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Sample Preparation — the Key to SEM Studies of Failed Concrete

Stella L. Marusin

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

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Abstract

The proper selections of a representative specimen and the sample preparation technique to be used for a scanning electron microscope (SEM) study require a knowledge of the investigated material and the skill of an experienced scientist. Based on comparative SEM studies of concrete samples prepared as either traditional or 'modern' fluorescent epoxy-impregnated thin sections, as-polished or epoxy-impregnated surfaces, or as simply sawn unpolished and fractured surfaces, the sawn unpolished and the fractured surfaces proved to be the best for many SEM investigations. The sawn surfaces can disclose those cracking patterns and fine crystal formations that are usually destroyed by polishing and that cannot be seen on thin sections. Further, concrete components soluble in the preparation media can be removed by the preparation procedures, and impregnation materials can introduce elements that are not original components of the studied material, possibly leading to false diagnosis of the damage mechanism.

Keywords: Scanning electron microscopy, sample preparation, thin sections, polished surfaces, unpolished surfaces, fractured surfaces, concrete deterioration, false diagnosis, delayed ettringite formations.

INTRODUCTION

During the last 20 years a number of investigators have used an SEM equipped with an X-ray energy-dispersive analyser to perform research studies or determine the mechanism for concrete failure.

A beam of electrons with an accelerating voltage of 15 or 20 kV is often used in such studies, producing three major types of signal as a result of the interaction of this electron beam with a surface of the concrete specimen: secondary electrons, backscattered electrons and X-rays. The electron micrographs obtained using low-energy secondary electrons, SE, are capable of showing the morphology of the microstructure in two (or three) dimensions; those obtained by using high-energy backscattered electrons, BS or BE, reflect differences in atomic numbers and can distinguish between the particles present in the matrix on the basis of the variation in brightness of their images. The X-ray radiation allows elemental compositions to be obtained as: qualitative analyses printed on a chart, where each element is identified on a continuous spectrum by the position of its peak; a dot map where each dot represents the presence of a particular element; or a quantitative analysis by wt% of elements or oxides as calculated by a computer.

Investigators usually describe their laboratory testing program and their visual observations of the damage to a concrete structure, but seldom their method of selection of representative specimens or their SEM sample preparation techniques (e.g. Refs 1–6).

In the author's opinion and experience, sample preparation is a very important part of SEM studies: poor preparation techniques can lead to erroneous diagnoses of the concrete distress mechanism.

Based on a review of several hundred papers, there is a no specific or uniform procedure among researchers in their approach to this problem. Some use polished concrete sections,[7,8,9] broken[10,11] or fractured surfaces,[12,13]

or thin sections.[14–17] Some specimens are described as dried at 50°C,[10] or oven-dried in a CO_2-free atmosphere.[18] Some specimens are cut with a fine diamond-impregnated wire saw without a coolant,[8] others are cut from resin-impregnated samples using a diamond saw.[9] Some surfaces are lapped using an alumina grit and then polished by a diamond grit,[9] others are polished by 'two kinds of diamond paste suspended in water or oil'.[8]

In accordance with Stutzman,[19] 'any sample type can be examined by SE imaging', but 'the best use of the BE imaging is examining flat, polished surfaces'. He also suggests that BE samples be prepared 'in the same manner as those used for analysis with the light microscope except that they are not etched', using a procedure described by Campbell.[20] He recommends using an ultra-low–viscosity embedding material, a low-speed lap wheel and hand pressure, a series of diamond pastes, propylene glycol as a polishing lubricant and immersion in dried ethanol in an ultrasonic bath.

Since SEM images may require identification by the X-ray elemental analysis method, there are recommendations regarding sample preparation for this technique (see Ref. 21, and various operating manuals). Generally, it is recommended that quantitative X-ray analysis requires a homogeneous, 'infinitely thick' (to the radiation) sample with a flat polished surface.

If the above described recommendations are adhered to, X-ray elemental analyses should probably not be used on concrete samples since concrete is not a homogeneous material and because polishing operations can lead to significant errors. Based on our experience, however, X-ray analyses (especially dot maps) of unpolished surfaces provide very useful information. Further, the results of X-ray analyses of unpolished samples at high magnification are not significantly influenced by 'saw grooves' or other imperfections that are visible at low magnification. Small areas, as well as crystal surfaces, provide, at high magnification, sufficiently homogeneous and flat surfaces for X-ray examination.

To avoid distorted SE and BS images, the sample must to be coated to allow discharge of electron build-up on the examined surface. A thin metal coating decreases the build–up of negative charge on the specimen surface by forming a conducting path for the electrons to avoid the distorted images. The thin metal coating (sputter coating) was applied by bombarding the metal with atoms of heavy gases and directing the atoms on to the specimen's surface. However, if the images are to be accompanied by X-ray analysis, it is obvious that a carbon coating cannot be used if a carbonation process is to be studied, and a gold sputter coating such as has been reportedly used to study the microstructure of concrete[13] gives a peak almost at the same position as sulfur.

SEM and light microscopy petrography are different tools, and sample preparation must be suited to these different approaches.

The importance of sample preparation and the advantages or disadvantages of different techniques are discussed below in connection with our SEM studies of SE and BS images and X-ray analyses of concrete damaged by delayed ettringite formations (DEF).

SEM STUDIES OF TRADITIONALLY PREPARED THIN SECTIONS (TS)

As shown in Fig. 1, an SE image at relatively low magnification exhibited 'gel-like' material at the aggregate particle/paste interface.

Petrographic examination identified this location as a dark rim of alkali–silica gel. Using the dot map study in Fig. 2 and the dispersive X-ray elemental analysis in Fig. 3 we were able to

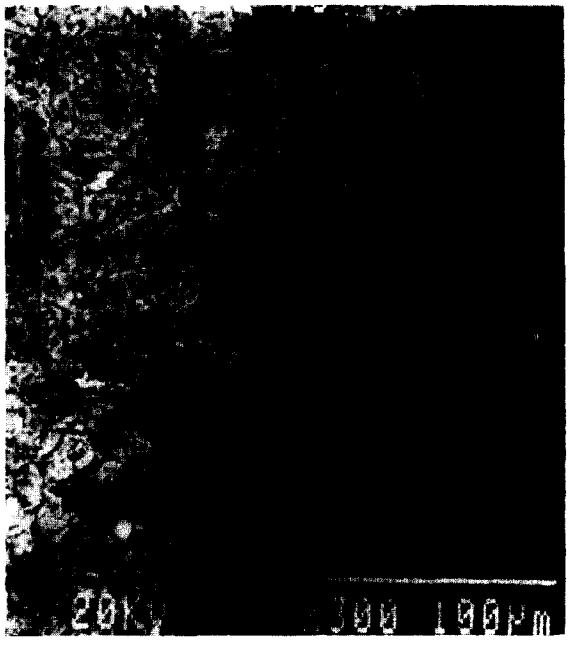

Fig. 1. TS — SE micrograph of 'gel like' DEF at aggregate particle and paste interface at 300×.

identify this 'rim' as an ettringite formation. However, as shown in Fig. 4, even if high magnification is used, a thin section sample does not allow us to see typical needles of ettringite crystals, or to study the crystalline morphology present in the matrix.

Depending on the technique used for thin section preparation, some elements (or components) can be washed away or destroyed by the preparation processes (e.g. by heating). Also, components can be spread over the surface during polishing, preventing effective use of dot map studies. Further, new cracks can be introduced and original cracks 'healed' or widened by the epoxy-impregnated thin section preparation.

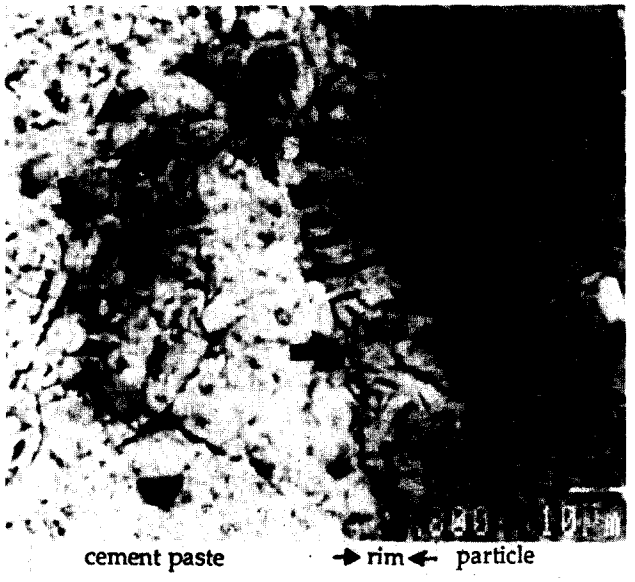

Fig. 4. TS–SE micrograph of 'gel like' DEF at aggregate particle and paste interface of area arrowed in Fig. 1 at 800×.

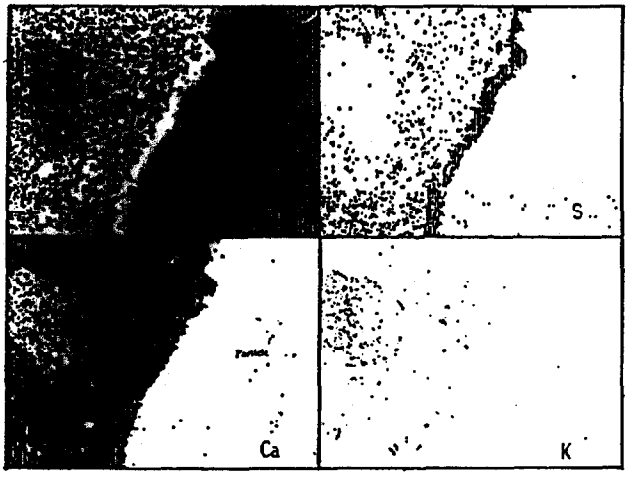

Fig. 2. TS — dot map study showing distribution of silicon (Si), sulfur (S), calcium (Ca) and potassium (K) of location in Fig. 1.

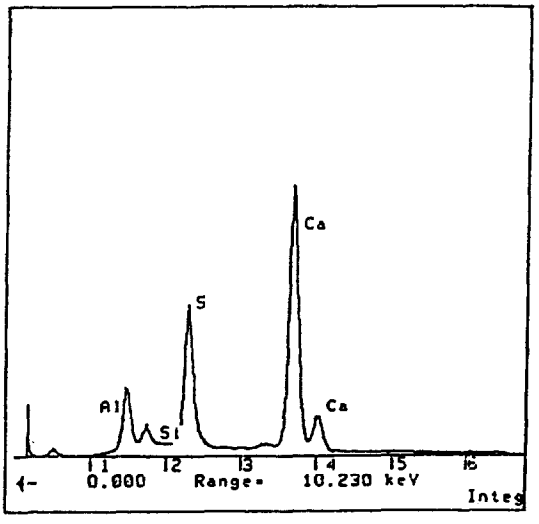

Fig. 3. TS — X-ray elemental analysis of 'gel like' material at aggregate particle and paste interface in Fig. 1.

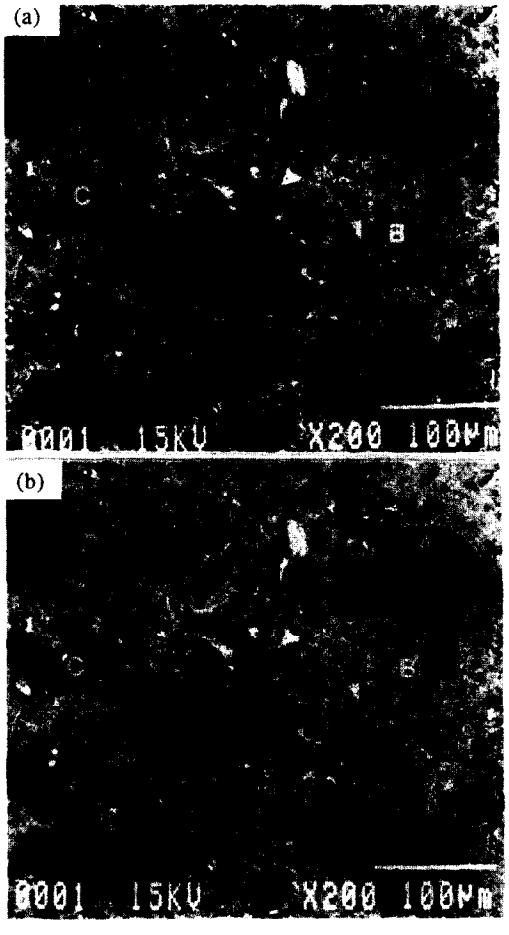

Fig. 5. FTS — SE and BS micrographs showing no significant differences between both images for FTS sample at 200×; note the hardly visible DEF in air void A and almost undetectable FED in paste (arrowed); high magnification micrograph of badly damaged DEF crystals in location B is in Fig. 6, and in location C is in Fig. 7.

SEM STUDIES OF FLUORESCENT EPOXY-IMPREGNATED THIN SECTIONS (FTS)

Based on our experience, FTS (preparation described by Gudmunson *et al.*[22]) may not be suitable for many SEM studies. In addition to all the disadvantages described with ordinary TS, the original or newly created cracks and voids are filled and widened with fluorescent material. Such a typical and important feature of DEF as the cracks radiating from DEF in paste are destroyed by the sample preparation. As shown in Fig. 5 there is no significant difference between SE and BS images for FTS. DEF, identified by our X-ray studies, is hardly visible in a large void (A), and it is almost invisible in the paste and at the aggregate particle–paste interface (see arrows). Due to the FTS preparation, SEM investigations must be done almost exclusively on BS images. As shown in Figs 6–8, some locations are so badly damaged by the preparation that it is not possible to identify DEF (or other crystals) in SE micrographs, even if high magnification is used. An SE micrograph of badly damaged DEF of location B in Fig. 5 is in Fig. 6, and of location C is in Fig. 7. Presence of DEF in both locations was identified by X-ray elemental analysis. Another SE micrograph of the badly damaged concrete samples in Fig. 8 does not provide any useful information. Even the presence of the aggregate particle P is undetectable without a dot map study in Fig. 9. Although sulfur accumulations shown in the dot map study of the arrowed location in Fig. 8 were identified as ettringite by X-ray elemental analysis, the smearing of com-

Fig. 6. FTS — BS micrograph showing typical image of damaged DEF crystals of location B in Fig. 5 due to FTS preparation at 2000×; note dark location of epoxy penetration.

Fig. 7. FTS — another SE micrograph of badly damaged DEF of location C in Fig. 5 at 8000×.

Fig. 8. FTS — another SE micrograph of a badly damaged concrete sample; note the sulfur accumulation of arrowed area and presence of aggregate particles P in a dot map study in Fig. 9 (1000×).

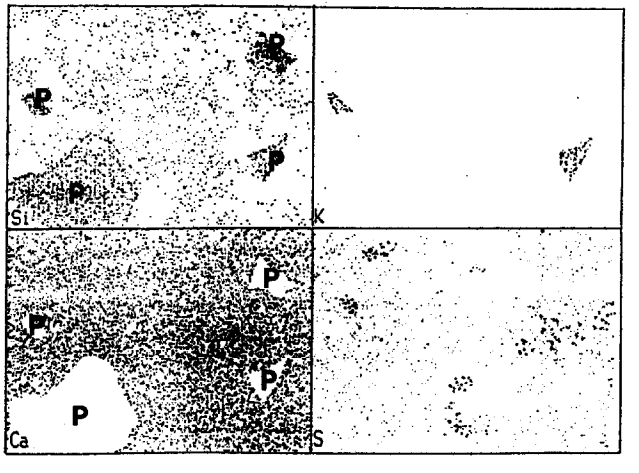

Fig. 9. FTS — dot map study showing distribution of silicon (Si) and potassium (K) at aggregate particles P, calcium (Ca) and sulfur (S) in cement paste of location in Fig. 8; locations of sulfur accumulation were identified by X-ray as DEF.

ponents on the surface made dot map studies inapplicable in many locations. A typical BS image of crack locations in cement paste where crystalline DEF was destroyed by grinding at location B in Fig. 5 and the cracks filled with an epoxy are shown in Fig. 6.

SEM STUDIES OF EPOXY-IMPREGNATED SAWN POLISHED SURFACES (ESPS)

The smooth highly polished surfaces (prepared by sawing and then polishing with successively finer silicon-carbide grit) exhibited all the disadvantages of epoxy-impregnated thin sections. Figure 10 shows an aggregate particle–paste interface where the ettringite crystals were typically damaged by the preparation technique and by mounting in epoxy. Figure 11 shows an X-ray analysis graph that displays chlorine (Cl) from the particular epoxy used and palladium (Pd) from the palladium sputter coating. Due to a very low percentage of gold in the sputter coating, a gold peak is not present.

SEM STUDIES OF SAWN POLISHED SURFACES (SPS)

The identification of the crystalline morphology and the presence of original cracks on SE and BS micrographs depends on the manner of polishing. Both SE and BS images can be used to study lightly polished (or lapped) surfaces. However, as shown in Fig. 12, the cross–section

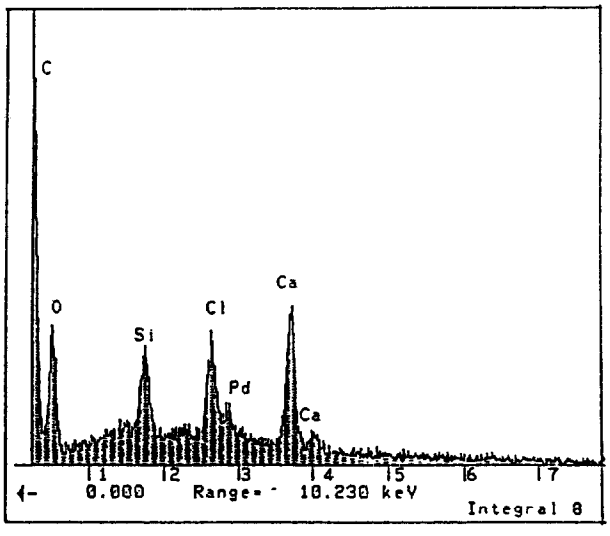

Fig. 11. ESPS — X-ray elemental analysis of paste location showing presence of chlorine (Cl) due to epoxy and palladium (Pd) due to coating.

Fig. 10. ESPS — SE micrograph showing typically damaged crystals of DEF at aggregate and particle-paste interface, at 2000 ×.

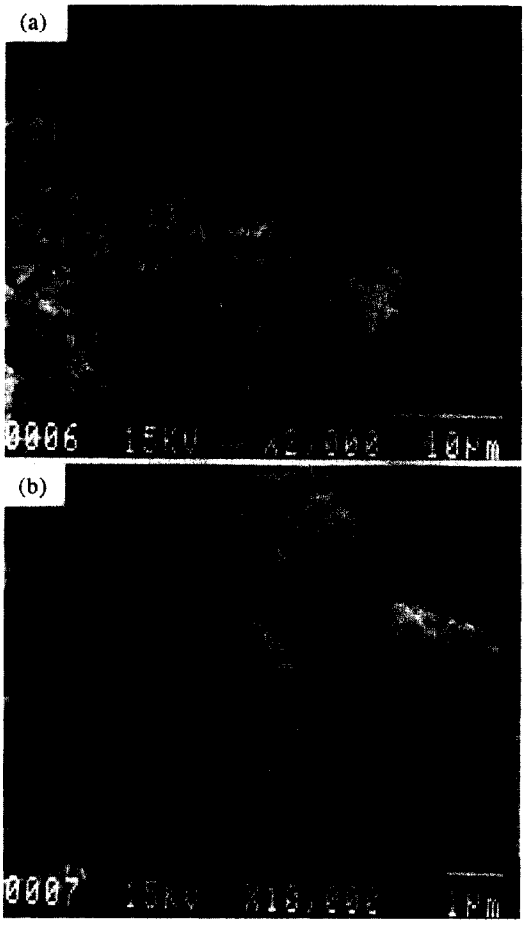

Fig. 12. SPS — SE micrographs of typical images of DEF crystals in cement paste at 2000 and 10000 ×.

image of a needle type DEF can be easily misinterpreted as a gel formation.

SEM STUDIES OF SAWN UNPOLISHED SURFACES (SUS)

Unpolished surfaces, obtained by cutting the sample with a diamond bladed saw, retain original cracking patterns and crystals. As shown in Fig. 13, both SE and BS images can be successfully used for this investigation. As shown in Fig. 14, sulfur accumulations are clearly shown in dot map studies and, as shown in Fig. 15, crystalline morphology can usually be clearly seen on SE images at high magnifications. A graph of the X-ray elemental analysis and an oxide calculation of the DEF of Fig. 15 are shown in Fig. 16. A typical example of DEF crystals in cement paste with cracks radiating into the surrounding locations is shown in Fig. 17.

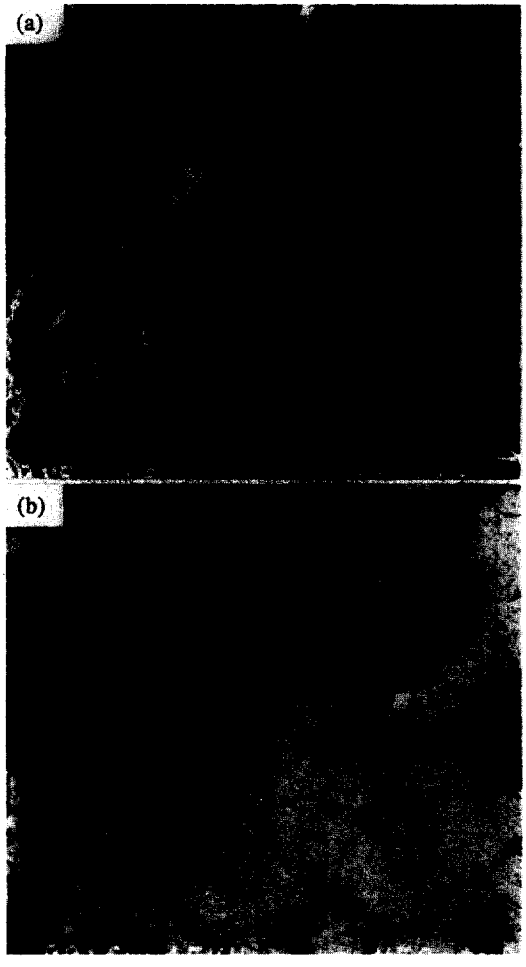

Fig. 13. SUS — SE and BS micrographs of DEF at aggregate particle/paste interface at 50×.

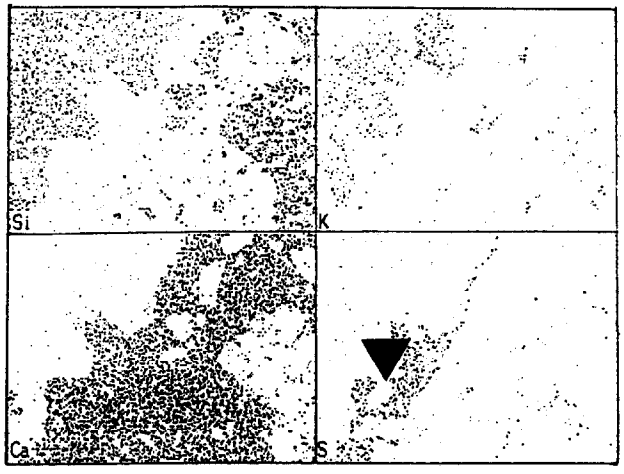

Fig. 14. SUS — dot map study showing distribution of silicon (Si) and potassium (K) at aggregate particles, calcium (Ca) and sulfur (S) of location in Fig. 13; note the sulfur accumulation atgel like' location at edge of aggregate particle; DEF crystals of area ▼ are in Fig. 15 and X-ray elemental analysis is in Fig. 16.

Fig. 15. SUS — SE micrograph of DEF crystals at location ▼ in Fig. 14 at 6000×.

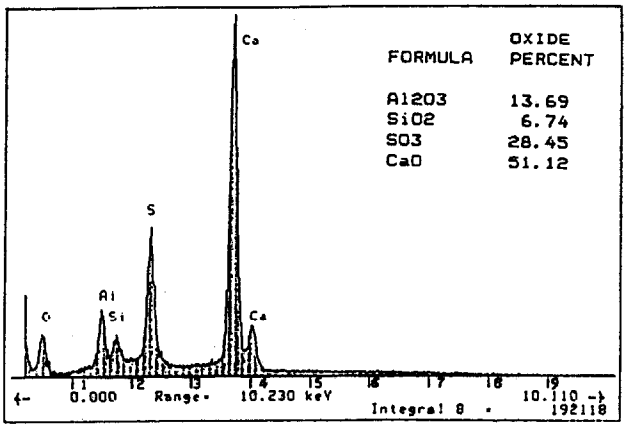

Fig. 16. SUS — X-ray elemental analysis and computer oxide calculation of DEF at location ▼ in Fig. 14.

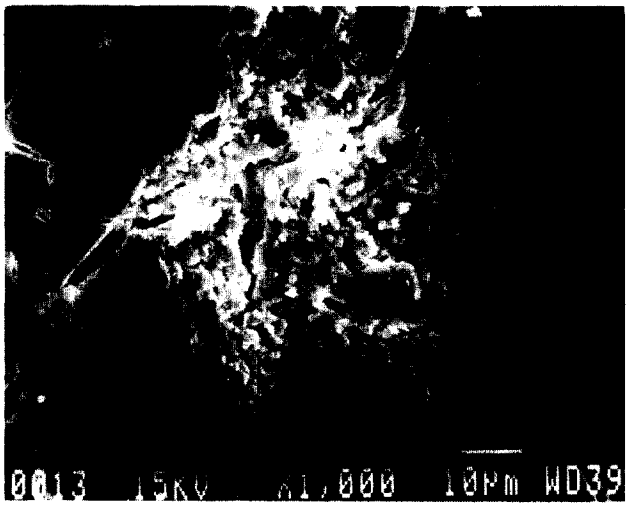

Fig. 17. SUS — SE micrograph showing typical radiating cracks from DEF crystals into surrounding cement paste.

SEM STUDIES OF FRACTURED SURFACES (FS)

Since additional cracks can be introduced by fracturing the specimen by hammer blows and fractured surfaces are unrepresentative of a concrete sample as a whole, concrete investigations cannot be solely based on fractured samples. The fractured surfaces cannot be used to study cracking patterns in a cement matrix or the cracking of aggregate particles. They can be used in conjunction with studies of unpolished sawn sections. As shown in Fig. 18, the fractured surfaces are excellent for showing crystals of DEF in paste or at aggregate particle–paste interfaces.

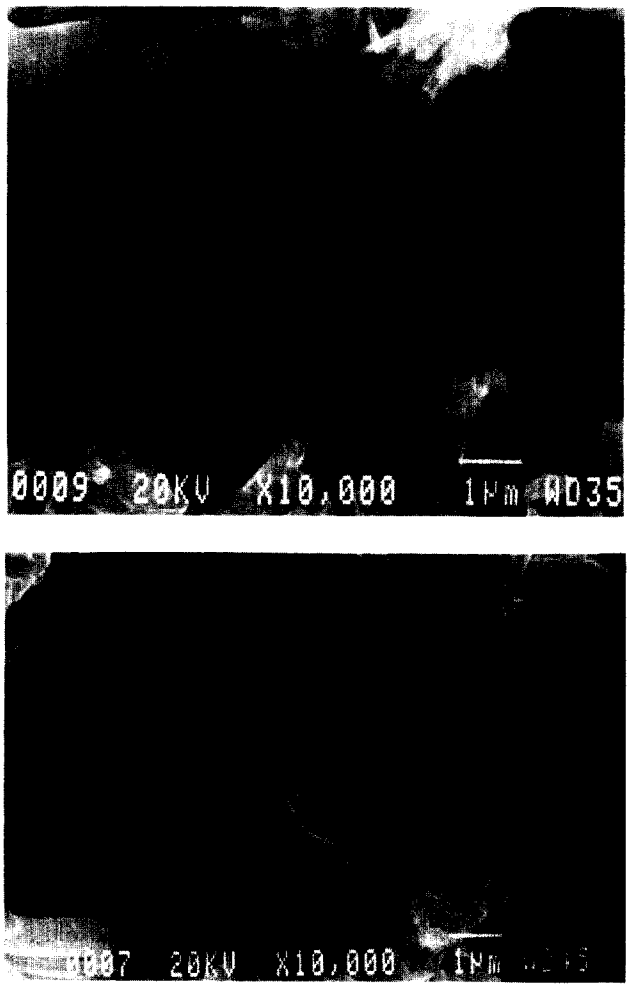

Fig. 18. FS — SE micrographs of DEF crystals at 10000×.

CONCLUSIONS

Based on a comparison of SEM studies of DEF development in concrete using 'traditional' or fluorescent epoxy impregnated thin sections, polished and epoxy–impregnated samples, or unpolished sawn and fractured samples, the sawn unpolished and the fracture surfaces appear to be best for SEM investigations of DEF and possibly all concrete distress mechanisms.

Thin sections or polished, epoxy-impregnated samples can lead to incorrect diagnoses of concrete failure causes. Surfaces damaged by sample preparation cannot be used to study crack patterns or crystalline materials originally present in the concrete. Ultrafine crystal locations can be mistakingly identified as 'a gel', and new elements can be introduced into the studied system (aluminum, chlorine, etc.), leading to incorrect conclusions. It is our opinion that fluorescent epoxy-impregnated thin sections may effectively prevent both useful SE images and, in many cases, dot map studies, and thus cannot be recommended for SEM investigations of concrete samples. Both SE and BS images and X-ray elemental analyses (graphs, dot maps, oxide calculations) on unpolished sawn surfaces must be employed in order to assume correct identification of such concrete failure causes as DEF.

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REFERENCES

1. Regourd, M. & Hornain, H., Microstructure of reaction products. In *Proc. of the 7th Int. Conf. on Concrete Alkali–Aggregate Reactions*, Ottawa, Canada, 1986, pp. 375–80.
2. Mullick, A. K. & Samuel, G., Reaction products of alkali–silica reaction — a microstructural study. *Ibid.*, pp. 381–85.
3. Baronio, G. & Berra, M., The occurrence of AAR in a concrete structure in Italy. In *Proc. of the 8th Int. Conf. on Alkali–Aggregate Reaction*, Kyoto, Japan, 1989, pp. 71–6.
4. Katayama, T. & Futagawa, T., Alkali–aggregate reaction in New Brunswick, Eastern Canada — petrographic diagnosis of the deterioration. *Ibid.*, 1989, pp. 531–6.
5. Brouxel, M. & Valiere, A., Thaumasite as the final product of alkali–aggregate reaction: a case study. In *Proc. of the 9th Int. Conf. on Alkali–Aggregate Reaction in Concrete*, London, 1992, pp. 136–43.
6. Prin, D. & Brouxel, M., Alkali–aggregate reaction in northern France: a review. *Ibid.*, 1992, pp. 790–6.
7. Grattan-Bellew, P. E. & Lefebvre, P. V., Effect of confinement on deterioration of concrete made with alkali–carbonate reactive aggregate. In *Proc. of the 7th Int. Conf. on Concrete Alkali–Aggregate Reactions*, Ottawa, Canada, 1986, pp. 280–5.
8. Kodama, K. & Nishino, T., Observation around the cracked region due to alkali–aggregate reaction by analytical electron microscope. *Ibid.*, 1986, pp. 398–402.
9. Laing, S. V., Scrivener, K. L & Pratt, P. L., An investigation of alkali–silica reaction in seven-year old and model concretes using SEM and EDS. *Ibid.*, 1992, pp. 579–83.
10. Shayan, A. & Quick, G., Microstructure and composition of AAR products in conventional standard and new accelerated testing. In *Proc. of the 8th Int. Conf. on Alkali–Aggregate Reaction*, Kyoto, Japan, 1989, pp. 475–82.
11. Carles-Gibergus, A., Oilivier, J. P., Fournier, B., & Bérubé, M. A., *A new approach to the study of alkali–aggregate reaction mechanisms*, *Ibid.* 1989, pp. 161–6.
12. Shayan, A. & Quick, G. W., Sequence of formation of deleterious AAR products and secondary ettringite in the same mortar and concrete specimens. In *Proc. of the 14th Int. Conf. on Cement Microscopy*, Costa Mesa, California, 1992 pp. 11–21.
13. Oberholster, R. E., Maree, H. & Brand, J. H. B, Cracked prestressed concrete railway sleepers: alkali–silica reaction or delayed ettringite formation. In *Proc. of the 9th Int. Conf. on Alkali–Aggregate Reaction in Concrete*, London, 1992, 1992, pp. 740–9.
14. Meland, I., Alkali–silica reaction in tile covered concrete. In *Proc. of the 8th Int. Conf. on Alkali–Aggregate Reaction*, Kyoto, Japan, 1989, pp. 107–12.
15. Shayan, A. & Quick, G. W., Microscopic features of cracked and uncracked concrete railway sleepers. *ACI Materials J.*, **89** (1992) 348–61.
16. Thaulow, N., Holm, J. & Andersen, K. T., Petrographic examination and chemical analysis of the Lucinda Jetty prestressed concrete roadway. In *Proc. of the 8th Int. Conf. on Alkali–Aggregate Reaction*, Kyoto, Japan, 1989, pp. 573–81.
17. Thaulow, N. Lee, R. J. & Holm, J., An integrated optical–SEM method for the identification of alkali–silica reaction in concrete sleepers. *Proc. of the Int. Symp. on Precast Concrete Railway Sleepers*, Madrid, 1991.
18 Wang, H. & Gillott, J. E., The effect of superplasticizers on alkali–silica reactivity. In *Proc. of the 8th Int. Conf. on Alkali–Aggregate Reaction*, Kyoto, Japan, 1989, pp. 182–92.
19. Stutzman, P., Cement clinker characterization by scanning electron microscopy. *Cement, Concrete & Aggregates*, **13** (1991) 109–14.
20. Campbell, D. H., *Microscopical Examination and Interpretation of Portland Cement and Clinker*. Portland Cement Association, 1986.
21. Small, J. A., Quantitative particle analysis in electron beam instruments. *Scanning Electron Microscopy J.*, **1** (1981) 447–61.
22. Gudmundsson, H., Chatterji, S., Jensen, A. D., Thaulow, N. & Christensen, P., Quantitative microscopy as a tool for the quality control of concrete. In *Proc. of the 3rd Int. Conf. on Cement Microscopy*, 1981, pp. 228–37.