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ELUCIDATION OF THE ROLE OF CHEMICAL ADMIXTURES IN HYDRATING CEMENTS BY DTA TECHNIQUE*

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ABSTRACT

Many types of admixtures are being used in concrete for obtaining better workability, retardation or acceleration of setting, improved mechanical properties, etc. There is no doubt that for more judicial and efficient use and also for the development of new types of admixtures, a basic understanding of their action in cement is essential. The mechanism is involved and complex and hence attempts are being made to explore new methods of approach.

The technique of differential thermal analysis (DTA) has largely been used as an adjunct or a subsidiary technique to investigate the role of admixtures. It is possible, by a systematic approach, to use DTA as the main source of information in many cases. Thermograms may be used to study the kinetics of hydration, the mechanism of action of admixtures, and for the identification and estimation of new products that may form in the presence of admixtures. In some instances thermograms provide information not easily obtainable by other techniques.

By means of typical examples this paper attempts to examine the application of DTA to a study of the different aspects of the action of various types of admixtures on the hydration of cement.

INTRODUCTION

An admixture is defined as a material other than water, aggregates and hydraulic cement, that is used as an ingredient of concrete or mortar and is added to the batch immediately before or during its mixing[1]. Most concrete in use in North America contains at least one admixture.

Admixtures can be grouped as follows: (*1*) chemical admixtures; (*2*) air-entraining admixtures; (*3*) pozzolans; and (*4*) miscellaneous (used for special purposes such as grouting, coloring, flocculating, damp-proofing and corrosion inhibition).

Chemical admixtures are widely used in concrete practice and are classified

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into five groups[2]. They are: Type *A*, water-reducing; Type B, retarding; Type C, accelerating; Type *D*, water-reducing and retarding; Type *E*, water-reducing and accelerating.

Most published data in the field of chemical admixtures relate to their influence on the engineering properties of concrete, and comparatively less attention has been directed to the basic understanding of the mechanism of their action. There is little doubt that the mechanism is complex and involved. At present no single mechanism offers a tangible explanation of the various changes in the physical, chemical and mechanical effects observed in concrete due to the use of any of the well-known admixtures. Hence, there is an ever-increasing awareness of the need for new approaches and techniques to investigate the action of the chemical admixtures.

The DTA technique has been used extensively in clay mineralogy and only recently has it been applied in cement chemistry. There is still a tendency to use it only as an adjunct or a subsidiary technique to other well-known methods of investigation[3]. A better appreciation of the DTA technique and the recent tremendous advance in the instrumentation have resulted in excellent contributions in the field of organic, inorganic and physical chemistry[4–12].

Among the various thermal techniques, the DTA method appears to be more extensively used than others because of its ability to detect both physical and chemical changes occurring in a substance. The full potential of this technique has not yet been realized in cement chemistry and, more particularly, in the field of admixtures. Valuable data can be obtained only if a systematic investigation of the hydration process is followed sequentially, *i.e.* the samples for investigation should be hydrated for different lengths of time, if required, from a few minutes to several months[13,14]. It is also essential that, for a proper interpretation of the inflections in the thermograms that may decrease or increase in intensity during hydration (including the inflections that may emerge), certain physical or chemical treatments should be carried out on the sample. In many instances slight modifications in the DTA equipment will yield useful information. Resolution and interpretation of the thermal effects may be effected by a manipulation of the furnace atmosphere and pressure, rate of heating or cooling, or sensitivity. Where additional evidence is needed for interpretation, the sample should preferably be subjected to a simultaneous analysis using thermogravimetry, effluent gas analysis, mass spectrometry, electrical conductivity, dilatometry, X-ray analysis, etc.

This paper attempts to show how, by using DTA as the main technique of investigation, useful information may be obtained on the role of chemical admixtures in the hydration of cements. Thermograms provide knowledge on the kinetics of hydration and the mechanism of hydration in the presence of admixtures; enable detection and identification of new products that may develop during hydration; and in certain instances yield data not easily obtained by other techniques. It is hoped that these examples will lead to a better appreciation and wider application of DTA in the admixture field in cement chemistry and in other related fields.

RESULTS AND DISCUSSION

Water reducing, retarding and water reducing–retarding admixtures

In the ASTM designation C494, the chemical admixtures are classified into five types. Of these, types *A*, *B* and *D* may be grouped together. In this group the type *D* is used in about 50–60 billion cubic yards of concrete per year in North America[15]. Under types *A* and *D* the following five classes are recognized: *1*, lignosulfonic acids and their salts; *2*, modifications and derivatives of lignosulfonic acids and their salts (classes *1* and *2* consist of Ca, Na or NH_4 salts of lignosulfonic acid); *3*, hydroxylated carboxylic acids and their salts; *4*, modifications and derivatives of hydroxylated carboxylic acids and their salts (examples for class *3* are Na, Ca or triethanolamine salts of acids such as adipic acid and gluconic acid. Class *4* may be a combination of class *3* and some organic or inorganic compounds acting as accelerators or retarders); *5*, carbohydrates, including modifications and derivatives (examples are sucrose, glucose and maltose).

Type *B* is an admixture that retards setting. Hence chemicals under *D* will also meet the requirements of *B*. Type *B* materials include some salts of zinc and water-soluble borates and phosphates.

Of the types discussed above the most commonly used admixture is the water-reducing and -retarding type, which enables retardation of setting and development of better strengths in concrete. Lignosulfonic acid and its salts are more widely used than others and they are known to extend the setting time by 30–60%, to reduce the water requirement from 5–10%, and to increase the compressive strength at 28 days by 10–20%. Table I shows the influence of a lignosulfonate on some of the properties of concrete[16].

TABLE I

EFFECT OF LIGNOSULFONATE ON THE PROPERTIES OF PORTLAND CEMENT CONCRETE

Admixture of cement (% by wt.)	*Water:cement ratio*	*Water reduction (%)*	*Setting time (h) for penetration resistance of*		*Compressive strength, % of the control*			
			0.5 N/mm^2	*3.5* N/mm^2	*24 h*	*3 days*	*7 days*	*28 days*
0	0.630		3-1/4	5	100	100	100	100
0.07	0.599	5	4	5-3/4	101	104	103	102
0.13	0.599	5	4	6-1/4	95	108	111	101
0.18	0.580	8	4-3/4	7-1/2	100	110	107	109
0.26	0.580	8	5-1/4	8-1/4	107	115	112	115

As can be seen in Table I, that addition of lignosulfonate results in retardation of setting, decreased water requirements for the same workability, and increased compressive strength. Attempts have been made to explain these effects by different mechanisms and there is still no general agreement. Portland cement is a mixture of several components and in the presence of lignosulfonate these, individually and in combination, mutually influence the hydration sequence. Since it is rather difficult to follow these complex effects, some attempts have been made to study the effect of lignosulfonate on the hydration of the individual components of cement. Once the effects on each phase are completely understood. the studies may then be extended to the binary and ternary systems and ultimately to the interpretation of the behavior of the cement itself.

Hydration of $3CaO,Al_2O_3$ in the presence of lignosulfonate. — The tricalcium aluminate phase (C_3A)*, although it constitutes only a small proportion in portland cement, exerts a significant influence on the setting property. It is hence logical to assume that the set-retardation effects of portland cement in the presence of lignosol may be related to the predominating influence of lignosol on this phase.

The C_3A phase is known to hydrate to a mixture of the two metastable phases of composition C_4AH_x and C_2AH_x (hexagonal) before final conversion to a stable cubic phase of composition C_3AH_6. The addition of lignosulfonate retards conversion of C_3A to these hydrates to different extents depending on the amount of admixture, water:solid ratio, temperature, and the particular size of C_3A.

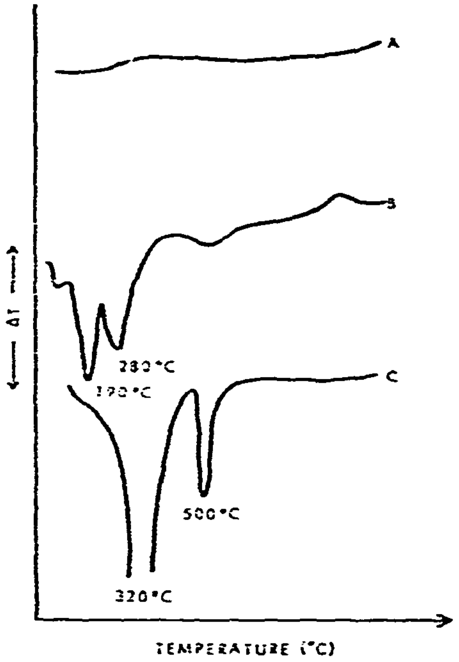

Fig. 1. DTA of C_3A and its hydrates (A = C_3A; B = hexagonal phase; C = cubic phase).

The technique of DTA is eminently suited to follow both qualitatively and quantitatively the interconversion effects during the hydration of C_3A. The DTA

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*The following nomenclature in cement chemistry will be used where necessary: C=CaO, S=SiO_2, A=Al_2O_3, and H=H_2O.

technique is sometimes so sensitive in the identification of phases such as C_3AH_6 that it is preferred to X-ray diffraction procedures. In thermograms the C_3A phase normally shows no perceptible effects. The hexagonal phases show two prominent endothermal effects, the first below 150–200°C and the second at 200–280°C. The cubic phase shows characteristic endothermal effects at about 300–350°C and 500–550°C (Fig. 1)*.

The retardation effects in the hydration of C_3A in the presence of small amounts of calcium lignosulfonate, and at a low water:solid ratio, may be illustrated by the thermograms in Fig. 2. It may be seen that without the addition of calcium lignosulfonate, the cubic phase appears at 6 h and is the main phase existing at 7 days. In the sample treated with the admixture the cubic phase is not detectable even at 14 days. These observations show the extent to which the hexagonal phase is stabilized by the admixture.

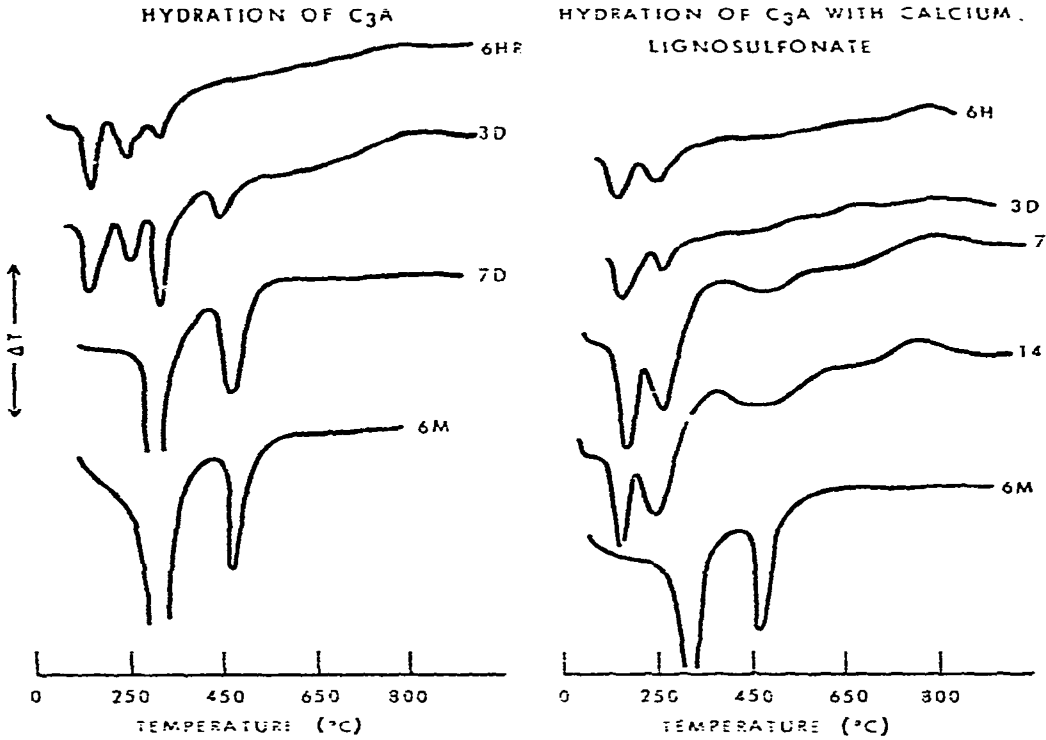

Fig. 2. Influence of calcium lignosulfonate on the hydration of C_3A.

In the above example, the retardation effect of lignosulfonate was studied as a function of time of hydration. Information on the degree of retardation achieved up to a particular period of hydration, using different amounts of lignosulfonate, would be a natural extension of the use of DTA. For example, thermograms of C_3A con-

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*These effects may occur at higher or lower temperatures, depending on the samples and experimental conditions, but in no way influence qualitative or quantitative aspects of identification and estimation.

taining 0–5% lignosulfonate and hydrated for 9 months show that with no admixture the hydrated product contains only the cubic phase[17]. Even with an addition of 0.5% admixture only the cubic phase is detected. At lignosulfonate concentration beyond 0.5% only the hexagonal phase is detectable. Thus the DTA method enables determination of the optimum amount of the admixture required to stabilize a particular phase for a predetermined period.

At very low concentrations of lignosulfonate the primary effect is the retardation of the conversion of the hexagonal to the cubic phase. Complex effects are observed when C_3A is treated with a large excess of lignosulfonate[18]. At calcium ligno-

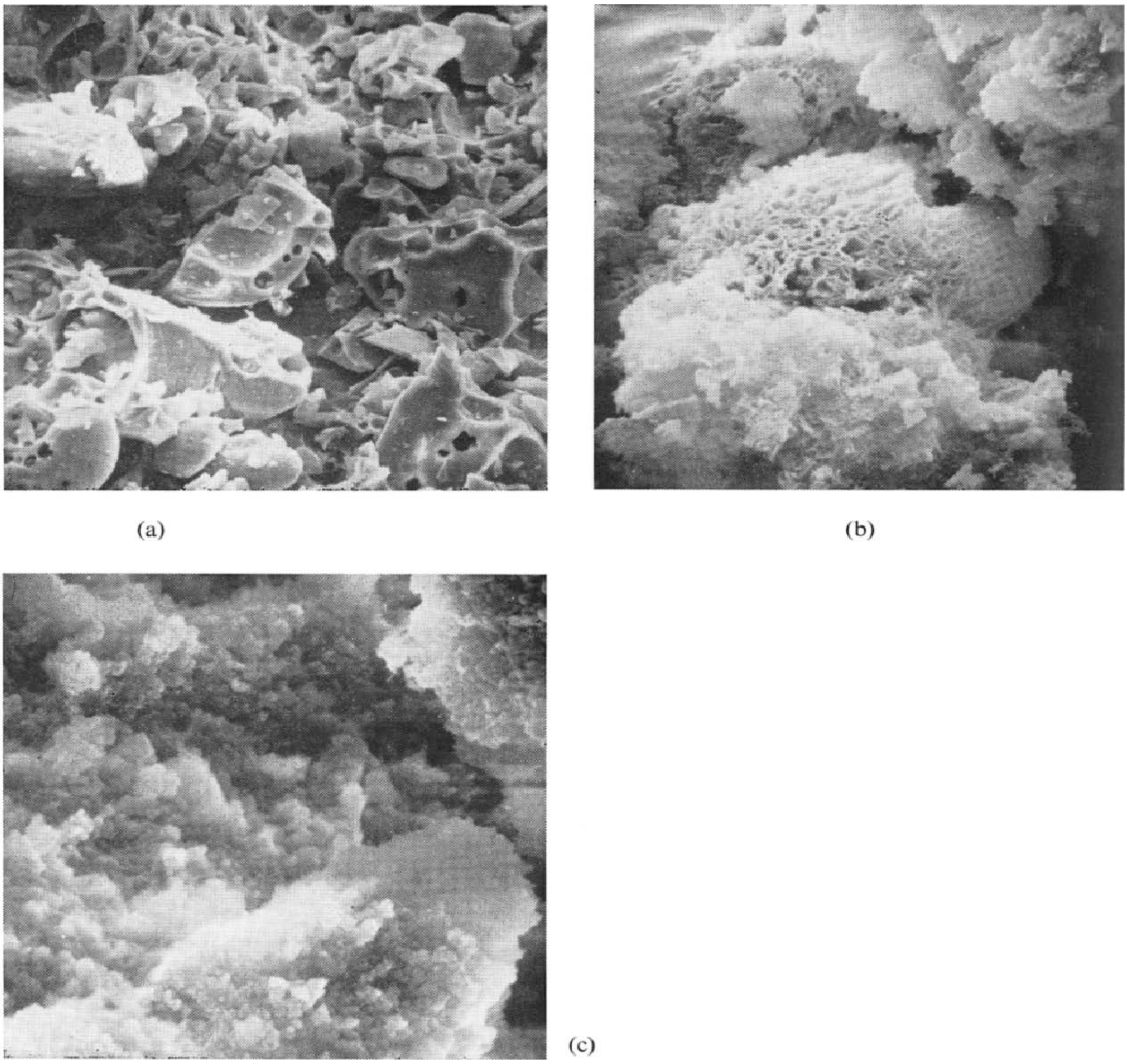
(a) (b) (c)

Fig. 3. (a), Electron micrographs of calcium lignosulfonate (× 420); (b), C_3A treated with 30% calcium lignosulfonate (× 1960); and (c), the gel-like material with C_3A treated with 100% calcium lignosulfonate (× 4900).

sulfonate concentration of 10–30%, there is evidence of a complex formed between C_3A and the lignosulfonate. The thermogram of this product is different from thermograms of pure calcium lignosulfonate or the aluminate hydrates. The electron microscopic examination of this product shows a honeycombed structure probably formed of twisted ribbon-like material (Fig. 3). At still higher concentrations of 50% or more, a gel-like material precipitates out. This gel-like material appears to be a basic calcium lignosulfonate with incorporated Al^{3+}. Unlike calcium lignosulfonate, it shows a large endothermal effect at about 100°C and an exothermic peak at about 730°C, has low solubility in water, has a different chemical composition, does not show any lines in the X-ray diffraction pattern and has a different morphology.

The mechanism by which the hexagonal phase of calcium aluminate hydrate is stabilized by calcium lignosulfonate is better understood by treating this phase directly with calcium lignosulfonate. Treatment of the hexagonal phase with increasing amounts of calcium lignosulfonate shows that this phase irreversibly adsorbs the lignosulfonate. There is evidence that lignosulfonate enters the interlayer positions in the hexagonal phase[18]. A thermogram of the phase containing about 10% irreversibly

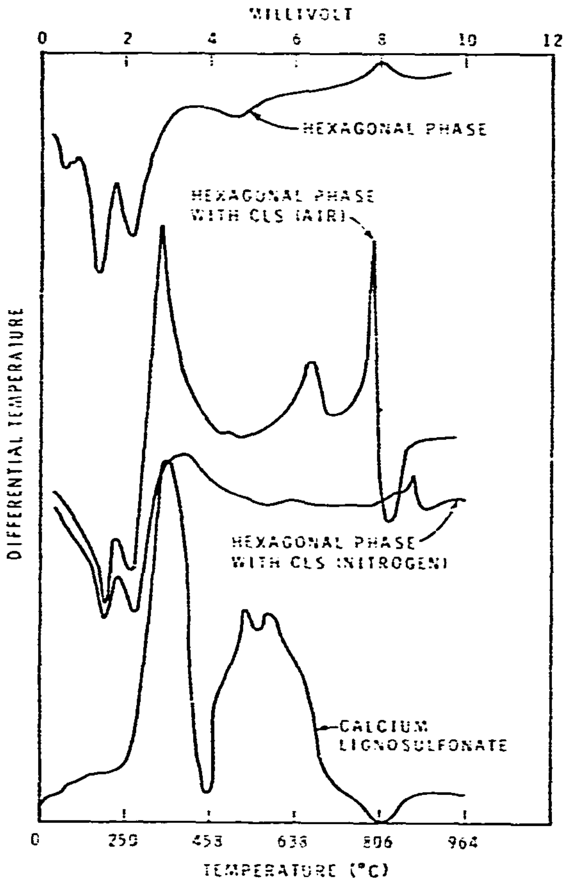

Fig. 4. Thermograms of the hexagonal phase treated with calcium lignosulfonate (CLS).

adsorbed calcium lignosulfonate (CLS) exhibits an intense exothermic peak at 790°C and an endothermic effect at 825°C (Fig. 4). The exothermic peak, which is absent in an N_2 atmosphere, is attributed to the oxidation of strongly bound lignosulfonate on the hexagonal phase. Calcium lignosulfonate itself is oxidized at a lower temperature. The lignosulfonate adsorbed in the interlayer positions may inhibit the free movement of the interlayer ions responsible for conversion of the hexagonal to the cubic phase.

Influence of lignosulfonate on the hydration of C_3A containing gypsum and lime. — Once knowledge is gained on the action of lignosulfonate on the hydration of C_3A, the next step would be to examine a mixture containing C_3A–gypsum and $Ca(OH)_2$. The study of hydration of this mixture would help understand the mechanism of hydration of cement at early stages. The DTA technique, though useful in following the hydration sequence in this system, has received little attention so far. Fig. 5 indicates the changes occurring in the thermograms[19] when a small amount of lignosulfonate is added to C_3A containing 10% gypsum and 5% $Ca(OH)_2$.

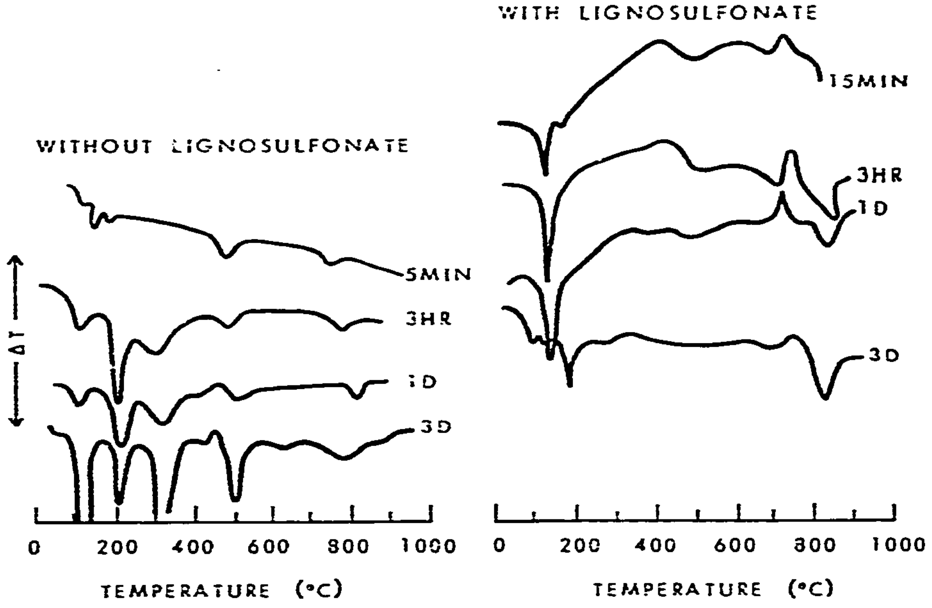

Fig. 5. Thermograms of C_3A hydrated in the presence of gypsum, lime, and lignosulfonate.

Without more extensive investigations all the thermal effects cannot be explained but certain general conclusions may be drawn. The high sulfoaluminate complex ($C_3A{\cdot}3CaSO_4{\cdot}31H_2O$) is recognized even within a few minutes in the mix containing the admixture by a strong endothermic effect at about 150°C. The conversion of the high to low sulfoaluminate form ($C_3A{\cdot}CaSO_4{\cdot}11H_2O$), or a solid solution, may be observed by the emergence of an endothermal effect at about 200°C. Thermograms readily show that it takes 3 days for high sulfoaluminate to convert to the lower form in the presence of lignosulfonate, whereas in the absence of this admixture the conversion is very rapid and occurs in about 3 h. Much more work may be needed to draw definite conclusions, but it does appear that the delay in set with the admixture may be connected with the rate of interconversion.

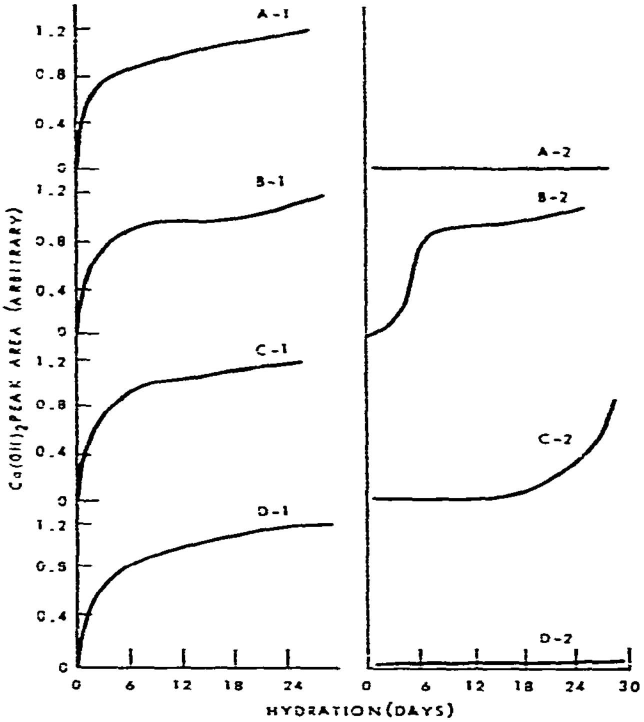

Fig. 6. Kinetics of the hydration of C_3S in the presence of calcium lignosulfonate, C_3A or its hydrates. A-1 = C_3S+H; A-2 = $C_3S+Lig+H$; B-1 = C_3S+C_3A+H; B-2 = $C_3S+C_3A+Lig+H$; C-1 = $C_3S+Hex+H$; C-2 = $C_3S+Hex+Lig+H$; D-1 = $C_3S+C_3AH_6+H$; and D-2 = $C_3S+C_3AH_6+Lig+H$.

Hydration of C_3S in presence of C_3A and calcium lignosulfonate. — Calcium lignosulfonate retards the hydration of C_3A but may inhibit the hydration of C_3S indefinitely. The extent to which this inhibiting effect of calcium lignosulfonate is counteracted by additions of C_3A, the hexagonal or the cubic aluminate hydrate, is of relevance to cement chemistry. In Fig. 6 the rates of hydration of C_3S in the presence of 5% C_3A and its hydrates are compared by estimation of $Ca(OH)_2$ through DTA. The following information may be gathered from these results. Addition of 0.5 % calcium lignosulfonate inhibits hydration of C_3S (Fig. 6, curves A-1, A-2). Addition of 5% C_3A is sufficient to promote hydration slowly at first and normally after 3 days (curves B-1, B-2). The hexagonal phase is less efficient than C_3A in counteracting the inhibitive action of lignosulfonate, the cubic phase being practically ineffective (C-1, C-2, D-1 and D-2). These results show that the rate and amount of irreversible uptake of lignosulfonate, which is in the order of $C_3A >$ hexagonal phase $>$ cubic phase, dictates the relative action on the hydration of C_3S. The greater inhibitive action of lignosulfonate when added to cements after 5 min of hydration may be explained on the basis of the hydrated products of C_3A having less adsorptive capacity than the C_3A itself.

The retarding action of sugars on C_3A hydration. — All saccharides with the exception of trehalose strongly retard the set of cement[20]. The sugars also possess a water-reducing property. The strong retarding actions of C_3A hydration by 1% sucrose, as opposed to the weak retarding action of 1% trehalose, is well substantiated by the DTA curves[21] of the hydrated C_3A (Fig. 7). The three endothermal effects in the vicinity of 100 and 200°C represent dehydration by a mixture of the hexagonal aluminate hydrates. The peaks at 300–350°C and 550°C are mainly due to the dehydration effects of the cubic aluminate hydrate phase. The relative amounts of the hexagonal and cubic phase formed at different periods may be followed by means of the thermograms. The hydration of C_3A without an admixture shows a strong endothermic peak at about 550°C as early as 3 h, indicating an early formation of the cubic phase. In the presence of sucrose a large amount of the hexagonal phase formed earlier persists even up to 90 days, as evidenced by the endothermal peaks below 250°C. As opposed to this, C_3A containing trehalose shows intense endothermal effects for the presence of the cubic phase after a relatively short time.

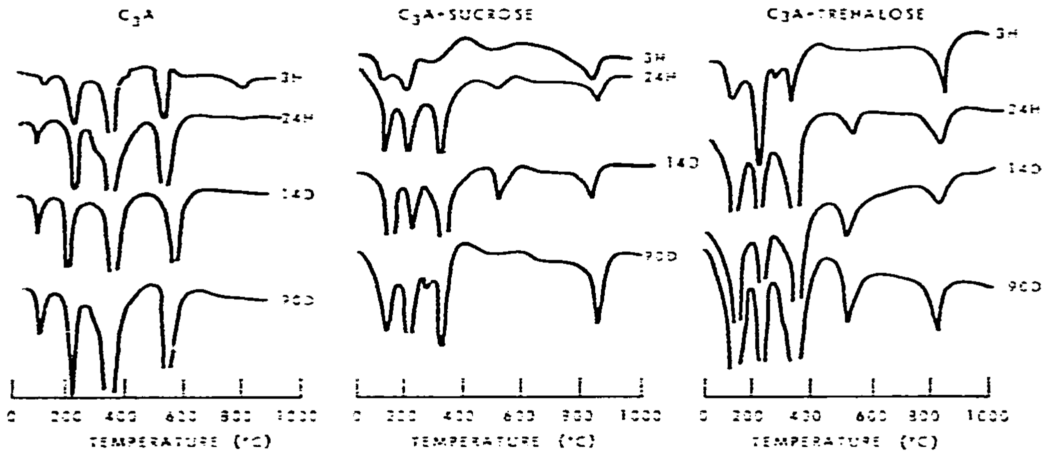

Fig. 7. Influence of sucrose and trehalose on the hydration of C_3A.

Influence of sugars on the hydration of C_3A–gypsum mixtures. — Addition of sugars except trehalose to C_3A–gypsum mixtures shows clearly a retardation of formation of the ettringite phase[21]. For example, at 14 days of hydration, the mixture containing sucrose has 24.8% of ettringite, and that without, 52.3% ettringite. With trehalose, the amount is 48.9%. Thermograms reveal that conversion of the ettringite to the low sulfoaluminate form is also retarded in the presence of sugars.

Experience indicates that it is not always possible to label an admixture as a retarder, an accelerator or a neutral type in the hydration of cement. In addition to other factors, the concentration of the admixture may determine whether it acts as a retarder or an accelerator. The following example[22] shows the influence of the concentration of sucrose on the hydration of C_3A (Fig. 8).

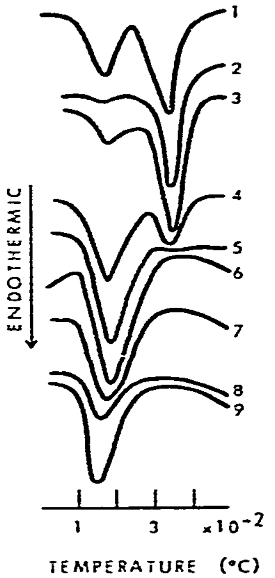

Fig. 8. Effect of different amounts of sucrose on the hydration behaviour of C_3A. Percentage of sucrose: 1 = 0.0; 2 = 0.025; 3 = 0.05; 4 = 0.1; 5 = 0.2; 6 = 0.5; 7 = 1.0; 8 = 2.0; 9 = 5.0.

The thermograms for all the samples were taken after 10 months of hydration. The C_3A sample without the admixture indicates two endothermal effects: at 140–180°C and 330–340°C for the presence of the hexagonal and the cubic aluminate hydrate respectively. At sucrose concentrations of 0.025 and 0.05%, the peaks due to the cubic phase are intensified and those due to the hexagonal phase are decreased. This shows that at these concentrations there is an accelerated conversion of the hexagonal to the cubic form. At concentrations 0.1–0.5%, increasing amounts of hexagonal aluminate hydrate are stabilized. At concentrations of 2–5%, even the amount of hexagonal form diminishes revealing that the hydration of C_3A itself is retarded.

No systematic DTA work has been done on the progress of hydration of cements using sugars. It may not be easy to interpret all the thermal curves below 300°C in this system; however, careful work, even for such difficult systems, may yield quantitative data on the products of hydration[23].

If the composition of the hydrated silicate is assumed to be constant during the hydration of C_3S or C_2S, an estimation of $Ca(OH)_2$ formed at different periods of hydration is a good index of the degree of hydration. The relative retardation effects of different amounts of citric acid on the hydration of portland cement and calcium silicates may be cited as an example in which this method could be used[24].

Accelerators (calcium chloride)

An accelerating admixture is used to reduce the setting time of concrete and to increase the rate of development of early compressive strengths. This is a type *C* admixture according to the ASTM designation C-494. Calcium chloride is by far the best known and most widely used accelerator in concrete practice.

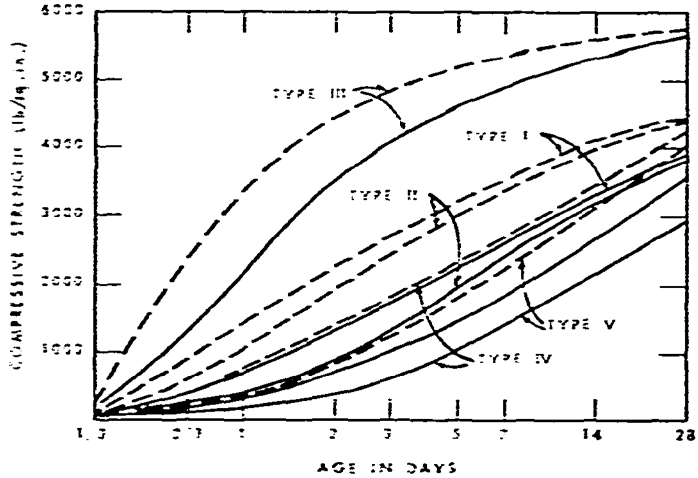

Fig. 9. Influence of $CaCl_2$ on the strength development in different types of cement. ——— no $CaCl_2$; – – – – – 2% $CaCl_2$.

Addition of $CaCl_2$ has been shown to increase the compressive strength of all types of cements[25] (Fig. 9). The degree to which $CaCl_2$ reduces the setting time of portland cement concrete may be seen from the following example. A portland cement concrete having an initial setting time of 3 h and a final setting time of 4½ h will show a reduction in these times by 2 and 3 h, respectively, at a $CaCl_2$ content of 3%.

The accelerating influence of $CaCl_2$ has been known for nearly 90 years, but as yet the exact mechanism involved has not been discovered. Little success has been achieved by studying directly the role of $CaCl_2$ in the hydration of portland cement. It seems essential first to gain an understanding of the influence of the accelerator on the individual phases of cement.

Hydration of C_3A in the presence of $CaCl_2$. — The C_3A phase in portland cement exerts a significant influence on the heat development and setting property, and hence the mechanism of interaction between C_3A and $CaCl_2$ becomes important for the study of the accelerating effect of $CaCl_2$. There is still some controversy as to which chloroaluminate forms when C_3A reacts with $CaCl_2$, *viz.*, $C_3A{\cdot}CaCl_2{\cdot}xH_2O$ or $C_3A{\cdot}3CaCl_2{\cdot}yH_2O$. It is generally believed that the low form is the main product that exists under the practical conditions of hydration. The DTA technique has been used to differentiate between the two forms of chloroaluminate and also the formation of other hydrated phases. For example, endotherms at about 190°C and 350°C identify the monochloroaluminate and the endotherm at about 160°C may correspond to the higher chloroaluminate. Other compounds detected include calcium hydroxychloride with peaks at about 130, 145 and 485 °C, the hexagonal calcium aluminate hydrates, and solid solutions.

Based on the thermal investigations, the following important conclusions may be drawn about the influence of $CaCl_2$ on the hydration of C_3A.

Both the high and low forms of chloroaluminate may be detected when C_3A is hydrated in the presence of $CaCl_2$ and saturated $Ca(OH)_2$ solution. The high form predominates at high $CaCl_2$ concentrations[26,30].

Tricalcium aluminate reacts with $CaCl_2$ more slowly in saturated $Ca(OH)_2$ solution than in water.

Addition of $CaCl_2$ does not prevent the formation of ettringite ($C_3A \cdot 3CaSO_4 \cdot 31H_2O$) when C_3A is hydrated in the presence of gypsum[27].

The cubic calcium aluminate hydrate (C_3AH_6) also reacts with $CaCl_2$ to form monochloroaluminate, but the reaction is slower than that using C_3A as the starting material[28].

The DTA of monochloroaluminate shows an exothermal effect at 500 °C corresponding to a crystallization effect which cannot be detected by the X-ray procedures[29].

Hydration of C_3S in presence of $CaCl_2$. — Several explanations have been offered for the accelerating action of $CaCl_2$ in cements. In earlier work it was assumed that a complex between C_3A and $CaCl_2$ was responsible for early setting and strength development. As already stated complexes are formed between C_3A and $CaCl_2$ in water or $Ca(OH)_2$ solution, but these may not play a major role in the accelerated action. In the first six hours of hydration in portland cement the concentration of chloride in the solution phase does not change. It appears that in the presence of $CaCl_2$ and gypsum, C_3A preferentially reacts with gypsum[31]. Also, it is difficult to conceive how the small amount of complex formed by C_3A and $CaCl_2$ could improve the strength development of cement to the extent that is usually observed. Therefore, the rapid setting and strength development should be related in some man-

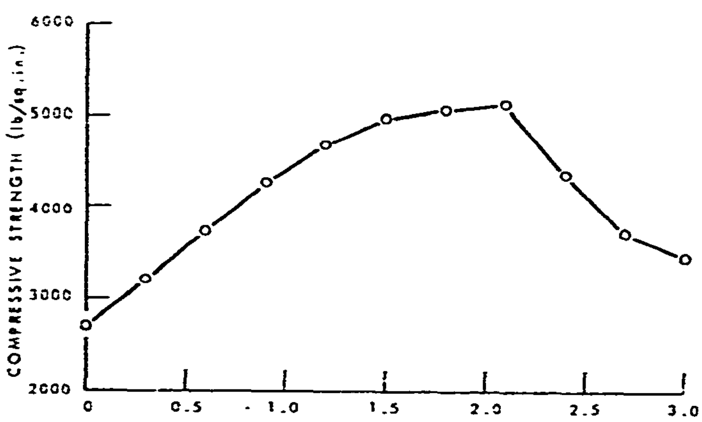

Fig. 10. Effect of $CaCl_2$ on the 28-day strength development in C_3S pastes.

ner with the action of $CaCl_2$ on the silicate phases. Recent studies have in fact conclusively shown that $CaCl_2$ accelerates the hydration of the C_3S phase. Fig. 10 shows that small additions of $CaCl_2$ increase the compressive strength of C_3S pastes, but higher amounts are deleterious[32]. It is thus imperative to gain knowledge of the action of $CaCl_2$ on C_3S hydration.

A sequential thermal study of the hydration of C_3S in presence of $CaCl_2$ yields data on the kinetics of hydration, identification of new phases and the possible mechanism of the accelerators[33,34].

The kinetics of hydration of C_3S may be followed by DTA either by estimating the amount of $Ca(OH)_2$ formed at different times or by the reduction in the amount of the C_3S phase[35]. The following features emerge when the endothermal area of $Ca(OH)_2$ decomposition is taken[33] as the basis of the degree of hydration of C_3S in presence of 0, 1 or 4% $CaCl_2$ (Fig. 11). The extent of hydration at 6 h is in the order of $C_3S + 4\%$ $CaCl_2 > C_3S + 1\%$ $CaCl_2 > C_3S + 0\%$ $CaCl_2$, and at 30 days, $C_3S + 1\%$ $CaCl_2 > C_3S + 0\%$ $CaCl_2 > C_3S + 4\%$ $CaCl_2$. In terms of the disappearance of C_3S, however, the extent of hydration at 6 h or 30 days is in the order $C_3S + 4\%$ $CaCl_2 > C_3S + 1\%$ $CaCl_2 > C_3S + 0\%$ $CaCl_2$. These results reveal that in the presence of 4% $CaCl_2$, C_3S hydrates to form a C–S–H product with a higher C:S ratio than that with 0% $CaCl_2$. The surface area values and morphological studies also show

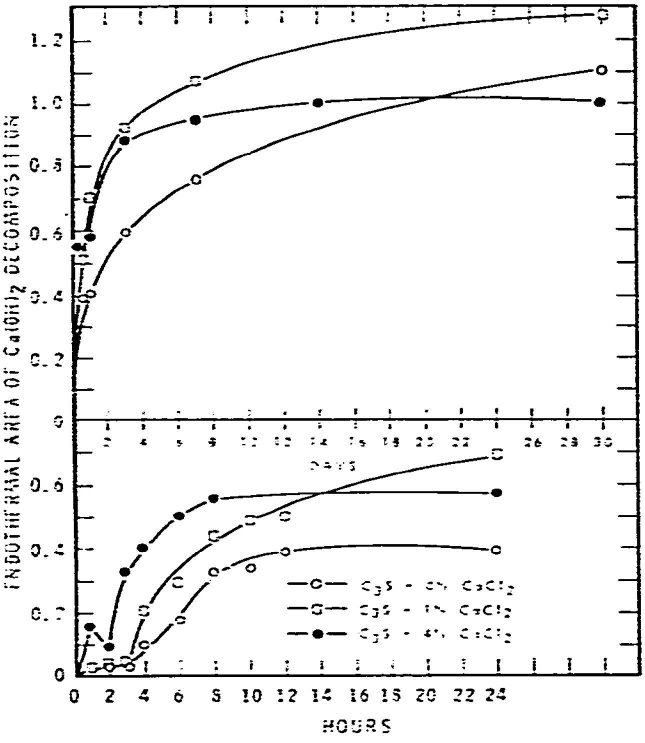

Fig. 11. Estimation of $Ca(OH)_2$ at different periods of hydration of $3CaO \cdot SiO_2$ by DTA.

distinct differences between C_3S containing no $CaCl_2$ and that with 1% or 4% $CaCl_2$. In Fig. 10 it is shown that the compressive strength of the C_3S paste decreases beyond 2% $CaCl_2$. The lower strengths at higher $CaCl_2$ contents seem to be due to the formation of C–S–H with a high C:S ratio. The C–S–H product that forms with low $CaCl_2$ concentrations has low C:S ratios and higher strengths. Thermograms in fact indicate formation of a product with a low C:S ratio in presence of 1% $CaCl_2$. It is obvious from these results that the compressive strength is not proportional to the degree of hydration if the C–S–H products formed do not have the same C:S ratios. This is shown in Fig. 12. All the points in the curve were obtained[32] at 28 days of hydration but with different amounts of $CaCl_2$.

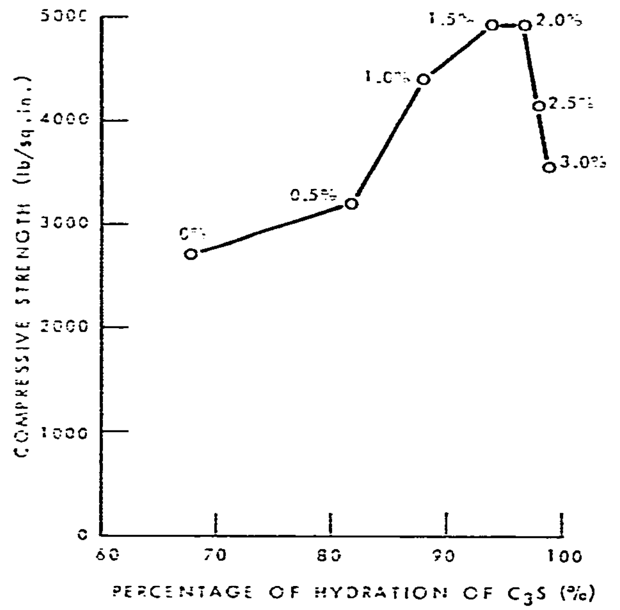

Fig. 12. Compressive strength of C_3S as a function of the degree of hydration with different amounts of $CaCl_2$.

Thermograms make possible a study of the influence of $CaCl_2$ on the dormant period in the hydration of C_3S. During the dormant period the reaction rate is very slow and at the end of this period the reaction is accelerated and is reflected in the emergence of peaks of the hydrated phase. For example, with 5% $CaCl_2$ the dormant period is reduced from 4 to 2 h.

In the presence of $CaCl_2$ new peaks emerge during the hydration of C_3S in addition to the changes in the endothermal peak intensities due to $Ca(OH)_2$ (Fig. 13). In $CaCl_2$ an endothermal effect is registered at about 570°C after 15 min of hydration: it increases in intensity in the first few hours and becomes undetectable at later periods. There is also an exothermic peak after 3 h at 640°C which intensifies with hydration: this peak is always followed by an endothermal dip in the range 810–850°C. An explanation of the above effects required certain treatments to the sample, and also

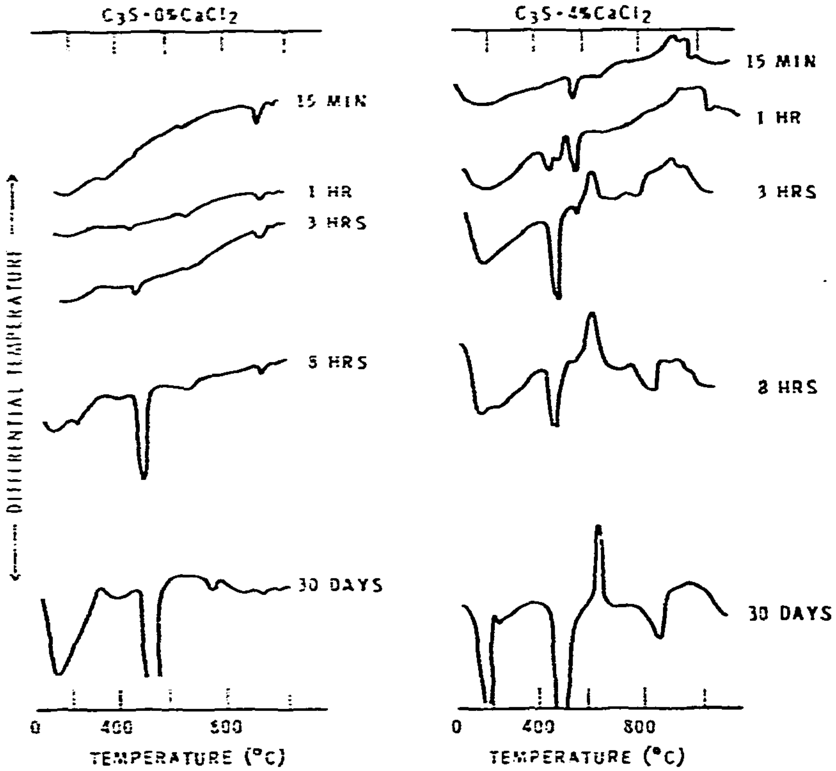

Fig. 13. Differential thermal characteristics of C_3S hydrated in the presence of $CaCl_2$.

a re-examination by DTA. Using DTA as the main source of information, the following conclusions may be drawn. Calcium chloride may exist in four or five states including complexes in hydrating C_3S, depending on the admixture content and duration of hydration. Calcium chloride exists in a free state in the early periods of hydration. In the dormant period the chloride is also adsorbed on the C_3S surface. In the acceleratory period and later, the chloride is chemisorbed on the C–S–H surface with some existing in interlayer positions. At later periods a considerable amount is incorporated strongly into the C–S–H lattice. An approximate estimation of the chloride with different modes of fixation in the hydrating C_3S is indicated in Fig. 14.

Accelerators other than $CaCl_2$

There is a general reluctance to use $CaCl_2$ as an accelerator in reinforced concrete and particularly in prestressed concrete. The enhanced corrosion effect of $CaCl_2$ on the prestressed wires is well known. There is hence a continued interest in developing an accelerator with nearly as much accelerating capacity as $CaCl_2$ but having no corrosive action.

Calcium thiosulfate. — There are many substances that have been suggested as alternative accelerators, but the recently reported chemical, calcium thiosulfate, has received some attention. In Table II a comparison is made of the action of three

TABEL II

INFLUENCE OF THE ACCELERATORS ON SETTING AND STRENGTH DEVELOPMENT IN PORTLAND CEMENT

Admixture	*Percentage admixture*	*Initial setting time (min)*	*Final setting time (min)*	*Compressive strength (kg/cm²)*			
				1 day	*3 days*	*7 days*	*28 days*
None	0	160	250	39	120	221	379
$CaCl_2$	0.5	118	195				
	1.0	78	122	69.5	150	291	381
	2.0			82.5	172	243	352
	3.0	45	80	85.3	177	265	364
$Ca(NO_3)_2$	0.5	112	132				
	1.0	95	160				
	2.0			18.7	113	193	316
	3.0	100	210				
CaS_2O_3	1.0			44.7	117	210	341
	1.2	81	114				
	1.8	64	99				
	2.0			46.7	127	203	328
	3.0	23	40	55.8	130	237	366

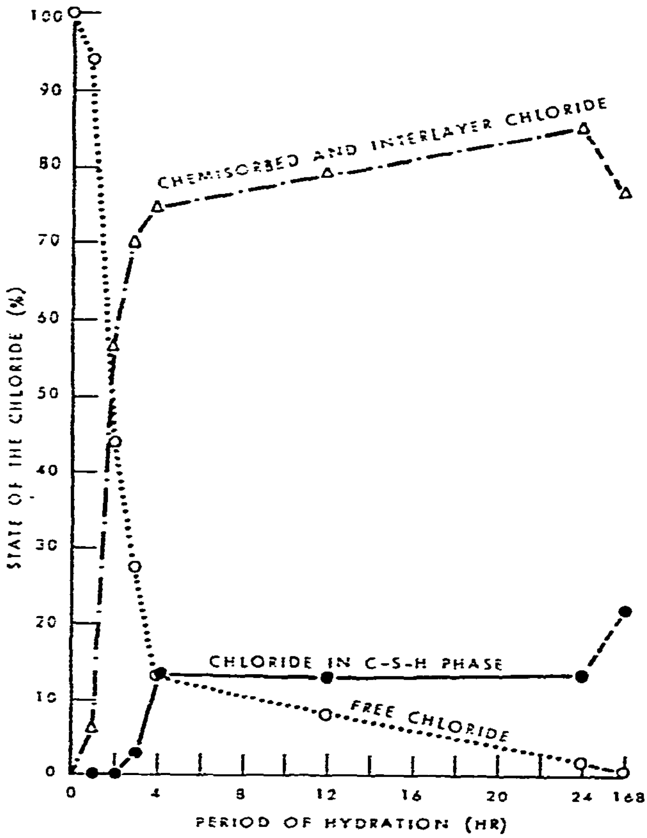

Fig. 14. Possible states of the chloride in tricalcium silicate hydrated for different periods.

accelerators on the setting property and strength development in a portland cement paste and mortar, respectively[36]. It may be generalized from the results that at low concentrations all three salts act as accelerators of setting. However, in terms of the early strength development $CaCl_2$ is by far the best among them. However, reinforced mortars containing 2–5% $CaCl_2$ showed signs of corrosion within a month, whereas those containing 5% CaS_2O_3 or $Ca(NO_3)_2$ did not exhibit any corrosion even after exposure for 6 months[36].

The relative accelerating capacities of the above accelerators may be conveniently followed by DTA. This may be illustrated with respect to C_3S hydrated for 7 h in the presence of 3% of each of these admixtures (Fig. 15)[36]. The low-temperature endothermal effect below 200 °C is due to C–S–H. The relative intensities of this effect for the three accelerators clearly demonstrate that $CaCl_2$ accelerates the hydration to the maximum extent. The same conclusions may also be drawn by an estimation of the intensities of the $Ca(OH)_2$ peaks occurring at about 550 °C. A small endothermal dip just before the $Ca(OH)_2$ peak is probably due to the dehydration of the amorphous form of $Ca(OH)_2$. The exothermal effects observable in the presence of $CaCl_2$ and CaS_2O_3 may possibly be due to the crystallization of C–S–H or to a reaction involving the chemisorbed complex of the admixture on the C–S–H phase.

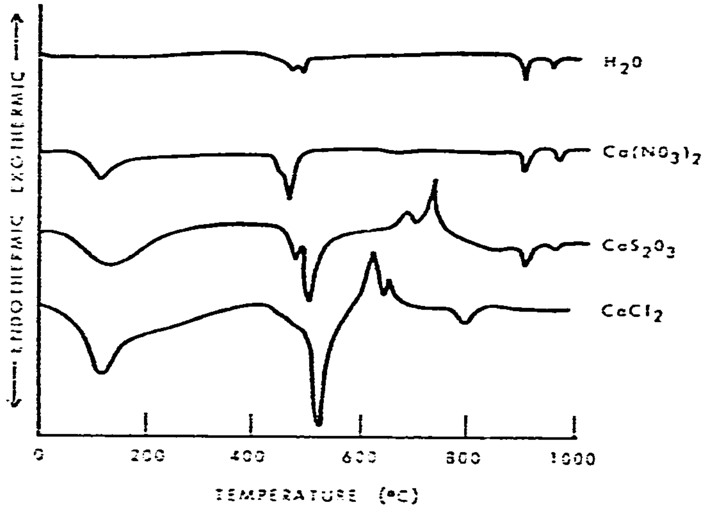

Fig. 15. DTA curves of the hydration products of C_3S in the presence of calcium salts.

In the hydration of C_3A in the presence of 3% of $CaCl_2$, $Ca(NO_3)_2$ or CaS_2O_3, the thermograms show some differences. With chloride and thiosulfate the formation of C_2AH_8, $C_3A{\cdot}Ca(OH)_2{\cdot}xH_2O$ or of products substituting Cl^- or $S_2O_3^=$ for $(OH)_2$ in the structure is indicated. The $Ca(NO_3)_2$ is different from others because it promotes hydration of C_3A to the cubic C_3AH_6.

Oxalic acid. — Oxalic acid in small amounts has been shown to accelerate the set and strength development in cements[37]. By an addition of 2% oxalic acid the initial set of cement paste is reduced by 43% and the final set by 44%. The compressive strength of the cement paste is increased by 12%, 10% and 9% at 5, 15 and 28 days, respectively.

A comparison of the hydrated cement with and without oxalic acid by DTA shows perceptible differences. In the cement containing oxalic acid four endothermal effects are observed at 300, 480, 550 and 620°C that could be ascribed to the existence of calcium oxalate. It appears that much of the strength development may be due to the formation of calcium oxalate during hydration.

Carbonates. — Carbonates such as $CaCO_3$, $MgCO_3$ and $CaCO_3 \cdot MgCO_3$ either as minerals or chemicals are known to react with the C_3A component of cement forming carboaluminate complexes. An addition of finely ground carbonates would increase the strength substantially. For example, a C_3A paste may show a compressive strength of only 6–12 kg/cm^2 between 3 days and 12 months, whereas this paste with marble may yield strengths at corresponding periods equivalent to 77–431 kg/cm^2, and with dolomites[38] 98–750 kg/cm^2. There seems to be some potentiality for using these admixtures in cement.

The strength development in C_3A pastes containing $CaCO_3$ or $CaCO_3 \cdot MgCO_3$ is attributed mainly to the formation of a carboaluminate complex of composition $3CaO \cdot Al_2O_3 \cdot CaCO_3 \cdot 11H_2O$. The paste containing $MgCO_3$ shows much lower strengths. For instance, at 28 days of hydration, the strengths for $CaCO_3$, $CaCO_3 \cdot MgCO_3$ and $MgCO_3$ are, respectively, 102, 160 and 44 kg/cm^2. The cause of low strengths developed with $MgCO_3$ admixture may be explained by a thermal investigation[38] (Fig. 16).

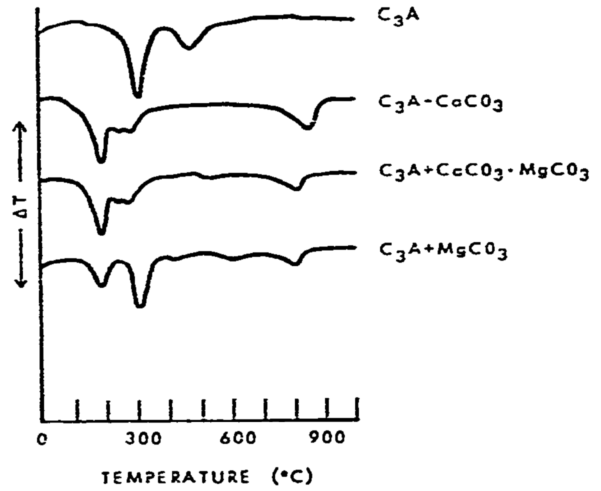

Fig. 16. Thermograms of C_3A hydrated with carbonate admixtures (28 days).

Tricalcium aluminate paste shows a sharp endothermal effect at 300°C and a broad endotherm of moderate intensity at about 450°C. These two effects are typical of C_3AH_6. In the presence of $CaCO_3$ or $CaCO_3 \cdot MgCO_3$, thermograms indicate a large endotherm at about 200°C, and a very small endotherm at about 300°C. The peak at 200°C corresponds to the formation of the carboaluminate complex. In presence of $MgCO_3$ only a small amount of the carboaluminate complex is formed, as evidenced by a small endotherm at about 200°C. A considerable amount of C_3AH_6 is indicated in the paste containing $MgCO_3$. A small quantity of carboaluminate and a large quantity of the C_3AH_6 phase present in the $MgCO_3$-treated C_3A sample should explain the lower strengths developed in this mixture.

Water-reducing and accelerating admixtures

The use of the type *D* admixtures provides good workability at low water: cement ratios and also results in increased compressive strengths. In many instances where only the water reduction is required but not the retarding action, certain formulations are made in which a material is added to counteract the retarding action and to accelerate the reaction. Calcium chloride, calcium formate and triethanolamine are typical of the materials used in these formulations.

Since triethanolamine is used to counteract the retarding action of an admixture, it is assumed that, used by itself, triethanolamine should be an accelerator. Not much published work is available on the effect of triethanolamine on the hydration of portland cement, but there is some evidence that it may not act as an accelerator[16].

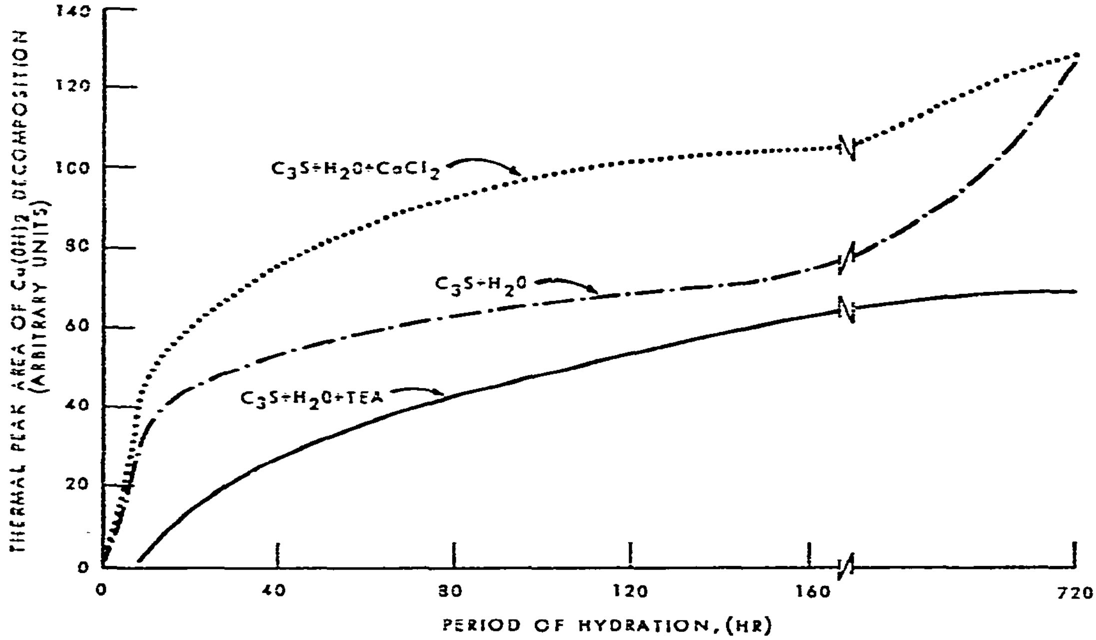

Fig. 17. The rate of hydration of tricalcium silicate in presence of calcium chloride and triethanolamine (TEA).

The apparently contradictory behaviour of triethanolamine can be understood only if its action on the individual phases in cement is understood. In Fig. 17 the rate of hydration of C_3S is compared with that containing $CaCl_2$ or triethanolamine. The calcium hydroxide content at different stages of hydration was obtained by estimating the peak area of the endothermal decomposition of $Ca(OH)_2$. It appears from the results that at any period of hydration the amount of calcium hydroxide formed in the presence of triethanolamine is less than that present in C_3S hydrated with water only and much less than that with $CaCl_2$. These results agree with those obtained by TG and X-ray analysis. The effect of different amounts of triethanolamine should be studied before its retarding or accelerating action is established. The influence of triethanolamine on the hydration of C_2S shows a similar trend (Fig. 18). At any stage of hydration the intensity of the endothermal effect corresponding to the dehydration of calcium hydroxide is much less in samples containing triethanolamine. Thermograms also reveal a twin endothermal effect in triethanolamine-treated samples, indicating a possible formation of an amorphous type of $Ca(OH)_2$. A systematic investigation of the effect of triethanolamine on the individual phases in cement has provided a basis for the mechanism of its action[39].

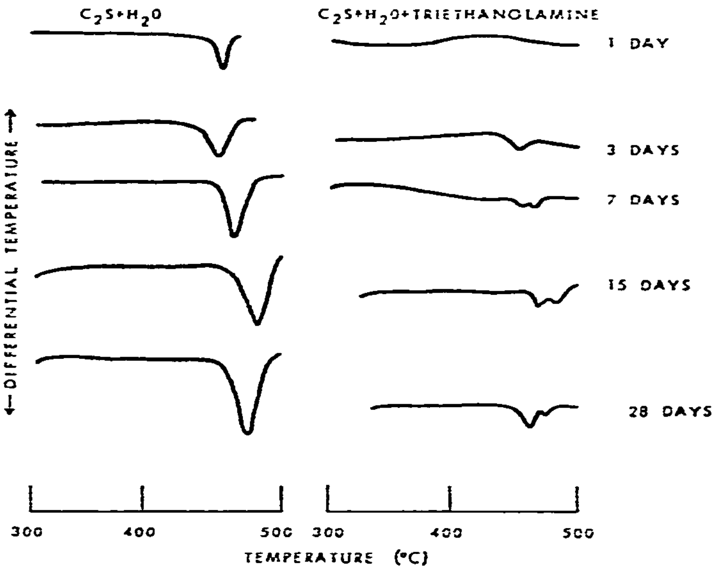

Fig. 18. Thermograms of C_2S hydrated in the presence of triethanolamine.

Polymers

Recently, there has been an upsurge in research on polymer concretes. Polymers improve significantly the compressive and tensile strengths of normal concrete. Typically, a cement mortar is hardened and physically-held water is removed either by ovendrying or by evacuation and then impregnated with a monomer (preformed). Subsequently, polymerization is carried out either with gamma radiation or by thermal catalytic means. In the so-called premixing method the monomer is added to the cement during mixing with water, it is then hardened and finally polymerized as before. Though the increase in strength characteristics obtained by this method is not as significant as that obtained by the impregnation method, it may yield some information on the mechanism of strength development in the composite.

The definition of admixtures requires that the admixture be added before or during mixing of concrete. Polymer concrete obtained by the premixing method should be included under the class of admixtures.

The use of DTA in polymer chemistry is well known, but its application to polymer concrete is only recent[40]. Though much more work would be needed before firm conclusions can be drawn using DTA in this field, the following example provides some idea of the future possibilities of its application.

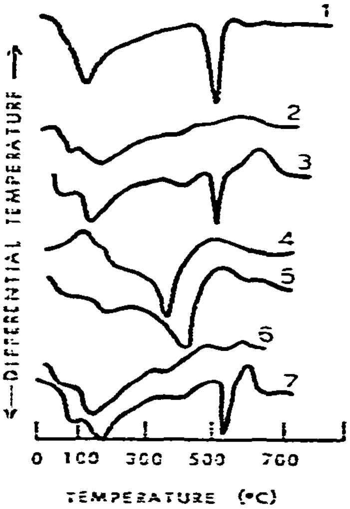

Fig. 19. DTA of cement paste containing polymers. (1), cement paste; (2), cement paste (PMMA) premixed; (3), cement paste (polystyrene) premixed; (4), PMMA; (5), polystyrene; (6), cement paste (PMMA) preformed; (7), cement paste (polystyrene) preformed.

The source of the great strength of polymer concrete is not yet known. It is not certain whether the increased strengths are due to the decreased porosity or some surface chemical effect or both. The DTA investigation of some of the polymer concretes reveals certain differences in thermal characteristics (Fig. 19)[40]. A comparison of the thermal curves for cement paste and for cement paste with premixed polymethylmethacrylate (PMMA) or polystyrene shows that, in the PMMA-treated sample, there is practically no evidence of $Ca(OH)_2$. In the polystyrene-containing sample there is a large amount of $Ca(OH)_2$. It may be inferred that hydration has proceeded to a greater extent in the polystyrene-containing sample than that with PMMA, which is in consonance with the low strength development in PMMA-treated samples (Table III)[40]. It should be noted that the extent of hydration is not the only guide of strength development. In paste containing polystyrene the exothermal hump may indicate a surface complex of the polymer with the hydrated product. Caution should also be exercised in the estimation of the intensities of the peaks because of the possibility of interference effects from the oxidation–decomposition effects of the polymer itself.

In preformed samples both PMMA and polystyrene yield high strengths (Table III)[40]. The PMMA-treated sample shows no $Ca(OH)_2$ peak, suggesting that there is an interaction with the polymer or monomer. However, the polystyrene-treated sample shows a large peak for $Ca(OH)_2$. It is possible that the strength development in this case is due to accelerated hydration.

TABLE III

SOME PROPERTIES OF POLYMER–CEMENT MORTARS

No.	*Material*	*Formation*	*Combined water (%)*	*Water absorption*	*Compressive strength (p.s.i.)*
1	No polymer		16.1	7.18	7,830
2	Polymethyl Methacrylate	Premix	5.1	7.50	4,140
3	Polystyrene	Premix	13.5	1.55	10,060
4	Polymethyl Methacrylate	Preform		0.25	23,440
5	Polystyrene	Preform		0.18	19,420

A hydrated portland cement treated with a water repellent based on the silane derivative of tallow or other fats or olefins shows certain thermal features common to the above. The $Ca(OH)_2$ peak does not appear in the treated sample, probably due to the interaction of $Ca(OH)_2$ and the water repellent[41].

Organo phosphorosilicon polymers. — Polymers based on small quantities of an organo-phosphorosilicon have been reported to increase the strength of concrete. By an addition of 0.38% of the polymer the strengths at 1, 3,7 and 28 days are increased, respectively, by 53, 48, 43 and 34% of the blank concrete specimen. In an effort to explain the possible causes leading to the strength development, the individual cement components were treated with the admixture and the thermograms of the hydrated products examined after 38 h and 3 years[42]. The thermograms of the polymer-treated C_3S showed increased amounts of the hydration products compared with C_3S containing no admixture. In the C_3A–polymer mixtures, in addition to larger amounts of hydration products at any stage of hydration, there was an evidence of formation of very finely divided product. This was reflected in an exotherm at 430°C due to crystallization.

CONCLUSIONS

DTA has great potential for use as a major technique in cement chemistry, especially for the investigation of the role of admixtures. This technique enables a study of the kinetics of hydration, interconversion effects, the emergence of new phases and their estimation, the mechanism of hydration, etc. In many instances the DTA technique provides information that cannot easily be obtained by using other well-known methods.

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REFERENCES

1 *Book ASTM Stand.*, Philadelphia, 1970, Part 10, p. 80.
2 Standard Specifications for Chemical Admixtures for Concrete, *Book A.S.T.M. Stand.*, Philadelphia, 1970, Part 10, p. 318.
3 V. S. Ramachandran, *Applications of DTA in Cement Chemistry*, Chemical Publishing Co., New York, 1969.
4 R. C. Mackenzie (Ed.), *Differential Thermal Analysis*, Academic Press, London, 1970.
5 J. P. Redfern (Ed.), *Therm. Anal. Proc. Int. Conf. 1st.*, Aberdeen, MacMillan & Co., 1965.
6 R. F. Schwenker and P. D. Garn (Eds.), *Therm. Anal. Proc. Int. Conf. 2nd.*, Worcester, Mass., Academic Press, New York, 1968.
7 *Therm. Anal. Int. Conf. 3rd.*, Davos, Switzerland, Abstracts of Papers, 1971.
8 W. W. Wendlandt, *Thermal Methods of Analysis*, Interscience Publishers, New York, 1964.
9 W. H. Smothers and Yao Chiang, *Handbook of Differential Thermal Analysis*, Chemical Publishing Co., New York, 1966.
10 D. Schultze, *Differential Thermoanalyse*, Verlag Chemie, Weinheim, 1969.
11 W. W. Wendlandt (Ed.), *Thermochim. Acta*, Elsevier Publishing Co., Netherlands, Bimonthly journal, first publication March 1970.
12 E. Buzagh and J. Simon (Eds.), *J. Therm. Anal.*, Heydon and Son Ltd., London, and Akademiai Kiado, Budapest, quarterly journal, first publication 1969.
13 R. F. Feldman and V. S. Ramachandran, *J. Amer. Ceram. Soc.*, 49 (1966) 268.
14 R. F. Feldman and V. S. Ramachandran, *Mag. Concr. Res.*, 18 (1966) 185.
15 *Admixtures in Concrete*, Special Report 119, Highway Research Board, Washington, 1971.
16 K. E. Fletcher, *Concrete*, 5 (1971) 142.
17 Z. A. Abueva and O. I. Lukyanova, *Kollod. Zh.*, 31 (1969) 315.
18 V. S. Ramachandran and R. F. Feldman, *Mater. Constr.*, 5 (1972) 67.
19 J. F. Young, *Mag. Concr. Res.*, 14 (1962) 137.
20 G. M. Bruere, *Nature*, 212 (1966) 502.
21 J. F. Young, *Proc. Int. Symp. Chem. Cements 5th*, Tokyo, 2 (1968) 256–267.
22 Z. A. Abueva, O. I. Lukyanova and T. K. Brutskus, *Kolloid. Zh.*, 31 (1969) 641.
23 G. L. Kalousek, *Mater. Res. Stand.*, 5 (1965) 292.
24 F. Tamas and G. Liptay, *Proc. Conf. Silicate Ind., 8th*, Budapest, (1966) 299–305.
25 J. J. Shideler, *Proc. Amer. Concr. Inst.*, 48 (1952) 537.
26 N. P. Stukalova and E. P. Andreeva, *Kolloid. Zh.*, 31 (1969) 446.
27 J. Skalny and I. Odler, *Mag. Concr. Res.*, 19 (1967) 203.
28 E. P. Andreeva, E. E. Segalova and E. E. Volynets, *Dokl. Akad. Nauk. SSSR*, 123 (1958) 1052.
29 S. J. Ahmed, L. S. Dent Glasser and H. F. W. Taylor, *Proc. Int. Symp. Chem. Cements 5th*, Tokyo, 2 (1968) 118–127.
30 N. N. Serb-Serbina, Yu. A. Savvina and V. S. Zhurina, *Dokl. Akad. Nauk. SSSR*, 111 (1956) 659.
31 M. H. Roberts, *Int. Symp. Admixtures for Mortar and Concrete*, Brussels, 2 (1967) 5–29.
32 H. G. Kurczyk and H. E. Schwiete, *Tonind. Z.*, 84 (1960) 585.
33 V. S. Ramachandran, *Thermochim. Acta*, 2 (1971) 41.
34 V. S. Ramachandran, *Mater. Constr.*, 4 (1971) 3.
35 V. S. Ramachandran, *J. Therm. Anal.*, 3 (1971) 181.
36 K. Murakami and H. Tanaka, *Int. Symp. Chem. Cements 5th*, Tokyo, 2 (1968) 422–436.
37 N. B. Djabarov, *Zem. Kalk Gips*, 23 (1970) 88.
38 P. P. Budnikov, V. M. Kolbasov and A. S. Penteleev, *Tsement*, 27 (1961) 5.
39 V. S. Ramachandran, unpublished results.
40 J. Gebauer and R. W. Coughlin, *Cem. Concr. Res.*, 1 (1971) 187.
41 D. M. Doty, *Cem. Lime Manuf.*, 44 (1969) 107.
42 V. S. Khramova and V. S. Gorshkov, *J. Appl. Chem. USSR*, 43 (1970) 855.