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Farid Begarin, Sandrine Garrault, André Nonat, Luc Nicoleau. Hydration of alite containing alumimium. 29th Cement and Concrete Science Congress, Sep 2009, Leeds, United Kingdom. pp.9-12. <hal-00452386>

HAL Id: hal-00452386

<https://hal.science/hal-00452386v1>

Submitted on 2 Feb 2010

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Hydration of alite containing aluminium

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Abstract: The most important phase in cement is tricalcium silicate which leads during its hydration to the nucleation and growth of calcium silicate hydrate (referred to C-S-H $(\text{CaO})_x\text{-SiO}_2\text{-(H}_2\text{O)}_y$). The development of this hydrate around the cement grains is responsible for the setting and hardening of cement pastes. The general term for designating the tricalcium silicate in cements is alite. This name relates to all polymorphs containing various foreign ions inserted in their structure. These ions may influence the intrinsic reactivity and once released during the dissolution, they may interact also with C-S-H. The melt phase during clinkering is rich in aluminium and moreover the pore solution during hydration contains aluminate ions. For these reasons, the aluminium is one of the most important ion and one the most likely to influence the hydration of alite. In order to investigate these effects, an alite containing 0.1% of aluminium by weight has been synthesised. Following its hydration and comparing with pure tricalcium silicate hydration, it has been observed that aluminium presence increases the delay before reaction acceleration. The ions concentrations evolution at very early age show the formation of a C-S-H containing aluminium ions and it has been evidence that this hydrate does not act as nuclei to C-S-H growth.

1. Introduction

The cement is a material composed mainly of calcium silicate and calcium aluminate phases [1]. The most important one in terms by weight and reactivity is tricalcium silicate, C_3S . Its hydration follows dissolution-precipitation processes [2,3] leading to the heterogeneous precipitation of a calcium silicate hydrate referred to C-S-H $((\text{CaO})_x\text{-SiO}_2\text{-(H}_2\text{O)}_y)$ which is responsible for the setting and hardening of cement pastes [4,5]. Various foreign ions can be inserted in the tricalcium silicate structure modifying its crystallinity [6] and giving different polymorphs depending on ions inserted and on the manufacture process. These polymorphs have

different reactivity and consequently ions insertion might influence the dissolution and/or the heterogeneous nucleation of C-S-H. One of the most likely to be inserted in the alite structure is the aluminium. It is aimed here to study the aluminium insertion on the early hydration. The Al-rich alite hydration is compared with pure tricalcium silicate hydration in water.

2. Materials and Methods

The C_3S and the alite, composed of 0.1% of aluminium by weight of alite, used in this study have both same specific surfaces around $1\text{m}^2.\text{g}^{-1}$.

The C-S-H was synthesised in water under nitrogen atmosphere, from an appropriate amounts of lime freshly decarbonated at 1000°C and a fine silica at a liquid to solid ratio equal to 50. To obtain C-A-S-H, 40mg of previously synthesised C-S-H was equilibrated during 12 hours in 200ml of a hydrated tricalcium aluminate solution. This solution was prepared by hydrating during 11 days 0.5g of tricalcium aluminate in 500ml of water.

To monitor the ion concentrations, 13 solution samples were regularly taken during the very early C_3S hydration realized at liquid to solid ratio equal to 250. Those samples were filtrated on a $0.1\mu\text{m}$ porosity filter. Each sample was then titrated with an ICP-AES VISTA PRO Varian with axial detection system.

To follow the C_3S and alite hydration reaction degree of hydration [3] some conductimetry experiments were carried out with continuous mechanical stirring under nitrogen atmosphere at liquid to solid ratio equal to 250 at 25°C . A Tacussel CDM210 device with CDC 241-9 Radiometer probe was used here.

3. Results & Discussion

3.1. Comparison of alite and pure tricalcium silicate hydration

On figure 1 are represented the conductivity evolutions versus time carried out during hydration in the same conditions of pure tricalcium silicate and alite containing aluminium. During alite hydration the period during which the conductivity remains at the same level is clearly prolonged. The accelerating period, corresponding to C-S-H growth, is delayed. In addition, the level of the conductivity value on the plateau is lower indicating a smaller calcium hydroxide concentration. As it has been previously shown [7, 8] this period is mainly depending on the C-S-H nucleation, the monitoring of ionic species in solution have been performed in both cases during the first 30 minutes of hydration.

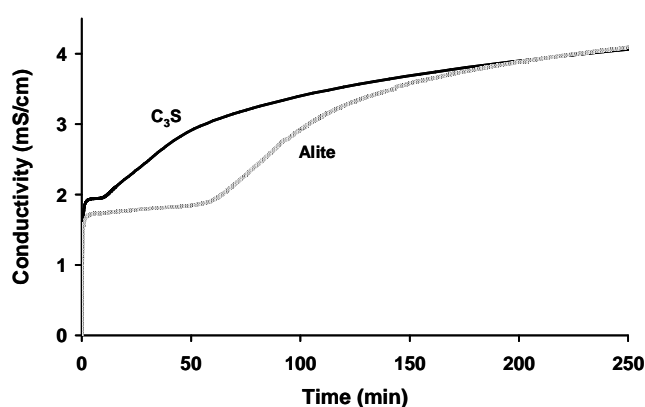


Figure 1: Evolution over the time of the electrical conductivity during hydration of tricalcium silicate and alite into pure water, $L/S=250$.

3.2. Evolution of concentrations at early age of C_3S and Al-doped alite hydration

The evolutions over the time of the ionic species concentrations in solution during the hydration of Al-doped alite and pure C_3S into water are plotted figure 2. It can be observed an initial increase of the calcium, silica and aluminum concentrations in the very early minutes of alite hydration due to the anhydrous phase dissolution. However the calcium and silica concentrations do not reach the same values than those obtained in case of pure tricalcium silicate. This is in agreement with the electric conductivity evolution of the solution.

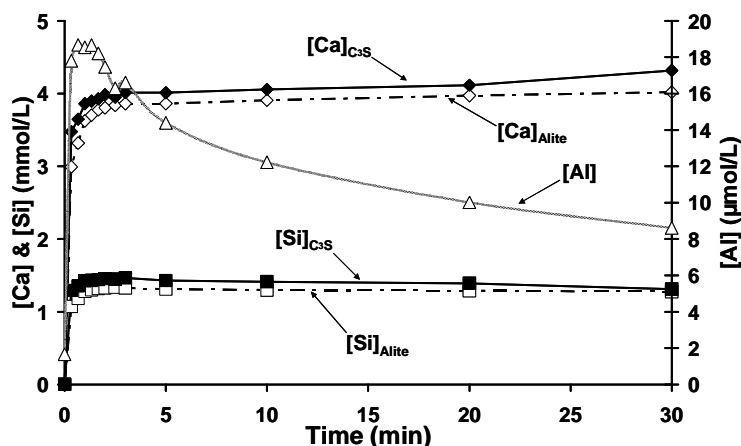


Figure 2: Evolution of concentrations of the calcium, silicate and aluminates ions in the suspension during the first 30 minutes of hydration of pure tricalcium silicate and alite in water.

After the initial increase of all ionic species due to the dissolution, there is a decrease of silicon and aluminium concentrations when the calcium concentration stands on a plateau. This behaviour reveals the precipitation of a calcium aluminosilicate hydrate. Nevertheless the identification of this precipitate is impossible via classical characterisation techniques because the precipitated substance amount is too small. Thanks to some thermodynamics calculations performed by PHREEQC software with the maximum concentrations reached in solution it is possible to say that C-S-H are more likely precipitating. It had been shown that at such aluminates ions concentration in solution some silicates could be substituted by aluminates in the C-S-H formed. Those C-S-H are calcium aluminosilicates hydrates noted C-A-S-H in cement chemistry notation. Via a mass balance calculation, it is possible to know the stoichiometry of the C-A-S-H that are precipitating. Using the difference of Ca/Si between 2min 30s and 30min and the difference of Al/Si between the same due dates, it can be found that $Ca_{2.73}Al_{0.005}SiH_2O_x$ precipitates.

This result indicates that the difference of reactivity between C_3S and alite in our case is due to aluminate ions passing into solution as soon as alite is in contact with water. This induces the precipitation of C-A-S-H which seems to not be able to grow and accelerate the hydration as C-S-H does. To verify this hypothesis seeding experiments of alite hydration have been made with both C-S-H and C-A-S-H.

3.3. Effect of seeding on alite hydration

Seeding a pure C_3S suspension more or less concentrated with synthesised C-S-H strongly accelerates its hydration. This experiment is reported on figure 3 in the case of a diluted

suspension in water; $50 \cdot 10^{-3}$ g of C-S-H are added and the acceleration occurs immediately when it only occurs 40 minutes later without adding C-S-H. On the contrary, the addition of the same amount of C-A-S-H does not shorten at all the delay existing before the acceleration of the hydration. It is clear that C-A-S-H do not play the role of surface of growth for new C-S-H as C-S-H itself does. The difference of growth ability of C-A-S-H and C-S-H has already been reported [9].

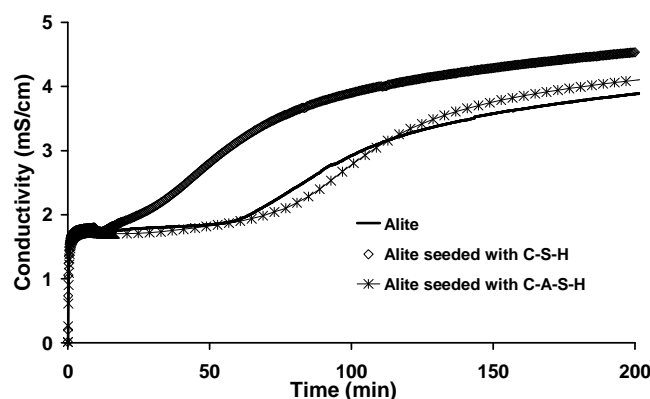


Figure 3. Evolution of electrical conductivity during the hydration of alite in water and alite seeded with C-S-H and C-A-S-H (L/S=250).

4. Conclusion

Comparatively to pure C_3S hydration in water, alite containing aluminium hydration shows a longer delay before the acceleration occurs. The experiments described here prove that the delay before hydration acceleration is linked to the aluminium which passes into solution at the early beginning. Due to aluminates in solution, C-A-S-H precipitates instead of C-S-H those first nuclei do not grow and do not act as a support for growth as the pure C-S-H does.

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