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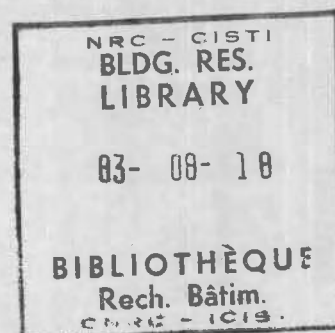
# ESTIMATION OF $\text{Ca}(\text{OH})_2$ AND $\text{Mg}(\text{OH})_2$ — IMPLICATIONS IN CEMENT CHEMISTRY

by V.S. Ramachandran

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## RÉSUMÉ

Le ciment Portland, le ciment Portland hydraté, l'oxychlorure et l'oxysulfate de magnésium et les enduits en général sont des systèmes à base de liant inorganique dans lesquels différentes quantités de  $MgO$ ,  $CaO$ ,  $Ca(OH)_2$  et  $Mg(OH)_2$  sont présentes. En identifiant et en évaluant les quantités d'oxyde et d'hydroxyde de Ca et de Mg au moyen d'une analyse thermique différentielle (ATS), on obtient des renseignements qui peuvent à leur tour être utilisés pour diverses études: mécanisme d'hydratation du  $CaO$ , réactivité des silicates de calcium, essai d'identification des ciments défectueux à l'autoclave, interactions dans les mortiers, effets de divers adjuvants sur le ciment et des compositions des caractéristiques, composition chimique, composition, activité chimique, hydratation de la résine, et d'oxysulfate et d'enduits au plâtre.

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# Estimation of $\text{Ca}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$ — Implications in Cement Chemistry

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**Abstract.** Portland cement, hydrated Portland cement, magnesium oxychloride, magnesium oxysulphate and plasters are inorganic cementitious systems in which different amounts of  $\text{MgO}$ ,  $\text{CaO}$ ,  $\text{Ca}(\text{OH})_2$  and  $\text{Mg}(\text{OH})_2$  are present. Identifying and estimating the Ca- and Mg-oxides and hydroxides by DTA provides information that can, in turn, be used for studying the mechanism of hydration of  $\text{CaO}$ , reactivity of calcium silicates, the relevance of the autoclave test for determining the unsoundness of cements, interactions occurring in polymer-impregnated cement, the effect of various admixtures on the hydration kinetics of cement and cement compounds, the contribution of  $\text{Ca}(\text{OH})_2$  to the physico-mechanical properties of cement, the composition of the hydrated silicates, mechanism of hydration, chemical activity of blended cements, strength development in magnesium-oxychloride and magnesium-oxysulphate cements and causes of failure of gypsum plasters.

## INTRODUCTION

Almost all inorganic cements such as Portland cement, high alumina cement, sorel cement, pozzolanic cement, gypsum plaster, and expansive and regulated-set cements contain calcium and magnesium compounds. Portland cement, which is far more widely used than all other cements, comprises 50–70% tricalcium silicate, 20–38% dicalcium silicate, 5–12% tricalcium aluminate, 5–12% ferrite phase (tetracalcium aluminoferrite), 3–5% gypsum, and small amounts of  $\text{MgO}$ ,  $\text{CaO}$  and alkali sulphates.<sup>1</sup> Sorel cement (magnesium oxychloride cement) is formed by adding an aqueous solution of  $\text{MgCl}_2$  to  $\text{MgO}$ . Magnesium oxysulphate cement is formed on addition of an aqueous solution of  $\text{MgSO}_4$  to  $\text{MgO}$ . White coat plasters are produced by hydrating a mixture of gypsum hemihydrate ( $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ ) and dolomitic lime ( $\text{CaO} \cdot \text{MgO}$ ).

Several methods, including calorimetric, X-ray, conductometric titration, thermal techniques and the chemical extraction method have been used for estimating amounts of  $\text{Ca}(\text{OH})_2$  and  $\text{Mg}(\text{OH})_2$  in cements. The chemical extraction method appears to be the most popular, although it is quite time-consuming and there is a distinct possibility that the solvent will attack compounds other than  $\text{Ca}(\text{OH})_2$ , especially when it is used for Portland cements. Ramachandran<sup>2</sup> and Midgley<sup>3</sup> have both suggested recently that DTA is a useful alternative to chemical methods; it is less time-consuming, needs only small amounts of sample, and appears to be reliable.

In the present paper the amount of  $\text{Ca}(\text{OH})_2$  and  $\text{Mg}(\text{OH})_2$  in various cementitious systems was determined by DTA with a view to investigating the mechanism of hydration, composition of products, kinetics of hydration, strength development, role of admixtures, and long-term durability aspects.

## EXPERIMENTAL

The types of material, preparation of samples and experimental procedures varied from system to system and are therefore described separately under relevant headings.

### Portland Cement

**Reactivity.** Analytical reagent quality  $\text{Ca}(\text{OH})_2$  and  $\text{AgNO}_3$  were used to prepare a mixture of the two compounds. The tricalcium silicate and  $\beta$ -dicalcium silicate samples used in this work are described under the subheading hydrated Portland cement. DTA was carried out in air using a DuPont-900 thermal analyser at a heating rate of  $20^\circ\text{C}/\text{min}$ .

**Unsoundness.** Portland cement of the following composition was used:  $\text{C}_3\text{S} = 46.5\%$ ,  $\text{C}_2\text{S} = 24.6\%$ ,  $\text{C}_3\text{A} = 10.4\%$ ,  $\text{C}_4\text{AF} = 9.3\%$ ,  $\text{MgO} = 3.46\%$ . It had a Blaine surface area =  $327.9 \text{ m}^2/\text{kg}$ , and was hydrated for 15 years at a water: cement ratio of 1:1. In each experiment 20 mg of sample was heated at  $20^\circ\text{C}/\text{min}$  to obtain differential thermograms. The DuPont 1090 thermal analysis system was used. DTG was carried out using the TGA module supplied with the 1090 system.

### Hydrated Portland Cement

**Estimation of  $\text{Ca}(\text{OH})_2$ .** Calcium hydroxide used for calibration purposes was obtained by calcining Analar Grade  $\text{CaCO}_3$  to  $1000^\circ\text{C}$  for 3 h and hydrating the resulting  $\text{CaO}$  in distilled water. The purity of  $\text{Ca}(\text{OH})_2$  was checked by TGA and considered satisfactory for use in construction of a calibration curve. Portland cement Type I, composition  $\text{C}_3\text{S} = 51.5\%$ ,  $\text{C}_2\text{S} = 19.8\%$ ,  $\text{C}_3\text{A} = 12.8\%$  and  $\text{C}_4\text{AF} = 6.6\%$ , was used. The sample of tricalcium silicate had the following composition:  $\text{C}_3\text{S} = 99.33\%$ ,  $\text{C}_2\text{S} = 0.00\%$ ,  $\text{C}_3\text{A} = 0.21\%$  and  $\text{CaO} = 0.46\%$ . Blaine surface area was  $331.0 \text{ m}^2/\text{kg}$ .

DSC cell, supplied as a module to a DuPont thermal analysis system 990, was used to obtain thermograms in a temperature range from room temperature to  $550^\circ\text{C}$ . In each experiment 20 mg of sample was heated in air at  $10^\circ\text{C}/\text{min}$ . The endothermal peak areas were determined using a planimeter. All samples were dried in vacuum for 3 h at  $110^\circ\text{C}$  prior to thermal analysis. The solvent variation method, consisting of extraction with a mixture of ethyl acetoacetate and isobutyl alcohol in a 3:20 ratio by volume, was used for estimating  $\text{Ca}(\text{OH})_2$  in some samples.

**$\text{Ca}(\text{OH})_2$ -free cement or  $\text{C}_3\text{S}$  paste.** The cement and  $\text{C}_3\text{S}$  samples were similar to those used above. The procedure used to extract  $\text{Ca}(\text{OH})_2$  from hydrated Portland cement or hydrated  $\text{C}_3\text{S}$  was as follows: Discs 0.64 to 0.76 mm thick were cut from cylinders prepared by hydration of  $\text{C}_3\text{S}$  or Portland cement at a water:solid ratio of 0.5 for about 10 years. They were placed in a cage and exposed to 5 L of an aqueous solution containing 9.5

mmol/L of CaO. Slicing and extraction were carried out in a CO<sub>2</sub>-free atmosphere.

**Role of admixtures.** The  $\beta$ -C<sub>2</sub>S sample used in this work had a Blaine surface area of 331.0 m<sup>2</sup>/kg. Triethanolamine of certified grade was supplied by Fisher Scientific Co.

The DTA procedure was similar to that adopted for studying reactivity. X-ray diffractograms were obtained by a Hilger and Watts unit using a CuK $\alpha$  source. Mg(OH)<sub>2</sub> provided an internal standard for estimating the amount of C<sub>2</sub>S. The unhydrated C<sub>2</sub>S was also estimated by DTA procedure by determining the endothermal peak area, at 915°C.

The hydration of C<sub>2</sub>S was studied by mixing it with double-distilled water at a water:silicate ratio of 0.5. Hydration was carried out in tightly covered polyethylene containers rotated continuously over rollers. At specified time intervals varying from a few minutes to 28 days each sample was ground in cold ethyl alcohol, placed in a desiccator, and continuously evacuated for 24 h using liquid air in the trap. Care was taken to prevent contamination with CO<sub>2</sub>.

**Polymer impregnation.** Portland cement paste was obtained by hydrating a high-early-strength Portland cement for 271 days at a water:cement ratio of 0.37. The sample had hydrated to about 93% and had a porosity of 19.9%. Polymer-impregnated cement was obtained as follows: Portland cement paste was dried to a constant weight at 110°C, evacuated for 4 h, and soaked in methyl methacrylate monomer containing 0.5% azobisisobutyronitrile as an initiator for 24 h. Samples were then polymerized for 48 h at 80°C under a pressure of 1.16 MPa followed by a further period of 48 h at 110°C. Polymethyl methacrylate was produced by the polymerization of the methyl methacrylate monomer. The material was obtained in a powdered form by filing of the solid piece of the polymer. The Portland cement paste-polymer mixture was prepared by mixing Portland cement (passing a 100-mesh sieve) with the polymer in the ratio of 4:1.

DTA was carried out using a DuPont 900 thermal analyser. The reference material was ignited  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. In each run, 50 mg of sample passing a 100-mesh sieve was packed at a moderate pressure. Thermograms were run in air or in a continuous flow of N<sub>2</sub> at 1.2 ft<sup>3</sup>/h. The rate of heating was 10°C/min.

**Blended cement.** Normal Type I cement was mixed with a fly ash to give a blend containing 35% of the addition. Another blend contained 70% slag. The fly ash had 85% of the particles between 45 and 12  $\mu$ m. The fly ash and slag contained 55.6 and 31.5% SiO<sub>2</sub> and 13.3 and 36% CaO, respectively. Hydration was carried out at a water:cement ratio of 0.45. Cubes were made and cured for 24 h and sliced into discs 32 mm in diameter and 1.3 mm thick. Various measurements were taken at hydration periods of 2, 7, 14 and 28 days. The procedure adopted for obtaining thermograms was similar to that described for estimating Ca(OH)<sub>2</sub>.

#### Mg-oxychloride and Mg-oxysulphate

**Magnesium oxychloride.** MgO used for making the magnesium oxychloride cements had the following characteristics: N<sub>2</sub> surface area, 20 m<sup>2</sup>/g; active CaO 1.5%; ignition loss 4%; fraction passing a 200-mesh 98%. An aqueous solution of magnesium chloride of specific gravity 1.18 was prepared by mixing MgCl<sub>2</sub>·6H<sub>2</sub>O in a dry form with distilled water. Cement paste samples were prepared at MgCl<sub>2</sub>·6H<sub>2</sub>O/MgO solution: solid ratios of 0.59, 0.64, 0.71, 0.77 and 0.86 by weight. Mixes were cured at 50% RH for periods of up to 10 months. Compacted discs were fabricated by grinding the samples and subjecting them to compaction pressures varying from 133 to 1665 MPa. A series of compacts was prepared by immersion in water at 22°C followed by heating at 85°C for 5 h. Porosity was measured by using methanol displacement employing Archimedes principle. X-ray examination was carried out with a Debye-Scherrer camera. Differential thermograms were obtained according to the procedure described for the estimation of Ca(OH)<sub>2</sub>.

**Magnesium oxysulphate.** Magnesium oxide has been described under Magnesium Oxychloride. An aqueous solution of specific gravity 1.18 was prepared by mixing MgSO<sub>4</sub>·7H<sub>2</sub>O in a dry form with distilled water. X-ray diffraction and thermal techniques were the same as those used for the oxychloride cements.

#### White Coat Plasters

**Plaster failure.** Three white coat plasters were collected from three buildings. Two samples had failed and one appeared to be sound. They were carefully separated from the base, dried, and powdered to pass a 200-mesh sieve. Fragments of white coat plaster from which the paint had been scraped and compacts (1.25 in. diam) formed from the powder with a steel mould at a load of 10,000 to 20,000 lb were used to study the length changes after autoclaving at 300 lb/in<sup>2</sup> for 3 h. A Cahn balance was used for TGA. DTA was carried out using an automatic recording unit. All samples were ground to pass a 200-mesh sieve. The rate of heating was maintained at 10°C/min.

**Estimation of MgO and Mg(OH)<sub>2</sub>.** Three white coat plasters were used; two were designated as failed and the third was found to be sound. Analytical reagent quality chemicals CaSO<sub>4</sub>·2H<sub>2</sub>O, Mg(OH)<sub>2</sub>, Ca(OH)<sub>2</sub> and CaCO<sub>3</sub> were used for calibration purposes. The purity of the compounds was assessed and corrections were made in the calibration curves where necessary. A differential scanning calorimetric cell supplied as a module to the DuPont 990 thermal analysis system was used to obtain thermograms in a temperature range from room temperature to 550°C. The rate of heating was 20°C/min and  $\Delta T = 5$  m cal s<sup>-1</sup> in.<sup>-1</sup>. All the thermograms were obtained in air with a constant quantity of the sample. DTA in the range from 550 to 850°C was obtained with a DuPont 990 apparatus.

### RESULTS AND DISCUSSION

#### Portland Cement

**Reactivity.** According to Hedvall effect many solids exhibit an increased reactivity during and as a consequence of crystalline transition.<sup>4</sup> Silver nitrate has a crystalline transition point at 160°C. A study was made to determine the reactivity of AgNO<sub>3</sub> with CaO, Ca(OH)<sub>2</sub> and completely hydrated C<sub>2</sub>S\* (containing a mixture of calcium silicate hydrate and calcium hydroxide) by estimating the amount of AgNO<sub>3</sub> that reacts with these compounds when heated in a DTA apparatus. The procedure was to heat different proportions of AgNO<sub>3</sub> and the Ca-compounds up to 250°C. An exothermal peak resulted at 192°C, on cooling, corresponding to the crystallization of unreacted AgNO<sub>3</sub>.<sup>5</sup> A calibration curve was constructed relating the amount of AgNO<sub>3</sub> with peak height (Fig. 1). From the intensity of the exothermic peak and the amount of AgNO<sub>3</sub> originally added, the amount of AgNO<sub>3</sub> reacted with the Ca-bearing compounds could be determined.

The reaction between Ca(OH)<sub>2</sub> and AgNO<sub>3</sub> and between hydrated C<sub>2</sub>S and AgNO<sub>3</sub> was stoichiometric. In the mixture of CaO and AgNO<sub>3</sub>, 96% CaO reacted and 4% was non-reactive. These results suggest that DTA can be used to estimate Ca(OH)<sub>2</sub> and to determine the reactivity of CaO formed by the calcination of limestone (one of the major raw materials used for the production of Portland cement).

**Unsoundness.** Portland cement clinker is formed between 1400 and 1500°C. At these temperatures some free MgO exists in the "dead burnt" state in the form of

\* Cement nomenclature: CaO = C, S = SiO<sub>2</sub>, H = H<sub>2</sub>O, F = Fe<sub>2</sub>O<sub>3</sub> and A = Al<sub>2</sub>O<sub>3</sub>.

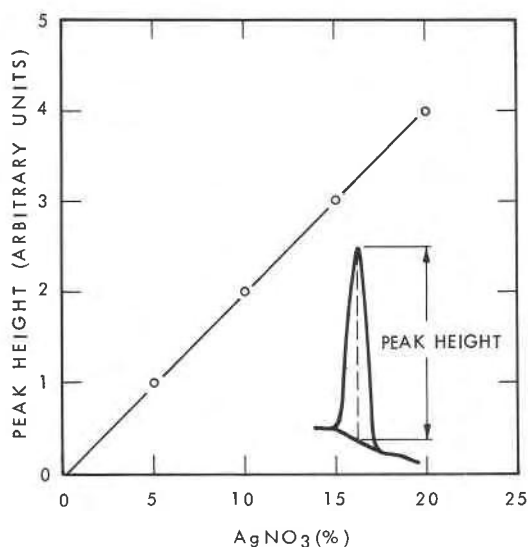


Fig. 1. Calibration curve for the estimation of  $\text{AgNO}_3$  by DTA peak heights.

periclase. Under normal conditions of exposure it may take several years for periclase to hydrate. As the conversion of  $\text{MgO}$  to  $\text{Mg}(\text{OH})_2$  involves a molar volume expansion of 117%, it may lead to unsoundness of concrete in the form of expansion and cracking. An accelerated test for potential expansion due to  $\text{MgO}$  has been devised for cements. In the ASTM (American Society for Testing and Materials) and CSA (Canadian Standards Association) methods the cement paste is autoclaved at a pressure of 2 MPa for 3 h; expansion should not exceed 0.8 and 1.0%, respectively. The relevance of the autoclave test has been questioned because of the possibility that  $\text{MgO}$  remains virtually inert in concrete under normal conditions of exposure.<sup>6</sup> A preliminary DTA test was therefore carried out to determine whether the free  $\text{MgO}$  present in a cement had hydrated after a normal curing period of 15 years.

Figure 2 shows that a normal cement cured for 28 days

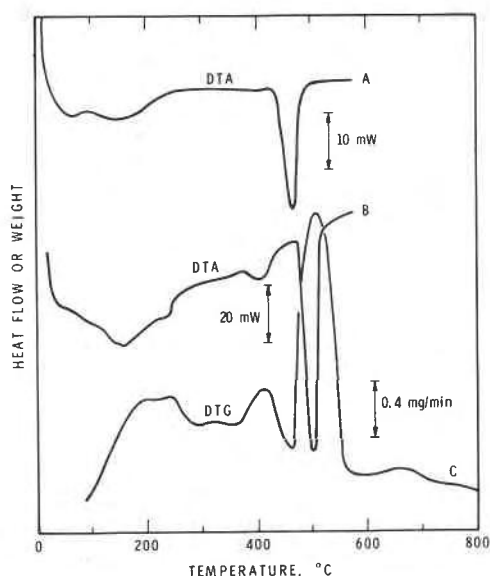


Fig. 2. Thermograms of hydrated cement (A: 28 days; B and C: 15 years).

indicates the presence of  $\text{Ca}(\text{OH})_2$  by an endothermal effect at 450 to 500°C. After 15 years of hydration, a cement containing 3.5%  $\text{MgO}$  indicates an additional endothermal effect at about 400°C caused by  $\text{Mg}(\text{OH})_2$  decomposition. The peak area corresponds to 3.2%  $\text{MgO}$ . DTA also indicates a weight loss occurring at a peak temperature of about 400°C. The DTA method thus indicates the possibility that  $\text{MgO}$  hydrates after several years of normal curing. More extensive work should be done to confirm these results and to examine their applicability in the case of concrete.

#### Hydrated Portland Cement

**Estimation of  $\text{Ca}(\text{OH})_2$ .** The dominant phases in Portland cement comprising  $\text{C}_3\text{S}$  and  $\text{C}_2\text{S}$  produce calcium silicate hydrate and  $\text{Ca}(\text{OH})_2$  on hydration. Calcium hydroxide exerts a significant influence on the physico-chemical characteristics of the hardened hydrated cement. DTA may be applied to determine the amount of  $\text{Ca}(\text{OH})_2$  formed in hydrated Portland cement.<sup>2</sup> Figure 3 presents the calibration curve of the endothermal peak areas due to  $\text{Ca}(\text{OH})_2$  decomposition in  $\text{Ca}(\text{OH})_2$ - $\text{C}_3\text{S}$  mixtures containing different amounts of  $\text{Ca}(\text{OH})_2$ . A good linear relation attests to the applicability of the DTA technique for estimating  $\text{Ca}(\text{OH})_2$  levels. At higher sensitivity DTA permits estimation of amounts as low as 0.1%  $\text{Ca}(\text{OH})_2$ .

The estimated  $\text{Ca}(\text{OH})_2$  content of Portland cement paste and hydrated  $\text{C}_3\text{S}$  provided by chemical analysis is generally higher than that obtained by using thermal methods. This is probably due to attack of the C—S—H phase by the solvent used in chemical analysis.

**$\text{Ca}(\text{OH})_2$ -free cement or  $\text{C}_3\text{S}$  paste.** One method of investigating the role of  $\text{Ca}(\text{OH})_2$  in hydrated Portland cement or hydrated  $\text{C}_3\text{S}$  is through study of the hydrated product from which free CH is extracted without affecting other hydrates. The material is placed in an unsaturated  $\text{Ca}(\text{OH})_2$  solution and the amount of extracted  $\text{Ca}(\text{OH})_2$  is monitored by DTA determination of the amount of free  $\text{Ca}(\text{OH})_2$  remaining in the material.<sup>7</sup> Figure 4 shows the amount of free CH remaining at different times of extraction and that at about 12 days most of the free CH has been extracted from the hydrated  $\text{C}_3\text{S}$ . This is proved by the disappearance of the endothermal peak due to  $\text{Ca}(\text{OH})_2$  decomposition. Further extraction beyond this period may destabilize the C—S—H phase.

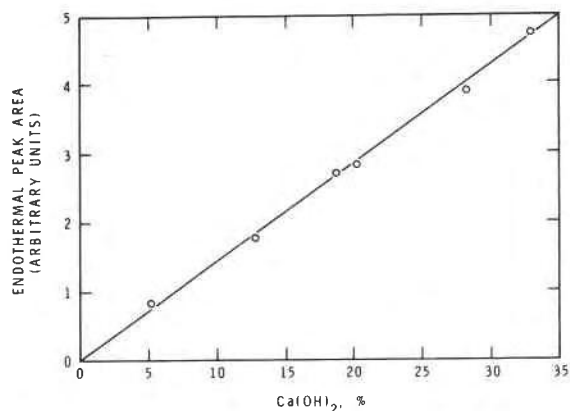


Fig. 3. Calibration curve for estimation of  $\text{Ca}(\text{OH})_2$  by differential thermal technique.

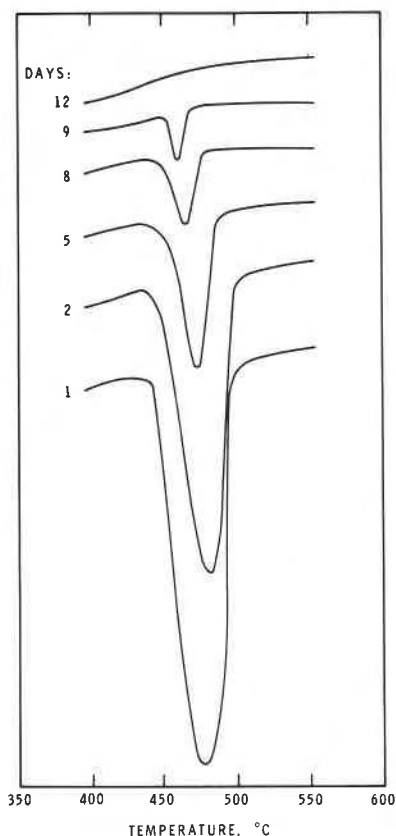


Fig. 4. Endothermal effect due to  $\text{Ca}(\text{OH})_2$  in hydrated  $\text{C}_3\text{S}$  exposed to different times of extraction.

**Role of admixtures.** Admixtures are chemicals that influence the rate of hydration, rheology, and other physical and mechanical properties of the resultant paste when added in small amounts to Portland cement. The kinetics of hydration may be followed by estimating the amount of CH formed at different times during hydration of Portland cement,  $\text{C}_3\text{S}$  or  $\text{C}_2\text{S}$  in the presence of admixtures such as  $\text{CaCl}_2$ , calcium lignosulphonate, triethanolamine, formates, nitrates, and sulphates.

Figure 5 presents the sequence of hydration of  $\text{C}_2\text{S}$  in the presence of triethanolamine.<sup>7</sup> The endothermal peak occurring in the vicinity of  $500^\circ\text{C}$  represents the decomposition of CH. The sample containing no admixture hydrates at a faster rate than that containing triethanolamine. The relatively low intensity of the peaks shows that triethanolamine acts as a retarder in the hydration of  $\text{C}_2\text{S}$ . In addition, dual peaks in the presence of this admixture indicate the possibility of the formation of non-crystalline as well as crystalline CH. Thermal analysis may also be used to compare the relative influence of various admixtures by comparing the CH peak areas of the hydrated products at a particular period of hydration.<sup>7</sup> Hydration of  $\text{C}_3\text{S}$  results in the formation of CH and calcium silicate hydrate of general formula  $\text{C}-\text{S}-\text{H}$ , having a C/S ratio of 1.4 to 1.6.<sup>1</sup> This ratio may change, depending on the conditions of hydration; in the presence of larger amounts of admixture there is evidence that the C/S ratio increases.<sup>8-10</sup> The ratio of C/S in  $\text{C}-\text{S}-\text{H}$  in hydrated  $\text{C}_3\text{S}$  can be determined by estimating CH and unhydrated  $\text{C}_3\text{S}$ . The unhydrated  $\text{C}_3\text{S}$

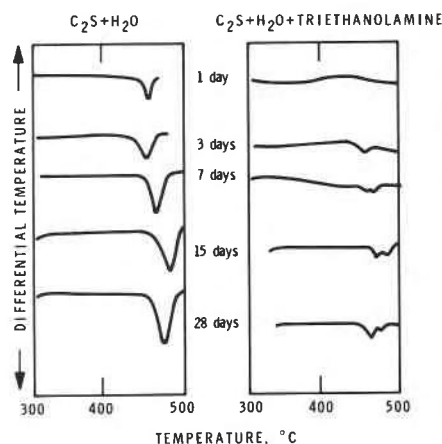


Fig. 5. Thermograms of  $2\text{CaO}\cdot\text{SiO}_2$  hydrated in the presence of triethanolamine (obtained in a  $\text{N}_2$  atmosphere).

may be determined by DTA or X-ray analysis and the amount of CH by DTA. In the hydration of  $\text{C}_3\text{S}$  in the presence of 0.5 to 1.0% triethanolamine, the amounts of CH formed at different times are lower than those formed in the absence of the admixture (Fig. 6).<sup>8</sup> These results indicate that triethanolamine is a retarder in the hydration of  $\text{C}_3\text{S}$ . The data, however, indicate that between 1 and 28 days more  $\text{C}_3\text{S}$  remains unhydrated in samples lacking triethanolamine. This can be explained as due to the formation of a  $\text{C}-\text{S}-\text{H}$  product with a C/S ratio which is higher than that formed in  $\text{C}_3\text{S}$  hydrated in the absence of the admixture. Similar conclusions may be drawn for products formed during the hydration of Portland cements in the presence of calcium chloride.<sup>11</sup>

**Polymer impregnation.** Concrete impregnated with an acrylic-type polymer is known to exhibit a two- to three-fold increase in compressive and tensile strengths. This could be attributed largely to a decrease in porosity although there may be other reasons for this effect. Evidence of the possible interaction between hydrated cement and polymethyl methacrylate (PMMA) has been sought by applying DTA.<sup>12-13</sup> Gebauer and Coughlin<sup>12</sup> found that in PMMA-impregnated cement the endothermal peak due to  $\text{Ca}(\text{OH})_2$  is practically absent. They concluded that interaction occurred between the polymer and the cement. In Auskern's<sup>13</sup> experiments polymerization of an intimate mixture of  $\text{Ca}(\text{OH})_2$  and methyl methacrylate resulted in a new peak at about  $430^\circ\text{C}$ , attributed to the presence of Ca-salt of methacrylic acid. Further studies were carried out to analyse these conclusions.<sup>14</sup>

In Fig. 7, curve A-1 refers to reference Portland cement hydrated to 83%; curve B-1 is cement impregnated with PMMA and curve C-1 refers to an intimate mixture of powdered PMMA and cement. These samples were analysed in air. Samples designated A-2, B-2 and C-2 were analysed in an atmosphere of  $\text{N}_2$ . Comparison of samples A-1 and B-1 shows that the impregnated cement exhibits several complex effects in addition to a decreased peak intensity for the endothermic peak at about  $500^\circ\text{C}$  corresponding to decomposition of  $\text{Ca}(\text{OH})_2$ . This decrease has been attributed previously to a bulk reaction between PMMA and hydrated cement.<sup>12</sup> Other possibilities include: a masking of the exothermic effects occurring at about the same temperature as the



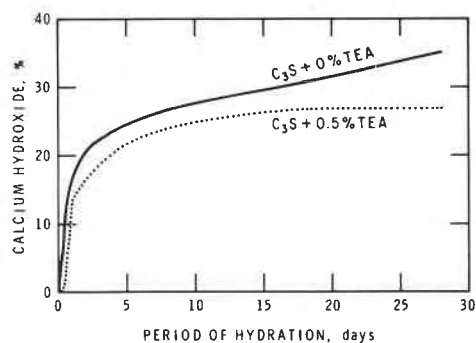


Fig. 6. Amounts of  $\text{Ca(OH)}_2$  estimated by S.V.M. method in  $3\text{CaO} \cdot \text{SiO}_2$  pastes (ignited basis).

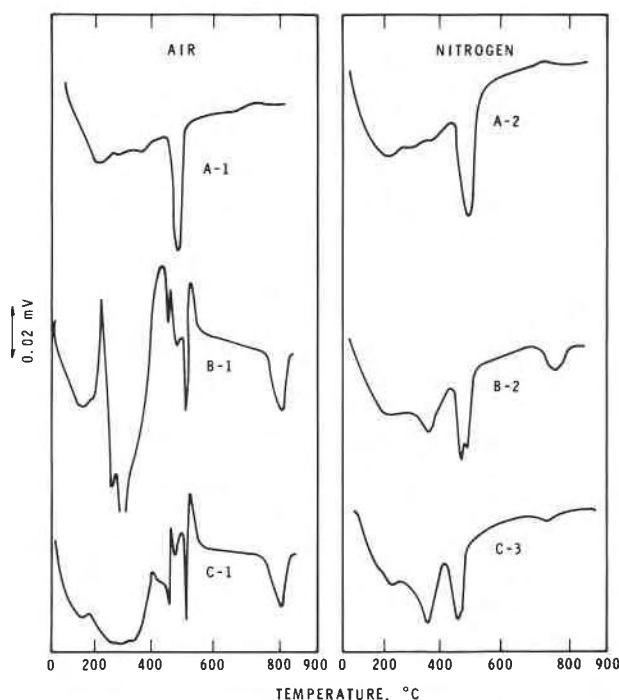


Fig. 7. Thermograms of polymethyl methacrylate-impregnated Portland cement paste ( $w/c = 0.37$ ). A: unimpregnated Portland cement paste. B: PMMA-impregnated Portland cement paste. C: Portland cement paste-PMMA mixture.

decomposition temperature of  $\text{Ca(OH)}_2$ , and a dilution effect resulting from the fact that the impregnated cement contains less cement than the reference cement A-1.

A close study of thermograms B-1 and C-1 shows that they are similar in terms of exothermic and endothermic effects. The absence of a few peaks in sample C-1 is ascribed to the better drying procedure adopted for the impregnated paste. It appears that the emergence of many of the new thermal effects and the decreased intensity of the CH peak in the impregnated system is not due to the compounds formed during impregnation but to reactions occurring between hydrated cement and the decomposition products of PMMA during heating in the DTA apparatus. It is possible that some reaction occurs between the PMMA and cement at the interface, but it would represent only a small portion of the total polymer and DTA may not detect it.

**Blended cement.** A blended cement contains a mixture of pozzolana or slag and cement. Fly ash is a pozzolana that reacts with lime in the presence of water to form the same types of hydrate as are found in the hydration of Portland cement. In hydration of Portland cement containing fly ash, lime liberated from Portland cement reacts with the fly ash to form hydrates. The rate of reaction and amount of lime reacting with the fly ash may determine the physical and chemical properties of the blended cement.

DTA may be utilized to determine the amount of  $\text{Ca(OH)}_2$  that has reacted with fly ash. Table 1 compares the amounts of  $\text{Ca(OH)}_2$  formed in the reference cement with those in two blends containing 35% fly ash or 70% slag. In cement the amount of  $\text{Ca(OH)}_2$  steadily increases up to 14 days due to the hydration of the calcium silicate phases. The fly ash blend contains relatively smaller detectable amounts of  $\text{Ca(OH)}_2$ . A dilution effect due to replacement of cement with fly ash may at least partly explain these results. Although there is practically no increase in the amount of lime in the reference cement, there is a considerable decrease from 14.1 to 9.9% in the fly ash blend which occurs between 14 and 28 days. This indicates that during this period there is a significant reaction between  $\text{Ca(OH)}_2$  and fly ash. In slag blends the total amount of  $\text{Ca(OH)}_2$  is considerably reduced. The amount of cement is only 30%. The low amounts of lime indicate, however, that some reaction does take place between  $\text{Ca(OH)}_2$  and slag.

Table 1. Amount of  $\text{Ca(OH)}_2$  Formed in Blended Cements

Time of hydration (days)	Cement	Cement + fly ash	Cement + slag
2	16.8	10.9	3.3
7	18.6	12.3	2.8
14	19.7	14.1	3.1
28	19.6	9.9	2.6

#### Mg-oxychloride and Mg-oxy sulphate cements

**Magnesium oxychloride.** This cement is formed by mixing finely divided  $\text{MgO}$  with an aqueous solution of  $\text{MgCl}_2$ . Four oxychloride complexes may be formed with the general formula  $2-9\text{Mg(OH)}_2 \cdot \text{MgCl}_2 \cdot 5-8\text{H}_2\text{O}$ , depending upon the conditions of preparation. This cement may also contain some  $\text{Mg(OH)}_2$  and  $\text{MgCl}_2$ . DTA may be applied to confirm the presence of  $\text{Mg(OH)}_2$  in these cements. A set of compacted discs of various porosities was prepared by subjecting a ground oxychloride cement (formed at  $22^\circ\text{C}$ ) to different pressures. Another set was prepared by immersing the discs in water at  $85^\circ\text{C}$ . A plot of the porosity against log strength yielded two straight lines of different slopes.<sup>15</sup> The sample prepared at  $85^\circ\text{C}$  exhibited a higher strength than the one prepared at room temperature at any particular porosity. Comparison of the thermographs of these two sets of materials showed that the sample prepared at  $22^\circ\text{C}$  exhibited two endothermal peaks, whereas that exposed to a temperature of  $85^\circ\text{C}$  indicated one peak corresponding to the decomposition of  $\text{Mg(OH)}_2$ . It may be concluded that treatment at  $85^\circ\text{C}$  results in decomposition of the oxychloride. X-ray diffraction confirmed this.



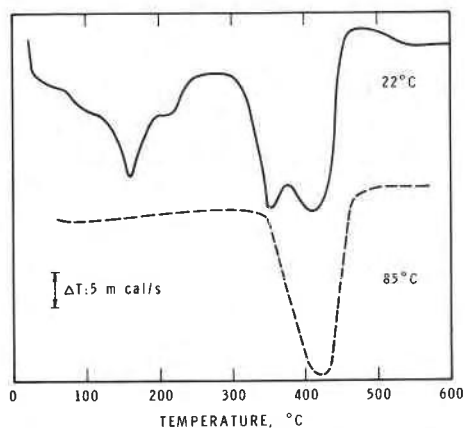


Fig. 8. Differential scanning calorimetric curves of magnesium oxysulphate.

**Magnesium oxysulphate.** Magnesium oxysulphate cement is formed by mixing finely divided  $\text{MgO}$  with an aqueous solution of  $\text{MgSO}_4$ . Four oxysulphate complexes are known to be formed with the general formula  $1-5 \text{Mg}(\text{OH})_2 \cdot 1-2 \text{MgSO}_4 \cdot 2-8 \text{H}_2\text{O}$  depending on the temperature at which reaction is carried out and conditions of formation. DTA was applied to examine the cements for unreacted  $\text{Mg}(\text{OH})_2$ . Such data can be used to interpret the mechanical properties of oxysulphate cements.<sup>16</sup> Series (I) was prepared by mixing an aqueous solution of  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  of specific gravity 1.18 with various amounts of  $\text{MgO}$ . Series (II) was prepared using a saturated solution of  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  of specific gravity 1.3. The X-ray diffraction results showed that series (I) samples contained larger amounts of oxysulphate than those of series (II).

Differential thermograms of the two series show that the amount of  $\text{Mg}(\text{OH})_2$  formed in series (II) is less than that formed in series (I) (Fig. 9), indicating that in samples in (II)  $\text{MgO}$  has reacted preferentially to form the oxysulphate complex, leaving less  $\text{Mg}(\text{OH})_2$ . Estimation of  $\text{Mg}(\text{OH})_2$  thus provides an indication of the amount of cementing agent produced.

#### White Coat Plasters

**Plaster failure.** Several investigators have reported popping and bulging in white coat plaster prepared from

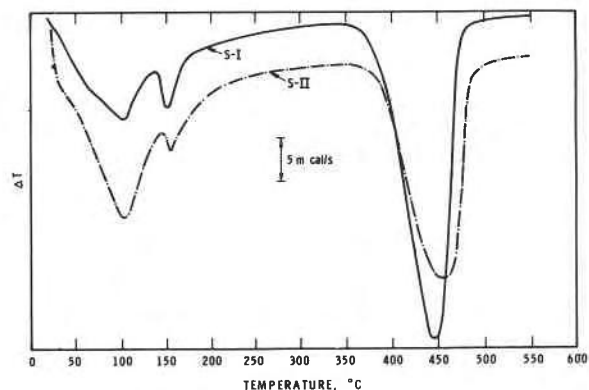


Fig. 9. Differential thermogram for magnesium oxysulphate cement.

dolomitic lime putty gauged with plaster of Paris. The onset of this phenomenon is generally noticed after 5 to 15 years. This plaster contains plaster of Paris,  $\text{CaO}$  and  $\text{MgO}$  before application. These are converted to gypsum,  $\text{Ca}(\text{OH})_2$ ,  $\text{CaCO}_3$  and  $\text{Mg}(\text{OH})_2$  on hydration, as a result of exposure.

DTA may be applied to the study of the mechanism of failure of white coat plaster (Fig. 10).<sup>17-18</sup> The doublet peaks at 142° and 158°C are typical of a stepwise dehydration which may be attributed to gypsum. The endothermic peak at about 400°C corresponds to the decomposition of  $\text{Mg}(\text{OH})_2$  and the peak at 465°C is the result of the decomposition of  $\text{Ca}(\text{OH})_2$ . A large endothermic peak at 800°C is caused by decomposition of  $\text{CaCO}_3$ . This endothermic effect resulting from  $\text{Mg}(\text{OH})_2$  decomposition was intensified when this plaster was subjected to an autoclave pressure of 295 lb/in.<sup>2</sup> for 1 h (Fig. 10). Autoclave treatment must have caused hydration of  $\text{MgO}$  in the failed plaster. The autoclaved plaster showed a linear expansion of about 13.5% due to hydration of  $\text{MgO}$ .

Differential thermograms indicated that the failed plaster had a higher amount of  $\text{Mg}(\text{OH})_2$  than the sound plaster from adjacent walls.<sup>18</sup> TGA, DTA, and autoclave experiments confirmed that delayed hydration of  $\text{MgO}$  is mainly responsible for bulging in white coat plaster.

**Estimation of  $\text{MgO}$  and  $\text{Mg}(\text{OH})_2$ .** One method of assessing the quality of plaster mix is to identify the constituents and estimate the quantities before the mix is applied to a wall so that its potential for failure can be predicted. The major components of plaster are  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ,  $\text{Mg}(\text{OH})_2$ ,  $\text{Ca}(\text{OH})_2$ ,  $\text{MgO}$  and  $\text{CaCO}_3$ .<sup>19</sup>  $\text{Mg}(\text{OH})_2$  and  $\text{MgO}$  are of special interest as far as the problem of plaster failure is concerned.<sup>19</sup>

Dehydration of  $\text{Mg}(\text{OH})_2$  is represented by an endothermic peak at about 390 to 400°C. A calibration curve can be constructed by plotting the percentage of  $\text{Mg}(\text{OH})_2$  against endothermal peak area of different pure mixtures  $\text{Mg}(\text{OH})_2$  and  $\alpha\text{-Al}_2\text{O}_3$ . This can be used for estimation of  $\text{Mg}(\text{OH})_2$  in the plaster samples. Magnesium oxide cannot be estimated directly because it exhibits no thermal inflection. It can, however, be esti-

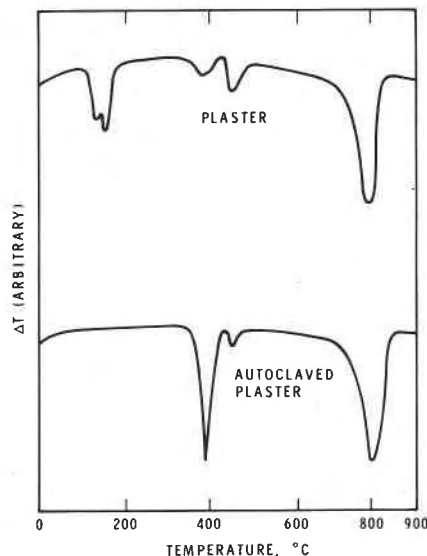
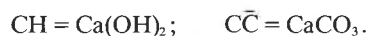


Fig. 10. DTA of plasters.

mated indirectly by autoclaving the plaster samples. In this treatment all MgO is converted to  $\text{Mg}(\text{OH})_2$ . The area of the endothermal peak occurring at about  $400^\circ\text{C}$  in the autoclaved material accounts for all Mg present as  $\text{Mg}(\text{OH})_2$ . Separate calibration curves can be established for estimating  $\text{Ca}(\text{OH})_2$ ,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  and  $\text{CaCO}_3$ . The amount of unhydrated MgO present in the plaster may be estimated according to the following equation:

$$0.69 \left[ \frac{W_{\text{MH}}(100 - 0.31 W_{\text{MH}} - 0.21 W_{\text{CSH}_2} - 0.24 W_{\text{CH}} - 0.44 W_{\text{CC}})}{(100 - 0.31 W_{\text{MH}} - 0.24 W_{\text{CH}} - 0.44 W_{\text{CC}})} - W_{\text{MH}} \right]$$

where  $W$  represents the percentage weight of a component in the original sample. The subscripts refer to the component estimated.



$W'$  represents the percentage weight of a component in the autoclaved sample.

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