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The influence of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ upon the hydration character of $3\text{CaO} \cdot \text{Al}_2\text{O}_3$

by R. F. Feldman and V. S. Ramachandran

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Influence du $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ sur les caractéristiques d'hydratation du $3\text{CaO} \cdot \text{Al}_2\text{O}_3$

SOMMAIRE

Les auteurs donnent dans le présent exposé une interprétation quantitative des résultats de l'analyse calorimétrique différentielle de mélanges hydratés à 2°, 12°, 23° et 52°C de gypse et d'aluminate tricalcique contenant zéro, 0,25, 2,5, 10 ou 20 pour cent de gypse. Ils en comparent les résultats avec les variations de longueur des éléments constitués de ces mélanges comprimés et hydratés. Les valeurs des vitesses relatives des réactions calculées d'après les aires des pointes endothermiques des thermogrammes et celles qui sont obtenues par la mesure des modifications de longueur des éléments au cours de ces réactions correspondent étroitement, bien que leur interprétation ait été faite prudemment.

Les auteurs en ont conclu que la formation d'ettringite (aluminate trisulfaté) n'a pas d'effet direct sur les vitesses de réaction mais que la réactivité de l'aluminate tricalcique était réduite par l'adsorption d'ions SO_4 en des points actifs de sa surface. La présence de gypse réduit la vitesse de transformation des aluminates hydratés de type hexagonal en aluminates hexa-hydratés de type cubique probablement aussi par adsorption d'ions SO_4 , constituant ainsi un second mécanisme retardant l'hydratation normale de l'aluminate tricalcique. La durée de ce retard causé par l'addition d'une certaine quantité de gypse dépend, à une température donnée, de l'équilibre entre: (1) la concentration des ions SO_4 à la surface de l'aluminate tricalcique et à son voisinage; (2) la vitesse de réaction des ions SO_4 avec les aluminates hydratés de type hexagonal; et (3) l'épaisseur de la couche d'aluminate hydraté de type hexagonal autour des particules d'aluminate tricalcique. Les auteurs étudient les réactions selon les variations des paramètres ci-dessus à diverses températures.



ANALYZED

The influence of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ upon the hydration character of $3\text{CaO} \cdot \text{Al}_2\text{O}_3$

by R. F. Feldman* and V. S. Ramachandran†

NATIONAL RESEARCH COUNCIL, CANADA: DIVISION OF BUILDING RESEARCH

SUMMARY

This paper presents a quantitative interpretation of results of differential thermal analysis of hydration reactions at 2, 12, 23 and 52°C of $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ mixed with 0, 0.25, 2.5, 10 or 20% gypsum, and compares these with length changes obtained from the hydration of compacts of these mixtures. Estimates of the relative reaction rates from d.t.a. peak areas and measurement of length change during these reactions showed marked agreement, although interpretation had to be made with caution. It was concluded that the formation of ettringite (high sulpho-aluminate) had no direct effect upon reaction rate, but that the reactivity of $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ was reduced by the sorption of $(\text{SO}_4)^{2-}$ ions on active sites of its surface. Gypsum reduces the rate of conversion of the hexagonal hydro-aluminates to the cubic hexahydrate, probably also by sorption of $(\text{SO}_4)^{2-}$ ions, and thus is a second mechanism by which they can retard the normal hydration of $3\text{CaO} \cdot \text{Al}_2\text{O}_3$. The degree to which a given addition of gypsum retards the hydration of $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ at a particular temperature is affected by a balance between (1) the concentration of $(\text{SO}_4)^{2-}$ ions on and around the surface of the $3\text{CaO} \cdot \text{Al}_2\text{O}_3$; (2) the rate of reaction of $(\text{SO}_4)^{2-}$ ions with the hexagonal hydro-aluminates; (3) the thickness of the hexagonal hydro-aluminate layer around the $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ grain. Reactions at the various temperatures are discussed in terms of the above parameters.

Introduction

It is common practice to use $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ in commercial Portland cement to control the reaction rate of C_3A ‡, the constituent of cement that reacts most rapidly with water.

Jones⁽¹⁾ studied the equilibria of the quaternary system $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaSO}_4 \cdot \text{H}_2\text{O}$ and found that the quaternary compound $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 31\text{--}32\text{H}_2\text{O}$ (high sulpho-aluminate) was the stable one, although a compound $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaSO}_4 \cdot 12\text{H}_2\text{O}$ (low sulpho-aluminate) does exist. Later work by Jones⁽²⁾ and Kalousek^(3, 4) showed how the hexagonal hydro-aluminates may form solid solutions with lime and calcium sulphate. The idea that the cubic $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ probably did not form in the presence of sulphate ions was presented in this work.

The actual mechanism of the retarding action of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ is in some doubt, however, although much work⁽⁴⁾ has been done in this field. A previous paper⁽⁵⁾ studied the hydration of C_3A in the presence of a small quantity of $\text{Ca}(\text{OH})_2$ by differential thermal analysis, length-change analysis and other techniques.

This paper presents a differential thermal analysis (d.t.a.) of the kinetics of the hydration reactions of mixtures of C_3A and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ at four temperatures, with four different gypsum concentrations, 0.25, 2.5, 10 and 20%. As the C_3A was prepared in the same way as for the study of C_3A hydration and contained approximately 2% free CaO, a direct comparison between the two systems is possible. A semi-quantitative evaluation of the results is made, and a comparison is made with some length-change results. Experiments in the latter were carried out at the same four temperatures, 2, 12, 23 and 52°C, as were used for the d.t.a. investigation and with gypsum concentrations of 0, 2.5, 10 and 20%; the hydration was made with the mixtures in compact form, yielding a water/solid ratio of approximately 0.1.

Many theories regarding the action of gypsum have

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‡ The following nomenclature used in cement chemistry will be used where appropriate:

C = CaO A = Al_2O_3 H = H_2O

been suggested in the past and these have been reviewed in detail by both Bogue⁽⁶⁾ and Steinour⁽⁴⁾. Lerch⁽⁷⁾ and Klein and Phillips⁽⁸⁾ brought forward the theory of reduced solubility of C₃A. Roller⁽⁹⁾ considered that retardation is due to the action of gypsum with free alkali in the clinker, and other workers^(4, 10) have suggested that the 'low' sulpho-aluminate is deposited on the C₃A grain, forming an impermeable film. Several workers⁽¹¹⁻¹⁴⁾ have now shown that the 'high' sulpho-aluminate forms first and current thinking suggests that this compound forms an impermeable film.

Experimental

Details concerning the preparation of C₃A have been reported⁽⁵⁾. The C₃A contained 2.2% free CaO.

The preparation was mixed with reagent-grade CaSO₄.2H₂O so as to give mixtures containing 0.25, 2.5, 10 and 20% by weight of gypsum. The 2.5 and 10% mixtures were hydrated at 2, 12, 23 and 52°C; the 0.25% at 2, 12 and 23°C; and the 20% at 23°C. The samples were mixed in a double-armed rotating mixer, containing steel balls, for 24 h.

The hydration procedure and the procedure for stopping the reaction were the same as described in a

previous paper⁽⁵⁾; the sample was in compact form, the pore volume being such that, when it was filled with water, a water/solid ratio of 0.12 was produced.

D.t.a. was performed in the absence of air, a heating rate of 10degC per minute being used. X-ray diffraction patterns were obtained on a few samples at each condition. In general, it was found that the lines, except those of C₃A and C₃AH₆, were diffuse. The results were useful only where a large amount of product was formed and provided confirmation in some cases only of the presence of a specific compound.

Length-change measurements were made by introducing water to a 1 in. long sample of C₃A + gypsum mixture, which had been made by compaction at 48,000 lb/in²; this was mounted on an extensometer in a vacuum chamber into which water at the required temperature could be introduced. Measurements could be taken to an accuracy of 4 × 10⁻⁶ in/in.

Results

D. T. A. INTERPRETATION AND QUANTITATIVE ESTIMATION

Thermograms for the hydration of C₃A + 0.25%

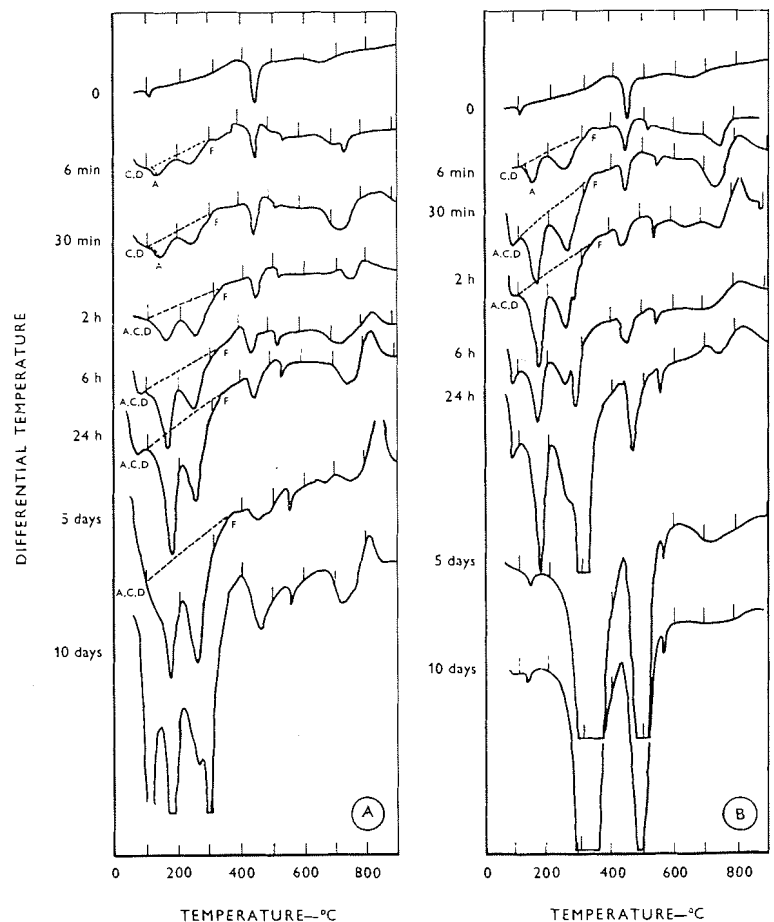


Figure 1: Thermograms for the C₃A + 0.25% gypsum mixture hydrated at (a) 2°C (b) 23°C.

gypsum mixtures are shown in Figure 1. The hexagonal hydro-aluminates of C_2AH_8 and C_4AH_{13} were observed to form from 5 minutes' to 5 days' hydration at 2°C . After ten days, a significant proportion of the cubic hydrate C_3AH_6 had formed. The time of first appearance of C_3AH_6 and the rate of conversion to C_3AH_6 increased with temperature, as did the rate of formation of the hexagonal hydro-aluminates; this was observed for 2, 12 and 23°C . Some of these results are illustrated in Figure 2b. A fixed procedure for extrapolation was used in the quantitative estimations, and is shown in most of the thermograms; the extrapolation for gypsum is lettered ABC; for the high sulpho-aluminate + C_2AH_8 , ACDE; for all the products, ACDF. The letter 'C' on some of the curves (e.g. 3a and 3b) signifies that some C_3AH_6 had formed and so the peak areas at these points would be too low. On comparing the hydration of the same C_3A preparation at the same temperatures, one observes that the reactions in all cases are retarded by the addition of gypsum (compare Figures 2a and 2b). No new compound

(sulpho-aluminate) was observed to form, but it may have been concealed by the large quantity of hexagonal hydro-aluminate. The retarding effect persisted, however, long after the gypsum had disappeared.

Thermograms for the hydration of $\text{C}_3\text{A} + 2.5\%$ gypsum mixtures at 2, 12, 23 and 52°C are shown in Figure 3. At 2, 12 and 23°C , hexagonal hydro-aluminates and the high sulpho-aluminate were observed to form simultaneously, the gypsum having practically disappeared after 30 min at 23°C and after 6 h at 12 and 2°C . It is shown in Figure 2b that the quantities of products at the three temperatures are not significantly different, but after 24 h at 23°C some C_3AH_6 had formed. Figure 2a shows how the rate of hydration of the $\text{C}_3\text{A} + 2.5\%$ mixture at 23°C is much lower than the rate of C_3A even at 2°C , although the gypsum had vanished after hydration for $\frac{1}{2}$ h. It was found in general that the rates of formation of hexagonal hydro-aluminate and C_3AH_6 were decreased and that the first appearance of C_3AH_6 was delayed by the addition of gypsum. At 52°C , the hydration was rapid,

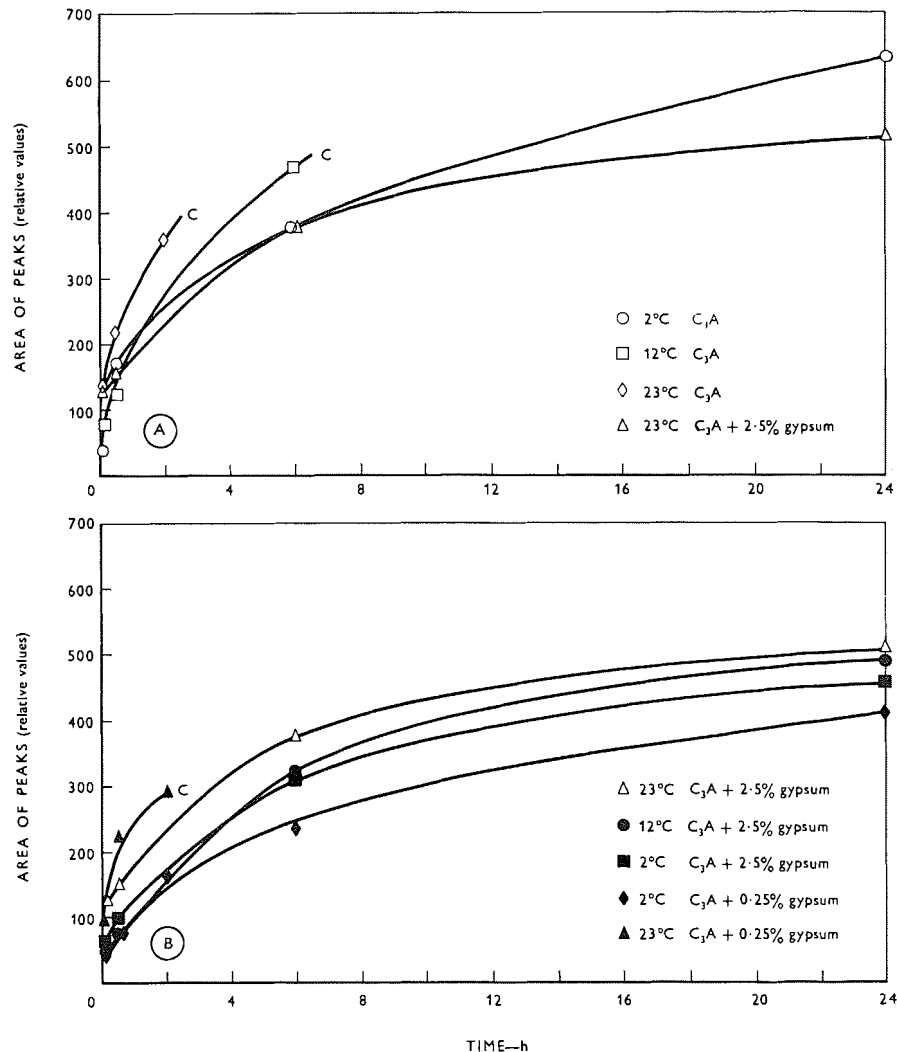


Figure 2: Relative rate of formation of products for $\text{C}_3\text{A} + \text{gypsum}$ mixtures hydrated at various temperatures.

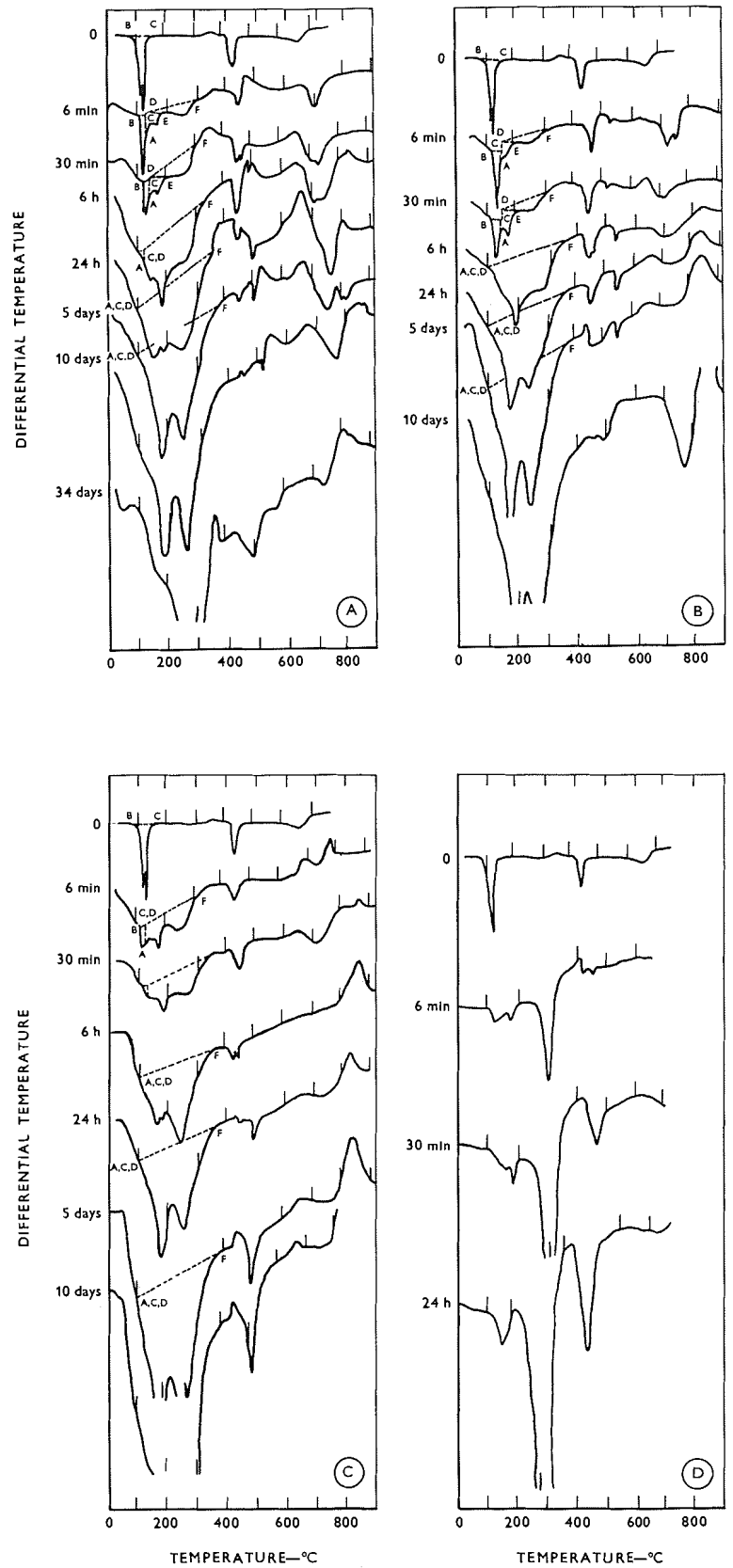


Figure 3: Thermograms for the $C_3A + 2.5\%$ gypsum mixture hydrated at (a) $2^\circ C$ (b) $12^\circ C$ (c) $23^\circ C$ (d) $52^\circ C$.

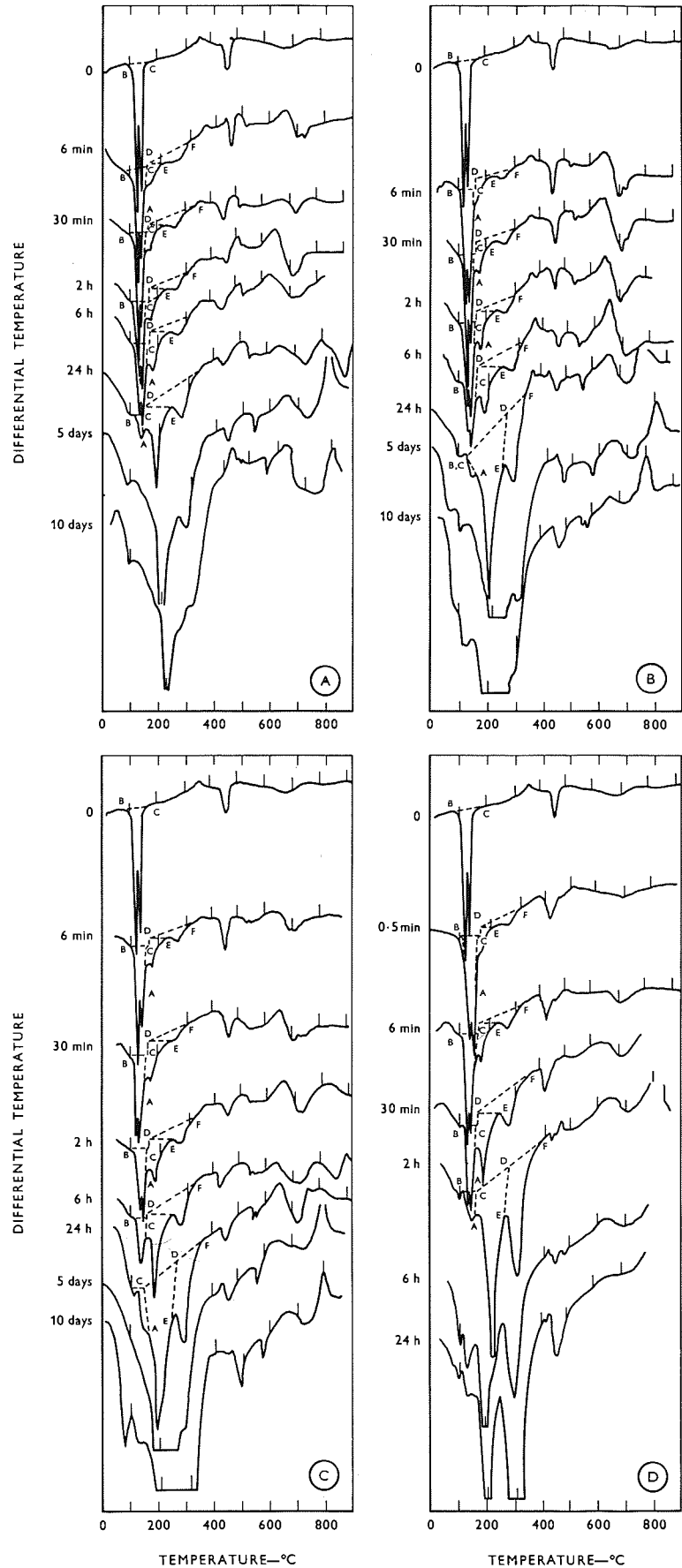


Figure 4: Thermograms for the $\text{C}_3\text{A} + 10\%$ gypsum mixture hydrated at (a) 2°C (b) 12°C (c) 23°C (d) 52°C .

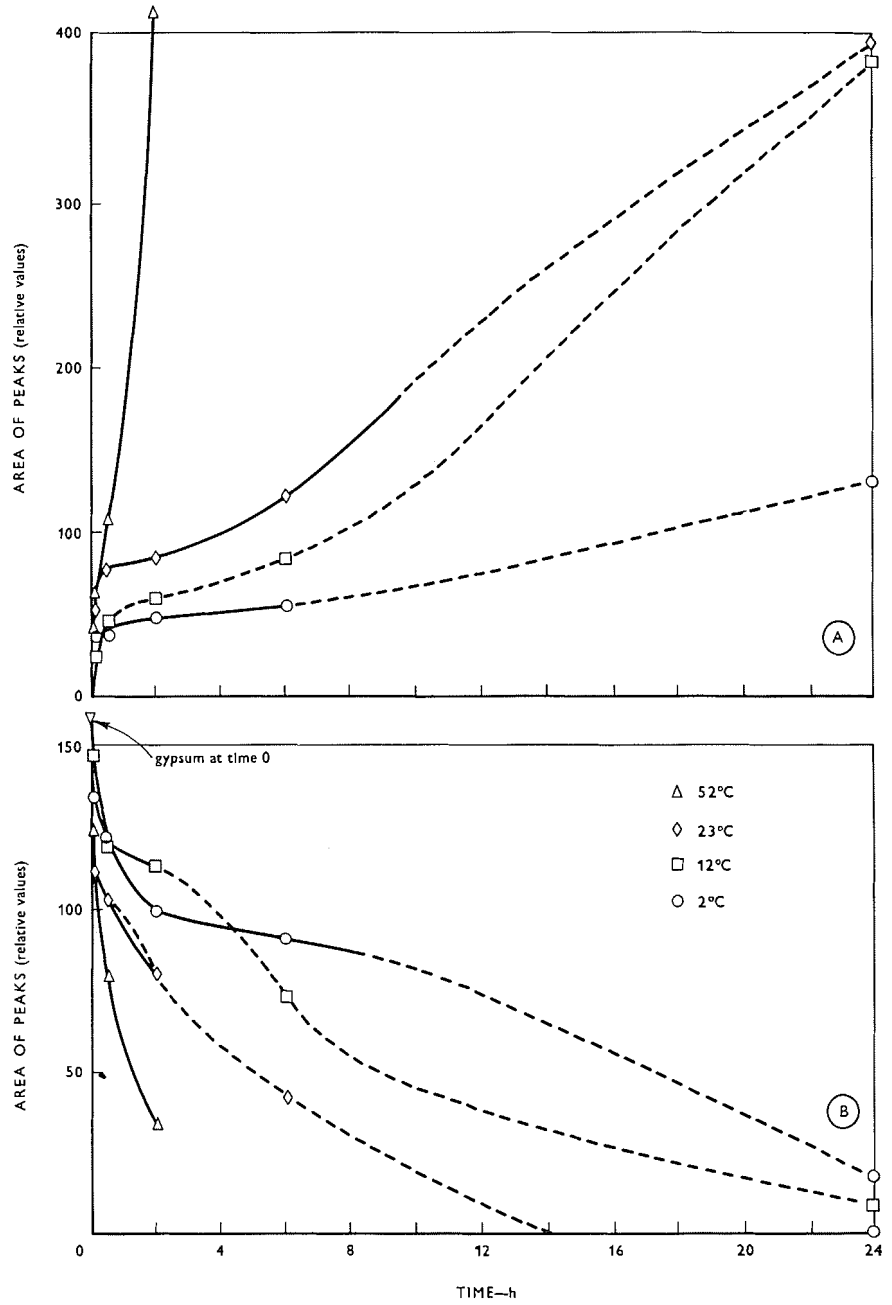


Figure 5: Relative rates of reaction of $C_3A + 10\%$ gypsum at various temperatures: (a) formation of sulpho-aluminate + C_2AH_8 ; (b) consumption of gypsum.

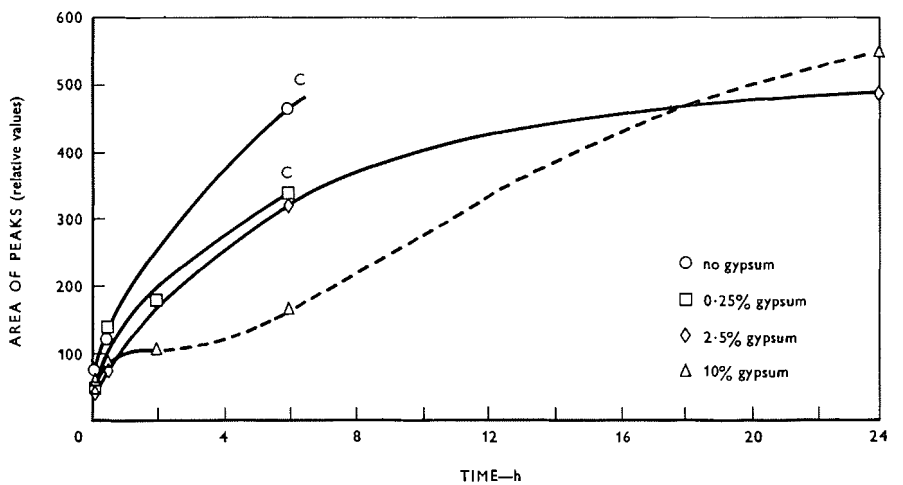


Figure 6: Relative rate of formation of total products during hydration of various $C_3A +$ gypsum mixtures at 12°C.

C_3AH_6 being formed together with high sulpho-aluminate and a small quantity of hexagonal aluminates at 6 min. However, the formation of C_3AH_6 was retarded by the addition of gypsum, but the reaction here may be complicated by the fact that, without gypsum, the C_3AH_6 formation retarded its own reaction⁽⁵⁾ and the presence of gypsum may partially interfere with this mechanism.

Thermograms for the hydration of $\text{C}_3\text{A} + 10\%$ gypsum mixtures at 2, 12, 23 and 52°C are shown in Figure 4. At 2, 12 and 23°C both the high sulpho-aluminate and the hexagonal hydro-aluminates are present at the earliest time studied (6 min). The quantity of sulpho-aluminate increases slowly, the rate increasing with temperature, but the quantity of hexagonal aluminates remains relatively constant. This is shown in Figure 5a, where a quantitative estimate is made for the sulpho-aluminate + C_2AH_6 . An estimate of the 'total products' was also made, and this showed that the reaction increases with temperature and a region of low rate followed by an acceleration occurs at 2° and 12° and possible at 23°C . The lower the temperature, the longer is this period of low rate. After 24 h at 2°C , 6 h at 12°C and 2 h at 23°C , increases in the hexagonal hydro-aluminates were observed, together with further increases in the sulpho-aluminate and significant decreases in the gypsum, although considerable quantities of the latter remain. Figure 5b shows the rate of decrease of gypsum; a region of low rate followed by an acceleration is again exhibited by these curves in a manner analogous to the other estimations. The gypsum has disappeared after hydration for 5 days at 2 and 12°C and after 24 h at 23°C . A small amount of C_3AH_6 has formed after 10 days at 23°C . At 52°C , after only half-a-minute's hydration, significant quantities of both hexagonal hydro-aluminate and sulpho-aluminate are formed (Figures 5a and 5b). Most of the gypsum has been consumed after 6 h. After hydration for 24 h, some C_3AH_6 has formed.

It is significant that the addition of 10% gypsum can prevent formation of C_3AH_6 for so long at 52°C . With the 2.5% addition, C_3AH_6 had formed in large quantities after only 6 min, even though gypsum still remained at this time. It must be concluded from this that the hydration of a $\text{C}_3\text{A} +$ gypsum mixture cannot be considered as equivalent to a system where C_3A is in a homogeneous solution, saturated with $(\text{SO}_4)^{2-}$ ions and where this homogeneous solution remains saturated until all the gypsum has been taken up.

The hydration reaction for $\text{C}_3\text{A} + 20\%$ gypsum at 23°C proceeds similarly to that for the 10% mixture at the same temperature, but the hexagonal hydro-aluminates, although clearly present in small quantities at the early times ($\frac{1}{2}$ min to 6 h), seem to decrease somewhat, and it appears that the sulpho-aluminate forms at least partly at the expense of the hexagonal hydro-aluminates.

COMPARISON OF THE REACTIONS FOR THE DIFFERENT GYPSUM CONTENTS

A comparison of the hydration at 12°C for the different gypsum contents is illustrated in Figure 6. The degree of retardation for 2.5% gypsum is much greater than for 0.25%, and for the 10% content greater than the 2.5%. With the larger additions of gypsum, however, this is not a completely true representation of reaction rate on the basis of C_3A reacted. The area of the sulpho-aluminate peak also would constitute a larger area than the hexagonal hydro-aluminates.

A comparison of the hydration at 2°C for the different gypsum contents may be made from Figures 1a, 3a and 4a. The larger addition of gypsum does more effectively prevent the formation of C_3AH_6 , and the 10% addition does suppress the formation of hexagonal hydro-aluminates further than with the 2.5% addition, although they are always present.

At 23°C (Figures 1b, 3c and 4c), the effect of 0.25% gypsum is not very great, and the comparison between this and the 2.5% addition is marked. With the latter addition, the formation of hexagonal hydro-aluminates is slowed as well as the formation of C_3AH_6 and its first appearance is delayed considerably. The 10% and 20% gypsum additions have even greater retarding effects.

At 52°C (Figures 3d and 4d), the 2.5% gypsum addition is insufficient to prevent C_3AH_6 formation as early as 6 min, even though gypsum still remains at this hydration time. The 10% addition slows down the over-all reaction to a much greater extent than the 2.5% addition and prevents C_3AH_6 formation until 24 h.

LENGTH-CHANGE MEASUREMENTS

Typical results of the length-change measurements during hydration of the $\text{C}_3\text{A} + 2.5\%$ gypsum mixture at 2, 12, 23 and 52°C are shown in Figure 7a. At 2, 12 and 23°C , little significant difference is observed when the full 48 h period is considered. This result is very similar to that obtained from the d.t.a. shown in Figure 2b. At 52°C , a marked reduction in expansion rate is observed after 5 h.

Results of length-change measurements during hydration of the $\text{C}_3\text{A} + 10\%$ gypsum mixture at 2, 12, 23 and 52°C are shown on Figures 7b and 7c. At each temperature the expansion rate in the first 3 min is high; this is followed by a lower, relatively constant rate; the higher the temperature of hydration the higher the rate of expansion at 2, 12 and 23°C . Expansion at 52°C , although greater initially, is less than at 23°C after 10 min. A constant rate of expansion is followed by a period where the rates increase rapidly after approximately 50 min, 2 h and 9 h respectively for hydration temperatures of 23, 12 and 2°C . Hydration at 52°C shows an increase in rate of expansion

after 45 min, but this rate remains constant (linear expansion with time) until approximately $3\frac{1}{2}$ h, after which it decreases sharply. These results (Figures 7b and 7c) show remarkable similarities to those obtained from the d.t.a. (Figures 5a and 5b), and emphasize the relationship between expansion rate and hydration rate.

The results at 52°C, however, do not conform to

this relationship; despite a high rate and degree of hydration, the expansion is relatively low, and after hydration for 5 days a strong sample with a low pore volume (9.3%) is produced. The products of hydration, although similar to the products formed at the other temperatures, may differ in morphology and may be more accommodative. On the other hand, greater quantities of hexagonal hydro-aluminates, forming

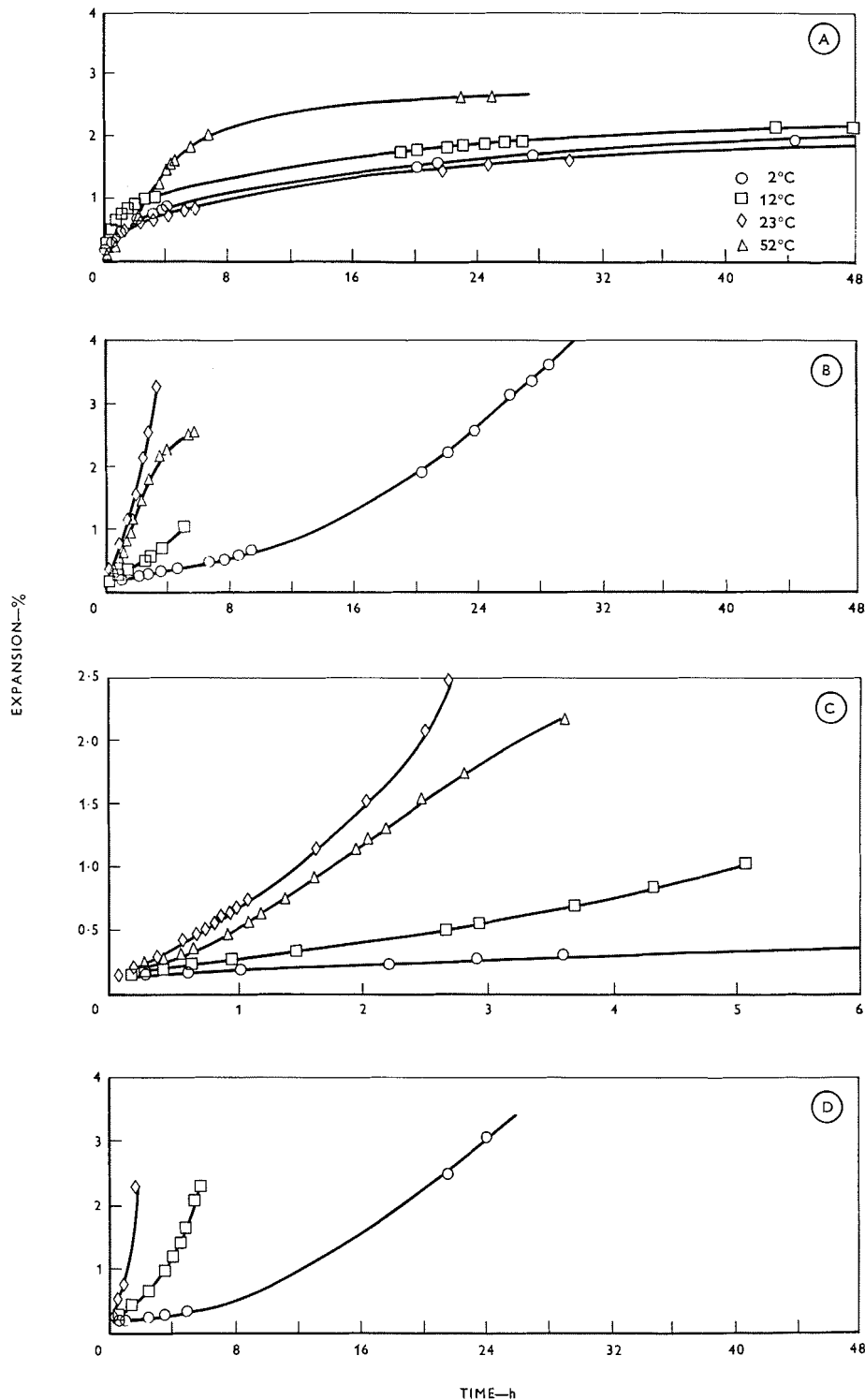


Figure 7: Length change for C_3A + gypsum mixtures hydrated at various temperatures
 (a) 2.5% gypsum
 (b) and (c) 10% gypsum
 (d) 20% gypsum

together with the 'high' sulpho-aluminate, may account for the low expansion. Hydration of the $\text{C}_3\text{A} + 10\%$ gypsum mixture at 23°C caused the sample to disintegrate after a few hours.

Results of length-change measurements during hydration of the $\text{C}_3\text{A} + 20\%$ gypsum mixture at 2, 12 and 23°C are indicated in Figure 7d and are similar to those observed for the 10% gypsum addition, except

that the increase in expansion rate began after approximately 50 min, 1.5 h and 6 h respectively for hydration at 23, 12 and 2°C .

The length-change results are plotted so that the effect of gypsum content may be observed at each temperature and are shown in Figures 8a to d. On comparison with the gypsum-free sample, the 2.5% gypsum sample shows a greater difference as the tem-

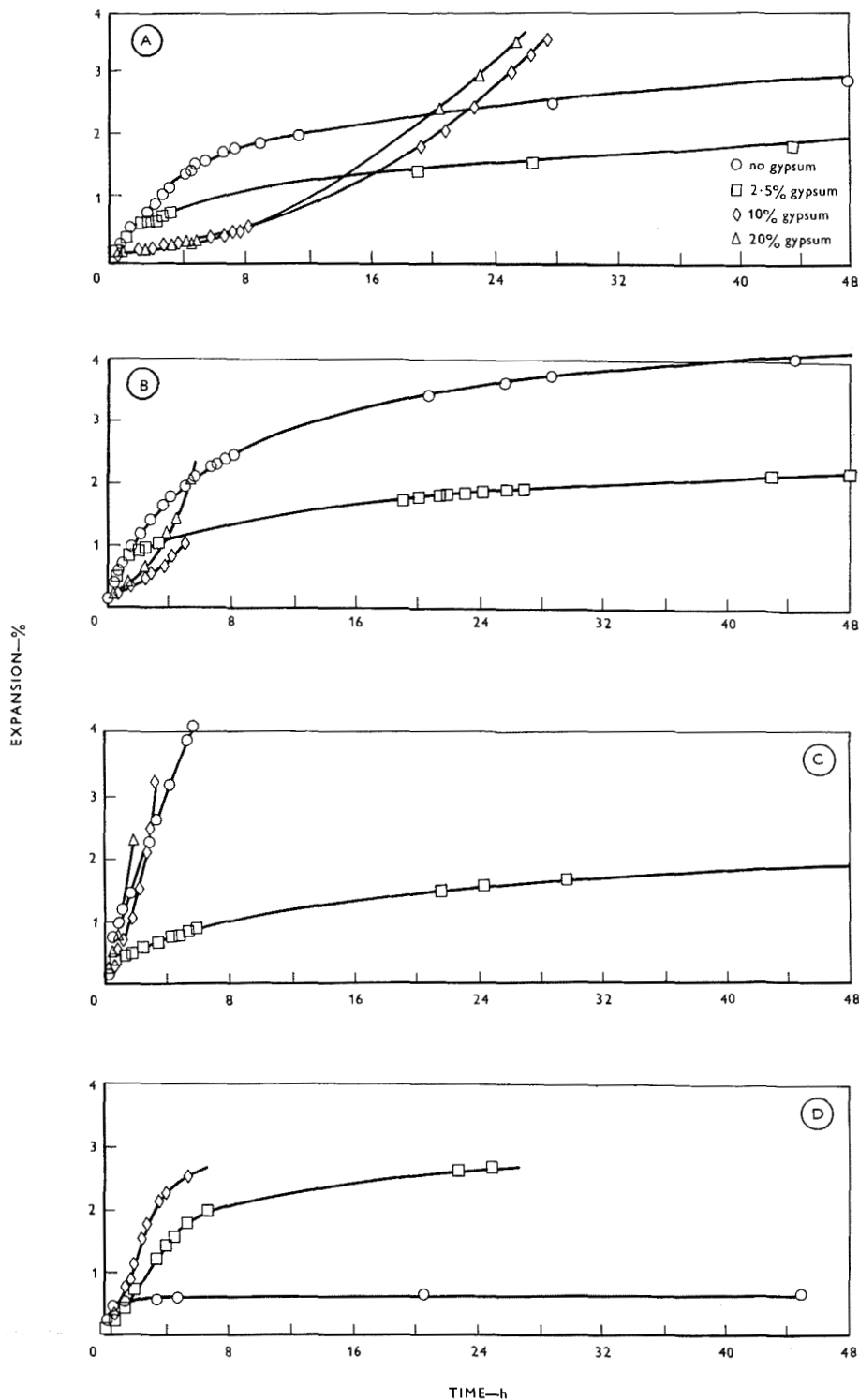


Figure 8: Length change for various $\text{C}_3\text{A} +$ gypsum mixtures hydrated at (a) 2°C (b) 12°C (c) 23°C (d) 52°C .

perature increases from 2 to 23°C. The higher the temperature, the earlier the expansion of the 10 and 20% mixtures exceeds that of the 2.5% and gypsum-free samples. The very large expansion of the 0, 10 and 20% gypsum mixtures for hydration at 23°C (Figure 8c) are apparent, whilst the 2.5% gypsum expands slowly despite the fact that the gypsum has been consumed shortly after $\frac{1}{2}$ h. At 52°C, the 2.5 and 10% gypsum samples expand steadily for some time and do not exhibit the abrupt halt shown by the gypsum-free C₃A.

Discussion

A detailed discussion of the interpretation of the d.t.a. thermograms for the hydration of C₃A has already been published⁽⁵⁾. The d.t.a. characteristics for the high sulpho-aluminate have been given by several workers⁽¹⁵⁻¹⁷⁾ as an endothermic peak at approximately 180°C (varying from 170 to 190°C), and it appears certain that this is the compound formed in this work and represented by an endothermic peak shifting from 170 to 200°C depending on the quantity formed. Some investigators⁽¹²⁻¹³⁾ have recently reported that the high sulpho-aluminate forms first at early times and is the only sulpho compound observed initially. The above fact and the general trend of results at the various temperatures and concentrations, where the peaks could be observed to grow and recede, indicate strongly that the endothermic peak between 240 and 285°C is due to the hexagonal hydro-aluminate C₄AH₁₃.

The results indicate that the hexagonal hydro-aluminates form immediately on contact with water; this has been stated by Lerch⁽⁷⁾ but challenged by other workers⁽¹⁸⁾. The gypsum reacts partly with the hexagonal hydro-aluminates to form the high sulpho-aluminate. The rates of reaction of both C₃A and gypsum in the mixture increase with temperature, but the retarding action of gypsum is similar in effect to the lowering of the temperature during hydration of C₃A; the rate of formation of hexagonal aluminates, and rate of conversion to C₃AH₆ are decreased. In general, retardation continued beyond the stage where the gypsum was totally consumed and it appears that the formation of the high sulpho-aluminate does not have any direct role in the retardation of the hydration reaction.

Unhydrated C₃A remained in all mixtures during the period of observation because of the low water/solid ratio used in this work. It is probable that the later stages of the reaction, the formation of low sulpho-aluminate and solid solutions, are also delayed in these experiments for the same reason. Most of the observations were thus made at the earlier stages of the reaction but conditions in some ways simulate those of the earliest reactions in Portland cement.

The rate of reaction is not defined necessarily by the solubility of a material undergoing hydration or of the

products, but by the rate of dissolution and decomposition. Dislocation density on the surface contributes to the rate of dissolution as it does to the rate of chemical attack⁽¹⁹⁻²¹⁾.

Environmental factors affect the operation of various types of surface source of dislocation. It has been suggested⁽²²⁾ that adsorbed polar molecules on these sites can hinder the operation of these sources. Adsorption on kinks can inhibit their movement along ledges on a crystal surface and greatly reduce its dissolution rate. It is suggested that the presence of CaSO₄ in solution decreases the rate of reaction of C₃A by sorption of (SO₄)²⁻ ions in a manner similar to one of the above.

Budnikov et al.⁽²³⁾ discussed the change of reactivity of C₃A due to small additions of electrolyte in terms of their surface-active properties, and Solov'eva and Segalova⁽²⁴⁾ observed that small quantities of calcium ligno-sulphonate caused a marked reduction of the initial rate of reaction of the C₃A.

Environment may determine the rate of nucleation of a metastable crystal into its stable form. Sersale⁽²⁵⁾ observed that, at room temperature, the addition of a small amount of calcium ligno-sulphonate retards the process of conversion of the hexagonal hydro-aluminates to C₃AH₆; at higher temperatures, the retarding effect of this additive was less noticeable.

These observations agree well with the results and conclusions from the d.t.a. and length-change analysis; gypsum additions reduced the rate of conversion of the hexagonals to the cubic. This process would remove them from the surface of the grain and would cause an acceleration. The tendency to suppress this reaction is a second mechanism by which (SO₄)²⁻ ions can retard the normal hydration of C₃A.

The fact that gypsum reacts with C₃A will modify the retardative processes discussed above. The concentration of (SO₄)²⁻ close to the surface of the C₃A grain will be reduced. Also the hexagonal aluminates surrounding the C₃A may break away because of the reaction with gypsum to form the high-volume product, high sulpho-aluminate. This may tend to accelerate the reaction by removing the barrier of hexagonal aluminate around the C₃A grain. This explains the increase in rate observed for the 10% mixture. The rate is controlled by both (SO₄)²⁻ ion sorption and the layer of products. The large volume of sulpho-aluminate product may contribute to a general decrease in porosity of the system of C₃A grains, but there is no reason to assume that this product will be any less permeable per unit thickness than the hexagonal hydro-aluminates. A layer of the type that completely stopped the hydration of C₃A at 52°C does not exist at all in the formation of the high sulpho-aluminate. A gypsum addition at 52°C may act as an accelerator in so far as it prevents the special layer of C₃AH₆ from forming. The 2.5% addition does not supply the sulphate ions at a high enough rate to prevent the

formation of C_3AH_6 , but a 10% addition successfully achieves this for a considerable time, thus preventing the formation of the layer.

The sequence of the reactions

On the basis of the above discussion, it is possible to give an approximate description of the reactions that take place.

As water first enters the specimen, the hexagonal hydro-aluminates form rapidly on the surface of the grains of C_3A . $(\text{SO}_4)^{2-}$ ions sorbing on the C_3A surface retard this reaction, the concentration of $(\text{SO}_4)^{2-}$ depending upon the initial quantity of gypsum in the mixture, and upon the temperature of the reaction. $(\text{SO}_4)^{2-}$ also retards the formation of C_3AH_6 and reacts with the hexagonal aluminates; the demand for $(\text{SO}_4)^{2-}$ ions will tend to reduce its concentration on and around the C_3A surface. When the quantity of gypsum in the mixture is sufficient (10 and 20% at 2, 12 or 23°C), the rate of reaction of the hexagonal aluminates with gypsum may exceed their rate of formation and thus remove the layer of hexagonal aluminates from the grain by rupturing. It is improbable that the sulpho-aluminate will remain in the same position as the hexagonal aluminate because a large disruptive expansion accompanies the reaction as was observed from the length change results. This does not agree with the suggestion⁽¹²⁾ that a layer of sulpho-aluminate is the cause of retardation of the C_3A and that this layer directly on the C_3A is more effective than a layer on the surrounding hexagonal aluminates. There is a balance between the retarding effect due to the concentration of $(\text{SO}_4)^{2-}$ ions on the surface, their rate of reaction with the hexagonal aluminates and the thickness of the hexagonal layer. It is possible that at some stage sulpho-aluminate is formed by direct action of $(\text{SO}_4)^{2-}$ ions with the C_3A .

As the concentration of $(\text{SO}_4)^{2-}$ ions diminishes, the reaction should accelerate owing to the reduction of sorbed ions on the C_3A surface, so that the low sulpho-aluminate and solid solutions of this and the hexagonal aluminate C_4AH_{19} should form. C_3AH_6 should also form in areas where the concentration of $(\text{SO}_4)^{2-}$ ions is very low. Although C_3AH_6 was observed at the later stages, interpretation of the peaks with respect to low sulpho-aluminate and solid solutions was not possible because of merging.

Conclusions

- (1) Estimates of relative reaction rates from peak areas obtained from differential thermal analysis and measurements of length change during these reactions show marked agreement, although interpretation must be made with caution.
- (2) Gypsum decreases the reactivity of C_3A by sorption of $(\text{SO}_4)^{2-}$ ions.
- (3) Gypsum reduces the rate of conversion of hexagonal

hydro-aluminates to the cubic hexahydrate by sorption of $(\text{SO}_4)^{2-}$ ions.

- (4) The large volume of sulpho-aluminate product may contribute to a general decrease in porosity of a system of C_3A grains and retard the reaction of C_3A in this way; the disruptive expansions that occur when the sulpho-aluminate is formed suggest that it cannot form an impermeable layer.
- (5) A large enough addition of gypsum may affect hydration at high temperatures (52°C) by preventing the impermeable growth of C_3AH_6 over the C_3A layer. Under these circumstances, the gypsum may thus be regarded as an accelerator.
- (6) The degree to which a given addition of gypsum retards the hydration of C_3A at a particular temperature is affected by a balance between (a) the concentration of $(\text{SO}_4)^{2-}$ ions on and around the surface of the C_3A ; (b) the rate of reaction of $(\text{SO}_4)^{2-}$ ions with the hexagonal hydro-aluminates; (c) the thickness of the hexagonal hydro-aluminate layer around the C_3A grains.

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