Pergamon

Cement and Concrete Research, Vol 27, No 9, pp 1407–1417, 1997
Copyright © 1997 Elsevier Science Ltd
Printed in the USA All rights reserved
0008-8846/97 $17 00 + 00

PII S0008-8846(97)00123-3

A SIMPLE ENVIRONMENTALLY FRIENDLY, AND CHEMICALLY SPECIFIC METHOD FOR THE IDENTIFICATION AND EVALUATION OF THE ALKALI-SILICA REACTION

George D. Guthrie, Jr. and J. William Carey
Geology and Geochemistry Group, Los Alamos National Laboratory

(Refereed)
(Received February 13, 1997; in final form July 9, 1997)

ABSTRACT

A rapid, dual staining method is described whereby reaction products associated with the alkali-silica reaction (ASR) are readily identified by their pink or yellow color following treatment in the laboratory or field. The method is based on both the compositional and physical characteristics of the ASR gel; hence, it provides greater information than non-chemical-specific techniques (such as the uranyl acetate method). In addition, the chemicals used in the staining method pose minimal health risks and are environmentally benign. © *1997 Elsevier Science Ltd*

Introduction

One of the principal mechanisms of premature degradation of concrete is alkali silica reaction (ASR), in which an alkali-rich silica gel forms around and within some reactive aggregate grains, in pores, along fractures, and within paste (1). This reaction can dramatically impact the strength and durability of a concrete structure and significantly shorten its lifetime.

ASR results from an interaction between high pH pore fluid, some aggregate constituents (e.g., poorly crystalline silica phases), and alkali cations (Na^+ and K^+) released by the cement and/or aggregate (2,3). As the alkali content of the pore fluid (and, hence, the pH) rises, the solubility of the silica phases increases, resulting in a release of silica to form an alkali-calcium-silica-hydrate gel (commonly referred to as "ASR gel"). Gel formation leads to an increase in volume relative to the reacting silica phases, which causes internal pressure in the concrete and eventually results in fractures. This process can be exacerbated by freeze-thaw cycles and by salting of road surfaces.

Methods for Identifying ASR Gel. Identification of ASR as the cause of a structure's demise is critical to a number of practical needs. The recognition that a particular aggregate is prone to ASR is probably the prime method used to ensure that ASR is avoided. Although several rapid tests (4,5) offer the ability to screen aggregates for their potential reactivity, field experience shows that these do not always accurately predict an aggregate's performance in a particular mix. Thus, identification of ASR in a degrading structure is the ultimate check of an aggregates's reactivity. In addition, potential treatment methods—such as the application of a lithium compound to a structure—are likely to be most effective if ASR can be identified as early as possible. Finally, identification of ASR is an important component of the management of a transportation infrastructure (e.g., by allowing long-term scheduling and budgeting of repair and replacement). Hence, the identification of ASR has been the focus of a number of efforts, including the Strategic Highway Research Program (SHRP).

There are two principal methods used to identify ASR gel in a concrete structure: petrographic analysis and labeling with uranyl acetate. The most common type of petrographic analysis relies on morphological and optical identification of the ASR gel product using binocular and petrographic microscopes. Less common methods of petrographic analysis involve morphological and chemical identification using a scanning electron microscope (SEM). Each of these methods requires specialized training and equipment; hence, petrographic analysis is typically performed by a private laboratory, making ASR verification costly and time-consuming (requiring days to weeks or longer).

One recent outcome of SHRP (6) was the evaluation of a technique by Natesaiyer and Hover (7,8) in which uranyl acetate [$UO_2(C_2H_3O_2)_2$] is applied to a concrete surface and rinsed off, leaving uranyl (UO_2^{2+}) sorbed to the negatively charged ASR gel. The distribution of the uranyl ion is monitored by its yellow-green fluorescence under ultraviolet light, thereby showing the distribution of the ASR gel.

Development of the uranyl-acetate technique was an important contribution to the practical needs of individuals interested in identifying ASR products in the field or in their own laboratory. Nevertheless, there are several potential concerns with the uranyl-acetate method, including: personnel are exposed to uranium-containing solutions and uranium-contaminated solids; uranium contaminated wastes are generated; the method requires the use of an ultraviolet light source in nearly complete darkness; and, the method is somewhat nonspecific for ASR gel because the uranyl ion is capable of binding to any negatively charged surface.

These first two issues are often believed to be insignificant because of the relatively small amount of uranyl acetate that is used. However, the amount of uranium present in a typical uranyl acetate test is significant from a regulatory standpoint. OSHA provides three values for assessing exposure to uranium compounds, the most relevant of which for short-term exposures is the ceiling limit (which is the concentration that should not be exceeded in an occupational setting). The ceiling limit for inhalation of uranium compounds is 0.6 mg U/m^3. In comparison, the treatment of a concrete core with ~5 ml of 0.125 molal uranyl acetate solution (5 gm/100 mL acetic acid) involves 150 mg U.* In other words, the ceiling limit may be reached by a person using the uranyl acetate method if only about 0.4% of the applied uranium becomes airborne in a meter-cubed of air. Some practices (e.g., vacuuming of a bush-hammered, treated surface) may result in short exposures at significant levels. In addition, environmentally responsible disposal of the uranium-contaminated liquid and solid waste generated by this method is costly.

The necessity of viewing the sample in ultraviolet light to see the presence of sorbed uranyl ions greatly restricts the analyst's ability to interpret the distribution of ASR gel. One cannot

---

*Even if uranyl acetate is made with depleted uranium, it is still both a radiological and a toxicological hazard. In fact, all isotopes of uranium are radioactive. The primary difference between natural and depleted uranium is the ^{235}U content (0.7 wt% vs. 0.2 wt%). This has only a minor effect on the radioactivity and no known effect on the toxicity.

observe simultaneously both the fluorescing gel and the aggregate, pore space, fractures, and past, because these latter components are difficult to observe in the UV light. Consequently, the uranyl acetate method does not help in a petrographic analysis aimed at understanding the extent and nature of ASR damage, unless one uses specialized petrographic equipment (8). In addition, the uranyl acetate method can be inconvenient to conduct in the field where it is difficult for the eyes to adjust from the brightness of daylight to the dimness of the ultraviolet viewing box.

The final issue—the non-specificity of the uranyl ion—raises the concern that the method can lead to false positives, particularly if the analysis is based solely on the presence of fluorescence. The non-specificity arises because the uranyl ion in solution will readily exchange with most cations associated with solids in the concrete (9), including K^+, Na^+, and Ca^{2+}. Any negatively charged surface (e.g., most silicates that are commonly present in concrete) can potentially sorb the uranyl ion by an ion-exchange process, so any negatively charged, high surface area material may test positive with the uranyl acetate technique. In addition, the non-specificity results in a loss of information concerning the nature of the ASR products (i.e., gels of different compositions are not differentiated). This non-specificity combined with the need to view the concrete under UV light limits the uranyl acetate method as a petrographic tool.

A New Method for Identifying ASR Gel. We report an alternative method for identifying ASR gel and its distribution in hand specimen using a dual staining technique (10). The method overcomes many of the limitations of the uranyl acetate method: the technique is based on environmentally friendly chemicals with relatively minor health concerns; the stains are chemically specific for ASR gel, and they are visible in normal light. The method allows ASR gel to be identified by individuals lacking extensive training in petrographic analysis while greatly improving the petrographic investigations by trained individuals. The method is capable of revealing the detailed reaction and distribution of ASR gel with respect to aggregate type, pore structure, and fractures. Finally, the method provides an overview of the abundance and distribution of two chemically distinct ASR gel products which are indistinguishable by both standard petrographic analysis and the uranyl-acetate technique.

The Staining Method

The staining method is based on two chemicals that are diagnostic for two components of gels associated with ASR: potassium and calcium.

Gel produced by ASR is typically enriched in both sodium and potassium (1,11), which are believed to originate largely from the cement. Most cements have potassium as their dominant alkali contaminant (12); likewise, ASR gels often have more potassium than sodium (e.g., Ref. 8; see also summary of reported compositions in Ref. 1). In our observations of ASR gels (primarily in samples from New Mexico), potassium is always the dominant alkali cation as determined by energy-dispersive spectroscopy (EDS) analysis. In contrast, typical calcium-silica-hydrate (CSH) gels produced by hydration of cement phases do not contain appreciable potassium. Consequently, one of the probes we selected for ASR gel was sodium cobaltinitrite, $Na_3Co(NO_2)_6$. Sodium cobaltinitrite is well known in analytical chemistry for use in the determination of the potassium content of a fluid (13), wherein the dissolved sodium cobaltinitrite reacts with potassium to form a $K_2NaCo(NO_2)_6 6H_2O$ precipitate. It has also been used in the geological sciences for staining potassium feldspars that have been etched in hydrofluoric acid (14–16). In the present method, sodium cobaltinitrite solution is allowed to react directly with the concrete surface (following a simple pre-wetting of the surface with deionized water but without an acid-etching step), ultimately resulting in the deposition of a yellowish precipitate—presumably $K_2NaCo(NO_2)_66H_2O$—on the surface of K-rich ASR gels.

Calcium is also a common constituent of both ASR and CSH gels; hence, we selected rhodamine B ($C_{28}H_{31}N_2O_3Cl$) as a stain for calcium, initially in an attempt to improve the contrast between the yellow-stained and non-yellow-stained areas. However, the rhodamine B did not appear to sorb to ordinary CSH but did sorb to a calcium-rich, potassium-poor silica gel that is apparently associated with ASR (as will be discussed below). In addition, rhodamine B may sorb to some but not all calcium carbonate. As discussed below, parts of some limestone aggregates and some layers within a travertine-like deposit were stained lightly by rhodamine B, but most calcium carbonate remained unstained. We do not known why only some calcium carbonate reacts with the rhodamine B (e.g., whether it reflects grain size, defect density, or some other property).

Both rhodamine B and sodium cobaltinitrite can be purchased as chemical reagents. The working solutions were prepared as saturated aqueous solutions (i.e., excess solid was present in the solutions). Sodium cobaltinitrite can be stabilized for longer periods when a small amount of acetic acid is added to the solution (17). Both simple aqueous solutions of sodium cobaltinitrite and solutions with weak acetic acid were tested, but no significant difference in behavior was found over the course of several weeks (i.e., both solutions remained effective as stains). Solutions were, however, prepared with deionized water in an attempt to minimize external sources of potassium.

Concrete samples were tested by briefly rinsing the surface to be examined with deionized water followed by treatment with the staining solutions. Each solution was applied to the surface in turn and allowed to remain on the surface for approximately 30–60 seconds followed by a thorough rinse of the surface with deionized water. The effect of differing staining sequences was examined, including the use of both stains simultaneously. the best results appeared to be obtained with the following sequence: rinse—sodium cobaltinitrite treatment—rinse—rhodamine B treatment—rinse. After final rinsing, stained regions could be seen clearly on the concrete surfaces; however, stained regions were most easily observed following drying of the surface. The intensity of the staining appeared to fade over the course of weeks to months; however, the original staining intensity could be achieved with a re-treatment of the concrete surface.

Results

The following observations are based on treatment of numerous samples from approximately 20 different concrete structures of various ages. The concrete structures include sections of highways and roads, bridges, and sidewalks exhibiting field conditions ranging from good to highly distressed. Cores were available from most localities, but bush hammering was used only on a few localities. Some samples were treated immediately following coring, whereas other samples were examined years after coring.

Yellow-Stained Regions. In hand sample, yellow staining was always associated with a "gel-like" material occurring as halos around some coarse aggregates, as precipitates in voids, and occasionally as precipitates on fracture surfaces (Figs. 1–2, 4). No other occur-

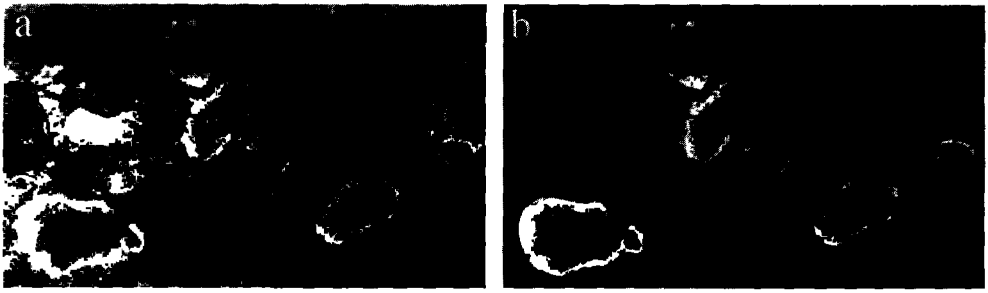

FIG. 1.
a) Optical scan of a treated concrete core from a highly distressed gutter at Los Alamos National Laboratory. Surface showed yellow-stained gel but no pink-stained gel. b) Processed image from (a) showing distribution of yellow staining. Images are approximately 47 mm along the bottom edge.

rences of yellow staining were observed (e.g., feldspars associated with coarse aggregates did not stain yellow). Some gel-like precipitates on fractures initially stained a faint yellow but were subsequently stained pink by rhodamine B. However, most regions that stained deeply yellow remained yellow following treatment with rhodamine B.

At higher magnification (i.e., with a 10× hand lens or at up to ~500× in a binocular microscope), the yellow staining was clearly associated with either a massive or granular precipitate. The massive precipitate had a distinctive gel-like morphology (smooth surface; desiccation cracks). The granular precipitate typically formed particles approximately 10–100 μm across and appeared to consist of aggregates of tiny crystals that may have grown from the gel. The granular precipiates typically occurred toward the interiors of the reacting

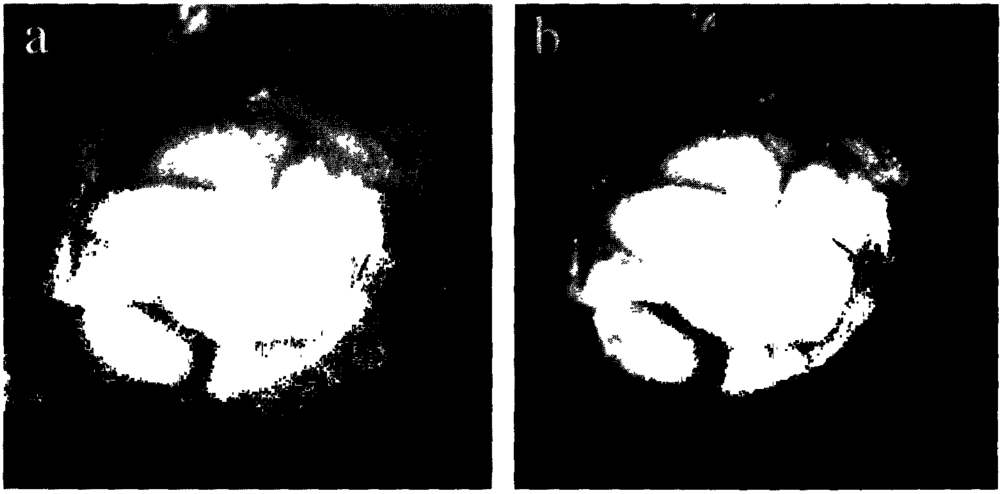

FIG. 2.
a) Photograph of a treated concrete core from US 20 in Iowa. A few voids were filled with yellow-stained gel, but most voids were empty. b) Processed image from (a) showing distribution of yellow staining. Images are approximately 1 mm along the bottom edge.

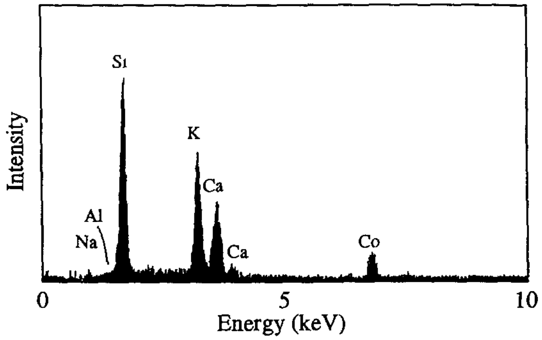

FIG. 3.
Representative chemical analysis of yellow-stained gel.

aggregates, whereas the massive precipitate occurred toward the rims. With the naked eye, the massive and granular precipitates could not readily be differentiated.

Samples of the massive material were examined in a petrographic microscope and found to be isotropic.

Samples of both the massive and granular materials that had stained yellow were hand picked for examination by EDS in the SEM.† All such materials were dominantly Si with large amounts of K and Ca (Fig. 3). In addition, they contained Co (from the stain), Na and, in some cases, minor Al or S. The relative amounts of the elements varied from sample to sample. No attempt was made to quantify these data, because of the general difficulties associated with EDS data and because of the problems associated with the geometry of the rough surfaces examined. Hence, it is difficult to determine from these data whether the (Ca+K+Na)/Si ratio (or, perhaps, the (Ca+2K+2Na)/Si ratio) is similar between the two gels (see also Fig. 5).

Based on these observations, we conclude that the yellow-stained materials were K+Ca+Si±Na gels resulting from ASR.

Pink Staining Regions. Pink staining was generally less common than yellow staining and was typically found in samples from structures exhibiting a higher degree of deterioration. In all but two instances (discussed below under "Non-ASR-Related Pink-Staining Regions"), pink staining only occurred when extensive yellow staining was present in the sample.

In hand sample, pink staining generally occurred on fracture surfaces, immediately adjacent to a reacting aggregate (with a yellow-stained rim) (Fig. 4). In such examples, the pink staining occurred on patches of the surface that were coated with a white precipitate prior to staining, where the white precipitate also included the material comprising the "reaction rim" around reactive aggregates. However, the actual reaction rim always stained yellow (although some rims additionally exhibited a slight pinkish hue), and there was a sharp break between the reaction rim and the pink-stained precipitate covering the rest of the fracture surface. Prior

---

†Plots were obtained by EDS analysis in an SEM of stained, carbon-coated gels hand picked from concrete cores. We used a Be-windowed detector that is insensitive to X-rays from elements with atomic numbers less than F.

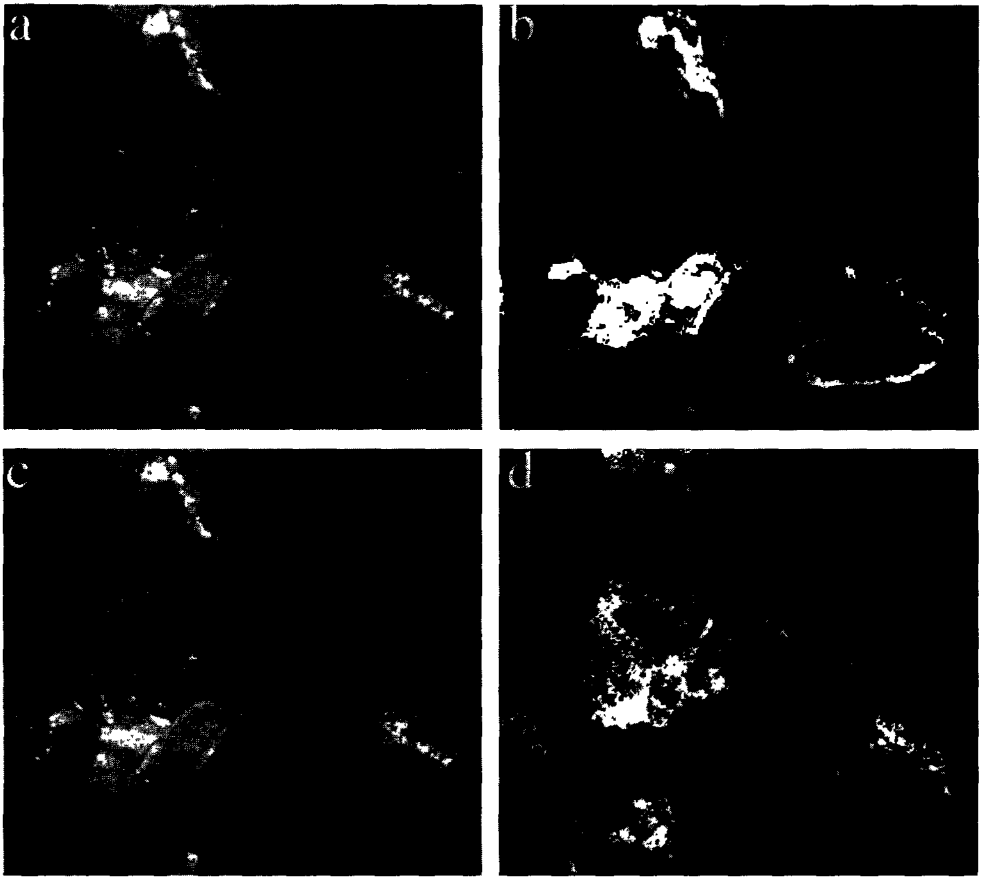

FIG. 4.

a & c) Optical scan of a treated concrete core from a highly distressed bridge along I-25 near Pecos, NM. Surface exhibited yellow-stained gel around some aggregate particles and pink-stained gel on much of the fracture surface. b) Processed image from (a & c) showing distribution of yellow staining. d) Processed image from (a & c) showing distribution of pink staining. Images are approximately 55 mm along the bottom edge.

to staining, no obvious difference could be observed between the white precipitate on the fracture surface and the white precipitate associated with the reaction rims. In some cases, the white precipitate adjacent to a reacting rim was stained yellow following sodium cobaltinitrite treatment but would then become pink following treatment with rhodamine B.

At higher magnification, like the yellow staining, the pink staining was clearly associated with either a massive or granular precipitate that had morphologies like the yellow-stained analogs. An additional occurrence for the pink staining was within portions of the paste in some concrete samples. These pink-staining materials occurred in what appeared to be "normal" past (i.e., bona fide CSH); however, in general, CSH did not stain pink in most concrete samples we investigated.

Samples of both the massive and granular pink-stained materials were hand picked for

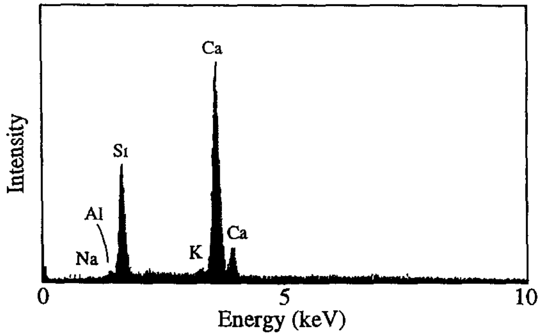

FIG. 5.
Representative chemical analysis of pink-staining gel.

examination by EDS in the SEM. All such materials were dominantly Si with large amounts of Ca (Fig. 5). In addition, they occasionally contained minor amounts of K and perhaps Na.

Based on these observations, we conclude that the pink-staining materials were alkali poor Ca+Si gels associated in some way with advanced ASR. Based on petrographic observations, it appears that these pink-staining gels are derived from the yellow-staining gels. The pink-staining gels may have formed directly from the alkali-rich (yellow) gels by leaching of the alkalis or by reacting with the cement paste or other components in the fractures (e.g., perhaps CO_2).

Non-ASR-Related Pink-Staining Regions. Two other examples of pink-staining materials were observed: some calcium carbonate and some "gel-free" fractures in two distressed cores.

Some occurrences of calcium carbonate were susceptible to rhodamine B. Although we have not undertaken any systematic investigation of staining of calcium carbonates, we noted two instances in which calcite was stained pink. In one instance, a travetine-like deposit (a layered deposit of calcium carbonate) had formed on the side of a highly distressed bridge with advanced ASR. Some layers within this deposit stained pink, whereas others did not. The other instance was in the case of a limestone aggregate used in a concrete exhibiting minor ASR and delayed ettringite formation (DEF). Parts of the limestone aggregate were lightly stained pink; however, much of the limestone aggregate remained unstained. (As an aside, it is possible, perhaps likely, that some of the "gels" we have investigated with our staining procedure have wholly or in part carbonated following exposure to the atmosphere; hence, other precipitates that we've observed to stain yellow or pink may in fact contain carbonates derived from gels.)

Another occurrence of pink staining was along some fracture surfaces of cores from a section of a concrete road that is exhibiting distress in the field. These particular cores showed no signs of ASR and had no occurrences of yellow-stained gel. The distress mechanism for these road sections remains undetermined, and we do not know why some fracture surfaces from these cores stained pink. The surfaces did not have any observable precipitate and were indistinguishable from other fracture surfaces that did not stain pink. (We did not collect the core, so we could not determine which fractures might have been associated with cracks in the concrete that were present prior to coring). One possibility is that these pink-stained surfaces were coated with a very thin carbonate precipitate that was unobservable prior to staining.

Comparison With the Uranyl Acetate Method. We have compared our dual stain approach with the uranyl acetate method on several samples of concrete suffering from ASR as well as some apparently free of ASR. These comparisons have been made on matched fracture surfaces (i.e., where one face was stained by our approach and the other stained by uranyl acetate) and on individual surfaces that were treated by both methods (either uranyl acetate first followed by the dual staining treatment or vice versa). In all cases, our dual staining method identified the same materials that the uranyl acetate method tagged. Interestingly, the uranyl acetate method tagged both the pink- and yellow-staining materials; hence, the dual staining method provided greater information on the nature of the ASR in a given concrete (i.e., it identified two chemically distinct gels). This improvement relates directly to the non-specificity of the uranyl acetate technique, as discussed in the Introduction.

In addition to providing greater information, the dual staining method was superior to the uranyl acetate method because it augmented standard petrographic examination of the concrete. Unlike the uranyl ion (which requires a UV source and nearly complete darkness to be seen), these colored stains allowed the reaction products to be identified concurrent with identification of aggregate lithology and the gross morphology of the concrete. Furthermore, the stains can be seen in a binocular microscope or hand lens, which greatly improved our petrographic examination of cores.

The staining method was particularly useful in our examination of one core from a distressed highway in Iowa. This concrete had been examined by several experts, and the distress mechanism remains hotly debated. At issue is whether the concrete contains ASR or DEF and, if so, how much. Standard petrographic examination of the core would lead to conclude that most of the voids contain both a gel-like precipitate and ettringite. Following staining, however, the extent and distribution of pink- and yellow-stained gels was readily apparent, and ettringite (unstained) was readily differentiated from the ASR gels in the core as a whole.

Effect of Staining on Ettringite. One sample of a core from a highway section known to contain ettringite-filled vugs was examined by the staining procedure. Both pink- and yellow-stained gel were observed in the core following treatment. However, clearly identifiable ettringite crystals—fine needles seen with a binocular microscope; presence of Ca, Al, and S verified by energy dispersive spectroscopy (EDS) analysis in the scanning electron microscope (SEM)—did not stain either pink or yellow. Some voids containing a pink-stained gel covered with unstained ettringite crystals were also observed. We cannot rule out the possibility that microcrystalline ettringite might have stained pink, but we believe, based on the non-staining of the larger crystals, that this is probably unlikely. Furthermore, ettringite should not stain yellow, because it lacks potassium.

Preparation of Concrete Specimen. In our evaluations of this dual staining method, we concluded (like other workers) that bush hammered surfaces do not provide readily interpretable information on the nature of ASR in the particular structure. We evaluated the staining method on several bush hammered surfaces from structures for which we also had cores. Although some staining could be seen on bush hammered surfaces, the staining was not nearly as striking as staining on fractured surfaces from the cores. Moreover, it was clear from the cores that in some cases ASR was more pronounced in the upper 0.1 m of the structure, whereas in other cases it was more pronounced in the lower portions of the structure. Hence, a bush hammered surface would not be expected to provide an adequate assessment of ASR within a concrete structure.

Another concern expressed by some workers is that method such as uranyl acetate must be applied to freshly fractured surfaces. In contrast, the dual staining method reported here appeared to work adequately both on freshly fractured surfaces and on aged (up to several years) surfaces.

Conclusions

The dual staining method described above provides a simple means for evaluating the extent and distribution of gel-related products associated with ASR. The method results in pink- and yellow-stained areas that give the observer a rapid indication of the degree to which ASR has affected the concrete and that are easy to interpret (even for someone not experienced in petrographic analysis).

For experienced petrographers, the method greatly improves the evaluation of ASR in a concrete, because the extent and distribution of ASR are readily determined and because the method provides additional information on the distribution of two different gels (a yellow-staining gel that is alkali-rich and a pink-staining gel that is alkali-poor). Like the uranyl acetate method, the dual staining method allows individuals to evaluate concrete for ASR in house and even in the field. Unlike the uranyl acetate method, the dual staining method does not require the use of a source of UV illumination in a light-tight environment and, more importantly, does not involve the use of uranium. In addition, the dual staining technique described above differs markedly from other staining techniques such as with cuprammonium sulphate (18) (which is non-chemical-specific, like uranyl acetate) or pH indicators such as phenolpthalien. Finally, false positives will be uncommon with this technique, because only materials that can cation-exchange potassium should stain yellow. Hence, common rock forming minerals such as feldspars, micas, and illite remain unstained. Less common minerals such as K-rich smectites and K-rich zeolites (most smectites and zeolites are not K-rich) may stain yellow. In general, however, these "false positives" should be easily recognized in hand specimen, particularly in light of the unique staining pattern (yellow within aggregates and pink surrounding aggregates) that appears to be typical of advanced ASR.

Acknowledgements

This work was supported by the Department of Energy through contract no. W-7405-ENG-36 to Los Alamos National Laboratory via a Laboratory-Directed Research and Development grant. We have benefited greatly from our interactions and discussions with a number of concrete experts, including Joe Barela, Wendell Dubberke, Steve Forster, David Gress, Ron Gorver, Vernon Marks, and Roger Surdahl. In addition, we wish to thank Robert Raymond for extensive discussions on ASR and for help on SEM examination; and Dave Vaniman and two anonymous reviewers for critical reviews of the manuscript.

References

1. R. Helmuth, Alkali-Silica Reactivity: An Overview of Research, p. 105, National Research Council Washington, 1993.
2. S. Diamond, Cem. Concr. Res. 5, 329 (1975).
3. H.F.W. Taylor, Cement Chemistry, p. 301, Academic Press, New York, 1990.
4. R.E. Oberholster and G. Davies, Cem. Concr. Res. 16, 181 (1986).
5. P.E. Grattan-Bellew, Proc. 8th Int. Alkali Conf., 279 (1989).
6. D. Stark, Handbook for the Identification of Alkali-Silica Reactivity in Highway Structures, National Research Council, Washington, 1991.
7. K. Natesaiyer and K.C. Hover, Cem. Concr. Res. 18, 455 (1988).
8. K.C. Natesaiyer and K.C. Hover, Cem. Concr. Res. 19, 770, (1989).
9. S. Ahrland, I. Grenthe and B. Noren, Acta Chem. Scand. 14, 1059 (1960).
10. G.D. Guthrie, Jr. and J.W. Carey, Detection of Alkali-Silica Reaction Swelling in Concrete by Staining, patent filed 11/7/96 (1996).
11. G. Davies and R.E. Oberholster, Cem. Concr. Res. 18, 621 (1988).
12. F.M. Lea, The Chemistry of Cement and Concrete, 3rd edition, p. 727, Chemical Publishing Company, Inc., New York, 1971.
13. P.J. Van Rysselberge, Ind. Eng. Chem. 3, 3 (1931).
14. A. Gabriel and E.P. Cox, Am. Mineral. 14, 290 (1929).
15. M.L Keith, Am. Mineral. 24, 561 (1939).
16. F. Chayes, Am. Mineral. 37, 337 (1952).
17. S. Budavari, The Merck Index, 11th edition, Merck & Co., Rahway, NJ, 1989.
18. A.B. Poole, A. McLachlan and D.J. Ellis, Cem. Concr. Res. 18, 116 (1988).