Application of Differential Thermal Analysis in Cement Research

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Differential thermal analysis (DTA) has recently attained increasing importance as a research tool in cement chemistry. DTA is normally used in identifying various materials but could also be employed to follow reactions by heating the reactants gradually to elevated temperatures. Use of sensitive equipment and proper calibration facilitate quantitative estimation of materials. Certain poorly crystallized compounds not easily identifiable by x-ray diffraction give characteristic thermal peaks.

This review presents the application of DTA to portland cement. Other cements are included to illustrate the importance of DTA to an understanding of the chemistry of cement in general and also of the potentialities of the method itself.

●THE TECHNIQUE of differential thermal analysis (DTA) is widely applied in clay mineralogy, but only recently has it been extended to other fields. The method consists of measuring the heat changes associated with physical or chemical transformations occurring during the gradual heating of a substance. Thermal changes, such as dehydration, crystalline transition, lattice destruction, oxidation and decomposition, are generally accompanied by an appreciable rise or fall in temperature and are amenable to DTA investigation. The DTA technique has found application in diverse fields such as criminology, pyrotechnics, catalysis, coal chemistry, polymer systems, radioactivity, soap and lubricating systems and will continue to be introduced to various branches of study.

The DTA method had its origin in 1887 when Le Chatelier applied thermal analysis to the study of the constitution of clays (1 - 4). However, although one of the pioneers in the field of cement chemistry, he did not realize the potentialities of the method to the study of cements. Kalousek et al. (5) were probably first to introduce DTA in cement chemistry. The usefulness of the method was realized and discussed at the Third International Symposium on the Chemistry of Cements held in London in 1952, and since then several papers have appeared dealing with the DTA of cementitious materials. The remarks made by R. H. Bogue (6) at the London symposium are significant:

> Our ability to detect and measure small temperature differentials
> has been greatly extended by new electronic instruments capable of
> rapid and automatic recording of minute changes in energy levels.
> With these instruments, differential thermal-analytical methods
> are replacing the older quenching techniques for following phase
> relations with the assurance that energy changes too small or too
> rapid otherwise to be observed will be identified.

Between 1952 and 1960, increasing attention was paid to the application of DTA in cement chemistry and at the Fourth International Symposium on the Chemistry of Cement, held in 1960, several investigators interpreted their results through thermographic analysis.

DESCRIPTION OF THE METHOD

Essentially the DTA equipment consists of a furnace, a temperature regulator, a specimen block, thermocouples, and a temperature-recording system. Several types of apparatus are in use. Refinements have been suggested from time to time to give greater accuracy in results and to widen the scope of the method.

The sample to be studied is placed in one of the cavities of the specimen block (Fig. 1). In the second cavity is placed calcined alumina, α-Al_2O_3, which does not experience any thermal change within the temperature range usually used in the study. Two thermo-couples, constituting the differential thermocouple, are connected as shown. In the third cavity of the block a separate thermocouple is embedded to measure the temperature of the specimen. The temperature can also be measured by connecting the thermocouple ends a-b from the inert material as shown in Figure 1b.

The block with the specimen to be studied and inert material, α-Al_2O_3, is placed in a furnace and the temperature is raised at a uniform rate. The differential couple re-cords zero potential difference when the specimen is not undergoing any thermal change. During a thermal transformation, the increase or decrease in the temperature of the specimen, relative to that of the inert material, will depend on the exo- or endothermal character of the change. With the completion of the thermal change, the specimen usu-ally reattains the temperature of the inert material. In some cases, the zero line shows a drift after a thermal transformation and is attributed to the differences in thermal characteristics between the specimen and the inert material. The differential tem-perature is recorded as a function of time or the temperature of the specimen block. In the thermograms, usually the differen-tial temperature, ΔT, and the block tem-perature, T, are recorded or plotted in such a manner that the endothermic peaks are shown downwards and the exothermic peaks, upwards with respect to the base-line, $\Delta T = 0$. The details of the DTA technique, theory, and varied applications are discussed in various sources (7 - 14).

The discussion herein pertains mainly to the application of DTA in the field of portland cement. The inclusion of the re-lated work was necessitated to indicate its importance to an understanding of the chemistry of cement and of the potential-ities of the method itself.

PORTLAND CEMENT CLINKER

Raw Materials

Portland cement is formed by firing chalk, limestone, marl or marine shells with shale or clay or other siliceous mate-rials to a temperature of 1400 to 1500 C, mixing the resulting sintered clinker with 4 to 5 percent gypsum, and grinding to a very fine powder of average diameter of 10 μ. In some cement plants gypsum is replaced by anhydrite or a mixture of an-hydrite and gypsum.

In the formation of cement clinker, the clay contributes SiO_2, Al_2O_3, and, pos-sibly, iron, alkalies and alkaline earths,
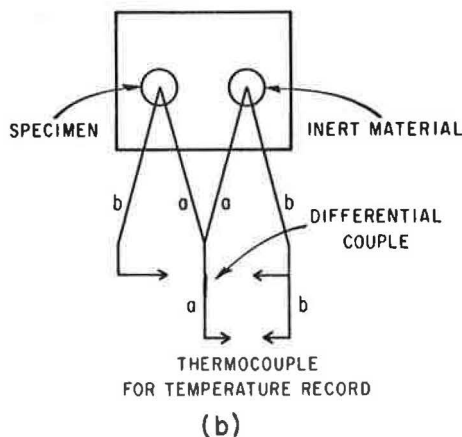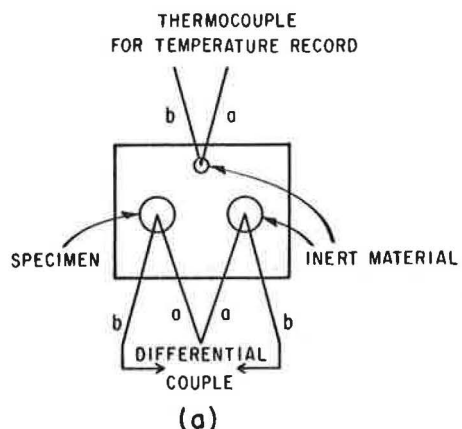

Figure 1. Specimen block with thermocouple connections.

depending on the clay mineral composition. More than 5 percent MgO in cement causes unsoundness of concrete. Consequently, clay minerals rich in Mg, such as attapulgite, sepiolite and chlorite, do not make suitable raw materials for cement manufacture. Kaolinite comprises mainly SiO_2 and Al_2O_3 and, hence, is suitable as a raw material, especially for the manufacture of white portland cement. Illite and montmorillonite clay minerals normally form suitable raw materials. Schweite (15) observed that kaolinite is much more suitable for wet manufacturing process because it exhibits better burning characteristics and produces less dusting during grinding. Caution should be exercised in choosing a suitable lime source. If the original limestone contains MgO in the form of dolomite, the resultant cement will be unsound.

The application of DTA to the examination of raw materials for cement production should prove useful in assessing their suitability. Figure 2 shows typical thermograms of some raw materials. The temperature of the peak, the endo- or exothermal character, the intensity and other general characteristics are used to identify each material.
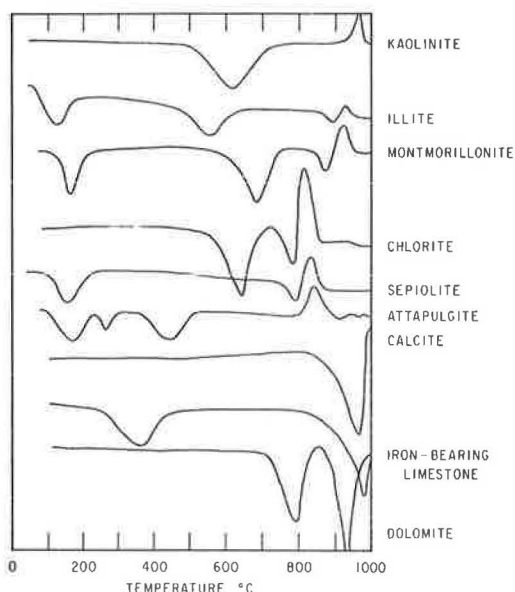

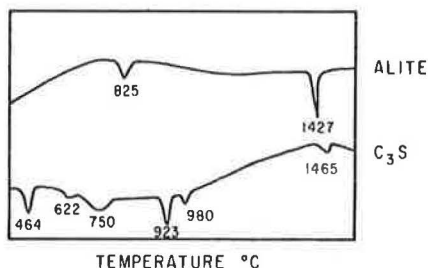Figure 2. DTA of some raw materials for manufacture of cement.

Figure 3. Thermograms of alite and pure tricalcium silicate.

Nature of Cement Clinker

Portland cement clinker contains a mixture of four major phases, C_3S, β-C_2S, C_3A and a ferrite phase extending in composition from C_4AF to C_6AF_2 (16). (Symbols used are defined as follows: C = CaO, S = SiO_2, A = Al_2O_3, F = Fe_2O_3, M = MgO, K = K_2O, N = Na_2O and H = H_2O.) The C_3S phase contains some Al and Mg in solid solution, whereas the C_2S phase contains some K_2O and the C_3A phase, some Na_2O. The clinker has a glassy phase ranging from 2 to 20 percent, and frequently the greater proportion of C_3A and ferrite exists in this phase. According to some workers there is essentially no glassy phase in the clinker.

Le Chatelier designated the predominant component of portland cement clinker as "alite" with a probable formula, C_3S. Nurse and Welch (17) carried out DTA of pure C_3S, alite and a cement clinker rich in alite. In Figure 3 are shown the DTA of pure C_3S and alite in the range 150 to 1500 C as obtained by them. Six endothermal transformations are observed in pure C_3S. The peak at 464 C is due to loss of water of hydration from the surface of CaO grains and those at 622 and 750 C are due to $\beta \rightarrow \alpha'$ and $\gamma \rightarrow \alpha'$ transformations of C_2S, respectively. The peak at 1465 C is attributed to $\alpha' \rightarrow \alpha$ transformation. The thermal effects at 923 and 980 C for C_3S are more speculative and are ascribed to either, triclinic $\xrightarrow{923\ C}$ monoclinic $\xrightarrow{980\ C}$ trigonal or triclinic $\rightarrow$ trigonal $\rightarrow$ trigonal + rotation of anions. Synthetic alite ($C_{54}S_{16} \cdot M \cdot A$) exhibits two endothermic peaks at 825 and 1427 C. The peak at 825 C is due to monoclinic $\rightarrow$ trigonal transformation and the higher temperature endothermic peak

is due to transformation in C_2S. A cement containing 60 percent C_3S, however, indicated no thermal transformations that could be ascribed to C_3S. The metastable inversions at 923 and 980 C in pure C_3S and at 850 C in alite reported by Nurse and Welch were confirmed by others (18, 99, 100).

There are four polymorphic forms of C_2S (γ, β, α' and α) stable in the range 0 to 1600 C. Only the β and, occasionally, the γ forms are likely to occur in the cement clinker. Minute quantities of α' form were observed under exceptional conditions (19). It should also be noted that α, α', and β forms are not stable at room temperature in absence of stabilizers. DTA has successfully provided the accurate inversion temperatures of the four forms of C_2S and has played an important role in establishing the interrelationship of the various forms (20). The quenching technique would not prove useful in this investigation because neither the α nor the α' form is stable at room temperature. Newman and Wells and Vasenin (21, 22) studied the transformations in C_2S, and the work carried out at the British Building Research Station has provided accurate inversion points of various forms of C_2S (23). The results are presented in Figure 4. Curve A shows two peaks obtained by heating γ-C_2S. At first sight these transformations could be mistaken for γ - β and $\gamma \rightarrow \beta$ transformations. A better interpretation is based on the cooling curve of the same substance. Curve B shows three peaks corresponding to three inversions. If the cooling is stopped at about 600 C and heating restarted, curve C results instead of curve A. Curve A is reproducible if the material is allowed to cool to room temperature before heating is re-started. The interpretation of these curves is as follows: on heating the γ-C_2S, the phase change is in the sequence $\gamma \rightarrow \alpha' \rightarrow \alpha$, the β-form appearing only on the cooling cycle below 600 C; the $\beta \rightarrow \gamma$ inversion takes place on slow cooling or $\beta \rightarrow \alpha' \rightarrow \alpha$ inversion on heating. These results were confirmed by de Keyser (24).

The stabilizing influence of barium orthosilicate on C_2S was studied by DTA. C_2S treated with various amounts of the stabilizing agent indicated absence of $\gamma \rightarrow \alpha'$ inversion on addition of more than 10 percent (25).

Systems With CaO, Al_2O_3, SiO_2 and Fe_2O_3

The thermal reactions in the binary, ternary and quaternary systems involving CaO, SiO_2, Fe_2O_3, and Al_2O_3 are of great importance in the study of the chemistry of cement clinker. Rapid heating of these mixtures in a thermal analyser results in the appearance of thermal inflections caused by the formation of various products.

Budnikov and Sologubova (26) applied DTA to the study of the reaction between kaolin and calcium carbonate in the production of white cement. The formation of $CaO \cdot Al_2O_3$ was indicated by an exothermal peak above 1000 C. The mortars cured for 28 days exhibited an endothermic effect at 320 to 340 C which was attributed to dehydration of $2CaO \cdot Al_2O_3 \cdot 7H_2O$. The formation of tricalcium silicate by the interaction of calcium carbonate and silica has been studied by DTA (27). De Keyser has done extensive work
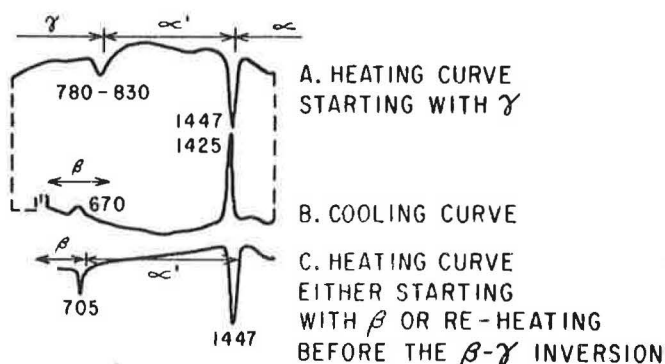

Figure 4. Inversions in C_2S.

on various oxide systems. He heated a mixture of SiO_2-CaO-Al_2O_3 and also a CaO-kaolin mixture between 1000 and 1400 C and studied the reaction by DTA [28]. Between 1200 and 1300 C, the reaction was controlled by the diffusion of oxides. In CaO-kaolin, gehlenite (C_2AS) was found to form between 900 and 1000 C, contrary to the results of Budnikov and Sologubova [26]. At higher temperatures CA converted to C_5A_3. A mixture of $Ca(OH)_2$ and SiO_2, when heated rapidly in a thermal analyser, exhibited several inflections in the thermograms. Samples were withdrawn at various temperatures corresponding to thermal inflections and examined by x-ray diffraction. Three endothermic peaks at 148, 490 and 555 C and three exothermic peaks at 800, 846 and 970 C were observed. The x-ray results showed at about 480 C the presence of γ-C_2S which converted to β-C_2S at 960 C.

Further work by de Keyser [29] on the system $2\,CaO$, Fe_2O_3, $6\,CaO + Al_2O_3 + 2\,Fe_2O_3$, $4\,CaO + Al_2O_3 + Fe_2O_3$ and $6\,CaO + 2\,Al_2O_3 + Fe_2O_3$ in the range 500 to 1300 C indicated that all these mixtures form $2\,CaO\cdot Fe_2O_3$ from 800 C and $CaO\cdot Fe_2O_3$ at higher temperatures. At still higher temperatures, $CaO\cdot Fe_2O_3$ reacted, with CaO to form $2\,CaO\cdot Fe_2O_3$ with the maximum rate of formation at 1200 C. For mixtures containing Al_2O_3, $3\,Al_2O_3\cdot 5\,CaO$ was the product between 1000 to 1250 C.

A systematic work has been carried out by Barta and co-workers [101-104] to follow the reaction when different mixtures of CaO, Al_2O_3, SiO_2 and Fe_2O_3 are gradually heated in the DTA furnace. DTA gives valuable information on the temperature of transformations, though the values may be different from those obtained from equilibrium studies. Some of the results obtained are shown in Figures 5 to 8.

Figure 5 shows the DTA behavior of $3\,CaO + SiO_2$ and also the effect of additions of Al_2O_3 and mixtures of $Al_2O_3 + Fe_2O_3$ on the temperature of formation of C_3S. The exothermic peak at 1450 C indicates the formation of C_3S. The peak temperature decreases to 1380, 1350 and 1320 C with additions of 5 percent Al_2O_3, 2 percent Al_2O_3 + 2 percent Fe_2O_3 and 5 percent Al_2O_3 + 5 percent Fe_2O_3, respectively.

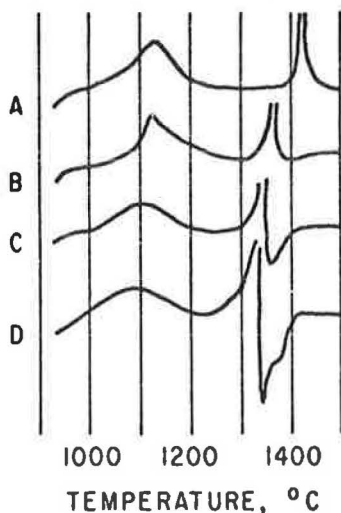Figure 5. Thermograms of $3\,CaO + SiO_2$: A, $3\,CaO + SiO_2$; B, with 5% Al_2O_3; C, with 2% Al_2O_3 + 2% Fe_2O_3; D, with 5% Al_2O_3 + 5% Fe_2O_3.
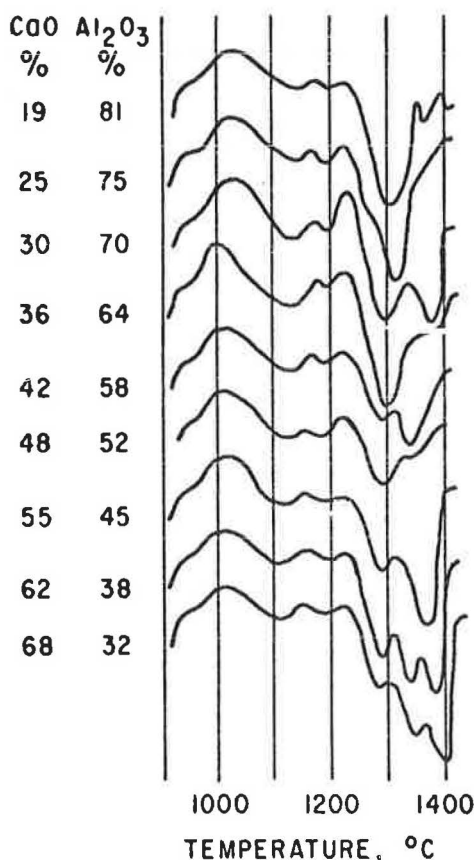
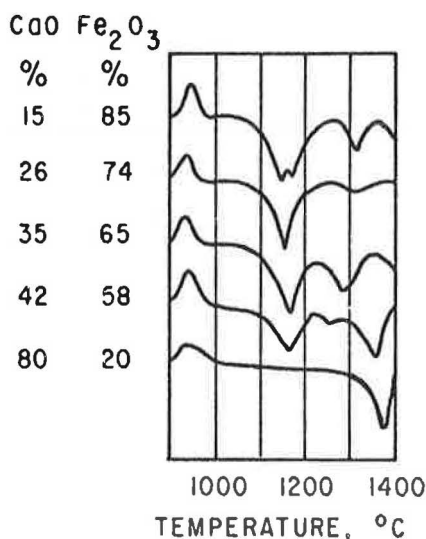Figure 6. Thermograms of mixtures of CaO and Al_2O_3.
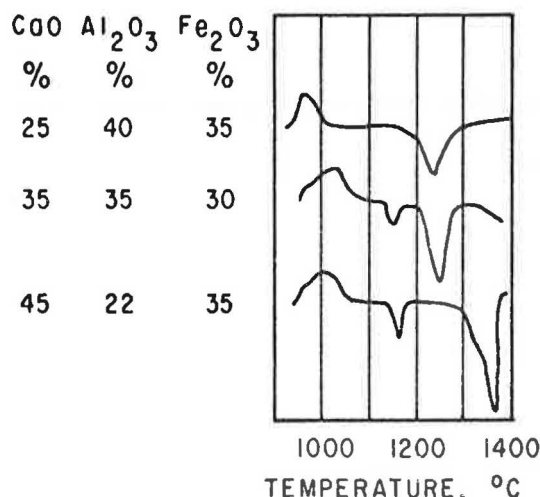
Figure 7. Thermograms of mixtures of CaO and Fe_2O_3.

Figure 8. Thermograms of ternary mixture containing CaO, Al_2O_3 and Fe_2O_3.

In Figure 6, the DTA curves of different proportions of CaO in Al_2O_3 are shown. The exothermic effect at 950 to 1000 C is attributed to a simultaneous formation of CA and $C_{12}A_7$. The dip at 1170 C represents the change of γ-Al_2O_3 to α form and the other at 1200 C corresponds to the beginning of formation of C_3A. The endothermic peak at 1300 C indicates melting in the system. Other endothermic effects at higher temperatures are not discussed.

Reactions of different mixes of CaO and Fe_2O_3 are represented by thermograms in Figure 7. The exothermic maximum at 950 C is due to formation of CF and is independent of the relative proportions of CaO and Fe_2O_3. Melting effect is shown by an endothermic effect at 1150 C and is lower than the eutectic temperature of 1200 C in the phase diagram. The compound C_2F is formed subsequently, the minimum at 1300 C corresponding to an incongruent melting of the mixture.

The reactions in the ternary mixture containing CaO, Fe_2O_3 and Al_2O_3 are shown in Figure 8. An exothermic effect occurs at about 980 C owing to the formation of C_4AF. At lower contents of Al_2O_3, C_2F is also formed, indicated by an endothermic dip at about 1160 C.

The effect of various mineralizers, present in the mass or in the oven atmosphere, on the reaction products in cement manufacture has also been studied by DTA by Barta and co-workers.

HYDRATION REACTIONS

Hydration of Individual Phases in Cement Clinker

A study of the hydration of the individual components of the clinker compounds provides a better understanding of the complex reactions taking place in the cement. C_3S reacts quickly with water, producing $Ca(OH)_2$ and an ill-crystallized compound with C/S ratio of 1.5 to 1.8. The compound is nearly related to natural tobermorite, $C_5S_6H_5$, and is designated tobermorite gel.

Midgley studied the hydration product obtained by curing C_3S in water for 2 yr in the paste form (30). Thermograms indicated the presence of $Ca(OH)_2$, $CaCO_3$ and calcium silicate hydrate with the formula $1.77\,CaO \cdot SiO_2 \cdot 3\,H_2O$ (CaO/SiO$_2$ = 1.77) representing a poorly crystalline tobermorite, CSH(II). The gel gave a characteristic endothermic peak at about 120 C. Gaze and Robertson (31) studied by DTA the calcium silicate hydrate in commercial products. The exothermic reaction between 800 and 850 C was

attributed to the transformation of CSH(I) to β-wollastonite. An endothermic peak at 760 C represented the presence of $CaCO_3$. Van Bemst (32) also studied the DTA of hydrates obtained by hydration of di- and tricalcium silicates. β-C_2S reacts at a slower rate and forms compounds similar to those resulting from C_3S. C_3A reacts very rapidly to form C_3AH_6, but its formation in cement is much debated. The DTA results of Kalousek et al (5) did not indicate the presence of C_3AH_6 in most of the cement pastes.

The DTA of C_3A after treatment with water shows a prominent bulge at 315 to 330 C (5, 105). Young (33) and Jones (64), however, found two endothermic effects corresponding to the stepwise dehydration of C_3AH_6. Gohlert (106) reported three peaks for C_3A pastes after 3 and 28 days of hydration. Budnikov et al. (107) and Sauman (108) also obtained three peaks. Govorov (109), however, reported four peaks. The differences in behavior of the hydrated C_3A reported by different workers could be attributed to the degree of purity of the sample, the temperature and quantity of water used, and the period of hydration. The sensitivity of the DTA apparatus is another factor which might have caused the nonregistration of minute effects.

The hydration reactions in the ferrite phase, C_4AF, proceed at a slower rate, contrary to earlier belief, and are much more complicated. Jones (34) has suggested that the ferrite phase forms a solid solution of $C_4A(aq)$-$C_4F(aq)$ as a first step in the transformation to $C_3A(aq)$-$C_3F(aq)$ solid solution.

Kalousek and Adams (35) followed the hydration of C_4AF by DTA. Thermal curves for hydrates of C_4AF with and without addition of gypsum are shown in Figure 9. The 7-day samples without gypsum showed the presence of the hydrogarnets and a small amount of hexagonal plates of $C_4A \cdot 13 H_2O$. With increasing age, hydrogarnets decreased and $C_4A \cdot 13 H_2O$ or a related phase increased, with a peak temperature at about 250 C. Hydrogarnets were represented by an endothermic effect at 300 to 400 C.

In cements, C_3A reacts with the retarder, gypsum, to form sulfoaluminates of compositions, $C_3A \cdot 3 CaSO_4 \cdot 32 H_2O$ or $3 C_3A \cdot CaSO_4 \cdot 12 H_2O$. It is not established which forms first in cement. In cements the formation of analogous sulfoferrites is also reported.

Hydration of Cement

DTA is considered one of the most powerful tools in the investigation of the hydration of cement pastes. Thermograms have yielded useful results on the cement hydrated for various lengths of time under different conditions (5, 30, 36, 37, 38, 39). Typical thermograms of portland cement hydrated for various periods as obtained by Greene (36) are shown in Figure 10. The unhydrated cement exhibits two endothermic peaks at 140 and 170 C due to stepwise dehydration of gypsum. The endothermal dent below 500 C is attributed to $Ca(OH)_2$ formed during exposure to air. The broad endothermic effect in the range 700 to 800 C is caused by the decomposition of $CaCO_3$, also formed by exposure to air. Five
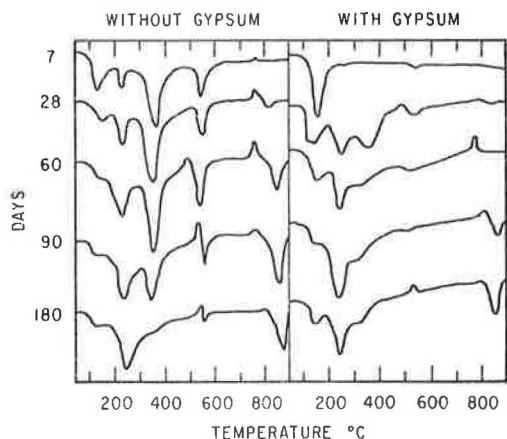

Figure 9. Thermal curves of C_4AF without and with gypsum and hydrated for various periods of time.
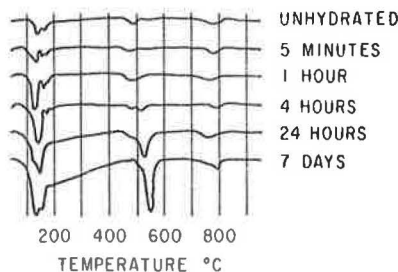

Figure 10. Thermograms of portland cement hydrated for various lengths of time.

minutes after hydration, an endothermic peak appears at 130 C due to the formation of high-sulfate calcium sulfoaluminate, $3\,CaO \cdot Al_2O_3 \cdot 3\,CaSO_4 \cdot 31\,H_2O$. The decrease in gypsum content is evident from the reduction of the gypsum peaks. An hour after hydration, the intensities of the gypsum peaks decrease further and the peak due to sulfoaluminate becomes more pronounced. At 4 hr, an additional endothermic peak above 500 C is observed. The peak below 500 C is believed to be due to chemisorbed water on the surface of free lime particles, and that above 500 C to the more coarsely crystalline $Ca(OH)_2$ formed by crystallization through solution. After 24 hr of hydration, the double peak due to gypsum disappears and a small endothermic shoulder appears on the low temperature flank of the sulfoaluminate peak due to calcium silicate hydrate. After 7 days this endothermic peak increases. The appearance of a small endothermic peak at 200 C may be due to either the low-sulfate calcium sulfoaluminate, $3\,CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 12\,H_2O$, or to a solid solution of this compound with tetracalcium aluminate hy-
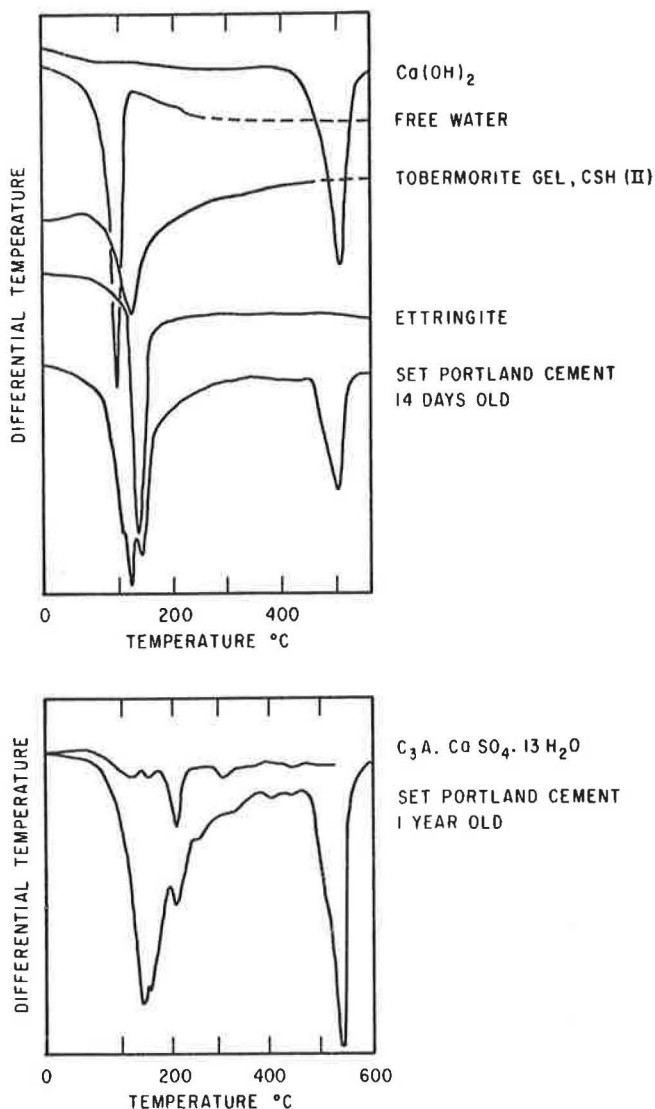

Figure 11. DTA curves of set portland cement and constituents.

drate, $4\,CaO\cdot Al_2O_3\cdot 13\,H_2O$. The other important feature of the 24-hr and 7-day curves is the gradual loss of water in the range 200 to 500 C and increase in $Ca(OH)_2$ and $CaCO_3$ contents.

The thermal effects below 200 C in hydrated cements are of great interest in the interpretation of various reactions. Midgley (30) has discussed the endothermic peak effects obtained in a 14-day and 1-yr set cement. The three endothermic effects occurring very close to one another could be identified by comparing the standard thermograms of purer systems, such as $Ca(OH)_2$, free water, tobermorite gel CSH(II), ettringite and low sulfoaluminate (Fig. 11). The 14-day hydrated compound gives three peaks at 114, 127 and 147 C due to free water, CSH gel and ettringite, respectively. The set cement after 1 yr shows two endothermic peaks below 200 C and a peak above 200 C. The peak above 200 C corresponds to one of the peaks of the low sulfoaluminate. A quantitative estimation of tobermorite, ettringite and $Ca(OH)_2$ contents was attempted by Midgley by calibrating the peak area with different amounts of the purer substances. The estimation of $Ca(OH)_2$ content is relatively accurate. The figures given for tobermorite and ettringite are open to question, however, because there is no way of separating the individual peaks from the triple peak effect in the range 100 to 200 C.

There is some controversy regarding the type of sulfoaluminate that forms initially in cements, although it is widely held that the high sulfoaluminate forms first. Figure 12 obtained by Greene gives the DTA curves of cement clinker hydrated for various periods of time without the addition of gypsum. At 5 min, the curve shows a peak at 200 C due to either $4\,CaO\cdot Al_2O_3\cdot 13\,H_2O$ or a related solid solution. The curve does not exhibit a low-temperature endothermic peak at 130 C, indicating that pure clinker compounds by themselves are not responsible for the peak. Addition of 2 percent gypsum produces a fairly large amount of high-sulfate form and prevents the formation of $4\,CaO\cdot Al_2O_3\cdot 13\,H_2O$, indicated by the absence of a 200 C peak. The results do not seem to be conclusive and much more systematic work is needed to establish the products in the initial stages of hydration. For example, the endothermic peak at 200 C for sample containing 1 percent gypsum may be partly due to the presence of low-sulfoaluminate form which may convert to high form at higher gypsum concentrations. The low sulfoaluminate is reported to be the preferred product in presence of $Ca(OH)_2$ and $CaSO_4$ (40). The DTA work of Greene, in which the cement was hydrated for 2 min in distilled water as well as in saturated $Ca(OH)_2$-$CaSO_4$ solutions, showed only the endothermic peak corresponding to high-sulfoaluminate form in distilled water and the absence of any sulfoaluminate in $Ca(OH)_2$-$CaSO_4$. Turriziani and Schippa (41, 42) believed that DTA can be used to estimate semiquantitatively the sulfoaluminate phases in cement.

In the DTA of hydrated cement, a single peak at about 130 C is attributed to the high form of calcium sulfoaluminate hydrate, whereas the peak at about 200 C is attributed to the low-sulfate form. The DTA of purer sulfoaluminate, however, shows three peaks. The thermograms of the high- and low-sulfate forms obtained by Nemecek and Barta (110) are shown in Figure 13. The higher form containing 31 molecules of H_2O loses 21 molecules (zeolitically held) at 180 C, 3 molecules at 280 C, and the rest at 370 C. The monosulfate containing 12 molecules of H_2O loses 8 molecules (zeolitically held) at 160 C, 2 molecules at 230 C, and the most strongly held at 300 C.
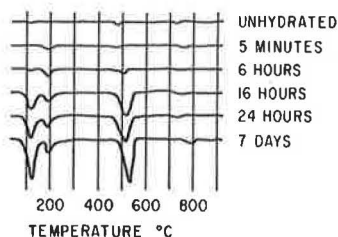

Figure 12. DTA curves of portland cement hydrated without gypsum.
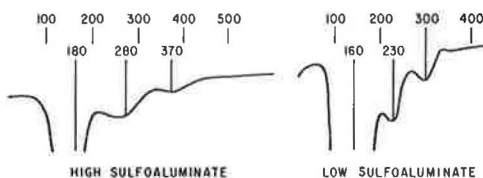

Figure 13. DTA of high and low calcium sulfoaluminate hydrates.

Figure 12 shows no indication of formation of the hexahydrate of C_3A in cement hydrated without gypsum. Kalousek et al. (5), however, reported the evidence of formation of C_3AH_6 in some clinkers by an endothermic effect at about 315 to 330 C. The other clinkers treated with gypsum did not exhibit the endothermic peak at 315 to 330 C. Only small amounts of SO_4 ions were required to suppress the formation of the hexahydrate.

Kalousek et al. believe that a solid solution is formed between $3\,CaO \cdot Al_2O_3 \cdot 3\,CaSO_4$ (aq) and $3\,CaO \cdot Al_2O_3 \cdot 3\,Ca(OH)_2$ (aq) and also between the low sulfoaluminate $3\,CaO \cdot Al_2O_3 \cdot CaSO_4$ (aq) and $3\,CaO \cdot Al_2O_3 \cdot Ca(OH)_2$ (aq). Midgley and Rosaman (43) carried out DTA of three cements and found the first phase was pure calcium sulfoaluminate, with the solid solution containing calcium hydroxy aluminate hydrate after longer periods. Thermograms of the likely complexes of C_3A and C_3F are shown in Figure 14.

The role of ferrite phases in cement has been a subject of much controversy and is much more obscure. Malquori and Cirilli (44) and Schippa (45) presented evidence to show that calcium sulfoferrites analogous to high sulfate and low sulfate are formed. Watanabe and Iwai (46), by using x-ray and DTA, observed no compound corresponding to the composition $3\,CaO \cdot Fe_2O_3 \cdot 3\,CaSO_4 \cdot 31\,H_2O$ in the hydration of $C_2F\text{-}CaSO_4$. Budnikov and Gorshkov (47) discussed the relative stabilities of calcium hydro sulfoaluminate and calcium hydro sulfoferrite by DTA. Kalousek et al. (5, 35) carried out DTA to ascertain whether C_4AF produced hydrogarnet or a related hexagonal crystalline compound. The 7-day sample without gypsum (Fig. 9) shows an endothermic peak at about 350 C, indicating the presence of hydrogarnet, and one at 220 C, indicating the presence of a small amount of $4\,CaO \cdot Al_2O_3 \cdot 13\,H_2O$. At longer periods of hydration, hydrogarnet decreases and C_4AH_{13} or a related phase increases. The reaction is modified by gypsum. The 7-day sample after treatment with gypsum is essentially the sulfoaluminate and sulfoferrite of calcium. At 90 days, the product has a maximum of solid solution of $C_3A \cdot Al_2O_3 \cdot CaSO_4 \cdot 12\,H_2O\text{-}3\,CaO \cdot Al_2O_3 \cdot Ca(OH)_2 \cdot 12\,H_2O$ and, presumably, $3\,CaO \cdot Fe_2O_3 \cdot CaSO_4 \cdot 12\,H_2O\text{-}3\,CaO \cdot Fe_2O_3 \cdot Ca(OH)_2 \cdot 12\,H_2O$. In presence of gypsum, the hydration of $4\,CaO \cdot Al_2O_3 \cdot Fe_2O_3$ proceeds rapidly without the formation of hydrogarnets. Attempts were made to follow the effect of $Ca(OH)_2$ and gypsum on the hydration of $C_2F + C_4AF$. Several endothermic effects were observed, and the interpretation of the effects was incomplete (5).

The effect of humid air on the products obtained during the storage of cements has been followed by DTA (48). Water combines first with $CaSO_4$ and then with CaO and calcium silicate. The exothermic peak at 600 to 700 C found in the thermograms of cements was traced to the presence of sulfides.

Systems Containing CaO, SiO_2, Al_2O_3, Fe_2O_3, Etc., in H_2O

Studies on systems containing CaO, SiO_2, Al_2O_3, Fe_2O_3, alkalies and $CaSO_4$ in H_2O are of great importance in the chemistry and morphology of hydrous calcium-complex compounds. Kalousek (49-53) did extensive work on the $CaO\text{-}SiO_2\text{-}H_2O$ system. The systems containing $CaO\text{-}SiO_2\text{-}H_2O$ and $CaO\text{-}Al_2O_3\text{-}H_2O$ were studied at room temperature by Kalousek et al. (5) and Jambor (54). The lime-silica gels show irregular exothermal bulges starting from 350 to 400 C and extending up to 500 C and an exothermic bulge at 800 to 890 C. Substitution of Al_2O_3 for silica
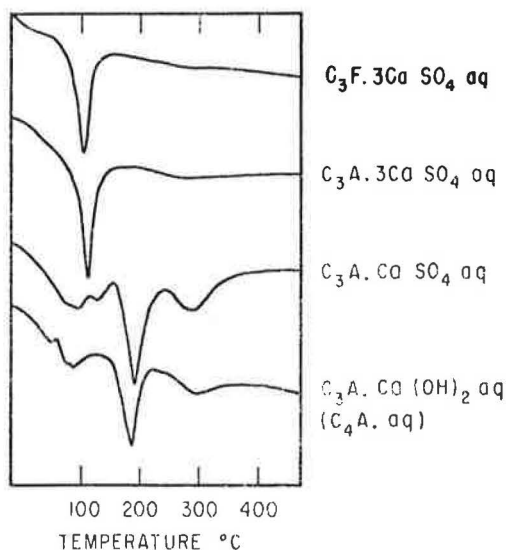

$C_3F \cdot 3Ca\,SO_4\ aq$

$C_3A \cdot 3Ca\,SO_4\ aq$

$C_3A \cdot Ca\,SO_4\ aq$

$C_3A \cdot Ca\,(OH)_2\ aq$
$(C_4A \cdot aq)$

100 200 300 400
TEMPERATURE °C

Figure 14. Thermograms of C_3A and C_3A-complexes.

gels shows, at 7, 14, and 28 days of aging, an endothermic bulge at 200 to 210 C and 470 C. The bulge at 200 to 210 C indicates the presence of $3\,CaO \cdot Al_2O_3 \cdot Ca(OH)_2 \cdot 12\,H_2O$. Newman (55) examined 15 mixtures containing $Ca(OH)_2$-SiO_2-H_2O in different molar ratios by DTA. Samples with different $Ca(OH)_2/SiO_2$ ratios and storage times and temperatures show characteristic thermal behavior. Some samples showed the presence of $C_3S_2H_2$. The behaviors of hydrous calcium silicates formed in the system CaO-SiO_2-H_2O with various C/S ratios were studied by DTA (56, 57), x-ray and electron microscopy. Tobermorite exhibited an endothermic effect at 260 C. The phase with C/S of 0.8 to 1.33 showed exothermic peaks at 830 and 900 C, and those with C/S of 1.5 to 2.0 exhibited peaks at variable temperatures. The DTA in conjunction with x-ray could be applied to differentiate 0.8 to 1.33 and 1.5 to 2.0 C/S hydrates.

The reactions in the system $Ca(OH)_2$-quartz (or silica) between 125 and 175 C in the molar composition range, $0.8\,CaO/SiO_2$ to $1.25\,CaO/SiO_2$, were studied by DTA (58). X-rays failed to differentiate between different compositions, whereas thermograms exhibited characteristic peaks. Figure 15 represents the DTA of products made with CaO-SiO_2 with 0.8 C/S (S = quartz) and autoclaved at 175 C for different periods (58). The 1-hr product shows the presence of $Ca(OH)_2$ by an endothermic effect between 500 and 600 C. At 1.5 hr, about two-thirds of $Ca(OH)_2$ is consumed to form poorly crystallized α-type hydrate. At 3.5 hr, there is almost complete absence of $Ca(OH)_2$ with an appearance of α-hydrate of 1.75 C/S. At longer periods reaction occurs between the lime-rich phase and the residual quartz. The formula for the 1.75 C/S product is $C_7S_4H_n$. The various steps in the reaction could be given as follows on the basis of thermograms:

$$7C + 4S + aq \rightarrow C_7S_4H_n$$

$$C_5S_4H_n + S \rightarrow 5\,CSH_n$$

$$4\,CSH_n + S \rightarrow C_4S_5H_n$$
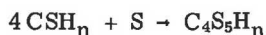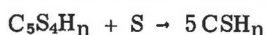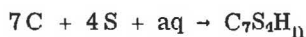
$C_4S_5H_n$ converts to tobermorite, indicated by the 8-hr curve. Products of $Ca(OH)_2$-silicic acid mixture also followed a similar sequence, but the reaction was comparatively faster.

Midgley and Chopra (59) studied the lime-rich part in the system CaO-SiO_2-H_2O. Thermograms were obtained for mixes containing CaO/SiO_2 = 2:1 and autoclaved at 150 C. The mixture autoclaved for 30 days indicated a thermal peak at 460 C for the presence of α-C_2S hydrate. After 14 days of autoclaving at 180 C, DTA again showed the presence of α-C_2S hydrate. At 90 days, the presence of α- and β-C_2S hydrate was indicated. The peak at about 500 C was attributed to α-hydrate and that at 550 C to the β-hydrate. The mixture with CaO/SiO_2 ratio of 1 formed crystallized tobermorite. In another series of experiments, the autoclaved product of CSH(I) and lime resulted in an initial formation of Flint's CSH(A) and C_2S-α hydrate. With the starting material as β-C_2S, the product was C_2S-γ hydrate. β-C_2S and lime gave C_2S α-hydrate. With C_3S as the starting material, the product was $C_3S \cdot 1\frac{1}{2}\,H_2O$. The representative thermograms of various hydrates formed in an autoclaved-treated system are given in Figure 16. Bozhenov et al. (60) studied by DTA the hydrothermal reactions at 8.25 and 100
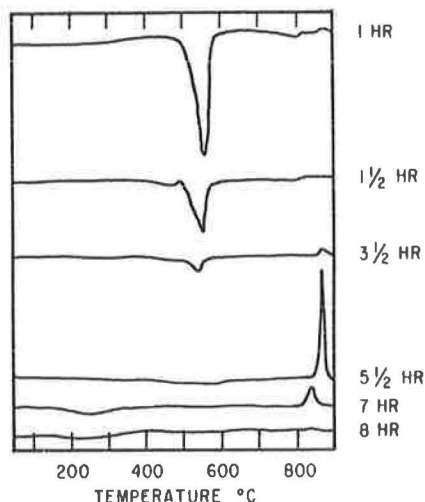

Figure 15. DTA of products obtained by autoclaving 0.8 C/S mixture at 175 C.

atm by adding various quantities of CaO and SiO$_2$ to β-C$_2$S. Lime-sand autoclaved products showed many endothermic effects. The effect in the range 120 to 400 C was due to dehydration of zeolitic water from the gel structural component, at 450 C it was due to Mg(OH)$_2$ decomposition, at 573 C to the $\alpha \rightarrow \beta$ conversion in quartz, at 680 to 750 C it corresponded to the dehydration of crystalline calcium hydrosilicate. Recrystallization of dehydrated silicates was manifested by a sharp exothermic reaction in the range 800 to 850 C. Further information on CaO-SiO$_2$-H$_2$O under hydrothermal conditions has been published recently (61).

Figure 16. Differential thermograms of various calcium silicate hydrates.

The DTA of products formed by hydrothermal interaction of lime, with or without addition of cement, with siliceous aggregates such as silica, pumice, expanded shale or slag showed certain characteristic properties of the products (51, 62). Autoclaved products with cement-lime and silica (or quartz) consist of a series of hydrates having a composition from about 0.9 to 1.3 C/S. The mixes different in silica fines formed a poorly crystalline lime-rich phase. With pumice, cement-lime formed hydrates structurally similar to those made from quartz but with C/S ratio higher than 1.3. DTA successfully differentiated between phases of different compositions. The DTA was applied by Midgley and Chopra (63) to identify the compounds formed by hydrothermal reaction of lime with aggregates such as fuel ash, expanded colliery shale, ground quartz, granulated and foamed blast furnace slag. Tobermorite and a hydrogarnet were formed with pulverized fuel ash or shale as aggregates, tobermorite and zonotlite with quartz, poorly crystalline tobermorite, dicalcium silicate α-hydrate and a hydrogarnet with slag.

Attempts have been made to study the DTA of quaternary system, CaO-Al$_2$O$_3$-CaSO$_4$-H$_2$O (41). DTA shows the presence of new phases, C$_4$A·13 H$_2$O and C$_3$A·CaSO$_4$·12 H$_2$O. Majumdar and Roy (64) used DTA to study the system CaO-Al$_2$O$_3$-H$_2$O between 100 and 1000 C under water pressures up to 3000 atm. DTA showed only endothermic peaks for the presence of Ca(OH)$_2$, C$_3$AH$_6$ and C$_4$A$_3$H$_3$.

Autoclaved Portland Cement Products

Setting and hardening of concrete products can be accelerated by curing them in steam at 180 C and at a pressure of 100 to 200 psi. In this type of curing, the cement is mixed with about 60 percent of its weight with fine quartz or other reactive silica and aggregate. Crystalline tobermorite is the main product formed by autoclave treatment. In absence of reactive silica, α-C$_2$S is the product responsible for low strengths. No free Ca(OH)$_2$ is detected. The reaction of C$_3$A and the ferrite phase is not well known.

Kalousek and Adams (35) carried out a systematic investigation of the cement-silica (finely ground quartz) mixtures by autoclaving at 175 C. The DTA of the products containing SiO$_2$ up to 60 percent is given in Figure 17. The peak due to decomposition of Ca(OH)$_2$ at 560 C is observed only in the products containing less than 9 percent SiO$_2$. The absence of
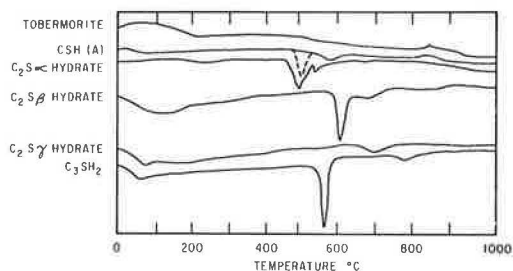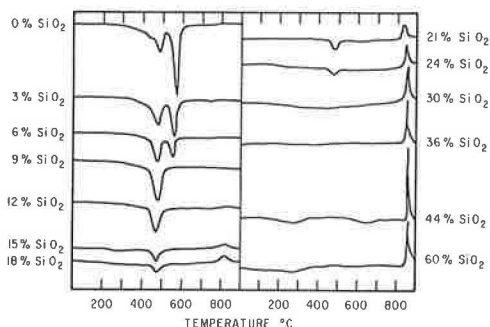

Figure 17. Thermal analysis of cement-silica mixtures processed at 175 C for 24 hr.

$Ca(OH)_2$ decomposition peak is due to the reaction between SiO_2 and $Ca(OH)_2$. The endo-thermic effect at 470 to 480 C was identified as plate-like dicalcium silicate hydrate and was present in larger amounts up to 9 percent SiO_2, after which it decreased pro-gressively. Menzel (65) had reported earlier that 8 to 10 percent SiO_2 product corre-sponded to minimum strength and at this composition, a maximum amount of plate-like dicalcium hydrate was observed. At higher SiO_2 concentrations, an exothermic peak appears at 840 C, with a maximum inflection at a composition of 40 to 45 percent SiO_2; this also corresponds to greatest strength. Hence, the high strength was ascribed to the phase responsible for the exothermic peak and was designated monocalcium hydrate. Subsequent studies showed that high strengths in the autoclaved products were due to the presence of tobermorite. The formation of α-C_2S always resulted in articles of poor strength. Bozhenov et al. (60, 66) presented results of DTA on autoclaved cement pastes obtained at 8 to 100 atm. Thermograms of products formed from C_2S in admix-ture with CaO and SiO_2 were examined. Evidence was found for an interaction between β-C_2S and SiO_2 with the formation of basic calcium hydrosilicates (67). DTA was ap-plied by Kalousek (51) to examine the autoclaved products obtained with different raw materials made of lime-cement and aggregates such as silica, pumice, expanded shale or expanded slag. The salient results obtained by him have already been discussed.

EFFECT OF EXTRANEOUS COMPOUNDS ON CEMENT HYDRATION

Reactions of $CaCO_3$ and CO_2 With Cement

The possibility of formation of complex compounds such as carboaluminates in cements in presence of CO_2, $CaCO_3$ or alkali carbonates has received some attention in recent years. Bessey (68) prepared the high- and low-carbonate forms, $3\,CaO \cdot Al_2O_3 \cdot CaCO_3 \cdot x\,H_2O$ and $3\,CaO \cdot Al_2O_3 \cdot 3\,CaCO_3 \cdot x\,H_2O$. Turriziani and Schippa (69) identified the low-carbonate form in alumina cement pastes cured for 2 yr. Carlson and Berman (70) obtained a product of the probable formula, $3\,CaO \cdot Al_2O_3 \cdot CaCO_3 \cdot 11\,H_2O$, in mixtures of CaO-Al_2O_3-H_2O exposed to CO_2. Greene (36) found a difference in the thermograms of cement hydrated with water and that hydrated with 2 percent Na_2CO_3 for 24 hr. The difference was attributed to the formation of carboaluminate. These thermograms for carboaluminates are shown in Figure 18 for comparison. Although these may repre-sent the carboaluminates, it is rather difficult to believe they are identical. No attempt has been made by any of these workers to discuss various peaks, and much more sys-tematic work seems to be needed to establish definitely the thermal behavior of carbo-aluminates.

Manabe et al. (71) carried out TGA of the system C_3A-$CaCO_3$-H_2O and reported the formation of $3\,CaO \cdot Al_2O_3 \cdot CaCO_3 \cdot 10.6\,H_2O$. The carboaluminate was formed after 3 days in a mixture of cement and $CaCO_3$.

Cole and Kroone (72) carried out DTA to investigate how CO_2 reacted with portland cement mortar and calcium silicate hydrate. Contrary to earlier views that only cal-cite is formed, poorly crystallized vaterite and aragonite in addition to some calcite were found.

The possibility of the occurrence of calcium silicoaluminates analogous to sulfoalu-minates has been reported by Flint and Wells (73). The compound $3\,CaO \cdot Al_2O_3 \cdot 3\,CaSiO_3 \cdot 30$-$32\,H_2O$ reported by Flint was re-examined by DTA by Carlson and Berman (70). The compound which had been exposed to CO_2 indicated an endothermic effect for the expulsion of water at the same temperature found for $3\,CaO \cdot Al_2O_3 \cdot 3\,CaCO_3 \cdot 32\,H_2O$. The endothermal peak found at 815 C was due to CO_2 evolution. The exothermic effect at 850 C was due to lime-silica reaction. The significance of other irregularities in the thermal curves was not discussed. The conclusion, however, was that the silico-aluminate in presence of CO_2 forms a mixture of aluminate silicate and carboaluminate.

Work on the effect of various amounts of $CaCO_3$ on the hydration of C_3A has been carried out at the Division of Building Research by the authors (results unpublished). The results of dimensional changes in the compacts formed from C_3A and C_3A-$CaCO_3$ and hydrated in water were correlated with those obtained by DTA. Thermograms showed that hydrated C_3A exhibits an intense endothermal effect with a peak at 310 C and additions of $CaCO_3$ suppress this peak. A carboaluminate complex formed on the surface of the C_3A grains also appeared to inhibit further hydration.
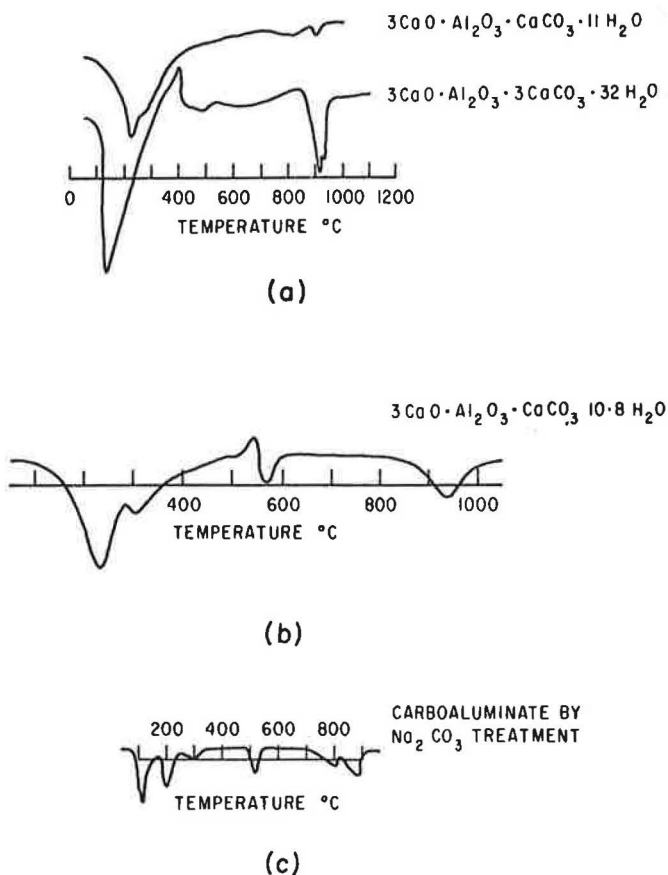
Figure 18. DTA of carboaluminates: (a) Carlson and Berman; (b) Turriziani and Schippa; and (c) Greene.

Surface Active Agents

Addition of small quantities of salts of lignosulfonic acid to concrete lowers the water requirement and retards the setting of the concrete mix. DTA was applied by Young (33) to study the role of lignosulfonate on the hydration behavior of C_3A alone and in presence of gypsum and lime. No attempts were made to explain some of the thermal peaks. It was concluded that in pastes of C_3A, lignosulfonates favor the formation of C_2AH_8 and C_4AH_{13} and modify their crystal habit. In presence of gypsum and lime, formation of low sulfoaluminate form is favored. In Figure 19 are represented the DTA of the typical mixtures obtained by Young. The C_3A hydrated product shows two endothermic peaks; the one at 300 to 400 C was also reported by others as being due to C_3AH_6. In presence of lignosulfonate, three endothermic peaks are obtained below 400 C and are attributed to a mixture of C_4AH_{13} and C_2AH_8. The exothermic peak at 520 C was not satisfactorily explained. C_3A paste with gypsum and lime shows endothermal effects at 100, 210, 320, 520 and 820 C. These are due to low-sulfoaluminate form, C_2AH_8 and C_4AH_{13}. The same mixture in presence of lignosulfonate gave less intense endothermal effects due to retardation of the hydration reaction.

False Set

Some cements exhibit the phenomenon of "false set" or premature stiffening. Various theories of false set have been reviewed by Blanks and Gilliland (74). According
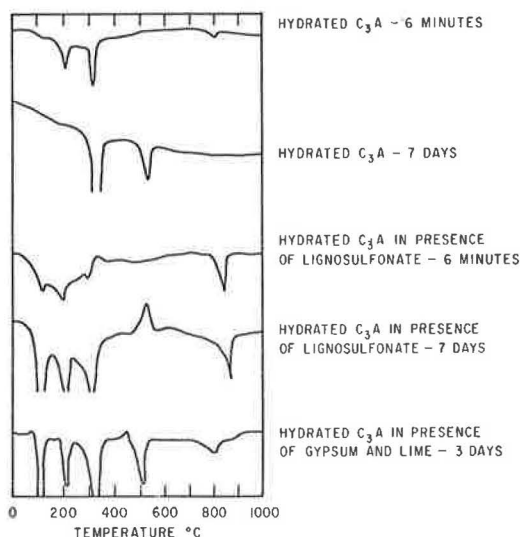
Figure 19. DTA of C₃A hydrated in presence of lignosulfonate and gypsum and lime.

to general views, false set is due to dehydrated gypsum in the form of hemihydrate or soluble anhydrite or both, rapidly precipitating as gypsum without the evolution of much heat.

Takemoto et al. (75) studied by DTA the extent to which gypsum had dehydrated during grinding of a mixture of clinker and gypsum in an experimental mill. The DTA curves showed that the hemihydrate was formed at 85 C when ground for 40 min. The soluble anhydrite was formed at 130 C when the grinding time was 80 min. Gilliland (76) studied the DTA behaviors of gypsum, hemihydrate, insoluble anhydrite, and a cement as received and when heated to 300 C. Gypsum showed two endothermic peaks at 190 and 210 C due to loss of $1\frac{1}{2}$ molecules and $\frac{1}{2}$ molecule of water, respectively. The exothermic peak at 380 C initiated the conversion of soluble to insoluble anhydrite. The hemihydrate exhibited an intense endothermic peak above 200 C owing to the loss of $\frac{1}{2}$ molecule of water. No thermal effect was observed for $CaSO_4$ (insoluble). A commercially ground cement showed two peaks at 140 and 160 C; that the latter was larger was attributed to the formation of hemihydrate from the gypsum present in the cement. The soluble anhydrite was formed by heating the cement at 300 C and then cooling. Soluble anhydrite partially converted to hemihydrate on exposure to air, showing a peak at 130 to 135 C. Fischer (111) evaluated quantitatively the degree of dehydration of gypsum in cement by DTA.

OTHER CEMENTS

Alumina Cement

The special type of cement known as "aluminous cement," characterized by a high early strength is formed by firing limestone or chalk with bauxite to a temperature of 1550 to 1600 C.

Alumina cement contains compounds such as unstable C_5A_3, CA and C_2AS. CA, the most important constituent, reacts with water at room temperature to form CAH_{10}, the principal cementing agent. Under hot humid conditions, CAH_{10} transforms to C_3AH_6 with a loss in strength. Pole and Moore (77) and Schneider (112) obtained DTA of alumina cement paste. The endothermic effect between 250 and 350 C showed the presence of C_3AH_6. An exothermic peak extending over a wide range of 400 to 1000 C was perhaps due to the burning of carbon present in the cement slag. Nagai and Harada (78, 79) studied three alumina cements, CA and C_3A_5 by DTA. Rey (38) showed by DTA that the aluminous cement hydrated for 7 days exhibits peaks corresponding to tetracalcium aluminate hydrate and at 13 days to dicalcium aluminate hydrate. The various inflections in the thermograms were not accounted for.

Pozzolanas and Pozzolanic Cements

Pozzolanas are materials which combine with lime at ordinary temperatures in presence of water to form stable insoluble compounds possessing cementing properties. Pozzolanic cements are obtained by grinding together portland cement clinker and pozzolana or mixing together a hydrated lime and a pozzolana (80). There is every reason to believe that pozzolanic materials form cementitious compounds similar to those obtained by the hydration of portland cement clinker.

Turriziani (81, 82) has applied the DTA technique extensively to a study of the chemistry of the pozzolanic activity. He reported that a pozzolana treated with saturated lime solution gave a low temperature endothermic peak at 140 C, indicating the presence of Taylor's silicate, CSH(I). The second effect at 200 C was ascribed to the presence of C_4AH_{13}. Continued work (83) on the products with different proportions of $Ca(OH)_2$ and pozzolana and on mortars confirmed the presence of calcium silicate of tobermorite type. In mortars, DTA showed the presence of C_4AH_{13}. The reaction at 45 C gave the product with a peak corresponding to C_3AH_6 (cubic). This agrees with results obtained by Malquori and Cirilli (84). The formation of small amounts of C_2SAH_x was also considered. The determination of free $Ca(OH)_2$ in pozzolanic cements by DTA showed that after long curing the quantity is much smaller than that ordinarily formed in portland cement pastes (85). The products of portland cement-pozzolanas examined up to a period of 1 yr showed the presence of tobermorite type of calcium silicate hydrate, tetracalcium aluminate hydrate, high-sulfate sulfoaluminate and low $Ca(OH)_2$ content. A mixture of pozzolana, hydrated lime and gypsum in water shows an endothermal peak corresponding to the formation of $3\,CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 32\,H_2O$ and under certain conditions, $3\,CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 12\,H_2O$ (86, 87). Rey (38) also presented a typical curve for $Ca(OH)_2$-pozzolana mixture. Surovkin and Krylov (88) studied the interaction of lime and calcined clay. DTA showed exothermic peaks at 310 and 890 C and an endothermic peak at 540 C for the reaction between calcined clay and $Ca(OH)_2$. Benton (113) carried out a systematic investigation of the lime-pozzolan and cement-pozzolan reactions by DTA and x-ray. The pozzolans used for the study included pumicite, diatomite, kaolinite, bentonite, illite, gibbsite, quartz and fly ash. The DTA of all lime-pozzolan mixtures except quartz showed endothermic peaks at about 200 C for the presence of C_4AH_{13}. All mixtures exhibited endothermic peaks between 500 and 600 C, corresponding to $Ca(OH)_2$ decomposition, and the intensity of the peak was used to determine the reactivity of the pozzolans in lime-pozzolan and pozzolan-cement mixtures. In cement-pozzolan mixtures, high-temperature exothermic peaks increased in intensity for more active cements; this was correlated with dehydration of products into such minerals as wollastonite, β-C_2S and melilite. A much more systematic work should be undertaken to study the interaction between clay minerals fired to different temperatures and treated with limes of varying reactivity.

Slag Cements

Slag cements are obtained by grinding granulated blast furnace slag (by quenching the slag issuing from the blast furnace at 1400 to 1500 C) with activators such as portland cement clinker or hydrated lime and a mixture of one or other of these with gypsum or anhydrite.

The chemistry of slag cements is less clear than that of portland cement. Lommatzsch (89) tried to obtain an understanding of binding and setting processes of granulated blast furnace slags under sulfate activation. The thermal changes in the range 800 to 900 C were thought to be due to modifications and formations typical of the hydraulic basic slags. The formation of glass in the slag was studied by Kondo (90). Williams and Chopra (91) found that Indian slags containing 25 percent $CaSO_4$ and 5 percent cement clinker formed a good-quality supersulfated cement. The DTA of this mix indicated the presence of ettringite at curing periods extending from 3 to 90 days. The intensity of the endothermic effect at 160 C gave an indication of the amount of ettringite formed. DTA has been applied by some workers to characterize the blast furnace slags (92, 93). Mchedlov-Petrosyan et al. (94) recently found that DTA is a rapid test method for the detection of glass in slags.

The mechanism of activation of slags was studied by Samaddar and Lahiri (114). Synthetic slags with a constant SiO_2/Al_2O_3 ratio and varying CaO contents were prepared with lime-gypsum mixture. DTA results showed the presence of C_4AH_{13} as an initial product on the surface. During hydration the hydrate liberates lime which reacts further with mass of the slag.

CONCLUSIONS

The introduction of DTA technique into the field of cement chemistry is only recent and it is certain that the method would play a role especially in the investigation of materials not easily discernible by x-ray diffraction.

The thermographic characteristics of similar materials reported by different workers vary considerably. Hence, factors such as heating rate, particle size, weight of the sample, furnace atmosphere, type of the specimen block, purity of the material (where possible), and method of drying must be specified.

The low-temperature endothermic peaks in cements provide a basis for the identification of the starting material. The method of drying is very critical in hydrating cements and, without proper precautions, may interfere with the low-temperature effects.

The identification of any material in cement in terms of peak temperatures presents difficulties because of the shift in the peak temperature caused by the presence of other materials. It would be helpful to calibrate the peak temperatures by running a DTA of mixtures of known amount of materials present or formed during a treatment.

For substances exhibiting small energy changes over a wide temperature range, the rate of heating should not be high so as to outstrip the rate of attainment of equilibrium. Spurious results, such as the development of two depressions in place of one, are not uncommon.

DTA, as any other technique, has certain limitations and the results should be interpreted cautiously and preferably in conjunction with other techniques. DTA could advantageously be used for quantitative work. Many attempts have been made to increase the sensitivity of the method so that it could be used as a quantitative tool (95-98, 115-120).

Another field of study in which DTA offers promise is in the investigation of the nature of water alone and in presence of salts in porous systems at fairly low temperatures.

The progress in the DTA of cement chemistry may be compared to the parrallel development in its application in clay mineralogy. It is reasonable to expect that the application of this technique in cement chemistry will greatly increase. In the field of clay mineralogy, with the introduction of DTA, there was a tendency among clay workers to apply the method rather indiscriminately without regard to precautions and limitations. Consequently, thermograms reported for a particular mineral by one laboratory differed greatly from that reported by the other. It was in this context that an International Geological Congress was held in London in 1948 to recommend certain specifications for the standardization of the technique. It is perhaps pertinent to indicate in this connection that DTA will probably continue to enjoy popularity in cement chemistry and it is advisable at this stage to formulate certain standards to aid workers in the interpretation and comparison of results.

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