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The solution chemistry and early hydration of ordinary portland cement pastes with and without admixtures

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Abstract

Solution extraction and analysis in the first 3 h of hydration have been used to study the effects of calcium chloride, calcium nitrate, calcium thiocyanate, and sucrose on the hydration of Portland cement. Studies were made at a water : cement ratio of 0.5, which is similar to that to be expected in normal use. The addition of calcium salts has a pronounced effect on the calcium, hydroxyl and sulphate ion concentrations. This is in agreement with the results from X-ray diffraction and differential scanning calorimetry, which show rapid precipitation of more gypsum and calcium hydroxide within the first 5 min on adding these salts than in neat OPC pastes. The data for sucrose show opposite trends in line with the chelation of the calcium ion. No significant changes in sodium and potassium levels were observed in the first 3 h with any of the additions. Differences in degrees of hydration at early stages from the addition of calcium salts are attributed to different relative degrees of solvation of the ionic reactants and transition states, in addition to the nature and extent of sulphate and hydroxide formation from solution. The combined effect of cations and anions on the acceleration produced are discussed. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Portland cement; Gypsum; Concrete; Admixtures; Hydration

1. Introduction

A large number of compounds, both organic and inorganic, have been shown to accelerate the stiffening and strength development of ordinary Portland cement (OPC) [1–7], although only a few such compounds are found in commercial use [5,7]. Of these, calcium chloride has been the most widely used [6] because of its ready availability, low cost and successful application over several decades. Its use in reinforced concrete, however, is now severely limited by building codes [8,9] because of the effect of chloride ions on the corrosion of embedded steel [10].

A review [11] has shown that the calcium chloride has also been the subject of most of the research on accelerators of cement hydration. Despite this, the mechanism by which the accelerating effect is achieved is not fully understood. Some workers have limited their investigations by considering only accelerating effects on cement minerals [12,13] but this also has not produced a complete understanding. Rama-

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chandran [6] has listed 12 possible mechanisms of acceleration which have been suggested by various workers, none of which explain all the observed effects of calcium chloride. Various other additives have been used in the study of hydration of cements. These include sodium nitrate [14], and calcium nitrate [15]. In thermal analysis the aim is generally to study the formation of calcium hydroxide as a measure of hydration [16,17]. This aspect of the subject is reviewed by Bhatty et al. [18].

Despite considerable research, it is not possible to describe a unified theory of how, accelerating admixtures interact with the hydration of OPC. This is partially due to the wide choices of experimental conditions available, including varying cement compositions, type and dosage of accelerator used and the criteria on which its classification is made. The commercial description of an accelerator as a material that speeds setting and/or strength development does not specify the exact nature of the measurement being made. It also does not indicate the effects on the basic hydration process [12], although it is of practical benefit as it describes the manner in which the material will be used.

In this study, we have assessed the effects on the hydration process of three chemicals, calcium chloride, calcium nitrate and calcium thiocyanate, selected as representing some of the major commercially available accelerators. These three salts were selected because they are known to differ in their effects on setting and strength development, although all meet the commercial classifications. In each case, the calcium salt has been selected to eliminate any effects of cation variability, even if the sodium salt is used more often in practice. The three materials have been compared against a neat OPC system and one containing sucrose, a well known retarder.

A number of workers [19–32] have followed chemical reactions which take place over the early stages of the hydration of OPC pastes, both with and without admixtures present, by extracting and analysing the aqueous phase. With water soluble admixtures it is to be expected that the presence of additional ions in solution will have some influence on the concentration of species normally present and will therefore affect the hydration process. Changes in the composition of the liquid phase may therefore be highly significant in explaining the mechanisms of acceleration. Much of the published work has considered cement suspensions at high water : cement ratios. In this investigation, an approach has been developed to allow studies at a water : cement ratio more typical of those used in practice. Solution analysis of OPC pastes at a water : cement ratio of 0.5 have been made over the period from 5 min to 3 h after the addition of the water to the cement. Based on these results and those obtained from examination of the actual cement paste by differential scanning calorimetry and X-ray diffraction published elsewhere [33,34] an acceleration mechanism is proposed.

2. Experimental

2.1. Materials and sample preparation

The oxide analysis for the OPC used in this work is shown in Table 1. Deionised water, decarbonised by boiling and then allowing to cool, was employed throughout. Each mix contained 400 g of OPC and 200 g of deionised water, giving a water : cement ratio of 0.5. The introduction of the admixtures was effected by dissolving the required quantities of Analar grade chemicals in the mixing water. The three calcium salts were added at a dosage of 90.1 mmol/kg of OPC. This gives anion concentrations of 360.4 mmol/l and cation concentrations of 180.2 mmol/l in the deionised water prior to mixing with the cement. This method was chosen to give equimolar amounts of anion in each case, with the actual level chosen to correspond to a dosage of 1% calcium chloride by weight of cement, a typical level in commercial practice. Retarders tend to be much more effective at lower dosages than accelerators,

Table 1
Oxide analysis of OPC

Constituent	CaO	SiO_2	Al_2O_3	Fe_2O_3	SO_3	MgO	Na_2O	K_2O	Free CaO
% weight	64.9	20.8	4.6	2.9	2.6	1.2	0.1	0.6	1.0

therefore sucrose was added at the significantly lower level. At the start of each hydration, the cement was added to the mixing water, which contained any admixture used. The paste was mixed for 2 min using a low speed domestic food mixer, poured into a sealed polythene container and then roll mixed, at 22°C until required. The sample was then transferred from the polythene container to the filtering apparatus inside a glove box kept under a nitrogen atmosphere.

2.2. Fluid extraction and storage

Fluids were extracted from each sample using a Baroid type filter connected to a nitrogen cylinder. Extractions were generally made after hydration had proceeded for 5, 20, 40, 60, 90, 120 and 180 min in each system. The exception to this was for the system containing calcium chloride, from which it was not possible to extract any fluid after 180 min at the pressures used. In this case the final sample was taken at 150 min.

An extraction pressure of 0.35 MPa (50 psi) was employed throughout. Filtration was carried out through two Whatman No. 542 filter papers. The residues of selected samples were also ground under an excess of Analar acetone and analysed by X-ray diffraction (XRD). Fluids were collected and stored in polythene containers to avoid contamination by SiO_2, which is leached from glassware at high pH levels. Samples were squeezed, filtered, sampled and stored in a purged closed system at 22°C. The danger of colloid formation upsetting the filtration results in the extraction process merits further work, since in mature paste, 70% by volume is taken up by colloidal silicate hydrate [35].

2.3. Analytical techniques

Appropriate dilutions were prepared under a nitrogen atmosphere for the determinations of calcium, sodium, lithium, magnesium and iron by atomic absorption spectrophotometry, for potassium by flame photometry and for aluminium and silicon species by X-ray fluorescence, using standard methods. As a further check, silicon was occasionally measured colorimetrically by reaction with ammonium molybdate and reduction with sodium hydrogen sulphite and 1-amino-2-naphthol-4-sulphonic acid solution to form the molybdenum blue complex. The following summary describes the methods employed for determining anions and sucrose:

Sulphate: Turbidimetric method, reaction with barium chloride to produce barium sulphate of uniform size.

Chloride: Colorimetric analysis after treatment with ferric alum solution and alcoholic mercuric thiocyanate.

Nitrate: Determined directly by its strong absorption at 220 nm. Only carbonate, phosphate, and organic matter were found to give significant interferences. Carbonate can be removed by the addition of 1 M hydrochloric acid and the maximum levels of phosphates expected in the fluid extracts are insignificant. The organic absorbance was measured at 275 nm and a factor of 1.6 times this value was determined from control tests as a correction factor to the determination at 220 nm.

Thiocyanate: Colorimetric analysis after treatment with dilute nitric acid and ferric nitrate to form red ferric thiocyanate.

Hydroxyl: Titration against standard hydrochloric acid using methyl orange indicator.

Sucrose: Colorimetric analysis, by treatment with chilled concentrated sulphuric acid, heating in a water bath for 5 min, followed by cooling to room temperature before determining the absorbance at 330 nm. The absorbance thus determined depends on the strength of the acid, therefore a new calibration curve was set up every time, the new determinations were made.

Preliminary trials showed no significant difference in the composition of the extracts made at different pressures or at various stages during a single extraction. It has therefore been assumed that the values obtained are representative of the whole of the solution phase. No attempt has been made to make allowance for the fact that, as hydration proceeds, water is slowly bound within the paste and then cannot be removed under the conditions used. Clearly, as water becomes bound, the amount of the solution phase will reduce. This will have implications for the total mass, as opposed to concentration, of material in solution. If no solute was removed from the solution, the concentration of all species would be expected to rise steadily as more of the solvent becomes bound. Similarly, continued hydration of the solid phase might also be expected to lead to increased amounts of certain species in solution. In general terms this did not happen in the samples examined, any rises were generally restricted to the first parts of the period studied.

2.4. Examination of the cement paste

A full account of the procedure followed has been reported previously [33]. Samples were taken after hydration had proceeded for 5 min, 1, 3, 6, 24 h and 3 days. The same conditions and materials as those used in the solution analysis were employed throughout. XRD traces were obtained using a Philips PW-1050 diffractometer with Cu-Kα radiation, nickel filter and a scanning rate of 1° 2θ/min. Differential scanning calorimetry (DSC) curves were generated using a Perkin Elmer DSC4. The samples were heated at 20°C/min in a nitrogen atmosphere with empty crimped aluminium crucibles as the reference material.

3. Results and discussion: solution analysis

3.1. Neat OPC paste

As an essential preliminary to the study of the influence of admixtures, experiments were first carried out to examine the solution composition in neat cement pastes. Fig. 1. presents concentration vs time curves of the major species in solution during the first 3 h. Concentration ranges for the minor species are shown in Table 2.

Most species detected remained at relatively constant levels throughout the period. The potassium concentration increased slightly over the first hour whilst sodium and lithium remained almost unchanged after the first 5 min. Calcium was present within the range 12–15 mmol/l at all ages. The major

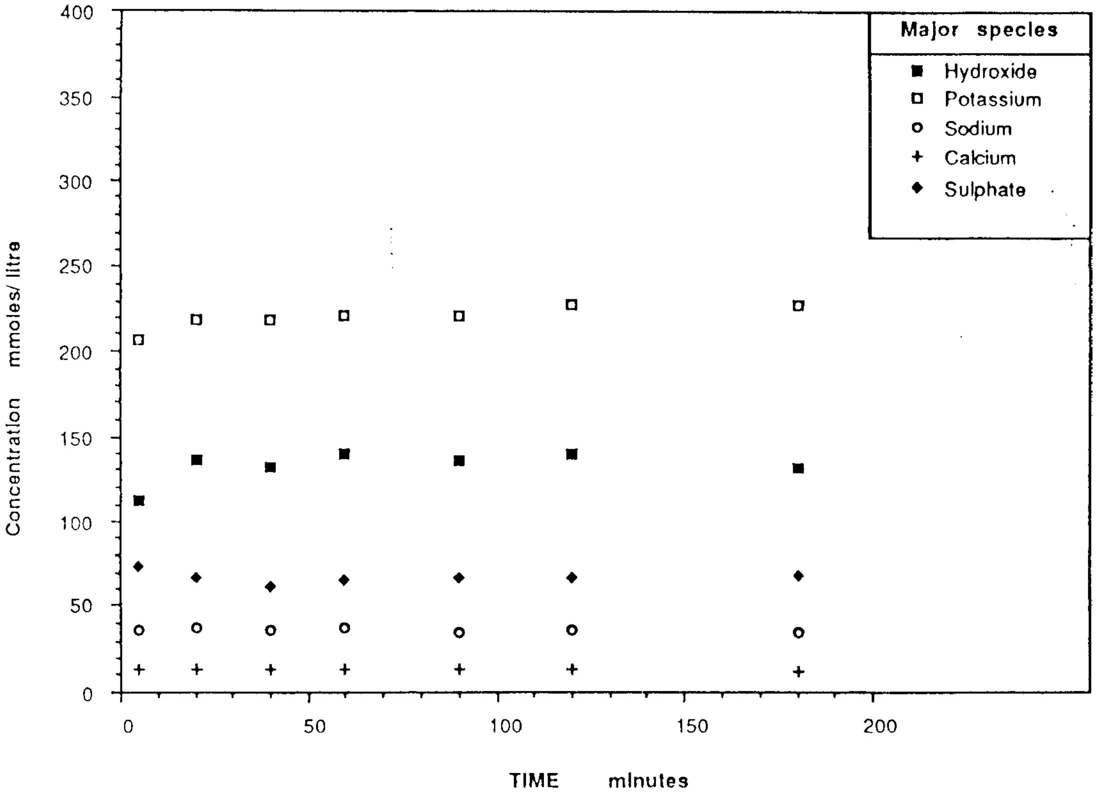

Fig. 1. Concentrations of major species in control system.

Table 2
Concentration ranges for minor constituents in neat OPC fluid[a]

Ion	Silicon	Lithium	Iron	Aluminium	Magnesium	Chloride
ppm	1.7–5.3	9.7–13.9	0–0.1	4.0–7.0	0–0.07	280–475
mmol/l	0.06–0.19	1.4–2.0	0–1.8 × 10^{-3}	0.15–0.26	0–2.8 × 10^{-3}	7.9–13.4

[a] The calculated pH values were 13.03 (5 min) increasing to 13.16 (180 min).

anions present were hydroxyl and sulphate, although low levels of chloride ion were also detected at all ages. The hydroxyl concentration rose steadily over the first hour, whereas that of sulphate dropped slightly over the same period, from 80 to 70 mmol/l. Other species, silicon, aluminium, magnesium and iron were only found at extremely low concentrations as has also been found by other workers [30,31].

The observed increase in hydroxyl and decrease in sulphate levels over the first hour, combined with the comparatively low level of calcium detected, suggests a combination of processes. Initially, alkali sulphates and possibly anhydrite, dissolve, followed by a removal of some sulphate from solution as the calcium salt, paralleled by liberation of hydroxyl from continuing hydration. The sulphate precipitation is probably governed by solubility product criteria of the calcium sulphate due to initial supersaturation of solution.

3.2. Calcium chloride

Fig. 2 shows the solution concentrations for OPC hydrated in the presence of calcium chloride. Although the initial chloride levels measured corre-

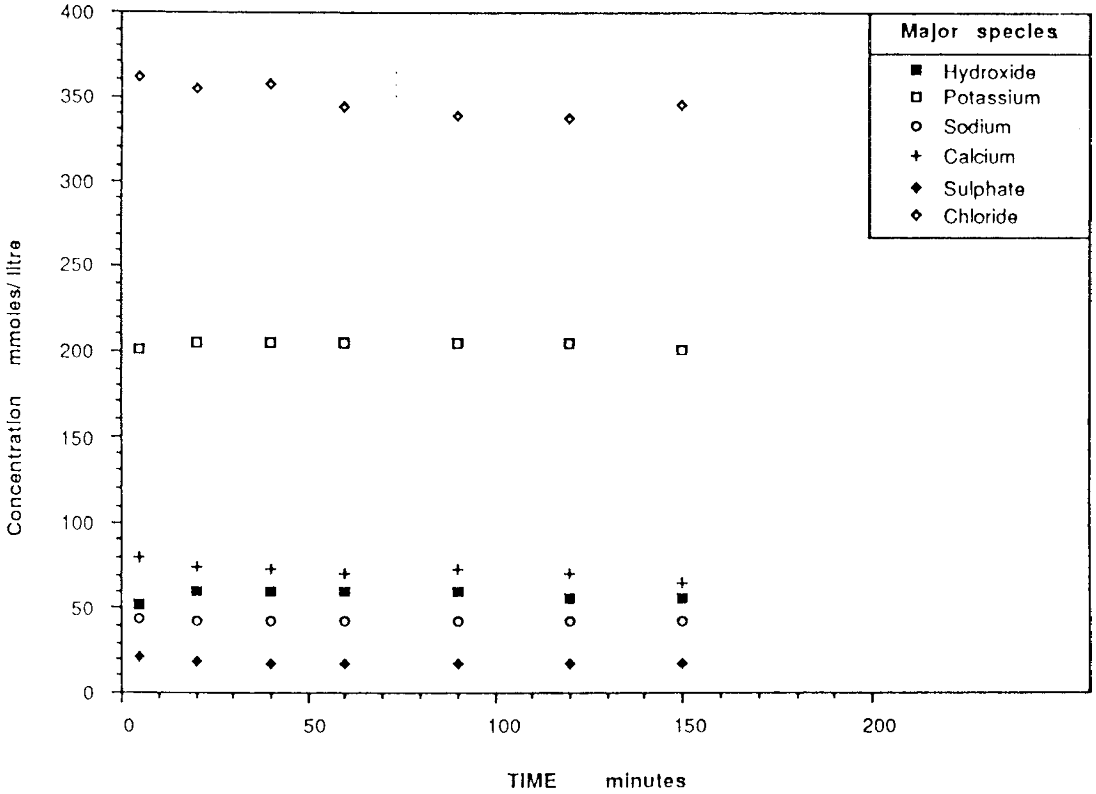

Fig. 2. Concentrations of major species in chloride system.

sponded reasonably well to those added, the amount of calcium detected was significantly less, the level measured at 5 min being less then 50% of that added. Levels of both ions decreased slightly with time. The addition of the calcium chloride also changed the detected levels of other ions, particularly sulphate and hydroxyl. Levels of both these anions were suppressed, although the general directional trends remained similar to those found in the control system. Sulphate was reduced from initial levels of 80 mmol/l in the control case to approximately 20 mmol/l. The general hydroxyl level was reduced from 140 to 60 mmol/l. Levels of sodium and other minor components were not significantly affected, although the potassium levels were slightly reduced.

It would appear that the aqueous phase becomes supersaturated very rapidly with respect to calcium sulphate and calcium hydroxide when calcium chloride is added. This suggests the precipitation of calcium sulphate and calcium hydroxide within the first 5 min to satisfy solubility product criteria. The presence of the chloride ion may also influence the solubility of calcium hydroxide and consequently the alkalinity of the extracts. The apparent decrease in chloride level may be due to the accuracy of the measurement. Statistical analyses carried out on chloride determinations indicated that absolute values thus determined are not totally reliable. The standard deviation at 96% confidence levels was estimated to be $\sim$10%. Clearly, this indicates that the variations reported in the chloride levels are well within the limits of experimental error. It should be noted that in other experiments using the same batch of cement but from a different drum, the levels of chloride were found to reduce considerably over the first hour, increase, then decrease again [36]. This variation in the chloride results may be due to experimental variation or might be attributed to the variation in the capacity of the cement for binding the chloride. It has been reported that the chloride binding capacity is influenced by the fineness, alkalinity of the cement and the chloride cation type [37–39]. Samples of the system studied were therefore taken from a blended sample of the respective drum.

3.3. Calcium nitrate

The concentration vs time curves for the different species present in the aqueous phase, after the addition of calcium nitrate, are shown in Fig. 3. The expected initial increase in calcium levels and decreases in sulphate and hydroxyl were found, although with differences from those seen with calcium chloride. Initial calcium levels were slightly lower compared with those found with chloride and continued to fall whilst the initial hydroxyl and sulphate levels were marginally higher. Sulphate levels continued to decrease towards the end of the period studied, whilst hydroxyl levels increased. The other significant difference was that the nitrate level dropped with time to a much greater extent than observed with the chloride, falling to 240 mmol/l after 3 h. There was very little variation in the levels and trends for other ions as compared with control values, as was the case in the chloride system.

The differences between these values and those for calcium chloride suggest that there may be changes in solubility product as the nitrate replaces the chloride in the aqueous phase, leading to different proportions of calcium and the major ion species.

3.4. Calcium thiocyanate

The composition of the aqueous phase for OPC hydration in the presence of calcium thiocyanate is shown in Fig. 4. Again the expected changes in calcium, sulphate and hydroxyl levels were found. Other species were present at similar levels to those found in the plain OPC system, with the exception of the potassium which was lower. The level of thiocyanate detected, although somewhat scattered, was approximately 320 mmol/l after the first 5 min and appeared to change only within the limits of experimental error after long hydration times. This level is only slightly lower than that would be expected from the initial addition level.

Calcium levels in this system were higher than those in either the chloride or nitrate systems, as were the hydroxyl levels. However, sulphate levels were comparable, if not slightly lower. It would therefore seem reasonable to expect the formation of less calcium hydroxide from solution in this system. Again, there is also the indication that the anion type has an effect on the solubility product balance.

3.5. Sucrose

The effect of a known retarder, sucrose, on the solution concentrations is shown in Fig. 5. The trends

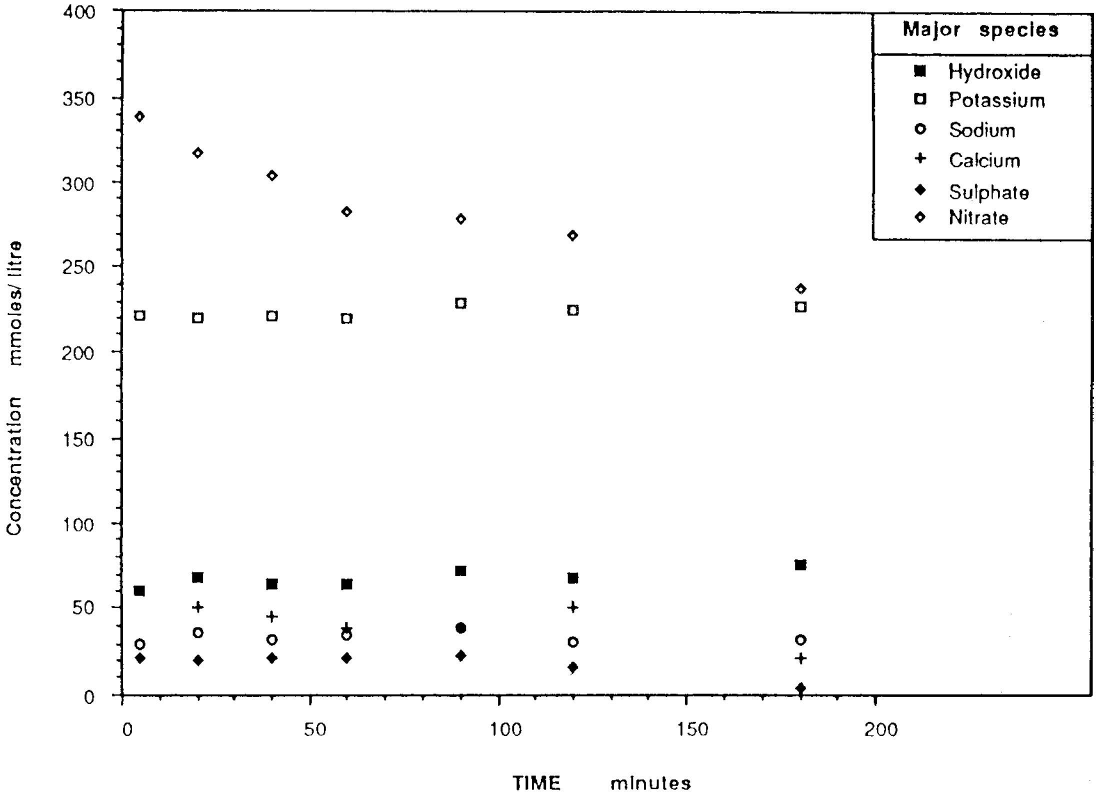

Fig. 3. Concentrations of major species in nitrate system.

found were clearly different from those for the previous systems. Hydroxyl levels rose over a longer period and reached higher levels even than those found in the plain OPC system. Calcium and sulphate levels were also higher than those for the plain system. There was still an initial drop in the sulphate level. The levels of other ions were similar to those found with plain OPC. The sucrose level detected after 5 min was 2.92 mmol/l compared with 5.85 mmol/l prior to the addition of cement, suggesting a loss of about 50% of that added initially.

The increased concentrations of sulphate and hydroxyl as well as calcium, when they would be expected to precipitate due to exceeded solubility product, suggests that the sucrose in some way removes calcium from the solubility product whilst holding it in solution. A possible mechanism for this would be chelation.

4. Summary of XRD and DSC examination of the cement paste

The examination of the solid phase by XRD and DSC methods have been reported in full elsewhere [33,34,36]. In each system, gypsum, ettringite and calcium hydroxide were the main new crystalline phases detected during the first hour, although the levels varied slightly between systems. After hydration for periods longer than 3 h, calcium hydroxide gave increasingly intense XRD peaks and was the major crystalline product in all systems. The major differences noted between the systems containing admixtures were as follows: Overall, the systems containing chloride and thiocyanate gave the highest levels of calcium hydroxide and the sucrose system, the lowest. The sample containing calcium nitrate had as much calcium hydroxide as that containing thio-

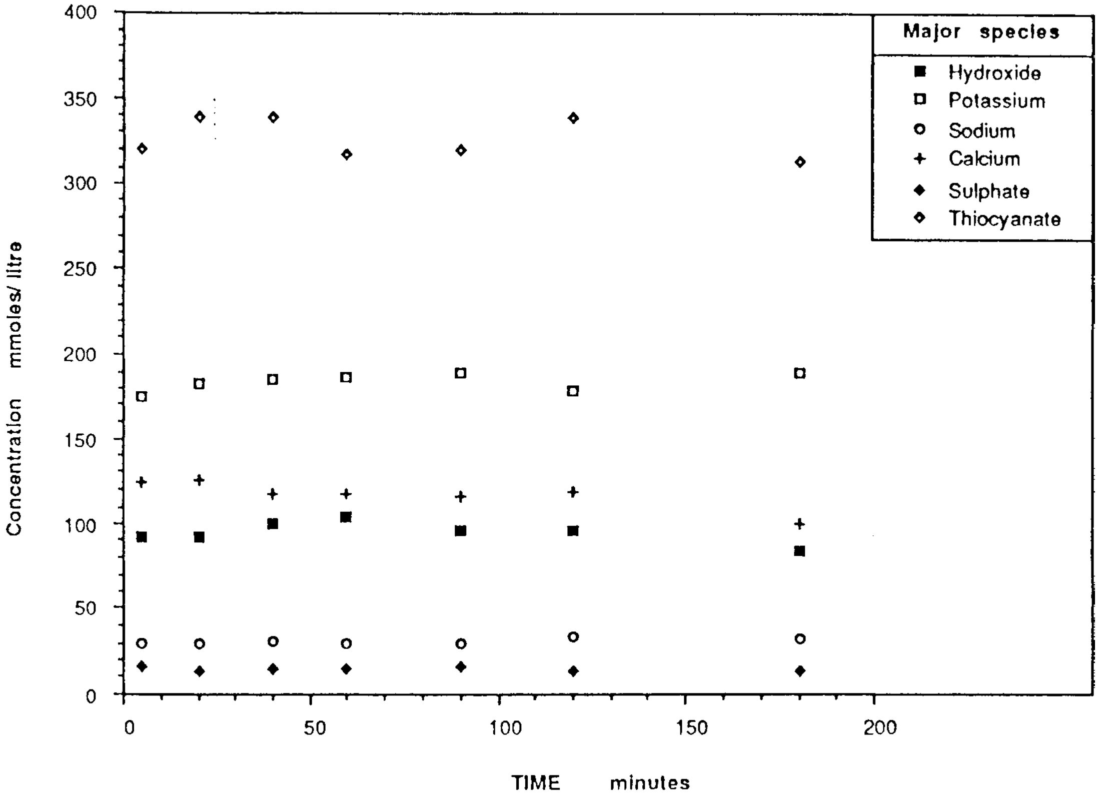

Fig. 4. Concentrations of major species in thiocyanate system.

cyanate during the first 4 h, but the levels detected after 12 h and at later ages were lower than for the control and after 3 days were even lower than those in the sucrose system. Comparisons made using the total energy absorbed as a measure of the degree of hydration confirmed the above trends, with the only difference being that nitrate was more effective than chloride and thiocyanate during the first 7 h. This presumably indicates the increased effect of nitrate on the formation of ettringite in this period.

A summary of the results obtained for sulphate containing phases is shown in Fig. 6. Three sets of data are shown on the same time axis for ease of comparison. The upper set of curves shows DSC values attributable to the presence of gypsum, which was not present in the anhydrous cement. Gypsum was formed in the first few minutes in each case and then consumed, none was detected after hydration for 3 h in the nitrate and sucrose systems or after 6 h in the other three mixes. The gypsum so formed and consumed can now be considered. The lower set of curves on Fig. 6 shows the XRD intensity, in scale values, attributable to the gypsum referred to above and the anhydrite present in the original cement. The changes in intensity reflect the consumption of these materials. The central set of curves shows the XRD values attributable to ettringite formation. Despite the differing degrees of hydration, there was little qualitative difference in the products of hydration except after hydration for 3 days. After this time, a C_4AH_{13}-chloroaluminate solid solution was identified in the chloride sample. However, the possibility of C_4AH_{13} being present cannot be ruled out, since both phases give the same XRD peak and DSC endotherm [33]. The results indicate that at earlier stages ettringite preferentially bind to any chloride containing product, with the latter being formed at later ages when sulphate levels are depleted. A C_4AH_{13}-monosulphate solid solution was detected in the corresponding sample containing nitrtate. By contrast, monosulphate was

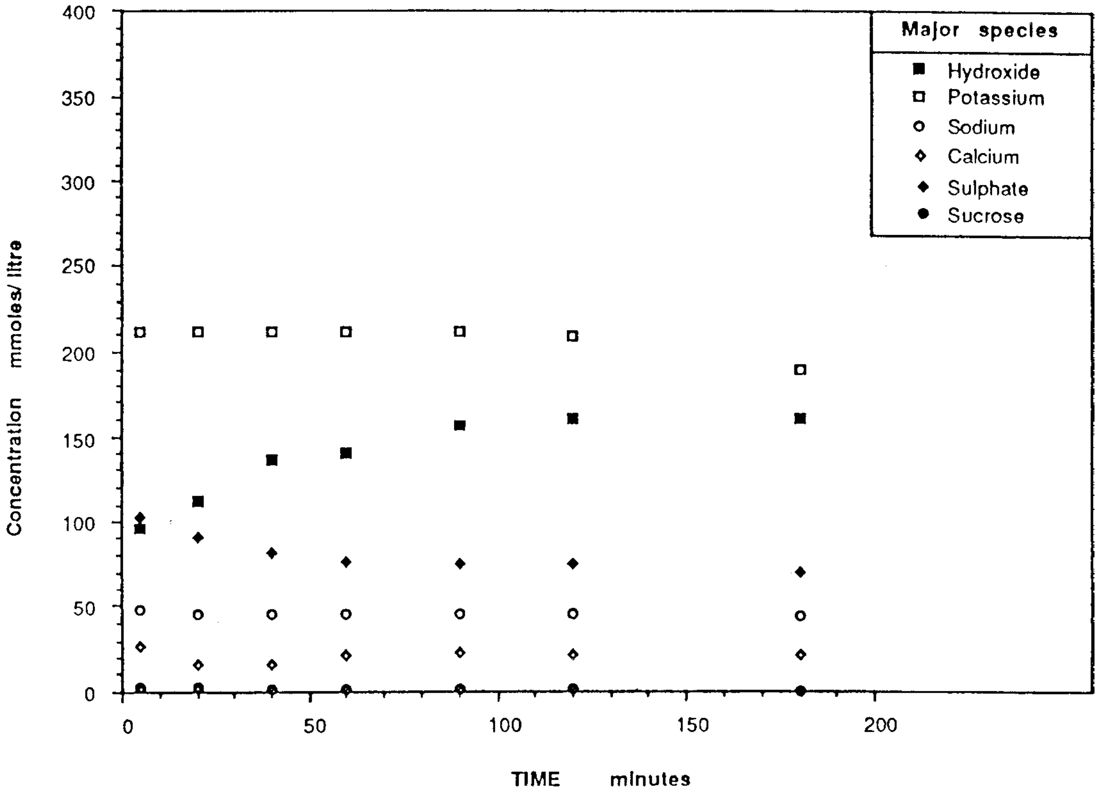

Fig. 5. Concentrations of major species in sucrose system.

the phase found after hydration for 3 days when calcium thiocyanate was the additive. No such phase was detected in the plain OPC or sucrose mixes.

5. Discussion

5.1. *Effects on sulphate*

Taken as a whole, the results indicate the formation of gypsum from solution in each system studied. In all cases there was a slight decrease with time of both calcium and sulphate levels in solution. The addition of sucrose gave more calcium and sulphate in solution than in the control case. When the three calcium salts were added, the analysis of the aqueous phases showed significant depressions of sulphate levels from those in the control system. The depression was possibly slightly more in the thiocyanate case. Calcium levels were higher than those for the control with each of the calcium salts, with the thiocyanate system being the highest. As the amount of calcium added in each case was the same, the anion added appears to have an effect on the solubility of calcium sulphate.

DSC and XRD results show that gypsum is an initial reaction product in each case, even though it was not present in the anhydrous cement. This corresponds to the initial decline in levels of calcium and sulphate ions in the aqueous phase. The addition of sucrose produced less gypsum formation than the control, corresponding to increased levels of sulphate ion in solution and therefore increased calcium sulphate solubility. Quantitative estimation of the levels of precipitated gypsum in the various systems, Fig. 6, indicates that the amount formed was markedly increased by the addition of the calcium salts, especially after the first 5 min. Comparisons between the three calcium salts at this stage shows that additions of the chloride or nitrate produced approximately equal amounts of gypsum with slightly more being detected when thiocyanate was the added. The levels of gypsum

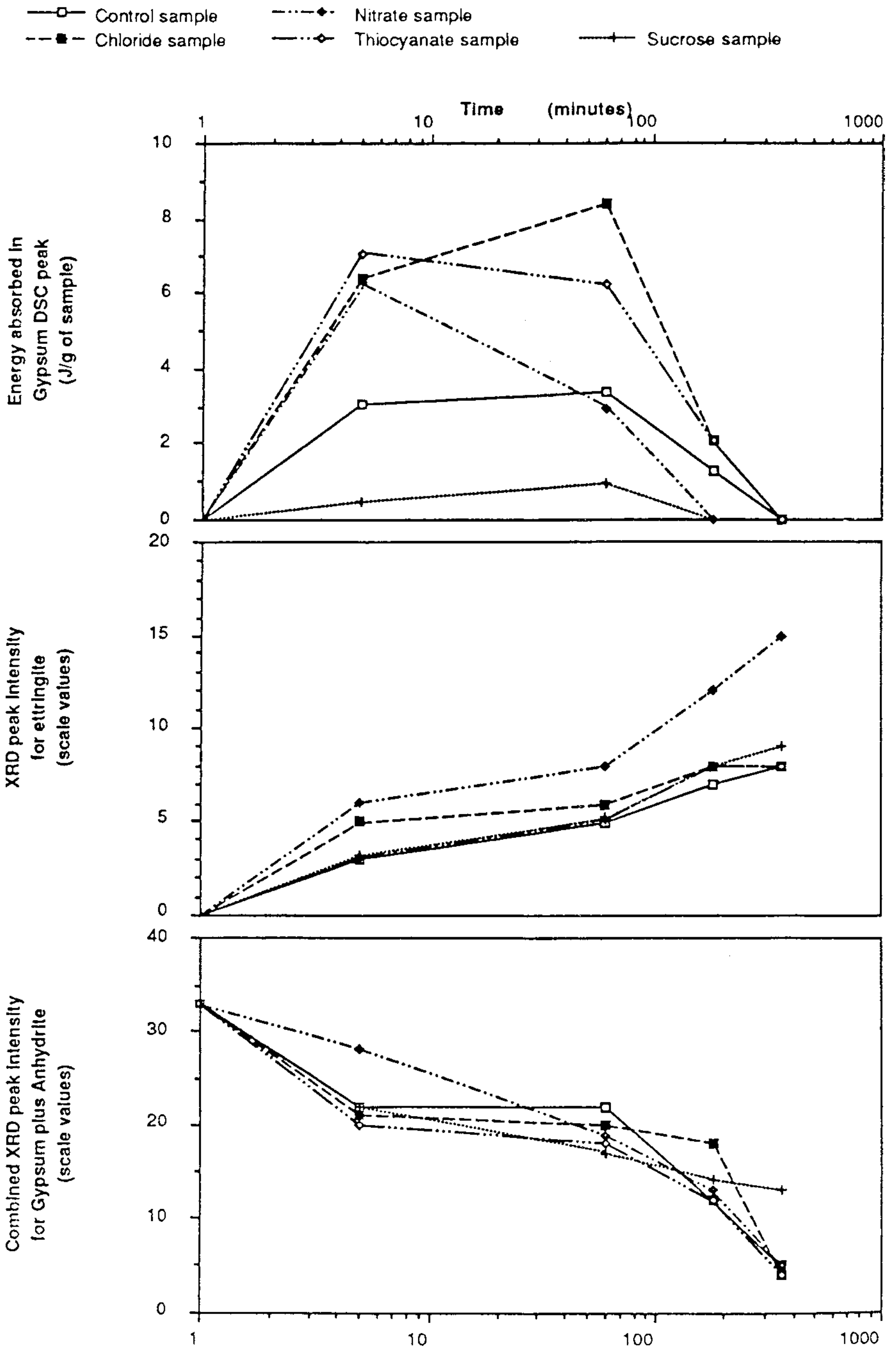

Fig. 6. Summary of XRD and DSC values for sulphate containing phases.

present after longer hydrations are clearly different. After 1 h, the levels of gypsum in the nitrate mix are diminished to values comparable to those for the neat paste, whilst that formed in the chloride mix continues to increase. In the thiocyanate case, gypsum decreased slightly after the first hour with none detected after 6 h hydration.

There are also variations in the levels of other sulphate containing phases, such as ettringite. Ettringite formation occurs rapidly in the 1–3 h period with the addition of the admixtures, as the source of sulphate, gypsum and anhydrite become available in the early stages of hydration, the more soluble gypsum being consumed first. This is important in the setting process and ultimate strength properties [40,41]. Significantly more ettringite is formed at all ages in the nitrate system. The amounts of ettringite detected in the thiocyanite mix during the first hour are identical to those in the neat OPC paste and sucrose systems, with chloride giving slightly higher values. After 3 h, however, slightly more ettringite is detected in the thiocyanate and sucrose mixes than in the neat paste. At this stage the formation of ettringite in the nitrate and sucrose systems continued to take place, even though the levels of gypsum were completely exhausted. Therefore, it must be assumed that anhydrite or sulphate ions in solution are the only sources involved in continuing the reaction.

It is of interest to note that between 3 and 6 h, the formation of ettringite is still much greater in the nitrate mix than in any of the others, while levels of the total sulphate continue to fall at much the same rate in each case. This would suggest that, at this time, sulphate is being incorporated into other hydration products in the systems other than the nitrate. Although there must be reservations about the reliability of the levels of sulphate determined by XRD, the results for gypsum from DSC also support the above trend. This is in line with the findings of Menetrier et al. who showed that CSH can accommodate substantial amounts of sulphate ion [42].

5.2. *Effects on hydroxide*

When hydroxyl levels in solution are compared, all three calcium salts depressed the control levels, with the thiocyanate being least effective. There is very little difference between the hydroxyl levels with nitrate and chloride additions, although the nitrate shows marginally higher values. These results again suggest different effects on solubility, this time on calcium hydroxide, between the three anions. The effect of the sucrose on the hydroxyl levels is less easy to determine. Levels after 3 h are higher than for the control system but at earlier ages the levels are lower. As calcium levels are higher than in the control at all ages, it would appear that there has been some slight effect of increasing the solubility of the calcium hydroxide in the presence of sucrose.

It might be expected that a greater depression of the hydroxyl ion concentrations would lead to higher levels of precipitated calcium hydroxide, particularly, as there is little apparent effect on the alkali metal levels from adding the calcium salts. The lack of significant differences in the solid phases, however, may be due to the fact that the differences in calcium hydroxide formed from solution are so small as not to be detected by DSC. Additionally, there may be an effect from any solid phase hydration also contributing to the detected levels which cannot be separately assessed.

6. Summary

The major differences between the systems studied, both in the solution and solid phases, are in the sulphate and hydroxyl containing species. There are also variations in the level of calcium ions present. Added calcium ion is responsible for the precipitation of sulphate and hydroxide, forming gypsum and calcium hydroxide from solution. This is presumably to satisfy solubility product criteria. There is also an effect from anion type, the different calcium salts having slightly different effects on the sulphate and hydroxide solubilities. This secondary effect is most noticeable in solution with the hydroxyl levels and in the solid with the sulphate containing phases. In the presence of sucrose, calcium levels are again increased but in this case the effect is to allow supersaturation of calcium salts, possibly by chelation of the calcium ion, so reducing the formation of gypsum and calcium hydroxide. Although there are some changes in concentration at later ages, the bulk of these variations, or the driving force behind them, seem to occur within the first 5 min. Since solution phenomena are likely to dominate in the first 5 min of hydration, the contribution from solution is expected to be highly significant. In high pH environments, as exist in these systems, different complexes can form, especially hydroxy complexes, involving the cations and anions which are significant components of the systems studied. Variations, caused by the different pH levels in the various samples are to be expected. Although direct experimental evidence is not available, it is likely that the nature and extent of these complex formations will determine the rate of dissolution of the cement materials and the solubility of calcium hydroxide. This in turn governs the amount of calcium hydroxide, CSH and other phases formed, and therefore the degree of hydration.

7. Discussion of mechanism of acceleration

The results discussed above shows that clear differences in the degree of hydration and the solution chemistry of the liquid phase are brought about by the addition of admixtures. These differences, although apparently somewhat minor, are the only factors to give rise to the major effects of admixtures which have a practical use in speeding up the setting and strength gain of hydrating OPC. Therefore, a model based on these observations and building upon them with information from other systems with different cation–anion combinations, may be able to probe the mechanistic aspects of acceleration.

It is generally accepted that the addition of gypsum, or other similar sulphate phases, to Portland cement, not only controls setting, but also influences other properties. There is an optimum amount of addition required which varies with the composition of the cement, especially the alkali and tri-calcium aluminate contents. This study and others have shown that the alkali sulphates come into solution immediately after adding cement to water. Other sulphate sources are the added calcium sulphate phases added to the cement clinker. It is the dissolution of these sulphates which leads to the formation of gypsum from solution. This precipitates and then is consumed, apparently in preference to the remaining anhydrite, in the formation of ettringite with the tri-calcium aluminate present in the cement. Ettringite may have a direct effect on stiffening or strength development and there is no doubt that the binding of water and the evolution of heat due to its formation will cause partial loss in the plasticity of the paste. Moreover, the extent of ettringite formation can determine whether or not sulphate is incorporated in the CSH structure, which has been reported to result in a substantial increase in the 24 h strength of hydrated tri-calcium silicate [43].

The addition of calcium salts as admixtures leads to the formation of more gypsum and calcium hydroxide, which are the major products of the hydration process, than in the plain OPC paste. The significance of this is many fold. The gypsum and calcium hydroxide formed from solution are well crystallized and would not be expected to limit access of water to the cement grains. In addition, gypsum is important for the formation of ettringite which, at least indirectly, affects the stiffening process and determines the extent of gypsum substitution in the CSH gel and consequently its strength. Finally, the formation of more calcium hydroxide and gypsum than in a plain OPC paste of the same age would lead to the evolution of more heat due to their hydration and precipitation. Despite the fact that some of the heat so produced will be lost to the surroundings, rising the initial temperature of the cement mix by a few degrees can affect the hydration process considerably. It is likely that the initial peak in isothermal heat evolution curves is in part due to these precipitations and work is in progress to verify this fact. It should be noted, however, that it has been shown that overall increases in the formation of gypsum and calcium hydroxide cannot be achieved through the addition of excessive amounts of admixture, since the sulphate and hydroxyl ions are the limiting reactants [44]. It appears therefore that a specific amount of admixture is needed to achieve the optimum early formation of calcium hydroxide and gypsum. This explains why a certain amount of admixture is required to achieve the maximum degree of acceleration, since further additions may upset this balance and result in the formation of other compounds.

Alongside the variations in the solid phase discussed above, the effects of the hydration processes and admixture additions will also produce changes in the composition of the solution phase with the various ions being present in differing ratios. The precipitation of sulphate and hydroxide phases removes their cations from solution, to be replaced, at least in part, by the cation added in the admixture. If the solution phase is considered as a collection of salts in solution, by pairing cations and anions, the composition of the solution is significantly affected. There are also other factors that will affect the solution, its composition at any particular time, and whether this is in equilibrium, metastable or transitory state. Three potential factors are disorder, the dielectric constant of the solvent, and the energy of interactions between the solvent molecules and the solute ions. Of these, the last is the most important, particularly if considered alongside the formation of complex ions between the various cations and anions present. Complexes are more likely at the high pH levels found in these systems and their formation will then affect the hydration of the cement minerals. The nature of complexed species found and the solubility of calcium hydroxide will also vary with the concentration of the salt added. Since solution equilibria appear to be major factors in the initial stages of hydration, the relative degree of solvation of ionic reactants and the presence of transition states are likely to be the primary factor in determining the reaction rate. Unfortunately, the lack of data on the stability and nature of these species at such a high pH makes it difficult to determine or predict their likely effects in such a complicated system.

8. Conclusions

A number of changes to the chemistry of the liquid and solid phases of cement paste are caused by the addition of different admixtures. Of particular importance is the formation of more gypsum and calcium hydroxide from solution within the first 5 min, together with the depression of calcium, sulphate and hydroxyl ion concentrations found with the addition of calcium salts. Despite the lack of detailed understanding, the results of this work clearly support the idea that both cation and anion are active in the acceleration mechanism. The possible formation of transition and complexed states and the relative degree of solvation of these and other ionic species appear to be the major factors governing acceleration.

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