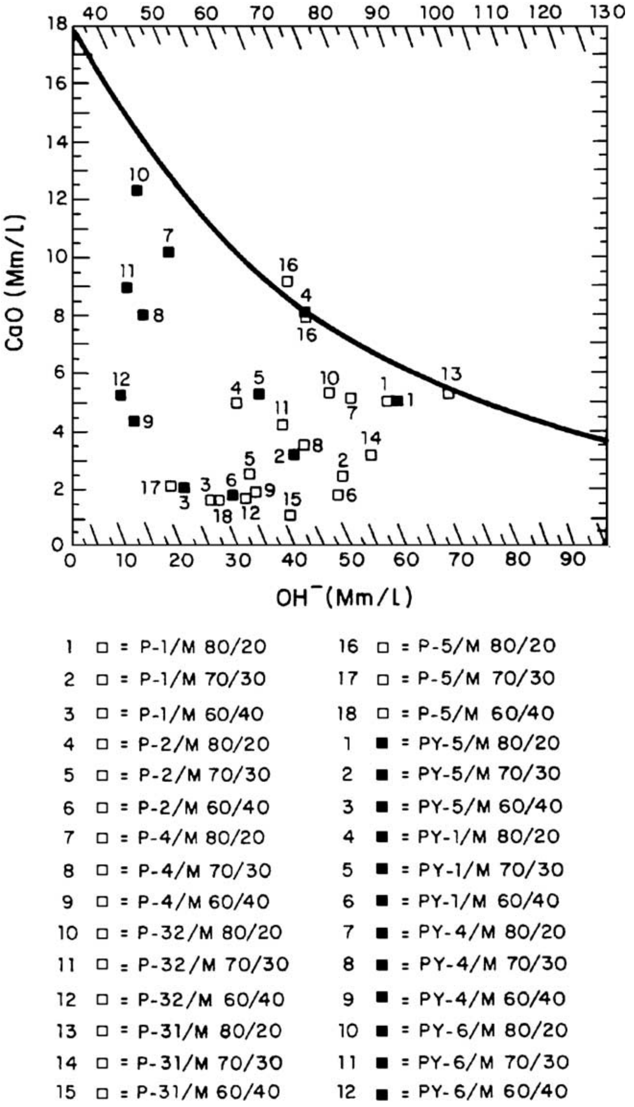

Fig. 1. Frattini test of the 30 POZCs. Ages: 28 and/or 7 days.

were manufactured with each PC and POZC, to determine their increase in length (%), ΔL (%), along with three additional specimens to ratify any questionable doubtful ΔL (%) (the leftover mortar amount was practically always the same). Length was measured a 1, 7, 14, 21, 28, 60, 90 days or even later, depending on the purpose. In this study, length measurements were taken for up to 2 years. Thus, first, the direct parameter, ΔL (%), was measured, after which the indirect or relative parameter Vcl(=ΔL (%)/day) was mathematically calculated by dividing the measured ΔL (%) by the amount of time lapsing since the last measurement in each case. For instance: [$\Delta L_{14\ \mathrm{days}}$ (%)$-\Delta L_{7\ \mathrm{days}}$ (%)]/[difference between 14 and 7 days=7 days], or more generally, the number of days between two successive length measurements which for other cases would be 60–28 days, 90–60 days, 270–180 days, 365–270 days and so forth. This means that the rate is not a rate at a specific moment, but the average rate between zero (=any considered age) and a moment in time (=up to the following considered age) (Figs. 2 and 3).

Other complementary determinations were: chemical analysis of cementing materials used (Table 1), specific properties of some cements tested (Table 5) and SEM examination and XDA patterns of ettringites. These latter two analysis were performed on 20 g of each PC or POZC (with 33.33% [5,6] of gypsum instead of 15.05% [1]), stored, after setting, in the same curing water as the respective specimens.

4. Results, discussion and interpretation

The experimental results for Vcl parameter are shown in Figs. 2(a)–(f) and 3(a)–(d). In the discussion and interpretation that follows, the curves are grouped on the basis of their similarity to a Gauss curve (specifically, the right and/or left arm of a normal curve).

4.1. Observations

4.1.1. Plain OPCs—6—and plain SRPCs—4 (Figs. 2 and 3)

The origin, evolution and development of the Vcl values for the 10 PCs tested can generally be compared to 2

Table 2
Pozzolanicity (Frattini test): results at 2 days

Cements	Frattini test: results at 2 days							
	Without 7.0% SO_3				With 7.0% SO_3			
	*	[OH^-]	*	[CaO]	*	[OH^-]	*	[CaO]
P-1		72.50		7.60		51.00		22.75
P-1/M 80/20	58.00	**55.00**	6.08	**6.35**	40.80	**59.00**	18.20	**6.00**
P-1/M 70/30	50.75	**48.50**	5.32	**5.50**	35.70	**49.50**	15.93	**5.55**
P-1/M 60/40	43.50	**35.00**	4.56	**2.15**	30.60	**44.50**	13.65	**5.45**
PY-6		42.50		21.50		42.50		31.10
PY-6/M 80/20	34.00	41.00	17.20	16.60	34.00	33.00	24.88	26.50
PY-6/M 70/30	29.75	**34.50**	15.05	**13.50**	29.75	**30.00**	21.77	**25.00**
PY-6/M 60/40	25.50	**28.00**	12.90	**11.15**	25.50	**25.50**	18.66	**18.50**

*Values assuming inertness of the metakaolin.

1. The paired values in **bold** mean that the point is in the subsaturation region (=+ result).
2. The rest of POZCs reached similar order values for each chemical parameter.

Table 3
Mechanical strengths from OPCs, P-1 and P-2, SRPC PY-6 and their POZCs with M pozzolan

CEMENTS	Mechanical strengths, MS (cement mortar types: -7.0% SO_3 → EN 196 - 1; + 7.0% SO_3 → ASTM C452 - 68)							
	Flexural strength, FS(MPa)				Compressive strength, CS (MPa)			
	28 days		90 days		28 days		90 days	
	-7.0% SO_3	+7.0% SO_3	-7.0% SO_3	+7.0% SO_3	-7.0% SO_3	+7.0% SO_3	-7.0% SO_3	+7.0% SO_3
P-1	**7.0**	**4.4**	**7.3**	**8.9**	**47.7**	**27.7**	**50.3**	**53.0**
P-1/M 80/20	**8.2**	**9.7**	**8.4**	**10.3**	**54.9**	**40.1**	**55.9**	**39.3**
P-1/M 70/30	**8.7**	**8.9**	**8.9**	**9.8**	**53.3**	**32.6**	**54.3**	**48.6**
P-1/M 60/40	**8.6**	**8.5**	**8.8**	**8.9**	**48.3**	**43.6**	**49.2**	**45.7**
P-2	**4.0**	**4.4**	**4.2**	**5.2**	**27.3**	**18.3**	**32.4**	**29.7**
P-2/M 80/20	**8.2**	**9.8**	**8.4**	**10.5**	**60.8**	**38.0**	**61.9**	**43.6**
P-2/M 70/30	**9.7**	**9.5**	**9.9**	**9.7**	**49.7**	**38.8**	**50.6**	**45.4**
P-2/M 60/40	**7.7**	**8.6**	**7.9**	**8.9**	**45.7**	**41.1**	**46.5**	**43.3**
PY-6	**7.8**	**6.1**	**7.3**	**7.4**	**54.3**	**30.9**	**63.0**	**32.7**
PY-6/M 80/20	**8.8**	**6.5**	**9.8**	**9.3**	**59.8**	**47.3**	**71.6**	**54.5**
PY-6/M 70/30	**9.5**	**9.2**	**10.4**	**11.0**	**57.2**	**32.1**	**68.4**	**47.8**
PY-6/M 60/40	**7.3**	**10.1**	**8.1**	**10.7**	**54.3**	**39.3**	**54.6**	**46.4**

The rest of the cements (OPCs, SRPCs and their POZCs) reached similar order values for each parameter.

successive Gauss curves joined at the downward arm of the first, and the upward arm of the second curve. But in any case, the final negative slopes (left arm of the second Gauss curve) have very small absolute values, decreasing to zero in all cases after a given age. The areas defined by plain PC curves are logically proportional to their C_3A (%) content.

NOTE: No initial point, i.e., the day when the specimens were manufactured or day 0 is shown in these figures (Figs. 2 and 3). Therefore, the initial point for 1 day, $Vcl_{1\ day}$, should be considered to be joined by an imaginary line to the day 0 point, $Vcl_{0\ day}$. This imaginary line must be considered together with the left arm of the first Gauss curve.

The following observations may be made with respect to 4.1.1.:

(a_o) It cannot be said without any more ado that $Vcl_{7\ days}$ value of the first Gauss curve for the 10 PCs tested is the highest value of all the points of that Gauss curve,

(b_o) On the other hand, maximum $Vcl_{7\ days}$ value of the second Gauss curve was reached at an age that was inversely proportional to the C_3A (%) content present in the PC,

(c_o) Both $Vcl_{7\ days}$ values, (a_o) and (b_o), were directly proportional to the C_3A (%) content of the PC, and

(d_o) $Vcl_{x\ days}$ (=Vcl_{xd}) values of the inflexion point(s) or minimum Vcl_{xd} values joining both Gauss curves maintained the same relationship to the C_3A (%) content of the PC as described in (b_o) and (c_o) above.

4.1.2. POZCs—30

Attention must first be drawn to the fact that the areas defined by POZC curves must also be proportional to their [C_3A (%)+$Al_2O_3^{r-}$ (%)] contents, although in some cases the results obtained are less exact than their respective PC curves.

Table 4
Normal consistencies, times of setting and stabilities of volume of several PCs and their POZCs with M pozzolan

Cements			Normal Consistency (%)	Times of setting (h, min) (Vicat Needle)			Le Chatelier needles (mm)							
							Water (days)							
							Hot 100°C	Cold (21±2°C)						
				initial	final	time of setting	7	7	14	21	28	60	90	120
P-1/M+“x”% SO_3	+3.50%	100/00	26.0	2 h,00 min	2 h,39 min	0 h,39 min	0.7	1.70	1.70	1.70	1.70	1.70	1.70	1.70
	+7.0%	80/20	29.6	3 h,15 min	4 h,10 min	0 h,55 min	0.5	3.33	5.65	7.20	9.35	12.00	12.15	12.15
	+7.0%	70/30	30.8	3 h,05 min	4 h,10 min	1 h,05 min	0.5	5.15	6.00	6.33	6.65	6.71	6.75	7.75
	+7.0%	60/40	32.8	3 h,15 min	4 h,10 min	0 h,55 min	0.5	5.75	5.75	5.75	5.75	5.75	5.75	5.75
P-2/M+“x”% SO_3	+4.94%	100/00	24.0	2 h,10 min	3 h,09 min	0 h,59 min	0.8	2.60	2.60	2.60	2.60	2.60	2.60	2.60
	+7.0%	80/20	28.7	4 h,40 min	7 h,30 min	2 h,50 min	0.5	5.83	8.16	10.00	11.50	15.33	16.33	16.33
	+7.0%	70/30	29.9	5 h,35 min	7 h,55 min	2 h,20 min	0.5	6.00	7.50	8.00	8.16	8.17	8.00	8.00
	+7.0%	60/40	32.2	4 h,35 min	7 h,15 min	2 h,40 min	0.5	7.33	7.33	7.33	7.33	7.33	7.33	7.33
PY-6/M+“x”% SO_3	+2.34%	100/00	21.2	0 h,05 min	0 h,25 min	0 h,20 min	1.0	0.30	0.30	0.30	0.30	0.30	0.30	0.30
	+7.0%	80/20	27.2	6 h,15 min	8 h,10 min	1 h,55 min	0.5	2.00	3.50	3.55	3.60	3.90	4.00	4.50
	+7.0%	70/30	28.8	5 h,45 min	6 h,55 min	1 h,10 min	0.0	3.20	3.70	3.80	4.00	4.60	4.60	4.70
	+7.0%	60/40	31.6	5 h,50 min	7 h,35 min	1 h,45 min	0.5	5.00	5.00	5.00	5.00	5.00	5.00	5.00

NOTE:The rest of the cements (OPCs, SRPCs and their POZCs) reached similar order values for each parameter.

The following observations may be made with respect to 4.1.2.: (a) In all ASTM C 452-68 specimens made with the 30 POZCs, by the end of the test, the Vcl values declined to zero from the 7-day figure. It will also be noted that, in all 30 POZCs, the Vcl values always peaked during the first 28 days, and usually during the first 7 days, but in any event always earlier than in the respective plain PCs (Figs. 2 and 3), and at even earlier ages when higher proportions of M pozzolan were added.

In other words, Vcl always dropped faster for any family of POZC tested than for its respective plain PC (P-n° or PY-n°), and faster yet as the M pozzolan content increased. The values began to decrease immediately after peaking, normally at the age of 7 days.

(b) $Vcl_{7-14\ \text{days}}$ values generally increased as the amount of M pozzolan increased for all OPCs (=P-n°) and SRPCs (=PY-n°) considered. The $Vcl_{7-14\ \text{days}}$ values fit the following inequality:

$$<Vcl<P-n^{\circ}/\mathrm{M}\ \text{or}\ \mathrm{PY}-\mathrm{n}^{\circ}/\mathrm{M}\ 100/00$$

$$<80/20<70/30<60/40,\ \text{at 7 and/or 14 days} \qquad (1)$$

Hence, the relationship described in Eq. (1) and the high $Vcl_{7-14\ \text{days}}$ values found were the direct result of replacing PC with M pozzolan, i.e., $Al_2O_3^{r-}$ present in the M pozzolan when converted in **ett-rf** [3–6] prevailed. This is tantamount to saying that **ett-rf** must necessarily be the chief cause of relationship [1] and the high $Vcl_{7-14\ \text{days}}$ values obtained for all POZC families tested. Furthermore, the order of magnitude of Vcl was infinitely smaller after than before 14 days for most cases studied, decreasing as the M pozzolan content increased in all cases.

(c) Vcl value for any plain OPC (=P-n°) or SRPC (=PY-n°) tested was a direct consequence of its daily ΔL only; this is due to the **ett-lf** from the C_3A present in the OPC and SRPC [3–6]. Nevertheless, when M pozzolan was added, the Vcl values increased proportionally, particularly, at early ages. Furthermore, the peak $Vcl_{7\ \text{days}}$ values rose as more M pozzolan was added, see Figs. 2 and 3, and the additional M pozzolan transformed two combined Gauss curves for each PC (whose C_3A (%) content differed from all the other PCs, be it recalled) into one curve for the respective POZC, where the Vcl

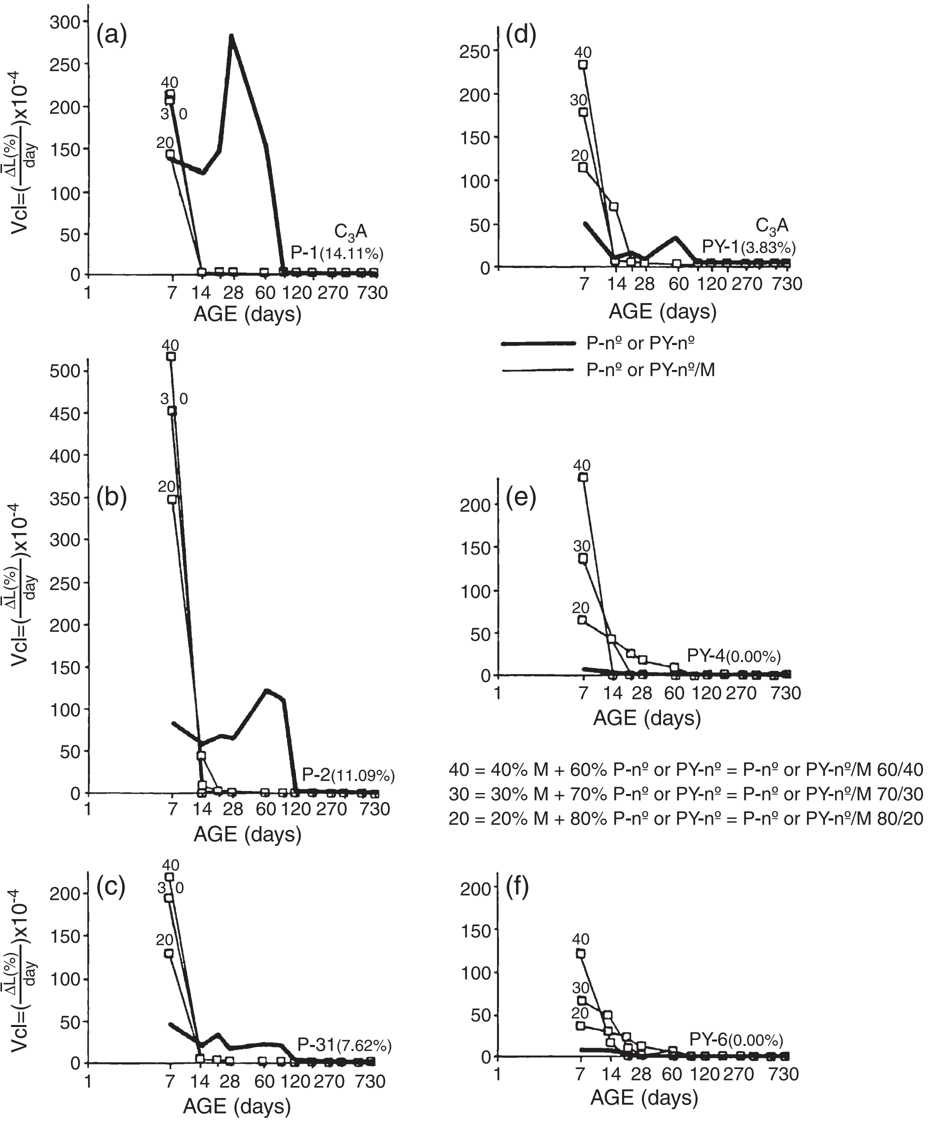

Fig. 2. Mortars: ASTM C 452-68; specimens: 1″ ×1″ ×11 1/4″; parameter: Vcl (=ΔL (%)/day); cements: 3 OPC(=P−n°), 3 SRPC(=PY−n°) and 15 POZC; pozzolan: M.

value always peaked earlier–generally speaking, at 7 days–than in the respective plain PC.

Once again, the chief cause must be the $Al_2O_3^{r-}$ prepresent in M pozzolan, when converted into **ett-rf** [3–6], as a result of its particular pozzolanic activity in gypsum and water environments (ASTM C 452-68 specimens) (Table 2).

(d) The lower the C_3A (%) content of the PC, the more closely its Gauss curve resembled its 80/20 POZC curve, and vice versa (see Figs. 2 and 3, but particularly Fig. 3(b)).

4.2. Prior consideration

The aim of the kinetic-chemistry is to study the evolution of chemical system(s) in terms of time. Kinetic-chemistry deals particularly with measurement and interpretation of reaction rates, which are to be defined as $R=dX/dt$ [2]. For a reaction that takes place across a solid–liquid interface–as it occurs with ettringites–, if the interface area is not known, as is usually the case, different definitions for the “rate” should be used, such as: $R=(1/W)(dX/dt)$ [3] or $r=(1/V')(dX/dt)$ [4], where W and V' are weight and volume of the solid particles dispersed within the liquid phase. Vcl was nevertheless considered sufficiently representative for the primary objective of this study, since:

- Both W and V' and the parameters for the corresponding reaction products formed (in this study, ettringite of different origins, namely $Al_2O_3^{r-}$ and C_3A), are very difficult to separate and accurately quantify;

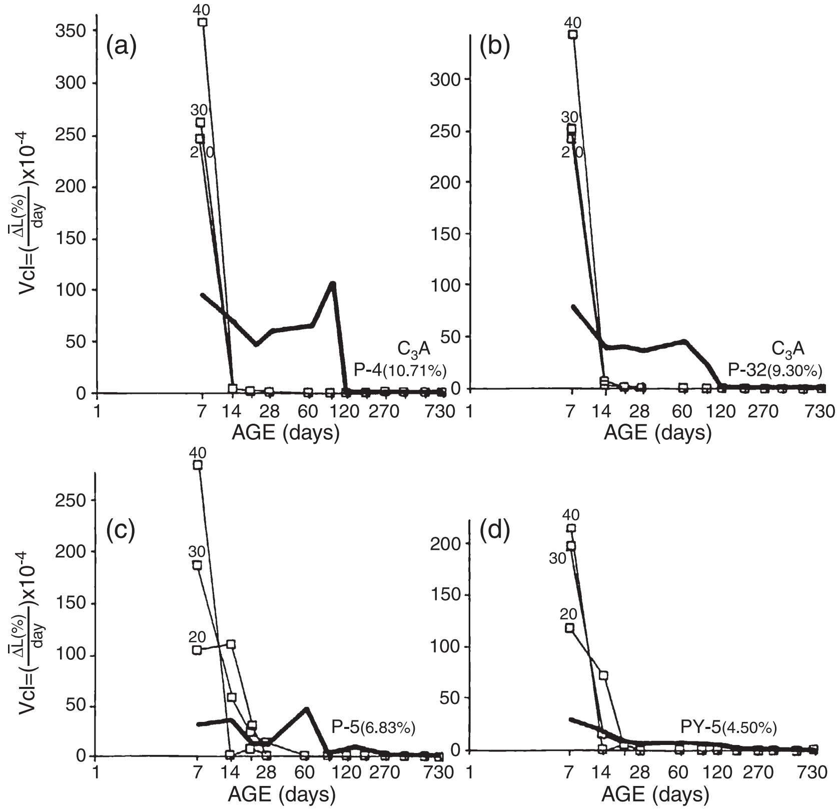

Fig. 3. Mortars: ASTM C 452-68; specimens: 1″ ×1″ ×11 1/4″; parameter: Vcl (=Δ*L* (%)/day); cements: 3 OPC(=P−n°), 1 SRPC(=PY−n°) and 12 POZC; pozzolan: M.

- Since the reaction rate must to be proportional to the derivative of the advance of the reaction over time, it is irrelevant whether expression [3] or [4] is used;
- The course of the ettringite formation reaction may be represented by the "total" increase in specimen size or by its length (*L*); the pattern of change in the *length growth rate*=Δ*L* (%)/day=Vcl is represented for ASTM C 452-68 specimens (Figs. 2 and 3).

4.2.1. Deductions from the observations 4.1.1.:

(a_1) The chemical reaction forming **ett-lf** in ASTM C 452-68 specimens takes place largely during the first 28 days of the test. The higher the C_3A (%) content in the OPC, the earlier the reaction reaches completion. This behaviour constitutes further proof that the TPQ mechanism with prior dissolution must prevail over the TS mechanism; otherwise, OPCs P-1, P-2, P-4, P-32 and P-31 would have formed the same first Gauss curve. Precisely, the opposite behaviour

Table 5
Times of setting and specific surfaces of several Portland cements

Portland cements	C_3A (%)	C_3S (%)	C_2S (%)	Times of setting (h, min)			BSS (cm^2/g)
				Initial	Final	Time of setting	
P-1	14.11	51.05	16.48	2h, 0 min	2h, 39 min	0h, 39 min	3192
P-2	11.09	33.47	30.26	2h, 10 min	3h, 9 min	0h, 59 min	3015
PY-4	0.00	58.19	19.46	2h, 15 min	2h, 65 min	0h, 50 min	3233
PY-6	0.00	79.43	2.29	0h, 05 min	0h, 25 min	0h, 20 min	3287

was observed, however. The contrary assumption must, therefore, be ruled out.

(b_1) The dual “filling-in<>expansion” process, which must be produced by **ett-lf** formation, linked to the TPQ mechanism with prior dissolution, prevailing over TS mechanism, must make that the first maximum Vcl value of the first Gauss curve reaches its minimum value later, and with smaller (“filling-in”), the lower C_3A (%) content of the PC (“expansion”) is, as obtained in this research. See 10 PC curves in Figs. 2 and 3.

Finally, it may be deduced from these observations as well that most of the slow formation of ettringite from C_3A present in PC or **ett-rf** [3–6] takes place during the first 28 days in ASTM C 452-68 specimens [1]. For this reason, the optional standard physical requirement $\Delta L_{14\ \mathrm{days}} \leq 0.040\%$ [56], which is presently used to differentiate SRPCs from OPCs, unlike the formerly $\Delta L_{28\ \mathrm{days}} \leq 0.054\%$ criterion, “predicts” rather than “assures” the probable behaviour of a PC under gypsum attack.

4.2.2. Deductions from the observations 4.1.2.:

According to observations (a_1) and (b_2), the larger/smaller the negative slope of the Vcl curve is, the larger/smaller must the respective positive slope be. The positive slope corresponds to the first 7 days. These observations support the following reasoning: examining firstly only the plain PCs (OPCs=P-n° and SRPCs=PY-n°) curves, the maximum Vcl value at 7, 14, 21, 28 or 60 days is found to increase–by and large–, with PC C_3A content (%) in the PC. According to this, for the OPC P-2 specimens to reach the same $Vcl_{7\ \mathrm{days}}$ value as recorded for the P-2/M 60/40 specimens, C_3A (%) content of OPC P-2 would have had to be $\approx$68.84%, a quantity that corresponds to an expansive **S** type clinker [57], but this was not the case. Consequently, the reason that the POZC containing 60% of OPC P-2 and 40% of M pozzolan showed a higher 7-day $Vcl_{7\ \mathrm{days}}$ value than the plain OPC P-2 was, once again, the presence of M pozzolan (40%), or more precisely, the $Al_2O_3^{r-}$ present in M pozzolan, which prompted the rapid formation of ettringite, **ett-rf** [3–6].

However, the most interesting deduction that can be drawn from the above observations is as follows: Considering that the excess mortar was of the same order of magnitude and thus could be regarded to be equivalent for all cements, the total area defined by OPC P-2 Vcl curve must match the formation of 144.22 g of **ett-lf** from C_3A present in OPC P-2 (11.09%), whereas the corresponding areas for PY-4/M 60/40 specimens must match at the most the formation of 144.22 g of **ett-rf**, mainly, from 11.886 g of $Al_2O_3^{r-}$ present in M pozzolan, assuming that all is reactive, and if all is not reactive, which probably would be the case [3,5], it would be still better for the final conclusion of this reasoning. Nevertheless, both areas ratio at 7 days is at the most $\approx$1:2. Here, it can be seen once again [3,5] that there is a great paradox between behaviours (Vcl values vs. time) and theoretical stoichiometric calculations [3,5], but behaviours holding priority.

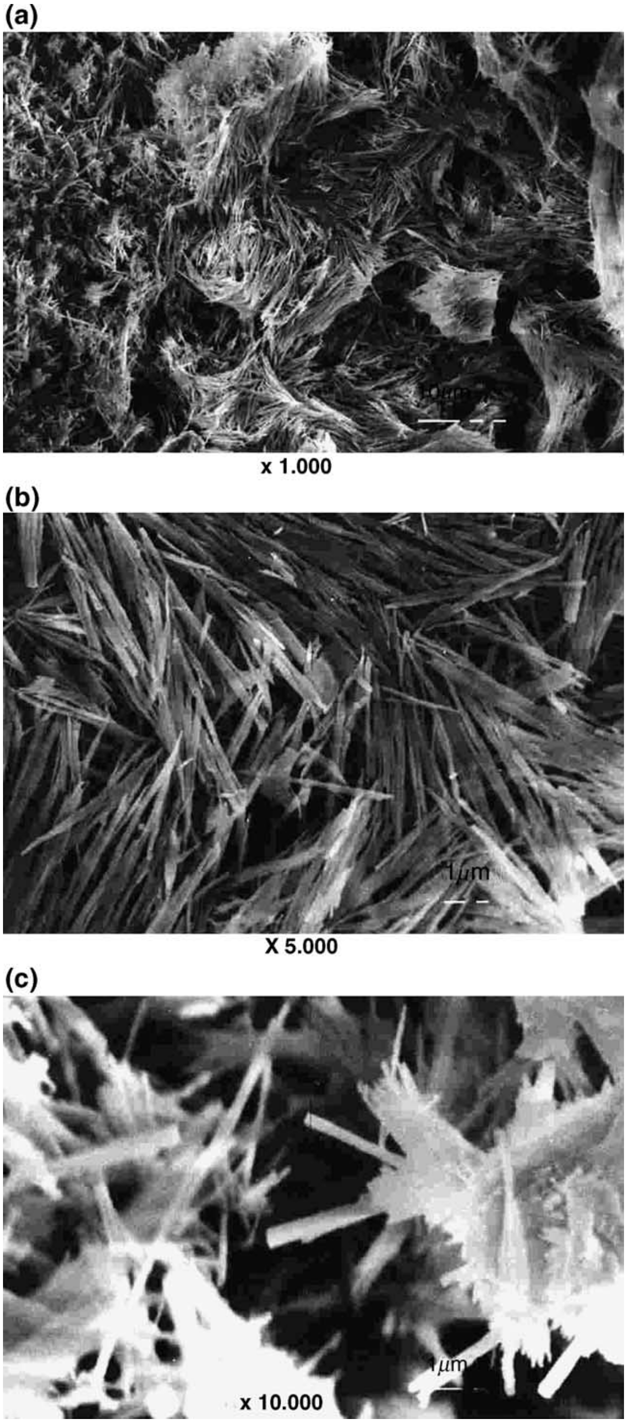

Fig. 4. 1.1. Ettringites of “rapid” formation (ett-rf). (a) Ettringites of “rapid” formation (ett-rf). (b) Ettringites of “rapid” formation (ett-rf). (c) Ettringites of the “rapid” formation (ett-rf).

Therefore, the only possible explanation of such remarkable paradox is that some alumina, of M pozzolan reacting to form ettringite must be substantially more reactive than the C_3A from the OPC P-2. For this reason, the M pozzolan would form the ettringite much faster than that of the C_3A from OPC, although the quantity formed is equal in the two cases. It may therefore be sustained that such high reactivity

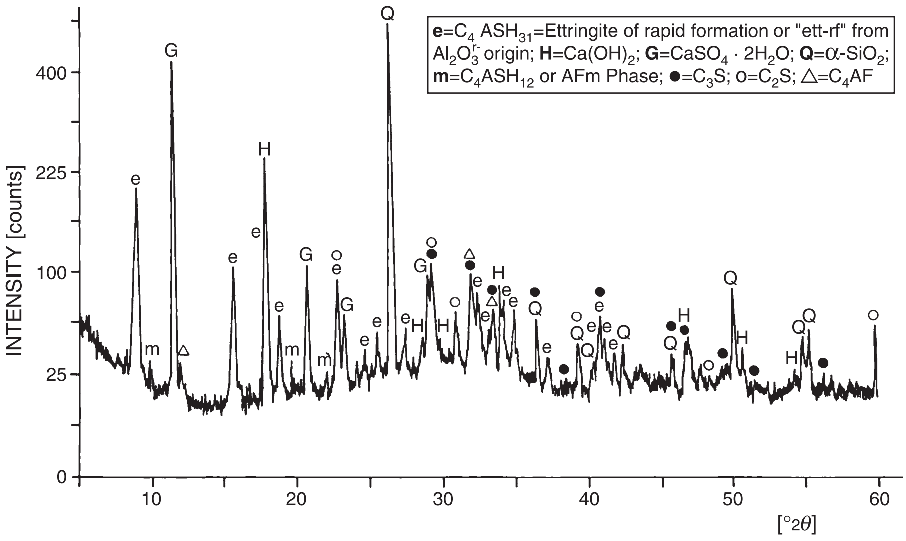

Fig. 4 (*continued*).

of the alumina may be the result of its IDEAL physical–chemical state for this process (reactive alumina $Al_2O_3^{r-}$ or, perhaps better, solid tetra- or penta-coordinated alumina [2]). The C_3A would, on the contrary, be in a NON IDEAL, or at least, less ideal form to reach the same result. Moreover, the rate at which it forms ettringite declines substantially, i.e., the C_3A reacts more slowly after the first very few hours of its initial hydration [5].

It might nevertheless be thought that **V_f ett-rf** is =**V_f ett-lf**, their common value being the **V_f ett-lf**. Under this assumption, the curves for any POZC family should be the same as their respective PC curve, i.e., P-n° or PY-n°/M 80/20,70/30 and 60/40 curves should be identical to their respective plain P-n° or PY-n° curve. But this was not in fact observed in the empirical results, which, rather, fit the relationship described in Eq. (1).

Both sets of curves were generated by plotting Vcl versus time and all Vcl values were due to the ettringites' expansion. Furthermore, the formation of ettringite from C_3A present in OPC was verified by previous paper [3–5]. It was likewise shown that M pozzolan also forms ettringite when exposed to the same sulfate bearing solution (gypsum in water) [3–5], such as in ASTM C 452-68 specimens, for instance (see Figs. 2 and 3).

To summarize, when PY-6/M 60/40 and PY-4/M 60/40 curves (with one maximum point or peak only) were compared to a P-1 curve (with two maximum points or peaks), the shapes of the curves and the areas they described were found to differ; the same observation was made when comparing P-1/M 80/20, 70/30 and 60/40 curves to a P-1 curve, while the differences were even greater between P-2/M 80/20, 70/30 and 60/40 curves and the respective P-2 curve. The higher the proportion of M pozzolan in OPC P-1 or P-2, the larger were the difference between the curves and the higher the Vcl peak values and the earlier the age at which they were reached. Consequently, the foregoing assumption that **ett-rf=ett-lf** would appear to be mistaken and either **V_f ett-rf<V_f ett-lf** or **V_f ett-rf>V_f ett-f**. But **V_f ett-rf** cannot be less than **V_f ett-lf** for the following reasons.

1. Although, at 7 days, ettringite amounts obtained for each cement–P-2 and PY-4/M 60/40–are equal, as both are short in gypsum (7.0% SO_3), the respective areas are completely different. Consequently, their respective formation rates are also completely different, for instance:

- Vcl for OPC P-2 specimens=0.00829%/day (worst case, at 7 days) and 0.0120%/day (best case, at 60 days), and
- Vcl for 60/40 POZC PY-4/M specimens=0.02286%/day (best case, at 7 days) and 0.00013%/day (worst case, at 60 days),

(the 0.00829%/day observed for OPC P-2 specimens at 7 days is clearly lower than 0.02286%/day for 60/40 POZC PY-4/M specimens; on the other hand, the 0.00829%/day is also clearly lower than 0.0120%/day, i.e., **ett-lf** is forming from 7 up to 60 days; in contrast, 0.02286%/day is higher than 0.00013%/day, i.e., **ett-lf** has almost completed its formation). Differences were also observed for these two samples in parameters such as mechanical strengths, times of setting and volume stabilities (Le Chatelier's needles), although they can be seen more vividly in the comparison between the two equivalent POZC families, P-2/M and PY-6/M (see Tables 3 and 4).

This shows that ettringite would form at a much higher rate from the reactive alumina, $Al_2O_3^{r-}$, present in M pozzolan than from C_3A (in the PC), and concomitantly, according to the Von Weimar's and Garrido's set patterns [58,59], **ett-rf** would be much smaller in size than **ett-lf** (see Figs. 4 and 5). Von Weimarn and Garrido both proved that the precipitation rate of a salt is directly proportional to the supersaturation grade and inversely proportional to its solubility. Besides, the set pattern of Von Weimarn and Garrido underlines that the more insoluble a salt is (ettringite is clearly insoluble, varying from 0.255 to 0.024 g ett/l in water solutions with $Ca(OH)_2$ a content of from 0.056 to 1.08 g CaO/l, while the solubility of $Ca(OH)_2$ in water is 1.2 g CaO/l at 18°C), the more difficult it is to induce slow precipitation with large and well formed crystals (see Figs. 4 and 5).

Thus, according to Von Weimarn's and Garrido's set patterns, if reagents are mixed so that high supersaturation takes palce–as it happen for the reactive alumina, $Al_2O_3^{r-}$, present in some pozzolans–fast precipitation occurs, and gelatinous precipitate is obtained. This originates small crystals which are formed quickly (**ett-rf**, in this case). On the contrary, if the precipitating agent is slowly added in diluted solution–as it is required for the C_3A present in OPC–, slow supersaturation is produced and precipitate, constituted by macrocrystals, appears slowly (**ett-lf**, in this case). That is to say, the initial rate of precipitation is proportional to $[(Q-S)/S]$, where Q is the total concentration of the substance that precipitate, S is the concentration of the solution in balance with the precipitate and, finally, $Q-S$ is the supersaturation when the precipitation stars. In summary, the particle size of precipitates decreases (**ett-rf**, in this case), when the concentration of the reacting substances increases (pozzolan or its reactive alumina, $Al_2O_3^{r-}$, in this case), and on the contrary, if crystalline precipitate (large and well-formed crystals) is preferred, $[(Q-S)/S)]$ has to be as small as possible.

Moreover, according to Garrido, crystals that result from weak supersaturation are the same as those that originate from the vapour phase (that is, without solvent) smaller size and growth rates correspond to faces which have an electric field. However, an inversion of the growth order originates when the growth is performed with strong supersaturation and the faces with strong electric field have a minimum growth rate. This inversion can be explained taking into account that when solution is strongly supersaturated, ions in solution and dipoles assume a different configuration than when the solution match to saturation. In crystal-solution contact, different phenomena happen. As the solution is poorer in solvent with strong supersaturation, it must give as result a reverse solvation, which is easier to obtain in the reticular surfaces with weak electric field which makes that these surfaces increase their growth rate enabling to exceed the rate at the surface with strong electric field. The higher the supersaturation grade (it brings about the change of facies), the stronger the solvent–crystal link and the lower the salt solubility (and the solubility of ettringite is already low enough). Hence, there is a very marked interaction between the solvent and the crystal, and the F forms, which appears in balance stage, may be replaced by S or K forms.

2. At 7 days,

– 60/40 POZCs PY-4/M and PY-6/M, with $Vcl_{7\ \mathrm{days}}$ values of: 0.02286%/day and 0.0120%/day, respectively,
– OPC P-2, with $Vcl_{7\ \mathrm{days}}$ value of 0.00829%/day ≈0.0083%/day, being 60%=0.00498%/day and 40%=0.00332%/day, and
– 60/40 POZC P-2/M, with $Vcl_{7\ \mathrm{days}}$ value of:
  - theoretical value: 0.00498%/day+(0.02286%/day+0.0120%/day)/2=0.02241%/day, which is greater than 0.00498%/day and than 0.0083%/day, and

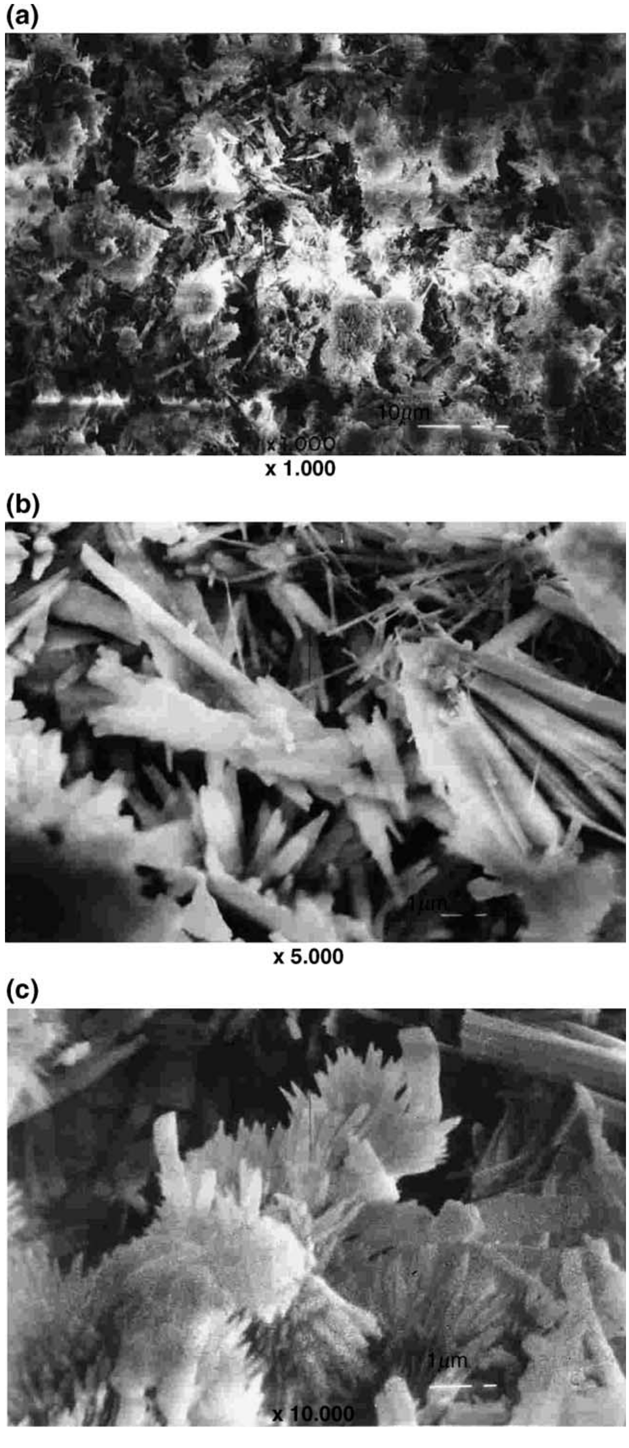

Fig. 5. 1.1. Ettringites of "slow" formation (ett-lf). (a) Ettringites of "slow" formation (ett-lf). (b) Ettringites of the "slow" formation (ett-lf). (c) Ettringites of the "slow" formation (ett-lf).

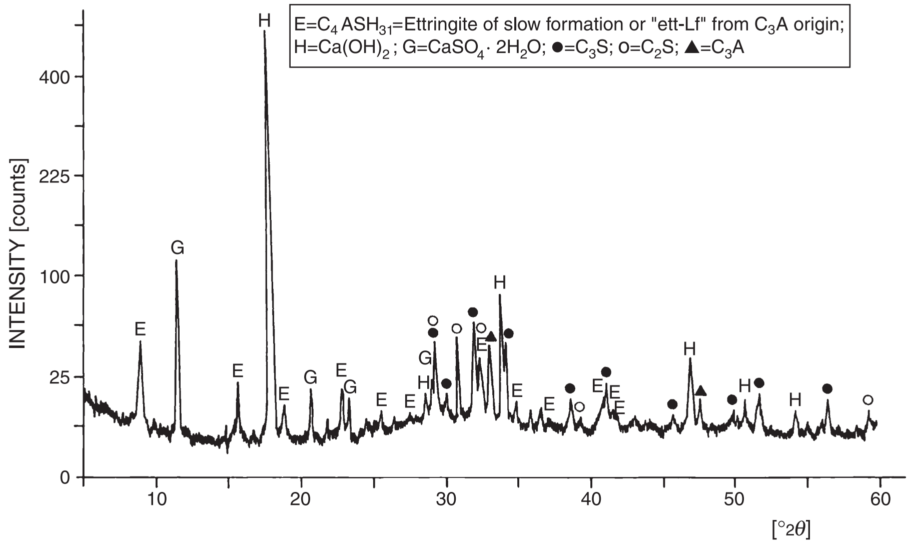

Fig. 5 (*continued*).

- real value: 0.05143%/day, but 0.05143%/day−0.00498%/day=0.04645%/day, which is also remarkably greater than 0.00498%/day and than 0.0083%/day.

These calculations point out that, in any case, $Vcl_{7\ days}$ value for 60/40 POZC P-2/M is much larger than $Vcl_{7\ days}$ value for plain OPC P-2, but according to the results obtained, real values prevailed, i.e., the empirical value is more than twice as large as theoretically expected.

These results and the reasoning put forward in this study contribute to a more detailed understanding of and explanation for many of the questions about ettringite morphology and size differences posed by Mehta [14].

Moreover, for all ASTM C 452-68 specimens of POZC, most of the reactions leading to the formation of ettringite of both $Al_2O_3^{r-}$ and C_3A origin take place during the first 28 days of age. And the larger the amount of M pozzolan added, the faster is the reaction–in the first 7 days–, and vice versa. This provides further ratification that the TPQ mechanism with prior dissolution prevails over the TS mechanism.

Finally, the ettringite formation reaction is complete when the Vcl declines to has 0.00(%)/day after having peaked. Indeed, as Figs. 2 and 3 show, most of the area defined by the curves for all the cements studied correspond to ages 0 to 28 days. Furthermore, in ASTM C 452-68 specimens to which M pozzolan is added, the higher the content of M pozzolan, the sooner the zero value is reached (14 days). Therefore, the above empirical evidence constitutes sufficient grounds to sustain the following.

1. The relationship expressed in Eq. (1) is a direct consequence of the $Al_2O_3^{r-}$ present in M pozzolan when converted into **ett-rf** [3–6].

2. The $\mathbf{V_f}$ of the **ett-rf** (or from $Al_2O_3^{r-}$ present in M pozzolan) is considerably higher than the $\mathbf{V_f}$ of **ett-lf** (from C_3A present in PC).

3. The pozzolanic reactions from $Al_2O_3^{r-}$ origin–present in M pozzolan–, in a gypsum and water environment–ASTM C 452-68 specimens–, have taken place during the first 28 days of age, and even earlier–during the first 14 days (Figs. 2 and 3) (and even perhaps much earlier, at 2 days, because their Frattini test results were already by then positive (Table 2); we do not think this is the case, due to the fact that their Frattini test results at 7 days, i.e. 5 days later, showed an even clearer positive result)–, in most cases studied, and by an large, the larger the C_3A content in the PC and more M pozzolan added, the sooner these reactions finished (14 days). According to the latest experimental results and their respective Vcl values obtained, those particular pozzolanic reactions owing to $Al_2O_3^{r-}$ were not sufficiently interfered with the corresponding pozzolanic reactions deriving from the reactive silica, SiO_2^{r-} [60,61], also present in M pozzolan (38.4% [62]). This also justifies the deduction set out in observation 4 below.

4. Observation 4 justifies without further ado that **ett-rf** and **ett-lf** formation must not take place independently from one another, but inter-dependently in a joint way or interactive way, i.e., both types of ettringite are obtained to a greater or lesser extent when dealing with gypsum and water environments—ASTM C 452-68 specimens. Nevertheless, the reaction products must be closer to **ett-rf** than **ett-lf**, when more M pozzolan is added (40%) and the PC has more C_3A and C_3S contents and Blaine specific surface (BSS), and vice versa (20%). Under such circumstances, the **ett**−Total=**ett**−**T**=**ett-rf**+**ett-lf** must logically resemble **ett-rf** more closely than **ett-lf**. This is because POZC 80/20 curves are more similar to its respective plain PC curve, followed by the 70/30 POZC curves for the SRPC, mainly; especially if C_3A (%) content is less than moderate (Figs. 2(c)–(f) and 3(c) and (d), but specially Fig. 3(c)).

Nevertheless, it can be shown, as noted in earlier papers, that the closer the $Al_2O_3^{r-}$ and C_3A particles are, to one another, the more inter-dependent this formation is. Such conditions, i.e., a high proportion of M pozzolan (40%) and a OPC with high C_3A (%) content, can be found in this study in the 60/40 and 70/30 mixes, namely, the P-2/M and P-5/M POZC families, as compared, for instance, with PY-6/M family (SRPC PY-6 without C_3A). Further proof of this hypothesis can be deduced from the following:

- POZC family P-2/M:
  - Vcl$_{7\ \text{days}}$ value for POZC P-2/M 80/20=0.05143%/day=80%×Vcl$_{7\ \text{days}}$ for OPC P-2(=0.0083%/day)+Vcl$_{7\ \text{days}}$ for 20% of M pozzolan, Vcl$_{7\ \text{days}}$ for 20% of M pozzolan=0.05143%/day−0.00664%/day=0.04479%/day;
  - Vcl$_{7\ \text{days}}$ value for POZC P-2/M 70/30=0.04486%/day=70%×Vcl$_{7\ \text{days}}$ for OPC P-2+Vcl$_{7\ \text{days}}$ for 30% of M pozzolan, Vcl$_{7\ \text{days}}$ for 30% of M pozzolan=0.04486%/day−0.00581%/day=0.03905%/day; and
  - Vcl$_{7\ \text{days}}$ value for POZC P-2/M 60/40=0.03457%/day=60%×Vcl$_{7\ \text{days}}$ for OPC P-2+Vcl$_{7\ \text{days}}$ for 40% of M pozzolan, Vcl$_{7\ \text{days}}$ for 40% of M pozzolan=0.03457%/day−0.00498%/day=0.02959%/day.
- POZC family P-5/M:
  - Vcl$_{7\ \text{days}}$ value for POZC P-5/M 80/20=0.02814%/day=80%×Vcl$_{7\ \text{days}}$ for OPC P-5(=0.0031%/day)+Vcl$_{7\ \text{days}}$ for 20% of M pozzolan, Vcl$_{7\ \text{days}}$ for 20% of M pozzolan=0.02814%/day−0.00248%/day=0.02566%/day;
  - Vcl$_{7\ \text{days}}$ value for POZC P-5/M 70/30=0.01843%/day=70%×Vcl$_{7\ \text{days}}$ for OPC P-5+Vcl$_{7\ \text{days}}$ for 30% of M pozzolan, Vcl$_{7\ \text{days}}$ for 30% of M pozzolan=0.01843%/day−0.00217%/day=0.01626%/day; and
  - Vcl$_{7\ \text{days}}$ value for POZC P-5/M 60/40=0.01029%/day=60%×Vcl$_{7\ \text{days}}$ for OPC P-5+Vcl$_{7\ \text{days}}$ for 40% of M pozzolan, Vcl$_{7\ \text{days}}$ for 40% of M pozzolan=0.01029%/day−0.00186%/day=0.00843%/day.
- POZC family PY-6/M:
  - Vcl$_{7\ \text{days}}$ value for POZC PY-6/M 80/20=0.01201%/day=80%×Vcl$_{7\ \text{days}}$ for OPC PY-6(=0.0006%/day)+Vcl$_{7\ \text{days}}$ for 20% of M pozzolan, Vcl$_{7\ \text{days}}$ for 20% of M pozzolan=0.01201%/day−0.00048%/day=0.01153%/day;
  - Vcl$_{7\ \text{days}}$ value for POZC PY-6/M 70/30=0.00657%/day=70%×Vcl$_{7\ \text{days}}$ for OPC PY-6+Vcl$_{7\ \text{days}}$ for 30% of M pozzolan, Vcl$_{7\ \text{days}}$ for 30% of M pozzolan=0.00657%/day−0.00042%/day=0.00615%/day; and
  - Vcl$_{7\ \text{days}}$ value for POZC PY-6/M 60/40=0.00357%/day=60%×Vcl$_{7\ \text{days}}$ for OPC PY-6+Vcl$_{7\ \text{days}}$ for 40% of M pozzolan, Vcl$_{7\ \text{days}}$ for 40% of M pozzolan=0.00357%/day−0.00036%/day=0.00321%/day.

It must nonetheless be acknowledged that, if POZC families P-1/M, P-31/M and PY-4/M had been chosen for analysis, the hypothesis could scarcely have been verified, if at all. Why? Simply because mineralogical composition, BSS, setting times and the other chemical and physical characteristics are less propitious, as discussed in observation 5 below.

5. With regard to the M pozzolan content, all the POZCs should have generated practically the same amount of ettringite under gypsum attack (7.0% SO_3⇒16.77% ettringite) because there was insufficient gypsum amount to react with their $Al_2O_3^{r-}$ (%) content, i.e., they should have yielded identical Vcl value. Since they do not, the following characteristics of the PC clearly influence the results of the ASTM C 452-68 test for these 30 POZCs: primarily, the mineralogical composition (C_3A (%), C_3S (%) and C_2S (%) contents), BSS and times of setting, mainly, and secondarily, the w/c ratio of the mortars and specimens porosity. Evidence for this assertion can be found by comparing the curves Figs. 2(a) and (b) to 3(d) and (e): OPCs P-1 and P-2 differ in their C_3A (%), C_3S (%) and C_2S (%) contents, BSS and setting times, and SRPCs PY-4 and PY-6 in their C_3S (%) and C_2S (%) contents (see Tables 1 and 5).

Following this line of reasoning, if such BSS had been more similar, for instance, by grinding all the cements before running the ASTM C 452-68 test, as it is done at the beginning of the *Le Chatelier–Ansttet* test [4–6,10,60], the Vcl for the POZC families P-1/M and P-2/M would have differed much less widely, in accordance with findings reported in previous papers [4–6]. This can be clearly illustrated by comparing Figs. 2 and 3 in this paper to Fig. 2 in both [5,6].

Finally, it may also be deduced from the observations discussed under 4.1.2. above that most of the ettringite formed from the $Al_2O_3^{r-}$ origin present in the M pozzolan or **ett-rf** [3–6] is also generated during the first 28 days of the ASTM C 452-68 test, and even during the first 14 days, in many cases. Nevertheless, according to the mandatory Frattini test [53] and EN 450 Standard [63], which must be applied to the natural or artificial pozzolan prior to the ASTM C 452-68 test, the most appropriate–and in fact mandatory–physical criterion for differentiating high SRPOZC from low SRPOZC is $\Delta L_{28\ \text{days}} \leq 0.054\%\Delta$ [4,64]. This physical requirement would, then, the more important than any other, whether chemical–pozzolanicity (Frattini test [53]), etc.–, or physical-pozzolanic activity index [65,66], etc.

5. Conclusions

In the present discussion and interpretation of the Vcl values, the following conclusions were drawn:

1. ASTM C 452-68 test: the Vcl parameter has shown that at the least in the first very few hours following initial hydration in both the OPCs and their respective POZCs with M pozzolan:

   1.1 The $\mathbf{V_f}$ of the ettringite formed from $Al_2O_3^{r-}$ present in M pozzolan, **ett-rf**, is considerably higher than the $\mathbf{V_f}$ of the ettringite formed from the C_3A present in OPC, **ett-lf**, a finding that concurs with the conclusions and proposals of earlier studies [3–6].
   1.2 As a result, the **ett-rf** is much smaller in size than the **ett-lf**.
2. The pozzolanic reactions from $Al_2O_3^{r-}$ origin–present in M pozzolan–, in a gypsum and water environment–ASTM C 452-68 specimens–, forming **ett-rf** reached completion in the first 28 days or even earlier, in 14 days, in most cases studied; by and large, the higher the C_3A content in the PC and more M pozzolan was added, the sooner those pozzolanic reactions came to an end, irrespective of whether the mineralogical composition, chemical and physical characteristics, BSS and setting times of plain OPC and SRPC, were more or less appropriate. This is discussed in greater detail in conclusion 3 below.
3. The combined formation of the **ett-rf** and **ett-lf** in ASTM C 452-68 specimens has not taken place independently from one another, but inter-dependently in a joint way or interactive way, to a larger or smaller extent, and the reaction products are closer **ett-rf** than **ett-lf** when more M pozzolan is added (40%), and vice versa (20%); but in any event, TPQ mechanism with prior dissolution must be preponderant over TS mechanism. In contrast, the formation of **ett-rf** and **ett-vlf** must be logically independent rather than inter-dependent or combined.
   Initially, the term proposed here for the result of the inter-dependent formation of **ett-rf** and **ett-lf** is the synergic expansive effect (SEE). The proof or demonstration, quantification, explanation, justification and practical consequences of this effect will be presented in subsequent papers.
4. The criterion presently used to differentiate OPC from SRPC–namely $\Delta L_{14\ \mathrm{days}} \leq 0.040\%$–laid down in ASTM C 150 [56] standard "predicts" rather than "assures" the performance of PCs under gypsum attack, by contrast to the criterion formerly used–$\Delta L_{28\ \mathrm{days}} \geq 0.054\%$–for this purpose, as inferred in the title of the ASTM C 452-68 standard.

6. Deductions

According to conclusions 1, 2 and 3 above, after positive result is obtained in the Frattini test (EN 196-5 [53]), at 28 and/or 7 days only, instead of at 15 and/or 8 days only, as well as in the tests set out in standards EN 196-1 [54], EN 196-3 [55] and UNE-EN 450 [63] and/or ASTM C 311-94b [65], mainly, the ASTM C 452-68 test can be validly used to characterize and to differentiate 28-days, POZCs prepared with this M pozzolan or with any other from natural or artificial (fly ash) pozzolan, which may or may not give rise to the development of low, moderate or high sulfate resistance (SR) [4,64]. The only requisite would be to establish suitable standard physical–chemical requirements and specifications [4,53–55,64–66].

This way, many questions about sulfate attack concrete and the further need of researching it brought up by Cohen and Mather [67] can now be explained in detail and with a better understanding, but specially those about:

- establishing a standard methodology for systematic data analysis and development of hypothesis (perhaps more precisely, thesis [4,25,60,61]),
- establishing methods for accelerating sulfate attack [4–6,60],
- establishing relationship between paste [3–6], mortar [4,47,60,64] and concrete [47] durability,
- assessing the role of pozzolans in sulfate attack [4,60,61,67–72], chloride attack [73–76] and heat emitted in the early phases of hydration reactions [61,77,78], and
- examining effect of ettringite [3–6] (and this paper).

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Errata

Our previous paper about this subject, Ref. [5] cited above, contained five minor typographical errors, as follows:

1. On page 710, point (1.2.2), $AL_2O_3^{r-}$ should read $Al_2O_3^{r-}$.
2. On page 712, paragraph (ii) 2nd. **ett-lf** should read **ett-rf**,
3. On page 713, 0.50<0.87% should read 0.50%<0.87%,
4. On page 714, 19.95–8.23%=11.72% and 21.20–7.11%=13.80% should read: 19.95%–8.23%=11.72% and 21.20%–7.11%=14.09%, and
5. Table 2, footnote: **TS** should read **FS** (=flexural strength).

None of these minor errors affects the reasoning and/or conclusions reached in any way.