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Alkali carbonation of calcium aluminate cements: influence of set-retarding admixtures under hydrothermal conditions

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The preferential uptake of aluminium ions by lactone and carboxylic acid groups in glucuronic-6,3-lactone and gluconic acid suggested that these organic admixtures have a high potential as set-retarding admixtures of high-temperature calcium aluminate cement slurry. However, the liberation of abundant free calcium ions caused by the adsorption of aluminium ions by the admixtures, increased the carbonation rate of hydrated cement pastes after exposure to Na_2CO_3-laden water at 300 °C. Using inorganic acid admixtures, such as boric acid and sodium tetraborate decahydrate, the retarding ability of colloidal $Ca(BO_2)_2 \cdot nH_2O$ and aluminium hydroxide yielded by the reaction between admixture and cement was less than that of the reaction products derived from organic acid admixtures. Although $Ca(BO_2)_2 \cdot nH_2O$ in hot Na_2CO_3 solution was converted into $CaCO_3$, the rate of alkali carbonation was almost the same as that of admixture-free calcium aluminate cement pastes.

1. Introduction

Well cements resistive to high-temperature (~300 °C) brine containing carbon dioxide (CO_2) are needed for use in completing geothermal wells. Conventional cement systems used to complete wells through aquifers containing ~1000 p.p.m. CO_2 at ~130 °C have all shown severe deterioration, with failure of the cement and casing after only 90 days in service. The cause of such severe damage was the combination of the attack of CO_2-laden hot brine, and the alkali metal-catalysed hydrolysis of the cement hydrates brought about by sodium cations. Thus, formulation of an alkali carbonation-resistant hydrothermal cement is an important way to ensure a long service-life of the cementing materials which support the intermediate casing pip and protect the casing from corrosive fluids and gases. In our recent study of alkali carbonation of autoclave-treated polymer–calcium aluminate cements [1], we found that the major reason for the considerable loss in strength of polymer-unmodified cements exposed to Na_2CO_3-laden water at 300 °C was the high conversion rate of calcite into water-soluble calcium bicarbonate salts, which directly reflect the formation of the porous microstructure in the hydraulic cement matrix. In contrast, we found that the Ca–OOC complexed polymer structure formed in polymer-modified cements inhibits the alkali carbonation reaction of cement hydration products.

When cementing materials are applied in practical geothermal wells at an elevated temperature, set-retarding admixtures must be incorporated into the cement slurry to provide a thickening time long enough for filling up the space between the casing pip and the ground wall. This requirement suggested to us that the influence of set-retarding admixtures in inhibiting or accelerating alkali carbonation of the calcium aluminate (CA) cement hydrates should be investigated as part of an ongoing research programme to formulate a hydrothermally and CO_2-resistant cement. Accordingly, our emphasis was directed toward a fundamental understanding of how the set-retarding functions of organic and inorganic admixtures inhibit and accelerate the alkali carbonation reaction of hydrated CA cement pastes in the Na_2CO_3-laden water at 300 °C. Our approach to gaining this information was by using the combined techniques of atomic absorption spectrophotometry (AA), X-ray photoelectron spectroscopy (XPS), infrared (IR) spectroscopy and thermogravimetric analysis (TGA). From a literature survey [2–5], we selected five representative retarding admixtures; glucuronic-6,3-lactone (GL) and gluconic acid (GA) as organic species, and boric acid (BA),

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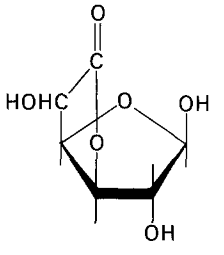
sodium tetraborate decahydrate (Borax) and sodium pyrophosphate (Na–P) as inorganic ones.

2. Experimental procedure

2.1. Materials

The organic and inorganic reagents, glucuronic-6,3-lactone, GL (I), gluconic acid, GA (II), boric acid, BA, (H_3BO_4), sodium tetraborate decahydrate, Borax ($Na_2B_4O_7 \cdot 10H_2O$), and sodium pyrophosphate, Na–P ($Na_4P_2O_7$), were employed as cement set-retarding admixtures. Calcium aluminate, CA, cement was the high-temperature cementing material. The typical chemical composition of the cement was 46.5 wt % Al_2O_3, 35.5 wt % CaO, 6.0 wt % Fe_2O_3, 8.5 wt % SiO_2, 0.7 wt % MgO, and 2.0 wt % SO_3.



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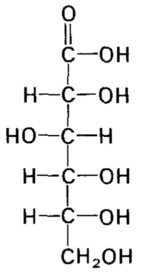


(II)

2.2. Measurements

To obtain information on the ion uptake of the retarding admixtures, the concentrations of ionic species, such as calcium and aluminium were determined by atomic absorption spectrophotometry (AA) in the liquid extracted from the admixture-modified cement slurry. The pH of the extracted liquids was measured before the AA analysis. The samples for AA were prepared in the following sequence. First, 12.6 g retarding admixture was thoroughly mixed with the 144 g water. Then 210 g CA cement was incorporated into the retarding solution, and agitated with a magnetic stirrer at room temperature for 10, 30, 60, 300 or 1440 min. The aqueous phase was then extracted by centrifugal separation.

The thickening time of the retarded cement slurries at hydrothermal temperatures of 50, 70, 120 and 170 °C under a nitrogen gas-pressure of 35.5, 35.8, 70.3 and 110.9 MPa, respectively, was measured using a Halliburton High Pressure Consistometer. Tests were conducted in accordance with the following procedure: approximately 1000 g mixed slurry was poured into a consistometer slurry container which was then pressurized with nitrogen gas before raising the temperature. The pressurized fluid mixtures were stirred by the paddle at a speed of ~100 r.p.m., and the viscosity (units of consistency) was monitored with the d.c. voltage indicator as a function of stirring times at the isothermal temperature.

The amount of $CaCO_3$ formed in the retarded cements after exposure for 24 h to hot 0.05 M Na_2CO_3 solution was measured by thermogravimetric analysis (TGA) and by the weight loss at which the thermal decompositions of $CaCO_3$ occur over the range 600–770 °C. In preparing TGA samples, all the retarder-modified CA cement pastes (consisting of 67 parts CA cement and 33 parts water with the admixture of up to 10% by weight of CA cement mass) were exposed to 300 °C water.

X-ray photoelectron (XPS) and infrared (IR) spectroscopy analyses were conducted to identify the reaction products formed by the interaction between the retarder and the cement paste. Two different samples, a cement liquid extracted by centrifugal separation of a 60 g CA cement-40 g water slurry, and the retarder-saturated aqueous solution, were mixed using a magnetic stirrer for 10 min, then left for 24 h at room temperature to complete the precipitation of the colloidal reaction products. The precipitated reaction products were dried at 110 °C to give samples of powder for XPS, IR and TGA measurements.

3. Results and discussion

3.1. Retarding admixture

Fig. 1 shows the variations in concentration of calcium and aluminium ions dissociated from the inorganic and organic retarder-modified CA cement solutions at room temperature. The amounts of both calcium and aluminium ions in the unmodified CA cement solution (denoted as the control) increased with agitating time until the concentration reached a peak of ~8.0×10^{-3} mol l^{-1} for calcium and ~3.2×10^{-2} mol l^{-1} for aluminium after 60 min. The concentrations then decrease gradually to ~1.2

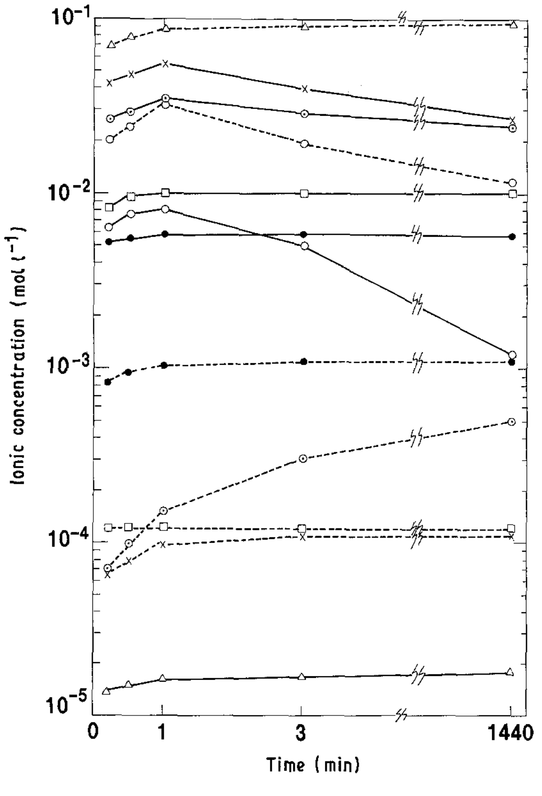


Figure 1 Changes in calcium and aluminium ion concentrations as a function of agitating time for CA cement slurries modified with admixtures; (○) control (△) Na–P, (●) Borax, (□) BA, (⊙) GA, (x) GL. (——) Calcium ions, (– – – –) aluminium ions.

$\times 10^{-3}$ mol l^{-1} for calcium and $\sim 1.2 \times 10^{-2}$ mol l^{-1} for aluminium after 1440 min. The curves also indicated that amount of aluminium ions liberated from the cement pastes is higher than of calcium. The control appears to liberate a large amount of calcium and aluminium ions from the surfaces of the paste during 1 h agitation: thereafter, we believe that a nucleating reaction might occur, precipitating the $CaO–Al_2O_3–H_2O$ system. The latter phenomenon can be postulated from the decrease in the amount of dissociated calcium and aluminium ions. With the sodium pyrophosphate (Na–P) admixture, we observed a dramatic reduction of free Ca^{2+} ions to a very low level, ranging from 1.4×10^{-5} to 1.7×10^{-5} mol l^{-1} after agitating for up to 1440 min, while a large number of aluminium ions dissociated from the cement pastes.

Of particular interest is the suppression by organic and inorganic acid admixtures of the dissociation of aluminium ions from the cements. Because the alkali-catalysed hydrolysis of lactone groups leads to their transformation into carboxylic acid groups [6], the glucuronic-6,3-lactone (GL) admixture also was categorized as a species of mild acid-type retarder. As is evident from the data (Fig. 1), aluminium ions are greatly reduced by adding boric acid (BA) and GL, whereas abundant calcium ions are liberated from the cement in the aqueous medium. Although the retarded cement solution was continuously agitated for 1440 min, the concentration of aluminium ions detected was only 1×10^{-4} mol l^{-1}, two orders of magnitude less than that of the control. Gluconic acid (GA) also inhibits the dissociation of aluminium ions initially. However, prolongation of stirring resulted in a conspicuous increase in concentration of the dissociated aluminium ion. By comparison with these acidic admixtures, the ion-trapping behaviour of the sodium tetraborate decahydrate (Borax), which is a salt compound of boric acid, differed; Borax not only absorbed the aluminium ions at a relatively high level, but also trapped some calcium ions. As a result, the magnitude of liberation of free calcium ions caused by aluminium uptake was in the order GL > GA > BA > Borax. These data also suggested that the extent of uptake of aluminium and calcium ions depends on the pH of the cement solution modified with the admixtures. The acidic admixtures have an affinity for aluminium ions. Fig. 2, which shows the correlations between the ion concentration and the pH for the admixture-modified cement solutions, clearly supports the concepts on distinctive ion uptake described above. The figure shows that a lowering of pH value by incorporating GL and GA into the cement solution corresponds to a low aluminium ion and a high calcium ion dissociation. In contrast, the Na–P cement solution which has a pH < 11.0 is indicative of low calcium and high aluminium ion concentrations.

To investigate the practical retarding activities of these acid- and base-type admixtures, we measured the thickening time for the retarded cement slurry samples consisting of 61 wt % CA cement, 30 wt % water and 9 wt % admixture using the Halliburton High Pressure Consistometer at an isothermal condition of 50, 70, 120 and 170 °C, respectively. Fig. 3 shows a typical relationship of viscosity–stirring time for the slurry samples at 50 °C. When the slurry starts to gel, the viscosity value (arbitrary unit), denoted as units of consistency, increases rapidly. The thickening time, T_t, of the samples was estimated from the curves by finding the intersection point of two linear extrapolations. Without retarder (control), the slurry gels after stirring for $\sim$20 min at 50 °C, and with acidic admixtures, the thickening time was extended to > 120 min. In particular, the effect of BA and GL admixtures on extending thickening time was outstanding. In contrast, the alkaline Na–P admixture seems to accelerate the gelation of cement slurry, showing that the thickening time of slurries is shorter than that of the control. Thus, we decide to eliminate Na–P in evaluating the retarding ability of admixtures at higher temperatures and pressures. Table I summarizes the thickening time for these samples at isothermal temperatures up to 170 °C. The extent of effectiveness on the retarding activity of acidic admixtures was GL > GA > BA > Borax. The inclusion of GL, which is the most effective admixture resulted in a thickening time of 210 min at 50 °C, 190 min at 70 °C, 150 min at 120 °C, and 85 min at 170 °C.

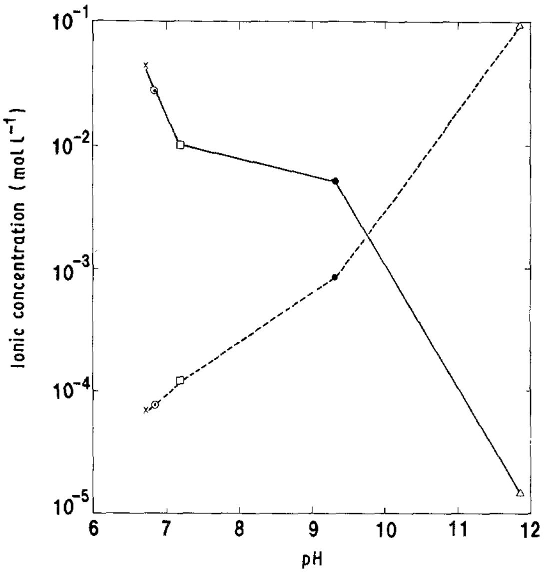


Figure 2 Degree of calcium and aluminium uptake versus pH of admixture-modified cement slurries: (△) Na–P, (●) Borax, (□) BA, (○) GA, (×) GL. (——) Calcium ions, (– · –) aluminium ions.

On the basis of this information, we identified the GL–, BA–, and Borax–cement paste reaction products which retard the setting of CA cement slurries, using XPS and IR analytical tools. Fig. 4 shows XPS survey scans for the colloidal reaction products precipitated by the interaction betwen CA cement solution and the GL-, BA-, or Borax-saturated solutions. The spectrum (a) for the GL–cement reaction products indicates the presence of an intense O_{1s} and C_{1s} in the additional aluminium signals. No evidence of a signal for the calcium atom was found, suggesting that GL preferentially reacts with aluminium ions dissociated from the CA cement. The emergence of a calcium signal, with relatively weak intensity can be seen in Spectrum (b) of BA–cement reaction products. In conjunction with the

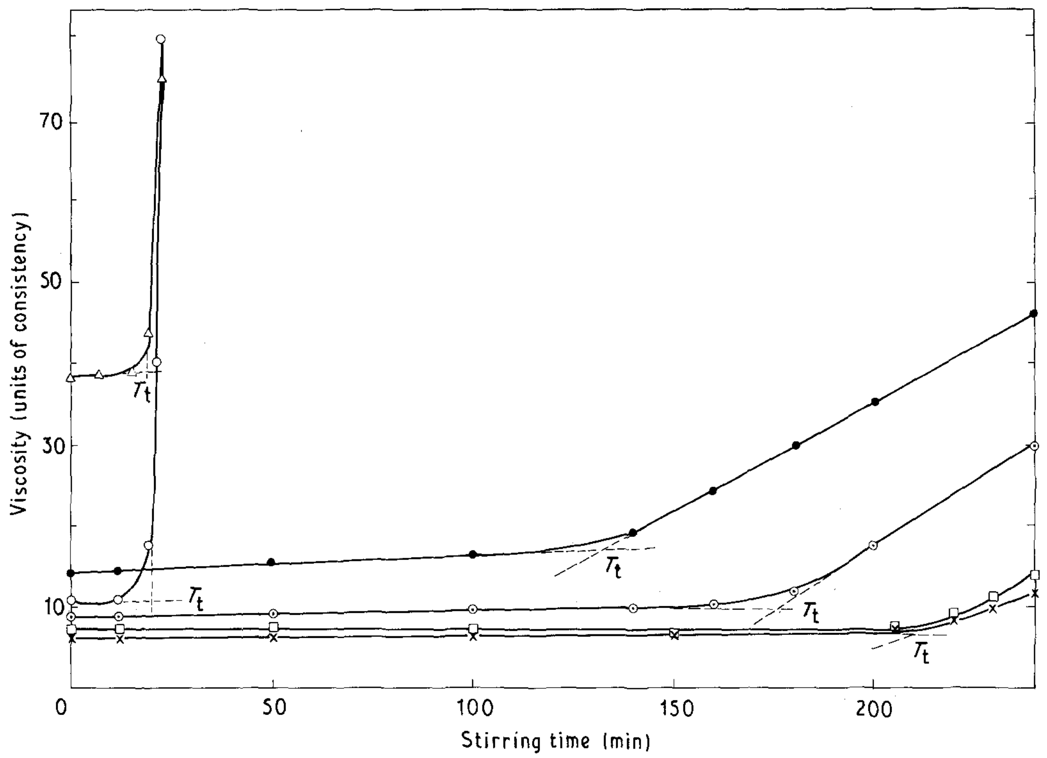
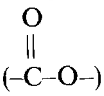


Figure 3 Viscosity–stirring time relations of retarded CA cement slurries at an isothermal temperature of 50 °C under the pressure of 35.5 MPa: (○) control, (△) Na–P, (●) Borax, (□) BA, (⊙) GA, (x) GL.

TABLE I Thickening times of admixture-modified cement slurries as a function of isothermal temperatures

Retarding admixture	Thickening time[a] (min)			
	50 °C	70 °C	120 °C	170 °C
Control	20	14	–	–
Borax	132	108	40	22
BA	210	135	58	26
GA	176	125	100	55
GL	210	190	150	85

[a] Averaged values of three specimens.

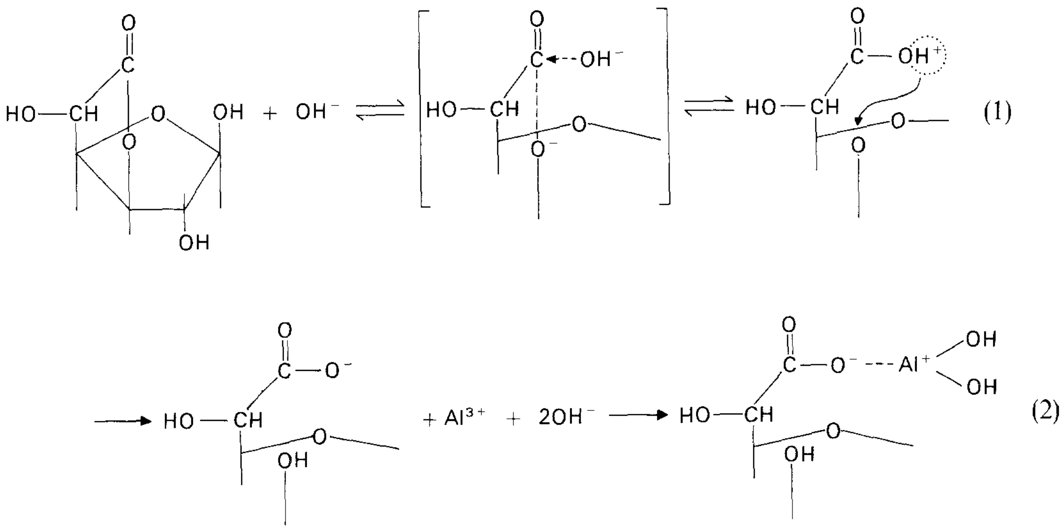
presence of a strong aluminium signal, the data imply that although the major reaction products refer to the aluminium-related compounds, some calcium-related compounds also precipitate as a colloidal reaction products. More calcium-related reaction products are formed as the cement solution was mixed with Borax solution. In fact, the calcium peak has a stronger signal intensity than that of aluminium on the depicted Spectrum c. The XPS high-resolution core level for the Al_{2p}, C_{1s}, $Ca_{2p3/2}$, and B_{1s} signals provided more detailed information on the reaction products. For the scale in all the XPS spectra, the binding energy, BE, was calibrated with the C_{1s} of the principal hydrocarbon-type carbon peak fixed at 285.0 eV as an internal reference standard. The Al_{2p} and C_{1s} core-level photoemission spectra for the GL–cement reaction products are shown in Fig. 5. The Al_{2p} region features a symmetrical single peak at 75.1 eV, that is assignable to the aluminium in the Al–O bonds [7]. The C_{1s} signal could be resolved into at least three Gaussian components, at 285.0, 286.5, and 288.5 eV. The dominant peak of the principal component at 285.0 eV corresponds to the carbon in the $-CH_2-$ groups, and the less intense line at 286.5 eV is attributable to the carbon–oxygen single bond in the C–OH groups. The interesting peak emerging at the BE position of 288.5 eV is located between the carbonyl carbon (C=O) at ~288.0 eV and the lactone  $(-\overset{\overset{O}{\|}}{C}-O-)$ at ~289.5 eV. From our previous XPS studies [8], we can reasonably conclude that this peak represents the formation of COO–metal complexes; the metallic element in this sample is aluminium. Fig. 6 gives the Al_{2p}, $Ca_{2p3/2}$, and B_{1s} regions for the Borax–cement reaction products. The line at 74.6 eV in the Al_{2p} region may be due to the aluminium in the aluminium hydroxide compounds [9, 10]. The B_{1s} region has an assymmetrical shape, with a main peak at 192.4 eV and a shoulder peak at 192.0 eV. According to the literature [11], the former peak is associated with boron in either the metaborate or the boric oxide compounds. An additional line at 192.0 eV, corresponding a shift of about 0.9 eV to a lower BE site than that of the main peak, may indicate the presence of tetraborate-based alkali metal compounds, distinguishable from the metaborate and boric oxides [11]. Thus, the line at 347.9 eV in the $Ca_{2p3/2}$ region may be due to the borate-related calcium compounds.

To support these findings, the reaction products were investigated using IR. Fig. 7 illustrates the IR spectra for these samples, over the frequency range 1900–600 cm^{-1}. The IR absorption spectrum (a) of GL–cement reaction products has three clearly identifiable bands at 1760, 1630, and 1380 cm^{-1}. The weak band at 1760 cm^{-1} is assignable to the carbonyl

(C=O) stretching vibrations in lactone [12]. The two remarkable peaks at 1630 and 1380 cm^{-1} are due to the ionized carboxylate (COO^-) structure [13]. For those reaction products shown by XPS to contain only the aluminium atom, the subsequent IR results verified that the functional group in GL contributing to the uptake of aluminium ions is the ionized carboxyl group, transformed by the alkali-catalysed hydrolysis of lactone groups in the GL formula. The ionized carboxyl reacts favourably with the aluminium ions dissociated from the cement, precipitating colloidal aluminium-complexed GL salts. Such an Al–GL salt complex may be formed through the following hypothetical reaction steps 1 and 2.

As seen above, lactone undergoes bond breakage of the C–O linkage caused by nucleophilic attack of the OH^- ion on the carbonyl carbon, which leads to the formation of an intermediate compound containing a carboxylate anion. The carboxylate anion readily reacts with the aluminium cation, forming aluminium-complexed carboxylate GL salts. We assume that similar reaction products can be derived from the interaction between a cement solution and GA admixture having COOH groups [14, 15].

The assignment of individual peaks indicated in the IR spectrum (b) for the BA–cement reaction products can be interpreted as follows: (1) a shoulder peak at 1625 cm^{-1} reveals the bending vibration mode of



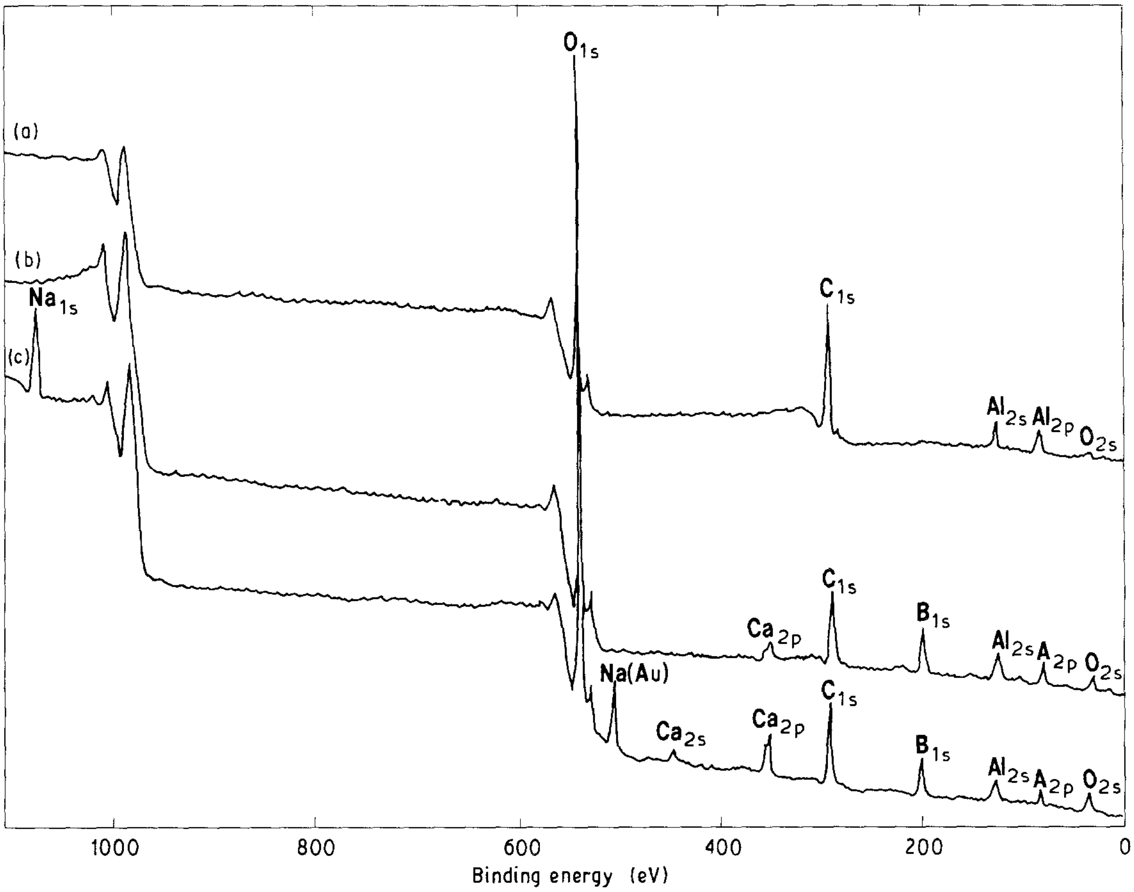


Figure 4 XPS survey scans for colloidal reaction products precipitated by reaction between CA cement solution and (a) GL-, (b) BA-, and (c) Borax-saturated solutions.

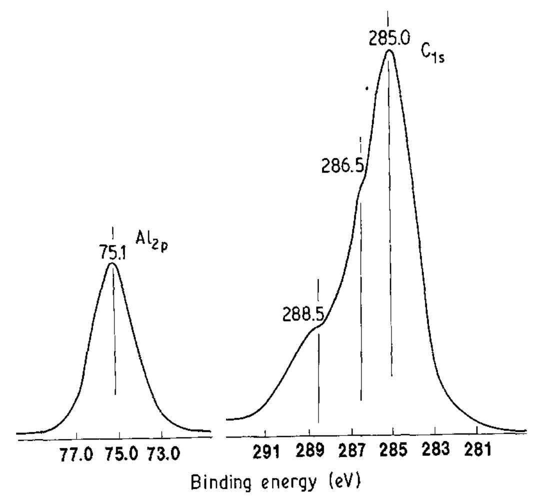


Figure 5 XPS high-resolution core level spectra of Al_{2p} and C_{1s} signals for GL–cement reaction products.

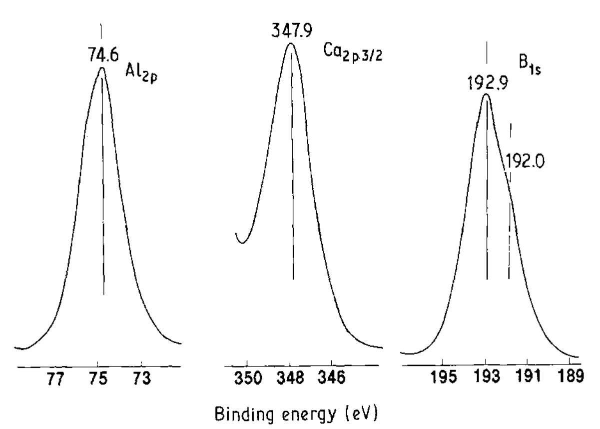


Figure 6 XPS spectra of Al_{2p}, $Ca_{2p3/2}$, and B_{1s} regions for Borax–cement reaction products.

H-O-H in the water; (2) a broad band near $1350\,cm^{-1}$ is attributable to the B–O stretching frequency in the BO_2^- ion [16, 17]; (3) the tetraborate ions ($B_4O_7^{2-}$) refer to the peak near $1000\,cm^{-1}$; and (4) other peaks at 1060, 890 and $700\,cm^{-1}$ reflect the presence of aluminium oxyhydroxide [18]. The spectrum of the Borax-cement reaction products (c) showed similar features. These data suggested that, in the case of BA, the precipitation of calcium metaborate, $Ca(BO_2)_2$, as a reaction product may commence through the following sequence: when BA comes in to contact with water, the reactive borate anions (BO_2^-) are released by the hydrolysis of BA [19]. The dissociated BO_2^- ions have an affinity for the Ca^{2+} ions from the cement pastes, and the ionic reaction between BO_2^- and Ca^{2+} leads to the formation of colloidal $Ca(BO_2)_2 \cdot nH_2O$ [20]. This reaction process is

$$4H_3BO_3 + 2OH^- \rightleftharpoons B_4O_7^{2-} + 7H_2O \quad (3)$$

$$B_4O_7^{2-} + 2OH^- \rightarrow 4BO_2^- + H_2O \quad (4)$$

$$2Ca^{2+} + 4BO_2^- \rightarrow 2Ca(BO_2)_2. \quad (5)$$

Because $Ca(BO_2)_2$ is also derived from Borax, a similar reaction would occur

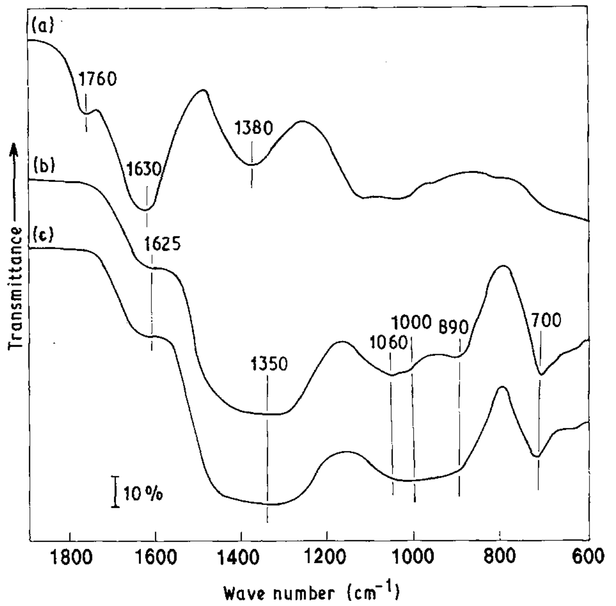


Figure 7 Infrared absorption spectra for (a) GL–, (b) BA–, and (c) Borax–cement reaction products.

$$Na_2B_4O_7 \cdot 10H_2O \rightleftharpoons 2Na^+ + B_4O_7^{2-} \quad (6)$$

$$B_4O_7^{2-} + 2OH^- \rightarrow 4BO_2^- + H_2O \quad (7)$$

$$2Ca^{2+} + 4BO_2^- \rightarrow 2Ca(BO_2)_2. \quad (8)$$

It should be noted here that such Ca^{2+} ion-trapping activities of the borate anion promote the precipitation of aluminium hydroxide.

Although the cement-retarding mechanisms are due to the precipitation of the conversion colloidal membrane coating, these effects are thought to delay the nucleation processes of $CaO–Al_2O_3–H_2O$ gel formation, and provide an effective barrier to the further hydration reaction between the cement and water until the gel is gradually destroyed by calcium and aluminium ions dissociated from the cement paste.

3.2. Alkali carbonation

Before estimating the rate of Na_2CO_3-induced carbonation of the retarded CA cement pastes, we investigated the vulnerability of the colloidal $Ca(BO_2)_2 \cdot nH_2O$, as calcium-related reaction products, to attack by a hot Na_2CO_3-laden water. This information was obtained using TGA, coupled with differential thermal analysis (DTA). In this test, the colloidal material formed by the chemical reaction between the cement solution and Borax was exposed to a 0.05 M Na_2CO_3 solution at 300 °C, and then dried at 150 °C for the TGA–DTA measurements. The 100 °C pre-heated colloidal material was used as the control. Typical TGA–DTA curves for these samples are given in Fig. 8. The TGA curve for the control (unbroken line) shows two pronounced decompositions, the first occurring between 25 and 300 °C, and the second from 350–650 °C. The first decomposition, which is associated with the endothermic peak at 210 °C, may be caused by the dehydration of colloidal $Ca(BO_2)_2 \cdot nH_2O$ reaction products, while the second, corresponding to the DTA peak at 460 °C, may be due

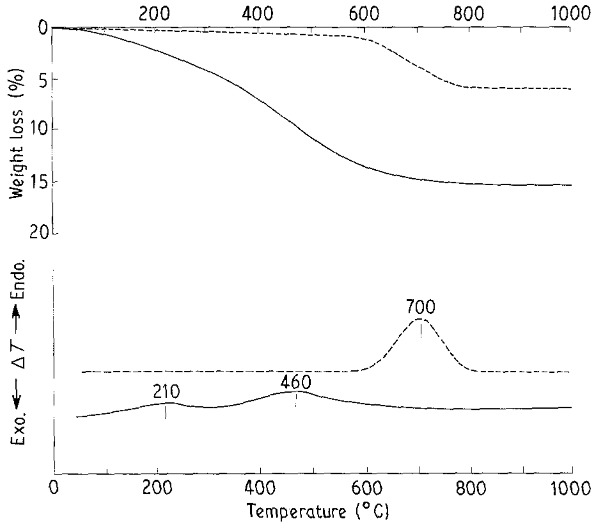


Figure 8 TGA–DTA curves of colloidal $Ca(BO_2)_2 \cdot nH_2O$ reaction products treated and untreated with Na_2CO_3-laden water at 300 °C.

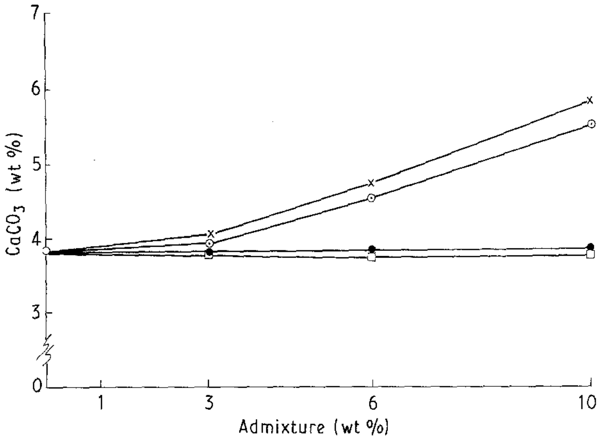


Figure 9 Concentration of $CaCO_3$ formed in admixture–cement hydrate after exposure for 24 h to 0.05 M Na_2CO_3 solution at 300 °C: (○) control, (●) Borax, (□) BA, (⊙) GA, (×) GL.

to the decomposition of $Ca(BO_2)_2$ compounds. Differences in the shape of the curve can be seen in the samples which were exposed to 300 °C Na_2CO_3 solution: the Na_2CO_3-induced carbonation of $Ca(BO_2)_2 \cdot nH_2O$ shifts the temperature of onset of thermal decomposition to a higher value. Because the thermal decompositions $CaCO_3$ occur over the range 600–770 °C [21], the weight loss occurring from 600–780 °C on TGA curve (dotted line), corresponding to the endothermic peak at 700 °C, reveals the formation of $CaCO_3$. Because the dissolution of Na_2CO_3 in a hot water liberates carbonic acid (HCO_3^-) and proton reactants, this finding reflects the favourable reaction of ionized $Ca(BO_2)_2$ with these reactants to precipitate the $CaCO_3$ in conjunction with the formation of metaboric acid (HBO_2). These reactions can be expressed as follows:

$$Na_2CO_3 + 2H_2O \rightarrow 2NaOH + H^+ + HCO_3^- \quad (9)$$

$$Ca^{2+} + 2BO_2^- + H^+ + HCO_3^- \rightarrow CaCO_3 + 2HBO_2 \quad (10)$$

Thus, we believe that the colloidal $Ca(BO_2)_2 \cdot nH_2O$ reaction products are also susceptive to alkali carbonation.

From this information, we estimated the rate of Na_2CO_3-induced carbonation for CA cement pastes modified with GL-, GA-, BA-, and Borax-retarding admixtures, ranging from 3–10 wt %, as the total amount of $CaCO_3$ formed in the cement body. Later data (see Fig. 9) indicated that, although the organic GL- and GA-admixtures have a high potential as set-retarders of high-temperature cementing materials, the concentration of $CaCO_3$ markedly increases with an increasing content of admixture. In contrast, the inorganic-type BA and Borax admixtures contain similar amounts of $CaCO_3$ to that of the control. This finding reflects the fact that the $Ca(BO_2)_2 \cdot nH_2O$ reaction product, which retards the setting of pastes, does not promote the carbonation reaction of cement hydrates. Contrarily, the formation of aluminium-complexed carboxylate salt complexes by adding GL and GA admixtures promotes the carbonating rates of cement body. Possibly, this occurs because the preferential uptake of aluminium ions by GL and GA liberates a large number of free Ca^{2+} ions, and then the free Ca ions are converted into $CaCO_3$ in the Na_2CO_3-dissolved aqueous medium, according to the following reaction:

$$Ca^{2+} + 2OH^- + H^+ + HCO_3^- \rightarrow CaCO_3 + 2H_2O \quad (11)$$

4. Conclusions

From our findings, we draw the following conclusions. When organic acid reagents such as glucuronic-6,3-lactone (GL) and gluconic acid (GA), as set-retarding admixtures of hydraulic cementitious materials were incorporated into calcium aluminate (CA) cement slurry under the hydrothermal conditions, the functional lactone and carboxylic acid groups in the GL and GA preferentially react with the aluminium ions dissociated from the CA, rather than calcium ions. This uptake of aluminium ions led to the formation of colloidal aluminium-complexed carboxylate salts, which greatly extended the setting time of the autoclaved CA cement slurries. However, although such organic acid reagents have a high potential as set-retarding admixtures of high-temperature CA cements, the generation of abundant free calcium ions caused by the preferential uptake of aluminium ions enhanced the rate of the alkali carbonation reactions in the Na_2CO_3-laden water at 300 °C, thereby increasing the amount of $CaCO_3$ in the cement body.

In contrast, the addition of inorganic acid-type retarders, such as boric acid (BA) and sodium tetraborate decahydrate (Borax), to the CA cement slurry, contributes to the precipitation of colloidal calcium metaborate [$Ca(BO_2)_2 \cdot nH_2O$] and to the formation of the aluminium hydroxides as reaction products between CA cement and BA or Borax in the aqueous media. The magnitude of retarding activity for these reaction products was lower than those derived from organic acids. With regard to the susceptibility of the retarded CA cement to alkali carbonation at 300 °C, we found that, despite the conversion of $Ca(BO_2)_2 \cdot nH_2O$ into $CaCO_3$, the rate of carbonation for the BA and Borax-modified CA cement pastes was almost the same as that of the unmodified CA paste.

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