

Mineralogy of C-S-H belite hydrates incorporating Zn-Al-Ti layered double hydroxides

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Abstract. Recently, the belitic cements with low alite content were the subject of several research works which aimed to replace the Ordinary Portland Clinker (OPC) for ecological reasons (reduction of CO₂ emissions), so to understand the reactivity of this cement, the hydration study of the C₂S "dicalcium silicate" phase is primordial research step. As well for a clean environment, the TiO₂ photocatalyst has been extensively applied in the science of building materials because of its ability to degrade the cement surface pollutants. New photocatalyst based layered double hydroxides (LDH) associated with zinc, aluminium and TiO₂ was introduced to increase the compatibility with mortars. The present work is subjected to investigate the effect of the layered double hydroxides on the hydration of C₂S in following the evolution of hydration by X-ray diffraction at 2, 7, 28 and 90 days and analyzing the calcium/silicon ratio of different formed hydrates.

1 Introduction

The ordinary Portland cement is a complex multi-phase system, the hydration includes several simultaneous processes of dissolution/precipitation [1]. As soon as the cement is contacted with the gauging water, the silicate phases C₃S and C₂S react rapidly with H₂O to form less soluble hydrates than these phases. Nevertheless, despite of the almost immediate forming of the first hydrates, the hydration may continue for many years to come [2]. When the cement is hydrated, the reactions during the gauging form the Calcium Silicate Hydrate C-S-H (notation in the cement industry C = CaO, S = SiO₂, and H = H₂O) by releasing Ca²⁺ and OH⁻ ions [3], these two species combine and form Portlandite. Dicalcium silicate C₂S gives the same products with low quantities and slow kinetics compared to C₃S. In Portland cement the dicalcium silicate has three polymorphic forms α -C₂S, β -C₂S and γ -C₂S (metastable) with a composition which varies between 20% and 25% in the clinker. The slower hydration of C₂S, after 28 days, leads to improved long-term strength. Tests on alite and belite showed that long term strengths are comparable and that only the hydration kinetics is different [4].

C-S-H is the predominant phase resulting from the hydration of dry cement, it is directly responsible for the evolution of mechanical properties. In the literature, several studies show that the tobermorite-like structure is the closest to that of C-S-H [5]. There are three isomorphous structures of tobermorite which are distinguished by their basal space (distance between the two basic plans of two first lamellas neighbors): 9.3 Å, 11

Å [6, 7] and 14 Å [8]. According to the ratio of water/cement and Ca/Si, the C-S-H can adopt one of the isomorphous structures. Tobermorite is generally considered as a valid analogy for the C-S-H with low ratios Ca/Si, while jennite structure is used to describe the structure of C-S-H with high ratios Ca/Si [9,10]. Similarities between C-S-H and tobermorite were also deduced from atomic simulations [11], although this model is the subject of criticism [12]. The chemical composition and the unit cell of the clinotobbermorite are closely linked to those of the tobermorite, it is very likely that the clinotobbermorite is a stable polymorph at a lower temperature than the tobermorite [13]. Studies of the structure and the kinetic of C-S-H are essential so as to understand the process of the cement setting and the "sticking" mechanism at the microscopic level, their chemical composition is variable. In particular, the ratio (Ca/Si) of calcium-silicon structure is commonly assumed to vary from 0.6 to 2.3, the highest ratio being found in the clean Portland cement, and the lowest in cements containing products such as fly ash or metakaolin [14,15].

The layered double hydroxides LDH have spurred the interest many researchers, they are more likely useful as additions in cements. Cement based materials containing the nanoparticles have shown several benefits under distinct perspectives for sustainable construction practice, as well as, the kinetics of hydration acceleration [16]. Photocatalytic phenomena have become an attractive field of studies in the last decade because of its great potentials for the purification of the environment and the ability to break down aquatic and air pollutants [17, 18].

Furthermore and as part of research on the reduction of pollutants in the atmosphere, the Portland cement is also studied for this aim by adding TiO_2 which allows the degradation of air pollutants by photocatalysis. The photocatalytic principles are based on the free-radical reaction initiated by light onto a concrete surface. Its efficiency depends on the mobility of electron-hole pairs that determines the probability of electrons and holes to achieve contact with active sites on the photocatalyst surface [19]. The most commonly used photocatalyst is TiO_2 due to its strong oxidizing power, its photo-stability and its non-toxicity. This oxide is already widely marketed for its properties and use in surface state [20, 21]. The titanium oxide properties can be improved when using double hydroxides lamellar based Zn-Al-Ti [22].

The introduction of the photocatalytic active inorganic-inorganic nanocomposites to the cement-based mortars improved overall mortar properties (micro-hardness and crystallinity) and showed that the synergetic effect between TiO_2 as traditional photocatalytic and Zn-Al-LDH contributes to the overall photocatalytic performances, improving also the compatibility of the photocatalytic active phase with the mortar matrix [23]. Zinc was selected as constituent LDH metal because of its photocatalytic and antimicrobial activity with the intention to possibly contribute to the overall activity of novel Ti-Zn-Al nanocomposite. ZnO is frequently looked as an alternative to TiO_2 , since it can absorb a larger energy fraction of the solar spectrum and more light quanta [24]. In our work, the LDH compounds after synthesis are added under a calcined form with a quantity of ZnTiO_3 , the compounds, thus introduced under a dried active form, are more likely to react to form again LDH structures that are themselves trapped in hydrates dicalcium silicate. Thermal treatment provides important physicochemical properties to LDH compounds [25]: a "memory effect" of the hydroxide lattice, which allows different anionic species to be incorporated into the LDH interlamellar space, a larger surface area, increasing adsorption of anions and elimination of the interlayer carbonate (CO_3^{2-}), which strongly hinders anion exchange processes in LDHs [26, 27].

In this paper we seek to use LDH compounds and exploit their memory effect by heat treatment and addition to the C_2S phase to study the evolution of hydrates formed in these mixtures. The purpose is to make a mineralogical study of the hydrates of dicalcium silicate in the presence of varying amounts (1% and 3 wt%) of layered double hydroxides Zn-Al-Ti, monitoring of phases used is carried out by XRD after 2, 7, 28 and 90 days of hydration to compare the polymorphism of phase formation and determine the Ca/Si in the formed phases.

2 Materials and methods

2.1 Synthesis of C_2S

The synthesis of the C_2S phase was performed by firing a silica source SiO_2 finely ground with calcite (CaCO_3) and of $(\text{NH}_4)_2\text{H}_2\text{PO}_4$ used as a dopant to stabilize the $\beta\text{-C}_2\text{S}$

variety, the mixture is subjected to a heat treatment at different temperatures 500 °C, 800 °C and 1000 °C for 24, 12 and 8h respectively, followed by rapid air cooling. The heat treatments are interspersed by milling with the addition of ethanol whose role is to increase the reactivity of the products.

2.2 Synthesis of Zn-Al-Ti Layered Double Hydroxides

In a beaker an acid solution of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ precursors and a basic solution of Na_2CO_3 and NaOH were simultaneously added (4cm³/min) so as to adjust a constant pH between 9 and 9.5 at a constant temperature of 45°C for 10 hours. A Zn-Al LDH white precipitate is formed after aging from 12h at 100°C in a stove and calcined for 5 hours at 500 °C. The wet impregnation of TiO_2 on the Zn-Al layered double hydroxide was used for the preparation of Zn-Al-Ti LDH. The wet impregnation process was carried out using TiO_2 suspension diluted (3% by weight) in a base solution 0.67M Na_2CO_3 and loaded on the calcined powder Zn-Al LDH. The excess water was removed in a stove at 100°C. The impregnated sample is dried for a second time 12 hours at 100°C and calcined for 5 hours at 500 °C to finally obtain the powder Zn-Al-Ti LDH.

2.3 Hydration of blended samples

The resulting binders and the hydrated samples were analyzed by the X-ray diffraction performed by a Siemens D5000 diffractometer. This unit uses the mounting BRAGG-BRENTANO ($\theta/2\theta$) and a radiation $\lambda_{\text{K}\alpha}\text{Cu} = 1.5406 \text{ \AA}$. The spectra 2θ interval is between 10 and 60 ° (with a step of 0.04°).

Two samples are prepared from the synthesized C_2S phase and the addition of 1% and 3% by weight of Zn-Al-Ti LDH. The adopted nomenclature is given in table 1. The designation for example of sample C2S3LDH7d means that the addition of 3% LDH is performed to C_2S and hydration of sample was followed for 7 days.

Table 1. Nomenclature of prepared samples

Hydration time	$\text{C}_2\text{S} + 1\% \text{ Zn-Al-Ti LDH}$	$\text{C}_2\text{S} + 3\% \text{ Zn-Al-Ti LDH}$
2 days	C2S1LDH2d	C2S3LDH2d
7 days	C2S1LDH7d	C2S3LDH7d
28 days	C2S1LDH28d	C2S3LDH28d
90 days	C2S1LDH90d	C2S3LDH90d

3 Results and discussion

3.1 X-ray diffraction of the anhydrous samples

The C_2S phase is synthesized by reacting of CaCO_3 and SiO_2 at 800°C and 1000°C. The $\alpha\text{-C}_2\text{S}$ form of

orthorhombic variety with a large amount of CaO is manifested at 800°C. At 1000°C the intensity of CaO peaks decreases with the appearance of a second form of C₂S (β-C₂S) which has a monoclinic crystal system.

The X-ray diffractograms of the Zn-Al LDH and Zn-Al-Ti LDH before and after calcinations are shown in Figures 1, 2, 3 and 4.

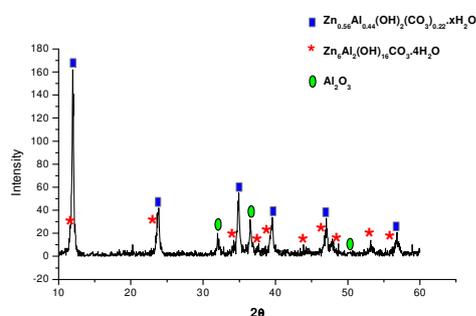


Fig. 1. XRD pattern of Zn-AL LDH phase before calcinations

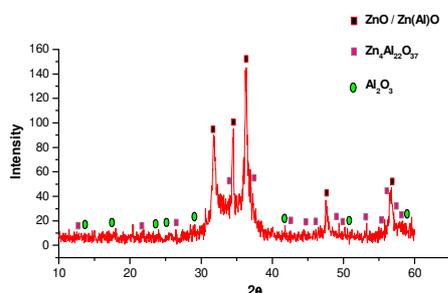


Fig. 2. XRD pattern of the Zn-Al LDH phase calcined at 500 °C

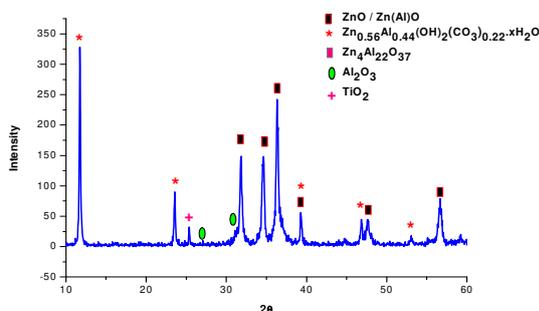


Fig. 3. XRD pattern of the Zn-Al-Ti LDH phase

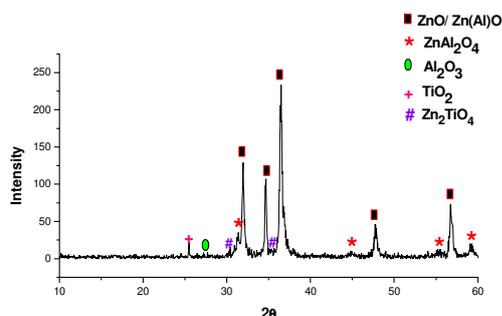


Fig. 4. XRD pattern of the Zn-Al-Ti LDH phase calcined at 500°C

The diffraction peaks demonstrates a LDH double layered hydroxides by forming two LDH phases: A stoichiometric phase Zn₆Al₂(OH)₁₆CO₃·4H₂O and a non-stoichiometric phase Zn_{0.56}Al_{0.44}(OH)₂(CO₃)_{0.22}·xH₂O was detected as the dominant phase. During the first calcination of Zn-Al LDH phase at 500°C we can note the disappearance of the diffraction peaks corresponding to LDH, the structure is destroyed which resulted in the appearance of ZnO, Al₂O₃ and Zn₄Al₂₂O₃₇ and the disappearance of carbonates (figure 2). After impregnation of TiO₂ onto Zn-Al LDH phase, TiO₂ was not detected in diffractograms because of its low concentration. However the appearance of zincite phase ZnO and aluminum oxide Al₂O₃ as well as Zn_{0.63}Al_{0.37}(OH)₂(CO₃)_{0.185}·xH₂O LDH phases were due to the hydration following the impregnation process (figure 3). After the second calcination the dominant phase detected is assigned to the mixed oxides of ZnO and Al₂O₃, since the origin of the ZnO phase is the Zn-Al LDH [28, 29], we also noticed the disappearance of the LDH phase such as what occurred in the first calcination (Figure 2), which resulted in the formation of stable phases of ZnO, ZnAl₂O₄ and Zn₂TiO₄. The reflections of the TiO₂ anatase phase were detected, probably due to the titanium oxide that did not react with ZnO (Figure 4). These results are consistent with the work of Milica Hadnadjev-Kostic et al. [30].

The interest of the calcination of Zn₆Al₂(OH)₁₆CO₃·4H₂O is to form Zn-Ti LDH by the reconstitution method, the formed LDH were calcinated at 500°C to remove nitrates and form the ZnO and Zn₂TiO₄ which is the essential final product for the photocatalytic activity [30]. The reconstruction of the LDH structure took place during the impregnation process under the effect of the mixed oxides of ZnAl who have the ability to re-establish the hydroxide lamellar structure when are exposed to water and anions [31], which will be used as an addition to the hydration of different samples of C₂S.

3.2 X-ray diffraction of hydrated samples

Figure 5 shows the diffraction patterns of C₂S samples + 1% of Zn-Al-Ti LDH hydrated for 2, 7, 28 and 90 days. Table 2 summarizes the semi-quantitative analysis of the formed hydrates and their Ca/Si ratios as a function of time. The global Ca/Si observed for total C-S-H phases is calculated as the sum of all proportions of each observed C-S-H phase multiplied by its own factor Ca/Si.

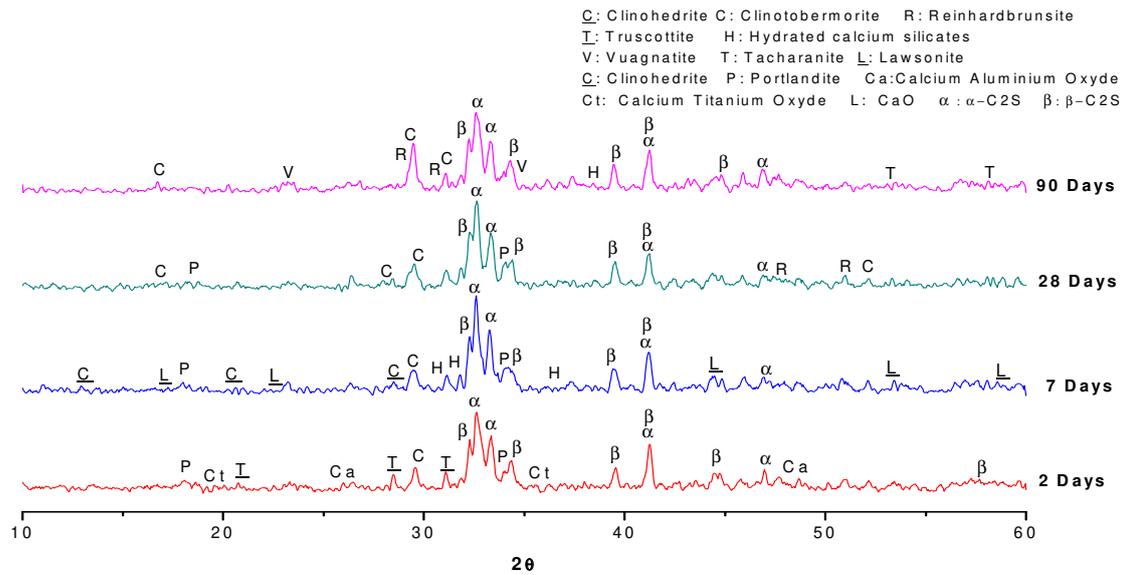


Fig. 5. XRD patterns of C₂S + 1% Zn-Al-Ti LDH hydrated samples

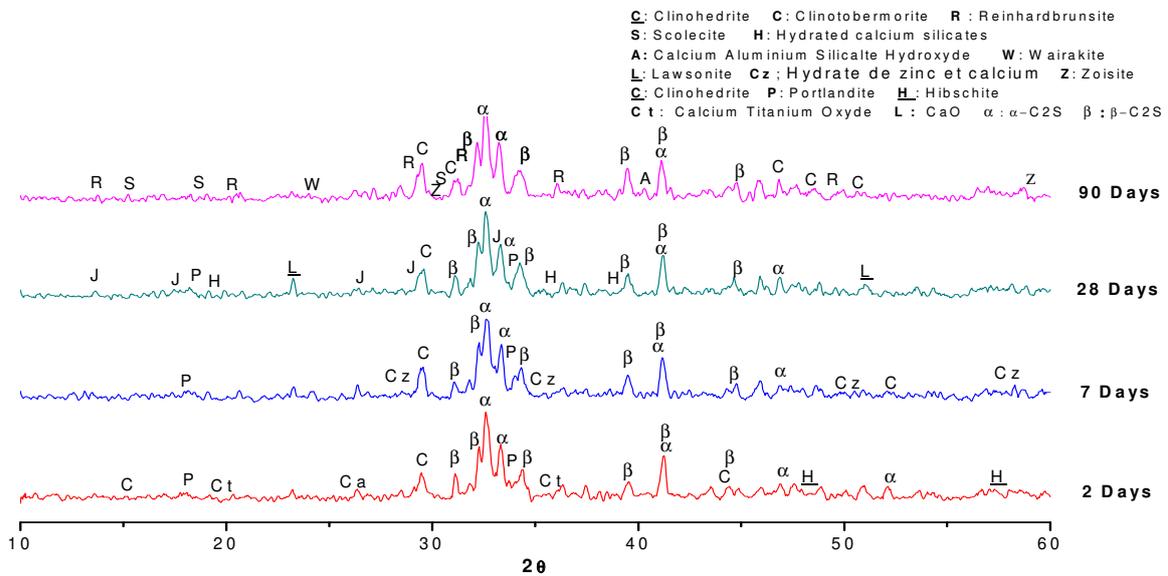


Fig. 6. XRD patterns of C₂S + 3% Zn-Al-Ti LDH hydrated samples

Table 2. Semi-quantitative analysis of hydrated samples with 1% Zn-Al-Ti LDH

	Phase nomenclature	Formulas	Percentages of hydrates				Ca/Si
			2 Days	7 Days	28 Days	90 Days	
Anhydrous phases	Dicalcique silicate	Ca_2SiO_4	41.27	34.59	23.62	20.13	-
	Calcium Titanium Oxyde	$\text{Ca}_4\text{Ti}_3\text{O}_{10}$	1.03	1.17	-	-	-
	Calcium Aluminium Oxyde	$\text{Ca}_3\text{Al}_2\text{O}_6$	6.05	-	-	-	-
Hydrated phases	Portlandite	$\text{Ca}(\text{OH})_2$	8.80	9.24	13.22	-	-
	Lawsonite (C-S-H-Al)	$\text{Ca}_4\text{Al}_8\text{Si}_{36}\text{O}_{48}\cdot 16\text{H}_2\text{O}$	-	13.73	-	-	0.11
	Clinobermorite (C-S-H)	$\text{Ca}_5(\text{Si}_6\text{O}_{17})(\text{H}_2\text{O})_5$	15.52	13.63	20.47	17.65	0.83
	Truscottite (C-S-H)	$\text{Ca}_{14}(\text{Si}_{24}\text{O}_{58})(\text{OH})_8(\text{H}_2\text{O})_2$	9.8	-	-	-	0.58
	Clinohedrite (C-S-H-Zn)	$\text{CaZn}(\text{SiO}_4)(\text{H}_2\text{O})$	-	12.22	-	-	1
	Hydrate calcium silicates (C-S-H)	$\text{Ca}_6\text{Si}_3\text{O}_{12}\cdot\text{H}_2\text{O}$	-	6.17	-	14.8	2
	Reinhardbraunsite (C-S-H)	$\text{Ca}_5(\text{SiO}_4)_2(\text{OH})_2$	-	-	12.78	10.38	2.5
	Tacharanite (C-S-H-Al)	$\text{Ca}_{12}\text{Al}_2\text{Si}_{18}\text{O}_{51}\cdot 18\text{H}_2\text{O}$	-	-	-	6.7	0.67
	Vuagnatite (C-S-H-Al)	$\text{CaAlSiO}_4(\text{OH})$	-	-	-	4.1	1
Global Ca/Si observed for total CSH phases			0.181	0.373	0.489	0.787	

Table 3. Semi-quantitative analysis of hydrated samples with 3% Zn-Al-Ti LDH

	Phase nomenclature	Formulas	Percentages of hydrates				Ca/Si
			2 Days	7 Days	28 Days	90 Days	
Anhydrous phases	Silicate bicalcique	Ca_2SiO_4	47.32	40.80	38.74	29.84	-
	Calcium Titanium Oxyde	$\text{Ca}_4\text{Ti}_3\text{O}_{10}$	10.03	-	-	-	-
	Calcium Zinc Titanium Oxyde	$\text{Ca}_2\text{Zn}_4\text{Ti}_{15}\text{O}_{36}$	7.8	-	-	-	-
Hydrated phases	Portlandite	$\text{Ca}(\text{OH})_2$	8.019	10.4	11.06	-	-
	Clinobermorite (C-S-H)	$\text{Ca}_5(\text{Si}_6\text{O}_{17})(\text{H}_2\text{O})_5$	16.77	19.93	19.20	15.29	0.83
	Hibschite (C-S-H-Al)	$\text{Ca}_3\text{Al}_2(\text{SiO}_4)_{1.53}(\text{OH})_{5.88}$	10.05	-	-	-	1.96
	Silicates de calcium hydratés (C-S-H)	$\text{Ca}_2\text{SiO}_4\cdot\text{H}_2\text{O}$	-	17.4	-	-	2
	Hydrate de zinc et calcium (C-S-H-Zn)	$\text{CaZn}_2(\text{OH})_6\cdot 2\text{H}_2\text{O}$	-	11.28	-	-	-
	Lawsonite (C-S-H-Al)	$\text{Ca}_4\text{Al}_8\text{Si}_{36}\text{O}_{48}\cdot 16\text{H}_2\text{O}$	-	-	11.84	-	0.11
	Jennite (CSH)	$\text{Ca}_9\text{H}_2\text{Si}_6\text{O}_{18}(\text{OH})_8\cdot 6\text{H}_2\text{O}$	-	-	10.95	-	1.5
	Hydrate calcium silicates (C-S-H)	$\text{Ca}_6\text{Si}_3\text{O}_{12}\cdot\text{H}_2\text{O}$	-	-	8.32	-	2
	Zoisite (C-S-H-Al)	$\text{Ca}_2\text{Al}_3\text{Si}_3\text{O}_{12}(\text{OH})$	-	-	-	14.97	0.05
	Wairakite (C-S-H-Al)	$\text{CaAl}_2\text{Si}_4\text{O}_{12}\cdot 2\text{H}_2\text{O}$	-	-	-	11.56	0.25
	Reinhardbraunsite (C-S-H)	$\text{Ca}_5(\text{SiO}_4)_2(\text{OH})_2$	-	-	-	9.77	2.5
	Scolecite (C-S-H-Al)	$\text{CaAlSi}_3\text{O}_{10}\cdot 3\text{H}_2\text{O}$	-	-	-	9.50	0.33
	Calcium Aluminium Silicate Hydroxyde (C-S-H-Al)	$\text{Ca}_3\text{Al}_2\text{SiO}_4(\text{OH})_8$	-	-	-	9.04	3
Global Ca/Si observed for total CSH phases			0.336	0.513	0.622	1.103	

Analysis of results shows that the main products of hydration of the C_2S phase + 1% Zn-Al-Ti LDH are α - C_2S and β - C_2S phases, Portlandite and hydrated calcium silicates. We notice that the C-S-H phases are present in forms of different solid solutions including different proportions of Al and Zn. On the 2nd day of hydration, we have a small amount of C-S-H phases whose presence is of formulas $Ca_5(Si_6O_{17})(H_2O)_5$ et $Ca_{14}(Si_{24}O_{58})(OH)_8(H_2O)_2$. On the 7th day of hydration, there is the appearance of other hydrates of formulas $Ca_6Si_3O_{12} \cdot H_2O$ and $CaZn(SiO_4)(H_2O)$ with decreasing percentage of Clinotobermorite, while the content of Portlandite continues to increase. After 28 days of hydration, we observe fluctuations in the amounts of this phase accompanied by appearance of other compounds such as hydrates incorporating the LDHs. These last phases have been identified in the forms of $CaZn(SiO_4)(H_2O)$ and $Ca_4Al_8Si_{36}O_{48} \cdot 16H_2O$. We observe also the formation of the $Ca_5(SiO_4)_2(OH)_2$ phase with a percentage of 12.78% with a slight decrease of C_2S phase and the total consumption of the Portlandite $Ca(OH)_2$, these results are consistent with the work of H. El-Didamony et al. [32]. The hydrated phases formed at a young age, before 7 days, are essentially constituted by crystalline phases with low ratio Ca/Si less than 1 while in the medium term, 28 to 90 days, the identified phases become more rich in calcium and the Ca/Si ratio increases and may exceed 2. The hydration of C_2S shows the presence of crystallized C-S-H compounds with percentages that increase and become more abundant in the 90th day, this is explained by the known character of this phase whose hydration is slow and participates in the creation of long-term resistances [2].

Figure 6 shows the diffraction patterns of C_2S samples + 3% of Zn-Al-Ti LDH hydrated for 2, 7, 28 and 90 days. Table 3 summarizes the semi-quantitative analysis of the formed hydrates and their Ca/Si ratios as a function of time. The observations for the sample with 3% Zn-Al-Ti LDH addition are similar to those attributed to the sample with 1% of the added. From the spectra of Figure 6 and table 3 we can see the formation of the clinotobermorite $Ca_5(Si_6O_{17})(H_2O)_5$ C-S-H type and Portlandite $Ca(OH)_2$ which are the main hydration products calcium silicates. Depending on the hydration time, the content of the clinotobermorite is variable and accompanied by the formation of jennite $Ca_9H_2Si_6O_{18}(OH)_8 \cdot 6H_2O$ (C-S-H). The Zn-Ti-Al LDH phases also interacted in this hydration by hydrate formation where Zn and Al are incorporated, these hydrates appear since the second day of hydration, they have formulas of $CaZn_2(OH)_6 \cdot 2H_2O$ and $Ca_4Al_8Si_{36}O_{48} \cdot 16H_2O$.

From the tables 2 and 3 we plot versus time the Ca/Si ratios of different hydrates formed (Figure 7), which clearly shows that in dependence of time the global Ca/Si ratio increases with time hydration, and that the Ca/Si ratios with the addition of 1% of Zn-Al-Ti LDH are lower than those with 3% of addition. These results agree well with several studies showing that the variation of the stoichiometry of C-S-H in terms of the ratio Ca/Si varies

with the concentration of lime in the solution in which it is in equilibrium, so the higher lime concentration, the ratio Ca/Si of C-S-H is higher [33,34].

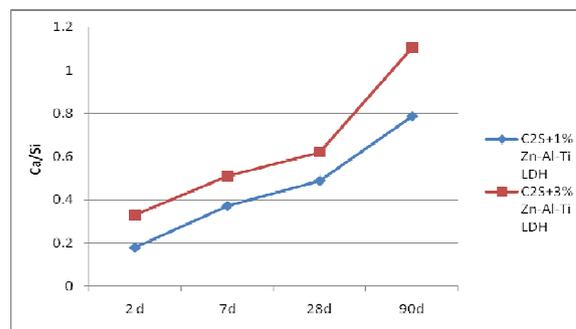


Fig. 7. Evolution of the global Ca/Si ratio of hydrated samples as a function of time

Conclusion

This study examines the mineralogical aspects of hydration of belite phase incorporating Zn-Al-Ti layered double hydroxides in time when the proportions of Zn-Al-Ti LDH varied of 1% and 3%. The results can be summarized as follows:

- As a function of the hydration time we observe a slow increasing of the formed C-S-H and a decrease in the Portlandite phase $Ca(OH)_2$, this may contribute to the increase of the mechanical resistances of the C_2S phase known having a slow hydration character and which participates essentially in the creation of long-term resistance.
- The basic elements of Zn-Ti-Al LDH interacted in the C-S-H phases that are presented in forms of different solid solutions including different proportions of Al and Zn.
- The hydrated phases formed (before 7 days), are essentially constituted by crystalline phases with low ratio Ca/Si less than 1 while in the medium term, 28 to 90 days, the identified phases become more rich in calcium and the Ca/Si ratio increases and may exceed 2 such as in the formation of Reinhardbraunsite $Ca_5(SiO_4)_2(OH)_2$.

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