

A staining technique for the identification of sulphates in aggregates and concretes

THE use of small amounts of gypsum and anhydrite as retarders in cements is well known. The presence of large quantities of these minerals leads to the slow expansion of the set cement (Lea, 1970), and in some examples of concretes excess gypsum in the aggregate is an important factor in the chemical reactions that lead to the rapid physical deterioration of the concrete (French and Poole, 1974).

Possible aggregate materials, particularly those from desert regions, sometimes contain gypsum or anhydrite as either sand grade particles (Kukal and Saadallah, 1973) or as veins or cavity infillings in the larger fragments. The importance of correctly identifying these sulphate minerals in aggregates and concretes is obvious, but simple physical tests are not always easy to apply when the minerals are present as fine grains. A simple solution to the problem of identification and assessment of proportion of sulphate mineral present in a given sample is to stain the mineral selectively so that it may easily be distinguished from other grains. A staining scheme for the identification of carbonate minerals devised by Friedman (1959) also included methods for the identification of gypsum and anhydrite. A simplified version of Friedman's scheme has proved very satisfactory for the differentiation between dolomitic and limestone aggregates on a routine basis in our laboratory, but the careful application of the scheme to the identification of sulphate minerals in concrete and aggregate samples has produced inconclusive results. There are relatively few common sulphate minerals that are likely to be present in concretes or concrete aggregates, the most common being ettringite, gypsum, and anhydrite. A simple staining technique has therefore been devised to produce a strong distinctive colour when applied to these minerals.

The staining procedure. An elementary test for the presence of sulphate is the formation of a white precipitate of barium sulphate from a solution containing SO_4^{2-} ions by the addition of Ba^{2+} ions. If such a solution also contains potassium permanganate, the permanganate co-precipitates with the barium sulphate, which will then contain permanganate molecules in the lattice. Thus any sulphates formed under these conditions will be stained purple. This co-precipitation of permanganate with barium sulphate has been adapted as a simple staining technique for the identification of ettringite, gypsum, and anhydrite, which may be exposed on broken surfaces, polished slabs, and sections and as individual grains in powders.

In principle the sample is immersed for 2 min in a mixed solution of barium chloride and potassium permanganate in water. The coloration due to excess permanganate is then removed by washing the sample in a saturated solution of oxalic acid.

Tests to determine the optimum ratio for the mixed solution, for the immersion time, and for solution stability have been carried out. These tests were made empirically

using gypsum powder and broken surfaces of massive microcrystalline gypsum. The colour produced by the staining was compared with an arbitrary colour-intensity scale of coloured discs ranging in 10 steps from white to intense magenta. The results of these tests indicated that a 2:1 ratio barium chloride to potassium permanganate is most appropriate for this solution, and using 6% solutions mixed in the 2:1 ratio near maximum intensity of stain colour was reached after 2 min immersion for both powder and broken surface test specimens. Extended immersion produced only small increases in colour intensity and powder immersed for 10 min showed considerable browning due to the formation of MnO_2 as a precipitate. Tests indicate that the shelf life of the mixed staining solution is at least six weeks if it is kept in a brown glass bottle.

Special concrete test specimens were prepared containing quartz, limestone, dolomite, and marlstone in addition to gypsum as fine aggregate materials. Although the more porous materials took up a purple coloration due to absorption of the permanganate during staining this coloration was entirely removed by washing the surface first with water and then with saturated oxalic acid solution; only the sulphate minerals retain their stain coloration.

The procedure described above is satisfactory for the identification of the sulphates gypsum, anhydrite, and ettringite but does not differentiate between them. Barytes and celestine, however, are not satisfactorily stained by this technique. According to the scheme published by Friedman gypsum and anhydrite may be differentiated using titan yellow in methanol: anhydrite remains unstained, but gypsum should stain orange red. Unfortunately this part of the Friedman staining scheme gave inconclusive results in a number of tests carried out in our own laboratories.

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