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REPRINT

A note on the occurrence of crystals of calcium hydroxide and ettringite in voids in hardened Portland cement paste

by J. E. Gillott, B.Sc., M.Sc., Ph.D. and T. Ritchie, B.A.Sc.

NATIONAL RESEARCH COUNCIL, CANADA : DIVISION OF BUILDING RESEARCH

SUMMARY

The occurrence of crystals of calcium hydroxide and of ettringite (calcium sulphoaluminate) in hardened Portland cement, reported previously by others, is confirmed. Samples of hardened Portland cement paste prepared half a century ago at one of Canada's earliest cement plants were, on examination, found to contain voids in which well developed crystals had formed. The crystals occurred as thin plates and needles that were identified by optical microscopy and X-ray diffraction as calcium hydroxide and ettringite, respectively. It is of interest that the calcium hydroxide had not been altered to carbonate even though the cement samples had been stored for a long time under conditions that would be expected to promote this change.

Cement samples

In the course of a study of the history of the manufacture of cement, a visit was made to the site of one of the first plants to produce Portland cement in Canada, that at Marlbank, Ontario, situated about 30 miles north-west of the city of Kingston. This plant had been constructed in 1891 and operated until 1914. In common with other early Canadian cement plants its manufacturing process was based on the use of marl and clay as the raw materials. During the examination of the ruins of the plant, test samples of cement were found that were of particular interest because of their age.

Two types of cement sample were obtained. " Pats " of neat cement paste about 3 to 4 in. in diameter and about ½ in. thick at the centre had been prepared in the plant laboratory to test the cement for time of setting. Similar pats were used to test it for soundness. Other samples were made of neat cement paste in " butterfly " shape, 1 in. square section at the narrowest point, for use in tests of the tensile strength of the cement. The samples had been used in the routine testing of cement and, after test, had been discarded on a slope near the laboratory. When they were gathered in 1963 they had lain on the ground for at least 49 years and at the most for 72 years; a few were dated 1909.

When cut by means of a diamond-bladed saw, it was observed that most of the samples contained small voids scattered throughout. Examination by means of the binocular microscope revealed well developed crystals of two kinds in the voids. The first occurred as very thin plates, which frequently extended from one side of the void to the other. These crystals were present in considerably larger quantity than the second kind, which occurred as radiating clusters of needles or spherulites (Figure 1).

Previous studies of hardened Portland cement have shown that calcium hydroxide forms as a result of the

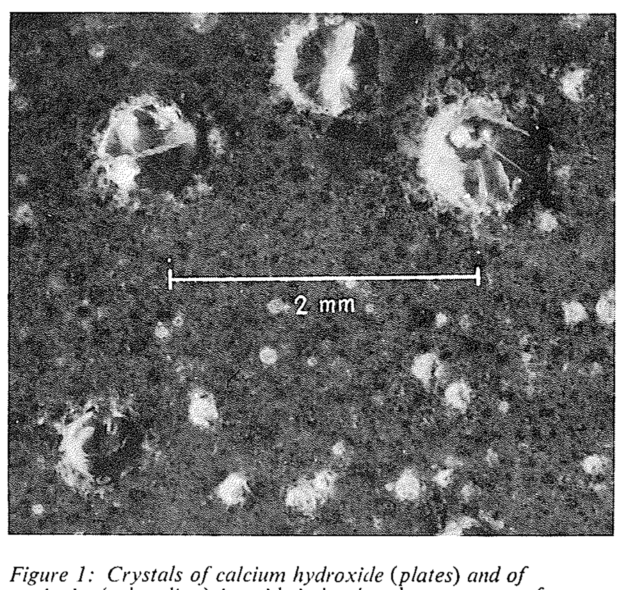

Figure 1: Crystals of calcium hydroxide (plates) and of ettringite (spherulites) in voids in hardened cement paste from Marlbank, Ontario, Canada.

hydration process and occurs as the only crystalline material readily detected under the microscope, although occasionally ettringite may be found.[1] The calcium hydroxide in set Portland cement usually takes the form of thin hexagonal plates[1], generally forming in hollow spaces[2]; ettringite occurs as clusters of needles radiating from a point[3].

Identification of crystals

The acicular and platy crystals were removed from the voids by the use of a needle under a binocular microscope. Initially no attempt was made to separate the two types and an X-ray powder photograph of the composite sample was taken with CuKα X-radiation, using a Nonius-Guinier quadruple-focusing camera. All the lines on the diffraction pattern obtained could be matched with calcium hydroxide, and it was concluded that the needle-like phase was present in an amount insufficient to register a pattern in competition with the dominant phase. A more careful separation was therefore made, restricting the concentrate as far as possible to the needle-like crystals. This was done by means of a glass fibre coated with a thin film of silicone grease so that the crystals would adhere. A Debye-Scherrer powder photograph was obtained from this material and the measured *d*-values were found to correspond closely with those published by the American Society for Testing and Materials for ettringite.[4] The identification was confirmed by examination of the crystals under the petrographic microscope. The crystals showed straight extinction, low birefringence, negative sign of elongation and refractive indices in agreement with published values for ettringite.[3,5,6]

It is of interest that on the X-ray powder pattern of the calcium hydroxide no lines were found that could be matched with calcium carbonate. As the samples are relatively thin and had lain on the ground under moist conditions in the presence of decomposing vegetation, one might have anticipated considerable carbonation.[7] It apparently had not progressed far enough, however, in a 50-year period to register as calcium carbonate even on an X-ray photograph of a concentrate of calcium hydroxide, normally regarded as the phase in Portland cement that is most reactive with carbon dioxide.

Conclusions

This study confirmed that crystals of calcium hydroxide and ettringite form in voids in hardened Portland cement. The crystals were found in samples prepared at least half a century ago and it is of interest that in this long period of time the calcium hydroxide apparently had not been altered by carbonation, even though the samples of cement were relatively thin ($\frac{1}{2}$ in.).

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