

Case study

The effect of the source of cement SO_3 on the expansion of mortarsSayed Horkoss^{a,b,c,*}, Gilles Escadeillas^b, Toufic Rizk^c, Roger Lteif^c^a Cimenterie Nationale S.A.L., Plant- Laboratory Department, Old Tripoli Road, Chekka, North Lebanon, P.O.Box. 11-5101 Riad El Solh, Beirut, Lebanon^b Université de Toulouse, UPS, INSA, LMDC (Laboratoire Matériaux et Durabilité des Constructions), 135av de Rangueil, F-31077 Toulouse Cedex 04, France^c Université Saint-Joseph, Faculté des Sciences, Mar Roukos, Mkillès, P.O.Box. 11-514 Riad El Solh, Beyrouth 1107-2050, Lebanon

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ABSTRACT

In order to evaluate the risk of the source and quantity of cement SO_3 on the expansion properties of mortars, this paper studied the influence of Gypsum, Bassanite and clinker sulfate on the cement paste expansion and the formation of delayed ettringite. The investigation covers the mortar cured at 20 °C and 80 °C and stored in water. In contradiction to many studies, the results showed that the cement produced with high sulfur clinker had lower expansion than that produced with classical gypsum or high soluble Bassanite. In addition to that, we have detected that the percentage of SO_3 , in the cement, could increase the risk of DEF if it surpasses the level of 3.5%. Also, the curing temperature at 80 °C affects the microstructure of concrete by generating cracks in the cement paste.

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1. Introduction

Internal sulfate attack is pathology of concrete. Over 40 years of researches, the scientists proved that the delayed ettringite formation (DEF) can lead to significant deterioration of concrete structure. However, the mechanisms of the DEF have still not been totally elucidated.

When ettringite occurs homogeneously and immediately in a fresh concrete, it does not cause any expansion but laterly when it forms heterogeneously in a hard concrete, it can produce cracks.

The heat treatment is one of the essential factors for the formation of delayed ettringite (Detwiler and Taylor, 2005). The maximum curing temperature should be kept at less than 70 °C in order to minimize the risk of DEF (Detwiler and Taylor, 2005).

The leaching of the alkali accelerates the formation of DEF. In order to minimize this risk, it is necessary to control the parameters that might affect the leaching of alkali compound during the curing period (Aubert et al., 2013).

Regarding cement composition, the important parameters, influencing the formation of DEF, appear to be the $\text{SO}_3/\text{Al}_2\text{O}_3$ ratio (Day, 1992), SO_3 , Na_2O , Na_2Oeq , MgO , CaO , C_3A content, specific surface area and possibly C_3S content (Shimada et al., 2005).

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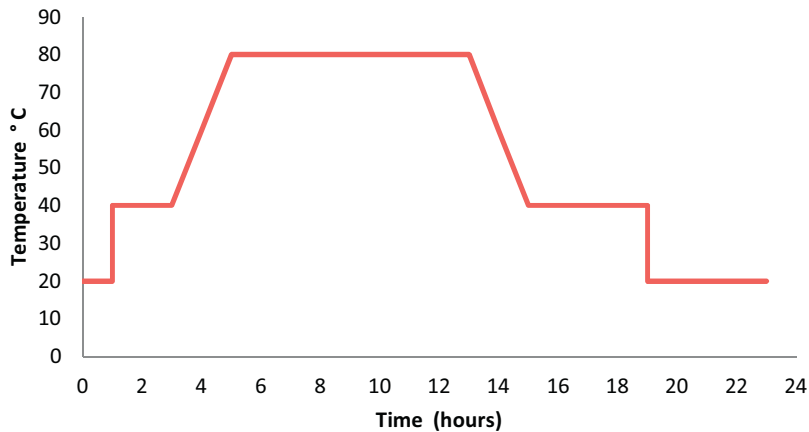


Fig. 1. Temperature cycle imposed on the heat cured specimens.

The type of sulfate plays an important factor in delayed ettringite formation (Escadeillas et al., 2007). No expansion was observed in the mortar containing calcium sulfate. In contrary the mortar containing sodium sulfate had remarkable expansion (Escadeillas et al., 2007). Literature references hypothesized that the high-sulfate clinker which is “slowly soluble” in ambient curing scenarios can cause distress (Hime, 1996; Mielenz et al., 1995) but this hypothesis contradicts the results of the most of investigations performed later (Herfort et al., 1997; Horkoss et al., 2011; Klemm and Müller, 1997; Michaud and Suderman, 1997; Michaud and Suderman, 1999; Shimosaka et al., 2002; Taylor, 1999; Tennis et al., 1999). (Collepari, 1999) assumed that the formation of the expansive heterogeneous ettringite, is based on the presence of three essential elements: micro-cracking, late sulfate release and exposure to water.

The objectives of this paper focus on the role of the form, solubility and quantity of cement setting regulator on cement paste expansion and on the delayed ettringite formation.

2. Experiment and methods

Over 100 years ago, it was found that cement produced from the rotary kiln was much more reactive than that made in the older shaft kilns. The cement tended to be much more quick setting or irregular setting, and this created marketing problems. Subsequently, de Navarro hired a French chemist by the name of Pierre I. Giron, who solved the problem by adding gypsum to the cement in order to control the setting time. Later on the cement producer optimized a mixture of all forms of calcium sulfate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, $\text{CaSO}_4 \cdot \text{H}_2\text{O}$, $\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$ and CaSO_4) in order to control the setting time and cement hydration. Actually the valorization of waste and the usage of high sulfur fuel led to increase the amount of sulfate in the clinker.

2.1. Material

In addition to the above facts, some additional requirements related to the cement composition and specification such as the amount of alkalis, the percentages of MgO and the ratio $\text{SO}_3/\text{Al}_2\text{O}_3$, were settled in order to eliminate the interference of these parameters on the results.

Based on these requirements three industrial cement samples were selected for the experience.

The samples were identified as follow:

Sample 1: It was sampled from certified cement (CEM I 52.5 R) according to the European standard EN 197. The manufacturer use natural gypsum as setting regulator. Since the natural gypsum is to be considered as the lower risky regulator of setting, we selected the sample that contained the higher amount of SO_3 for the test.

Sample 2: It was sampled from certified cement (CEM I 52.5 N) according to the European standard EN 197. The manufacturer used Bassanite as setting regulator. The cement mill outlet was optimized at 130 °C.

Sample 3: It was sampled from certified cement (CEM I 52.5 N) according to the European standard EN 197. The manufacturer ground only clinker with high SO_3 without adding any types of gypsum during cement production.

The forms of sulfate, in the three samples, are the globally utilized material for regulating the setting time of cement.

Table 1

The chemical analysis of the samples by XRF.

	L.O.I	CaO	SiO ₂	Al ₂ O ₃	TiO ₂	Fe ₂ O ₃	SO ₃	MgO	P ₂ O ₅	Na ₂ O	K ₂ O	IR	SO ₃ /Al ₂ O ₃	C ₃ S	C ₂ S	C ₃ A	C ₄ AF
1	2.50	65.66	20.18	4.41	0.21	2.40	3.37	0.66	0.05	0.06	0.14	0.26	0.76	71.20	4.14	7.63	7.30
2	1.09	65.64	20.46	4.87	0.42	3.27	2.35	0.89	0.38	0.07	0.33	0.34	0.48	67.56	7.69	7.37	9.95
3	0.79	65.45	20.67	4.76	0.35	3.70	2.31	0.74	0.55	0.08	0.37	0.21	0.49	65.43	9.90	6.35	11.26

Table 2

The mineralogical analysis of the sample by XRD.

	C ₃ S M ₃	C ₃ S M ₁	Total C ₃ S	C ₂ S beta	C ₂ S alpha	Total C ₂ S	C ₃ A cubique	C ₃ A Orthorm.	Total C ₃ A	C ₄ AF	Free lime	Periclase
1	9.80	50.80	60.60	16.30	1.00	17.3	4.20	0.20	4.40	7.30	0.40	0.10
2	20.20	38.80	59.00	11.40	5.60	17.0	3.70	1.30	5.00	12.00	0.50	0.20
3	10.42	44.51	54.93	28.42	0.00	28.42	2.05	0.82	2.87	11.39	0.85	0.00
	Quartz	Acranite	Gypsum	Bassanite		Anhydrite	Ca-langbenite		Aphthitalite		Portlandite	Calcite
1	0.30	0.90	2.20	0.80		1.70	0.00		0.30		0.10	3.70
2	0.00	0.60	0.10	3.20		0.00	0.00		0.30		1.10	0.90
3	0.00	0.45	0.00	0.00		0.18	0.87		0.04		0.00	0.00

2.2. Measurements

The determination of the chemical composition was done according to the ASTM C114. The analyses were conducted by ARL 9800-XRF machine, calibrated by NIST standards. The samples were prepared and fused automatically by Claiss machine.

The mineralogical analyses were conducted by Bruker D4 XRD diffractometer. All diffraction patterns were evaluated with the Diffrac program (Bruker-AXS) and quantified with the Topas Rietveld-package (Bruker-AXS).

The Blaine was performed by the semi-automatic Blaine ToniPERM 6568 calibrated with NIST standard. The particles size distribution was conducted by Malvern–Sirocco 2000.

The determination of strength, setting time and soundness were realized as per the European standard EN 196-1 and 3.

The mortars were prepared according to EN 196-1 and poured in specimen molds (25 by 25 by 285 mm prisms having a 250 mm gage length) in accordance with the requirements of the ASTM C490. The apparatus for measurement of the length changes conforms to the requirements of the ASTM C490 with an accuracy of 0.001 mm. The German Normensand standard DIN EN196-1 was used as siliceous aggregate. This type of sand was chosen because the expansion is influenced by the nature and the size grading of the aggregate (Heinz et al., 1989; Yang et al., 1999). Laboratory studies showed that the expansion is very slow in mortars made with limestone sand but faster with quartz aggregates (Heinz et al., 1989; Yang et al., 1999; Lawrence, 1999). In addition to that the sand size distribution is wider in the European norm than in the ASTM C 778. This feature may lead to better packing of particles, and hence potentially improved connectivity of the capillary pores, consecutively leading to better availability of the water necessary for formation of ettringite (Bhattacharja and Miller, 2005).

After casting, half of the mortar specimens were cured in a moist cabinet at 20 °C and over 95% humidity. The second half of the mortar specimens were cured according to the heat treatment presented in Fig. 1. This heat treatment is representative of the treatments used in some precast industries. The temperature was increase from 60 °C to 80 °C in order to increase the risk of delayed ettringie formation.

The mortar specimens were cured in their metallic molds, tightly covered by a metallic plate to prevent the evaporation of water during the heat treatment.

After 24 h of curing and in order to accelerate the expansion, the specimens (cured with and without heat treatment) were removed from the molds and stored in water at 20 °C. (Famy, 1999) confirmed that the expansion is faster and extensive in water; slower less extensive in moist air and still slower in a KOH solution. After each measurement, the curing water was replaced by fresh water. The renewal of the curing water affects positively the delayed ettringite formation (Leklou et al., 2013).

After one year, the microscopic examinations were carried out on polished section of mortar using a scanning Electron microscope (SEM) type JEOL 6380 LV equipped with backscattered electron (BSE) detector and an energy dispersive X-Ray analyzer. In addition to that the scans by XRD were conducted on the same samples.

2.3. Nomenclature of the specimens

1. The heat cured specimens are labeled: C 80.
2. The specimens cured at 20 °C are labeled: C 20.

Table 3

The physical and mechanical results of the samples.

	Compressive strength Mpa				Soundness by Lechatelier (mm)	Setting time (minutes)	Blaine (Cm ² /g)	Particles size distribution					
	1 day	2 days	7 days	28 days				≥ 9 μ (%)	≥ 75 μ (%)	≥ 45 μ (%)	≥ 35 μ (%)	≥ 3 μ (%)	3–35 μ (%)
1	25.40	38.90	57.0	71.25	0.50	120	4100	0.03	0.16	8.43	16.71	78.55	61.85
2	15.84	29.70	50.20	58.47	0.50	105	3590	0.27	1.16	8.30	14.60	77.07	62.47
3	10.60	26.10	48.50	66.40	0.50	200	3620	0.00	0.19	6.66	13.81	82.30	68.49

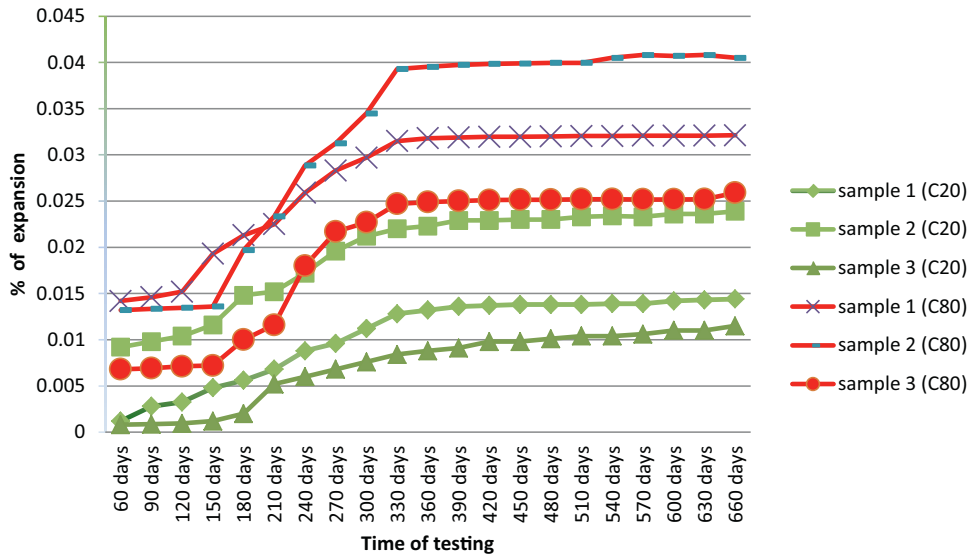


Fig. 2. Length variation of the specimens.

3. Results and discussions

3.1. General evaluation of the samples

The three samples are comparable to the Type III Portland cement according to ASTM C150. This type of cement is, according to some published researches papers, the most susceptible to DEF (Donald, 1998; Fu and Beaudoin, 1996; Grattan-Bellew, 2000).

The results of (Zhang et al., 2002) shows that the expansion occurs for mortars made from cements with ratio SO_3/Al_2O_3 falling between 0.85 and 1.5 while (Fu et al., 1997) and (Famy, 1999) found that this ratio should exceed 1.1. The three cement samples (Table 1) used in the experiments contained a SO_3/Al_2O_3 ratio lower than 0.85 (0.76 for sample 1 and around 0.50 for the 2 other samples) that eliminate the impact of the ratio of SO_3/Al_2O_3 on the results.

The high MgO content in the cement could generate expansion due to the hydration of periclase to brucite, more than to the formation of ettringite. Also it involves an interaction between Brucite and ettringite (Bhattacharja and Miller, 2005). The percentage of MgO (Table 1) in the three samples is very low (less than 0.9%) that eliminate any risk related to the Brucite formation.

The presence of alkali in the cement could increase the DEF. In one hand it has been claimed that alkali silica reaction (ASR) accelerated by high-temperature curing is the primary cause of concrete damage and subsequent ettringite formation, filling cracks and other cavities, promotes only minor expansion. This view originally developed from the frequent coexistence of DEF and ASR in concretes (Shimada et al., 2005). In other hand the presence of alkali increases the pH of the pore solution, which favors the presence of monosulfate rather than ettringite. The leaching of alkali hydroxide from the pore

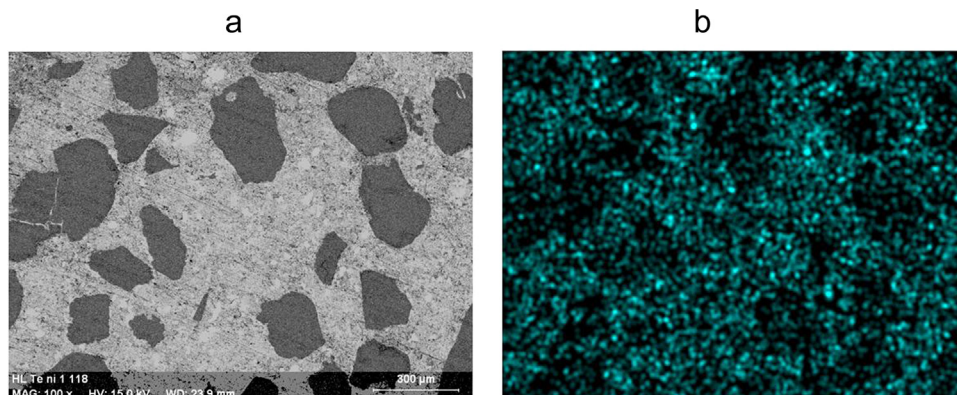


Fig. 3. (a) BSE of the mortar after one year of immersion in water (Sample 1- C20) (b) Elemental mapping of sulfur by EDS of Fig. 3a (Sample 1- C20).

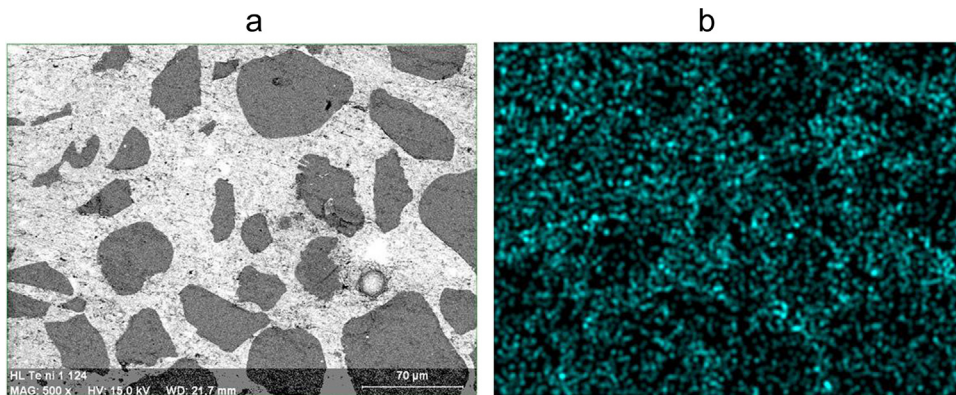


Fig. 5. (a) BSE of the mortar after one year of immersion in water (Sample 2- C20) (b) Elemental mapping of sulfur by EDS of Fig. 5a (Sample 2- C20).

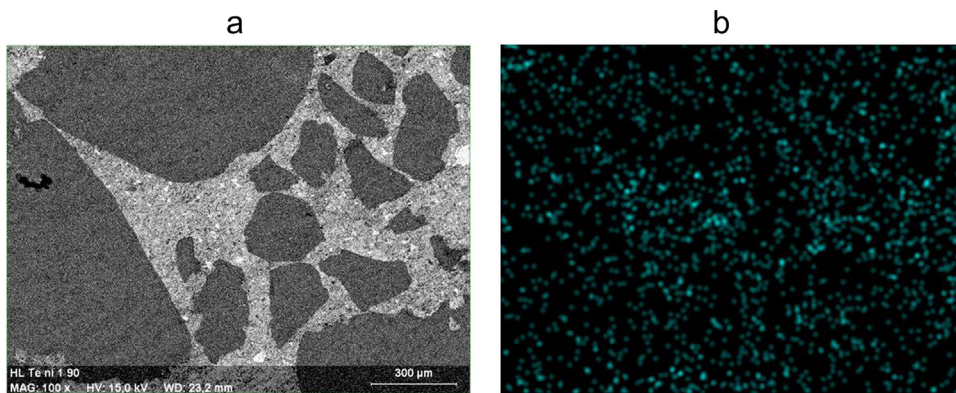


Fig. 7. (a) BSE of the mortar after one year of immersion in water (Sample 3- C20) (b) Elemental mapping of sulfur by EDS of Fig. 7a (Sample 3- C20).

solutions increases the risk of DEF (Escadeillas et al., 2007). In the three cement samples, the amount of Na_2O is less than 0.1%, that of K_2O is less than 0.4% and the equivalent Na_2O is less than 0.35. The amount of alkalis, in the 3 samples, is very low that eliminates the risk related to the alkali silica reaction and change of pH in the pore solution.

The calculated C_3A , in the three samples, is between 6.35 and 7.63 (Table 1) while that measured by XRD was between 2.87 and 5 (Table 2). The very low percentage of measured C_3A (2.87%), compared to the calculated one in sample 3 (6.35%), is related to the amount of sulfur in the clinker. Increasing the amount of SO_3 in the low alkali clinker decreases the percentages of C_3A due to the high incorporation of alumina in the silicate phases (Horkoss et al., 2011).

The calculated C_3S (Table 1), according to ASTM C150 formulas, is between 65.43 and 71.20. The highest one is sample 1. The amount of loss on ignition (Table 1) of this sample is higher than the other two samples. The XRD result (Table 2) shows the presence of about 3% of calcite. This finding is the result of less than 5% limestone added to the clinker during the milling process. The recalculation of the C_3S , after using only the reactive calcium oxide as it is required by the European standard EN 197, was around 64% for the three samples. The measured Alite (Table 2) is around 60% for sample 1 and 2 while it is 10% less for sample 3. The reason is attributed to the negative influence of sulfur, in the clinker, on the development of Alite (Horkoss et al., 2011).

The calculated C_2S (Table 1), according to ASTM C150 formulas, is between 4.14 and 9.9. The recalculated result according to EN 197-1 was around 10% for the three samples. The measured C_2S (Table 2) is around 17% in samples 1 and 2 while it reached 28.42 in sample 3. The incorporation of S^{6+} can increase Belite at the expense of Alite by as much as 10 to 15% (Herfort et al., 2010).

The presence of C_2S alpha in sample 2 (Table 2) indicated an increased temperature regime during the clinkering process.

The XRD result (Table 2) assured the previous information. The form of sulfate in sample 1 is mainly gypsum. The Acranite and Aphthitalite are coming from the alkali sulfate of the clinker. The form of sulfate in the sample 2 is mainly Bassanite while that of sample 3 is a mix of alkali sulfate and sulfur incorporated in the silicate phases (0.75%).

The XRF result showed that the percentage of SO_3 (Table 1) in sample 1 is 1% (3.37%) higher than the 2 other samples (around 2.35%) but still conforms to the European standard EN 197 (Max% of SO_3 is 3.5).

The setting time (Table 3) ranged from 100 min (Sample 2) to 200 min (Sample 3) depending on the reactivity of the C_3A and C_3S and on the solubility of the sulfate.

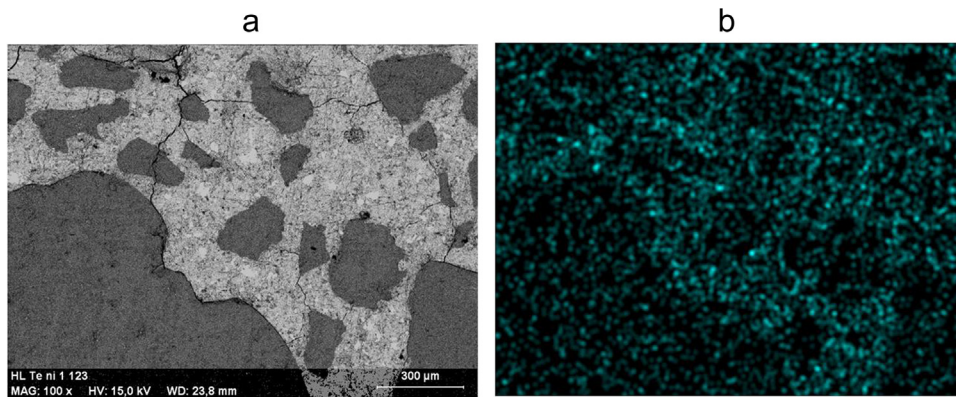


Fig. 4. (a) BSE of the mortar after one year of immersion in water (Sample 1- C80) (b) Elemental mapping of sulfur by EDS of Fig. 4a (Sample 1- C80).

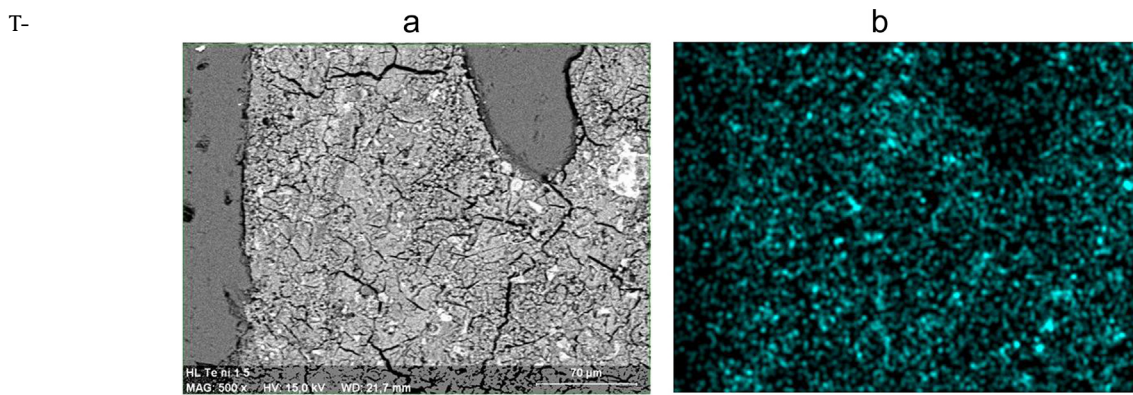


Fig. 6. (a) BSE of the mortar after one year of immersion in water (Sample 2- C80) (b) Elemental mapping of sulfur by EDS of Fig. 6a (Sample 2- C80).

he Blaine results (Table 3) were $4100 \text{ cm}^2/\text{g}$ for sample-1 and around $3600 \text{ cm}^2/\text{g}$ for the two other samples. The particles size distribution (Table 3) did not show remarkable difference between the three samples.

The compressive strength was very high and the soundness was very low for the three samples (Table 3).

3.2. The result of the expansion of the specimens

In general (Fig. 2) the results of the specimen's expansion, after 660 days of storage, were relatively low (less than 0.04%) (LCPC, 2007). The specimens that were cured at high temperature (C80) (Fig. 2) showed higher expansion than that cured at low temperature (C20) (Fig. 2).

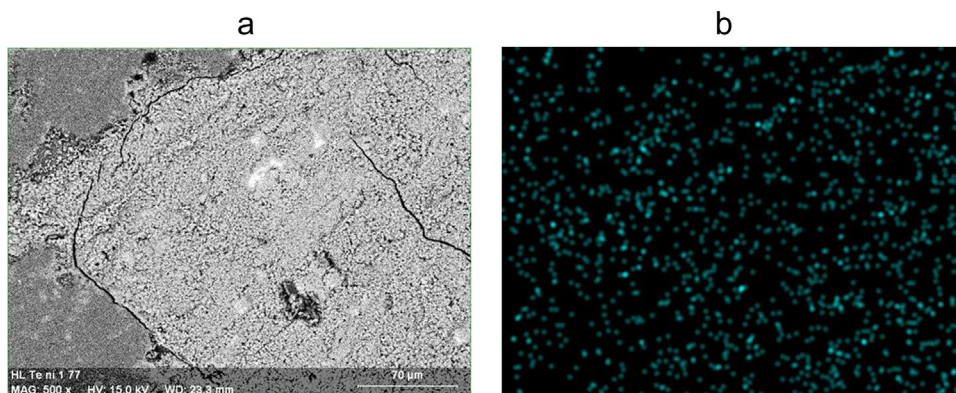


Fig. 8. (a) BSE of the mortar after one year of immersion in water (Sample 3- C80) (b) Elemental mapping of sulfur by EDS of Fig. 8a (Sample 3- C80).

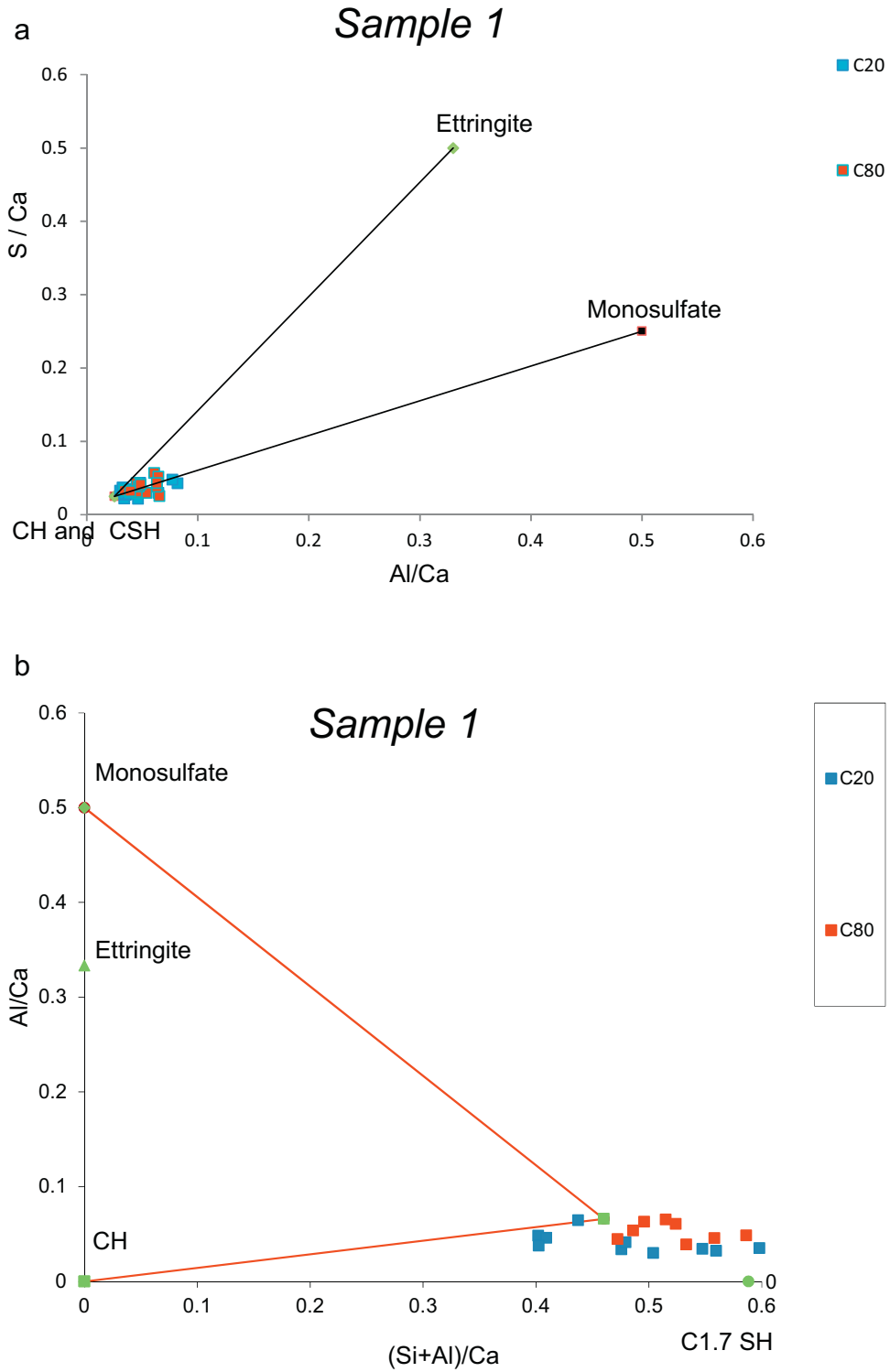


Fig. 9. (a) S/Ca atom ratio vs. Al/Ca atom ratios for sample-1 (b) Al/Ca atom ratio vs. (Si +Al)/Ca. atom ratios for sample-1.

The evaluation, of the expansion results of the specimens that were cured without heat treatment (Fig. 2), showed that the sample 2 had the highest expansion while the sample 3, that contains only clinker with high sulfate, had the lowest one.

As expected the expansion of the cement containing gypsum was low but in contradiction to many researches the cement containing slow soluble gypsum showed the lowest expansion at 20 and 80 °C cured temperature. Also the cement containing the highest soluble gypsum showed the highest expansion results.

The evaluation, of the expansion results of the specimens that were cured with heat treatment (Fig. 2), shows that the sample 3 had the lowest expansion while the sample 1 had the highest expansion till the 210 days of storage. After that sample 2 again had the highest expansion.

In one hand the specimens cured at 20 °C showed:

- The cement containing the Bassanite had the highest expansion

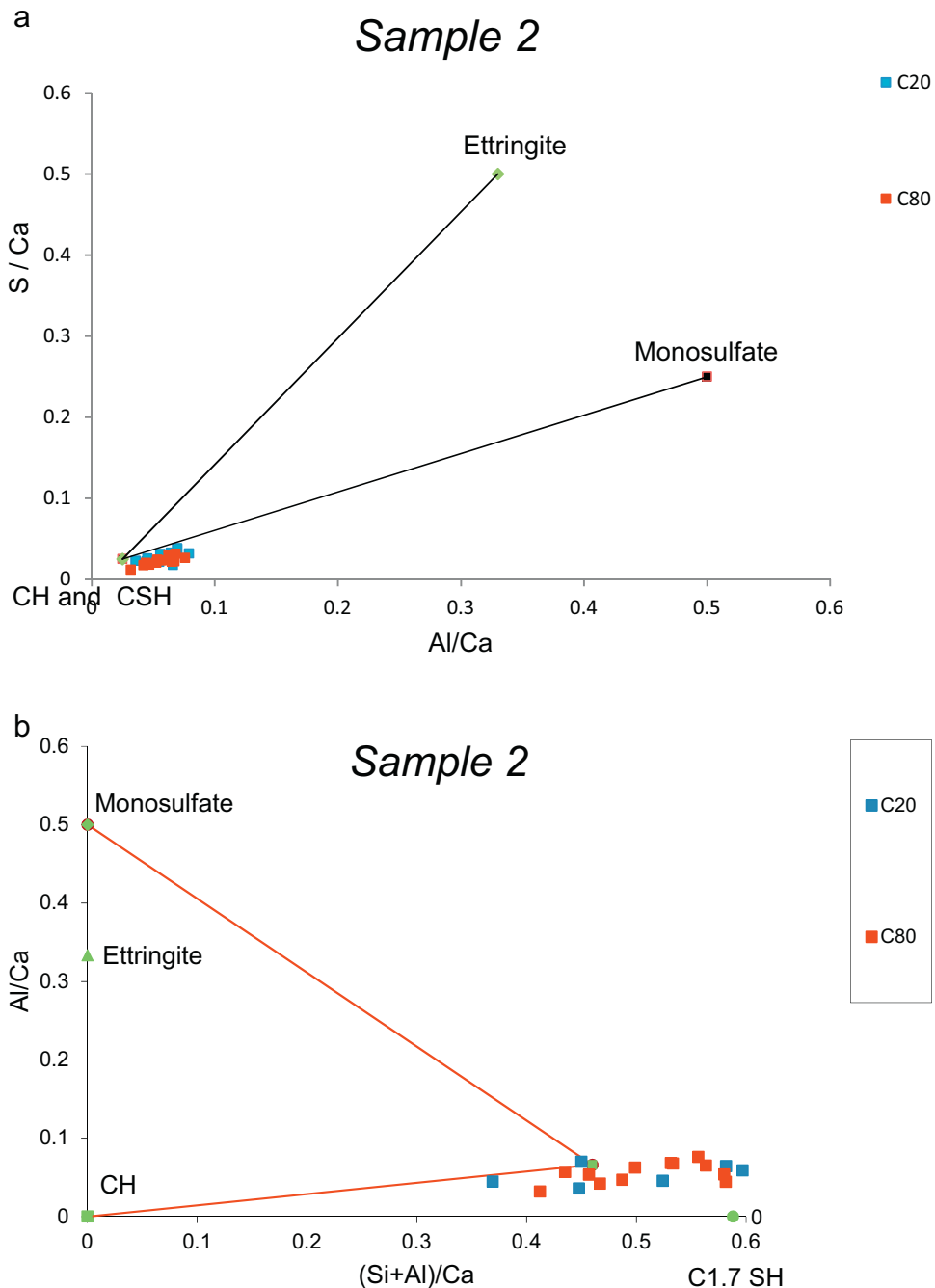


Fig. 10. (a) S/Ca atom ratio vs. Al/Ca atom ratios for sample-2 (b) Al/Ca atom ratio vs. (Si + Al)/Ca. atom ratios for sample-2.

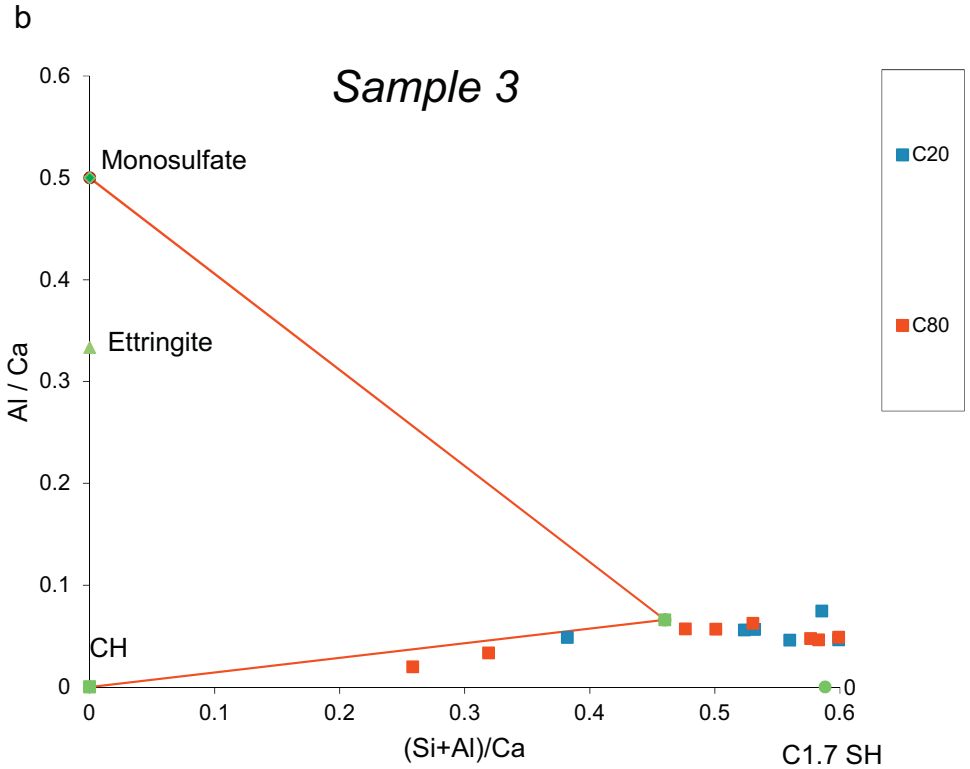
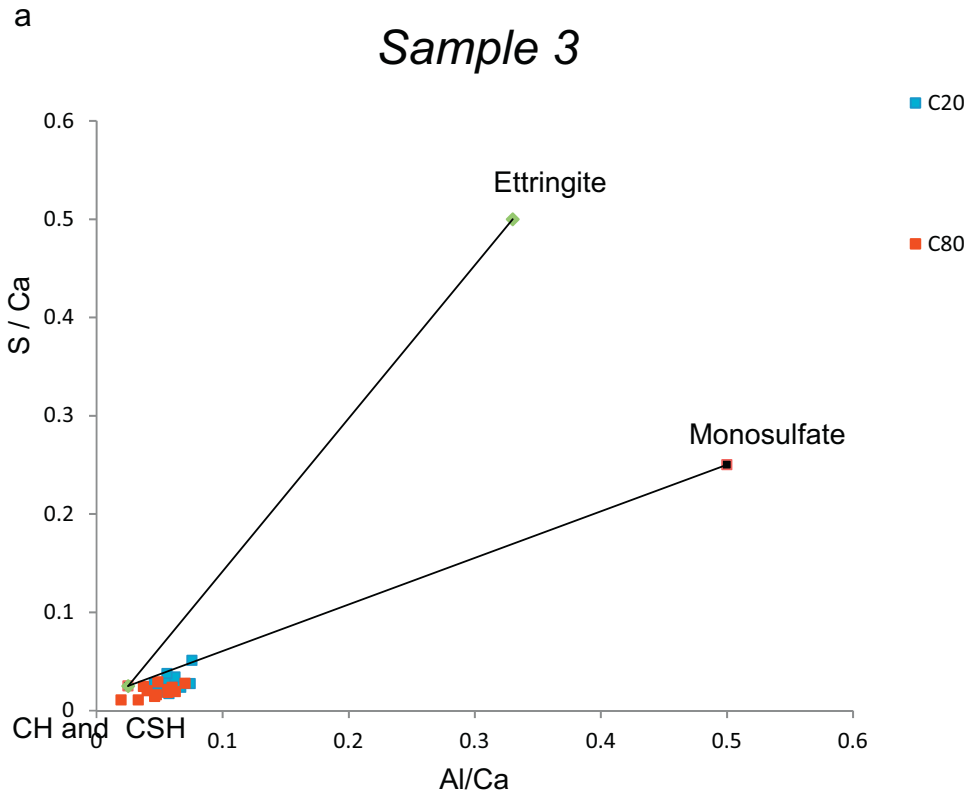


Fig. 11. (a) S/Ca atom ratio vs. Al/Ca atom ratios for sample-3 (b) Al/Ca atom ratio vs. (Si +Al)/Ca. atom ratios for sample-3.

- The cement produced with only clinker had the lowest expansion

In other hand the specimens cured at 80 °C showed:

- The expansion of the cement containing gypsum and clinker sulfate had higher expansion than the same cement cured at 20 °C but the tendency of the curves of the expansion were comparable in both case. The reason could be attributed to the impact of the curing temperature on the microstructure of the cement paste
- The tendencies of the expansion curves of the cement containing bassanite were different than the others two types of cement. The reason could be attributed to the impact of the curing temperature on the solubility of Bassanite.

3.3. The detection of the delayed ettringite formation

In order to detect the presence of the DEF, three techniques, XRD, SEM and graphical treatment of microanalysis by EDX, were used.

3.3.1. XRD analysis

A part of two centimetres in length of each hardened cement paste specimens was ground to pass 80 μm . The samples were scanned by XRD. The qualitative scan showed the absence of ettringite in all samples. The reason could be attributed to fact that the amount of DEF could be lower than the detection limit of the XRD.

3.3.2. Scanning Electron microscopy

After XRD, the samples were tested by the scanning electron microscopy. The results of the experiment are listed below.

The specimens (Figs. 3a, 5a and 7a) that were cured at 20 °C and stored in water did not show any cracks. No delayed ettringite development can be observed either in the cement paste or at the interfaces of the cement paste/aggregate. The sulfur is uniformly distributed in the paste (Figs. 3b, 5b and 7b).

The specimens (Figs. 4a, 6a and 8a) that were cured at 80 °C and stored in water showed:

1. Some cracks. These cracks could be the consequence of the tensile stress within the cement paste. At high temperature the water in the pore starts to exert pressure. The combined effect of the pore pressure and thermal stress causes a tensile stress within the body of the cement paste. This phenomenon generates some micro-cracks in the cement paste.
2. No delayed ettringite development can be observed either in the cement paste or at the interfaces of the cement paste/aggregate.

The sulfur is uniformly distributed in the paste (Figs. 4b, 6b and 8b).

3.3.3. The graphical treatment of microanalysis by energy-dispersive X-ray spectroscopy

In order to detect the form of sulfur (monosulfate or ettringite), (Scrivener, 2004) proposed to do a correlation of S/Ca atom ratio versus Al/Ca atom ratio. The graphical treatment of microanalysis by energy-dispersive X-ray spectroscopy (Figs. 9a,b, 10a,b, 11a,b) showed the presence of mainly CSH and some monosulfate. The risk of ettringite formation was not detected in all specimens regardless of the curing condition.

The only difference, between the sample 1 and the two other samples, is the ratio S/Ca. In the sample 1 this ratio (Fig. 9a) is higher than that of the two other samples (Figs. 10a and 11a). This observable fact could be attributed to the level of SO_3 in the cement samples. The amount of SO_3 in sample 1 is 1% higher than the 2 other samples (Table 1).

The laboratory studies may not predict the behavior of the field concrete but their results could help to better understand the influence of some parameters on the deterioration of concrete. The analysis explanation of the difference in performance of the three cement samples showed that the percentage of SO_3 in the cement plays an important role in the concrete expansion. Sample 3 that have the lower amount of SO_3 had the lowest expansion regardless of the curing condition. It is right that sample 1 that contains the highest amount of SO_3 had lower expansion than sample 2 but the graphical treatment of microanalysis by energy-dispersive X-ray spectroscopy showed that sample 1 had the highest risk of delayed ettringite formation. Based on that the limitation of SO_3 (Max 3%) in the ASTM C150 is less risky than that of European standard EN 197 (Max 3.5%) regarding concrete expansion and delayed ettringite formation.

The usage of classical natural gypsum is less risky than the usage of pre-heated gypsum such as Bassanite. The reason could be attributed to the fact that Bassanite is much more soluble than natural gypsum. In addition to that, the results of the tests show that the usage of low alkali high sulfur clinker had the lowest risk for concrete expansion and delayed ettringite formation.

Due to the absence of the expansion phases such as DEF, the difference on the mortar expansion schematic forms between the three cement types is most probably related to the solubility of the gypsum and to the behavior of each cement type in the complex system that involved chemical, thermodynamic, mineralogical and physical mechanisms and parameters such as the cement hydration, the reactivity, distribution and size of the cement phases, the strength development, the porosity

and permeability of the cement paste, the internal and external temperature, the internal and external humidity, the adsorbing behaviors of sulfate in the CSH gel, the leaching of the alkalis and $\text{Ca}(\text{OH})_2$ to the storage.

After one year of mortar storage it seems that this complicated system reached an equilibrium that reflects a minor change in the expansion.

4. Conclusion

The main conclusions of this study are:

1. The solubility of sulfate added to the cement as a regulator of setting time could have some impact on the specimen's expansion. It did not show any role on the delayed ettringite formation. The usage of high percentages of Bassanite as setting time regulator could increase the risk of expansion.
2. The graphical treatment of microanalysis by energy-dispersive X-ray spectroscopy showed that the amount of SO_3 in the cement is an important factor for the transformation of monosulfate to ettringite. Increasing the percentages of SO_3 in the cement increases the risk of delayed ettringite formation.
3. The heat curing generates micro-cracks in the cement paste. It could lead with the interference of many other external and internal factors to the formation of delayed ettringite.
4. In contradiction to many hypotheses, the cement produced with clinker containing high sulfate showed the lowest expansion and the lowest risk of ettringite formation.

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