Influence of the clinker SO_3 on the cement characteristics

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ABSTRACT

This paper aims to clarify the influence of the clinker SO_3 on the cement characteristics. The impact on the strength development rate and the level of sulfate resistance were studied .The results show that increasing the amount of clinker SO_3 at low alkali level reduces the percentages of the tricalcium aluminate (C_3A) and alite as well as the alite/belite ratio, leading to a modification in the cement quality.

For these reasons cements produced from a clinker containing high sulfate and low alkali, have slower strength development and higher sulfate resisting level than that produced with low sulfate clinker.

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1. Introduction

Portland cement clinker is a hydraulic material composed mainly of tricalcium silicate (C_3S), dicalcium silicate (C_2S), tricalcium aluminate (C_3A) and tetracalcium aluminoferrite (C_4AF). The abundance, size, reactivity and distribution of these phases are affected by complex interactions between the heating and cooling regime as well as the raw feed characteristics such as chemical and mineralogical composition, particles size distribution and homogenization.

The clinker nodules are ground with gypsum, which serves to control setting, to a fine powder named Portland cement.

The amount of cement SO_3 comprises the clinker SO_3 and that added during clinker grinding. In ordinary Portland cement clinker the SO_3 is usually below 1%. During the past years, the thermal valorization of industrial wastes, tires and solvents as well as the usage of high-sulfur fuel in the cement kilns have gained ground. This change has increased the sulfate levels in Portland cement clinker, which affects the chemical, mineralogical, physical and mechanical characteristics of the clinker and cement.

The objective of this paper is to evaluate the rate of strength development and the level of sulfate resistance for cements produced with high SO_3 clinker at low alkalis level.

2. Experiment and methods

Thirteen clinker samples were sampled during the production process at Cimenterie Nationale SAL. Based on the ASTM C150

requirements, the types of cement clinker samples were: Twelve moderates sulfate resistance (type II, the calculated $C_3A<8\%$) and one (number 6) high sulfate resistance (type V, the calculated $C_3A<5\%$). The clinker sulfate variation, in the type II clinker, was done by changing the fuel type from fuel oil (2% S) to petroleum coke (4.5 to 6% S).

In order to minimize the interaction of other factors with the influence of clinker sulfur on the clinker phases, the following parameters were monitored (Table 1):

1. The aluminum module in the Type II clinker was fixed at 1.2 ± 0.05 and that of type V at 1.1.
2. The SM was fixed at 2.40 ± 0.04.
3. The variation, in the percentages of P_2O_5, TiO_2, MgO, was controlled.
4. The percentages of alkalis were assured in the lowest level.

Due to the very low burnability of the kiln feed, the clinker was produced without any addition of fluxes or mineralizes. The sampling was done under stable kiln operation. The percentage of kiln inlet oxygen was maintained between 2 and 3%. The free lime of the clinker was ≤1%.

The clinker samples were crushed and ground in the laboratory mill. The evaluation of cement characteristics was done using the following standards:

1. ASTM C114 for the determination of the chemical composition. The chemical analysis was done using ARL 9800 – XRF machine, calibrated by NIST standard samples. The Claiss machine was used for samples preparation.
2. ASTM C1365 for the determination of the proportion of phases in Portland-cement clinker using X-Ray Powder. The ARL X'TRA Diffractometer with Copper tube, using Rietveld method was used.
3. ASTM C1356 for the evaluation of the clinker phases in clinker by microscope. The optic microscope (ZEISS – Axioskop 40) and the

Table 1
Chemical composition of the clinker samples.

	1	2	3	4	5	6	7	8	9	10	11	12	13
% L.O.I.	0.45	0.42	0.42	0.22	0.20	0.11	0.33	0.27	0.12	0.22	0.23	0.12	0.12
% SiO_2	20.30	20.92	20.39	20.56	20.42	20.76	20.49	20.10	20.88	20.51	20.22	20.95	20.91
% CaO	65.80	66.95	66.06	66.21	66.94	66.9	67.19	66.71	67.21	66.81	66.68	67.14	67.36
% Al_2O_3	4.65	4.62	4.73	4.84	4.51	4.45	4.45	4.55	4.53	4.74	4.51	4.63	4.75
% Fe_2O_3	3.90	3.88	3.81	3.87	3.85	4.10	3.79	3.7	3.89	3.95	3.82	3.86	3.91
% SO_3	2.45	0.69	1.73	1.52	2.23	1.14	1.28	2.76	1.08	1.63	1.65	1.27	1.28
% MgO	0.55	0.49	0.45	0.49	0.5	0.52	0.50	0.54	0.52	0.58	0.48	0.49	0.50
% P_2O_5	0.60	0.64	0.63	0.64	0.67	0.66	0.65	0.65	0.67	0.64	0.65	0.65	0.62
% TiO_2	0.35	0.31	0.33	0.33	0.32	0.32	0.32	0.31	0.33	0.34	0.32	0.31	0.31
% Na_2O	0.11	0.11	0.09	0.09	0.10	0.10	0.10	0.10	0.11	0.10	0.09	0.10	0.09
% K_2O	0.36	0.37	0.35	0.27	0.39	0.28	0.33	0.33	0.26	0.31	0.34	0.26	0.21
Free lime	0.82	0.67	0.84	0.78	0.77	0.70	1.00	1.00	0.60	0.82	0.92	0.83	0.88
AM	1.19	1.19	1.24	1.25	1.17	1.09	1.17	1.23	1.16	1.20	1.18	1.20	1.21
SM	2.37	2.46	2.39	2.36	2.44	2.43	2.49	2.44	2.48	2.36	2.43	2.47	2.41
SO_3/Al_2O_3	0.53	0.15	0.37	0.31	0.49	0.26	0.29	0.61	0.24	0.34	0.37	0.27	0.27

Struers – TegraPol-15 and TegraForce – were used. The etching of the samples was done by Nital (99 ml Iso-propyl-alcohol + 1 ml Concentrated HNO_3). Our objective was to detect the morphology, distribution and reactivity of the clinker phases.

4. ASTM C109 for the determination of the strength development rate. This test covers the determination of the compressive strength hydraulic cement mortars, using 50 mm cube specimens.
5. ASTM C1038 for the determination of the sulfate expansion in water. This test covers the determination of the length change of mortar bars stored in water. It was implemented to detect the volume stabilities of mortars bars (25 by 25 by 255 mm) after storing it, for one year, in water under controlled temperature.
6. ASTM C452 for the determination of the potential expansion of Portland cement mortars exposed to sulfate. This test covers the determination of the expansion of mortar bars made from a mixture of Portland cement and gypsum in such proportions that the mixture has a SO_3 content of 7%.
7. ASTM C1012 for the determination of the sulfate resistance level. This test covers the determination of length change of mortar bars immersed in 50 g/l Na_2SO_4 solution. For the first 24 h, the mortar bars and cubes must be stored in a water tank at 35 ± 3 °C.

3. Results and discussions

The chemical composition (Table 1) shows variation of the clinker SO_3 from 0.69 to 2.75%.

Concerning the strength according to ASTM C109 and the expansion and strength tests according to ASTM C1012, the cement samples were prepared based on 2.5% SO_3 content.

The clinker samples containing equal or over than 2.5% SO_3, were used without any gypsum. For that lower than 2.5% a quantity of grounded natural gypsum were added. The quantities of clinker and gypsum were listed in Table 2. The Gypsum fineness was: 0% over 90 μm, 2% over 75 μm and 7% over 45 μm.

The ground clinker samples that had over one hour's setting time (clinker $SO_3 > 1.5$%) were used without adding any gypsum quantity in the execution of the standard ASTM C1038.

3.1. General observations

During the investigation many observations were made.

1. The hardness of the clinker samples correlated with the clinker SO_3. This related to the influence of SO_3 on the ratio of C_3S/C_2S in the clinker (Fig. 1) and on alite crystal size (Table 4). In order to obtain a similar fineness (Blaine 3600 ± 50 cm^2/g), the time, for grinding the clinker with relatively high SO_3, was extended. The residue of the powder samples over 45 and 32 μm was also measured (Table 3). Except for clinker 1 which shows the lowest residue, the fineness of the other samples was comparable.
2. The measured percentage of C_3A (cubic and orthorhombic) is lower than that calculated (Fig. 2). For similar calculated C_3A amounts, the clinker having the lowest amount of SO_3 contains the highest percentages of C_3A and vice versa. This result is in contradiction with some previous investigations. Hamou and Sarker [8] detected that increasing clinker SO3 increases the amount of measured C_3A in the clinker while others reported that the composition of the matrix (aluminates and ferrites) is not altered by the level of SO3 in the clinker [7,13,22]. The substitution of AlO_4^{5-} and SO_4^{2-} for SiO_4^{4-} is easier in belite than alite [1]. The sulfate concentration in belite is between four to five times that in the alite [23]. Herfort and others [10] suggested that
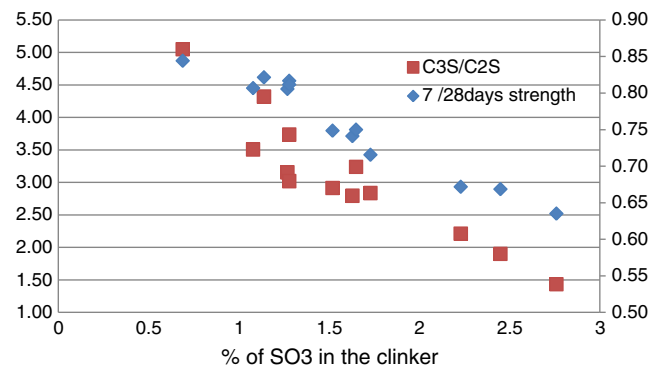
Fig. 1. Correlation between the C_3S/C_2S ratio, 7/28 days strength ratio and the percentage of clinker SO_3.

Table 2
The quantity of clinker and gypsum mixed to produce the cement samples.

	1	2	3	4	5	6	7	8	9	10	11	12	13
Clinker quantity (g)	500	479	490.9	488.5	496.75	484.2	485.75	500	483.6	436.9	490	485.65	485.75
Gypsum quantity (g)	0	21	9.1	11.5	3.25	15.8	14.25	0	16.4	63.1	10	14.35	14.25

Table 3
Residue over 32 and 45 µm.

Sample	1	2	3	4	5	6	7	8	9	10	11	12	13
Over 32 µm	12	16	18	23	25	22	26	20	21	25	23	20	21
Over 45 µm	2	4	4	5	7	5	6	7	4	7	6	5	5
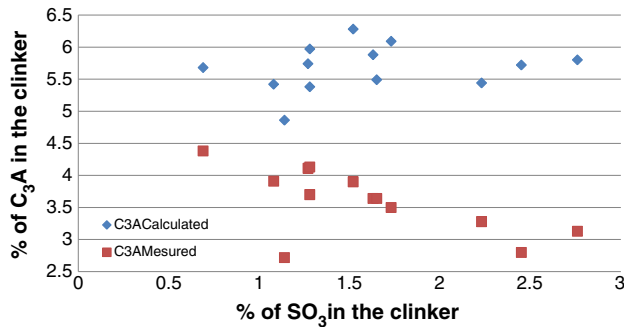
Fig. 2. Influence of the clinker SO_3 on the amount of C_3A.

substitution of S^{6+} for Si^{4+} is facilitated by a concomitant substitution of 2 Al^{3+} on the same site. As the amount of belite increase with the increase of sulfur there is more incorporation of Al^{3+} ions in this phase. This process reduces the amount of Al_2O_3 in the liquid phase leading to some reduction in the amount of C_3A.

3. The percentage of belite is higher than that calculated (Fig. 3). It is correlated to the amount of clinker SO_3. The percentage of alite is lower than that calculated (Fig. 4). The negative influence of the clinker SO_3 on the development of alite is related to the fact that belite is stabilized by the incorporation of sulfur. The reaction of CaO with belite, is inhibited and the formation of C_3S is suppressed [22]. This phenomenon increases the amount of belite and decreases that of alite in the clinker [6]. The same conclusion was reached in other studies [11,20,22]. Recently Herfort and others [12] found that the actual content of alite and belite are governed by the ratio of octahedral to tetrahedral sites rather than the ratios of Ca to Si (as per Bogue). The incorporation of S^{6+} and P^{5+} can increase belite at the expense of alite by as much as 10 to 15% [12]. In our cases both elements (S^{6+} and P^{5+}) had an influence on the increase of belite and the decrease of alite but the influence of phosphorous was not investigated in this study as it was present in the same amount in all clinker (P_2O_5 around 0.63%).

4. The percentage of the tetracalcium aluminoferrite is slightly higher than that calculated (Fig. 5) but isn't affected by the amount of clinker SO_3. This result is in agreement with previous investigations [7,13,22].
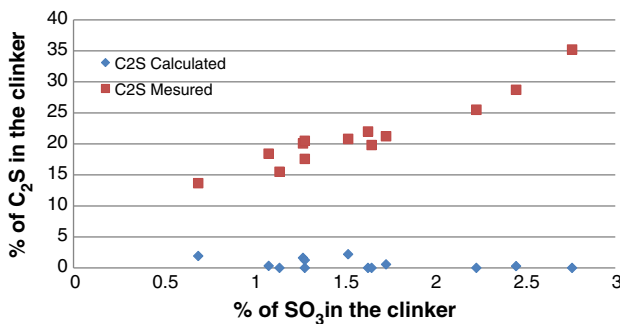

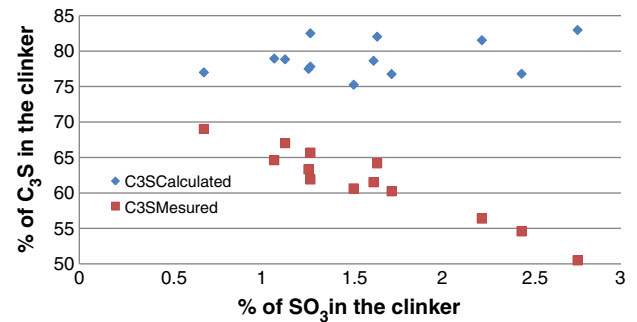Fig. 4. Influence of the clinker SO_3 on the amount of C_3S.

5. In the clinker containing high sulfur, the crystal size of the alite is heterogeneous ranging from small to very big crystals in the same clinker (Fig. 6). Campbell [4] found that alite size is related to bulk clinker SO_3 by the following linear equation: the median long diameter of alite $= 45 \times SO_3 + 20$ but his conclusion was based on classical clinker with total clinker SO_3 ranging from 0.09% to 1.1%. Strunge and others [22] found that increasing the clinker SO_3 content from 0 to 2.6% increases the alite crystal size from 0.05 mm to 0.150 mm.

6. In the low sulfur clinker, the crystal size is relatively homogenous ranging from medium to small size crystal (Table 4).

7. By microscopy, the presence of C_3A crystals was detected only in the sample containing over 3.3% of measured C_3A (Fig. 7). In the other samples this phase was not detected (Fig. 6). The reason for the limitations of their microscopic identification could come from the formation of very fine C_3A crystals in the interstitial material.

8. The percentage of K_2O varied from 0.21 to 0.39% but no alkali sulfate phases were detected by XRD. The very low percentages of K_2O and existence of several alkali sulfate compounds could mean that some sulfate phases were present at levels below the XRD detection capacity.

9. In the clinker samples containing less than 1.5%, SO_3 the setting time ranged from 10 to 35 min.

10. In the clinker containing more than 1.5% SO_3, anhydrite was detected and the setting time was over 1 h. Based on this observation we can conclude that the anhydrite in the clinker is not only soluble but it participates in regulating the setting time.

3.2. The influence of clinker SO_3 on the rate of strength development

Strunge and others [22] noticed that the strength of low alkali cement decreases by up to 10% with increasing SO_3 content of the clinker. They concluded that this decrease in strength is less than
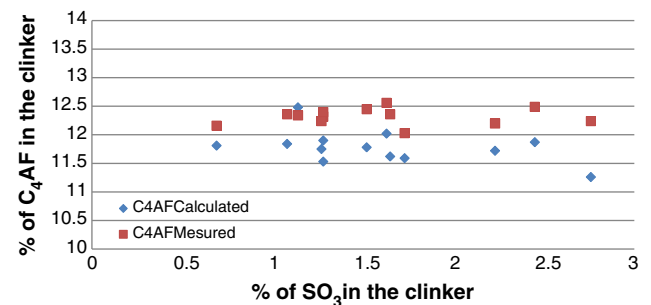

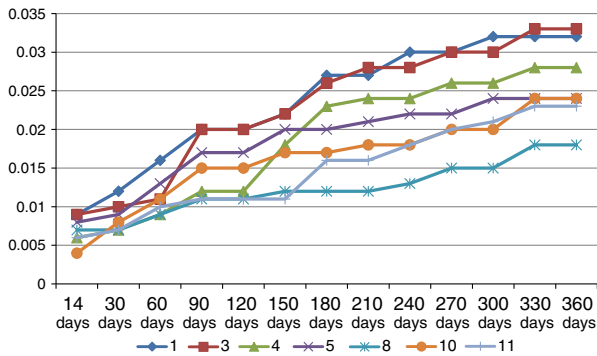Fig. 3. Influence of the clinker SO_3 on the amount of C_2S.

Fig. 5. Influence of the clinker SO_3 on the amount of C_4AF.

Fig. 6. Clinker number 8 (high clinker SO₃).

Fig. 7. Clinker number 12 (low clinker SO₃).

could be expected from the decrease in alite and its crystal development.

Older and Zhang [20] found that cements made with high SO₃ clinker exhibit an accelerated strength development.

Our results (Fig. 1) show a strong influence of the clinker SO₃ on the cement strength development. The ratio of 7/28 day strength decreased from 0.84 to 0.63 when the clinker SO₃ increased from 0.69 to 2.76%. This is related to the decrease of the C_3S/C_2S ratio. The correlation between the ratio of 7/28 day strength, the C_3S/C_2S ratio and the percentage of SO₃ is clearly shown in Fig. 1.

3.3. The influence of clinker SO₃ on the sulfate resistance level

In order to clarify the influence of the clinker SO₃ on the cement sulfate resistance level, this study was divided to two main parts. The first part sought to detect any dimensional instability due to the slow reacting of clinker sulfate and the second to study the sulfate resistance of the cement by adding an excessive amount of gypsum to the mortar or storing the cement mortar in a sulfate solution.

3.3.1. Dimensional stability due to slowly release of clinker sulfate

It is well known that excessive addition of sulfate may lead to dimensional instability. The test ASTM C1038 is designed to detect such situation. In addition it is known that exposure to high temperatures (>70 °C) during curing may result in subsequent expansion, known as delayed ettringite formation (DEF). Kelham [14] reported that DEF is mainly influenced by the curing temperature but it is increased by increasing the Na_2O_{eq}, C_3A, C_3S and MgO contents, as well as the specific surface area of cement. Mielenz et al. [17] also claimed that DEF could arise from the presence of slow soluble clinker sulfate, based on that, Hime [9] proposed to limit the

amount of clinker SO₃ below 1%. ; However this was widely discredited by several investigations [14,18,19,23,24], which showed that clinker sulfate reacts in a matter of days and did not cause long term expansion in samples cured at normal temperatures.

Collepardi [3] listed causes of internal sulfate sources as:

1. The cement with high sulfate content,
2. The gypsum-contaminated aggregate,
3. The thermal decomposition of "normal" ettringite in overheated concrete and the sulfate ions slowly released from that adsorbed on the C–S–H phase in high temperature steam-cured concrete.

In order to avoid any interaction or influence of the external gypsum, the ground clinker samples that had over one hour's setting time (clinker SO₃ >1.5%) were used without adding gypsum.

The result (Fig. 8) shows the expansion after one year of storage in water. The expansion of the specimens produced with the very high clinker SO₃ (sample number 8) was the lowest and did not exceed 0.018% while the maximum expansion of the other samples did not exceed 0.033%.

Regarding the samples (1 and 8) with relatively high clinker SO₃, the specimens which had been stored in water for one year, were ground to pass 80 µm and studied by XRD. The result (Fig. 9) did not show any presence of Delayed Ettringite formation (DEF).

3.3.2. External sulfate attack

Sulfate attack is potentially one of the most damaging degradation mechanisms. Regarding the cement, the amount of C_3A [5,16,25] is the major factor for the determination of cement sulfate resistance level while the ratio C_3S/C_2S [21] could play a role in this mechanism. The sulfate resistance of the samples in this study was studied by ASTM

Table 4
Evaluation of the samples by microscope.

Phase	Characteristics	1	2	3	4	5	6	7	8	9	10	11	12	13
C₃S	>150 µ	10%	0%	0%	0%	10%	0%	0%	30%	0%	0%	0%	0%	0%
	60<<150 µ	50%	0%	0%	10%	40%	0%	0%	30%	0%	30%	40%	0%	10%
	25<<60 µ	30%	80%	70%	80%	30%	90%	80%	25%	70%	60%	50%	70%	60%
	<25 µ	10%	20%	30%	10%	20%	10%	20%	15%	30%	10%	10%	30%	30%
	Reactivity	Good	Good	Fair	Fair	Good	Good	Good	Good	Good	Fair	Fair	Good	Good
	Fused alite	Yes	Yes	Yes	Yes	Yes	Yes	No	No	Yes	Yes	Yes	Yes	Yes
C₂S	>70 µ	0%	0%	0%	0%	0%	0%	0%	10%	0%	0%	10%	0%	0%
	40<<70 µ	40%	0%	0%	10%	20%	30%	25%	30%	0%	20%	30%	25%	30%
	20<<40 µ	60%	40%	90%	80%	80%	50%	70%	60%	90%	70%	50%	60%	60%
	<20 µ	0%	60%	10%	10%	0%	20%	5%	0%	10%	10%	10%	15%	10%
	Reactivity	Good	Good	Good	Poor	Good	Poor	Poor	Good	Poor	Poor	Good	Good	Good
C₃A	Detected	No	Yes	Yes	Yes	No	No	Yes	No	Yes	Yes	Yes	Yes	Yes
	Size	–	Mod.	Mod.	Small	–	–	Small	–	Small	Small	Small	Big	Big
C₄AF	Detected	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes

Fig. 8. The specimen's expansion after stored in water for one year.

Fig. 10. Correlation between the % of measured C_3A and the expansion after 14 days.

tests C452 (addition of extra gypsum to mortars bars) and C1012 (storage in Na_2SO_4 solution).

3.3.3. Influence of clinker sulfate on the potential sulfate expansion

ASTM C452 involves accelerating the expansion of mortars bars by adding sufficient gypsum to the dry Portland cement so that the mixture has a 7% sulfur trioxide (SO_3). According to requirement of the ASTM C150, type V (sulfate resistant) cement should have, after 14 days, less than 0.04% expansion when the amount of calculated C_3A exceeds 5%.

Clifton et al. [2] claimed that this method is rapid and does differentiate between high-C_3A and low-C_3A Portland cements.

The result (Fig. 10) shows that the specimen expansion after 14 days isn't related to the calculated amount of C_3A but to the measured one. Regardless of the clinker type and the amounts of calculated C_3A, the expansions after 14 days were lower than 0.04% when the percentage of measured C_3A was less than 3.3%.

Sample number 1 (type II clinker with calculated C_3A equal to 5.72%) and sample number 6 (type V clinker with calculated C_3A equal to 4.86%) both had similar expansions after 14 days. The reason is due to the amount of measured C_3A was very similar in both samples.

The results (Table 5) of the expansion, over 14 days and up to one year, were very low in all samples.

3.3.4. Influence of clinker sulfate on the external sulfate attack

External sulfate attack is determined by the chemical interaction of a sulfate-rich soil or water with the cement paste.

Lea [15] pointed out, there are apparently two chemical reactions involved in sulfate attack: The combination of sulfate with calcium ions liberated during to hydration of the cement to form gypsum and the combination of sulfate ion and hydrated calcium aluminate to form calcium sulfoaluminate.
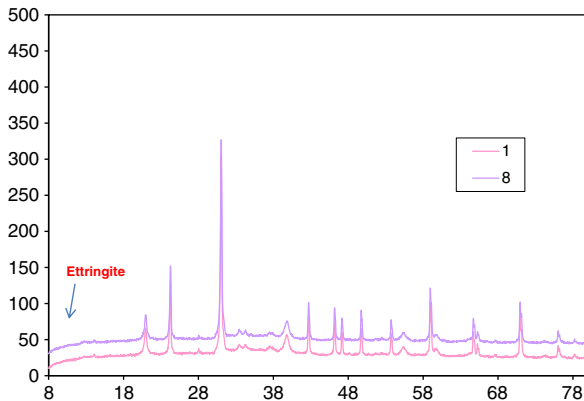

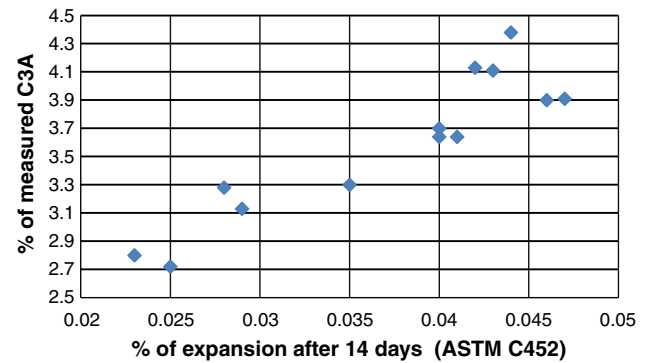Fig. 9. The XRD scan for the samples 1 & 8 after one year storage in water.

Expansion in external sulfate attack is usually related to the volume increase associated with the conversion of monosulfate to ettringite [2].

In order to produce mortars which were as similar as possible for the different cements the fineness of gypsum was controlled (0% over 90 μm, 2% over 75 μm and 7% over 45 μm) and the mixing, preparation and molding of the cubes and bars were done following the ASTM C1012 standard. The cubes for the compressive strength test and that for the sulfate resistance test were mixed following exactly the same mixing procedure. All the test results, even for many cubes at the same age, fulfilled the standard requirements.

The forms of the paste moulds have an influence on the external sulfate resistance. The cubes (Fig. 11) showed slower degradation than the prisms measured for expansion (Fig. 12). The trend of attack is similar for both specimens but the cubes take a relatively longer time to be affected.

The results (Fig. 13) showed that the expansions, after one year of the prisms stored in 5% Na_2SO_4 solution, ranged from 0.75% (sample number 1) to over 4.5% (sample number 13).

Based on these results, the samples were divided into four groups as follow:

1. Group I: expansions ≤1.5%.
2. Group II: expansion between 1.5 and 2.5%.
3. Group III: expansion between 2.5 and 3.5%.
4. Group IV: expansion ≥3.5%.

Group I contains only samples 1 and 6. These samples are type II clinker (calculated $C_3A = 5.72$ and $SO_3 = 2.45\%$) and type V clinker (calculated $C_3A = 4.82\%$ and $SO3 = 1.14\%$). Regardless of the percentages of the C_3A (calculated) and SO_3, both samples show good resistance to external sulfate attack. This performance is attributed to the fact that both samples have the lowest measured C_3A of less than 3%. According to the calculated C_3A content sample 6 (type V) would be expected to have less expansion than sample 1 (type II), but in fact the expansion of sample 1 was lower than that of sample 6 (Fig. 13). The difference could be due to the difference in the ratio of C_3S/C_2S, which is 1.90 in sample 1 and 4.32 in sample 6. The development of sample-1 strength (Table 6) was continued until 120 days while for sample 6 it stopped at 60 days. The difference of the strength development, between both samples, is due to the difference in the measured C_2S. The better grain size distribution of sample 1 could also play a role in improving the sulfate resistance.

The loss of strength (Table 6), after one year, showed the same trend as expansion (Fig. 13). The loss of sample 1 strength was 12.5% (47.43 MPa at 120 days to 41.50 MPa at 360 days) while sample 6 showed a loss of 28% (50.24 MPa at 60 days to 36.20 at 360 days).

Group II contains samples 5and 8. These samples are type II cement with calculated $C_3A = 5.44$ and 5.80% .The percentages of SO_3, in both samples, are high 2.23 and 2.76%. The measured amounts of C_3A, in both samples, are less than 3.3% and the ratios of measured

Table 5
The results of specimens expansion after one year of the sample prepared as per the standard ASTM C452.

	1	2	3	4	5	6	7	8	9	10	11	12	13
% of expansion after 14 days	0.023	0.044	0.035	0.046	0.028	0.025	0.040	0.029	0.047	0.041	0.040	0.043	0.042
% of expansion after 30 days	0.026	0.045	0.035	0.046	0.028	0.037	0.040	0.029	0.054	0.041	0.042	0.045	0.042
% of expansion after 60 days	0.027	0.045	0.036	0.049	0.030	0.044	0.043	0.035	0.055	0.042	0.044	0.047	0.054
% of expansion after 90 days	0.028	0.048	0.038	0.050	0.035	0.051	0.044	0.035	0.058	0.047	0.055	0.059	0.057
% of expansion after 120 days	0.029	0.048	0.040	0.052	0.041	0.060	0.044	0.039	0.064	0.050	0.057	0.059	0.057
% of expansion after 150 days	0.029	0.050	0.045	0.052	0.041	0.066	0.050	0.039	0.064	0.055	0.057	0.061	0.058
% of expansion after 180 days	0.029	0.050	0.062	0.055	0.045	0.067	0.053	0.040	0.064	0.055	0.067	0.061	0.058
% of expansion after 210 days	0.030	0.050	0.076	0.058	0.045	0.093	0.053	0.038	0.064	0.067	0.067	0.064	0.058
% of expansion after 240 days	0.030	0.050	0.088	0.058	0.049	0.095	0.053	0.038	0.065	0.067	0.067	0.064	0.060
% of expansion after 270 days	0.030	0.050	0.088	0.058	0.049	0.095	0.060	0.038	0.065	0.067	0.069	0.068	0.060
% of expansion after 300 days	0.030	0.050	0.097	0.060	0.049	0.100	0.060	0.040	0.068	0.070	0.069	0.068	0.060
% of expansion after 330 days	0.030	0.050	0.097	0.060	0.049	0.100	0.060	0.040	0.068	0.070	0.069	0.068	0.062
% of expansion after 360 days	0.030	0.050	0.097	0.060	0.049	0.100	0.060	0.040	0.068	0.070	0.069	0.068	0.062

C_3S/C_2S are less than 2.3. Both samples show acceptable resistance to external sulfate attack. Sample 8 has slightly lower expansion than number 5 because it has relatively lower C_3A and C_3S/C_2S ratio.

The loss of strength after one year showed the same trend as expansion. The loss of strength of sample 8 was 41% (46.05 MPa at 90 days to 27.23 MPa at 360 days) while sample 5 shows loss of 49% (46.20 MPa at 60 days to 23.50 at 360 days).

Group III contains four samples 3,7,10 and 11. These samples are type II cements. The calculated amounts of C_3A ranged from 5.38 to 6.09 and that for SO_3 ranged from 1.28% to 1.73%. However, the measured amounts of C_3A were all 3.6 ± 0.1. After one year of storage in 5% Na_2SO_4 solution, all samples showed relatively high expansion (Fig. 13) and strength loss (Table 6). The strength loss was 60 ± 0.5%. The expansion of sample number 7 shows a different expansion curve than others due to its relatively high early strength (32.9 MPa after 4 days).

Group V contains five samples 2, 4,9,12 and 13. These samples are type II cements. The percentage of SO_3 ranged from 0.69 to 1.52%. The calculated amount of C_3A ranged from 5.42 to 6.28. The measured amounts of C_3A are relatively higher than the samples in other groups, ranging from 3.9% to 4.38%. The C_3S/C_2S ratio is relatively high, ranging from 2.91 to 5.05.The cube strengths could not be measured after 300 days either due to the excessive increase in dimension of the cubes or from excessive degradation (Fig. 11). At this point the expansions of the prisms exceed 3.5%.

4. Conclusion

In high sulfate low alkali clinker, the calculated amount of C_3A does not give any indication regarding the level of cement sulfate resistance.

For such clinkers, the measured amount of C_3A seems to be the major indicator of sulfate resistance. It should be less than 3%. The C_3S/C_2S ratio could be considered as minor factor. It is preferable to be less than 2.5.

The clinker SO_3 doesn't have any direct influence on the strength development or sulfate resistance. The presence of SO_3 in the clinker
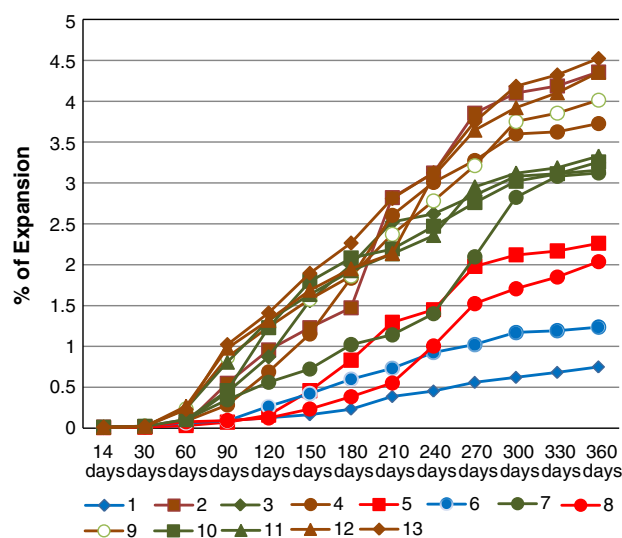

Fig. 12. Specimens stored, for one year, in the Na_2SO_4 solution.

Fig. 13. Specimens expansions results after one year storage in the Na_2SO_4 solution.

Fig. 11. Cubes stored, for one year, in the Na_2SO_4 solution.

Table 6
The strength development of the cubes stored in 5% Na$_2$SO$_4$ solution.

Strength (MPa)	1	2	3	4	5	6	7	8	9	10	11	12	13
4 days	20.23	34.79	24.63	23.23	29.92	22.63	32.91	28.56	28.84	24.84	26.60	30.04	30.23
14 days	37.72	53.12	38.00	38.63	39.84	45.24	38.68	35.63	45.75	37.43	36.11	35.04	37.91
30 days	41.84	55.91	40.95	40.88	44.56	50.15	42.36	42.52	46.63	42.56	42.47	44.31	43.50
60 days	43.15	56.35	39.00	41.20	46.20	50.24	45.84	45.59	45.84	41.30	41.08	42.25	41.60
90 days	45.00	52.72	35.63	41.47	45.23	49.31	44.10	46.05	44.80	40.10	39.59	40.50	39.70
120 days	47.43	51.59	30.80	38.50	43.32	48.43	42.60	43.80	39.50	36.50	37.76	36.79	38.36
150 day	46.56	48.15	25.15	36.36	40.84	46.79	39.72	42.07	38.65	34.70	34.68	34.30	36.59
180 day	45.00	45.88	21.36	33.60	38.10	45.04	36.27	37.50	37.31	32.10	34.76	29.83	30.80
210 day	43.59	43.40	19.10	28.56	37.52	44.50	32.84	33.00	30.10	31.08	32.11	24.04	21.07
240 day	43.56	40.50	18.50	22.30	36.71	44.30	30.21	29.07	21.56	29.60	30.04	19.39	15.30
270 days	43.15	35.40	17.90	18.23	33.82	42.75	26.45	28.68		28.36	27.25		
300 days	42.45		17.10		30.83	40.63	25.11	28.28		22.87	23.10		
330 days	41.85		16.80		25.50	39.15	19.50	28.12		22.15	19.60		
360 days	41.50		14.30		23.50	36.20	17.80	27.23		18.60	15.20		

lowers the amount of C$_3$A and the C$_3$S/C$_2$S ratio leading to slower strength development and higher the sulfate resistance level.

Based on the above results, the cement made with clinker containing somewhat high percentages of SO$_3$ and low alkali had relatively slower strength development and higher resistance to sulfate attack than classical cement with similar chemical composition.

References

[1] L. Bonafous, C. Bessada, D. Massiot, J. Coutures, B.L.E. Rolland, P. Colombet, Si MAS NMR study of dicalcium silicate: the structural influence of sulfate and alumina stabilizers, Journal of the American Ceramic Society 78 (10) (1995) 2603–2608.

[2] J. Clifton, J. Ponnersheim, Sulfate attack of cementitious materials: volumetric relations and expansions, National Institute of Standards and Technology NIST and U.S. Department of Commerce, NISTIR 5390, 1994.

[3] M. Collepardi, Damage by delayed ettringite formation – a holistic approach and new hypothesis, Concrete International 21 (1) (January 1999) 69–74.

[4] D. Campbell, Microscopical examination and interpretation of portland cement and clinker, Second edition, Portland Cement Association, 1999.

[5] H.F. Gonnerman, W. Lerch, Changes in characteristics of Portland cement as exhibited by laboratory over the period 1904 to 1950, Portland Cement Association Bulletin 39, Research Department, 1951.

[6] W. Gutt, M.A. Smith, Studies of the role of calcium sulfate in the manufacture of Portland cement clinker, Transactions of the British ceramic society 67 (10) (1968) 487–510.

[7] A. Gies, D. Knöfel, Influence of sulfur on the composition of Belite – rich cement clinker and the technological properties of the resulting cement, Cement and Concrete Research, 1987, pp. 317–328, Vol. 17.

[8] A. Hamou-Tagnit, S. Sarkar, The influence of varying sulfur content on the microstructure of commercial clinkers and the properties of cement, World Cement, September 1990, pp. 389–393.

[9] W.G. Hime, Clinker Sulfate: a Cause for Distress and a Need for Specification, Concrete for Environment Enhancement and Protection, E&FN Spon, London, U.K, 1996, pp. 387–395.

[10] D. Herfort, J. Soerensen, E. Couthard, Mineralogy of Sulfate Rich Clinker and the Potential for Internal Sulfate Attack, World Cement, May 1997, pp. 77–85.

[11] S. Horkoss, OPC Clinker with high SO$_3$, World Cement, June 2004, pp. 71–74.

[12] D. Herfort, G.K. Moir, V. Johansen, F. Sorrentino, H. Bolio Arceo, The Chemistry of Portland Cement Clinker, Advances in Cement Research, October 2010, pp. 187–194.

[13] D. Knöfel, E. Spohn, Der quantitative Phasengehalt in Portlandzementklinkern, ZEMENT –KALK- GIPS 10 (1969) 471–476 No.

[14] S. Kelham, The effect of cement composition associated with delayed ettringite formation 18 (3) (1996) 171–179 No.

[15] F.M. Lea, The Chemistry of Cement and Concrete, Third edition, 1970.

[16] F.R. McMillan, T.E. Stanton, I.L. Tyler, W.C. Hansen, F.R. McMillan, T.E. Stanton, I.L. Tyler, W.C. Hansen, Long-time Study of Cement Performance in Concrete – Concrete Exposed to Sulfate Soils, Portland Cement Association, Research Laboratory, 1949 Bulletin 30, et.

[17] R.C. Mielenz, S.L. Marusin, W.G. Hime, Z.T. Jugovic, Investigation of Pre-stressed Concrete Railway Tie Distress, Concrete International, 1995, pp. 62–68.

[18] V. Michaud, R.W. Suderman, Suderman, Sulfate Solubility in high SO$_3$ Clinkers, Proc. 10th Int. Cong. Chem. Cement Gothenburg, vol. 2, 1997, p. 2ii010-11.

[19] V. Michaud, R.W. Suderman, Anhydride in high sulfur trioxide (SO$_3$)/alkali clinker: dissolution kinetics and influence on concrete durability, cement, concrete and aggregate, ASTM Journal (1999).

[20] I. Older, H. Zhang, Investigation on high SO$_3$ Portland cement clinkers, World Cement Research and Development, 1996, pp. 73–77.

[21] Rasheeduzzafar, Influence of cement composition on concrete durability, ACI Materials journal 89 (1992) 574–586.

[22] J. Strunge, D. Knöfel, I. Dreizler, Influence of alkalis and sulfur on the properties of cement, Part 1: effect of the clinker SO$_3$ content on the cement properties, Zement, Kalk,Gips 3 (1985) 150–158 No.

[23] H.F.W. Taylor, Distribution of Sulfate Between Phases in Portland Cement Clinkers, Cement and Concrete Research, 1999, pp. 1173–1179.

[24] P. Tennis, S. Bhattacharja, W. Klemm, F.M. Miller, Assessing the distribution of sulfate in Portland cement and clinker and its influence on expansion in mortar, Cement, Concrete and Aggregates 21 (2) (1999) 212–216.

[25] G.J. Verbeck, Field and Laboratory Studies of the Sulphate Resistance of Concrete, Portland Cement Association, Research Department, 1967 Bulletin 227.