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Examination of Portland cement paste hydrated in the presence of malic acid

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Abstract

When malic acid (MA) solutions are added to ordinary Portland cement (OPC), rapid heat evolution takes place, but the hydration is retarded considerably at all the MA concentrations. To understand the mechanism of retardation, UV–visible and IR spectral studies were made and the results have revealed that some interaction occurs between MA and certain constituents of OPC. X-ray diffraction (XRD) and thermogravimetric (TG)/differential thermal analysis (DTA) studies have proved the formation of a new reaction product due to interaction between MA and some of the mineral phases of Portland cement. The retardation of the hydration of Portland cement may be attributed to the formation of this new compound.

Keywords: Malic acid; Admixture; Portland cement; Thermal analysis; SEM

1. Introduction

Admixtures that retard setting are of great value for concreting in hot weather and for other purposes such as oil well cementing. Several organic admixtures are known to retard the hydration [1–9]. Taplin [2] noted that most organic retarders contain one or more groups in which the oxygen atoms are attached to adjacent carbon atoms, such as HO–C–CO. However, exceptions to this generalisation are also known [10]. It has been suggested that retardation is due to adsorption and chelation of the organic admixtures on the surface of cements and hydration products. Ions of calcium, alumina, silica and iron are all potentially capable of chelating with organic compounds.

In practice, the most widely used retarders are chiefly hydroxyl carboxylic acids or their salts. It is reported that malic and tartaric acid retard the hydration of cements [1,2]. The retarding effect of tartaric acid has been studied in detail, and it was speculated that retardation may be due to the formation of a very stable chelate with alumina $\{\mathrm{Al\,(tartarate)}_3^{3-}\}$ [1]. However, the retarding effect of malic acid (MA) during the hydration of cements has not been studied in detail. The purpose of this article is to study the effect of MA on the hydration of ordinary Portland cement (OPC).

2. Experimental

2.1. Materials

OPC (Prism) was used for detailed hydration studies. The oxide and mineralogical compositions of the cement are given in Tables 1 and 2, respectively.

Malic acid (CDH) was used as an admixture. The concentration of MA is expressed as weight percent with respect to cement.

2.2. Methods

To prepare hydrated samples, 10 g of cement was taken in polythene bags and 5 ml water was added in each bag to have a water to cement (w/c) ratio of 0.5. It was thoroughly mixed by hand for 5 min. Air was removed from the bag to avoid carbonation and then the bag was sealed. In a similar fashion, hydrated samples were made in the presence of MA of different concentrations with a w/c ratio of 0.5. The MA concentration was with reference to cement. Hydration of OPC in polythene bags at room temperature (30 ± 2 °C) was

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Table 1
Oxide composition of Portland cement

Oxide	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	TiO_2	PbO	ZnO	MnO	P_2O_5	SO_3
Composition (wt.%)	19.75	4.84	3.26	62.66	4.19	0.54	0.06	0.44	0.07	0.09	0.15	0.03	2.13

stopped at different intervals of time (1, 3, 7, 15 and 28 days) by washing four to five times with isopropyl alcohol and ether. The hydrated samples were dried at 105 °C in an oven and stored in polythene bags. These bags were then kept in a desiccator.

To have an idea about the extent of hydration, the percentage of free lime (CaO) in the hydrated samples was determined by modified Franke extraction method [11].

Nonevaporable water contents were determined by heating approximately 1 g of the hydrated samples to 105 °C for 1 h and then to 1000 °C for another hour in ceramic crucibles. From the loss in weight, the nonevaporable water contents were determined.

Powder X-ray diffraction (XRD) patterns of both anhydrous and hydrated samples were recorded with the help of an X-ray diffractometer PW 3710 using CuK_α radiation at the Institut für Gesteinshüttenkunde, Technische Hochschule, Aachen, Germany.

Thermogravimetric (TG)/differential thermal analysis (DTA) studies of cement hydrated in the presence and absence of 2.0 wt.% MA for 1 day were made with a NETZSCH STA 409 at a heating rate of 10 °C/min under ambient conditions using Al_2O_3 as reference at the Institut für Gesteinshüttenkunde.

Maximum rise in temperature in the presence of different concentrations of MA during hydration was measured. Ten grams of cement were weighed in polythene bags and kept in a double-walled glass container (thermos flask). Five milliliters of MA solution of different concentrations was added to the cement, and the rise in temperature was measured with a precision thermometer as a function of time.

Pure C_3A was also prepared by preparing a stoichiometric mixture of $CaCO_3$ and Al_2O_3 at 3:1 molar ratio and by repeated firing at 1450 °C in the form of pellets. The free lime was 1.7%. C_3A (5 g) was mixed with 2.5 ml of water solution of 0.5 g MA (w/c = 0.5) and the maximum rise in temperature was noted.

The heat of hydration of cement was determined through a conduction calorimeter at the Institut für Gesteinshüttenkunde. Two grams of cement were weighed in a cylindrical cell and the same amount of finely ground quartz was weighed in another cylindrical cell. The two cells were then separately fitted with a pipette attached to a syringe containing 2 ml of distilled water or 1.0 wt.% MA solution to have a w/c ratio of 1.0. The two cells were then placed in a calorimeter kept at a constant temperature (20 °C). On thermal equilibration, water or MA solution was injected into the cells containing cement and quartz and the calorimeter chamber was shaken for 1 min for mixing. The rate of heat changes was recorded with a computer.

Table 2
Mineralogical composition of Portland cement (Bogue calculation)

Phase	C_3S	C_2S	C_3A	C_4AF
Composition (wt.%)	67.8	5.51	7.31	9.92

Ca^{2+} ion concentrations in the liquid phase extracted from the hydrating cement were determined by titrating against 0.01 N EDTA solution using Eriochrome Black T indicator.

Water consistency, setting times and compressive strengths were determined per Indian Standard IS 4031-1988 (Methods of Physical Tests for Hydraulic Cements). Compressive strengths of cement moulds (2 × 2 × 2 $in.^3$) were determined at different intervals of time. In the cement moulds, in the presence of 0.5–2.0 wt.% MA, cracks were developed within 1 or 2 days, and hence compressive strengths could not be determined. White solids came out from the moulds through the cracks and these were analysed by XRD technique.

UV–visible spectra of 0.4 wt.% MA solution was recorded with a Hitachi-U.2000 UV–visible spectrophotometer in the wavelength range of 190–500 nm. MA (0.4 wt.%) was mixed with OPC (w/c = 10.0) and the mixture was filtered after 2 and 60 min. The spectra of the filtrates were recorded.

IR spectra of OPC hydrated for 1 day in the presence and absence of MA were recorded in KBr phase.

Scanning electron microscopic (SEM) photographs of the hydrated samples (w/c = 0.5) were recorded.

3. Results and discussion

To determine the extent of hydration in the presence of different concentrations of MA, the nonevaporable water contents (W_n) were measured (Fig. 1). In the case of control, the values increased as the time of hydration

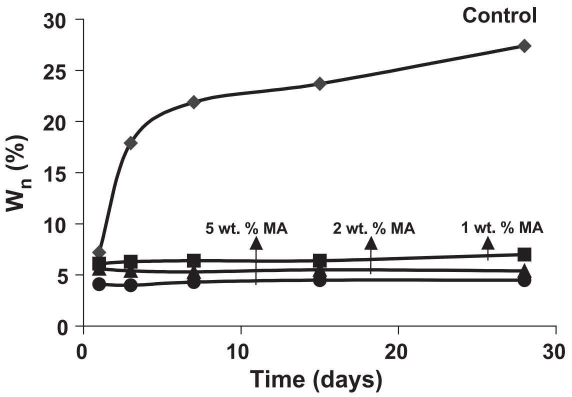


Fig. 1. Variation of nonevaporable water contents with hydration time.

Table 3
Effect of malic acid on water consistency and setting time

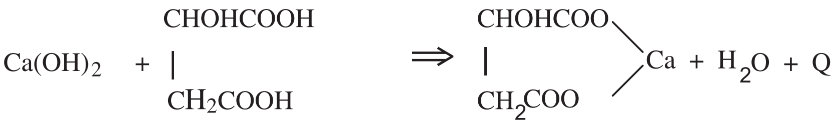
Concentration of MA (%)	w/c	IST (min)	FST (min)
0.0	0.304	155	250
0.5	0.288	198	273
1.0	0.304	446	531
2.0	0.344	475	590
3.0	0.336	227	337
4.0	0.360	15	30
5.0	0.400	8	19

progressed, indicating that the degree of hydration increased with hydration time. However, in the presence of 1.0, 2.0 and 5.0 wt.% MA, the W_n values were much lower and remained practically constant during 28 days of hydration, indicating that MA at all the concentrations acts as a strong retarder for the hydration of OPC. Free lime determinations also showed that in the presence of MA very little $Ca(OH)_2$ is formed, indicating again a strong retardation of hydration of OPC.

Variations of water consistency and setting time with MA concentration are given in Table 3. Up to 2.0 wt.% MA concentration, there is a continuous increase in both initial and final setting times indicating that MA retards the setting. Above 2.0 wt.% MA concentration, the setting time values decrease considerably. At 5.0 wt.% MA concentration, initial and final setting times become as low as 8 and 19 min, respectively. With the increase in MA concentration there is a rapid and high increase in temperature during the hydration, and this high temperature may be responsible for the decrease in setting time. In the presence of MA (5.0 wt.% and above), the setting time is decreased; however, hydration is retarded as indicated by nonevaporable water content and free lime determinations.

When solutions of different concentrations of MA were added to OPC, the temperature rose considerably indicating that chemical reactions occur. The maximum rise in temperature was obtained within 2 min of hydration. The variation of maximum rise in temperature with MA concentration is shown in Fig. 2. As the concentration is increased, the maximum rise in temperature is also increased. In the presence of 20 wt.% MA, the maximum rise in temperature was about 30 °C. The rise in temperature may be due to the following reasons.

(1) During hydration, an alkali $Ca(OH)_2$ is formed and this may react with MA evolving heat of neutralisation *Q*. Because in the presence of MA there is very little formation of $Ca(OH)_2$, such rise in temperature is not expected due to neutralization reaction only. The reaction will certainly occur, but the contribution toward temperature rise will be very small.



$$\mathrm{Ca(OH)_2} + \begin{array}{l}\mathrm{CHOHCOOH}\\ |\\ \mathrm{CH_2COOH}\end{array} \Rightarrow \left.\begin{array}{l}\mathrm{CHOHCOO}\\ |\\ \mathrm{CH_2COO}\end{array}\right\rangle \mathrm{Ca} + \mathrm{H_2O} + \mathrm{Q}$$

(2) The second possibility is that there is adsorption of MA on the surface of OPC with the evolution of heat. Again, the heat of adsorption will not be as high as it is detected.

(3) The MA may interact chemically and form a compound with some of the components of the OPC, thus causing a temperature rise. The higher the concentration of MA, the greater will be the amount of compound formed and the higher the rise in temperature. Since the maximum rise in temperature occurs within 2 min, the compound formation must occur very rapidly. The compound formed may hinder the hydration of OPC, and MA will act as a strong retarder for hydration. It is already reported that aluminium forms a stable chelate with tartaric acid [1]. However, XRD studies have shown that aluminate (C_3A) does not form any compound with MA. This has further been confirmed by the temperature rise measurements. When 2.5 ml of water solution containing 0.5 g MA was added to 5 g C_3A, a temperature rise of 13.5 °C was observed. This temperature rise was also observed in the absence of MA indicating that there is no interaction of MA with C_3A.

The rate of heat evolution is shown in Fig. 3a and b. In the case of control, as soon as OPC comes in contact with water, there is a rapid rate of heat evolution as a result of cement wetting and dissolution of ions. This immediately decreases to a very small value and remains practically constant up to 1 h (induction period) (Fig. 3a) and then increases with a broad peak at around 15 h of hydration (Fig. 3b). After this, the heat evolution decreases continuously. After the induction period, the increase in the rate of heat evolution is mainly due to the hydration of the silicate phase. However, in the presence of 1.0 wt.% MA there is a

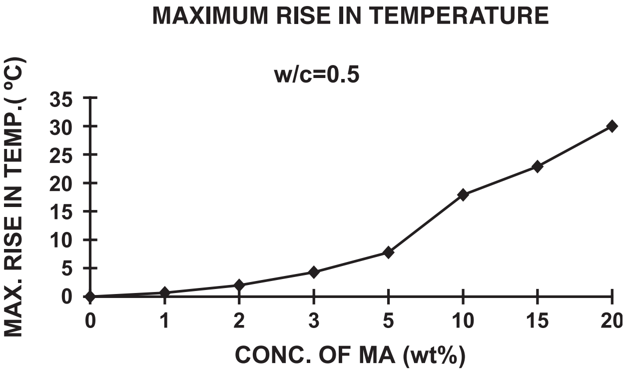


Fig. 2. Variation of maximum rise in temperature during the hydration of cement in the presence of different concentrations of MA.

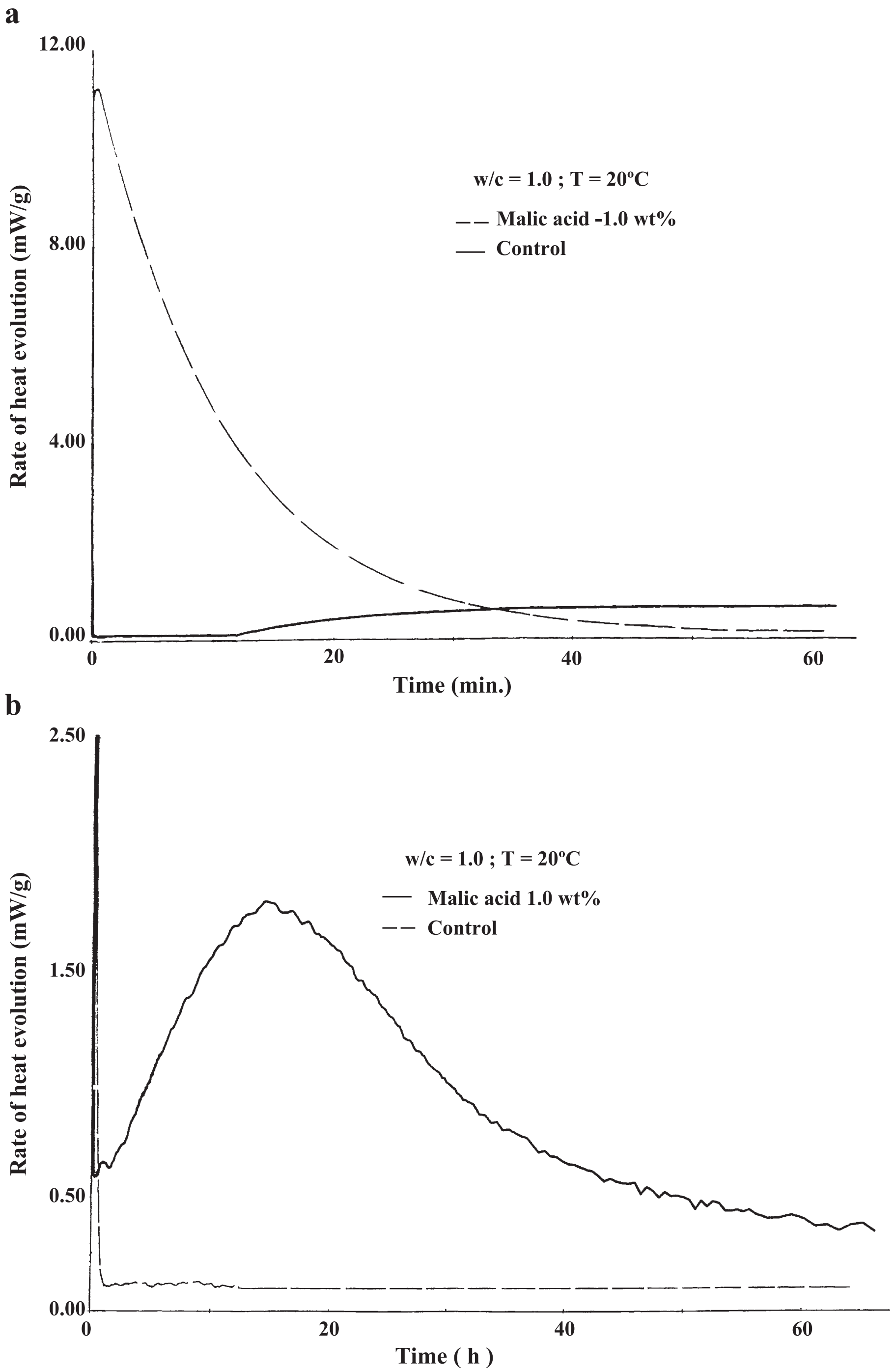


Fig. 3. Rate of heat evolution during the hydration of cement. (a) Rate of heat evolution up to 60 min (time of hydration in minutes). (b) Rate of heat evolution during the hydration of cement for total time period (time of hydration expressed in hours).

rapid heat evolution with a very strong peak at about 1 min of hydration (Fig. 3a); after that it decreases till 1 h of hydration and then becomes practically constant (Fig. 3b). This observation is in support of temperature rise measurements and confirms that MA is a strong retarder for cement hydration. The results confirm that whatever role MA plays for retardation, its influence is due to reaction with cement constituents within 1 or 2 min of the start of the hydration process.

Interaction of MA with cement can be indicated by the increase or decrease of concentrations of certain ions in the liquid phase. With this viewpoint, Ca^{2+} ion concentrations in the liquid phase were determined and its variation with hydration time is shown in Fig. 4. In the case of control, as soon as cement comes in contact with water, Ca^{2+} ions go into the solution. When it is saturated or supersaturated with respect to Ca^{2+} ions, precipitation of $Ca(OH)_2$ takes place. This results in the decrease of Ca^{2+} ion concentration in the

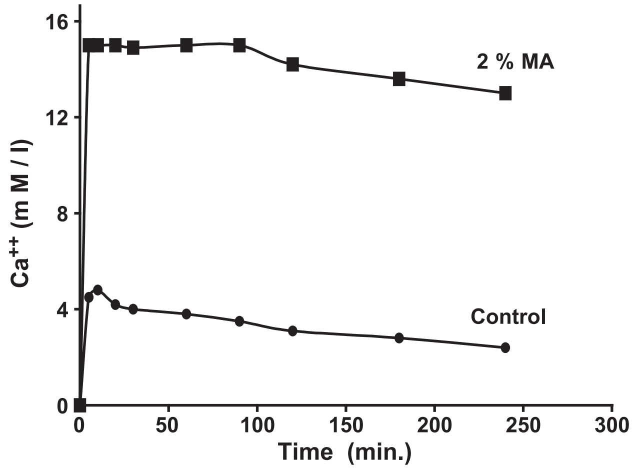


Fig. 4. Variation of Ca^{2+} ion concentration in the liquid phase during the hydration of cement.

liquid phase. In the presence of 2.0 wt.% MA the trend is similar, but the values are higher than those of the control. It appears that MA interacts with cement forming some compound of calcium, which in smaller amounts is soluble. However, when the concentration of this compound is increased, it starts precipitating with the lowering of Ca^{2+} concentration in the liquid phase.

Spectroscopic studies were also made to have an idea about the interaction between MA and OPC. The UV–visible spectra of MA and its interaction product with OPC was recorded. MA solution (0.4 wt.%) showed two peaks at wavelengths 204 and 220 nm. The absorption spectra of the filtrate of 0.4 wt.% MA shaken with OPC (w/c = 10) for 2 and 60 min are both similar and different from those of 0.4 wt.% MA solution. There is a broad peak between 350 and 375 nm and absorbance between 250 and 300 nm is higher than that of 0.4 wt.% MA solution. Below 250 nm the spectrum is similar to that of MA solution. The differences in spectra clearly indicate some sort of interaction between MA and some of the constituents of OPC. However, it is difficult to ascertain the exact nature of the interaction.

The IR spectra of anhydrous OPC and OPC hydrated for 1 day in the presence and absence of 2.0 wt.% MA are recorded. For the anhydrous OPC, bands at 929.8, 527.5 and 462 cm^{-1} are due to the Si–O asymmetric stretching vibration (ν_3), Si–O out of plane bending vibration (ν_4) and Si–O in plane bending vibration (ν_2), respectively. Due to hydration, the Si–O stretching vibration band (ν_3) at 929.8 cm^{-1} is shifted to 960 cm^{-1} with a decrease in intensity. This is due to polymerisation of the SiO_4^{4-} units present in alite and belite with the formation of C-S-H phase [12,13]. However, in the presence of MA this vibration (ν_3) appears at 939 cm^{-1} with almost the same intensity. A shift of only 10 cm^{-1} indicates that the extent of hydration is very low in the presence of MA. Si–O in plane bending vibration at 462 cm^{-1} observed in the anhydrous OPC disappeared due to hydration. This again showed the increased degree of polymerisation of SiO_4^{4-} tetrahedra during hydration. In the presence of MA, there is very little hydration even when this peak disappeared. The disappearance of Si–O in plane bending vibration indicates that MA is interacting with the silicate phase of OPC.

To have an idea about the extent of hydration and the formation of hydration products, XRD patterns of hydrated

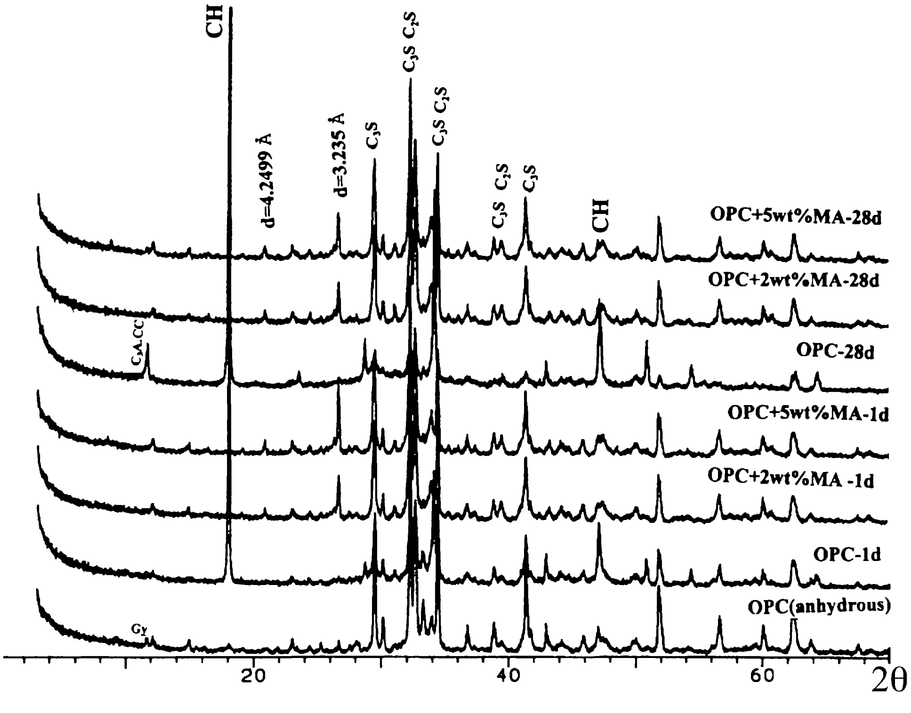


Fig. 5. Powder XRD patterns.

samples were recorded (Fig. 5). In the case of control, over time the intensity of the peak due to CH formation increased, the peak due to gypsum disappeared and the intensity of the peak corresponding to C_3S and C_2S decreased indicating that hydration increases with time. At 28 days of hydration there is a peak at $d = 7.57$ Å that is due to the formation of calcium aluminium oxide carbonate hydrate phase. This phase appears due to the carbonation during hydration. In the presence of 2.0 and 5.0 wt.% MA, there was no formation of CH phase, and practically no decrease in the intensities of C_3S and C_2S phases was observed. This indicated that essentially there was no hydration in the presence of MA. In the presence of MA there were appearances of new peaks at $2\theta = 20.900°$ and 27.550° ($d = 4.2499$ and 3.2350 Å, respectively), the intensity of which increased with the concentration of MA and decreased with the hydration time. The decrease in intensity with time indicates that the compound formed either dissociates or becomes less crystalline. These new peaks are due to the formation of some new compound because of the interaction of MA with one of the components of OPC (probably silicate phase). JC PDS database does not give any information about the compounds having these two peaks. The results show that the compound formed is new. However, a detailed investigation is needed to identify this new compound. This new compound formed may be responsible for the strong retarding action of the MA.

To have an idea regarding the formation of the new compound in the presence of MA, TG/DTA experiments of hydrated samples (1 day) were performed and are recorded in Fig. 6. In the case of control there is a sharp endotherm at 494.5 °C due to the decomposition of $Ca(OH)_2$ and an endotherm at 716.7 °C due to the decomposition of $CaCO_3$ formed as a result of carbonation. The total weight loss at 1000 °C is 10.27%. In the presence of 2.0 wt.% MA at 1 day of hydration, there is no formation of $Ca(OH)_2$, and hence there is no endotherm corresponding to the decomposition of $Ca(OH)_2$. There is a very large exotherm at 475.4 °C and a small exotherm at 556.4 °C. These two exotherms may be due to the decomposition of the new compound formed between MA and some of the phases of OPC.

SEM pictures of OPC hydrated in the absence and presence of 2.0 wt.% MA for 1 day are shown in Fig. 7a and b. In the absence of MA, rectangular crystals are seen indicating that probably ettringites are present. However, XRD studies ruled out the presence of ettringite. These crystals may be due to carboaluminate phase. In the presence of MA, very little hydration has taken place. It appears

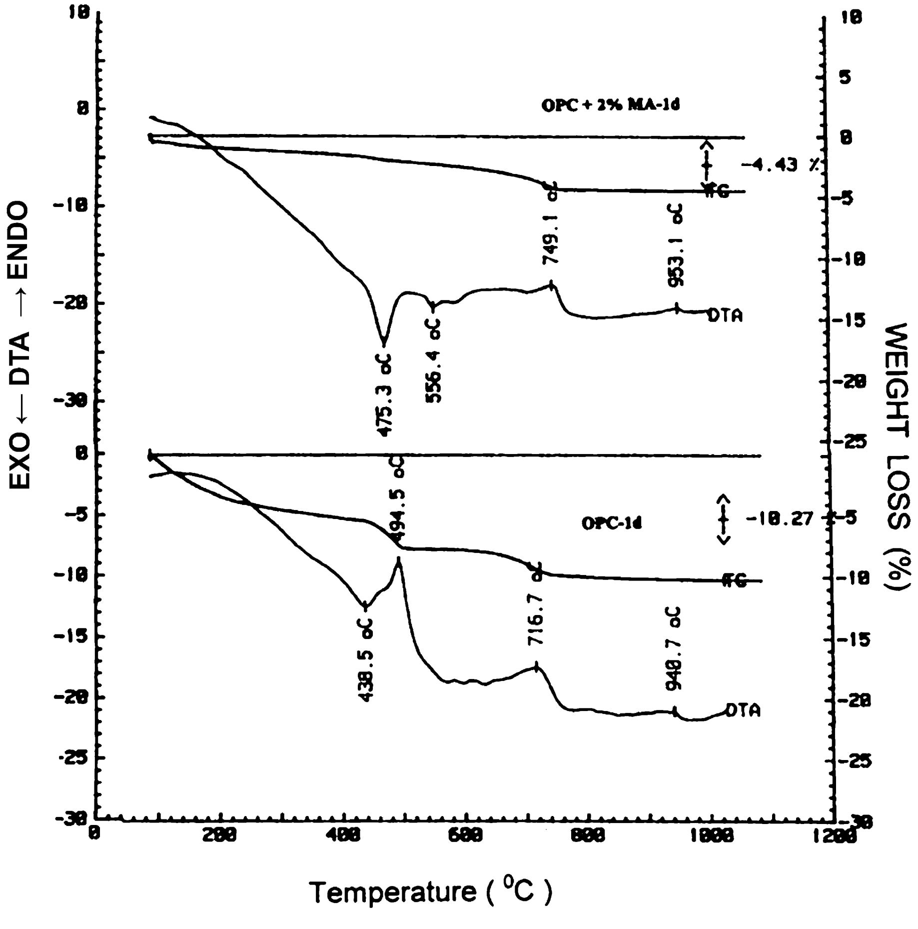


Fig. 6. TG and DTA curves of OPC hydrated for 1 day in the presence and absence of 2.0 wt.% MA.

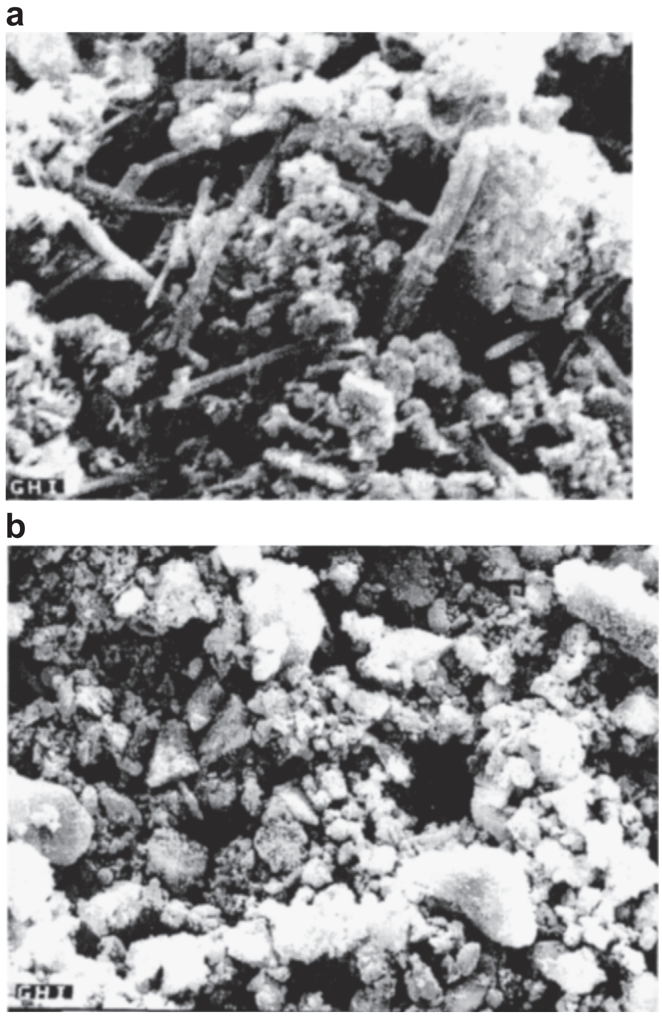


Fig. 7. SEM pictures of (a) cement hydrated for 1 day (w/c = 0.5); (b) cement hydrated in the presence of 2.0% MA for 1 day (w/c = 0.5).

that either MA hinders the hydration of OPC just by adsorption or it is the interaction product of MA with some mineral phases of OPC that is adsorbed on the surface of OPC and retards the hydration.

Compressive strengths of cubes in the case of control were also measured. The values increased with hydration time as is usually expected. However, in the presence of 0.5–2.0 wt.% MA, strengths were not developed in the cubes indicating strong retardation of hydration. After 1 or 2 days in the presence of MA, cracks were formed in the cubes, where white solid appeared. This was confirmed to be $CaCO_3$ by XRD technique. It appears that atmospheric CO_2 entered through the cracks and reacted with $Ca(OH)_2$ forming $CaCO_3$.

4. Conclusions

The results have shown that MA is a strong retarder for the hydration of cement. Spectroscopic studies have shown that some sort of interaction occurs between MA and some mineral phases of OPC (silicate phase) leading to the formation of some new compound. Liquid phase analysis has confirmed the formation of some soluble calcium compound of MA. XRD and DTA studies have supported the formation of a new compound in the presence of MA. The new compound formed may be responsible for the retardation of hydration of the cement.

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