

# The Mechanism of Action of Sodium Gluconate on the Fluidity and Set of Portland Cement

J-Ph. Perez

*Lafarge Centre de Recherche, 95 rue du Montmurier, 38291 St Quentin Fallavier*

## 1. Introduction

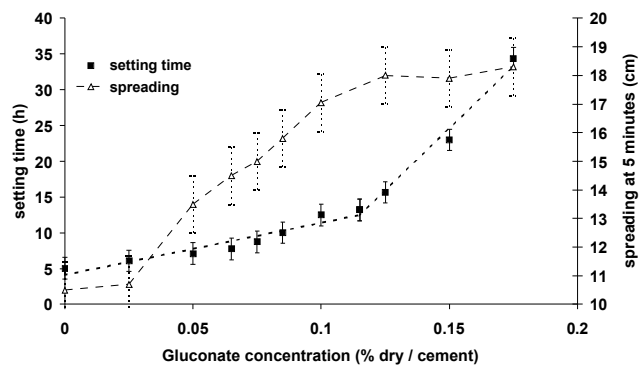
Portland cement in its purest (idealised) form is a complex multi-mineral powder composed essentially of the following five principal phases, for which the approximate pure phase compositions are given in brackets: alite ( $C_3S$ ), belite ( $C_2S$ ), tricalcium aluminate ( $C_3A$ ), calcium aluminoferrite ( $C_4AF$ ), and calcium sulfate ( $C\$\$ ). Portland cement hydrates in water following a dissolution-precipitation mechanism forming insoluble hydrates, and the resulting increase in solid volume coupled with the cohesive forces between the hydrates leads to the development of the mechanical properties that are needed for construction concretes [1, 2, 3]. The hydration kinetics of portland cements can be very complicated due to the fact that there are many possible physical and chemical interactions between the various phases in a real cement. However, we can simplify somewhat by considering two main chemical systems:

1. The silicate phases (alite and belite), hydration of which produces only calcium silicate hydrates (C-S-H) and portlandite ( $Ca(OH)_2$ ). C-S-H is usually assumed to be the main binding phase responsible for setting and development of mechanical strengths [4, 5].
2. The aluminate phases plus calcium sulfate, which react almost independently at early ages to form calcium aluminate hydrates, mainly ettringite ( $C_6A\$_3H_{32}$ ). These reactions are believed to have a major influence on the rheological properties of fresh concretes [6].

In order to modify the rheological and/or mechanical properties of concrete, chemical admixtures are often included in the concrete formulation. "Water Reducing Admixtures" (WRAs) are commonly used in Ready Mix Concrete applications at dosages of the order of about 0.1% per mass of dry cement. They are dispersants that allow concretes to be made with lower water/cement ratios (w/c) for the same initial flow, leading to better rheology and higher ultimate strengths, although they may also lead to some set retardation. Sodium gluconate is commonly used as a major component of commercial WRA formulations. It is a strong set-retarder but usually improves the flow properties of cement pastes at constant w/c. In order to explain this behaviour, many studies have been devoted to the interactions between cement and gluconates at early ages. Tenoutasse [7] showed that ettringite formation can be impeded, apparently due to the adsorption of gluconate molecule on  $C_3A$  surfaces,

hindering their hydration. Using optical rotation measurements, Casu [8] observed the rapid formation of an aqueous complex between gluconate and calcium ions ( $\text{Ca}^{2+}$ ) which then adsorbed onto  $\text{C}_3\text{A}$  surfaces. A similar mechanism has been observed for a calcium aluminate cement (“Ciment Fondu”) hydrated in presence of sodium gluconate [9]. Vidick *et al* [10] thought that small molecules such as gluconate used at low dosages, (glucoheptonate in their study), could not work by direct blockage of the surfaces of the anhydrous phases, and was more likely to act by poisoning the nucleation and/or growth of hydration products. However, their actual data do not clearly support this hypothesis. Milestone [11] simply assumed that poisoning of hydrate nucleation sites could explain his SEM observations of clean surface of  $\text{C}_3\text{S}$  grains hydrated for 50 days in presence of 0.1% of gluconate. But, in our opinion, the true mechanism of cement retardation by gluconates remains elusive.

The work in this paper was inspired by a simple observation, made when mortar tests were conducted to optimise the dosage of gluconate for use as a retarding water-reducer in concrete. The results, shown in Fig. 1, clearly show two successive linear domains for setting time, the first having a gentle slope and the second having a much steeper slope (i.e. there is a very rapid increase in set retardation with increasing dosage beyond the break point in the curve). This behaviour, which is crucial in field applications, has been reported before by Vernet [12], but no detailed explanation has yet been advanced. On the same graph we also show the mortar flow expressed as a spreading measurement after five minutes of hydration. Two separate domains can also be identified, the first one observed for very low dosages apparently corresponding to a “threshold dosage” needed to obtain any fluidifying effect, and the second one an increase towards an asymptotic flow value at high dosage which appears to correspond to a “saturation dosage” beyond which additional gluconate does not further increase the mortar workability. [Note that the asymptotic flow value observed here is not due to a physical limit on the flow measurement since higher flows can be obtained with the same mortar formulation by using other admixtures such as lignosulfonates, etc.].



**Figure 1: Variations of setting time and spreading at 5 minutes versus SG dosage measured on mortars made at  $w/c = 0.6$ ,  $T = 20^\circ\text{C}$ .**

The remainder of the work described herein was aimed at answering the following questions:

- What are the mechanisms of cement retardation by gluconate?
- Why are there two linear domains with different slopes?
- Is the adsorption of the gluconate at the origin of the retardation or fluidification?
- Can the saturation dosage for mortar flow be related to a maximum surface coverage?

## 2. Experimental

### 2.1. Materials

#### 2.1.1. Minerals

The composition of the Portland cement used is given in table 1. For selected experiments we used pure C<sub>3</sub>S made in our laboratory (triclinic form with free CaO less than 1%). The specific surface area determined by Blaine's method was 3600 cm<sup>2</sup>/g ( $\pm$  50 cm<sup>2</sup>/g) for both minerals.

**Table 1: Chemical and mineralogical analysis of Portland cement (CEM I – 52.5N)**

#### 1a: Chemical analysis

CaO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	SO <sub>3</sub>	K <sub>2</sub> O	Na <sub>2</sub> O	CaO f	Na <sub>2</sub> O eq sol
64.53	20.73	4.55	2.76	3.46	0.91	0.06	0.33	0.59

#### 1b: Bogue-calculated major phases, and calcium sulfates determined by DSC

C <sub>3</sub> S	C <sub>2</sub> S	C <sub>3</sub> A	C <sub>4</sub> AF	L.O.I.	SSB	Gypsum	Hemi-hydrate
60.7	12.5	7.4	8.4	1.2	3570	2.1	0.8

#### 2.1.2. : Organic additives

Sodium gluconate (SG) solutions were obtained by dissolving powder (D-gluconic acid sodium salt, 97%) in de-ionized water. All gluconate dosages are expressed as mass of gluconate ion per mass of solid.

### 2.2. : Methods

#### 2.2.1.: Gluconate Adsorption

Suspensions of cement or C<sub>3</sub>S in solutions of SG were prepared at a water/cement mass ratio of 5, and were stirred at 20°C for various times before being centrifuged and filtered prior to analysis by means of a TOC (Total Organic Carbon) apparatus. The fraction of gluconate adsorbed was estimated from the difference between the initial organic carbon concentration and the concentration measured in the supernatant minus the value obtained for the blank (admixture-free cement).

### 2.2.2.: Solution Chemistry

The procedures were essentially the same as described above, but the chemical evolution of the suspension was followed continuously by electrical conductivity measurements. In addition, liquid phase samples were withdrawn at various times, filtered on a 0.3  $\mu\text{m}$  filter, diluted with HCl, and analysed for total calcium and sulfur by means of an Inductively Coupled Plasma apparatus. Some additional experiments in which  $\text{C}_3\text{S}$  was suspended in portlandite-saturated solutions were conducted at a liquid/solid ratio of 50 rather than 5 as used above. In all cases the suspensions were maintained at  $20^\circ\text{C}$  ( $\pm 1^\circ\text{C}$ ) before filtration.

## 3. : Results and discussion

### 3.1. : Adsorption

#### 3.1.1.: Experimental results

Adsorption kinetics were initially studied at four different initial SG dosages (0.05%, 0.07%, 0.12% and 0.14%). This range was intentionally selected in order to bracket the "saturation dosage for spreading" of about 0.11% observed in mortar tests conducted on the same cement at  $w/c = 0.6$  (Fig. 1). Fig. 2 shows the fraction of the initial SG adsorbed vs. time in stirred cement suspensions at  $w/c = 5$ . It can be seen that, regardless of initial SG dosage, about 75% of it is adsorbed within the first 5 minutes and not much more after that time. In fact, all four percentage adsorption curves are identical within experimental error, which implies simple concentration-proportional adsorption.

A set of 5-minute adsorption experiments was conducted on the same cement at SG dosages up to 1%; results are shown in Fig. 3. A break point appears in the adsorption vs. dosage curve at a SG dosage of 0.38%, beyond which the fractional adsorption decreases rapidly from the initial plateau of 75%. This seems to imply some kind of saturation of the cement particle surfaces at a SG dosage over three times greater than that required for the maximum spreading in mortar (as estimated from Fig. 1.)

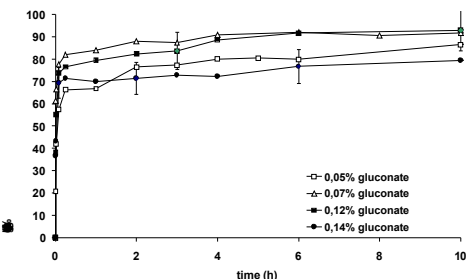


Figure 2: Evolution of the fractional gluconate adsorption vs. time for cement suspensions with different initial SG dosages. ( $T = 20^\circ\text{C}$ ; liquid/solid ratio:  $l/s = 5$ ).

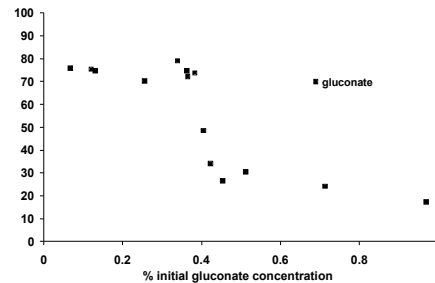


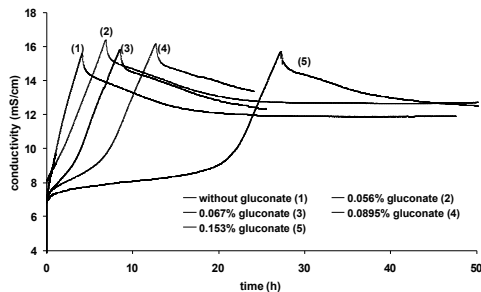
Figure 3: Fractional Gluconate adsorption at 5 minutes vs. initial Gluconate dosage. ( $l/s = 5$ ,  $T = 20^\circ\text{C}$ ).

### 3.2.: Hydration kinetics

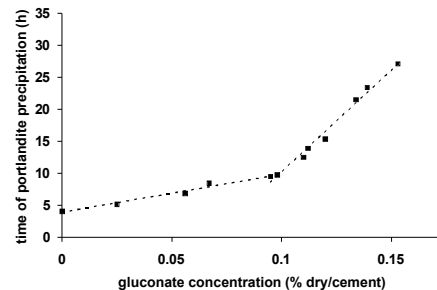
#### 3.2.1. : Electrical conductivity: cement

When  $C_3S$  reacts with water in dilute suspensions, calcium silicate hydrates (C-S-H) precipitate almost immediately but the concentrations of dissolved calcium and hydroxide ions (and thus the conductivity) increase slowly until the solution reaches the maximum supersaturation necessary for rapid massive portlandite precipitation. This precipitation point is easily identified as a sharp peak on conductivity vs. time traces of dilute  $C_3S$  suspensions, and can also usually be identified even in Portland cement suspensions, despite the simultaneous occurrence of other reactions that influence the absolute conductivity value.

Fig. 4a shows the electrical conductivity as a function of time and SG dosage for our cement slurries at  $w/c = 5$ . The results show that the time of rapid portlandite precipitation is strongly retarded by quite low dosages of SG. Fig. 4b plots the time of rapid portlandite precipitation versus initial SG dosage. Two successive linear domains are found which show a very similar SG dosage dependence to the setting time observed in the mortar tests, (fig.1). This is consistent with the widely-accepted view that setting of Portland cements is mainly related to  $C_3S$  hydration and the consequent formation of C-S-H and portlandite. The much longer timescale of the conductivity experiments can be explained by the fact that the  $w/c$  ratio in these suspensions is almost an order of magnitude higher than in the mortar tests.



**Figure 4a: Variation of electrical conductivity vs. time for cement slurries made with different initial SG dosages. ( $I/s = 5$ ,  $T = 20^\circ C$ ).**



**Figure 4b: Time of rapid portlandite precipitation vs. initial SG dosage ( $I/s = 5$ ,  $T = 20^\circ C$ ).**

#### 3.2.2. : Ionic concentrations

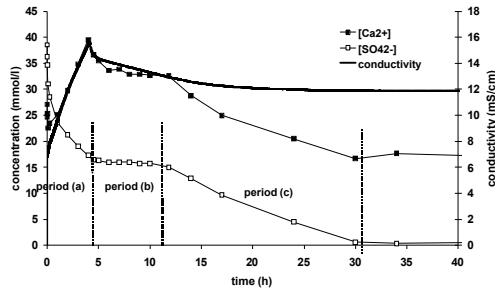
Fig. 5a shows the evolution of  $Ca^{2+}$  and  $SO_4^{2-}$  concentrations and electrical conductivity vs. time for the SG-free cement suspension at  $w/c = 5$ . Alkali ( $Na^+$ ,  $K^+$ ) concentrations are not shown because they remain roughly constant at a total of 35 mM throughout the whole period. The only other ion in solution at significant concentrations is hydroxide which can be estimated by difference by assuming charge balance. Other ionic species

such as aluminate, silicate or ferrite are only found at very low concentrations. It is usually found that the conductivity closely follows  $[\text{OH}^-]$  since this ion has by far the highest specific conductance and also usually the highest concentration except at very early ages. However, for most of the time before the end of period (b), changes in  $[\text{OH}^-]$  are roughly proportional to changes in  $[\text{Ca}^{2+}]$  because both alkali and sulfate concentrations are fairly constant, which explains the close correspondence between the conductivity and  $[\text{Ca}^{2+}]$  curves observed here. Ignoring the rapid changes in  $[\text{Ca}^{2+}]$  and  $[\text{SO}_4^{2-}]$  during the first few minutes, (which are due to rapid dissolution of calcium sulfate hemihydrate and precipitation of gypsum), we see a slow rise in  $[\text{Ca}^{2+}]$  during period (a), since  $[\text{Ca}^{2+}]$  provided by the dissolution of alite is only partly offset by C-S-H precipitation. At the same time,  $[\text{SO}_4^{2-}]$  decreases in order to maintain the solution saturated with respect to gypsum. Soon after the onset of rapid portlandite precipitation, a plateau in  $[\text{Ca}^{2+}]$  is obtained due to roughly constant portlandite and gypsum saturation levels until all of the solid gypsum has been consumed at the end of period (b). There is then a slow, almost linear decrease in  $[\text{SO}_4^{2-}]$  and  $[\text{Ca}^{2+}]$ , assumed to be due to continued ettringite formation, until  $[\text{SO}_4^{2-}]$  reaches almost zero at the end of period (c).  $[\text{Ca}^{2+}]$  finally approaches a steady state value is determined mainly by the solubility of portlandite in an alkali hydroxide solution, the concentration of which depends on the soluble alkali content of the cement at the w/c used.

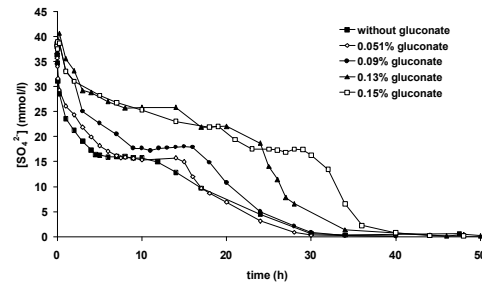
Fig. 5b show the evolution of  $[\text{SO}_4^{2-}]$  vs. time for similar suspensions as a function of SG dosage. It can be seen that SG alters the rate of sulfate uptake. Periods (a) and (c) are respectively lengthened and shortened by increasing SG dosage, while the duration of period (b) remains roughly constant for SG dosages up to at least 0.09%, leading to little change in the overall time to the sulfate exhaustion point (about 30 hours), which implies that the reactions of the silicate phases and the aluminate phases in the cement are almost completely independent at these lower SG dosages. At higher SG dosages, however, the time to the sulfate exhaustion point is extended significantly, suggesting that strong retardation of the silicate phase hydration can also have a slight retarding effect on aluminate phase hydration, perhaps simply by the blocking of some aluminate surfaces by unreacted silicate phases in multimineralic cement grains.

There is also an interesting change in the rate of decrease of  $[\text{SO}_4^{2-}]$  during period (c) which is usually assumed to be directly proportional to the rate of precipitation of ettringite, since it is thought that there is no longer any sulfate available in solid gypsum particles at this time, and so all of it must be coming from the solution. At lower SG dosages, the rate of ettringite precipitation first increases (twice/three times higher than without additive) and then evolves like the reference. Surprisingly, the shortening of period (c) is compensated by the lengthening in period (a) since the overall time to consume sulphate ions remains unchanged (fig 5b). This implies that the acceleration in period (c) is somehow influenced by the

initial retardation due to the presence of gluconate in period (a). For the higher SG concentrations (> 0.1%), typically 0.13% and 0.15%, the ettringite precipitation rate is also higher than that of the reference.



**Figure 5a: Ionic concentrations and electrical conductivity vs. time for a cement slurries ( $l/s = 5$ ;  $T = 20^\circ\text{C}$ ).**

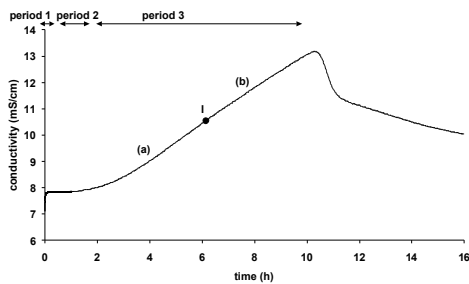


**Figure 5b: Sulfate concentrations vs. time for cement slurries with different SG dosages ( $l/s = 5$ ;  $T = 20^\circ\text{C}$ ).**

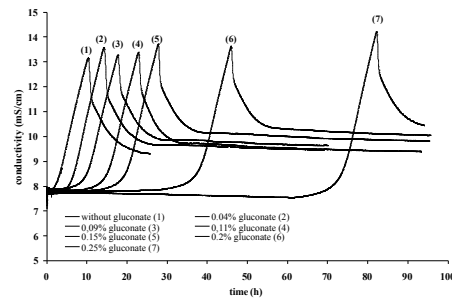
### 3.2.3. : Influence of SG on tricalcium silicate ( $C_3S$ ) hydration

Many studies have been devoted to the hydration mechanism of  $C_3S$ , which remains complex [1,2,6,13,14]. A typical conductivity curve for a dilute  $C_3S$  suspension in saturated limewater is shown in figure 6a. Period 1, which is only measurable at very high water/solid ratios, involves the congruent dissolution of  $C_3S$  to give mainly  $Ca^{2+}$ ,  $OH^-$  and  $H_3SiO_4^-$  ions. The conductivity hardly changes from the value of the saturated limewater, but the silica concentration increases very significantly (although it is still roughly three orders of magnitude lower than the calcium concentration) and solution quickly reaches supersaturation with respect to C-S-H, provoking heterogeneous nucleation of this hydrate on the surface of the  $C_3S$  particles. The "apparent induction period" of the kinetics (period 2) depends on the amount of C-S-H nuclei formed. After, C-S-H begins to grow from some of the initial nuclei, leading to an acceleratory period (period 3)[14]. Later on, this C-S-H begins to form a diffusion barrier around the grains, which is characterized by the onset of a second deceleration in the hydration rate at point I. So, in period 3a, C-S-H clusters grow on the very thin initial hydrate layer on the  $C_3S$  surface, but in period 3b, this reaction begins to be limited by diffusion of some species (probably silicate ions) through the layer of hydrates. Massive portlandite precipitate occurs at a certain "critical supersaturation" (represented here by a conductivity of a little over 13 mS/cm,) leading to a rapid sharp drop in conductivity, marking the end of period 3, and complexifying the interpretation of the conductivity curves beyond that point. At water/cement ratios more typical of ordinary concrete this point occurs much earlier and is often considered to mark the end of the "induction period" (period 2), which is usually very short at low w/c and especially in the absence of retarding admixtures such as gluconates.

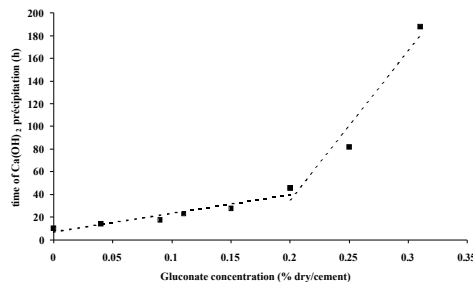
Fig.6b shows conductimetric curves for  $C_3S$  hydrated in saturated limewater at  $w/c = 50$  and with various SG dosages. The curves differ mainly by the length of period 2, but it is easier to measure the sharp peak representing the end of period 3. Plotting the time of the peak against SG dosage in Fig 6c, we see an initial linear domain at low dosages, followed by an upward curve which begins to diverge strongly above a SG dosage of about 0.15%. This result confirms that strong retarding effect of SG on the hydration of  $C_3S$  manifests itself during or before the “induction” period where stable C-S-H clusters nucleate. Once the nuclei begin to grow (period 3), all curves keep the same shape, implying that, at this time, the hydration kinetics remains similar regardless of the presence of SG, i.e. the C-S-H growth rate is not affected by gluconate. Within the framework of Garrault and Nonat’s model[14], this in turn implies that the number of stable C-S-H nuclei formed per unit of  $C_3S$  at the onset of the acceleratory period is the same whatever the gluconate dosage. However, no information could be directly obtained about the earliest hydration steps, (dissolution and hydrate nucleation) from these conductimetric curves.



**Figure 6a:** Typical conductivity curve for dilute  $C_3S$  suspensions in saturated limewater ( $l/s = 50$ ,  $T = 20^\circ C$ ).



**Figure 6b :** Conductivity vs. time for  $C_3S$  in saturated limewater at various SG dosages. ( $l/s = 50$ ;  $T = 20^\circ C$ ).



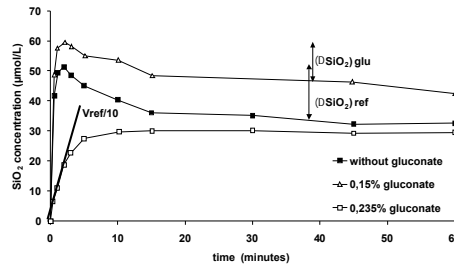
**Figure 6c:** Time of rapid portlandite precipitation vs. initial SG dosage for  $C_3S$  suspensions in saturated limewater ( $l/s = 50$ ;  $T = 20^\circ C$ ).

### 3.2.4. : Influence of gluconate on $C_3S$ dissolution and C-S-H nucleation

The influence of SG on very early  $C_3S$  hydration was studied by following the silica concentrations versus time in stirred suspensions at a  $w/c$  ratio



of 50. Two SG dosages were used: 0.15% (at the end of the first dosage domain, just before the breakpoint) and 0.235% (well into the second domain). Variations in calcium concentration are not shown because they are negligible with respect to the 22mM of the saturated limewater used to prepare the suspensions. This dilute suspension approach allows us to effectively buffer the lime concentration, which is the most important factor controlling the nucleation process [14]. The three  $[\text{SiO}_2]$  vs. time curves obtained are plotted in fig. 7.



**Figure 7: Dissolved silica concentration vs. time for  $\text{C}_3\text{S}$  suspensions in saturated lime water with and without SG additions. ( $l/s = 50$ ;  $T = 20^\circ\text{C}$ ).**

In the absence of SG, the very rapid initial increase of silicate concentration is ascribed to congruent  $\text{C}_3\text{S}$  dissolution. Based on the measured silica concentration of 0.042 mM after only 30 seconds (the earliest time at which a sample could be taken), one can estimate an initial dissolution rate for this  $\text{C}_3\text{S}$  suspension of at least  $1.3 \times 10^{-6}$  mol/L/s, which, considering the water/solid ratio used, implies a specific dissolution rate,  $da/dt$ , of at least  $1.5 \times 10^{-5}$  s $^{-1}$ . After this,  $[\text{SiO}_2]$  quickly reaches a maximum value which is believed to correspond to the maximum possible supersaturation with respect to C-S-H and which is then followed by a decrease due to C-S-H precipitation, leading to a steady state concentration supposedly in near equilibrium with respect to C-S-H, which seems to be reached after about 20 minutes at this w/c.

It is important to note that the initial dissolution rate is very fast compared to the later hydration of the  $\text{C}_3\text{S}$ . The apparent dissolution rate of  $1.3 \times 10^{-6}$  mol/L/s for silica can be multiplied by 1.3 for calcium if it is assumed that the solid C-S-H formed has a C/S ratio of 1.7. Garrault's model [14] assumes that  $\text{SiO}_2$ , the difference between the maximum  $[\text{SiO}_2]$  observed and the asymptotic value after apparent equilibrium with initial C-S-H is reached, is proportional to the number of C-S-H nuclei formed initially on the surface of the  $\text{C}_3\text{S}$ . The value obtained here for the reference sample without SG,  $(\text{SiO}_2)_{\text{ref}}$ , is about 16  $\mu\text{mol/l}$ , similar to the actual values obtained by Garrault. It can be seen that a SG dosage of 0.150%, (which represents a concentration of 154  $\mu\text{mol/l}$  at this dilution), reduces the apparent  $\text{SiO}_2$  slightly, to about 12  $\mu\text{mol/l}$ , but does not appear to change the initial dissolution rate (as estimated from the first data point). If anything, it seems to slightly reduce the number of C-S-H nuclei precipitated at a given time, but the asymptotic value of  $[\text{SiO}_2]$

remains higher than the value for the reference sample even after 60 minutes. Given that the gluconate molar concentration is more than two orders of magnitude lower than the lime concentration, it is hard to believe that this effect could be due to calcium chelation; it seems much more likely to be due either to silica chelation or else to the stabilization of dispersed C-S-H nuclei which can escape filtration.

At the higher Gluconate dosage tested here, (0.235%, equivalent to 241  $\mu\text{mol/l}$ ) the form of the early age  $[\text{SiO}_2]$  vs. time curve is very different. An apparent decrease in the initial  $\text{C}_3\text{S}$  dissolution rate by a factor of 10 with respect to the system hydrated without additive is observed, implying that gluconate at this concentration acts essentially instantaneously as a dissolution inhibitor. This result is similar to the observations of Rettel regarding the action of gluconates on a calcium aluminate (Fondu) cement [9]. Note that, at this high SG dosage, it is difficult to see an early-age maximum in  $[\text{SiO}_2]$ , but yet the later hydration of the suspension during period 3 still follows almost exactly the same conductivity profile as the others, despite a very long induction period. This seems to imply that the number of C-S-H formed after 60 minutes is very small. On the other hand, the asymptotic value of  $[\text{SiO}_2]$  after 60 minutes is not very different from that of the reference sample, which seems to imply that both solutions are in near-equilibrium with the same type of C-S-H and that the hypothesis of excess silica being chelated and thus maintained in solution by gluconate cannot be correct.

We are thus forced towards the hypothesis that the gluconate can adsorb directly onto  $\text{C}_3\text{S}$  dissolution sites fast enough to block them before they can release much silica into solution, thus avoiding the formation of many dispersed C-S-H nano-particles in the initial reaction.

The dissolution of  $\text{C}_3\text{S}$  in very dilute suspensions is presumably initially controlled by a surface reaction and is favoured at localized active sites where the reactions have lower activation energy. The actual initial dissolution rates can be much higher than those observed here, however. According to the calculation given in [6], Damidot and Nonat observed rates of at least  $1.4 \cdot 10^{-5} \text{ mol.s}^{-1}.\text{m}^{-2}$  in very dilute suspensions ( $w/c = 5000$ ) in pure water, whereas the highest rate that we observe here is only equivalent to about  $1.8 \cdot 10^{-7} \text{ mol.s}^{-1}.\text{m}^{-2}$ , suggesting that the presence of saturated limewater and the much lower dilutions used here already strongly retard dissolution. At low SG concentrations it appears that blockage of alite dissolution sites compete partially with all the other retarding processes and, up to a certain "break point" above which retardation increases rapidly with additional gluconate. For our sample of  $\text{C}_3\text{S}$ , this break point occurs somewhat above 0.15%, whereas for our cement it appears (Fig. 1) to occur at about 0.12%, which is not too unreasonable considering that the cement has roughly the same Blaine value as the  $\text{C}_3\text{S}$  and contains about 70% calcium silicates (mostly alite). If we assume that, at the break point, about 75% of the gluconate is adsorbed (as in Fig. 3) and that at this point this can block all of the active sites on  $\text{C}_3\text{S}$ , this implies that about 1.1g of SG (about 6 millimoles) can

block all the active sites on one kg of our C<sub>3</sub>S with a Blaine specific surface area of 360 m<sup>2</sup>/kg, giving a critical gluconate coverage of about 3.1 mg/m<sup>2</sup> or about 16 μmol/m<sup>2</sup>. If all of this gluconate were adsorbed, this would, (assuming a density of about 1g/ml spread over the Blaine specific surface area), represent an adsorbed gluconate layer of the order of 3nm in thickness, which should indeed be sufficient to completely block the surface.

Fig. 8a plots the time to the massive portlandite precipitation peak vs. SG dosage for three C<sub>3</sub>S samples having different granulometric curves (insert), the latter two produced by regrinding our original C<sub>3</sub>S. Clearly, the finer the C<sub>3</sub>S, the shorter the time to portlandite precipitation and the higher the SG dosage at the apparent breakpoint. Plotting the Gluconate dosage at the breakpoint against the percentage of particles below 3μm (fig. 8b) gives a linear correlation. These results validate the assumption of a strong interaction between gluconate and the C<sub>3</sub>S surface. The higher the C<sub>3</sub>S specific surface area, the higher the gluconate dosage needed to saturate it. Measurement of the actual specific surface area available for gluconate adsorption is not so easy, since the Blaine method is probably not really appropriate in this case.

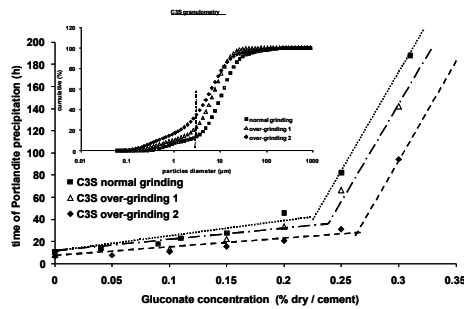


Figure 8a: Time of rapid portlandite precipitation vs. SG dosage for three C<sub>3</sub>S sample of different fineness, as detailed in insert. (Saturated limewater, l/s = 50; T = 20°C).

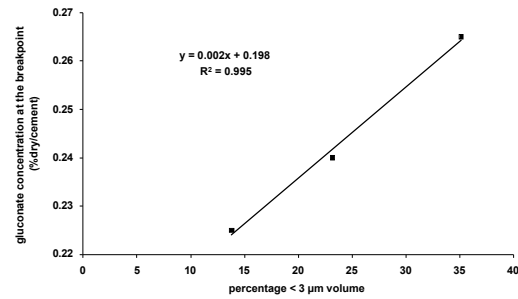


Figure 8b: SG dosage at the breakpoint vs. the percentage of C<sub>3</sub>S particles < 3μm.

#### 4. Discussion

The questions that still remain to be answered at this point are (a) why are dosages below the break point not nearly so effective at retarding C<sub>3</sub>S hydration as dosages above it, (b) why is the saturation value for initial SG adsorption on the cement (about 0.38%) so much higher than that apparently required to block all the adsorption sites on alite.

Question (a) in fact relates to the dissolution step and the length of the “induction period”, and what factors control them. According to [14] the length of the induction period only depends on the number of C-S-H nuclei while the growth mode of C-S-H mainly controls the acceleratory period. The fact that there is almost no induction period in the absence of a

retarder implies that the lengthening of the induction period is directly related to the surface interactions resulting from the presence of adsorbed retarder. The evidence cited earlier regarding the effect of gluconate on the evolution of silica concentrations in solution seems to imply that, for gluconate dosages below the break point, the  $C_3S$  dissolution rate is not changed but a small number of C-S-H nuclei is formed initially due to a gradual saturation of the active dissolution sites by the adsorbed gluconate. It is thus relatively easy to understand that this could lead to a roughly linear increase in the induction period with gluconate concentration in this dosage range, assuming that the length of the induction period shortens in proportion to the amount of C-S-H formed initially. However the number of C-S-H nuclei formed at the end of the induction period appears to be the same whatever the SG dosage since once the nuclei begin to grow during the period 3, all conductivity curves keep the same shape, implying that, at this time, the hydration kinetics remains similar regardless of the presence of SG, i.e. the C-S-H growth rate is not affected by gluconate.

Once the breakpoint is passed, we assume that there is enough gluconate to neutralize all the active dissolution sites. C-S-H nuclei form more slowly as the SG dosage increase.

To validate these assumptions, over-grinding of  $C_3S$  have been performed in order to increase the number of small particles and so the number of active dissolution sites. In this case, it appears that the finer the  $C_3S$ , the higher the gluconate concentration to obtain the breakpoint. This confirms a strong interaction between gluconate and reactive sites of  $C_3S$ : the higher the number of reactive sites, the higher the gluconate concentration needed to saturate the reactive sites.

About question b, the fact that the 5-minute SG adsorption isotherm on the cement (fig. 3.) shows a saturation point at about 0.38%, whereas one would have expected a much lower saturation point based on the break points in the setting time and conductivity curves, implies that adsorption on the non-silicate phases in the cement (presumably the aluminates and their hydrates) must account for the bulk of the adsorption. The adsorption on these phases may be weaker than that of the silicates, but must be present to some extent. Since it appears that gluconate do not have a strong retarding effect on the aluminate-sulfate reactions, and it is known that these reactions usually produce large amounts of hydrates (AFm phases and ettringite) during the first few minutes of hydration [6], they can give rise to a large additional surface area for possible gluconate adsorption. This type of adsorption can in many cases contribute to changing the rheology of the cement, although the rheological benefits appear at very low SG dosages in this case (fig. 1.), suggesting that they probably arise more from adsorption on alite than on the aluminate phases.

## 5. Conclusions

We have confirmed that gluconate adsorbs readily on cement particles to generate a weak fluidifying effect at fairly low dosages. However, the "saturation" dosage for maximal fluidification occurs well below the apparent adsorption saturation on the cement. Thus, the fluidification is probably mainly due to that fraction of the adsorption that occurs onto the "silicate-phase surfaces" (alite, belite, and any C-S-H that forms at early ages).

Gluconate is also a strong retarder for cement hydration, and we have shown by experiments with pure  $C_3S$  that this retardation also occurs mainly via adsorption onto alite. There is a "break point" in the retardation vs. dosage curve, beyond which the retardation rapidly becomes very severe. For both cement and  $C_3S$  of typical Blaine specific surface areas (about  $360 \text{ m}^2/\text{kg}$ ), this break point occurs at about 0.15 – 0.20 % SG per mass of alite. If the specific surface area of  $C_3S$  is increased, the break point dosage also increases roughly linearly, confirming that it must be related to specific surface adsorption sites on alite.

At dosages below this break point, gluconate seems to have little effect on the aluminate-sulfate reactions of the cement. At dosages above it there is an apparent retarding effect on the uptake of sulfate which we believe can probably best be explained by an indirect effect due to the strong retardation of the silicate phase hydration in multimineralic cement grains.

The mechanism by which gluconate retards alite hydration seems to involve two distinct dosage regimes. At lower dosages it is not capable of completely neutralize all the active dissolution sites of the alite. A higher dosages, beyond the apparent "break point", the gluconate can apparently adsorb on alite surfaces (or at least, on the active dissolution sites) rapidly enough to partially or completely inhibit any initial C-S-H formation greatly lengthening the induction period.

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