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THE EFFECT OF ADDITIONS OF ALKALINE-EARTH METAL CHLORIDES ON THE SETTING BEHAVIOR OF A REFRACTORY CALCIUM ALUMINATE CEMENT

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ABSTRACT

The literature concerned with the effect of alkaline and alkaline-earth metal chlorides on the hydration of calcium aluminate cements is confused. For example, some authors have suggested that magnesium chloride acts as a retarder, while others stated that it acts as an accelerator. Accordingly a thorough investigation has been carried out into the setting behaviour and early hydration of Secar 71, mixed with a range of concentrations of $MgCl_2$, $CaCl_2$, $SrCl_2$, and $BaCl_2$. At 12°C all chlorides brought about retardation of the setting time of the cement, which increased with increasing concentration of the admixture. At 20°C, at low concentrations they brought about acceleration of the set, but acted as retarders at higher concentrations. At 28°C and 36°C, retardation was observed and its extent increased with increasing concentration of the admixture.

Introduction

Although Parker as long ago as 1952 reported the effects on the setting time of various additions to aluminous cement pastes (1), there have been relatively few thorough investigations concerning the effect of various additions on the setting behaviour of calcium aluminate cements. The literature on the use of admixtures with calcium aluminate cement (CAC) has been reviewied recently by Cox and Sharp (2).

The effect of metal chlorides on the hydration behaviour is particularly important, because they are often present inadvertently in the water used to mix the cement paste. Furthermore, alkali and alkaline-earth metal chlorides come into contact with all forms of concrete in marine environments.

The effect of several metal chlorides on the setting of CAC was discussed by Parker (1), Robson (3) and Lea (4), who concluded that they generally acted as retarders, but that $MgCl_2$ and $CaCl_2$ can be accelerators when present in the gauging water in low concentrations. Rodger and Double

(5) drew attention to the dramatic acceleration brought about by lithium salts, including the chloride. To test whether other metal cations had a similar effect to that of lithium, they examined a range of mono-, di-, and tri-valent metal chloride salts and concluded that none of the cations tested had an accelerating effect comparable with that of lithium. Both calcium chloride and strontium chloride, which are set accelerators for Portland cement, showed a retarding effect with Ciment Fondu.

Overall Rodger and Double (5) summarised the action of alkali and alkaline-earth metal chlorides to be in the following series:

$$Li^{+} << Mg^{2+} < Ba^{2+} < \text{control} < K^{+} < Na^{+} < Sr^{2+} < Ca^{2+}$$

(Note: this sequence and those set out below are extracts from the papers concerned listing only the alkali and alkaline-earth metal cations)

Currell et al. (6) studied the acceleration and retardation of setting of Ciment Fondu in the presence of many additives. According to their investigation the set of low purity CAC pastes was considerably affected by the addition of very small amounts of chemical compounds. They concluded that both cations and anions have a profound effect on the chemical reactions which cause the hardening of CAC. The effect on the time of setting may be summarised as follows:

for cations

$$Li^{+} << Na^{+} < \text{control} < K^{+} < Ca^{2+} < Mg^{2+} < Sr^{2+}$$

for anions

$$OH^{-} << \text{control} < Cl^{-} < NO_3^{-} < Br^{-} < \text{acetate}$$

Griffiths et al. (7) also investigated the hydration reaction of Ciment Fondu in the presence of chlorides, sulphates and sea water. They stated that of all the chloride solutions the most interesting result was that of $CaCl_2$ which, although a well known accelerator for OPC, retards the hydration of CAC. The effect of chloride admixtures at different temperatures on the setting time was reported to be as follows :

$$Mg^{2+} < K^{+} < Na^{+} < Ba^{2+} < \text{control} < Ca^{2+} \qquad \text{at } 15^{\circ}C$$

$$Mg^{2+} < K^{+} < Na^{+} < \text{control} < Ca^{2+} < Ba^{2+} \qquad \text{at } 30^{\circ}C$$

$$Mg^{2+} < K^{+} < Na^{+} < \text{control} < Ca^{2+} < Ba^{2+} \qquad \text{at } 40^{\circ}C$$

They stated that the position of $MgCl_2$ is anomalous and represents the ease with which magnesium ions can replace calcium ions in the cement hydrate.

Murat and Sadok (8) considered the role of foreign cations in solution in the hydration kinetics of Ciment Fondu. From their report it is concluded that all chloride salts have an accelerating effect on the set of Secar 71. This conclusion differs from that reached in most other studies, summarised above.

All workers agree that lithium chloride has a dramatic accelerating effect, but disagree about the role of other cations. For example, Rodger and Double (5) reported that NaCl and KCl acted as retarders, whereas Griffiths et al. (7) and Murat and Sadok (8) have them as accelerators, while Currell et al. (6) reported NaCl to be an accelerator but KCl to be a retarder.

There are also differences when the effect of additions of alkaline-earth chlorides are compared. Rodger and Double (5) and Griffiths et al. (7) reported $MgCl_2$ to act as a mild accelerator, whereas Currell et al. (6) found it to act as a retarder. $CaCl_2$ is reported by all three groups to bring about retardation, but differing results were obtained with $BaCl_2$ additions. Only Rodger and Double (5) studied the effect of both Sr^{2+} and Ba^{2+} ions, which were reported to behave differently, yet they are chemically very similar and might be expected to act in a similar manner.

Clearly the literature is so confused that a thorough study of the effect of metal chlorides on the early hydration of calcium aluminate cement is timely. In this investigation, we have studied the effect of alkaline-earth metal chlorides at various concentrations at several different temperatures on the setting behaviour of a calcium aluminate cement. To avoid any confusion over conflicting reactions with the silicate and ferrite phases also present in Ciment Fondu, the cement used in this investigation was Secar 71, a relatively pure, refractory calcium aluminate cement with an Al_2O_3 content of approximately 70%.

Experimental

The Secar 71 used was kindly supplied by Lafarge Special Cements. Its chemical composition and mineralogical analysis is similar to that given by Bushnell-Watson and Sharp (9). The water to cement ratio (w:c) was 0.5 to compare with the work done by Rodger and Double (5) and most other previous workers.

A mixing time of two minutes was used throughout the study. The appropriate amount of additive in the form of the chloride salt was added to the gauging water prior to mixing. The salts were added as hydrates with composition $RCl_2.nH_2O$ (where n = 2 when R = Ca, Ba; n = 6 when R = Mg, Sr); molarities are quoted with respect to the concentration of R^{2+} ions in the solution. Every experiment was carried out using 30g of Secar 71 mixed with 15ml of boiled distilled water, which contained any admixture used in solution.

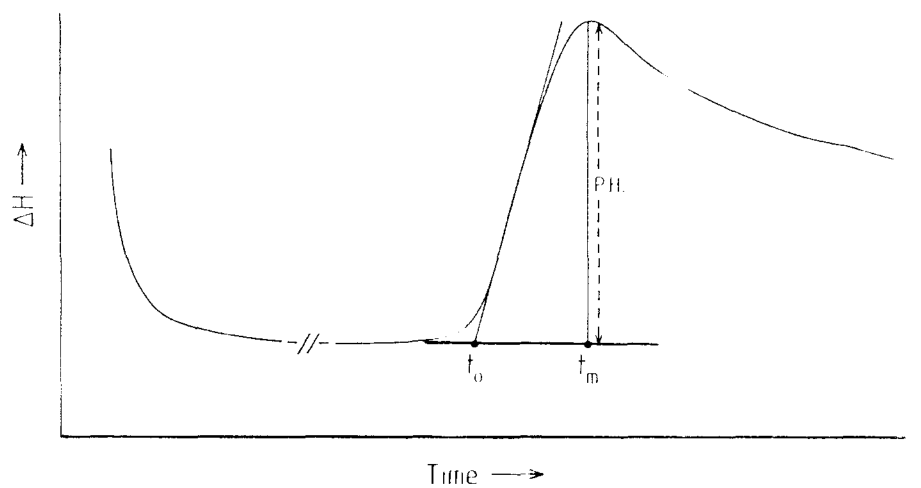

Fig. 1- The embedded thermocouple trace for Secar 71 hydrated at 12°C with 0.05M $SrCl_2$

The setting time parameters were determined by measuring the heat evolution by the embedded thermocouple technique. The procedure followed was that described by Bushnell-Watson and Sharp (9), as illustrated in Figure 1 for the sample of Secar 71 hydrated at 12°C in the presence of 0.05M $SrCl_2$ solution. Various concentrations of alkaline-earth chlorides dissolved in the water were investigated at four temperatures in the range 12-36°C. Many experiments were repeated to test the reproducibility of the results. The values of both t_o and t_m were found to be reproducible within 10 minutes for experiments in which the setting time parameters were 300 minutes or less, and within 30 minutes when these parameters were of the order of 1500 minutes.

Results

1 - Effect of addition of RCl_2 at 12°C

1 - 1 Effect of addition of $MgCl_2$ at 12°C

The effect of a range of concentrations from 0.025-0.5M of $MgCl_2$ on the setting time parameters of Secar 71at 12°C is shown in Table 1. The weight % of the admixture relates to the % relative to the weight of cement, whereas the molarity of the solution relates to the concentration obtained on dissolving this weight in 15ml of water. It can be seen that $MgCl_2$ brought about drastic retardation of the setting time parameters, t_o and t_m, and that the extent of retardation increased with increasing concentration of the admixture. When the the concentration of the admixture was 0.5M, the cement had not set after 48 hours and even after 7 days some parts of the paste were still soft. The difference, (t_m-t_o), increased with increasing concentration of $MgCl_2$, whereas the peak height (P.H.) decreased.

Table 1. Effect of different concentrations of $MgCl_2$ on the setting time of Secar 71 at 12°C

wt of admix. (g)	wt % of admix.	mol of admix.	mol of Cl^-	mol of Mg^{++}	t_o min	t_m min	t_m- t_o min	P.H. mm
--	--	--	---	---	165	196	31	123
0.076	0.25	0.025	0.05	0.025	194	219	25	129
0.304	1.01	0.10	0.20	0.10	279	324	45	112
0.762	2.54	0.25	0.50	0.25	732	858	126	80
1.525	5.08	0.50	1.00	0.50	>5500	>5500	--	--

1 - 2 Effect of addition of RCl_2 at 12°C (where R = Ca, Sr or Ba)

The results presented in Table 2 allow comparisons to be made between the various setting time parameters obtained for additions of $CaCl_2$, $SrCl_2$ and $BaCl_2$ with those already presented for $MgCl_2$. It can be seen that calcium chloride generally brought about retardation of the setting time of Secar 71 at 12°C. At very dilute concentration (0.025M), however, the addition of this salt seemed to bring about slight acceleration. On increasing the concentration of calcium chloride

Table 2. Effect of different concentrations of divalent metal chloride admixtures on the setting time parameters of Secar 71 at 12°C

Molarity of RCl_2	R = Mg		R = Ca		R = Sr		R = Ba	
	t_o min	t_m min	t_o min	t_m min	t_o min	t_m min	t_o min	t_m min
Control	165	196	165	196	165	196	165	196
0.025	194	219	158	176	--	--	167	183
0.05	--	--	--	--	166	189	--	--
0.1	279	324	374	421	229	265	227	261
0.25	732	858	--	--	473	561	583	668
0.5	>5500	>5500	833	996	>4000	>4000	>4000	>4000

to 0.1M, clear retardation was observed, which increased dramatically with a 0.5M addition. The time taken to reach the maximum evolution of heat, t_m, and the difference between t_m and t_o decreased slightly in the presence of 0.025M $CaCl_2$ solution, but then increased dramatically with increasing concentration of calcium chloride. The peak height corresponding to t_m decreased significantly on addition of 0.5M $CaCl_2$.

The addition of strontium chloride and barium chloride brought about similar effects to those observed in the presence of magnesium chloride and calcium chloride. At low concentrations of the admixture, t_o was hardly affected, while t_m and (t_m-t_o) were slightly reduced. At concentrations of 0.1M and above, the admixtures brought about retardation, which became more severe as the the concentration was increased. With addition of 0.1M and 0.25M solutions, (t_m-t_o) became longer, while the peak height was found to decrease. Setting was not observed within the 72 hours that the experiments were left running in the presence of 0.5M solutions, but in a separate experiment a paste with 0.5M addition of $BaCl_2$ had set after 7 days.

2 - Effect of addition of RCl_2 at 20°C

The setting time parameters obtained when several different concentrations of alkaline-earth metal chloride solutions were added to Secar 71 at 20°C are listed in Table 3. It can be seen that the addition of 0.025M solutions brought about acceleration of the setting time. Addition of 0.05M solutions resulted in setting time parameters that were closer to those in the absence of any admixture, but acceleration was still evident in the presence of $MgCl_2$ and $SrCl_2$. A further increase of admixture concentration to 0.1M brought about dramatic retardation of the setting behaviour in the presence of any of the four salts. When the concentration of the additive was increased to 0.5M, setting was not usually observed during the period that the experiment was running (for 3 days or more), but in a separate series of experiments the paste had always set after 7 days.

Table 3. Effect of different concentrations of divalent metal chloride admixtures on the setting time parameters of Secar 71 at 20°C

M of RCl_2	R = Mg		R = Ca		R = Sr		R = Ba	
	t_o min	t_m min	t_o min	t_m min	t_o min	t_m min	t_o min	t_m min
Control	270	334	270	334	270	334	270	334
0.025	224	288	220	276	200	234	245	286
0.05	258	302	301	355	258	301	282	319
0.1	748	900	1126	1174	1589	1789	1212	1476
0.25	--	--	--	--	--	--	4808	5171
0.5	>5000	>5000	3186	3414	>7200	>7200	>5760	>5760

The results obtained on the addition of the five different concentrations of $BaCl_2$ are given more fully in Table 4. Similar results were obtained with the three other metal chloride additions; additional detailed information on the setting time parameters found at each temperature in the presence of different concentrations of each alkaline-earth metal chloride is tabulated elsewhere (10). The addition of 0.025M $BaCl_2$ brought about acceleration of the setting time, whereas dramatic retardation was observed with 0.1M, 0.25M and 0.5M solutions. Variation of t_m followed a similar trend to that of t_o, and the parameter (t_m-t_o) also decreased initially and then increased with increasing concentration of $BaCl_2$. The peak height decreased with increasing concentration of $BaCl_2$.

Table 4. Effect of different concentrations of $BaCl_2$ on the setting time parameters of Secar 71 at 20°C

wt of admix.(g)	wt% of admix.	mol of admix.	mol Cl^-	mol Ba^{2+}	t_o min	t_m min	t_m- t_o min	P.H. mm
--	---	--	--	---	270	334	64	103
0.118	0.38	0.025	0.05	0.025	245	286	41	103
0.238	0.76	0.05	0.10	0.05	282	319	37	88
0.46	1.53	0.10	0.20	0.10	1212	1476	264	60
0.92	3.80	0.25	0.50	0.25	4808	5171	363	39
1.84	7.60	0.50	1.00	0.50	>5760	>5760	ND	ND

3 - Effect of addition of RCl_2 at 28°C

Table 5. Effect of different concentrations of divalent metal chlorides admixtures on the setting time parameters of Secar 71 at 28°C

M RCl_2	R = Mg		R = Ca		R = Sr		R = Ba	
	t_o min	t_m min	t_o min	t_m min	t_o min	t_m min	t_o min	t_m min
Control	996	1056	996	1056	996	1056	996	1056
0.05	1146	1256	1470	1688	1483	1584	1953	2277
0.1	1590	1792	1614	1866	>5760	>5760	2460	2850

At 28°C, the effect of two different concentrations of RCl_2 was investigated and the results are summarised in Table 5. It can be seen that 0.05M RCl_2 brought about retardation of the setting time parameters, while an increase in the concentration to 0.1M brought about even greater retardation. With addition of 0.1M $SrCl_2$ the paste did not set during the four days for which the embedded thermocouple experiment was followed. The parameter (t_m-t_o) also increased with the addition of 0.05M RCl_2, compared with the cement alone, and increased further in the presence of 0.1M solutions.

4 - Effect of addition of RCl_2 at 36°C

Table 6. Effect of different concentrations of divalent metal chlorides admixtures on the setting time parameters of Secar 71 at 36°C

M RCl_2	R = Mg		R = Ca		R = Sr		R = Ba	
	t_o min	t_m min	t_o min	t_m min	t_o min	t_m min	t_o min	t_m min
Control	196	224	196	224	196	224	196	224
0.05	220	242	275	298	448	550	600	696
0.1	244	264	328	348	730	864	702	896
0.5	1490	1556	601	617	>2160	>2160	3876	4098

Variations in the setting time parameters when the effect of different concentrations of RCl_2 on the setting time of Secar 71 was examined at 36°C are summarised in Table 6. With $MgCl_2$, t_o increased slightly with 0.05M and 0.1M solutions and then dramatically with further increase in the concentration of the admixture to 0.5M.. Similar effects were observed on t_m. The parameter (t_m-t_o) decreased slightly up to 0.1M and then increased with the 0.5M solution. The peak height increased up to 0.1M compared with Secar 71 alone, but then dramatically decreased with 0.5M concentration of $MgCl_2$.

Results obtained in the presence of calcium chloride were similar to those generated with magnesium chloride, except that the retardation was greater at low concentrations, but less at the highest concentration studied. In the cases of strontium chloride and barium chloride, the retardation was even greater than with the magnesium and calcium salts.

Discussion

It can be seen from the data presented that the setting time parameters depend in a subtle manner on both the concentration of the admixture and the temperature of hydration. For example, at 20°C at very low concentrations of the alkaline-earth metal chlorides, the setting of the cement was accelerated, but at higher concentrations it became dramatically retarded (see Table 3 and Fig. 2).

At 28°C (Table 5) and 36°C (Table 6), however, the set was retarded at all concentrations of the metal chloride solutions, whereas at 12°C it was hardly affected at low concentrations, but retarded at concentrations of 0.1M and above. In these cases the degree of retardation increased with increasing concentration of the additive. The parameter t_m varied with concentration of the admixture in a very similar manner to t_o. Generally the peak height varied inversely with (t_m-t_o), so that the area under the peak, which is related to the total amount of heat evolved (and that lost through the sides of the tubing during the experiment), was fairly constant.

Most previous workers are believed to have investigated the setting behaviour at about 20°C, i.e. they have either specified this temperature or have worked at "ambient temperatures", which we take to mean about 20°C. The results presented here at this temperature are in accordance with the statement quoted earlier from Lea (2), that although magnesium chloride and calcium chloride generally acted as retarders, they acted as accelerators at low concentrations. Thus the drastic retardation brought about by 0.1M solutions of these salts is clearly shown in Fig. 2. In contrast, it can be seen that with the addition of 0.025M solutions there was slight acceleration; all four metal chlorides showed similar effects, but that of $SrCl_2$ was the greatest. At the intermediate concentration of 0.05M, the effect of the additions was almost neutral; solutions containing Mg^{2+} and Sr^{2+} ions were accelerating whereas those with Ca^{2+} and Ba^{2+} ions were somewhat retarding. This concentration is the same as that used by most previous workers, who, it can now be seen, inadvertently selected the most difficult concentration to study, hence possibly accounting for some of the disagreement in the literature. The results presented here for 20°C, however, are closely similar to those reported by Currell et al. (6), who reported that the chlorides of Mg, Ca and Sr generally acted as retarders.

At the other temperatures studied, the effects observed were more straightforward. Thus at 12°C, the overall effect was to bring about retardation, although the lowest concentrations studied had

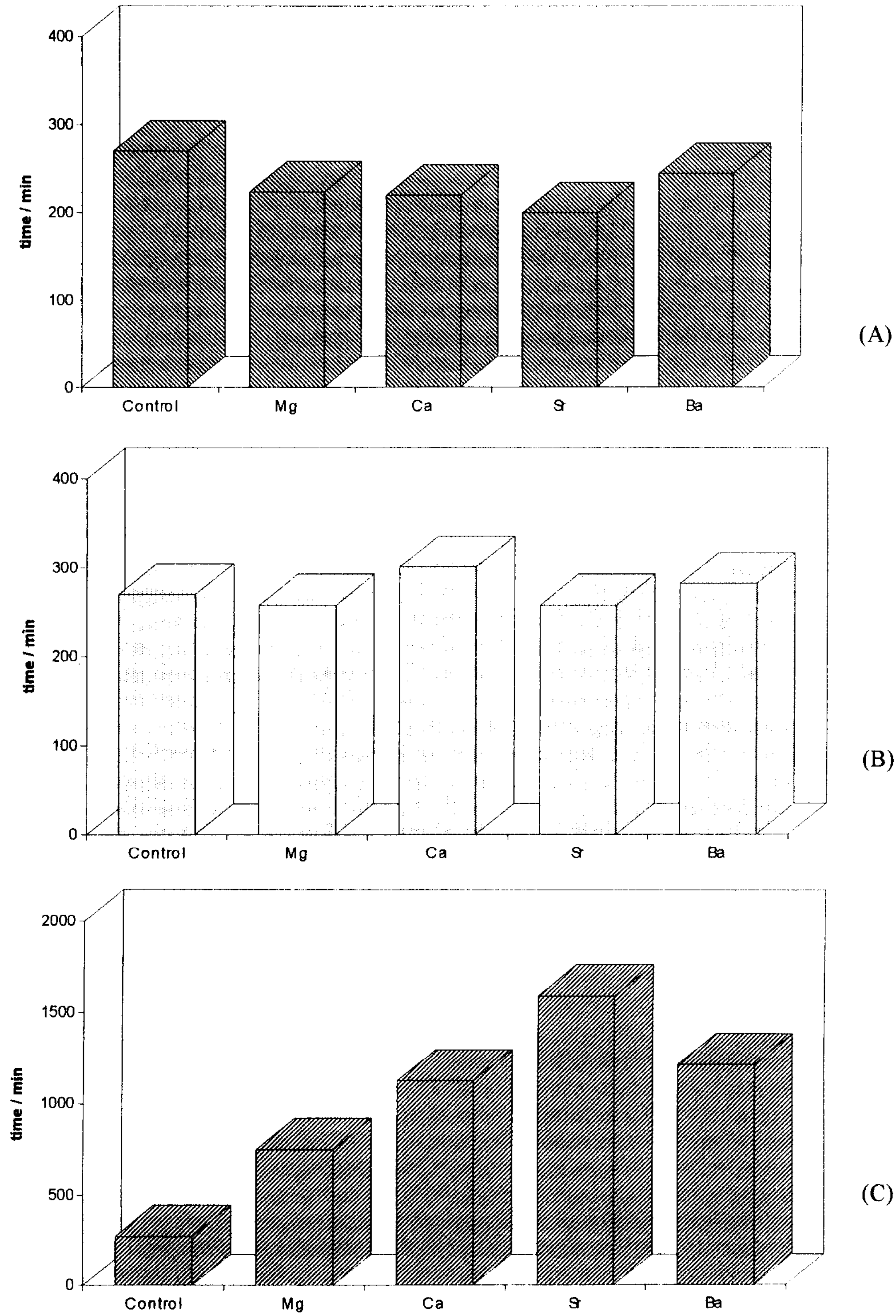

Fig. 2-The effect of chloride additives on the setting time parameter at 20°C
A: 0.025M B: 0.05M C: 0.1M

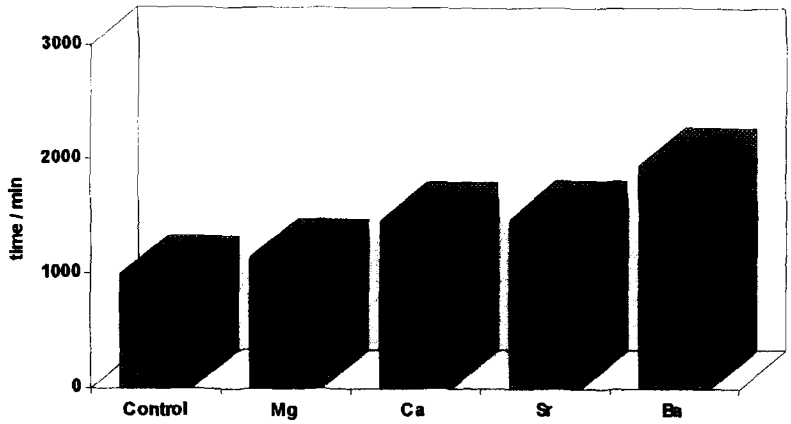

Fig. 3 - The effect of 0.05M chloride additives on the setting time parameter at 28°C

little effect on the setting time parameters. At 28°C and at 36°C, all concentrations of alkaline-earth metal chlorides were found to be retarding. Results obtained with 0.05M solutions of the four metal chlorides at 28°C are shown in Fig. 3 and those at 36°C in Fig. 4, by way of example.

Murat and Sadok (8) have suggested that the parameter, t_0, gives a measure of the nucleation time, whereas (t_m-t_0) is related to the growth of these nuclei. Assuming this to be correct, it seems that addition of alkaline-earth metal chlorides has a major effect on the nucleation phenomena, but a lesser effect on the subsequent growth of these nuclei. The nucleation of one or more of the metastable hexagonal hydrates is probably the rate controlling factor in the early hydration, and hence setting, of calcium aluminate cements based on calcium monoaluminate.

The anomalous dependence of the setting time parameter, t_0, with respect to the temperature of hydration, reported by Bushnell-Watson and Sharp (9,11,12) for CA, Secar 71 and other commercial CACs, is still evident, as shown in Fig. 5. Similar curves could be drawn for all concentrations of the four metal chlorides studied. Since the effect of these additions was to

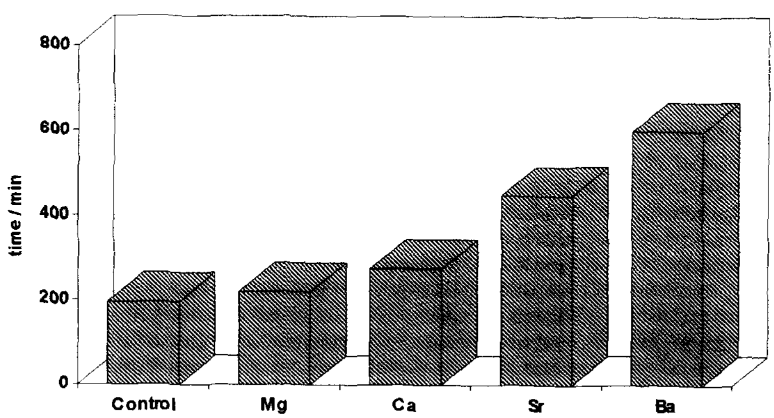

Fig. 4 - The effect of 0.05M chloride additives on the setting time parameter at 36°C

bring about enhanced retardation at 28°C, these curves are even more "anomalous" than that for Secar 71 in the absence of any admixture.

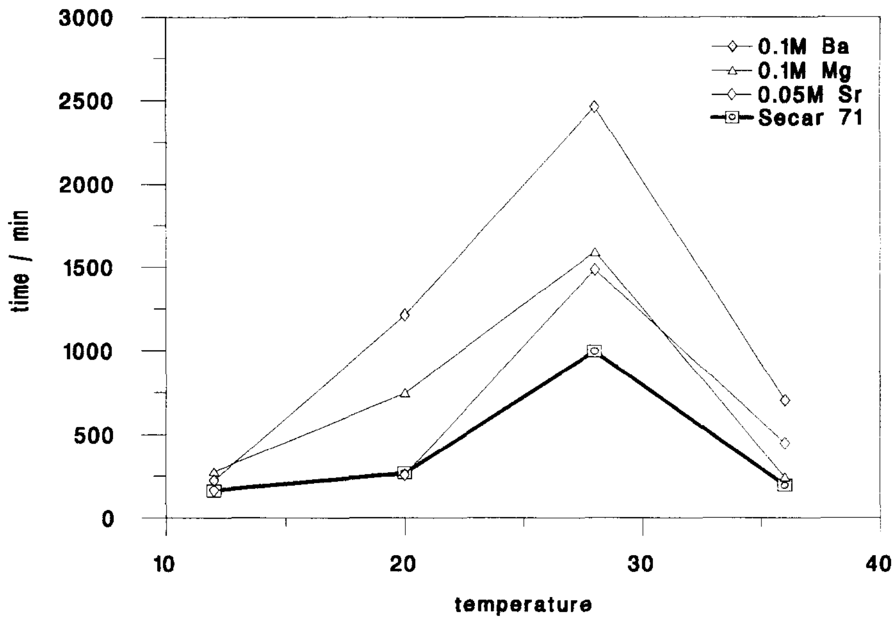

Fig. 5 - Effect of addition of RCl_2 and temperature on the setting time parameter (t_0) of Secar 71

It is apparent that at least two factors are affecting the setting time parameters in the presence of RCl_2. At low concentrations at 12°C and especially at 20°C, there is a slight acceleration, which is overwhelmed at higher concentrations by another factor that brings about dramatic retardation. This latter factor is dominant at all concentrations studied at 28°C and 36°C. In addition to the effect of the alkaline-earth metal ions on the setting behaviour of the refractory cement, the retarding effect of the chloride ions has to be considered. This is particularly important to remember when the oxidation state of the cation is changed. For example, when sodium chloride is considered the molarity of the chloride ions is only half that of RCl_2 for the same molarity of the solution. Further work is in progress, investigating the effects of other metal chlorides and various other admixtures. It is hoped that these studies will give additional information concerning the mechanism of the setting behaviour.

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