

Changes in Composition of the Aqueous Phase During Hydration of Cement Pastes and Suspensions

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The chemical reactions taking place in the early stages of the hydration of a number of portland cement-water pastes and suspensions have been followed by periodically extracting and analyzing the aqueous phase. Three reactions have been examined: the crystallization of calcium hydroxide; the release of alkali metal ions from the lattice of the C_3A phase on hydration; and the combination of the C_3A phase and calcium sulfate. The effects of alkali metal ions on these reactions have been investigated and the possible bearing these have on the hydration of commercial cements is discussed.

•THIS REPORT describes an investigation into the chemical reactions which take place in the first few hours after water has been added to commercial cements. It has proved possible to follow these reactions by successive separations and analyses of the aqueous phase from reacting cement-water pastes and suspensions. From the results obtained it appears justifiable to draw the following conclusions:

1. The rapid rise of the calcium hydroxide concentration to a peak value and its subsequent slow fall is the result of a slow crystallization of calcium hydroxide from the aqueous phase.
2. The acceleration in the rate at which sodium and potassium ions are released to the aqueous phase, after all the calcium sulfate has been combined in the formation of ettringite, is closely associated with the increased rate of hydration of the C_3A at this time, and it is deduced that sodium and potassium ions are incorporated in the C_3A phase present in cements studied in this investigation.
3. The kinetics of the combination of calcium sulfate with C_3A suggest that neither the diffusion of ions through the aqueous phase nor the diffusion of ions or water molecules through the accumulating hydration products is the rate-determining step of this reaction.

The composition of the aqueous phase in cement-water systems has been considered by Greenberg and Mehra (1), who, by application of the Debye-Hückel equation have calculated the activity coefficients of the ions present in the aqueous phase and, from data on the saturated systems C-S-H, C-A-H, and C-A-S-H, (C = CaO, S = SiO₂, H = H₂O, \bar{S} = SO₃, A = Al₂O₃), conclude that the Ca²⁺ and OH⁻ ion concentrations are above their respective equilibrium levels. The concentration of sulfate ions present is found to be at the equilibrium value so that the aqueous phase can be regarded as being composed essentially of a supersaturated calcium hydroxide solution saturated with calcium sulfate dihydrate. In the aqueous phase there are also sodium and potassium ions present at concentrations which are normally below "equilibrium" levels and these remain nearly constant during the early hydration processes. The aqueous phase also contains SiO₂ and Al₂O₃ but at concentrations which are very low and can be disregarded.

In the present work departures from equilibrium concentrations in the aqueous phase have been detected by comparing these cement extracts with solutions containing an equivalent concentration of alkali metal ion and which are in equilibrium with calcium hydroxide and calcium sulfate dihydrate crystals.

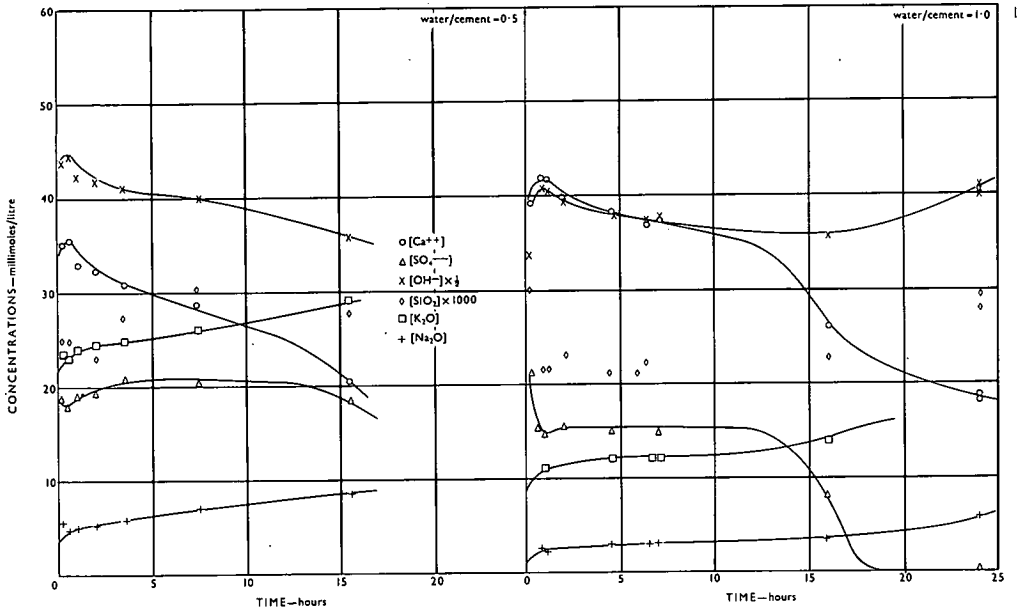


Figure 1. Composition of the solution phase in contact with hydrating cement 242 at 15 C.

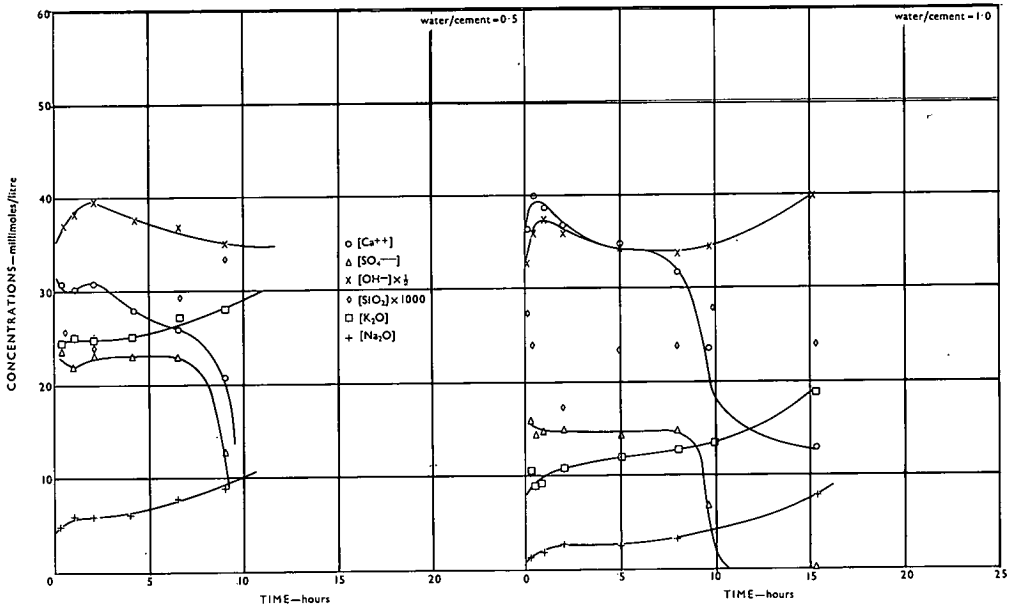


Figure 2. Composition of the solution phase in contact with hydrating cement 242 at 25 C.

Several reports of the influence of alkali metal salts on the performance of portland cements have been made (2, 3), and the part played by sodium and potassium ions in the early hydration reactions has been studied in this work.

Small amounts of sodium and potassium, equivalent to about one percent by weight of the cement as Na_2O and K_2O , are combined in most commercial portland cements. Part of the alkali is present as readily soluble sodium and potassium sulfates and part

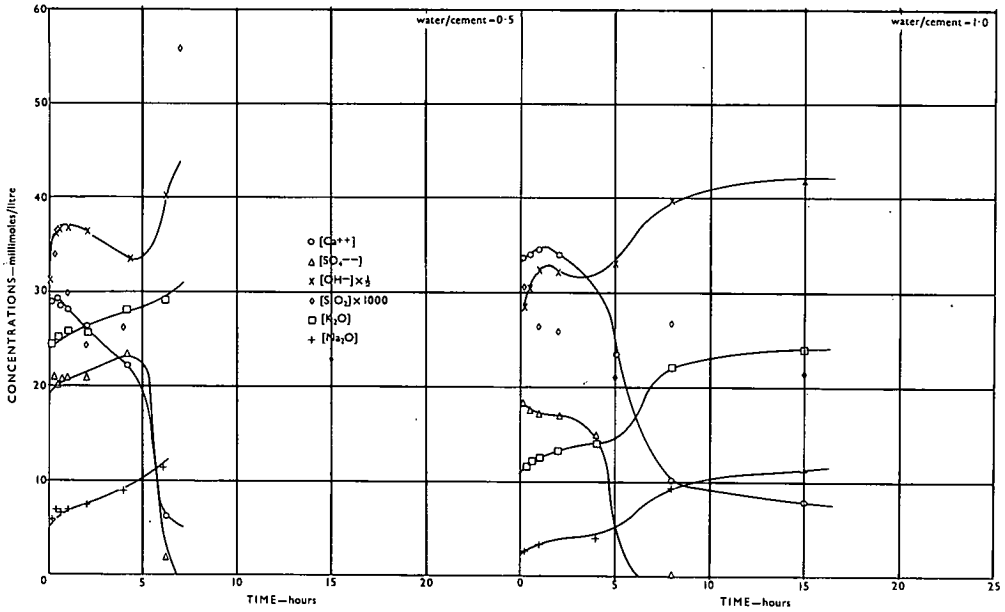


Figure 3. Composition of the solution phase in contact with hydrating cement 242 at 35 C.

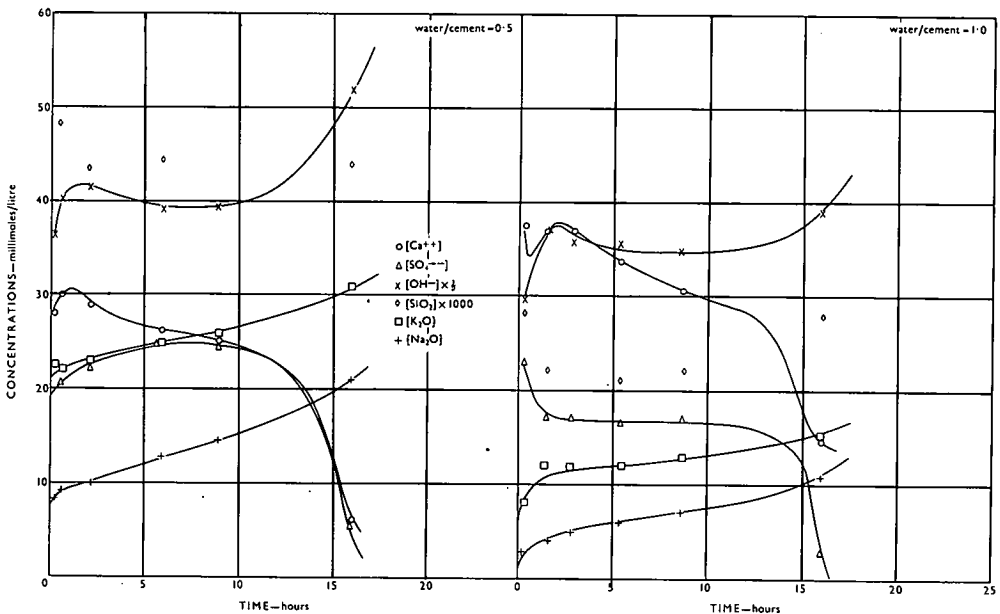


Figure 4. Composition of the solution phase in contact with hydrating cement B at 25 C.

is combined in the calcium silicate and aluminate phases, only being released to the aqueous phase when hydration occurs (4, 5). The manner in which these alkali metals are so combined is not completely resolved but the compounds NC_8A_3 , KC_8A_3 , and $KC_{23}S_{12}$ have been prepared under conditions which suggest that they may be present in cement clinker (4, 6). Additional evidence has been recently provided in this laboratory of a modified C_3A phase present in some cements and it was suggested that the incorporation of alkali metal ions into the C_3A lattice could have been responsible for the observed change in X-ray diffraction pattern (7).

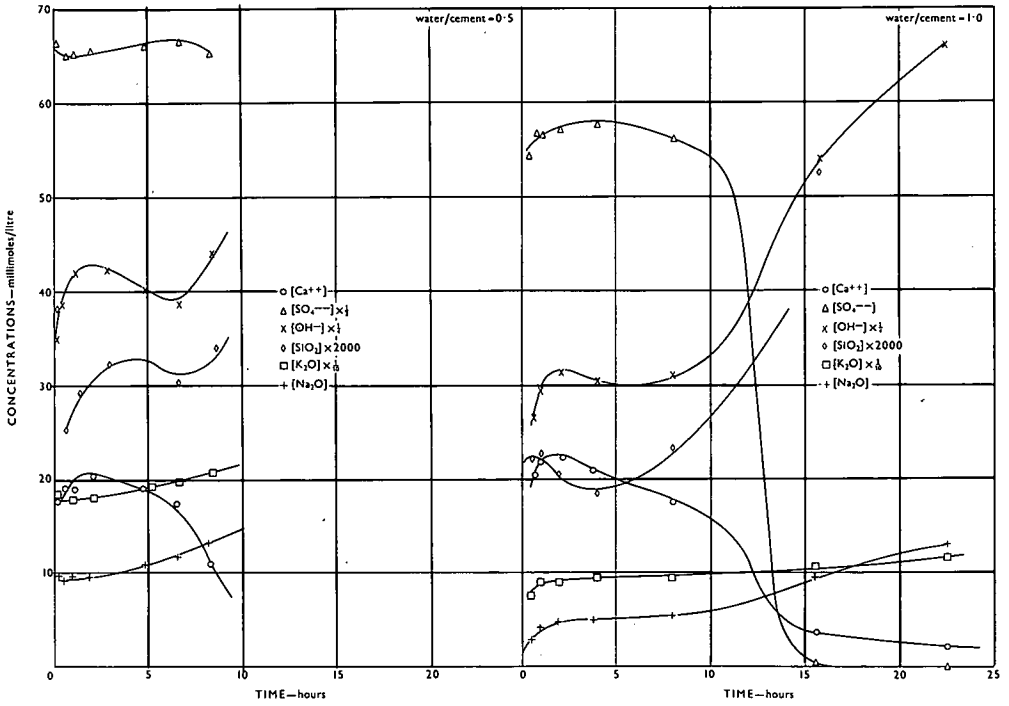


Figure 5. Composition of the solution phase in contact with hydrating cement 244 at 25 C.

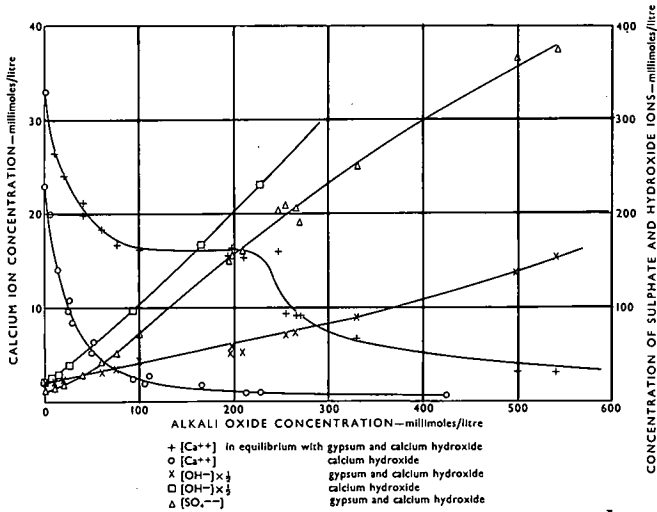


Figure 6. Composition of solution in equilibrium with calcium hydroxide and with both calcium hydroxide and gypsum in the presence of increasing amounts of alkali at 25 C.

The mechanism by which sulfate ions are able to retard the normally very rapid hydration of the C_3A present in most commercial cements is not fully understood. Stein (8) has suggested that ettringite, which is the reaction product during the retarded reaction, forms a protective layer around the C_3A crystals. It is not clear how this layer can be quickly rendered ineffective when there are no further sulfate ions in the

TABLE 1
CONCENTRATION OF IONIC SPECIES IN THE AQUEOUS PHASE IN
CONTACT WITH HYDRATING CEMENT

Cement	W/C Ratio	Time (hr)	Ionic Concentration as Percentage of Saturated Concentration at 25 C			
			Ca	OH	SO ₄	
242	0.5	1	141	146	105	
		2	141	154	100	
		3	136	144	98	
		5	129	132	95	
	1.0	1	150	169	105	
		2	146	166	100	
		3	139	164	100	
		5	136	148	100	
	244	0.5	1	125	145	86
			2	129	149	88
3			125	139	85	
5			118	134	83	
1.0		1	129	150	83	
		2	137	153	85	
		3	137	153	85	
		5	121	145	83	
B		0.5	1	138	158	95
			2	135	156	95
	3		133	152	100	
	5		129	143	100	
	1.0	1	135	159	105	
		2	148	167	100	
		3	148	157	100	
		5	142	146	100	

aqueous phase available for reaction. A modification of this theory was proposed recently by Schweite et al. (9) who deduced that the protective ettringite layer is continuously spalling off and being replaced by fresh ettringite as the reaction proceeds.

A study of the early hydration reactions of portland cement-water pastes has been made in this laboratory using a conduction calorimeter and the results support those obtained by Lerch and others who used similar techniques (10). The present work on the composition of the aqueous phase extracted from hydrating cement pastes and suspensions was intended to be a complementary investigation which would throw light on the chemical reactions responsible for the observed changes in rates of heat evolution.

REACTIONS OCCURRING IN CEMENT PASTES OF LOW WATER/CEMENT RATIO

Data were obtained from experiments (procedure is given in the Appendix) with cement pastes at cement/water ratios of 1:0.5 and 1:1, at temperatures of 15, 25 and 35 C, using three different commercial portland cements (Figs. 1 - 5). The values of Ca²⁺, SO₄²⁻, and OH⁻ ion concentrations in the aqueous phase of these pastes have been compared with the equilibrium concentrations of these ions in the Ca(OH)₂-CaSO₄·2H₂O-water system modified by the additions of sodium and potassium ions to give the same concentrations of these ions as measured in cement paste extracts (Fig. 6). Departures from equilibrium concentrations are indicated in Table 1. The data for two cements (242 and B) giving low sodium and potassium ion concentrations show that the aqueous phase was essentially saturated with respect to calcium sulfate dihydrate and supersaturated with respect to calcium hydroxide. The degree of supersaturation fell in the period one to five hours after mixing in experiments conducted at 25 C. X-ray diffraction photographs of the solid phase, i. e., the partially hydrated cement, indicated

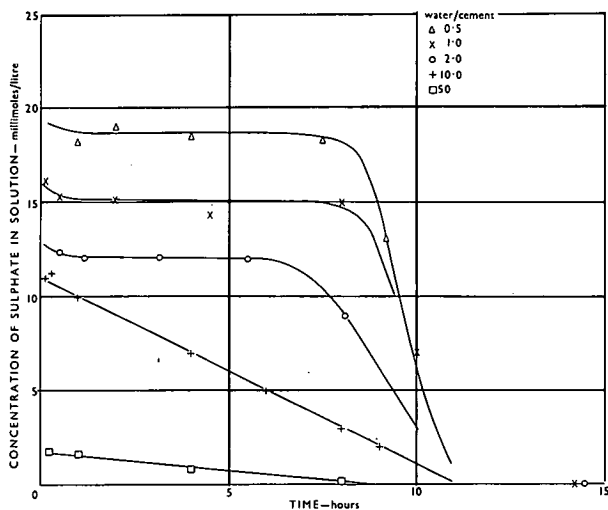


Figure 7. Influence of water/cement ratio on the absorption of sulfate by cement 242 at 25 C.

TABLE 2
AMOUNT OF ALKALI RELEASED TO SOLUTION PHASE AT DIFFERENT
WATER/CEMENT RATIOS

Cement	Temperature (deg C)	W/C Ratio	Alkali Released (millimole oxide/100 g cement)			
			After 1 hr		After 16 hr	
			Potassium	Sodium	Potassium	Sodium
242	15	50	17.4	8.05	17.4	13.4
		10	13.0	4.03	17.3	7.5
		2	12.5	3.22	14.2	4.9
		1	13.5	3.48	14.9	5.3
		0.5	12.5	3.0	15.2	4.7
	25	50	15.7	5.35	21.7	13.4
		10	13.2	3.75	19.4	7.52
		2	12.8	3.76	20.4	9.6
		1	13.2	3.48	20.0	8.1
		0.5	12.5	3.49		
	35	50			26.0	13.4
		10	14.5	4.30	20.1	8.6
		2	13.9	3.76	25.6	12.3
		1	12.8	3.75	25.6	12.1
		0.5	13.9	3.68		
244	25	50	108	10.1	111	13.4
		10	96	5.4	111	9.2
		2	96	5.4		
		1	95	5.4	111	9.7
		0.5	91	4.7		
B	25	50	14.1	8.4	15.2	11.7
		10	13.0	5.4	18.6	12.1
		2	13.0	5.4	17.4	14.1
		1	13.0	5.4	16.5	12.4
		0.5	11.9	4.7		

that relatively large calcium hydroxide crystals were forming in this period and it is probable that the fall in the degree of supersaturation arises simply because of the nucleation and growth of calcium hydroxide crystals from the aqueous phase.

The aqueous phase given by cement 244, which contains a high potassium ion concentration, was also supersaturated with respect to calcium hydroxide but had less than the equilibrium concentration of sulfate ions.

The concentration of silica in the aqueous phase does not show any marked decrease during the early stages of the hydration as might be expected to occur if nucleation and crystallization of calcium silicate hydrate were taking place from solution. The silica concentration is higher than the equilibrium value in the system C-S-S-H, and the aqueous phase is therefore probably highly supersaturated with respect to calcium silicate hydrate. This is supported by evidence from X-ray diffraction photographs which show that calcium silicate hydrate, formed synthetically from solutions highly supersaturated with respect to calcium hydroxide, shows a weak diffuse pattern similar to that given by the calcium silicate hydrate formed in the hydration of cement pastes. Calcium silicate hydrates produced by synthesis from colloidal silica and saturated calcium hydroxide solutions usually show a more detailed pattern which includes a strong line denoting a basal spacing at about 12 Å not present in the pattern shown by cement hydration products or solids synthesized from supersaturated solutions.

The concentrations of sodium and potassium ions in the aqueous phase in cement-water mixes rapidly increase in the first minutes of the reaction for all cement examined. They then remain nearly constant for some hours at a value which is inversely proportional to the water/cement ratio of the mix. Thus a constant fraction of the alkali metal ions combined in the cement is readily soluble independent of the water/cement ratio. A further rise in the alkali metal ion concentrations can be observed when all sulfate ions have been removed from the solution phase. This observation has been further investigated at high water/cement ratio where the reaction can be followed for longer periods of time without the difficulty of extracting solutions from partially set pastes; the results are given later.

When a high alkali metal ion concentration is present in the aqueous phase, the reduction of the large sulfate ion concentration present to zero after all the solid calcium sulfate initially present in the cement has been used up by reaction with C₃A to form insoluble ettringite can be seen to be accompanied by a large increase in the hydroxyl ion concentration (Fig. 5) indicating that calcium hydroxide has been dissolved by the aqueous phase at this point. If calcium hydroxide has to dissolve in aqueous phases containing high alkali metal ion concentration during the reduction of sulphate ion concentration to zero, the calcium hydroxide concentration in these solutions tends to be reduced to the saturated value. No calcium hydroxide need dissolve at this time if alkali metal ions are not present in the aqueous phase; in this case the solution can remain supersaturated with respect to calcium hydroxide after sulfate ions have been removed from the aqueous phase.

The time taken from the moment of mixing cement with water to the point at which the sulfate ion concentration in solution dropped to a negligible level was found to depend on the temperature at which the reaction took place. In order to obtain more information on the C₃A-calcium sulphate reaction and to be able to derive an activation energy for this reaction it is necessary to know the course of the reaction at earlier times in the hydration. The use of a higher water/cement ratio would allow this information to be obtained from successive concentration measurements in the aqueous phase during the reaction, but it was necessary first to establish that addition of excess water to the system did not change the character of the reaction, and accordingly a series of experiments was made to examine this point.

COMBINATION OF CALCIUM SULFATE AND RELEASE OF SODIUM AND POTASSIUM IONS

Effect of Water/Cement Ratio on Reaction Rates

Cement-water mixes having a range of water/cement ratios between 0.25 and 50 were examined using three different cements. As far as could be judged the rate of reaction of sulfate ions with the anhydrous cement (Fig. 7) and the percentage of alkali released at a given time (Table 2) were independent of the water/cement ratio, provided a saturated lime solution could be formed very quickly by the cement. The aqueous

phase became saturated with calcium hydroxide almost immediately using water/cement ratios between 0.25 and 10 but took several hours to reach saturation when a water/cement ratio of 50 was used. It follows that the concentration of water in these systems as measured by the water/cement ratio does not affect the rate of release of alkali or the rate of reaction of calcium sulfate in the opening stages of the reaction. Differences in behavior between the hydration of pastes and of dilute suspensions might be expected at later stages, as the water available for reaction is decreased by combination in the hydration products.

At a water/cement ratio of 10:1 the aqueous phase rapidly becomes saturated with gypsum and calcium hydroxide but after a short time the reaction of the sulfate ions with the cement reduces the sulfate concentration below the saturation level. This allows the amount of sulfate combined by the cement to be obtained a few minutes after mixing the cement with water from the analysis of the aqueous phase.

Release of Alkali to Solution Phase at 10:1 Water/Cement Ratio

The sodium and potassium ion concentrations in the aqueous phase rose rapidly in the first 15 minutes of hydration and thereafter increased slowly over the next six or seven hours. After this time the rate of release of alkali metal ions again increased, then finally dropped again after about ten hours' hydration to a slow rate of increase of alkali in solution (Fig. 8). The second acceleration in the rate of release of alkali occurred as or just before the sulfate ions were completely removed from solution. Addition of extra calcium sulfate to the system resulted in a delay before the second acceleration in rate of release of alkali and it again took place at the time when sulfate ions disappeared from solution (Fig. 9). The increase in rate of release of alkali then seems to be associated with the rapid reactions which occur on removal of sulfate ions from the aqueous phase. The most obvious reaction is the hydration of C_3A which is known to be delayed by the presence of sulfate ions in the solution phase. On this basis some of the alkali present in the cement is trapped in the crystal lattice of the C_3A phase and is released to the solution phase when hydration occurs.

An examination of the amounts of alkali released between two times of hydration, chosen to include the second increase in rate of alkali release to the aqueous phase, is illustrated in Table 3. It is interesting that cements which show a modified C_3A phase X-ray diffraction pattern also show an abnormally high release of potassium but not sodium ions during this period. This can be interpreted as showing that the modified C_3A phase contains considerable amounts of potassium in its lattice. This view is strengthened by the closeness of the modified C_3A phase diffraction pattern reported (7) and that of KC_8A_3 given by Suzukawa (6).

Kinetics of Reaction of Calcium Sulfate With Cement

The shape of the curve of amount of sulfate ion removed from solution against time indicates that the controlling step in the process takes place on the surface of the anhydrous grains of the cement rather than by a control mechanism depending on the diffusion of some species through a thickening layer of reaction products. If the latter diffusion mechanism is applicable, the rate would be very rapid at first and then fall off continuously as the layer of products built up. In fact, an almost constant rate of uptake of sulfate ion persists for several hours and then gradually tails off, possibly as the amount of C_3A surface available for reaction is decreased by the reaction. When extra calcium sulfate is added to the system the solution phase remains saturated for much of the reaction time with calcium sulfate as would be expected if the rate of solution of calcium sulfate was rapid compared to the rate of reaction of the sulfate ions with cement.

Addition of moderate amounts of sodium sulfate (anhydrous) in place of calcium sulfate does not change the rate of uptake of sulfate to any marked extent though some increase in rate could be detected for 20 percent and 30 percent additions (by weight of cement) after 65 hours' reaction at 35 C (Fig. 9). These weights of added sodium sulfate correspond to initial concentrations of approximately 140 and 210 millimole Na_2SO_4 per liter respectively in the aqueous phase and are probably near the maximum alkali concentration found in the aqueous phase of portland cement pastes. From this

result it appears that sulfate ion diffusion into the reacting cement, which would be influenced by the sulfate concentration in solution, is not a rate-determining step, and also that the influence of alkali on the reactions in cement pastes is not caused by changes in the rate of formation of ettringite.

Recent work on the hydration of C_3S , βC_2S , $CaSO_4 \cdot \frac{1}{2}H_2O$ and CaO and the conversion of C_3AH_6 to ettringite using radioactive tracers has led to the idea that surface mechanisms are applicable to these reactions (11). The present work, which proposes a surface mechanism for the formation of ettringite from C_3A and calcium sulfate, therefore seems to be in line with hydration reactions previously described by other workers.

The rate of combination of sulfate by a number of cements has been found to be not very different and it is possible to calculate, from the equivalent rate of ettringite formation, the rate of evolution of heat from this reaction for an average cement. Using the heat of formation of ettringite from aqueous suspensions of C_3A and calcium sulfate, given as 347 cal/g C_3A (12), it is calculated to be approximately 1×10^{-4} cal/g cement/sec at 25 C. This figure can be compared with between 2.5 and 5×10^{-4} cal/g cement/sec obtained experimentally for cement pastes after between two and five hours' hydration in this laboratory using a conduction calorimeter (13). The indications are that a sizable fraction of the heat output during this period of the hydration is produced in the conversion of C_3A and calcium sulfate to ettringite.

A considerable proportion of the sulfate present in the commercial cements is not soluble in saturated lime solution and must therefore be presumed to have either reacted very quickly when the aqueous phase was mixed with the cement or to be present as an insoluble compound which may have been formed either during the grinding of the cement clinker with gypsum or in the period of storage of the cement (Table 4). Bucchi (14) also gives evidence that a proportion of the calcium sulfate in portland cement is combined within a short period of time from mixing with water.

Derivation of Activation Energy

The reaction was repeated at four temperatures, 15, 25, 35 and 45 C, using several cements, and the logarithms of the initial rates of uptake of sulfate were plotted against the reciprocal of the absolute temperatures (the Arrhenius graph). An activation energy of 9.0 ± 0.5 Kcal/mole was obtained from the slope of this graph for all cements studied (Table 5). The rate of combination of sulfate was doubled by raising the temperature by 13 C.

This value of activation energy can be compared to the value of 3.6 Kcal/mole quoted (15) for the diffusion of simple ions in aqueous solution. The wide difference between this value and that obtained for the reaction of calcium sulfate with cement rules out a mechanism for this reaction involving the diffusion of simple ions through the solution phase as the rate determining step, though it is possible that a complex ion such as the aluminate ion, which is probably polymerized in these solutions, could have an increased activation energy of diffusion. The absence of influence of changes in the rate of stirring, which would be likely to change the speed with which ions diffused through the aqueous phase from the reacting solid to the crystallizing hydrate, supports the conclusion that solution phase diffusion is not the controlling step in this reaction.

Comparison of the value of activation energy obtained for the reaction of calcium sulfate with cement in this work can be made with that obtained by Copeland and Kantero from the heat evolved after periods of hydration at three different temperatures (12). After approximately three days' hydration at 25 C the apparent activation energy of the whole hydration process was 8 Kcal/mole. After approximately seven days' hydration at 25 C the apparent activation energy had fallen to 5.1 Kcal/mole. The value of 9.0 Kcal/mole obtained in this work then appears to be near that obtained by extrapolation of the values of the activation energy for the whole hydration process to the value after one day's hydration at 25 C. It is of interest that these activation energies are in agreement with one another in that it provides a further indication that the mechanisms by which the hydration reactions of the various phases present in portland cement take place may be fundamentally similar in character.

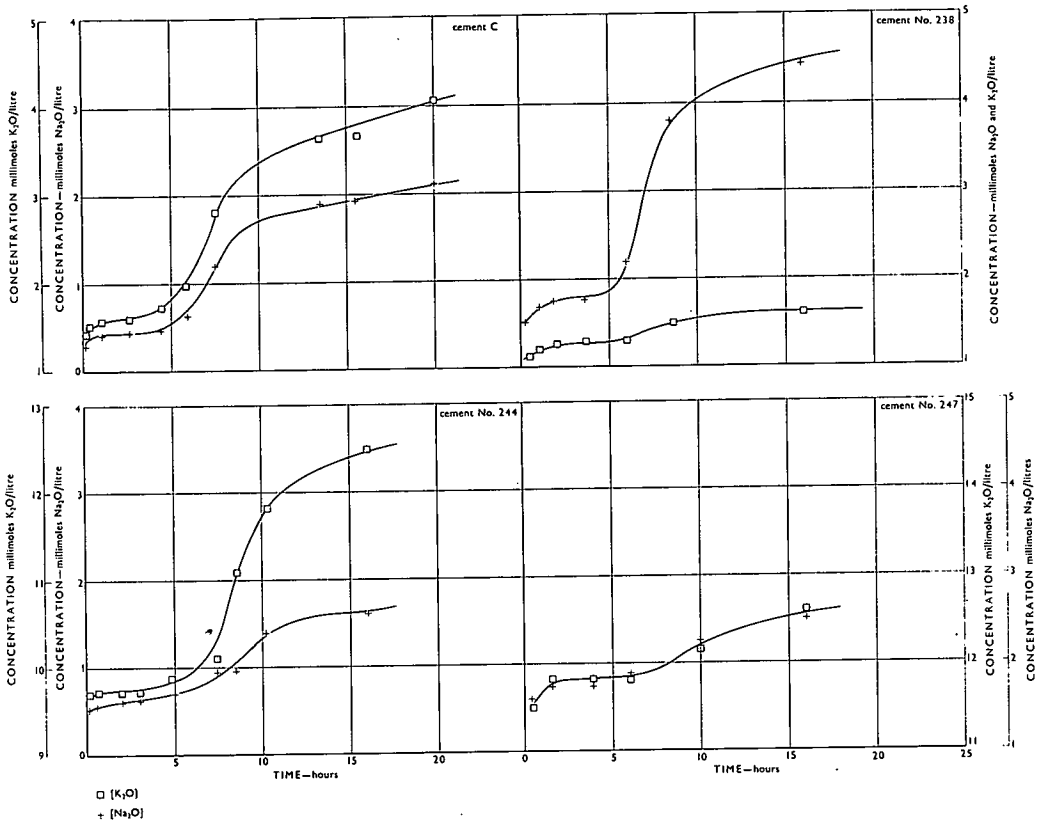


Figure 8. Release of alkali to solution phase in cement suspension at 35 C, water/cement = 10.

TABLE 3

RAPID INCREASE IN ALKALI CONTENT OF SOLUTION PHASE AFTER REMOVAL OF SULFATE FROM SOLUTION

Cement	Alkali Content of Solution Phase as Oxide Percentage of Cement					
	Before Sulfate Is Removed from Solution (after 1 hr)		After Sulfate Is Removed from Solution (after 16 hr)		Increase in Alkali Content of Solution During Period	
	Potassium	Sodium	Potassium	Sodium	Potassium	Sodium
242	0.14	0.03	0.19	0.05	0.05	0.02
*244	0.91	0.04	1.17	0.10	0.26	0.06
245	0.43	0.15	0.47	0.22	0.04	0.07
247	1.11	0.11	1.18	0.16	0.07	0.05
238	0.12	0.11	0.15	0.28	0.03	0.17
B	0.12	0.04	0.18	0.10	0.06	0.06
* C	0.15	0.03	0.38	0.13	0.23	0.10

*Cements showing new C₃A phase.

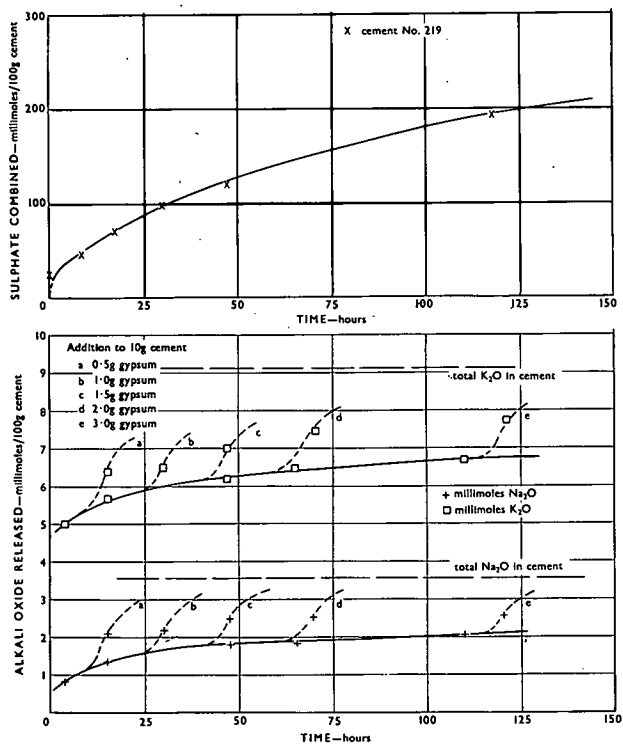


Figure 9a. Absorption of sulfate and release of alkali by cement 219 at water/cement = 10 and 35 C.

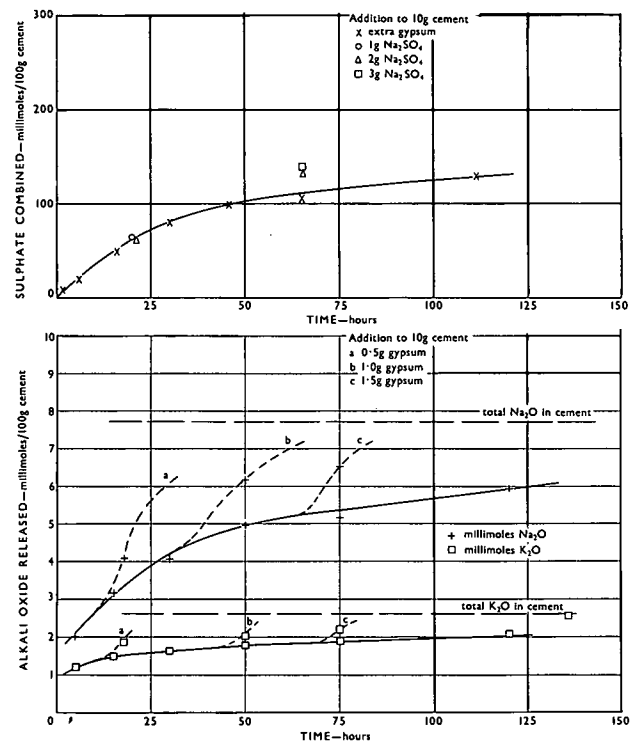


Figure 9b. Absorption of sulfate and release of alkali by cement 238 at water/cement = 10 and 35 C.

TABLE 4
PERCENTAGE OF SULFATE EXTRACTED BY
SATURATED LIME SOLUTION AT 25 C
IMMEDIATELY ON MIXING

Cement	Percentage SO ₃ in Aqueous Phase at Zero Time	Total Percentage SO ₃ in Cement
250	1.25	1.78
247	1.76	2.60
238	1.25	1.82
242	1.05	2.10
B	1.45	2.04
245	1.05	1.96

TABLE 5
EFFECT OF TEMPERATURE ON RATE OF
ABSORPTION OF SULFATE BY CEMENTS
AT WATER/CEMENT = 10

Cement	Rate of Absorption of Sulfate (millimoles/hr) SO ₄ ²⁻ /100 g cement/hr				Activation Energy (Kcal/mole)
	15 C	25 C	35 C	45 C	
238	0.70	1.25	2.00	3.10	9.0
242	0.50	1.10	1.60	2.90	9.5
244	0.65	1.10	2.00	3.80	9.5
245	0.70	1.05	2.10	3.20	9.5
247	0.80	1.40	2.00	3.50	9.0
250	0.50	0.95	1.40	2.30	9.0
A	0.70	1.10	1.80	3.10	9.0
B	0.65	1.15	1.60	2.50	8.5

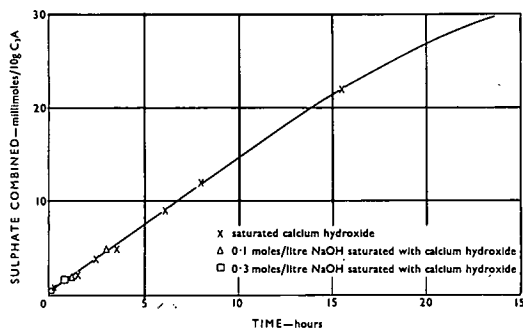


Figure 10. Absorption of sulfate by C₃A at 35 C in the presence of saturated lime solution (solid/liquid ratio = 200).

Reaction of Calcium Sulfate With Synthetic C₃A

The conclusions arrived at from the study of the combination of sulfate by cement were tested by repeating the experiment using synthetic C₃A in place of cement. A suspension of 1 g of C₃A in 100 ml of saturated calcium hydroxide solution containing measured amounts of calcium sulfate in solution was found to react at about the same rate as a suspension of 10 g of cement in 100 ml of water. The specific surface area of the C₃A used was 3200 cm²/g and was approximately the same as that of the portland cements studied.

The results confirmed that the sulfate was combined at a constant rate in the early stages of the reaction (Fig. 10). The only crystalline product detected by X-ray diffraction photography of the partially reacted C₃A was ettringite. When the sulfate ions had been completely removed from the aqueous phase by reaction with the C₃A, there was a rapid conversion of the ettringite originally formed, together with a large proportion of the remaining C₃A present, to the monosulfate (C₃A · CaSO₄ · 12H₂O). Additions of alkali hydroxide to the system to give NaOH concentrations up to 0.3 mole/liter, while at the same time maintaining the aqueous phase saturated with respect to calcium hydroxide (the actual concentration of calcium hydroxide is reduced by the presence of alkali metal ions in solution), had no effect on the initial rate of reaction of the sulfate ions present, and ettringite was again the only hydrated phase detected. In the presence of NaOH, however, the formation of monosulfate began at moderate sulfate ion concentrations, whereas, in the absence of alkali, it formed only at almost negligible sulfate ion concentrations.

A recently published study of the reactions of C₃A suspensions and calcium sulfate in the presence of calcium hydroxide supports some of the conclusions of this work

(9). The shape of the $C_3A-CaSO_4$ reaction curve is similar to that found in the present work over the first six or seven hours of the reaction though differences occur after this time. Ettringite is formed as the main product of the reaction in both studies in the opening stages. The mechanism proposed in this study involves the formation of a barrier of ettringite on the surface of the anhydrous C_3A crystals through which sulfate ions diffuse and combine at the C_3A surface to form more ettringite. It is proposed that the barrier of ettringite periodically spalls off as fresh ettringite is formed.

The kinetics of the C_3A -calcium sulfate reaction found in the present work support the ideas on the mechanism of the reaction proposed by this study except that the proposed diffusing species should possibly be changed from sulfate ions to water molecules. The mechanism then becomes very similar to that proposed in the hydration of C_3S and βC_2S (16) in that spalling of the products of the reaction, allowing further penetration of water molecules to the anhydrous crystal surface, is a common feature of these mechanisms.

A further point of similarity between the kinetics of the formation of ettringite found by these workers and that found in this study for the reaction of synthetic C_3A and calcium sulfate is the absence of any significant initial rapid absorption of sulfate by the C_3A . This contrasts with the large initial heat evolution found for this reaction by Stein (8) using a conduction calorimeter and ascribed by him to a rapid initial combination of the reactants. It is pointed out in his paper, however, that the initial heat evolution is affected by the handling of the samples and so may be exaggerated in his results.

CONCLUSIONS

The importance of the value of the concentration of calcium hydroxide in the aqueous phase in contact with hydrating cement compounds in determining the rate at which hydration proceeds has been well established. In this work it has been shown that the rate of crystallization of calcium hydroxide and the concentration of alkali metal ions control, at different stages in the hydration, the degree of supersaturation of the aqueous phase with respect to calcium hydroxide, and so would be expected to influence the rate of hydration of the cement compounds.

A proportion of both the sodium and potassium ions which are combined with the cement compounds has been shown to be located within the lattice of the C_3A phase.

The mechanism of the reaction of sulfate ions with the C_3A phase present in cements has been examined and similarities found between this reaction and other hydration reactions which have been studied by other workers, notably by using radioactive tracer techniques. It appears possible that a similar hydration mechanism can be adopted for all these reactions and that further studies on the C_3A -calcium sulfate reaction, which is relatively easy to follow by chemical analysis, will shed light on hydration reactions in general.

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Appendix

EXPERIMENTAL PROCEDURE

Cement-water suspensions were stirred in polythene bottles (500 cc capacity) using paddle-type stirrers entering through metal bearings set in the caps. The bottles were immersed in a thermostated water-bath controlled to ± 0.25 C and the mixtures agitated for measured times. They were then quickly transferred to a CO₂-free glove-box where the solid phase was filtered off through a Whatman No. 42 filter paper (close grained) supported on a demountable porcelain filter funnel. The speed of stirring was varied and found to have little influence on the rate of release of alkali or the uptake of sulfate and subsequently was kept at about 3.5 rev/sec throughout the series of experiments. The temperature of the suspension was not significantly above that of the water-bath at any time during the reaction. The filtering technique was checked to show that the concentrations of calcium hydroxyl, sulfate, silicate and aluminate ions in solution were not significantly changed by passing through this filter. A few results using a sintered glass filter showed that absorption of calcium hydroxide by, and dissolution of silica from, the filter was quite marked in this case. Strelkov (17) appears to have used a glass filter in his studies on the solution phase in cement pastes and this may have influenced his results. The solution was analyzed for calcium by E. D. T. A. titration, hydroxyl by standard acid and methyl red as indicator, sulfate by passing a sample through a cation exchange resin in the hydrogen form and titrating the resulting acid with standard alkali. Silicate was measured colorimetrically by forming the molybdenum blue color, and aluminate by reacting with solochrome cyanine R.

A limited number of experiments was attempted on pastes having a water/cement ratio of 0.25. The aqueous phase was extracted from these pastes using a piston and cylinder fitted at the lower end with a stainless-steel filter disc having a porosity equivalent to a No. 4 sintered glass filter. Clear extracts were obtained but the difficulty of maintaining a uniform temperature throughout an unstirred paste made interpretation of the results uncertain. A pressure of two ton/in.² allowed sufficient liquid to be extracted for analysis up to about eight hours after mixing.

X-ray diffraction photographs were taken of a selected number of partially hydrated solids after removal of water by evacuation. The hydration was stopped by washing with acetone. A Brindley semi-focusing camera was used and phases identified by comparison of the patterns with those produced by pure compounds on the same camera at the same focusing angle.