

Thermodynamic and structural study of the substitution of Si by Al in C-S-H

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Abstract

Al-substituted-C-S-H samples of varying Al/Si ratio have been prepared by introducing C-S-H (Ca/Si = 0.66) powders in tricalcium aluminate hydration solution at different solid weight concentrations. The characterization of the solids by EDS (TEM) and XRD ensures that pure Al-substituted-C-S-H phases have been synthesized. Once the equilibrium is reached, both solids and solutions have been analyzed to determine the Al/Si substitution ratio according to the aluminate equilibrium bulk concentration. The results showed that a maximum of Al/Si = 0.18 is reached. An equilibrium surface reaction accounting for the Al-substituted-C-S-H formation has been considered in the framework of a thermodynamic model. The preliminary results obtained are encouraging.

1. Introduction

Aluminate phases are the second most important constituents of cement [1], just after silicate phases. Therefore, when cement is hydrated, the main appearing component, calcium silicate hydrate (C-S-H)[2], produced by the silicate phases hydration, may be influenced by the present aluminate ions [3]. Actually, it is well known that aluminium can substitute silicon in C-S-H components [1, 4-8]. This substitution may induce some modifications in their properties. Despite the numerous studies devoted to the aluminium/silicon substitution in C-S-H components, the aluminium location in the structure is not well-defined, Kalousek[9] suggested that Aluminium occurs primarily in the tetrahedral sites substituting for Silicon. Komarneni [9-12] demonstrated that tetrahedral Al occurs in both Q² chain sites and Q³ sites that link across interlayer, and significantly affects its cation exchange properties. Indeed, the synthesized aluminium-substituted-C-S-H (note C-S-A-H) is never pure but mixed with others aluminates phases (often sodium aluminate) [1, 3, 5, 13-16] which confuse the results, because Lognot [17] proposed that sodium plays an important role in charge balancing Al[III] for Si[IV] substitution. For instance, NMR is a suitable tool to investigate inorganic solid structures, but it is also very sensitive to all present phases, even the minor ones. Though structural investigations of C-S-A-H have already been well documented, especially by NMR techniques. Faucon [4, 15, 18]

used MAS and (MQ MAS) ^{27}Al NMR to provide more detailed information about the number and spectroscopic characteristics of aluminium in precipitated, tobermorite-like C-S-H. They resolve two tetrahedral Al sites, one pentahedral Al site and one octahedral Al site that they assign to C-S-H. Schneider et al [19] confirmed the presence of two tetrahedral Al sites in C-S-H from slag cements, but did not assign the observed octahedral Al to the C-S-H phase. Richardson and co-workers [20-22] used ^{27}Al and ^{29}Si NMR and trimethylsilylation (TMS) to confirm that Al occurs as both tetrahedral and octahedral Al in C-S-H of slag containing cement pastes. In their data, the absence of Q^1 sites with 1 tetrahedral Al next-nearest neighbour ($Q^1(1\text{Al})$), the relative intensities of the ^{29}Si NMR resonances for different sites, and the relative abundances of the silicate polymers of different lengths observed in the TMS data are all consistent with tetrahedral Al occupying only the bridging tetrahedral sites of the drierkette chains.

Until now, there is not any determination for thermodynamic conditions required by such a substitution, neither its consequences on the cohesion of C-S-A-H particles whereas it is well known that the cohesion of cement paste originates in the C-S-H particles interactions [23-25]. The present work aims to determine the thermodynamic equilibrium conditions of a pure C-S-A-H system. After describing the experimental procedure to synthesize pure C-S-A-H, the characterization results will be presented proving that the system obtained is pure C-S-A-H without any other phase. Then, a thermodynamic model built on the solubility of C-S-H and surface reaction equilibria will be presented to describe the Al/Si substitution.

2. Experimental

2.1. Materials

Experiments were performed by using tricalcium aluminate (C_3A), calcium oxide, silica and water. Calcium oxide was obtained by overnight decarbonation, at 1000°C , of calcium carbonate provided by Aldrich. Silica was amorphous precipitated silica provided by Rhodia with a specific area of $230\text{ m}^2\text{g}^{-1}$ and we used freshly demineralized water. All the mixtures were stirred in a thermoregulated bath at 25°C . After equilibrium, the samples were filtered, the solutions were stocked for future analyses and the solids were washed firstly with an alcohol-water mix (two times), secondly with pure alcohol, dried in vacuum conditions for 5 days, and finally stocked in a dessicator.

2.2. Methods

The chemical analyses of the solids were carried out using a JEOL JED 2300T Energy Dispersive X-ray Spectrometer (EDS) which is attached to a JEOL 2100 200 kv Transmission Electron Microscope (TEM) fitted with a hairpin type LaB6 filament. The specimen preparation procedure used in

this study was the dispersion of the powder in an ethanol solution, the deposition onto a formvar/carbon film supported by a Copper grid and the evaporation in air of the drop of the liquid. X-ray Diffraction (XRD) data were recorded using an Inel CPS 120 position sensitive detector and a Cu K α radiation ($\lambda_{\text{CuK}\alpha 1} = 1.54056 \text{ \AA}$, acquisition time was one night, voltage 40kV and intensity 40mA). The sample filtrates were analyzed by Inductive Coupled Plasma Optical Emission Spectroscopy (ICP-OES) to determine their calcium, silicon and aluminate concentrations.

2.3. Synthesis of Al-substituted-C-S-H (C-S-A-H)

The synthesis of C-S-A-H samples consists in a three-step procedure. First, C-S-H (Ca/Si=0.66) was synthesized from calcium oxide, silica and water as described elsewhere [26]. The dried C-S-H(0.66) powder was recovered using the procedure described in the materials section (§ 3.1). The second step is the hydration of C₃A in order to get a solution containing aluminate ions. The hydration reaction was carried out with a water/C₃A = 1000, in container where the hydrating suspension could be kept in motion at 25°C for 10 days. Indeed, the results of our experiences showed that in these conditions, stable and reproducible ionic composition of the solution was obtained. Then the solutions were filtered on MILLIPORE system (0.1 μm) and analysed by ICP-OES in order to obtain the concentration of calcium and aluminate ions. In the third step, known masses of the previously synthesized C-S-H(0.66) were added in a given volume of C₃A hydration solution so as to obtain weight concentrations, $W_{\text{C-S-H}(0.66)}$ (g.L⁻¹), ranging from 0 to 3.2 g.L⁻¹. After one month stirred, the solids and the solutions were separated and analysed by XRD, EDS and ICP-OES respectively as described previously (§ 3.2).

3. Results and discussion

3.1. Solids characterization

The elemental composition of the samples was extracted from the EDS chemical analyses. The initial C-S-H(0.66) sample was firstly analysed. As expected, calcium, silicon and oxygen (proton are not detectable by EDS) were detected. No other element was observed except copper arising from the TEM grid in few experiments. Those were not taken into account not to false the semi-quantitative investigation. The Ca/Si ratio of 17 spectra, acquired from different areas of the sample is shown in Fig. 1. This curve, centered on Ca/Si = 0.66, is in good agreement with the expected ratio, according to the accuracy of the technique ($\pm 10\%$ on the atomic percentage).

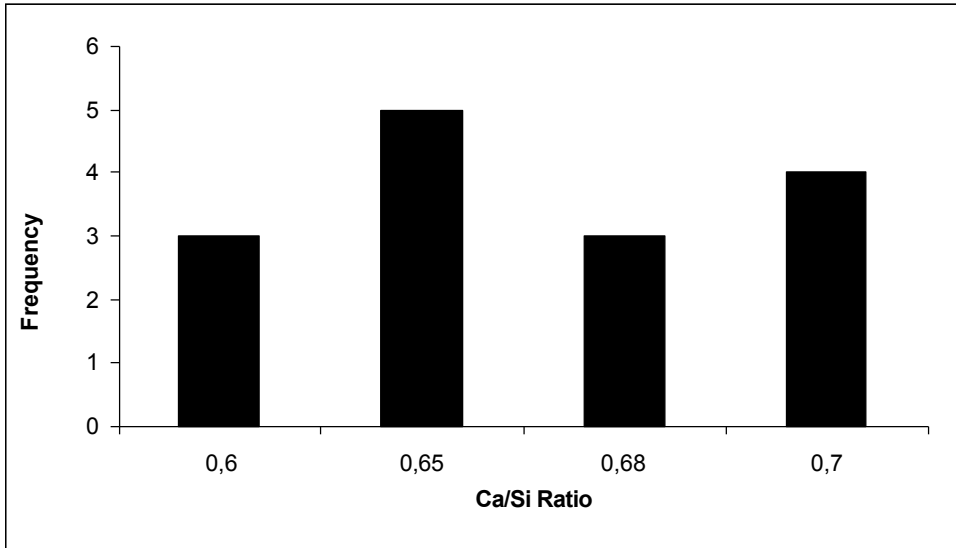


Fig.1. Ca/Si ratio frequency histogram for C-S-H(0.66)

The EDS analyses of the solids stemming from the C-S-A-H synthesis procedure showed the presence of aluminium (Fig. 2). This result has been confirmed for all our samples. The semi-quantitative analyses showed no significant variation of the Ca/(Si+Al) ratio for the various initial C-S-H concentrations $C_{C-S-H(0.66)}$. It remains nearly constant to 0.65 ± 0.03 . As already said, the results scattering cannot be interpreted as it is in the order of magnitude of the EDS technique accuracy.

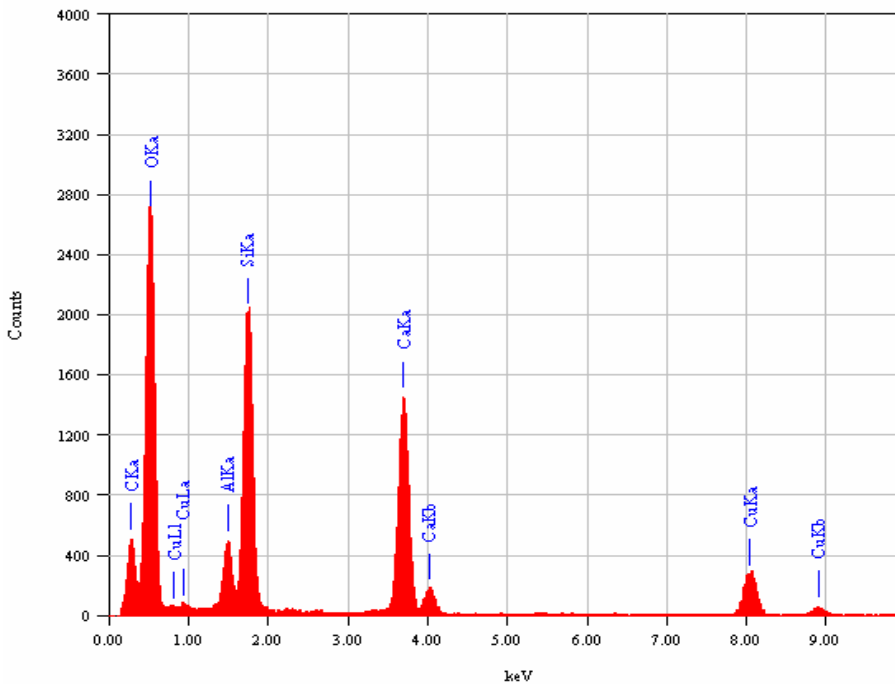


Fig. 2: Example of an EDS(TEM) analysis on a C-S-A-H sample.

The EDS analyses have been useful to prove that aluminum was present in all our samples, but XRD analyses are essential to indicate if aluminum has truly entered the C-S-H structure or if aluminate phases have precipitated besides C-S-H.

The XRD patterns of the original C-S-H(0.66) used for the C-S-A-H synthesis and of three C-S-A-H samples, the two extremes and one middle $W_{\text{C-S-H}}(\text{g.L}^{-1})$ are displayed in Fig. 3.

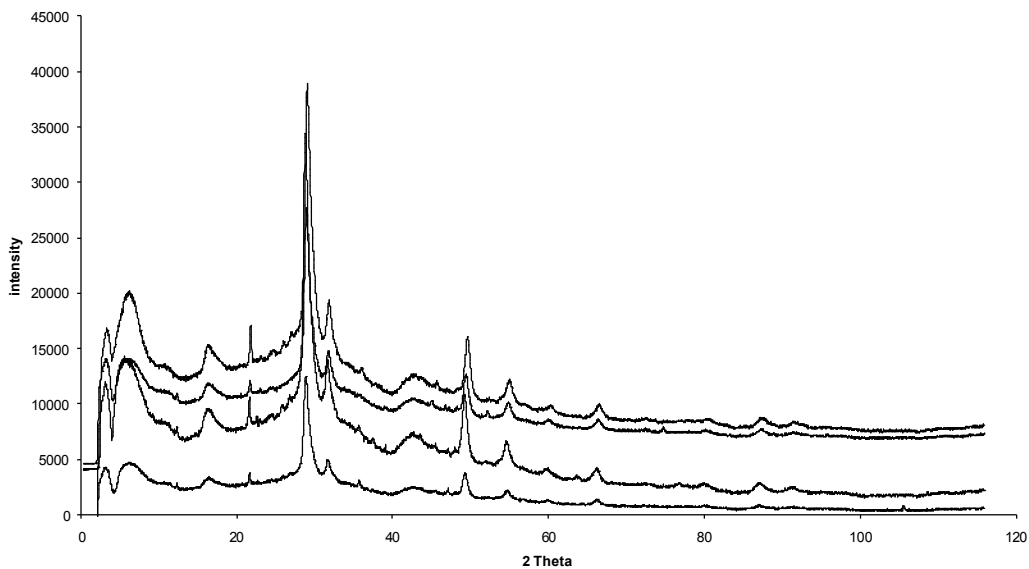


Fig. 3: X-rays diffraction patterns of three products obtained from the C-S-A-H synthesis and of the pure C-S-H(0.66). From top to bottom are C-S-H(0.66), C-S-A-H ($W_{\text{C-S-H}} = 0.4\text{g.L}^{-1}$), C-S-A-H ($W_{\text{C-S-H}} = 1.6\text{g.L}^{-1}$) and C-S-A-H ($W_{\text{C-S-H}} = 3.2\text{g.L}^{-1}$).

Fig. 3 show that only one single phase corresponding to the C-S-H(0.66) phase is present and that no other aluminate phase has crystallized besides. Therefore, we can now state that the aluminium observed by EDS analyses has entered the C-S-H structure and thus, that our synthesis of pure C-S-A-H compound has been successful. We would like to emphasize on this result because it is to our knowledge the first time that pure synthetic C-S-A-H has been obtained. Indeed, all the studies reported in the literature deal with multi-phasic systems[1, 8, 13, 14, 27, 28]. Moreover, one can notice in Fig. 3 that all the diagrams match each other. Therefore, the aluminium insertion in C-S-H does not imply any important structural modification. This feature seems to prove that aluminium substitutes silicon in existing structural positions, leaving the crystal unchanged. This is in accordance with what is generally accepted

in the literature *i.e.*, that aluminium substitutes silicon in the C-S-H bridging tetraedra [1, 10, 15-18, 21]

These results allow us to study the C-S-A-H thermodynamic equilibrium properties thanks to their aluminium content.

3.2. Determination of the Al/Si ratio

The filtrate of each sample was analyzed by ICP-OES to measure the calcium, silicon and aluminium concentrations. Fig. 4 presents these concentrations according to the initial C-S-H weight concentration W_{C-S-H} (g.L^{-1}) in the C_3A solution. The points at $W_{C-S-H} = 0 \text{ g.L}^{-1}$ correspond to the pure C_3A solution (without added C-S-H).

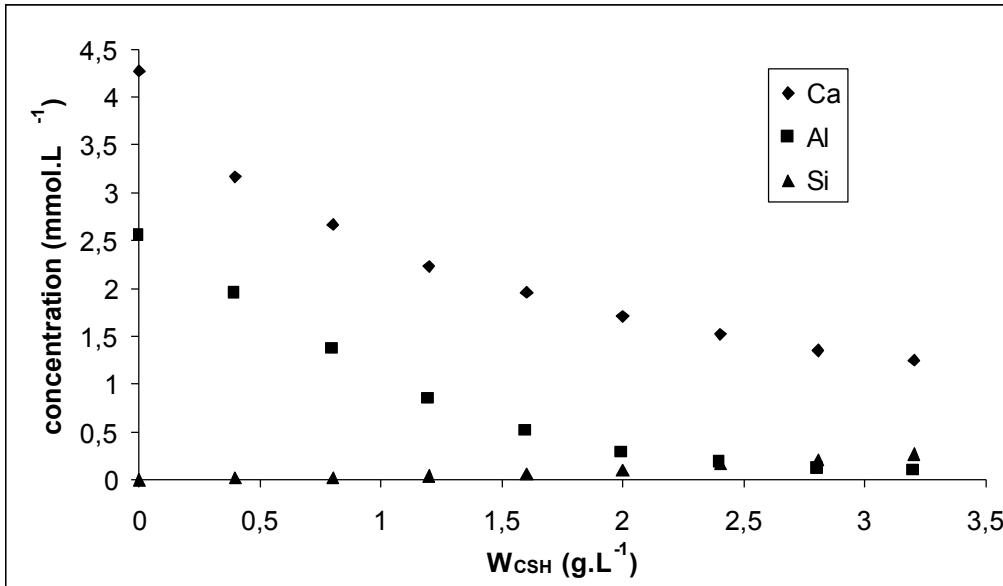


Fig. 4: Concentration of calcium, silicate and aluminate ions in the equilibrium solutions of C-S-A-H. W_{C-S-H} is the initial C-S-H weight concentration (g.L^{-1}).

The addition of C-S-H(0.66) in the C_3A hydration solution lead to a decrease of the calcium and aluminum concentrations. Afterwards, the concentration of silicate increased a few. It shows well that the more C-S-H(0.66) we added, the more aluminum disappeared from the solution and was thus incorporated into the C-S-H. The origin of the decrease in calcium concentration is twofold. First, the calcium content in the solid may increase to compensate the excess negative charge resulting from the Al/Si substitution (silicon bearing one more positive charge than aluminium). Furthermore, the solubility of the solid can also play an important role. Indeed, the EDS results showed that C-S-A-H samples keep a $\text{Ca}/(\text{Al}+\text{Si})$ ratio equal to 0.66. For this ratio, the C-S-H solubility curve points out a calcium concentration below 5 mmol.L^{-1} [26, 29-31]. The silicate concentration does not increase much with regard to the concentration of aluminate, because the silicon ions, substituted by the

aluminate ions, can continue to form C-S-H with the calcium ions present in the bulk. So the solubility of the solid also plays an important role.

From these results, it is possible to calculate the aluminium substitution rate in the C-S-A-H according to the aluminate bulk concentration. This is illustrated in Fig. 4 in terms of the Al/Si ratio in the C-S-A-H compounds. The amount of aluminum (mol) contained in a given C-S-A-H was calculated to be the difference between the aluminium amount (mol) in the initial C₃A hydration solution and in the corresponding equilibrium solution. The amount of silicon (mol) contained in the same C-S-A-H was the one present in the added C-S-H powder minus the silicon present in the C-S-A-H equilibrium solution. The quantity of silicon present in the C-S-H was estimated according to the initial quantity of SiO₂ used to react with the lime and the water and the remaining quantity of silicon in solution:

$$\frac{\text{Al}}{\text{Si}} = \frac{(n\text{Al})_{\text{in}} - (n\text{Al})_{\text{eq}}}{(n\text{Si})_{\text{C-S-H}} - (n\text{Si})_{\text{eq}}} \quad \text{Eq.1.}$$

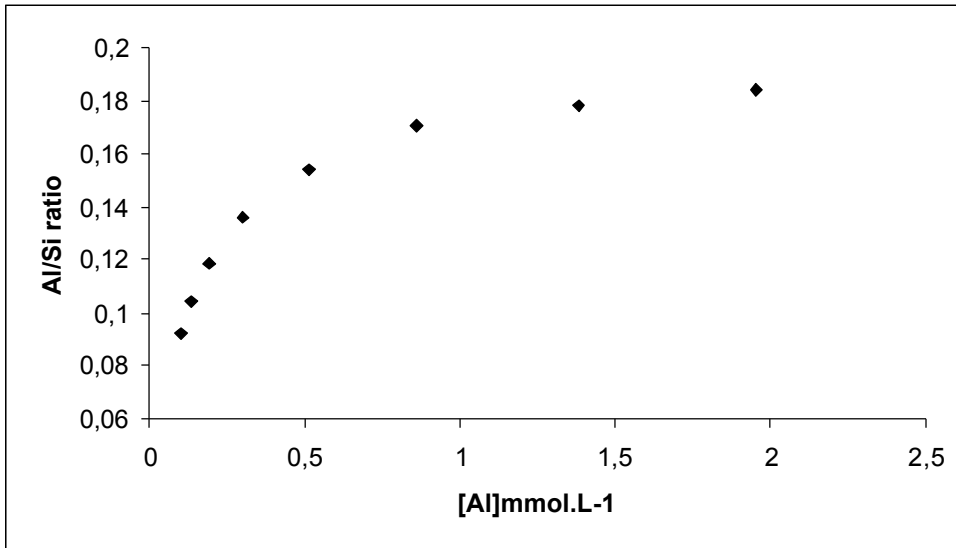
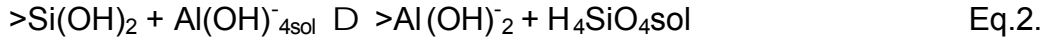


Fig. 5: Evolution of the Al/Si substitution ratio with aluminate concentration in the equilibrium solution.

Fig. 5 shows that the Al/Si substitution ratio increases up to an aluminate bulk concentration of about 0.8 mmol.L⁻¹. For a greater aluminate concentration, Al/Si aims towards a quasi-constant plateau, which would mean that the C-S-H aluminium saturation has been reached. This is in agreement with several studies of the literature reporting that the maximum Al/Si substitution rate is about half of the bridging tetrahedra [4, 15] that is one aluminium for five silicon *i.e.*, Al/Si=0.20 compared to 0.18 obtained in the present work.

3.3. Thermodynamic equilibrium constant

We aim to describe the formation of C-S-A-H in equilibrium with its interstitial solution by considering a thermodynamic equilibrium reactions. According to what has been demonstrated in the present work and to the literature [4,15], the following reaction has been chosen to account for aluminium insertion in the C-S-H structure:



that is, an aluminate tetrahedra comes and bridges two neighbour silicate dimers. Therefore, the aluminate tetraedra becomes a bridging tetraedra in the C-S-A-H structure. Hence, the following equilibrium constant is defined:

$$K = \frac{[\text{Al}(\text{OH})_2^-][\text{H}_4\text{SiO}_4]}{[\text{Si}(\text{OH})_2][\text{Al}(\text{OH})_4^-]} \quad \text{Eq.3}$$

A thermodynamic model built on the equilibrium solubility of C-S-H has been used [13]. This model has already been successfully employed in the case of C-S-H with varying Ca/Si ratio [32]. In this case, the model is described by experimentally observed changes: evolution of silicate chain length, introduction of calcium in the interlayer and inversion of surface charge. Equilibrium constants have been adjusted, taking into account the evolution of silicate chain length, surface charge of C-S-H, calcium and silicate concentrations at equilibrium in order to reproduce experimental results. For the present work, the reaction described by Eq.(1) has been added to the described model and the equilibrium constant K has been adjusted to reproduce the experimental bulk ionic concentrations and the Al/Si ratio in the solid. For this purpose the speciation software PHREEQC has been employed. The best fitted results, obtained with $\log K = -16.5$, are depicted in Figs. 6 and 7. The calculated points are in quasi-agreement with the experimental data. Actually, the trend of the concentrations and Al/Si ratio evolution is good but the calculated results do not match exactly the experimental ones. Therefore, the general ideas expressed above are good but the thermodynamic model should certainly be improved.

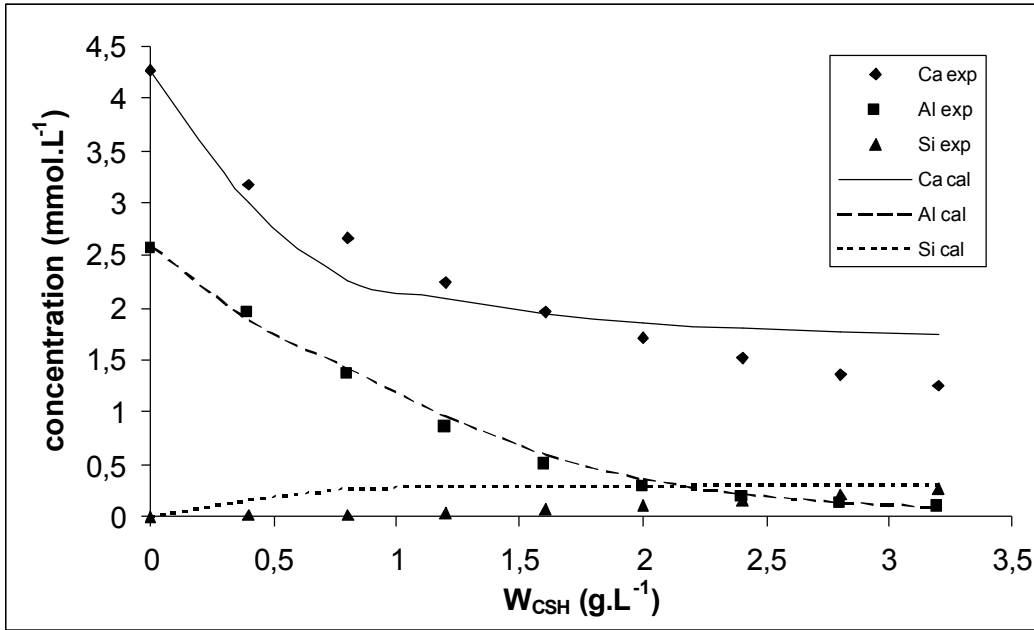


Fig.6. Same as Fig.4. The lines represent calculated bulk calcium, silicate and aluminate concentrations.

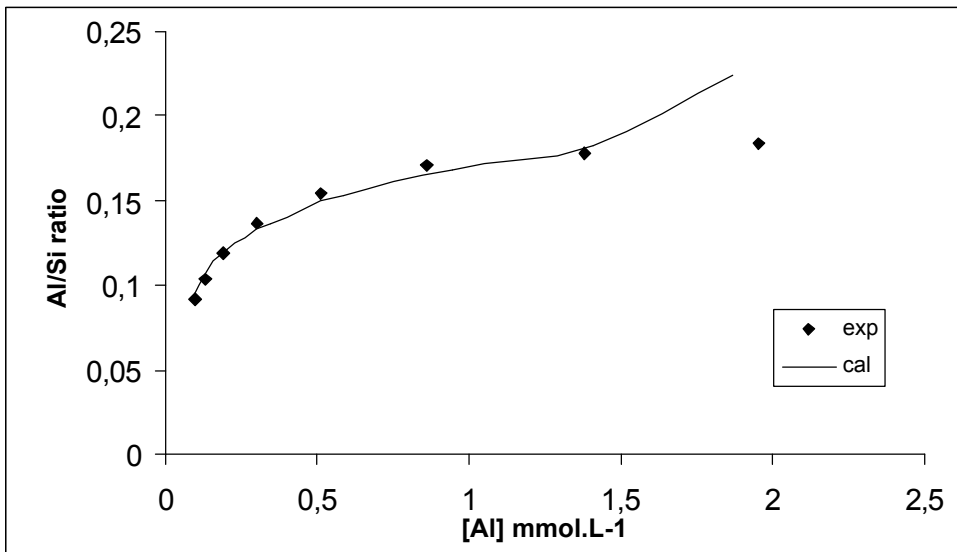


Fig.7. Same as Fig 5. The line represents the calculated Al/Si ratio versus the calculated bulk aluminate concentration.

4. Conclusion

In this study, the analyses of EDS and XRD show that we have succeeded in synthesis the pure C-S-A-H without forming any other phase. With the data of solution analyses, we have calculated the Al/Si substitution ratio according to the aluminate equilibrium bulk concentration. Finally we have used a thermodynamic model to adjust the equilibrium constant of the substitution reaction in order to reproduce experimental results.

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