Pergamon

Cement and Concrete Research 31 (2001) 1115–1116

CEMENT AND CONCRETE RESEARCH

Discussion

A discussion of the paper “The distributions of bound sulfates and chlorides in concrete subjected to mixed NaCl, $MgSO_4$, Na_2SO_4 attack” by P.W. Brown and Steven Badger☆

William G. Hime*, Stella L. Marusin

Wiss, Janney, Elstner Associates, Inc., 330 Pfingsten Road, Northbrook, IL 60062, USA

Received 13 February 2001

Abstract

The use of scanning electron microscopy (SEM) for investigating sulfate attack to concrete is fraught with pitfalls, including analyses of volumes only about one-trillionth of a cubic inch, extrapolation of elemental identifications to compounds, interpretation of results without a “zero-time” basis, and failure to consider optical petrography conclusions. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Ettringite; Salt hydration; SEM; Sulfate; Sulfate attack

---

Dr. Brown and Mr. Badger have used a technique that is relatively unique for “demonstrating” sulfate attack to residential concrete: scanning electron microscopy (SEM). Interestingly, several other teams of investigators have studied most or all of the same hundreds of residences and have come up with the opposite conclusion: there is little or no sulfate attack occurring. Most of those teams have used petrographic microscopy and found none of the conventional signs of sulfate attack: cracks filled with gypsum or ettringite near and parallel to the sulfate-exposed surfaces, expansion of the structure, and map cracking.

It is interesting that Brown and Badger found Friedel’s salt in the same concrete structures, but failed to point out that that chloride compound is destroyed in a sulfate environment. Its presence indeed demonstrates that the concrete likely had not been exposed to sulfate.

To use SEM to prove sulfate attack in the absence of petrographic evidence is fraught with potential perilous consequences, including removal of concrete that may be perfectly good. One great difficulty with SEM is that the portion of the sample being analyzed is extraordinarily small. For example, each of the EDS spectra presented by Brown and Badger represents a volume of about a trillionth of a cubic inch. An enormous study using, in our opinion, elemental mapping (“dot maps”) would have to be made to prove that the findings are representative of any general attack mechanism.

We have made concrete in the laboratory using the cements and aggregates from Orange County, CA, the location where most of Brown and Badger’s core samples were taken. We have been able to produce most of the spectra shown in their paper by using SEM analysis of our laboratory specimens, none of which were exposed to sulfate.

To illustrate, in Fig. 2 of their paper, they show the presence of “magnesium silicate,” but surprisingly admit that it may be a mixture of brucite and silica gel. We note the following:

1. In virtually no case have we, nor they, found layers of brucite near surfaces that were presumably exposed to magnesium salt solutions, although such layers are reported by many investigators to be the natural result of such exposure.
2. Magnesium silicate can be a component of Portland cement.
3. Many of the aggregates used in Southern California concrete consist of silicates of magnesium, aluminum, and alkalis. Fig. 1 shows the microstructure and EDS analysis of

---

☆ Cem. Concr. Res. 30 (2000) 1535–1542.

* Corresponding author. Tel.: +1-847-272-7400; fax: +1-847-291-5189.

E-mail address: whime@wje.com (W.G. Hime).

0008-8846/01/$ – see front matter © 2001 Elsevier Science Ltd. All rights reserved.
PII: S0008-8846(01)00520-8

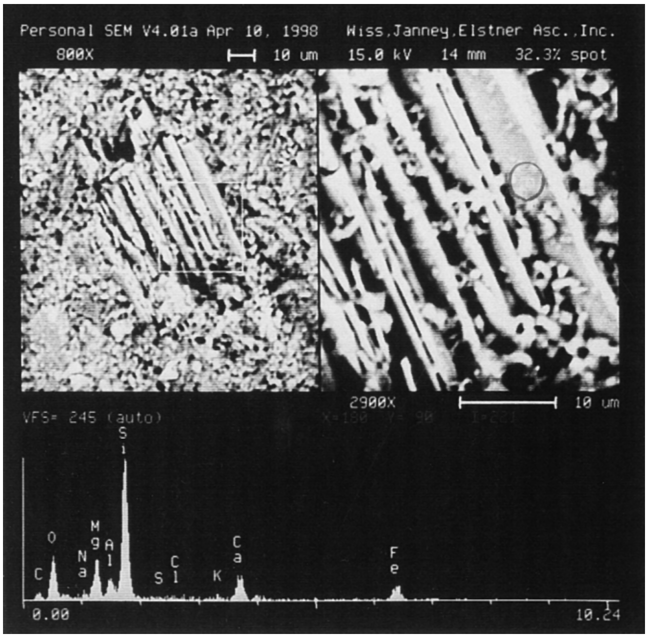

Fig. 1. SEM micrograph and EDS spectra of micaceous aggregate removed from Orange County residential concrete.

aggregate removed from concrete of the California residences. Note the resemblance to their Fig. 2 and the fact that some of the micaceous fibers are only a few microns wide.

As another example, Fig. 3 of their paper shows ettringite at paste–aggregate interfaces and in cement paste. They imply it is a result of sulfate intrusion. But ettringite preferentially occurs near paste–aggregate interfaces [1] and it also precipitates there if there is water gain under aggregate particles and the concrete is simply exposed to water. Ettringite is also a normal component of Portland cement concrete, and even more so with the use of present day cements that have a much higher S/A ratio (ratios for Type III cement now average 0.41 [2] compared to the 1940s when they averaged 0.23 [3]).

Fig. 3 evidences fly ash, which was not noted by the authors. Shaking most fly ashes with calcium hydroxide solution produces an almost instantaneous cloud of ettringite. Finding ettringite in the vicinity of, or even within, fly ash particles is common in our experience.

The finding of gypsum in concrete is uncommon by conventional petrographic microscopy, but our studies have shown several sources for it that do not involve migration of salts such as sodium sulfate into the concrete. Such sources are: components of the aggregate, components or reaction products of the fly ash, and advancing carbonation fronts (the carbonation converts monosulfoaluminate and ettringite to gypsum).

Finally, we note that there is distress to some of the concrete of the homes that Brown and Badger studied. It occurs as a “line” of efflorescence with underlying loss of concrete surface. It is due to, as we term it, salt hydration distress, the conversion of anhydrous sodium sulfate (thenardite) to the 10 hydrate (mirabilite). The result is an almost fourfold expansion. The source of the sodium sulfate is the soil; the process is the solution of the salt by daily irrigation (watering) and the wicking of such solutions up the surface of the concrete. Unfortunately, the sample preparation techniques used by Brown and Badger, and by many petrographers using thin sections, dissolve out the salt and it is not found.

References

[1] P.J.M. Monteiro, P.K. Mehta, Ettringite formation on the aggregate–cement paste interface, Cem. Concr. Res. 15 (1985) 378–380.

[2] R.F. Gebhardt, Survey of North American Portland cements: 1994, Cem. Concr., Aggregates (1994) 17 (2) 145–189 (December).

[3] W. Lerch, C.L. Ford, Chemical and physical tests of the cements, Long-Time Study of Cement Performance in Concrete, Am. Concr. Inst., Proc. 44 (1948) 743–795 (February–May, Chap. 3).