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The influence of an ion-exchange resin on the kinetics of hydration of tricalcium silicate

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ABSTRACT

The addition of a finely-ground ion-exchange resin makes it possible to modify the hydration kinetics of C_3S pastes. Analyses of the liquid phase in pastes and more dilute suspensions show that the resin exchanges calcium ions for sodium ions very rapidly during the early stage of hydration and therefore the concentration of silica in solution increases. The resin impacts the hydration of C_3S by other mechanisms which depends on the resin quantity added. For a high resin quantity, the induction period is very short, but the longer-term hydration is enhanced compared to a reference sample without resin. We hypothesize that the surface of the resin can provide sites for the nucleation and growth of C–S–H hydrates and/or portlandite far away from the surface of the C_3S grains. This consequently increases the quantity of hydrates that can precipitate before a continuous hydrate layer forms over the surfaces of C_3S particles.

Contents

I. Introduction

C_3S, or tricalcium silicate, is the major phase in Portland cement. The hydration of this compound, by a dissolution and precipitation process, leads to the formation of two types of hydrates depending on:

- the dissolution of C_3S: $Ca_3SiO_5 + 3H_2O \rightarrow 3Ca^{2+} + H_2SiO_4^{2-} + 4OH^-$
- the precipitation of C–S–H: $xCa^{2+} + 2(x-1)OH^- + H_2SiO_4^{2-} \rightarrow (CaO)_x\text{–}(SiO_2)\text{–}(H_2O)_y$
- the precipitation of portlandite: $Ca^{2+} + 2OH^- \rightarrow Ca(OH)_2$.

The main product is a calcium silicate hydrate (C–S–H) of variable composition [1,2]. This hydrate is a colloidal, nano-crystalline gel. In some cases these nano-crystals are thought to self-assemble into elementary bricks of about 60*30*5 nm [3] in size. C–S–H acts as a "glue" for the other solid components of mortar or concrete, strongly influencing the mechanical strength. The other product, portlandite

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$(Ca(OH)_2)$ is more highly crystalline and contributes less to the final mechanical strength. The mechanical strengths of a concrete or mortar also depend on the volume fraction filled by hydrates during the hydration reactions, and hence on the initial water/cement ratio and the degree of hydration of the cement, (mainly the degree of hydration of the C_3S) [4,5]. The curve of the degree of hydration versus time of the C_3S is sigmoidal and may be decomposed in to three time periods [6] as shown in Fig. 1. There is an initial part where the degree of hydration is still low. This corresponds to the precipitation of the C–S–H on the surface of the particles of C_3S. The part related to the free growth of the C–S–H on the surface of the particles of C_3S corresponds to the sudden increase of the degree of hydration. The research work done by Garrault et al. [6] shows that the nuclei of C–S–H develop parallel and perpendicular on the surface of the particles of C_3S. Finally the last part of the curve coincides with the complete covering of the anhydrous particle, which induces a slowing down of the reaction, then limited by the diffusion of reagents through the continuous layer of hydrates formed on the surface of the particle of C_3S [7–9]. Complete hydration, then governed by the diffusion regime could take several years.

It is possible to accelerate the cement's hydration process, notably the C_3S, by adding salts. The following two examples of hydration-accelerating salts are NaCl and $CaCl_2$. In the case of hydration of a suspension of C_3S in a solution of NaCl, Garrault-Gauffinet [10] showed that the hydration of C_3S begins more rapidly because the number of initially-precipitated C–S–H nuclei is greater. In the case of a paste of C_3S, Medala [11] showed that, within a 0.4 M to 1.8 M range, the addition of NaCl also modifies the growth mode of the C–S–H hydrates by favorably supporting a perpendicular (or axial) growth. This makes it possible to reach a higher hydration degree when passing to the diffusion regime than the reference sample without an addition. Furthermore, the addition of the calcium salt, $CaCl_2$, modifies the growth mode of the C–S–H nuclei: the perpendicular growth of the hydrates is privileged, allowing for a less rapid overlapping of the surface, hence reaching a higher hydration degree when passing to the diffusion regime. The addition of $CaCl_2$ however, does not have an impact on the number of initially-precipitated C–S–H nuclei.

This paper proposes a new way to manage the hydration of C_3S with the addition of ion-exchange resins. Comprehension of the modifications of the reactional mechanisms induced by these cationic exchange resins will be developed in the following paragraphs.

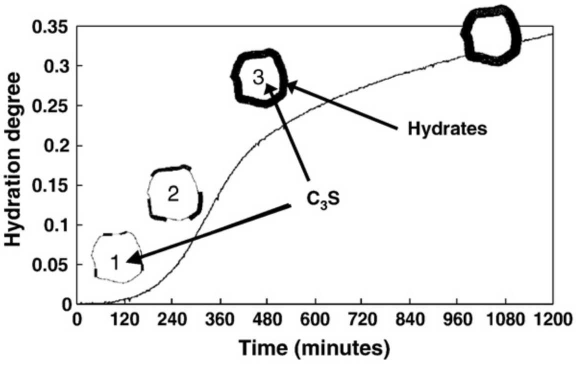

Fig. 1. Advancement curve of C_3S hydration. An initial phase is observed (1) during which the advancement is slow. The accelerated period (2) is related to the free growth of the C–S–H on the surface of the particle of C_3S. The complete covering of the anhydrous particle (3) induces a slowing down of the hydration reaction, which is then limited by the diffusion of reagents through the continuous layer of hydrates.

2. Experimental scope

2.1. C_3S preparation

For the preparation of 1 kg of C_3S, 1.316 kg of calcium carbonate, Rectapur (Prolabo), and 0.263 kg of ultra fine silica (Sifraco C600) were mixed and homogenized together using the wet method. The obtained homogenous mixture was dried in a drying oven at 110 °C over night. The obtained material was then granulated until obtaining the most homogenous sizes possible and heated to 110 °C for several hours to evaporate the water. The granules were then placed in a drying oven at 800 °C and the temperature of the sample was increased to 1600 °C by ranges of 200 °C/h followed by a one-hour plateau at 1600 °C. The C_3S was then quenched in air and crushed and ground to a finesse of 4000 cm^2/g (Fig. 2). After grinding, an analysis of the specific surface of the resin was done by nitrogen adsorption with the BET method. A specific surface of 0.9 m^2/g was obtained.

2.2. Cationic ion-exchange resin: Amberlite® IRC 747

Amberlite® IRC 747 is a cationic exchange resin produced by Rohm & Haas. Its macroporous structure is constituted of a polystyrenic matrix cross linked with Divynilbenzene and it contains the aminophosphonic group in the Na^+ form. This chelating resin has high calcium selectivity. The product such as it is presented is in the form of beads with diameters between 0.35 and 1 mm; humidity is close to 65%. The ion-exchange capacity (CEC) is 6.3 meq/g (dry resin).

The beads used in this study were dried and then ground: a batch of 240 g of resin was dried then ground using a planetary mill (the Retsch PM400 type). Four agate receptacles were used with 15 balls per receptacle and 60 g of material was put in each receptacle. The rotation speed was 300 trs/min. The grinding time of the resins was in the range of 10 min to obtain the particle size distribution curve shown in Fig. 2. An analysis of the specific surface of the resin was done after grinding by nitrogen adsorption with the BET method. A specific surface of 3.4 m^2/g was obtained.

2.3. Testing method for the treatment using Amberlite® IRC 747 in its calcium-exchange form

10 g of resins was immersed in saturated lime solution during 24 h so, a part of the sodium ions were exchanged with calcium ions. Saturated lime solution was prepared with lime freshly decarbonated at 1000 °C. Those samples were filtrated on a 0.1 µm porosity filter and dried by immersion in ethanol before new filtration.

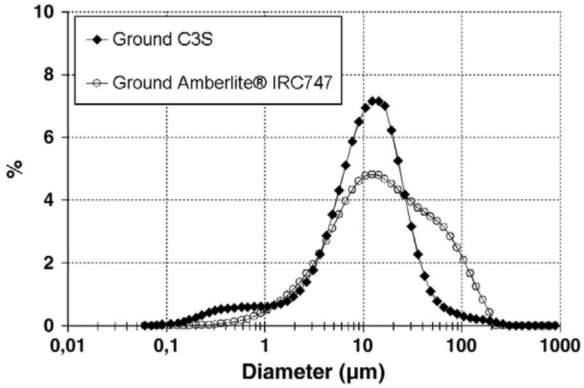

Fig. 2. Particle size analysis by laser diffraction of ground C_3S and ground Amberlite® IRC 747.

2.4. Isothermal calorimetric measurements

The hydration of cement pastes may be monitored by recording the evolution of the heat flux released during the first hours after mixing. Experiments were done using an isothermal micro calorimeter, TAM AIR 3115. The temperature of the apparatus was set at 25 °C. The introduction system of the paste in the micro calorimeter is such that it minimizes friction. The sample was lowered to the bottom of the measuring chamber using a long probe at the end of which an open capsule is attached. The mass of the sample introduced in the boat was approximately 1 g. For each dosage of resins, the calorimetric experiments are repeated three times.

2.5. Monitoring the ionic concentrations in diluted suspensions and in paste

The composition of the solutions was monitored using a spectrometer, ICP-OES Inductively Coupled Plasma-Optical Emission Spectrometry, VISTA PRO Varian. These analyses were done continuously on the diluted suspensions and by samplings on the paste. The medium to be dosed in the diluted suspension was agitated by a propeller attached to the center of a cell and connected to a motor turning at variable speeds. The cell was hermetically closed and scanned by an argon flow, derived from the main flow of the spectrometer, to prevent carbonation of the solution. Part of the solution was aspired through a filter (0.1 µm) using a peristaltic pump and entrained to the nebuliser. These experiments were done at a pump speed of 50 turns per minute. An insignificant amount was then directed towards the torch while the rest was reintroduced in the cell. This technical method makes it possible to maintain the liquid/solid ratio constant while the experiment is carried out. The measurements could therefore be done every 20 s. The dissolutions of C3S were carried out in suspensions diluted in 100 ml of de-ionized water for a liquid/solid ratio of 50.

In the case of pastes, the liquid/solid ratio was 0.4 for 20 g of C_3S. The paste was filtered using a vacuum pump after 45 s of mixing. A few micro-liters of liquid were thus recuperated after 1 min, then after 5 min at the end of the mixing operation. The samples were analyzed by ICP-OES spectrometry after being acidified.

Table 1 presents the wavelengths used to determine the concentrations of the different species.

Table 1
Wavelengths used to determine the concentrations of the different species.

Elements	Wavelengths/nm
Calcium	443.496 and 445.478
Silica	288.158
Sodium	568.821 and 589.492

3. Results and discussion

3.1. Overall description of the impact on the hydration of C_3S after adding Amberlite® IRC 747 resins

Analyses of pore solutions were done continuously on diluted suspensions to study the impact on the hydration of C_3S after the addition of finely ground Amberlite® IRC 747 ion-exchange resins. 2 g of C_3S was put in 100 ml of water, in the presence or absence of the ion-exchange resin. In the case of the resin additions, 0.36 g of ground Amberlite® IRC 747 was introduced, that is 18% of the mass of C_3S. Fig. 3 shows the definite rise of concentration of sodium in solution associated with a drop of the concentration of calcium when the resins were present: this confirms the exchange mechanism consisting of trapping the calcium ions by the resin and freeing the sodium ions in solution. For the exchange to be complete the addition of 0.36 g of resins would give a concentration of 22 mmol/L; we measured a concentration of 12 mmol/L and this resulted in an approximately 60% exchange yield.

This trapping of calcium ions, during the very first moments of the hydration, induced an increase of the maximum concentration of silica in solution; it passed from approximately 1.7 to 2.5 mmol/L. When the calcium ions are trapped by the resins, the maximum silicate increases to reach the C–S–H super-saturation level sufficient for nucleation. Thomas et al. [12] obtained similar results using a chelating agent of the calcium, Na_2EDTA. In their research work, they mixed the C_3S in water with a mass water/C_3S ratio equal to 5. An analysis of the aqueous phase was done after 20 s of mixing: comparing the silica concentrations, they passed from 0.05 mM to 5.7 mM in the control suspension without an addition and in the suspension with a concentration equal to 20 mmol/L of Na_2EDTA. This increase of concentration in silica in the presence of Na_2EDTA was associated to a drop of the initial concentration of calcium in solution. These changes of calcium and silica ions in solution can be explained by a constant solubility product for C–S–H. Thomas et al. [13] showed that by adding 50 mM of Na_2EDTA in a suspension of cement with a water/cement ratio equal to 2, an increase of the initial concentration of silica (measured after 20 s) would also be induced as well as a drop of the concentration in calcium. Nevertheless, the calorimetric curves obtained on a cement paste with a water/cement ratio equal to 0.5 showed that the addition of 50 mM of Na_2EDTA led to a delay of the hydration's initial kinetics compared to the control sample without an addition.

Fig. 4 shows the evolution of the total heat output, proportional to the hydration degree over time, during hydration of the C_3S with different quantities of ion-exchange resins. Two main points on this curve may be observed:

1. At the very beginning of hydration, one may observe that the start of hydration occurred earlier when resins were present; this acceleration was greater when there was a greater quantity of added resins. These results therefore confirm that an addition of resins accelerates the initial hydration.
2. After longer periods of time the addition of ion-exchange resins did not create a monotonic variation in the total heat output. Depending on the quantity of resin added to the C_3S, one may indeed distinguish three different trends:
   - For low levels of resins (from 0 to 0.6%) there was an increase of the released heat compared to the control sample without a resin addition.
   - From 0.6 to 2% of resins, a lower release of heat was observed on the longer term than the control sample. This drop of released heat corresponded to a lower degree of hydration when the reaction was limited by the diffusion of the reagents through the layer of formed C–S–H (for the added resins). This finding was always encountered for 4% levels but not as pronounced.
   - For high levels of resins, that is, higher than 6%, the released heat continued to increase over long time periods until exceeding the control sample without resin.

Hence, for long time periods, the hydration of C_3S in the presence of ion-exchange resins appears to react to antagonistic mechanisms. We consider that, depending on the quantity of ion-exchange resins introduced, certain mechanisms will have more impact than others, thus explaining this non-monotonous variation of the total heat output.

3.2. Impact of the liberation of sodium ions on the hydration of C_3S

In view of better understanding the impact of the liberation in solution of sodium ions on the hydration of the C_3S, complementary colorimetric measurements were monitored on paste with a mass water/C_3S ratio equal to 0.4. The first monitored hydration

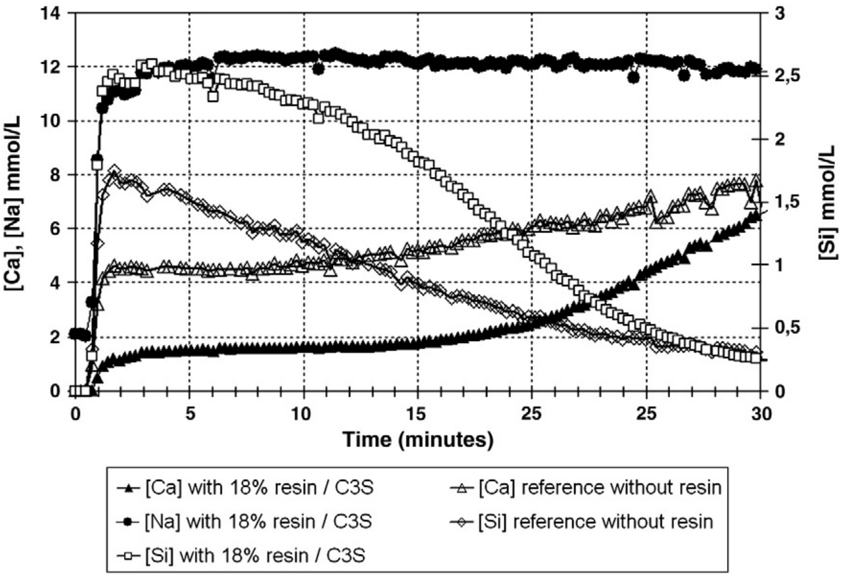

Fig. 3. Monitoring of calcium, sodium and silicon ion concentrations during hydration of the C_3S in the presence or absence of ion-exchange resins (water/solid ratio equal to 50).

measurement corresponded to a very low addition of resin equal to 0.6%. This addition of resin induced the liberation, during the very first moments of hydration, of sodium ions in the aqueous phase, due to the calcium–sodium exchange by the resin. By taking a 60% exchange yield into account, one obtained a liberation of 2.16 mmol of sodium, that is a concentration of approximately 50 mmol/L. The second monitored calorimetric measurement corresponded to the direct hydration of the C_3S in an equivalent solution of NaCl for a concentration of 50 mmol/L. Fig. 5 shows the almost similar evolution of these two calorimetric curves. There was an increase of the total heat output compared to the reference sample. This would tend to prove that for a low dosage of resin, the hydration kinetics is controlled by the liberation of sodium ions in solution; this creates an initial acceleration of the hydration process by the formation of a greater number of C–S–H nuclei on the surface of the particles of C_3S [10].

3.3. Impact of the increase of the concentration of silica on the hydration of C_3S

Our study will now focus on a paste of C_3S with a water/solid ratio equal to 0.4. Analyses of the aqueous phase were done to measure the concentration of sodium and silicate ions after 1 and 5 min of the mixing. In Table 2, one may observe that after 1 min of hydration, a 6% addition of resin induced a 453 mmol/L concentration of sodium (for a theoretical concentration of 900 mmol/L) compared to 0.7 mmol/L for the sample without an addition of resin. Here again there was an exchange yield of approximately 60% as in the diluted suspension. As previously developed, this liberation of sodium ions in solution would induce the abundant formation of C–S–H nuclei, hence an accelerated hydration start. Furthermore, in the case of the addition of ion-exchange resins, the concentration of silica after 1 min went from 1.2 mmol/L without resin to 42 mmol/L with an 6% addition of resins by mass relative to C_3S. The difference of concentration after 1 min and after 5 min was 40 times greater in the presence of resins compared to the reference sample: this means that the quantity of C–S–H, hence the initial precipitated nuclei were 40 times higher. Garrault et al. [14] did indeed show that the quantity of initially precipitated C–S–H nuclei over a given time was proportional to the variation of the concentration of silica during the same time period. This quantity of C–S–H nuclei is given by the following equation:$n_{C-S-H} = \frac{\Delta[SiO_2]*V}{\frac{X}{3}-1}$where X is the Ca/Si stoichiometric ratio of the C–S–H and V the volume of the solution.

Fig. 6 represents the total heat output for 3 different cases: hydration of C_3S in pure water, hydration of C_3S with a 6% addition of resins, and hydration of C_3S in a solution of NaCl (concentration: 500 mmol/L). All these tests were done with a mass water/C_3S ratio equal to 0.4. As already developed, the addition of 6% of resins induced a liberation of sodium ions close to 450 mmol/L. This is why the hydration of C_3S in a solution of NaCl (concentration: 500 mmol/L) was monitored. The aim was to only simulate the impact of the liberation of the sodium ions in solution. One may observe that the

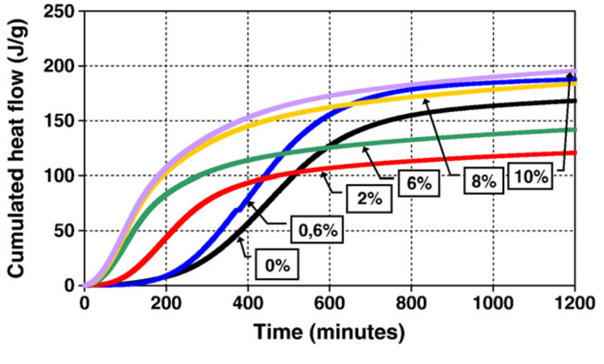

Fig. 4. Evolution over time of the total heat output of a paste of C_3S for different additions of ground Amberlite® IRC747 (% given in mass of added Amberlite® IRC747 relative to the mass of C_3S).

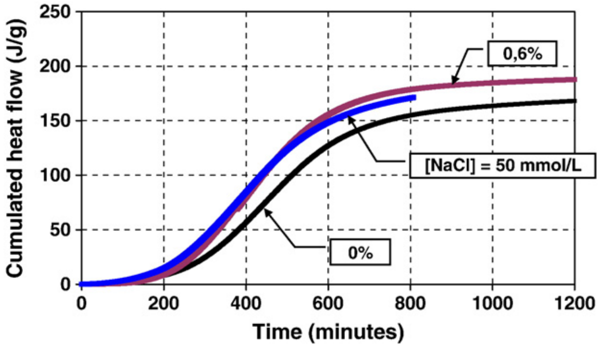

Fig. 5. Evolution of the total heat output during the hydration of a paste of C_3S with a water/C_3 S ratio equal to 0.4 with 0.6% of ground Amberlite® IRC747 and in an equivalent solution of NaCl, concentration: 50 mmol/L.

Table 2
Concentrations in sodium and silicon after 1 min and 5 min of hydration of a paste of C_3S in the presence or absence of ion-exchange resins (water/solid ratio equal to 0.4).

	C_3S		$C_3S + 6\%$ Amberlite® IRC747	
	Hydration at W/C = 0.40		Hydration at W/C = 0.40	
	At t = 1 min	At t = 5 min	At t = 1 min	At t = 5 min
[Na] in mmol/L	0.7	0.5	453	546
[Si] en mmol/L	1.21	0.24	42.4	3.8

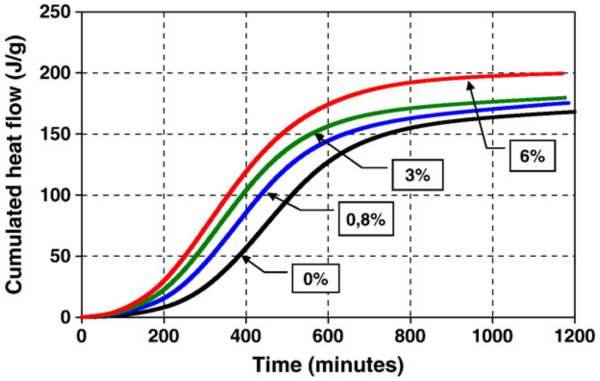

Fig. 7. Evolution of the total heat output during the hydration of a paste of C_3S with a water/C_3 S ratio equal to 0.4 for different additions of pre-treated Amberlite® IRC747 with calcium.

hydration kinetics during the very first moments of hydration was notably more accelerated in the sample where the resin was added than in a solution of NaCl at 500 mmol/L. This confirms the fact that in the case of additions of resins, there are two mechanisms at play cumulatively: the liberation of the sodium ions and the increase of the concentration of silica. These two effects make it possible to create a greater quantity of C–S–H nuclei than in the solution of NaCl. On the longer term, however, hydration of the C_3S slowed down for a lower level of hydrates in the sample with added resins compared to the solution with 500 mmol/L of NaCl. The C–S–H nuclei rapidly formed very close to or on the surface of the particles of anhydrous C_3S [14]. The multiplication of C–S–H nuclei, hence the island growth, led to a rapid covering of the surface of the particles of cement by the C–S–H hydrates; this subsequently slowed down the hydration reactions compared to the hydration of C_3S in the sample without resin. These results conform to the research work done by Garrault [6] who monitored the reaction percentage of C_3S over time according to the number of initial nuclei introduced and for different controlled concentrations of calcium hydroxide. According to this hypothesis, the greater the amount of resin introduced, the higher the concentration of silica during the first moments and the greater the amount of precipitated C–S–H nuclei, with the subsequent slowing down of the hydration on the long term.

This however does not explain how on the long term the degree of hydration, when the hydration of the C_3S has slowed down, re-increases for concentrations of resin greater than 6% (see Fig. 1) even exceeding that of the reference sample for 8 to 10% additions of resins relative to the C_3S.

3.4. Impact of the surface of the resin on the development of hydrate nuclei

We consider that the surface developed by the ion-exchange resins plays an organic support role for the nucleation and growth of such mineral hydrates as C–S–H and/or portlandite. The resin was pre-treated in a solution of lime to highlight this mechanism: this pre-treatment of the resins with calcium made an exchange possible between the calcium ions with the sodium ions of the solution. Once introduced in the paste of C_3S, during the mixing time, there would no longer be a calcium–sodium exchange mechanism between the aqueous phase and the resin because the latter would be already pre-saturated in calcium. There would also not be an increase of the maximum concentration of silica in solution nor formation of a great number of nuclei of C–S–H. In Fig. 7 the total heat output of C_3S in the presence of different quantities of pre-calcium treated resins is traced. On the long term, a monotonic increase of the total heat output relative to the quantity of pre-treated resin was observed in this case. The initial hydration acceleration was all that much greater when the quantity of added pre-treated resin was greater. We consider that this hydration-accelerating effect during the first moments is due to the more important creation of hydrate nuclei on the surface of the resin. An increase of the quantity of resin would increase its total developed surface, hence even more favorably support the quantity of precipitated nuclei. This acceleration mechanism is similar to that provoked by the addition of limestone fillers ground in a paste of cement or C_3S: it is well known that the surface of this filler makes nucleation of such hydrates as C–S–H or portlandite possible. The difference between a limestone filler and an ion-exchange resin is that in the latter case the growth of the hydrates occurs on an organic support. The greater number of nuclei remained however lower for the pre-calcium-treated resin than the resin initially neutralized with sodium because, for a same amount of resins added to the C_3S, the hydration acceleration was not as important as that of the pre-calcium-treated resin (Fig. 8).

In light of this hydrate germination hypothesis, on could expect that the growth of C–S–H and/or portlandite from these nuclei would allow part of the hydrates, which form «naturally» on the surface of the C_3S, to shift onto the surface of the resin. If part of the hydrates

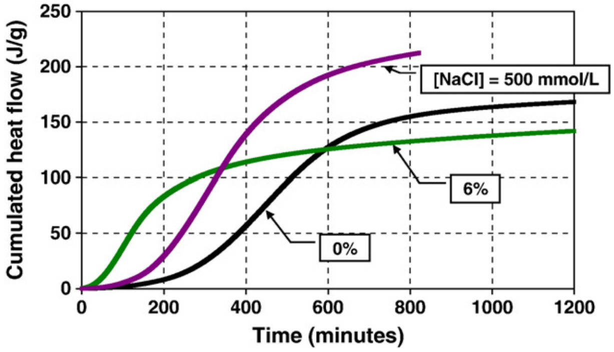

Fig. 6. Evolution of the total heat output during the hydration of a paste of C_3S with a water/C_3 S ratio equal to 0.4 with 6% of ground Amberlite® IRC747 and in an equivalent solution of NaCl, concentration: 500 mmol/L.

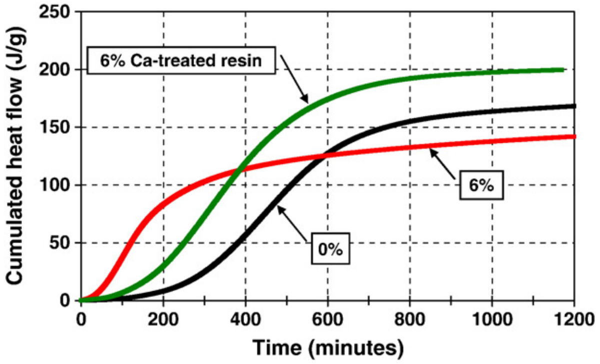

Fig. 8. Evolution of the total heat output during the hydration of a paste of C_3S with a water/C_3 S ratio equal to 0.4 for different additions of non-treated Amberlite® IRC747 and pre-treated Amberlite® IRC747 with calcium.

Table 3
Value of the total heat output during the hydration of a paste of C_3S with a water/C_3 S ratio equal to 0.4 and with different additions of pre-calcium-treated Amberlite® IRC747 with calcium, during the passage to the diffusion phase.

% Pre-calcium-treated resins	Cumulated heat flow (J/g)
0	155
3	170
6	190

shifted to the surface of the resin, at the expense of an accumulation on the surface of the particles of C_3S, this would increase the level of hydration when passing to the diffusion phase. This value of the total heat output at the passing time to the diffusion phase is determined by the intersection of two asymptotes: the first asymptote is applied to the free growth phase of C–S–H and the second to the more long-term hydration level marked by the hydration's slowing down. The values of the total heat output are listed in Table 3 for levels of resin between 0 and 6%. The total heat output increased by approximately 20% between the reference and the 6% resin samples and, in a same way, an addition of 6% of resins leads to an increase of 20% of the total surface area in the mixture (C_3S + resins).

4. Conclusions

The addition of ion-exchange resins such as Amberlite® IRC 747, in a paste of C_3S has a definite accelerating effect on early-age hydration. This acceleration is related to the abundant formation of C–S–H nuclei during the very first moments of the hydration process. On the longer term and depending on the amount of resin added to the C_3S, contradictory results may be obtained, that is, the hydration process will either slow down or on the contrary, the degree of hydration of the C_3S will increase, compared to a reference sample without an addition of resin. The advanced hypothesis aims at explaining this increase of the degree of hydration by considering the organic surface of the resin as a support for hydrate nucleation (C–S–H and/or portlandite). This increase of the degree of hydration would appear to indeed be co-related to the surface growth induced by the resin. This result would require more in-depth study: complementary tests using other types of resins or the same resin and varying the specific surface. This nucleation mechanism of the mineral hydrates on an organic support nevertheless offers new directions to broadly modify the hydration of the C_3S: this mechanism may be used to modify the setting and hardening kinetics, even in applications where the aim is to encourage mineral growth on an organic support and record the organic-mineral matrixes. Finally it would be interesting to pursue this research by carrying out tests on cement since it might not be possible to generalize all the mechanisms and phenomena observed on C_3S to cement.

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