Cement & Concrete Composites **14** (1992) 235–238

Chemical Composition of Mortars from the Ganga Canal System

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Abstract

Investigations of the chemical composition of the lime mortars from the Ganga Canal System do not indicate the presence of any calcium hydroxide in the free state. The samples, however, were found to be heavily carbonated, and several compounds have been indicated.

Keywords: Lime, burnt clay (surkhi), mortar, plaster, compressive strength, free lime, pozzolana, pH, chemical composition, X-ray diffraction.

INTRODUCTION

Fat lime, in conjunction with burnt clay (surkhi), has been utilized as a cementing material in India since very early times.[1] Numerous types of structures made in lime–surkhi have braved the ravages of centuries and are in service in excellent shape. A study of the extent of deterioration of the mortars in one of the oldest of such systems — the Ganga Canal — has recently been undertaken.[2]

Marchese[3] examined some ancient Italian non-hydraulic lime mortars and reported the presence of non-crystalline calcium hydroxide therein. Newton and Sharp[4] investigated some Renaissance lime plasters in the UK, and found little calcium hydroxide, either crystalline or amorphous.

During the course of our investigation of the mortars of the Ganga Canal System, we have made some interesting observations and these are reported here.

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GANGA CANAL SYSTEM

The Ganga Canal, one of the oldest water-carrying systems in India — the main canal stretches over 563 km and carries as much as 6750 cusecs of water — was constructed between AD 1839 and 1858. In all the canal works, lime and surkhi mixtures were used as the mortar.[5] Lime was obtained through calcination of highly calcareous limestone from the quarries of Dehradun or collected from river basins in the area; it generally is fat. Enhancement in hydraulic strength was achieved through the incorporation of surkhi and wet grinding of the mortar. Generally, one part of surkhi was mixed with one part of lime by volume.

EXPERIMENTAL

Twenty-five samples of the mortars were collected from different locations. These were subjected to thermogravimetry (TG) and differential thermogravimetry (DTG) analysis and differential thermal analysis (DTA), using an STA-1500. Simultaneous Thermal Analyser. The rates of heating were maintained at 10°C/min and the temperatures were measured with a platinum/platinum-rhodium thermocouple. A sample of alumina was used as the reference material. The X-ray diffraction (XRD) patterns were obtained by means of a Phillips X-ray diffractometer (Model PW 1730), using Ni-filtered CuK_α radiation. The powder specimens were placed in a recess in a plastic plate, and compacted under sufficient pressure to cause cohesion without the use of a binder. The results obtained were compared with data from the ASTM powder diffraction file.

To estimate free lime, 1 g of sample was refluxed with 10 ml of acetoacetic ester and 60 ml

Cement & Concrete Composites 0958-9465/93/$6.00

of isobutyl alcohol for 2 h, cooled, filtered under vacuum and titrated against standard perchloric acid solution, using Thymol Blue as indicator. The results are reported in Table 1.

For the determination of pH, 25 g of powdered samples were shaken for 2 h with 100 ml of double-distilled water, allowed to stand for 22 h, filtered and the pH determined (Table 1).

The results of investigations on three typical cases are reported below.

RESULTS AND DISCUSSION

The most prominent observation in DTA curves (Fig. 1) is a very strong endothermal effect observed between 734 and 832°C, characteristic of calcium carbonate decomposition. This observation is supported by strong peaks in the XRD (Fig. 2) TG (Fig. 3) and DTG (Fig. 4) curves. These changes can be assigned to the decomposition of the mineral calcite.

The DTA curves also show (i) fairly well-developed endotherms in the region 686–695°C; (ii) a weak yet sharp endotherm around 575°C; and (iii) a sharp exothermal effect at 174°C (only in one sample). The TG and DTG analyses show weight losses corresponding to (i) and (iii) only. Of these, the endotherms at 575°C (not shown by DTG) can be assigned to transformation of quartz. This fact is also strongly supported by the XRD results.

Table 1. Free lime contents and pH values of the samples

Sample	*Free lime (%)*	*pH*
LM-1	0·11	7·4
LM-2	0·15	7·8
LM-3	0·13	7·6

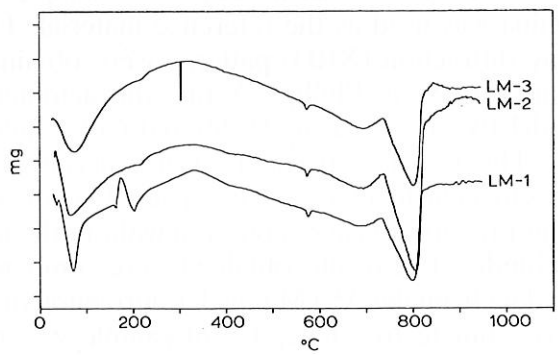

Fig. 1. Differential thermal analysis curves.

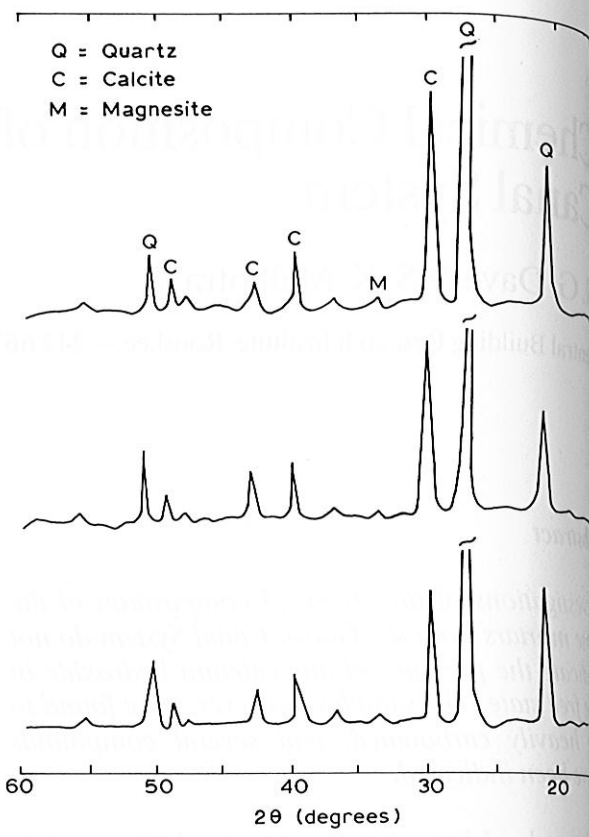

Fig. 2. X-ray diffraction curves.

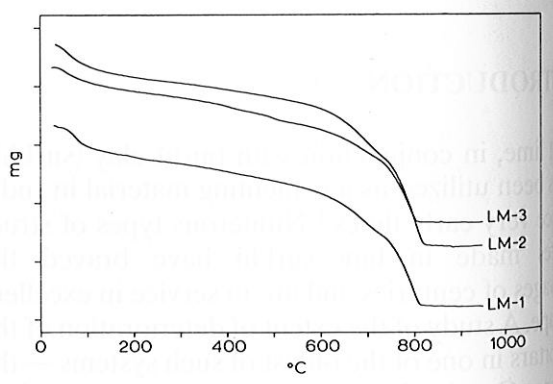

Fig. 3. Thermogravimetry curves.

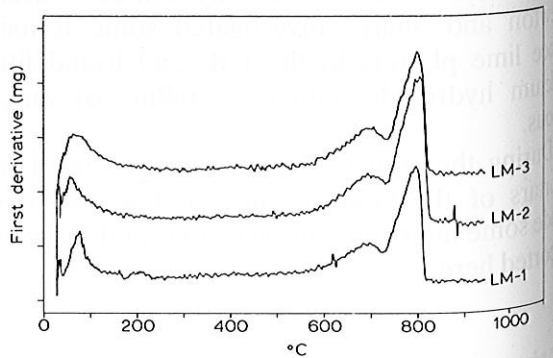

Fig. 4. Derivative thermogravimetry curves.

The exothermic peak around 174°C in sample LM-1 is also accompanied by a loss in the DTG curve. This appears to be due to the ignition of cellulosic material, which, as shown by the records,[5] was incorporated in the mortar in accordance with local practice.

Broad endothermal valleys observed in the DTA curves between 660 and 760°C, and supported by corresponding weight loss in TG curves, appear to have another explanation. In the pastes of lime and surkhi, atmospheric carbon dioxide enters by dissolution in water and is converted into HCO_3^- and CO_3^{2-} ions. These ions interact with Ca^{2+} present in the solution and generate sparingly soluble $CaCO_3$. As the reaction is exothermic, it results in the evaporation of water, thereby suddenly changing the concentration of calcium carbonate in solution and causing precipitation of amorphous or poorly crystalline material. The process is repeated continually. Even after the paste has set, the reaction continues in capillaries. Considerable quantities of such amorphous calcium carbonate can be produced — especially under tropical conditions. Cole and Kroone,[6] in their studies on the mortars of Portland cement, also observed this type of carbonate, and Moorehead[7] reported evidence for such calcium carbonate.

In these samples, the XRD, DTA and TG results gave no indication of the presence of calcium oxide or calcium hydroxide. 'Free lime' contents of these samples were determined by a modified Franke method,[8] and the results are given in Table 1. The pH values of the aqueous extracts were determined and are also reported in Table 1. Phenolphthalein tests were also found to be negative. All these experiments indicate the absence of free lime in any significant quantity.

It appears that in these types of mortars any protective mechanism for calcium oxide has not been operative. The presence of pozzolana particles resulted in the outer calcite layer becoming discontinuous and led to the formation of a large number of capillaries through which carbon dioxide could penetrate. Goodbrake *et al.*[9] also found the permeability of the mortars to be sufficiently large to allow atmospheric carbon dioxide to penetrate and convert calcium hydroxide into calcium carbonate. Consequently, it appears difficult to agree with the postulates of Marchese[3] or Lea.[10] These mortars seem to be similar in composition to some of those reported by Newton and Sharp.[4,11]

The XRD patterns also indicate the presence of small amounts of magnesite at 33° 2θ in all three samples, whereas there is no evidence in TG or DTG curves. Newton and Sharp[4] made the same observation in the TG curves of plasters with low magnesium content.

The records[5] show that the actual amounts of pozzolanic materials incorporated into these mortar mixtures were not substantial — at any rate, they were far from the optimum ratios of one part of lime to about three parts of pozzolana. Moreover, the pozzolanas were obtained by grinding bricks and consequently were not of very high reactivity. Considerable fractions of lime may therefore fail to enter into hydraulic reactions and may actually behave as a non-hydraulic lime. This is probably why there is little evidence of the presence of products of hydraulic reaction.

CONCLUSION

The plasters from the Ganga Canal System are heavily carbonated. There is no evidence of calcium hydroxide being present. On the other hand, there is evidence of the presence of poorly crystallized or amorphous calcium carbonate; this could have resulted from sudden changes in concentration of calcium carbonate or the carbonation of amorphous calcium hydroxide as it formed. The reaction products of lime and silica and/or lime and alumina reactions are scarcely present.

As the reactants are present in far from optimum concentrations, the hydraulic constituents may not have been formed in large quantities. Alternatively, they also might have undergone carbonation.

ACKNOWLEDGEMENTS

This work was carried out in the laboratories of the Central Building Research Institute, Roorkee, and is published with the permission of the Director. The authors also thank Dr J. M. Bhatnagar for carrying out XRD analyses.

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