

Investigation of Resistance of Cement Paste to Sulfate Attack

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•THE PRELIMINARY test described here was carried out to investigate the effect of the "density" of the cement paste on the course of the reaction, partly by means of microscopic examination of thin sections from the test specimens and partly by determining the quantity of sulfate consumed. The effect of the metal ions on the course of the reaction was also investigated by storing test specimens in sodium sulfate, magnesium sulfate, ferrous sulfate, and ferric sulfate. The effect of ferric sulfate will not be discussed in this connection.

The test specimens consisted of cement paste cubes with an edge length of 25 mm. Three different w/c ratios were used: 0.38, 0.34 and 0.30 (corrected for bleeding). After 7 days curing in water, the cubes were stored in 0.07 molar solutions of each of the four salts. The solutions were changed each month to keep the concentrations approximately constant.

After the specimens had been stored for about 2 months, systematic determination of the sulfate consumption was commenced. At the same time, the content of non-evaporable water in the cubes was ascertained and found to be $W_n = 0.255$ g/cc paste, regardless of the original w/c ratio. W_n was determined by the method given by Copeland and Hayes (1). There is, thus, every reason to believe that the gel porosity and specific surface of the cubes were identical at this time, regardless of the original w/c ratio, so that only the permeability varied.

RESULTS OF CHEMICAL ANALYSIS

There is a strong increase in the total sulfate consumption in the series, sodium sulfate, magnesium sulfate and ferrous sulfate, but the obvious differences between the solutions become apparent only after some time. The strong increase in sulfate consumption begins first with ferrous sulfate and last with sodium sulfate; the density of the cubes influences the quantity of sulfate transformed, the sulfate consumption being lowest in cubes cast with a w/c ratio of 0.30.

MICROSCOPIC INVESTIGATIONS

Examination of the thin sections showed gypsum is the predominant sulfate reaction product. Ettringite was found only in specimens that had been stored in sodium sulfate and, rather surprisingly, in a specimen stored for 1 month in ferric sulfate. It was further seen that the increases in sulfate consumption determined by chemical analysis coincided with observation of development of cracks in the thin sections.

The micrographs in Figures 1 through 4 give a general impression of how the deterioration appeared in thin sections. All specimens had been stored for 8 months.

Figure 1 shows a crack parallel to and near the surface of a specimen that had been stored in sodium sulfate. The crack is filled with gypsum. Only very limited deterioration appears to have taken place.

Figure 2 shows a corresponding parallel crack in a test specimen that had been stored in magnesium sulfate. The crack perpendicular to the surface is not filled with gypsum; it is probably a shrinkage crack that has occurred during preparation of the thin section. On the right of the photograph (torn off the surface) a band of gypsum and magnesium hydroxide can be seen. The gypsum is always precipitated on the surface and the magnesium hydroxide on the gypsum.

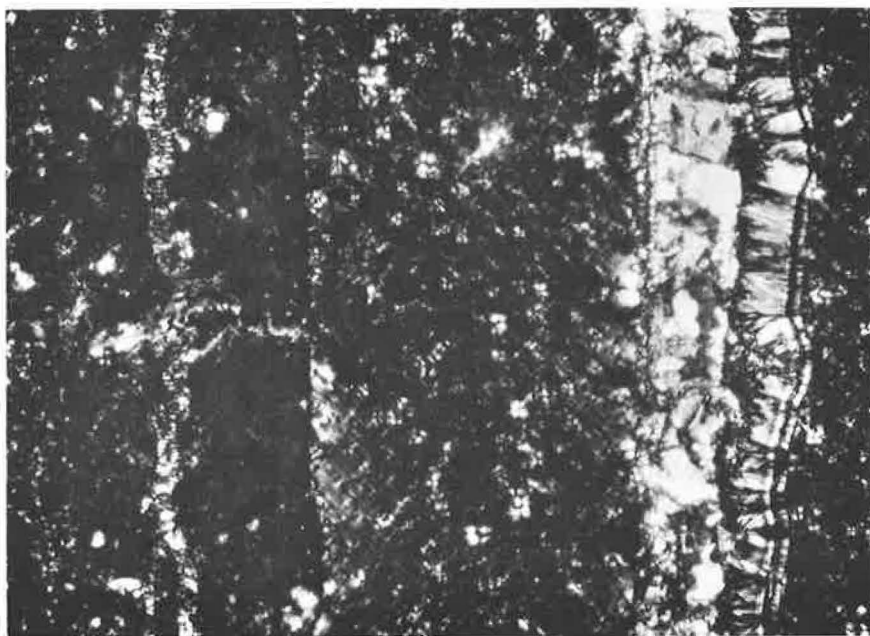


Figure 1. Thin section of cube stored 8 months in sodium sulfate, 120X magnification, parallel nicols.

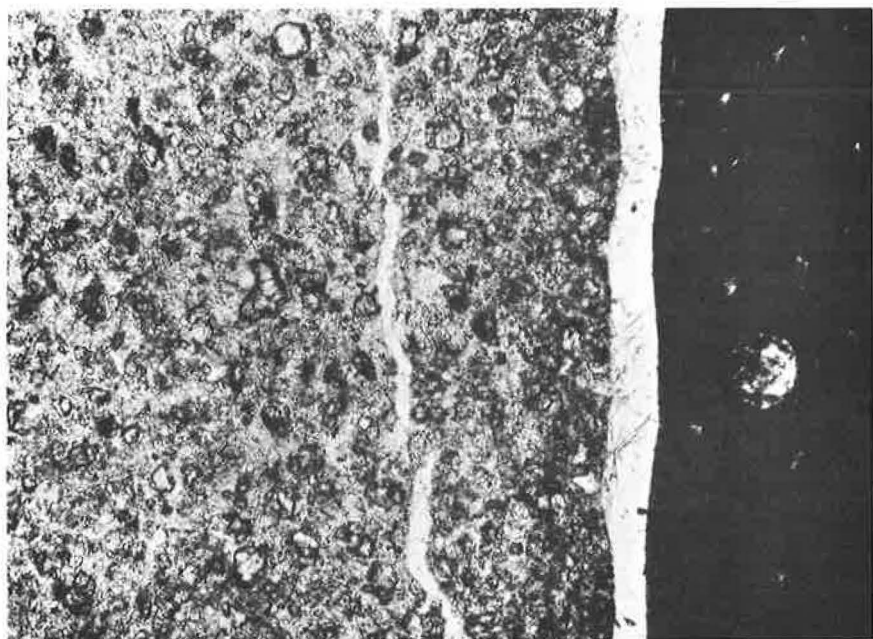


Figure 2. Thin section of cube stored 8 months in magnesium sulfate, 120X magnification, crossed nicols.

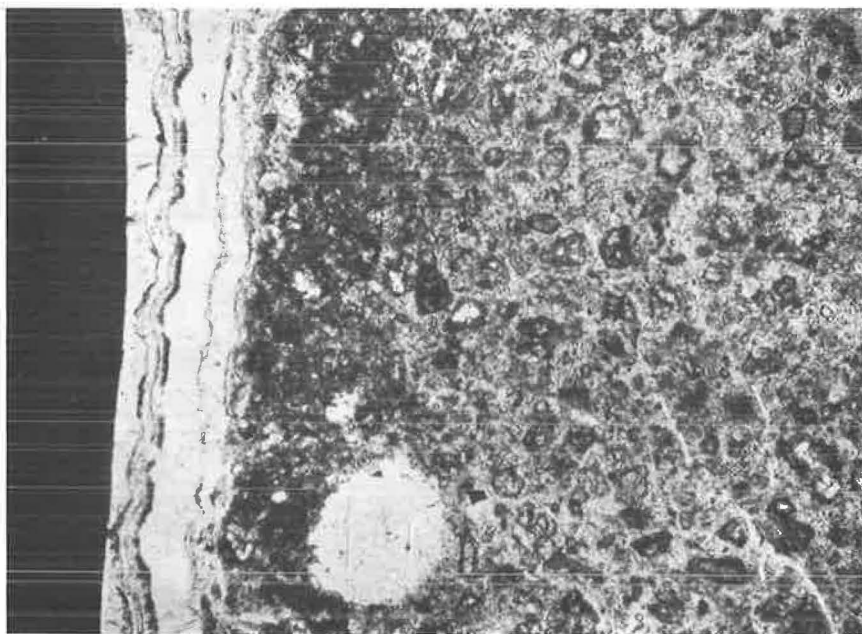


Figure 3. Bubble filled with gypsum in thin section stored 8 months in magnesium sulfate, 120X magnification, parallel nicols.

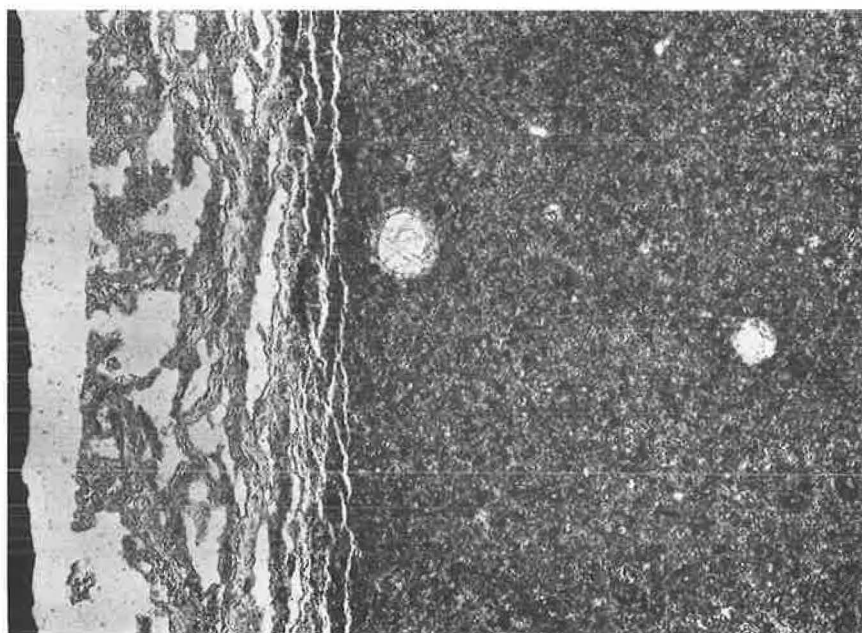


Figure 4. Thin section of cube stored 8 months in ferrous sulfate, 120X magnification, parallel nicols.

Figure 3 shows a bubble, in the same specimen as in Figure 2, that is almost completely filled with gypsum. The thin section gives a reason to believe that almost all magnesium hydroxide is precipitated on the surface; it might, therefore, have been expected that large quantities of ettringite would have formed in such a bubble. However, as can be seen, this is not the case.

Figure 4 shows a test specimen that had been stored in ferrous sulfate. As in other cases, gypsum is the dominant reaction product, together with various unidentified iron hydroxides. The general impression is that the deterioration has been much more comprehensive than in the other solutions.

CONCLUSION

From the rather limited investigations discussed, the following preliminary conclusions can be drawn:

1. All other things being equal, the aggressiveness of the solutions increases from sodium sulfate, over magnesium sulfate, to ferrous sulfate;
2. The resistance of the cement paste can be considerably improved by increasing its "density"; and
3. The thin-section examinations show that ettringite is rarely formed in sufficient quantities to be reasonably considered a cause of the crack formations.

These results seem to warrant more detailed investigation of the importance of the pore structure and the various sulfates to the durability of the concrete. It would be interesting to investigate the effect of ettringite, and to a certain extent the content of C_3A in the cement, on the resistance to sulfate attack. Ettringite crystals found in cracks after storage in sodium sulfate apparently formed after occurrence of the cracks.

REFERENCE

1. Copeland, L. E., and Hayes, J. C. The Determination of Nonevaporable Water in Hardened Portland Cement Paste. ASTM Bull., Vol. 194, pp. 70-74, 1953.