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CRACKS IN SOREL'S CEMENT POLISHING BRICKS AS A RESULT OF MAGNESIUM OXYCHLORIDE CARBONATATION

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ABSTRACT

A magnesium oxychloride polishing brick showed, after five months, both original planes bent towards the same side and two perpendicular systems of cracks. A powdered sample of the crust treated with distilled water, revealed two sedimentary layers. Brucite, oxychloride form 3, chlorocarbonate and traces of form 5 were identified in the lower level. Periclase, F5 and brucite were identified in the upper level.

The association of F3 with the basic chlorocarbonate suggests that the carbonatation takes place on this form. This carbonatation implies an increase volume producing enough stress to provoke the observed cracks. The CaO impurities yield aragonite, so this is formed simultaneously with chlorocarbonate due to the atmospheric CO_2 and magnesium ions act as inhibitors of the calcite formation.

Introduction

Magnesium oxychloride or Sorel's cement, may present four different forms (F2, F3, F5 and F9) which are named by the number of $Mg(OH)_2$ moles appearing in its formula in relation to each $MgCl_2$ mole (1). Form 3 and form 5 of oxychloride are the only stable ones at room temperature (< 100°C) (2).

This paper is a part of a wider research programme focused on improving the performance of the polishing bricks and therefore, all the materials employed have an industrial quality.

This paper deals with an unusual oxychloride application. Here the abrasive particulate is bonded by Sorel's cement in one type of polishing brick for ornamental stones.

Sometimes and after a storage period some cracks appear in unworked polishing bricks. These cracks impair the cement cohe-sion and consequently its mechanical performance shortening the working life of the brick.

This paper seeks to provide insight into the reason for the appearance of bent surfaces and cracks in the bricks.

Materials and Methods

Caustic-calcined magnesia (MgO) and magnesium chloride were mixed with water excess necessary for workability of paste, i. e., 7:1:13 molar ratio respectively.

The bricks after setting were packed inside a box. The pieces were in the form of an isosceles triangle with the following dimensions: b= 7.5 cm, h= 17 cm and 6.5 cm in thickness (Fig. 1A).

One piece (reference 94-4) was tested after five months. The two planes defined by the two equal sides of the isosceles triangles were remarkably bent toward the same side showing a concave and a convex surface (Fig. 1B).

Moreover a system of cracks more or less parallel to the bending axis and one very long and wide crack nearly perpendicular to the aforementioned system appeared on the convexly bent face.

It should be pointed out that there was a difference of colour between the core and the crust of the brick. The former was grey and the latter was dark-grey.

The crust of the concave surface was almost 1 cm thick, whereas the crust next to the convex surface exceeded 3 cm in thickness.

About 10 g of the crust powdered sample were placed inside a beaker with distilled water in an attempt to separate the brick cement phases.

The sample was leached several times by decanting the liquid. The solid residue was dried at room temperature. The sediment obtai-ned had a very typical distribution, with pronounced layers:

1 - The thicker lower level had a coarser grain size and was dark-grey in colour at the bottom of the beaker.

2 - The thinner upper level which was grey in colour had a smaller grain size showing the typical desiccation cracks.

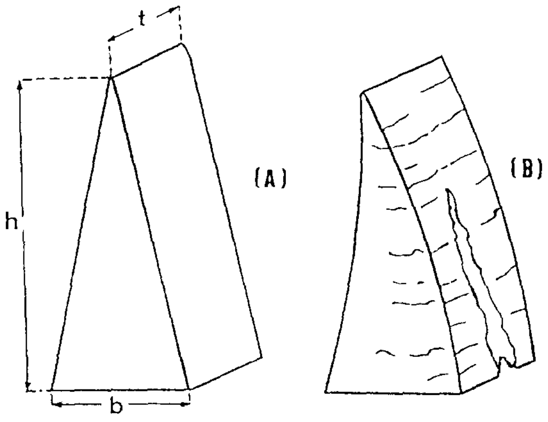

FIG. 1.

A - Shape and dimensions of a polishing brick, t = 6.5 cm, h = 17 cm, b = 7.5 cm.
B - shape of the brick after five months.

Both samples were gently ground by hand in order to avoid any transformation produced by the mechanical grinding. The crystal-line phases of different samples were identified by X-ray diffraction with a Siemens D500 automatic equipment coupled to a graphite monochromator for copper Kα radiation.

Results and Comments

The XRD identified phases in the lower level were: brucite, oxy-chloride form 3, aragonite, chlorocarbonate and traces of form 5.

The XRD identified phases in the upper level were: periclase, oxychloride form 5, brucite and traces of chlorocarbonate.

The coarsest fractions are the first to descend in any sedimen-tation process; therefore form 3 and chlorocarbonate had the largest grain size. This indicates that the carbonatation acts as a binder of particles producing aggregates of the two phases.

The identified active phases in the light and dark-grey samples are shown in Table 1, where a sharply increasing amount of basic magnesium chlorocarbonate may be observed in the dark-grey sample (traces increase to 789 c/s).

At the same time a sharp decrease in the highest intensity peak of F3 oxychloride is produced (557 c/s decreases to 127 c/s). It goes without saying that, the carbonatation takes place because of the CO_2 atmospheric action on form 3 in accordance with (2):

$$3Mg(0H)_2.MgCl_2.5H_2O + 2CO_2 \rightarrow$$
$$Mg(OH)_2.2MgCO_3.MgCl_2.6H_2O + H_2O$$

The fact that the two original symmetrical sloped faces (Fig.1A), were bent (Fig. 1B) indicates that there was a greater stress increase near the convex surface where the carbonatation is very strong as it is corroborated by the greater thickness of the dark-grey zone.

The carbonatation effect and the structural rearrangement would mean an increase in volume to produce stress that is sufficiently strong stress to cause the cracks.

Aragonite together with chlorocarbonate have only been identified in the dark-grey side of the sample, suggesting that the forma-tion of both carbonates was the result of two simultaneous pro-cesses.

The caustic-calcined magnesia is normally intermixed with calcium oxide as an impurity. Quick lime is more active than magnesium oxide so it could be inferred that given the large amount of wa-ter in the process to obtain oxychloride, the former is rapidly hydrated yielding portlandite [$Ca(OH)_2$]. The carbonatation of this hydroxide yields aragonite. This calcium carbonate poly-morph is widespread throughout the dark-grey colour mass. Despite the

TABLE 1

Active Phases Identified by XRD at the Two Sedimentary Layers. T: Majority Traces. t: Minority Traces, c/s: Counts Per Second

	Basic chlorocarbonate	Brucite	F3
Light-grey	t	T	557 c/s
Dark-grey	789 c/s	t	127 c/s

fact that the increase in CaO volume for yielding aragonite is about 160 %, the effect of its formation on the stress occur-rence would be negligible due to the small amount of calcium oxi-de impurities.

Slaked lime would normally generate calcite in the absence of an inhibitor agent like the magnesium chloride. Obviously the whole brick mass is rich in this chloride.

A lot of work has been carried out on magnesium ion as inhibitor of calcite formation. In this study we only refer to the most relevant papers on this subject (3, 4, 5, 6, 7, 8, 9).

The association of F3 with chlorocarbonate suggests that the carbonatation chiefly takes place on form 3 of oxychloride.

The free chlorocarbonate upper leve suggests that the carbona-tation of the oxychloride form 5 is more difficult. In other words, it is more stable than form 3. On the other hand form 5 would be protected by $Mg(OH)_2$ produced in its carbonatation process. This compound would coat the grains protecting them from the subsequent CO_2 action.

References

1. M.T. Ball, Cem. Concr. Res. 7, 575 (1977).
2. T. Demediuk, W.F Cole and H.V Heuber, Austr. J. Chem. 8, 215 (1955).
3. H. Leitmeier, Neues Jahrb. Mineral. 49 (1910).
4. H. Leitmeier, Neues Jahrb. Mineral. Bd. 40, 655 (1916).
5. J.W. Murray, J. Geol. 62, 481 (1954).
6. A.J. Eardley, Bull. Am. Ass. Petroleum Geol. 22, 1359 (1938).
7. D. Neev and K.O. Emery, Israel Geol. Survey Bull. 41, (1967)
8. P.H. Managhan and M.L. Lytle, J. Sediment. Petrol. 26, 111 (1956).
9. F. Lippmann, Sedimentary Carbonate Minerals, p 110, Springer-Verlag, Berlin, Heidelberg, New York (1973).