Mineralogical stabilization of Ternesite in Belite Sulfo-Aluminate Clinker elaborated from limestone, shale and phosphogypsum

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Abstract. This paper investigates the mineralogical evolution of sulfoaluminate clinker elaborated from moroccan prime materials limestone, shale and phosphogypsum as a byproduct from phosphoric acid factories. The advantage of the production of this type of clinker is related to the low clinkerisation temperature which is known around 1250°C, and to less consumption quantity of limestone thus enabling less CO₂ emissions during the decarbonation process compared to that of Portland cement. In this study we determine the stability conditions of belite sulfoaluminate clinker containing belite (C₂S) ye'elimite (C₄A₃\$) and ternesite (C₅S₂\$). The hydration compounds of this clinker are also investigated. The monitoring of the synthesized and hydrated phases is performed by X-Ray Diffraction and Infrared spectroscopy. The results show the formation of ternesite at 800°C and the stabilization of clinker containing y'elminite, belite and ternesite at temperatures between 1100 and 1250°C.

1 Introduction

The literature relating to sulfo-aluminate cement is abundant, but remains much less vast than that dealing with Portland cement. Sulfo-aluminate cements are relatively recent hydraulic binders, these cements are still little known differently than by specialists. They present unquestionable assets and many potential applications. Moreover, the ecological advantages of these cements also arouse the interest of the researchers. Its use thus seems an alternative of choice allowing the reduction of gas emissions for greenhouse effects, and constitutes one of the replacement solutions partial or total Portland cement for some applications.

The production of sulfo-aluminate cements indeed has two advantages compared to that of Portland cement: on the one hand, the temperature of firing is less high (approximately 1250°C) and on the other hand, the manufacturing of this cement requires the consumption of a less quantity of limestone, which reduces the CO₂ emissions during the decarbonation process, compared with that of Portland cement, the manufacturing of sulfo-aluminate cement makes it possible to reduce of almost 35% the carbon dioxide emissions [1]. Energy efficiency is also improved, as the lower burning temperature reduces fuel consumption by roughly 10% [1]. But knowledge on the properties related to its modified

chemical and mineralogical composition are less varied and requires advantage research to better understand of the mechanisms, temperatures and phase transformation stages in these cements.

The manufacturing of sulfo-aluminate cement is carried out from a source of aluminium like bauxite (40%) and of a source of sulphate (20%)[2]. The obtained sulfo-aluminate clinker is mainly composed of ye'elimite (C₄A₃\$ ≈ 65%), of bellite (C₂S ≈ 20%)(cement notation used throughout the document: A = Al₂O₃, C = CaO, F = Fe₂O₃, H = H₂O, K = K₂O, M = MgO, S = SiO₂, T = TiO₂, \$ = SO₃).

The formation of solid solutions of C₄A₃\$ is hindered by rich concentrations of additives, mainly due to the phosphorus effect that enlarges the stability field of the calcium aluminate phases at the expense of the calcium sulfoaluminate field. My.Y. Benarchid et al. [3] showed that the presence of the Cr₂O₃ and P₂O₅ oxides lowered the decomposition of CaCO₃. The enthalpy of decarbonation and the enthalpy of the formation of the solid solutions based on tricalcium aluminate formation decreased when the concentrations of additives increased. In another study [4] the authors showed that the maximum of the initial heat rate of the hydration process of C₄A₃\$ decreases with an increase in the concentration of Cr₂O₃ and P₂O₅ oxides. The incorporation of these oxides in the crystal lattice of C₄A₃\$ induces a long

induction period during the hydration reaction and the principal products of hydration are ettringite, calcium monosulfate and gibbsite.

The calcium sulfoaluminate phase, also named as Ye'elimite (C_4A_3S), has been known as hydraulic phase for several decades, but its potential in non-expansive cementitious materials has only recently been reported.

As a result of many researches [5], an optimized formulation based on a clinker containing C_4A_3S , belite (C_2S) and Ternesite (C_5S_2) was developed [6]. As a consequence, the clinkerization temperature of this type of cement is low (1200°C) compared to Ordinary Portland Cement ($1400\text{--}1450^{\circ}\text{C}$). It is thus currently attracting a great deal of interest worldwide [7, 8]. Its advantages include: i) reduced energy consumption during manufacturing, ii) low CO_2 emission during manufacturing [9], iii) acceptable setting times and high-early strength development, [10], iv) very good durability, particularly in marine constructions [11].

The ternesite phase C_5S_2 is a calcium sulphosilicate known also as sulphospurrite, its formation is based on the presence of belite and anhydrite [6] according to the formula (1)

When ternesite is formed or stabilised at temperatures above 1200°C , the use of a mineralizer such as phosphates or fluorides is required. Another possibility to form ternesite is a methodology, developed by Frank Bullerjahn and Al. [6], which is based upon a two-step clinkering procedure. In a first step, the clinker is sintered at a temperature of at least 1250°C . In a second step, a slow cooling or so called "second clinkering" is applied by decreasing the temperature from 1200 to 800°C .

Accordingly, the production of supposed ternesite belite calcium sulfo-aluminate ferrite clinkers offers facilitate potential for the beneficiation and the advancement of clinkers and bonds in view of calcium sulfo-aluminate. These clinker sorts could be produced utilizing a comparable process to belite calcium sulfo-aluminate clinkers, however inside a temperature scope of 900 to 1300°C .

2 Materials and methods

2.1 Mixture

The raw materials used in this study are: limestone, shale, and phosphogypsum. The chemical compositions determined by XRF are given in Table 1. In order to prepare the basic raw mixture, all of the raw materials are homogenized during 4 minutes in a disc crusher. The final mixtures were homogenized manually by using one ceramics mortar, a rammer and ethanol as a dispersive media to improve homogeneity of sample.

Table 1: Chemical composition of raw materials (Wt %)

	Limestone	Shale	Phosphogypsum
CaO	50,81	5,05	30,45
SiO ₂	7,67	35,34	9,50
Al ₂ O ₃	2,41	14,21	2,80
Fe ₂ O ₃	1,15	5,23	0,90
SO ₃	0,26	0,15	42,9
MgO	0,57	1,88	0,30
K ₂ O	0,16	0,30	0,10
P ₂ O ₅	0,29	0,11	0,63
LOI	36,68	37,73	12,42

The basic mixture made by the starting materials was carried out by a first approximation calculating raw believed to have a clinker at an approximate mineralogical composition wherein the produced phases would be within the average values of : 50% of belite (C_2S), 30% of ye'elimite (C_4A_3S) and 20% of ternesite (C_5S_2). The calculation is based, at a first approximation, on the quantitative distribution of the oxides CaO, SiO₂, Al₂O₃ and SO₃ of starting materials in the C_2S , C_4A_3S and C_5S_2 phases planned in the target clinker. Determining the composition of the mixture to achieve, from the chemical composition of raw materials, gives the intended composition shown in Table 2.

The clinkering of the samples were carried out in platinum crucible in a laboratory furnace at different temperatures: 800°C (24h), 1000°C (12h), 1100°C (12h), and 1250°C (6h), with an intermediate crushing in order to increase the homogeneity. The mineralogical evolutions of the various elaborated clinkers and their pastes are carried out using XR-Diffraction and IR spectroscopy. To do this, the hydrated samples were crushed, immersed in ethanol to stop the hydration and then dried in an oven set. In order to investigate the hydraulic behavior of sulfo-aluminate belite clinker, the synthesized clinkers were hydrated for up to 90 days at ambient temperature with the $w/c = 0.5$.

Table 2: Anticipated composition of raw basic mixture

	Limestone	shale	Phosphogypsum
Wt %	55.04	37.42	7.54

2.2 Characterization

X-ray Fluorescence (XRF) is a widely used technique for both qualitative and quantitative elemental analysis of solids, powders. The pearls were prepared by adding 5g of lithium tetraborate (melted) to 1g of crushed and grounded powder, the homogenized mixture was placed into a Platinum crucible and brought up to the complete melting until pearl level; the melt is poured into the mold and cooled up until the pearl detached from the mold.

X-ray diffraction analysis is performed in order to examine the mineralogical composition of the samples. The diagrams were collected using a Siemens D 500 Powder diffractometer equipped with a copper anticathode ($\text{CuK}\alpha=1.5418 \text{ \AA}$) at scanning speed of $0.04^\circ.\text{s}^{-1}$ from 10 to 60° .

The Infra-red Spectroscopy with Transform of Fourier (or FTIR: Fourier Transform Infra-Red Spectroscopy) is based on the infra-red absorption of radiation by analyzed material. The absorbed frequencies by molecular vibration are ranging between 4000 and 400 cm^{-1} . The used abbreviation to describe studied samples is detailed in Table 3

Table 3: Designation of burned and hydrated samples

Burned Sample designation	CSA1	CSA2	CSA3	CSA4
Burning temperature ($^\circ\text{C}$)	800	1000	1100	1250
Hydrated Sample designation	CSA5	CSA6	CSA7	CSA8
Hydration time (Days)	2	7	28	90

3. 3 Results and discussion

3.1 Elaboration and characterization of belite sulfo-aluminate clinker

Different phases are identified by X-ray diffraction for the anhydrous samples CSA1-CSA4. The spectra are presented in figure 1 and their percentages are respectively collected in table 4. These results are obtained by applying the Rietveld method for the determination of semi-quantitative proportions of present phases at each temperature. The observed mineralogy of the synthesized clinker, applying the sintering process described above, displays a composition close to that expected, showing a tendency to form a $\beta\text{-C}_2\text{S}$ polymorph of dicalcium silicate as a main formed phase observed at $2\theta = 32,50^\circ$ [12, 13], while $\text{C}_4\text{A}_3\text{S}$ is present in orthorhombic and cubic forms. Bullerjahn Frank et al. found the same phases using calcite powder, siliceous fly ash, and natural anhydrite as starting materials [6].

Figure 1: X-ray diffraction spectra of the synthesized clinker CSA1-CSA4

The decomposition of limestone is observed at 800°C , lower temperature compared to those typically known for this reaction (860°C), this result was also observed by Y. WANG et al. [14]. Comparing the amounts of the formed phases during clinkerization we observe that increasing the temperature above 1000°C leads to the reduction and cancellation of the amounts of CaO and SiO_2 and formation of the intermediate phase CaSiO_3 between 1000 and 1100°C according to the reaction (2).

Then, the percentage of C_2S grows beyond 1100°C according to the reaction (3) [15].

Table 4: Semi-quantitative identification of mineral phases in synthesized clinker CSA1-CSA4

	CSA1	CSA2	CSA3	CSA4
C_2S	11,51	53,09	49,01	52,92
$\text{C}_4\text{A}_3\text{S}$	15,85	22,02	24,96	28,09
$\text{C}_5\text{S}_2\text{S}$	12,60	17,80	18,45	18,90
CS	—	7,47	0,08	—
CaO	37,76	1,06	—	—
SiO_2	13,70	2,05	—	—
SO_3	8,5	3,01	—	—

The three phases C_2S , $\text{C}_4\text{A}_3\text{S}$ and $\text{C}_5\text{S}_2\text{S}$ form in small amounts from the temperature of 800°C , their quantities increase until the order of 53% for C_2S , 28% for $\text{C}_4\text{A}_3\text{S}$ and not exceed 18 to 20% for the ternesite phase, during all the treatment process up to 1250°C . It appears clearly that beyond the temperature of 1100°C , there is a joint stability of the three phases C_2S , $\text{C}_4\text{A}_3\text{S}$ and $\text{C}_5\text{S}_2\text{S}$, this result is of agreement with the many previous published results [6, 16-20]. The appropriate burning condition of

pure ternesite, is found to be 1200°C for 8 h. The secondary heat treatment between 1100 and 1250°C can significantly promote the formation of ternesite from the reaction of belite and anhydrite in sulfo-aluminate clinkers[18]. The increase of the SO₃ content in the raw meal leads to the replacement of large amounts of C₂S by ternesite, which is stable in the temperature ranging between 900 and 1250°C [6].

Figure 2: Infrared spectra of CSA1- CSA4 sample

The ternesite phase formed as a second major phase instead of C₂S and CS, in addition to C₄A₃\$. Upon hydration, this cement produced very high mechanical strength at early and later ages [20].

The infrared absorption spectra of CSA1-CSA4 samples reported in figure 2 and table 5 showed that the major absorption bands of the clinker phases are in the region 1600 to 400 cm⁻¹. The main vibration bands of the different groups are listed in Table 5. The Si-O2 stretching mode produces an absorption band at 991,879, and 847 cm⁻¹ in C₂S [21], while a broader band with peaks observed at 500 and 1000 cm⁻¹ is assigned to the same stretching mode in C₅S₂\$. The SO₄ groups are identified at 610, 613, 620 cm⁻¹ in C₄A₃\$ [22, 23], while bands with peaks observed at 1100 and 1150 cm⁻¹ are assigned to this vibration in C₅S₂\$. The AlO₄ groups vibration identified at 420, 600, and 870 cm⁻¹ are assigned to C₄A₃\$ phase.

Table 5: Major vibration bands observed by IR spectroscopy in CSA1- CSA4 samples

	CSA1	CSA2	CSA3	CSA4
Group SiO₂	1000 f	1000 M	1000 M	991 f
Group SiO₂	879 f	879 f	847 f	847 f
Group SiO₂	500 F	500 M	500 M	500 F
Group AlO₄	420 f	420 M	420 M	420 f
Group AlO₄	600 f	600 f	600 f	600 f
Group AlO₄	870 F	870 F	870 M	870 M
Group SO₄	610 f	613 f	615 f	620 f
Group SO₄	1100 M	1100M	1150 f	1150 f
Group H₂O	3620 f	3620 f		
Group H₂O	3400 f	3400 f		

Group CaO	1400 F	1400 F	1450 F	1450 F
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3.2 Hydration

The hydrated samples CSA5-CSA8 of the cement pastes has been investigated at 2 days, 7days, 28 days, and 90 days. XRD technique showed the formation of hydration product of ye'elimite, the ettringite phase characterized by the diffraction peaks of maximum intensities observed at 2θ = 9,65 (Figure 3 and Table 6) according to the reaction (4).

Figure 3: X-ray diffraction spectra of the hydrated samples CSA5-CSA8

The diffraction peaks relating to Gibbsite are identified at 2θ = 44,82 [15], and the peaks of monosulfate are detectable at 2θ = 10,3 , indicating the partial decomposition of ettringite and its transformation into monosulfate. This result is agrees with previous published results [18, 24, 25]. The strätlingite, C₂ASH₃, is formed from the reaction of belite which consumes a portion of AH₃ produced by hydration of ye'elimite according to the reaction (5)

Table 6: Semi-quantitative identification of mineral phases in hydrated samples CSA5-CSA8

	CSA5	CSA6	CSA7	CSA8
Calcuim slicate C₂S	8,68	4,43	1,93	0,53
Ye'elimite C₄A₃\$	6,27	3,21	1,32	0,94
Ternesite C₅S₂\$	17,22	17,17	17,02	7,85
Ettringite C₆A\$₃H₃₂	22,36	28,54	29,93	39,34
Monosulfoaluminate C₄A\$H₁₂	8,81	10,41	11,53	20,44
Gibbsite AH₃	16,61	9,26	6,74	1,24
Strätlingite, C₂ASH₃	11,45	19,56	24,43	24,65

Hexagonal hydrates	4,47	4,43	4,34	3,95
Gypsum C\$H	4,11	2,98	2,73	1,05

The same results, deduced here, are obtained by Y.Shen and al.[18] which have shown that the pure ternesite can hydrate at a slow rate, and the addition of ye'elimite promotes the hydration of ternesite and the formation of ettringite. The ettringite formation for the clinker containing ternesite mainly depends on the dissolution of gypsum originating from the hydration of ternesite.

Figure 4 and table 7 shows the infrared spectra of the hydrated samples CSA5-CSA8, main infrared vibrations are summarized in Table 7. We identify the vibrations corresponding to the group (SO_4) in the ettringite $C_6A_3H_{32}$ at 1100 cm^{-1} and in the monosulfoaluminate hydrated calcium $C_4A\$H_{12}$ at 420, 630 and 1000 cm^{-1} like it has been shown by some authors [26, 27]. Absorption localized at 530 cm^{-1} is due to binding of vibration (AlO_6) in the phase of ettringite, these results are the same obtained by M. Idrissi et al. [15]. on calcium sulfoaluminate phase elaborated by iron inclusion.

Figure 4: Infrared spectra of hydrated samples CSA5-CSA8

According to Table 6 we found that the percentage of increased ettringite in the sample CSA8 from 22% (at 2 days) to 39% (at 28 days), it may be due to the hydration of ternesite phases beyond 28 days, this result agrees with with previously mentioned results.

Previous studies reported that the ternesite is least reactive in pure ternesite system, the hydration of ternesite does not take place until 90 days, and gypsum has formed as new crystalline phase. The hydration process of ternesite starts by its partial dissolution, and after 28 days of hydration, only traces of ettringite are detectable while gypsum produced from the hydration of ternesite has almost been depleted [18], but in the presence of Yeelimite the ternesite hydration favors also the formation of gypsum and ettringite. [6].

Gallardo et al. [28] and Velazco et al. [29] were shown in the previously published results that the ettringite as the main hydration product although traces of monosulphate phase were also found. The addition of citric acid increased the setting time, modified the morphology of the ettringite needles, changed the microstructural configuration and prevented the decreasing in compressive strength of the samples caused by delayed

ettringite formation, also Bazaldúa et al. [30] demonstrated that the main hydration products of supersulphated cements were C-S-H and Ettringite. These products precipitated since the first hours of hydration, forming a porous and weak microstructure; with time and up to one year, the C-S-H and Ettringite consolidated the microstructure and increased the compressive strength. The cements showed hydraulic behavior after curing under water.

Table 7: Major vibration bands observed by IR spectroscopy in CSA5-CSA8 samples

	CSA5	CSA6	CSA7	CSA8
SO_4 corresponding to the ettringite hydrated calcium monosulfoaluminate	410 M	410 M	410 M	410 M
SO_4 corresponding to the ettringite hydrated calcium monosulfoaluminate	630 f	630 f	630 f	630 f
AlO_6 corresponding to the ettringite and strätlingite	520 M	520 M	530 f	530 f
AlO_6 corresponding to hexagonal hydrates	780 M	780 M	770 f	770 f
SO_4^{2-} corresponding to the ettringite	1100 f	1100 f	1100 f	1100 f
H ₂ O	1580 M	1580 M	1580 f	1580 f

Frank Bullerjahn et al. [6] found that the $C_5S_2\$$ phase in the clinker is more reactive than the C_2S , unlike previous studies that considered the ternesite as an inert phase or showing a low reactivity [19, 31-35]. These studies conclude on the low reactivity of ternesite based on the chemical bound water and the low quantities of hydrates formed, which were present in trace amounts only. It has also been reported [36-37] that $C_5S_2\$$ has better hydraulic properties after autoclaving, it transforms to a rapidly hardening and high strength compound [38]. Additionally, the hydration reaction of calcium sulphoaluminate initiates rapidly and forms ettringite and AH_3 [39], contributing to faster setting of CSA cement than Portland cement [40].

All these results indicate that ternesite can be hydrated at a long-term, adding yeelimite not only induces hydration ternesite but also favors the formation of gypsum [6, 18], this gypsum in the pastes leads to ettringite formation and reduced the amount of formed monosulfoaluminate [40]. In this work we have clearly shown the formation and joint stability at relatively moderate temperatures (1100-1250°C) of the three phases C_2S , $C_4A_3\$$ and $C_5S_2\$$. The hydration of this clinker shows the formation of usually known phases in relatively high proportions for Ettringite $C_6A_3H_{32}$ (22%) from the second day and the formation

of monosulfoaluminate $C_4A\$H_{12}$ and strätlingite C_2ASH_3 in large amounts at 28 days.

4 Conclusions

The sulfoaluminate cements bring innovating technical solutions, those hydraulic materials find more uses in building and civil engineering by presenting a favorable ecological assessment. This work concerned the sulfoaluminate clinker characterized by the presence of C_2S (belite), $C_4A_3\$$ (Ye'elimeite) and of $C_5S_2\$$ (ternesite). The clinker is elaborated by sintering raw materials at a temperature around 1100-1250°C. The blended raw material is made up of a source of alumina (Shale), limestone and a source of sulphate calcium (phosphogypsum derived from phosphoric acid factories). The sulfoaluminate clinker is characterized by a carbonic reduction from approximately 35% due to the use of less limestone and lower clinkerisation temperature. The formation of ternesite is observed at least of 1100°C, that is related to clinkering process. We observe also the stabilization of this phase at 1200°C. The hydration process shows that all hydrate phases are formed in the first two days except the ternesite hydrated phase which takes place at later ages (beyond 28 days).

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