

Differential Thermal and Thermogravimetric Analysis of Reacted Bentonite-Lime-Water Mixtures

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Thermal methods are applied to supplement previous results by X-ray diffraction of mixtures of bentonite with calcitic, monohydrated, and dihydrated dolomitic lime reacted in the presence of water at 23 C for 3 years in sealed containers. In addition, the cured mixtures were reacted at approximately 100 percent relative humidity at temperatures of 40 and 80 C for 4 to 5 days. These mixtures were then subjected to hydrothermal treatment at several intermediate temperatures to 170 C. X-ray diffraction indicated calcium silicate hydrate (CSH) gel, CSH I, and possibly CSH II in all room-cured mixtures, with C_4AH_{13} indicated only in calcitic and monohydrated lime mixtures. Better crystallized CSH phases, including tobermorite, resulted from hydrothermal treatment. In most instances, results by X-ray diffraction were confirmed using thermal methods. In addition there were new findings; it was possible to characterize reaction products having low degrees of crystallinity. A chlorite-like mineral was noted in all mixtures containing dolomitic lime. CSH II was also clearly identified as a reaction product in most of the mixtures, particularly those reacted at intermediate temperatures.

•A COMPLETE EVALUATION of a stabilized soil involves, among other factors, identification of products of the reaction between the additives and components in the soil. This is a difficult process, particularly when X ray diffraction is the only analysis technique employed and the reaction products have low degrees of crystallinity. This is often the case, particularly in soils stabilized with hydrated lime under field temperature conditions. One supplementary technique is Differential Thermal Analysis (DTA), accompanied sometimes by Differential Thermogravimetric (DTG) and Thermogravimetric (TG) analysis to obtain weight loss and other reaction data.

The present study applies these thermal techniques to the analysis of separate reacted mixtures of a pure clay mineral with 3 types of lime in water.

Previous studies by X-ray diffraction of these mixtures reacted at 23 C using calcitic and monohydrated dolomitic lime indicated formation of the tetracalcium aluminate hydrate (C_4AH_{11-12}). These mixtures as well as the one reacted at 23 C using dihydrated dolomitic lime showed that calcium silicate hydrate (CSH) gel, $CaCO_3$, CSH I, and possibly CSH II were also produced after curing for long periods, with apparently increasing degrees of crystallinity with longer reaction time. This phenomenon in the hydrothermally reacted mixtures was evident, with well-crystallized tobermorite appearing at the highest temperatures and with other CSH phases at intermediate temperatures. In all mixtures the products noted at 23 C were found to persist beyond the hydrothermal reaction at 105 C (1). Reexamination of the X-ray diffraction patterns of dolomitic monohydrated lime mixtures revealed that a 15.2 \AA nonexpanding mineral was produced in hydrothermal reactions at 105 C and above.

For obvious reasons, previous DTA, DTG, and TG studies of the 2 systems, $\text{CaO-SiO}_2\text{-H}_2\text{O}$ and $\text{CaO-Al}_2\text{O}_3\text{-H}_2\text{O}$, were selected from the literature and used in the present analysis.

DTA of the compound $\text{C}_4\text{AH}_{12-13}$ by Turriziani showed weak endotherms near 130 and 170 C with a strong endotherm near 230 C. Another weak endothermic peak near 330 C was followed by a broad weak exothermic bulge near 350 C (2). Carlson's studies of the calcium aluminoferrite hydrates explained the progressive dehydration of C_4AH_{13} to be as follows: The 11 hydrate is formed at 127 C; 4 additional molecules of water are lost at 194 C. Above 250 C the hexagonal hydrate goes to C_3AH_6 , the isometric form, accompanied by formation of Ca(OH)_2 . C_3AH_6 is decomposed near 350 C (3). TG studies of cement chemistry by Longuet essentially confirm these findings (4).

DTA of CSH gel prepared at room temperature by Brunauer and Greenberg shows only a strong endotherm near 200 C (5). Diamond noted this phenomenon, but his preparations also gave a small exotherm between 840 and 865 C (6). Kalousek found that CSH I having CaO/SiO_2 (C/S) ratios between 0.8 and 1.0 gave similar DTA patterns for both room temperature preparations and those hydrothermally reacted at 175 C. The peak temperatures increased with increases in C/S ratio but the exotherms were about 7 C lower for the room temperature preparations. After 4 days of autoclaving at 175 C, a 0.8 C/S mixture made with lime and silicic acid showed weak DTA effects, namely, an endotherm near 270 C and an exotherm near 840 C. At less reaction time, the low temperature endotherm moved from just below 200 C to slightly higher temperatures; this was accompanied by a progressive diminution in intensity of the 840 C exotherm. Kalousek indicated that an intermediate lime-rich phase (C/S = 1.75) interacted with unreacted quartz after about 6 hours (7, 8, 9). Gaze and Robertson hydrothermally reacted lime with quartz having a C/S ratio of 0.33 at 165 C to give a product showing a weak DTA endotherm at 570 C followed by a strong exotherm at 818 C (10). Diamond's hydrothermal preparations of tobermorite gave a noticeable endotherm near 275 C and a barely noticeable exotherm near 820 C. Aluminum substituted tobermorite produced the following changes in his DTA patterns: for 3 percent Al, the endotherm appeared at 810 C; for 5 percent Al, both endotherm and exotherm were 10 C lower than for pure tobermorite. Changes noted in the 10 percent Al pattern, as compared with that for 5 percent Al, included the appearance of a 630 C weak exothermic bulge and an 825 C exotherm; the 15 percent Al preparation showed 285 and 380 C medium endotherms, a 510 C weak exotherm, and an 835 C very strong exotherm (6).

Mackenzie reports that diluted 20 to 25 percent CaCO_3 mixtures show DTA peak temperatures between 830 and 940 C (11). Gaze and Robertson attribute a large endothermic effect at 780 C to calcite. This lower temperature is affirmed to be due to appreciable quantities of CO_2 . A similar result was noted by Mackenzie in DTA findings for a calcium carbonate sample from carbonation of Ca(OH)_2 . Lowering of the calcite peak temperature was attributed to the finer particle size of the secondary carbonate. Longuet reports a weight loss study in which decomposition of CaCO_3 in air commences at 630 C and terminates at 880 C (4, 10, 11).

Van Bemst presents DTA and DTG studies of CSH I (C/S = 1.36) and CSH II (C/S = 2.01). Exothermic effects near 155 and 800 C appeared on DTA patterns for both preparations. CSH I showed a very strong exotherm at 840 C while CSH II showed twin thermal effects between 340 and 380 C as well as weak exotherms at 850 and 920 C. The greatest rate of weight loss occurred below 200 C, as indicated by the DTG curve. Weak decomposition reactions also occurred near 400 C with intermediate reaction rates near 710 C for both compounds. The distinguishing features noted on the DTG patterns were the intermediate reaction at 260 C for CSH II and the one at 640 C for CSH I (12). Unidentified calcium aluminate hydrates and calcium silicate hydrates were found by X-ray diffraction in various lime-clay mixtures as early as 1960 (13, 14). DTA, as well as X-ray diffraction, was used in the analysis of lime reacted with several clay minerals to characterize reaction products, namely, C_4AH_{13} , 10 Å tobermorite, and monocarbonate aluminate (15).

Among the results of X-ray diffraction studies of products of lime-bentonite-water mixtures by McCaleb were the following: With Ca(OH)_2 , room temperature mixtures produced calcite and Ca-montmorillonite. With Mg(OH)_2 , Mg-montmorillonite, brucite,

and a small amount of vermiculite-chlorite-like mineral were formed. When both $\text{Ca}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$ were present, no such changes were noted. Hydrothermally reacted (168 C) mixtures contained a 12.8 Å and 15.7 Å montmorillonite as well as tobermorite and calcite. Little difference was noted between room temperature and hydrothermal preparations using $\text{Mg}(\text{OH})_2$. When both $\text{Ca}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$ were used, a 12.9 Å montmorillonite, a 14.7 Å vermiculite, and an 11.7 Å tobermorite were formed (16).

Caillere et al. treated montmorillonite with MgCl_2 and NH_4OH solutions and described the product as having characteristics between chlorite and vermiculite. The explanation of the phenomenon was that $\text{Mg}(\text{OH})_2$ rapidly precipitated between the structural layers of the montmorillonite. DTA results from artificially prepared chlorites showed a weak endotherm between 500 and 600 C and a weak exotherm near 850 C (17, 18, 19). Artificial pseudochlorites are reported by Mackenzie to show about 3 times the weight loss as that of a natural chlorite and that half occurs at about 300 C from interlayer water and a third near 400 C, attributed to brucite layer dehydration; the balance of the dehydration occurs slowly up to 525 C, at which temperature the montmorillonite layer decomposes (11).

Using X-ray diffraction, supplemented by DTA, Wang and Handy noted that MgO reacted at 23 C for 28 days with bentonite and water to produce a 15.2 Å nonexpanding material that was characterized as a chlorite-like mineral. The DTA peaks for this mixture reacted at 126 C for 1 day were as follows: weak endotherms at 540 and 810 C and a medium exotherm at 845 C. Curing for longer periods at 126 C resulted in an increased temperature and intensity for the low temperature endotherm and an increased intensity for the exotherm at a slightly lower temperature. After 8 months, the well-crystallized mineral serpentine was the final product, exhibiting longest X-ray diffraction spacing at 7.19 Å and DTA peaks as follows: a strong endotherm at 620 C and a very strong exotherm at 800 C. As the reaction proceeded from 1 day to 8 months, there was a progressive diminution of the 110 C hygroscopic moisture endotherm characteristic of montmorillonite (20).

McConnell performed a dehydration study of the natural 11.3 Å hydrate, tobermorite, from which he found that almost two-thirds of the weight loss occurred between 200 and 300 C. In the DTA of the same material, a strong endotherm was observed at 250 C. The 14.6 Å hydrate phase was also present in small quantity, which accounted for other dehydration effects at 105 C (21).

CSH phases with low degrees of crystallinity have always been difficult to identify by X-ray diffraction alone (1). The relationships between phase and degree of crystallinity of the various products are given in Table 1.

PROCEDURES

The clay mineral used was Otay, California, bentonite API reference clay mineral No. 24 (22). Lime, synthesized from reagent grade laboratory chemicals, was mixed with bentonite in water in the proportions given in Table 2.

Mixtures prepared in slurries were sealed in plastic containers to prevent loss of water or entry of carbon dioxide and cured at 23 C, ± 2 deg, for 3 years. Reactions at 40 C for 5 days and 80 C for 4 days, as well as hydrothermal reactions of the cured

TABLE 1
RELATIONSHIP BETWEEN PHASE AND DEGREE OF CRYSTALLINITY

Product C/S Ratio	Degree of Crystallinity		
	High	Low	Very Low
0.8 to 1.33	Tobermorite: 9.3, 11.3, and 14 Å Well-crystallized CSH I	CSH I	Plombierite (natural gel)
1.5 to 2.0	Tobermorite: 10 and 12.6 Å	CSH II	CSH gel
X-ray diffraction pattern	Complete, including h, k, l reflections	Poor, with basal and hk or hko reflections	Very poor, with one or more hk reflections and no basal reflections

mixtures at 105, 145, 156, and 170 C for 12 hours, were employed. The hydrothermal procedure involved reaction at the vapor pressure for steam in an apparatus manufactured by the Parr Instrument Company, Moline, Illinois.

Samples from which specimens were taken were allowed to equilibrate under vacuum over CaCl_2 for 24 hours; they were then ground to approximately 200 mesh size before mounting on the DTA apparatus.

All reacted mixtures were analyzed using a DTA apparatus equipped with an automatic temperature controller, providing for a heating rate of 10 C per minute to 1,000 C. A vertical furnace arrangement is used. Two vertical $\frac{3}{8}$ -in. diameter by $\frac{1}{2}$ in. deep sample holes were symmetrically located in a stainless steel block with centers 1 in. apart. Number 22 platinum-platinum 10 percent rhodium differential thermocouples were used. The furnace temperature couple was a separate chromel-alumel junction inserted in a $\frac{3}{8}$ -in. diameter by $\frac{1}{2}$ in. deep hole drilled into the bottom of the block. An inert sample of powdered alumina was placed in one hole with the sample in the remaining hole. Materials were tamped with a tightness from which reproducible results were obtainable.

In order to clarify certain of the thermal effects noted on the initial DTA curves, selected specimens from the desiccated samples that had been stored in capped bottles for periods exceeding a year were reexamined. DTG and TG curves as well as a second set of DTA curves were simultaneously obtained for mixtures using all 3 types of lime reacted at 23 C and for all hydrothermally reacted mixtures containing only the dolomitic monohydrated lime. The second apparatus, namely, the Mettler Thermo-analyzer, was used. It was operated at the same heating rate. This apparatus is designated as equipment A in Figures 3 and 4 for these mixtures whereas the other apparatus is designated as equipment B.

RESULTS

Results of the DTA for Otay bentonite shown at the top of Figures 1, 2, and 4 include an interlayer water endotherm near 150 C. Two other medium endotherms near 850 and 855 C are from expulsion of hydroxyl water. The sharp exotherm near 1,000 C is associated with the appearance of the second endothermic peak but its exact origin is unknown (11).

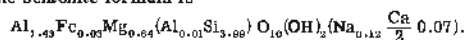
Mixtures Reacted at 23 C for 3 Years

Differential Thermal Effects Below 300 C for All Types of Lime—DTA curves for the mixtures using calcitic and dihydrated dolomitic lime are shown in Figures 1 and 2 respectively. DTG, TG, and DTA curves for the mixture using monohydrated dolomitic lime are shown in Figure 3; TG data for the other 2 mixtures are summarized in the text. The first reaction appears near 140 C and represents weight losses between 6 and $7\frac{1}{2}$ percent, representing expulsion of hygroscopic and interlayer water. Heat treatment of an identical sample in a 105 C oven for 24 hours resulted in a hygroscopic water loss of less than 3 percent; there was a 2 percent weight loss at the corresponding temperature on the TG curve, lower because of the relatively short period of heat application in the DTA apparatus. The total weight loss for the reaction near 140 C was low apparently because of additional desiccation during storage of the samples. Mixture constituents contributing to this initial thermal effect are unreacted bentonite, C_4AH_{13} , CSH gel, and CSH I, all of which were noted from previous X-ray diffraction study; thermal effects at higher temperatures that support these findings are noted later (1). Additional effects from C_4AH_{13} were detected in the mixtures using calcitic and monohydrated dolomitic lime. Dehydration of the hexagonal hydrate overlaps that

TABLE 2
LIME-BENTONITE-WATER MIXTURE

	Weight Ratio	Starting C/S Ratio of Mixture
A.	$\text{Ca}(\text{OH})_2$:bentonite: H_2O 0.45:1.00:1.62	0.69
B.	$\text{Ca}(\text{OH})_2$: MgO :bentonite: H_2O 0.45:1.00:1.62	0.45
C.	$\text{Ca}(\text{OH})_2$: $\text{Mg}(\text{OH})_2$:bentonite: H_2O 0.45:1.00:1.62	0.39

The bentonite formula is



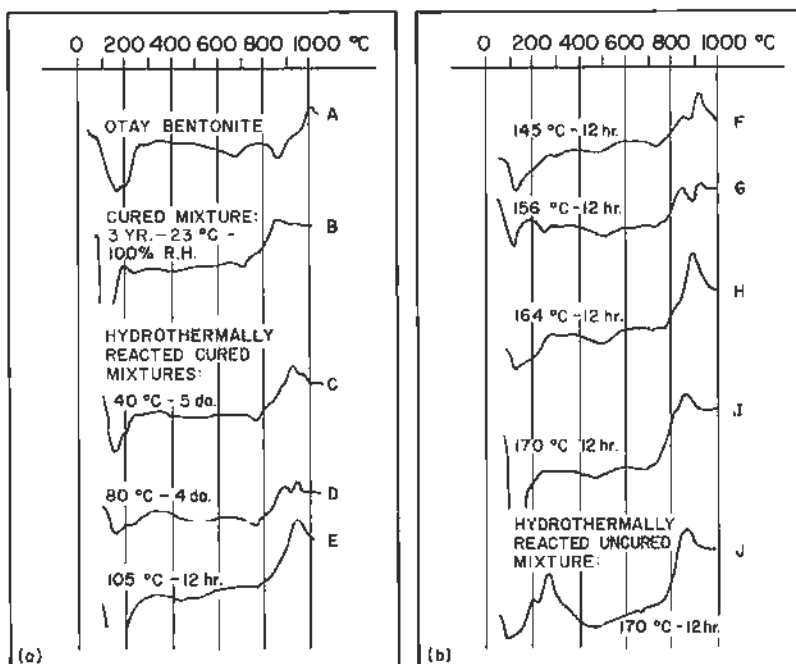


Figure 1. DTA curves of reacted mixtures of bentonite + $\text{Ca}(\text{OH})_2$ and H_2O .

for the constituents mentioned earlier near 100 and 200 C (2, 3, 4, 6). The endotherm centered near 250 C appears in all mixtures but stronger in the calcitic and monohydrated lime mixtures. This thermal effect may be associated with CSH I and II as well

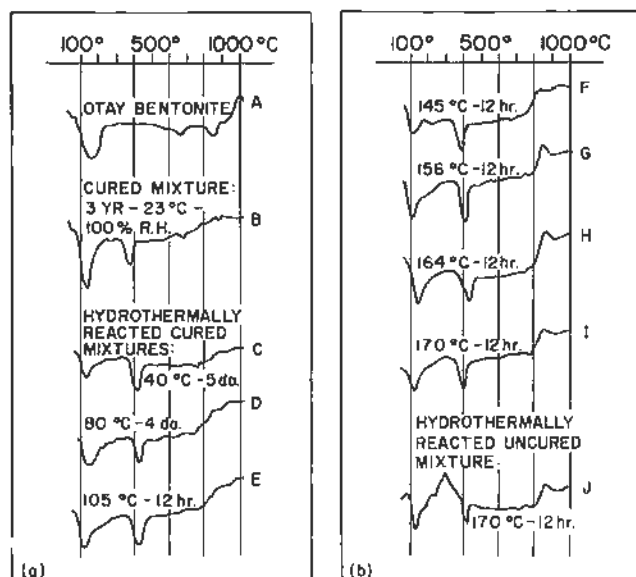


Figure 2. DTA curves of reacted mixtures of bentonite and $\text{Ca}(\text{OH})_2 + \text{Mg}(\text{OH})_2 + \text{H}_2\text{O}$.

as C_4AH_{13} ; the aluminate hydrate has its most prominent DTA peak at 230 C, corresponding closely with TG data. Weight losses at this temperature for the calcitic and monohydrated lime mixtures were 50 to 100 percent greater than for the dihydrated lime mixture that contained no C_4AH_{13} (1, 2, 9, 12).

Differential Thermal Effects Above 300 C for Calcitic Lime Mixtures—Shown on DTA curve B in Figure 1 for this mixture reacted at 23 C, there are broad, diffuse, weak endotherms near 400 and 700 C, with weak undulating effects just above 500 C. These are followed by more prominent endothermic effects near 800 C and a medium exotherm at 840 C.

Between 300 and 500 C, there was a total weight loss of $4\frac{1}{2}$ percent. There were no significant peaks in the DTG curve in this temperature range although the weight loss curve reflected an increased rate commencing near 400 C and terminating near 560 C. The $1\frac{1}{2}$ percent weight loss between 300 and 400 C may be associated with dehydration of the C_3AH_6 phase that normally terminates near 350 C. $Ca(OH)_2$ dehydration in air usually begins near 400 C and terminates in the vicinity of 500 C and is associated with the remaining 3 percent weight loss (3, 4). An overlapping endotherm at 380 C and weak exotherm at 510 C from CSH II may contribute (9).

Beginning near 600 C, the DTG rate increases gradually to a diffuse peak near 700 C; the DTG reaction rate is equal to that noted at 140 C and represents a total weight loss of over 7 percent. These effects are attributed to the loss of hydroxyl water from unreacted bentonite (11). This is followed by a distinct DTG peak at 815 C at double the rate of weight loss of the preceding peaks, amounting to a loss of over 5 percent of the sample weight. This weight loss essentially terminates at 840 C, coinciding with the only distinguishable exotherm in the DTA pattern. The 815 C endotherm and accompanying weight loss is attributed to $CaCO_3$ (4, 10, 11). CSH I and II have strong weight loss reactions near 700 C and are also contributory to this thermal effect. CSH I usually shows a stronger exotherm near 850 C than CSH II, which has a second very weak exotherm near 920 C. CSH II also has a high rate of weight loss near 260 C that aids in distinguishing it from CSH I (12). Also contributing slightly to the 840 C exotherm is CSH gel that earlier was noted by a low temperature endotherm as well (6).

Differential Thermal Effects Above 300 C for Dihydrated Dolomitic Lime Mixtures—Shown on DTA curve B in Figure 2 for this mixture reacted at 23 C, there is a strong endotherm near 400 C with an associated weight loss of 4 percent, and several weaker, broad, and somewhat diffuse peaks appear at higher temperature. Most prominent are the weak endotherm near 560 C and the medium endotherm near 700 C. A weak endotherm at 730 and, appearing as a shoulder at 810 C, another endothermic effect preceded medium double exotherms at 840 and 920 C.

There are 5 essential differences in the thermal effects noted for this mixture when compared with those for the calcitic lime mixture. The 415 C endotherm represents decomposition of $Mg(OH)_2$. Second, thermal effects for the calcium aluminate hydrates are absent. In the third place, the appearance of a definite DTG peak at 560 C is accompanied by approximately twice as much loss of weight, namely, 3 percent. The fourth difference is associated with the endothermic effects near 700 and 800 C, where the weight loss measurement for the dihydrated lime mixture is 40 percent lower than that obtained for the other mixture. No clear indication for $Ca(OH)_2$ can be distinguished although noted by X-ray diffraction (1). The fifth difference lies in the diminished 840 C exothermic effect.

With regard to the third and fourth items just cited, the peak near 560 C is probably due to the interaction of the $Mg(OH)_2$ with the bentonite to produce a chlorite-like mineral having a low degree of crystallinity. Wang and Handy found that curing of a similar mixture at 23 C for a year produced a reacted mixture that gave a weak hump at 7 \AA on the X-ray diffraction pattern. These findings were similar to those of McCaleb. However, X-ray diffraction of the Wang and Handy mixture, as well as that of the present mixture, indicated presence of expansive clay rather than the usual nonexpanding 15.2 \AA peak (1, 16, 18, 19, 20).

Diminished intensity of the exotherm at 840 C and the accompanying 920 C exotherm as well as distinctive endotherms below 300 C and another endotherm at 710 C provide

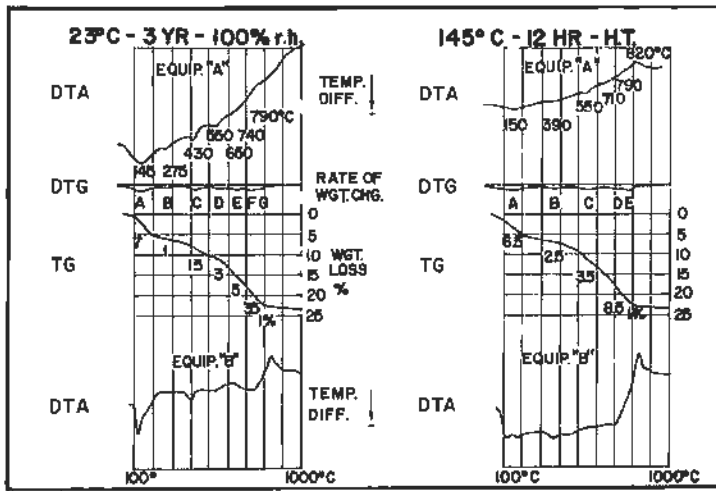


Figure 3. DTG, TG, and DTA curves of monohydrated dolomitic lime-bentonite-water mixtures.

the essential evidence for identification of CSH II in the mixture. It appears that contribution by CSH I to the 840 C exotherm is likely only if CSH I were present in small quantity and at a high degree of crystallinity (1, 7, 12).

Finally, the thermal effect near 700 C may be associated with dehydroxylation of unreacted bentonite as well as the aforementioned decomposition of CSH II (11, 12). The relatively lower weight loss for the dihydrated lime mixture at this temperature may be due to a diminished quantity of unreacted bentonite, due to its alteration to the chlorite-like mineral (16, 20).

Differential Thermal Effects Above 300 C for Monohydrated Dolomitic Lime Mixtures—On the left in Figure 3, the DTA for this mixture reacted at 23 C is shown. A medium endotherm at 430 C, with an associated DTG peak and weight loss of 1½ percent, is attributed to the decomposition of Mg(OH)₂. This effect is followed by a sim-

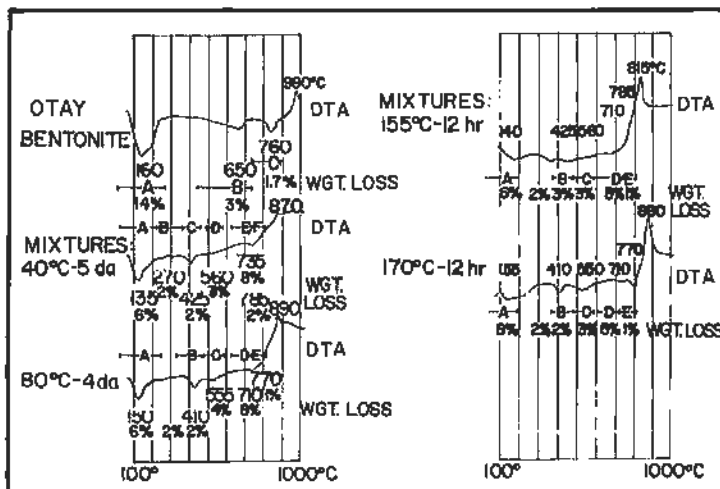


Figure 4. DTA curves of monohydrated dolomitic lime-bentonite-water mixtures.

ilar set of DTA and DTG peaks near 550 C, with a weight loss of 3 percent, which are associated with a chlorite-like mineral. Near 650 C the bentonite dehydroxylation peak appears on both DTA and DTG curves, accounting for a weight loss of 5 percent. Two DTG peaks appear to be combined into a medium endothermic effect between 700 and 800 C. The overall character of the 200 C endothermic effect and the associated exotherm at 840 C, noted particularly in the DTA curve by equipment B, is indicative of CSH I, to which the weight loss of $1\frac{1}{2}$ percent near 700 C is attributed. The breadth of the 700 to 800 C peak is probably associated with the 1 percent weight loss near 800 C. No distinguishable DTA effects are noted above 300 C for the final decomposition of the isometric phase of the initial C_4AH_{13} .

Hydrothermally Reacted Mixtures

40 C for 5 Days—DTA curves shown in Figures 1, 2, and 4 for all 3 mixtures differ most from those of mixtures cured at 23 C for 3 years by the diminished low temperature endothermic effects. Although evidence persists for the same constituents noted in the earlier discussion, the intensities are lower (2, 3, 6, 9). The second most striking change in the overall appearance of all 3 DTA curves is enhancement of the evidence for CSH II (9, 12). Effects may be noted for unreacted bentonite as well as $CaCO_3$ (4, 11, 12). $Mg(OH)_2$ decomposition may also be noted in Figures 2 and 4.

80 C for 4 Days—DTA curves shown in Figures 1, 2, and 4 appear about the same as for the 40 C reacted mixtures with respect to CSH gel, C_4AH_{13} , and $Mg(OH)_2$; however, the evidence for CSH II is enhanced in all mixtures, particularly by the 850 and 920 C exotherms. CSH I exothermic effects are also stronger in Figure 4 (9, 12). Some increase in intensity of the $Ca(OH)_2$ decomposition peak near 500 C is shown in Figure 1. The endothermic effects near 550 C in Figures 2 and 4 likely indicate the presence of a chlorite-like mineral (16, 18, 19, 20).

105 C for 12 Hours—DTA reactions at this temperature, shown in Figures 1 and 2, seem to be approximately the same as those at 40 C, so the same identifications are made.

145 C for 12 Hours—The DTA curves are almost identical for the monohydrated lime mixtures at 145 and 80 C, as shown in Figures 3 and 4 respectively. Those for the 145 and 80 C mixtures for dihydrated lime, shown in Figure 2, are also strikingly similar; therefore, identifications of constituents are the same as previously stated. The CSH I exotherm near 850 C is somewhat enhanced in the DTA of the monohydrated lime mixture as is the double exothermic effect for CSH II in the DTA of the dihydrated lime mixture (12).

The DTA curve shown in Figure 1 for the calcitic lime mixture may be characterized as predominantly CSH II with increased evidence for $Ca(OH)_2$ (3, 12).

156 C—The DTA curve shown in Figure 1 for the calcitic lime mixture is essentially that for CSH II with more evidence for $Ca(OH)_2$ than at lower temperatures (3, 12).

There is also more evidence in Figure 4 for the chlorite-like mineral and well-crystallized calcium silicate hydrate in the DTA curves for both types of dolomitic lime (6, 7, 9, 10). However, the nonexpanding 15.2 \AA X-ray diffraction peak was present only for the mixture using monohydrated lime (16, 19, 20). Although there is diminished evidence for CSH II in the dihydrated lime mixture, other constituent identifications remain the same as for the 145 C mixture.

164 and 170 C for 12 Hours—As shown in Figure 1, DTA curves for these 2 calcitic lime mixtures reflect a transition from CSH II to a lime-rich phase, with excess $Ca(OH)_2$ present as well; these effects are followed by their conversion to 11.3 \AA tobermorite at 170 C (6, 7, 9, 10).

Tobermorite is predominant in DTA curves for both of the dolomitic lime mixtures as shown in Figures 2 and 4, with more conclusive evidence for the chlorite-like mineral in the monohydrated lime mixture. In addition, some unreacted $Mg(OH)_2$ is indicated in both mixtures.

Because $CaCO_3$ is believed to be present in relatively small quantities, the lower temperature endothermic effects noted near 785 C are attributed to this compound (1, 4, 10, 11).

The low temperature exotherm is unexplained in curve J in Figures 1, 2, and 4 for identical freshly prepared mixtures using all 3 types of limes.

Analysis Summary of Weight Loss Data

A complete set of weight loss curves was obtained only for the monohydrated lime mixtures reacted over a long period of 23 C and subsequently reacted hydrothermally at 40, 80, 145, 155, and 170 C. Examination of these data for this mixture, shown in Figures 3 and 4, provides summary findings as follows: The weight losses below 300 C for the mixtures reacted hydrothermally at 170 C were 20 percent higher than for the 23 C mixture. There was also a slight upward shift in the DTA peaks. Weight loss above 700 C for the 145 C mixture is double that for 23 C. The 170 C mixture has a weight loss equal to one and one-half that for 23 C. These low temperature and high temperature thermal effects may be related as follows: As indicated in X-ray analysis of the 23 C mixture, CSH gel, CSH I, CaCO_3 , and C_4AH_{13} , as well as some unreacted lime and bentonite, were noted (1). The 145 C mixture was noted to contain predominantly CSH I, a chlorite-like mineral, some unreacted $\text{Mg}(\text{OH})_2$, and CaCO_3 . The 170 C mixture was predominantly 11.6 Å tobermorite with some 15.2 Å chlorite-like mineral, CaCO_3 , and unreacted $\text{Mg}(\text{OH})_2$. The evident influence of increase in temperature on the progression of the reaction may be summarized in the following way: Unreacted bentonite and $\text{Ca}(\text{OH})_2$ in the 23 C mixture provided materials for production of CSH compounds at intermediate hydrothermal reaction temperatures. These in turn are utilized in part to form tobermorite as the reaction temperatures approach 170 C. Concurrent decomposition of C_4AH_{13} above 156 C provided additional Ca^{++} ions and Al^{+++} ions. Substitution of aluminum in the tobermorite lattice may also have occurred. Starting at 23 C, long-term reaction between Mg^{++} ions and bentonite probably produced the poorly crystalline chlorite-like mineral. In the monohydrated lime mixture, the degree of crystallinity of this 156 C product was sufficient to clearly indicate a nonexpandable 15.2 Å X-ray diffraction peak; the 550 C DTA peak was also evident. The weight losses for the 550 C reactions were constant at all temperatures, and there was negligible change in either the $\text{Mg}(\text{OH})_2$ peak or associated weight loss with increase in hydrothermal reaction temperature. Thus one may conclude that only a progressive refinement in degree of crystallinity of initial chlorite-like material occurred with increased hydrothermal reaction temperature.

Mixtures using both types of dolomitic lime reacted at 23 C showed DTA peaks and equal weight losses near 550 C. Although not conclusively supported by X-ray diffraction results obtained on the dihydrated lime, this effect may be attributed to formation of the poorly crystalline chlorite-like mineral. Weight loss for $\text{Mg}(\text{OH})_2$ for the dihydrated lime mixture was 3 times that for the monohydrated lime. Losses near 140 and 700 C associated with CSH compounds were approximately the same for both types of lime. Carbonation of $\text{Ca}(\text{OH})_2$ in the dihydrated lime mixture was apparently 3 times that in the monohydrated lime mixture from comparison of weight loss data obtained near 800 C.

Comparison of the weight loss data for calcitic lime mixtures reacted at 23 C with the dolomitic lime mixtures indicates about equal CSH product formation. The CaCO_3 formation is almost double that for the dihydrated lime mixture.

CONCLUSIONS

1. DTA, especially when accompanied by DTG and TG analysis, provides valuable data supplementary to that obtained by X-ray diffraction, as noted later.
2. DTA delineates between CSH I and CSH II, which may occur as mixture constituents having approximately equal degrees of crystallinity. Although the compounds may be indistinguishable by X-ray diffraction, the characteristic CSH II thermal effects are evident in a DTA pattern of the mixture.
3. Mixture constituents, having such low degrees of crystallinity that no X-ray diffraction peaks are obtainable, may be inferred from analysis of weight loss measurements obtained simultaneously with DTA curves. Detection of a bentonite-magnesium

alteration product in dolomitic lime-bentonite mixtures reacted at room-temperature for long periods is an example.

4. Hydrothermal reactions at elevated temperatures (105 to 170 C) for relatively short periods (12 hours) produce reaction products (e. g., tobermorite) having higher degrees of crystallinity than obtained at 23 C (e. g., CSH gel) after long-term reaction (3 years). Products (e. g., CSH I and CSH II), obtained at slightly increased temperatures (40 to 80 C) reacted for 4 to 5 days, are similar to those obtained at elevated temperatures (105 to 145 C) for relatively short periods of time (12 hours).

5. The higher temperature hydrothermal reactions (155 to 170 C) utilize constituents produced in lower temperature reactions. This may be inferred from analysis of weight loss measurements obtained simultaneously with the DTA curves. An example is the formation of tobermorite from available CSH I and II and other possible sources of calcium that have interacted with bentonite in the presence of water at 156 C and above.

6. The extent of carbonation of $\text{Ca}(\text{OH})_2$ is clearly indicated from DTA and TG data to be greatest in the calcitic lime mixtures followed by those containing the dihydrated and monohydrated types of lime.

7. Very little difference is detectable in pozzolanic reaction at room temperatures between $\text{Ca}(\text{OH})_2$ and bentonite in water for either the calcitic or dolomitic types of lime.

8. There was no detectable carbonation of magnesium compounds in any of the reactions studied.

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