Forces of Hydration That Can Cause Havoc in Concrete

May the force not be with you

BY BERNARD ERLIN AND DIPAYAN JANA

Forces of nature are sometimes immediate (earthquakes, volcanoes, tornados, hurricanes, tsunamis and seiches, floods, lightning strikes) and are sometimes eons slow (erosion of mountains that create flanking, relatively flat piedmonts and the gradual building of mountains by the movements of tectonic plates). There are also forces that disrupt and deteriorate concrete, which are usually less cataclysmic than the previously mentioned ones. But, forces that deteriorate concrete can be ultradynamic if, for example, you are standing on a fired-clay tiled floor that erupts violently because of tile expansion (sometimes enhanced by concrete shrinkage) that was not accommodated.

Natural forces that deteriorate concrete are caused by cyclic freezing and thawing, cyclic wetting and drying, cyclic heating and cooling, corrosion of metal reinforcement, attrition by abrasion, cavitation, chemical attack—both internal and external—and the subject of this article, volume changes caused by hydration of water soluble salts and relatively insoluble anhydrous compounds. Each force is the result of an in-place solid volume change that causes the final solid product volume to occupy more space than the original solid volume of the reactants. The mechanisms that create the forces of deterioration are described and discussed in this article, along with examples of distress caused by each phenomenon. We also describe instances where these forces have been harnessed for useful purposes.

PUTTING THE FORCES TO WORK

Alexander Klein invented kleinite (calcium sulfoaluminate, $4CaO \cdot 3Al_2O_3 \cdot SO_3$, in cement chemist's notation C_4A_3S), the anhydrous counterpart of ettringite ($3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$), and the basic component of Type K shrinkage-compensating cement specified in ASTM C 845.[1] He took one of the end products of deleterious sulfate attack, ettringite (and its forceful expansion), and made something good of it (discussed later). The Japanese took free lime (CaO, uncombined lime), the anhydrous counterpart of epizet-strained calcium hydroxide ($Ca(OH)_2$) that forms from hydration of free lime (an expansive material), which causes a lesser-known distress to concrete, and controlled it. They used its tremendous force, calculated to be greater than 30,000 psi (200 MPa),[2] to implode concrete structures by packing it and moisture into drilled holes at selected locations in concrete columns. They also used lime for making shrinkage-compensating and self-stressing concrete by controlling the magnitude of the lime's expansion. Irreversible transformations of very low soluble or insoluble anhydrous compounds—the hydration of free lime to calcium hydroxide (epizet), magnesia (periclase) to magnesium hydroxide (brucite), metallic iron to iron hydroxide and iron oxide—can cause bulk concrete expansion, intrinsic structural distress, cracking, spalling, and popouts. The size and population density of the offensive particles, and the physical mechanisms involved, determine the magnitude and type of distress.

Other hydration reactions can create uncontrollable physical forces that cause distress in concrete. Lately, popularity has been given to reversible, cyclic conversions of highly water-soluble salts having various hydration states (for example, sodium sulfate and sodium carbonate) that can cause distress of concrete surfaces exposed to cyclic wetting and drying. Some of these phenomena are not new, as demonstrated by Hime et al.,[3] who coined the term "salt hydration distress (SHD)," and Haynes, O’Neill, and Mehta[4] each listed prior literature dealing with physical attack in concrete by sodium sulfate and carbonate salts. Each also reported that stone as well as concrete are vulnerable to SHD. The following supplements their work by presenting and discussing field examples of the SHD phenomena. Also discussed are other phenomena, along with explanations of mechanisms that cause “hydration” distress.

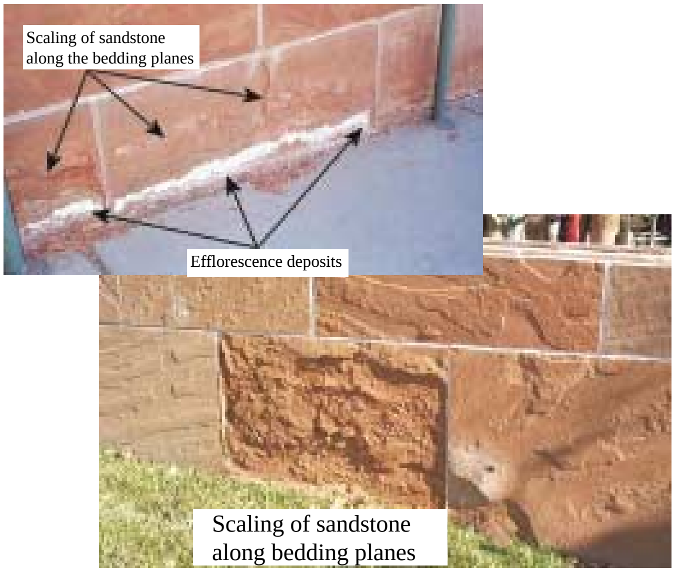

Fig. 1: Salt hydration distress of a masonry sandstone facade manifested as crumbling and scaling of the sandstone

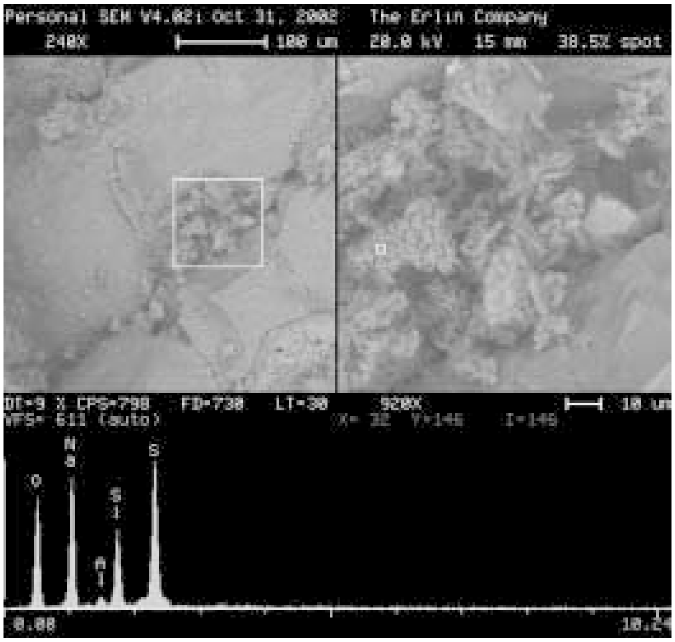

Fig. 2: Electron micrograph of white efflorescence in an embayment on the sandstone surface. The right micrograph is of the boxed area in the left micrograph. The x-ray spectrum is of the small boxed area in the right micrograph. The spectrum is indicative of sodium sulfate

SALT HYDRATION DISTRESS

This type of distress is restricted to concrete surfaces exposed to cyclic variations in ambient temperature and humidity. The following details a case study of the deterioration of a sandstone facade.

Distress evidence in nominally 2-in.-thick (50 mm) face-bedded ashlar sandstone units of a masonry façade exposed to a sulfate-rich soil environment manifested as crumbling and scaling—particularly along flanking bedding planes—and white efflorescence (Fig. 1). The distress is in the lower reaches of the facade where water-soluble sulfates from subgrade soils are from 0.80 to 1.33% by mass of the stone.

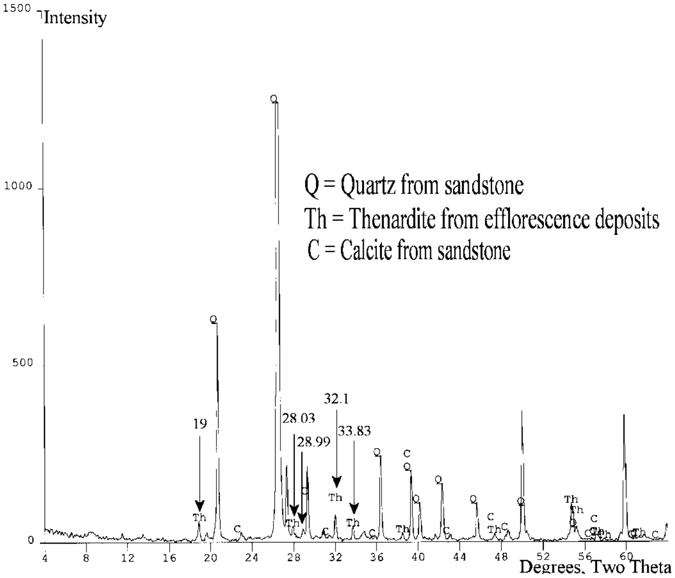

Fig. 3: XRD pattern of thenardite efflorescence scraped from the sandstone. The arrows point to several main peaks of thenardite

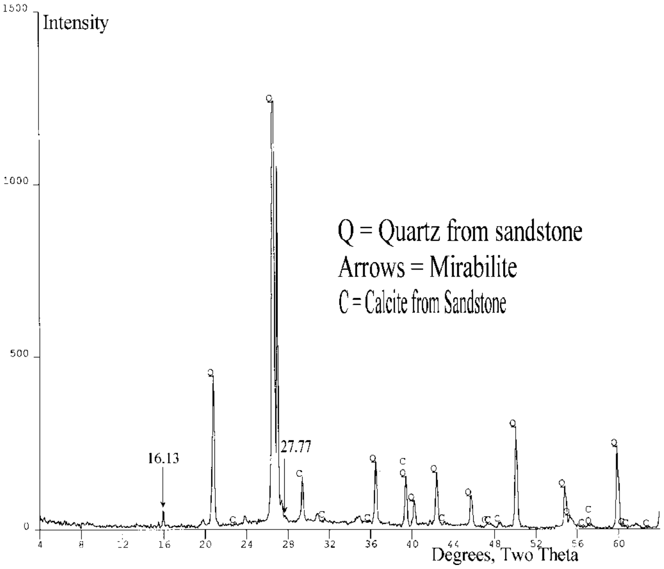

Fig. 4: XRD pattern after wetting the thenardite that produced the x-ray pattern in Fig. 3. Rerun of the sample that produced the pattern in Fig. 3 after exposure to a few drops of water. The arrows point to two main peaks of mirabilite

The distress extends up the facade for distances of about 2 ft (0.6 m). Associated with the distress are white, water-soluble efflorescence salt deposits (Fig. 1). Based on classical petrographic microscopy, x-ray diffraction (XRD), and scanning electron microscope energy-dispersive spectroscopy (SEM-EDS) analyses, the deposits were identified as thenardite (Na_2SO_4) (Fig. 2 and 3). The conversion of thenardite to mirabilite is shown in an XRD pattern (Fig. 4) of the thenardite after exposing it to moisture (by placing a few drops of water on the sample).

This is supporting proof of the Hime et al.[3] conclusion that distress is a result of expansion due to the repeated reconversion of thenardite (Na_2SO_4) to mirabilite ($Na_2SO_4 \cdot 10H_2O$) during cyclic wetting. A 315% in-place solid volume increase accompanies the thenardite-mirabilite conversion. The 2 ft (0.6 m) or so upward movement of sulfate-bearing solutions is, in part, due to the orientation of the sandstone whose vertical bedding planes (along which the solutions rapidly migrated) had appropriate permeability for sulfate solutions to wick upward on the surface of the facade. Neither jointing mortar nor concrete sidewalks that contacted the same façade are distressed.

Phase changes similar to the thenardite-mirabilite transformation include: (1) thermonatrite ($Na_2CO_3 \cdot H_2O$) to natron ($Na_2CO_3 \cdot 10H_2O$), which is accompanied by a 261% solid volume increase, and (2) thermonatrite to $Na_2CO_3 \cdot 7H_2O$, which is accompanied by a 179% solid volume increase. Hime et al.[3] listed the requirements for SHD: (1) highly soluble salts (Table 1); (2) exposure to a cyclic wetting environment; and (3) reversible transformations of the salts between different hydration states due to variations in ambient temperature and humidity.

The physical aspects of the thenardite-mirabilite transformation mechanism, however, are somewhat difficult to interpret because of thenardite and mirabilite's high solubility in water (Table 1). Unlike the hydration of free lime, which occurs in-place at the surface of the free lime (Fig. 5), hydration of thenardite to mirabilite may be in place, or through solution, or both. Additionally, if mirabilite is formed initially, when it converts to thenardite (which occupies a smaller volume), additional solutions will create new deposits to fill the vacated space so that subsequent conversions to mirabilite will have less space in which to form and enhance the magnitude of the stress.[5,6] For the voids to be filled with new deposits, the process must take place within the concrete. Hence, efflorescence (which by definition is a surface deposit) does no harm, but is an indicator of possible SHD.

Final solid volume—not the sum of the reactant volumes—is important

According to Haynes, O'Neil, and Mehta,[4] the thenardite-mirabilite transformation is not expansive based on molar volume calculations because the molar volume of thenardite plus 10 moles of water (53 + 180 = 233 cm^3) is greater than the molar volume of their

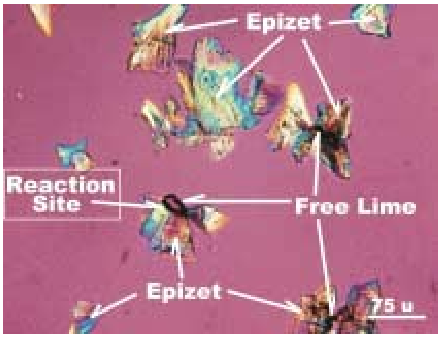

Fig. 5: Free lime encased by epizet. The hydration to epizet takes place at the surface of the free lime

TABLE 1:
SOLUBILITIES OF SOLID REACTANTS AND REACTION PRODUCTS INVOLVED IN THE HYDRATION REACTIONS (DATA FROM *CRC HANDBOOK OF CHEMISTRY AND PHYSICS*, 1995)

Hydration reactions	Solubility in water (g/L) at the indicated temperature	
	Solid reactant	Solid product
$CaO + H_2O = Ca(OH)_2$ (Free Lime) (Epizet)	1.31 (10 °C) to 0.7 (80 °C)	1.85 (0 °C) to 0.77 (100 °C)
$MgO + H_2O = Mg(OH)_2$ (Periclase) (Brucite)	0.0062 (0 °C) to 0.086 (30 °C)	0.009 (18 °C) to 0.04 (100 °C)
$CaSO_4 + 2H_2O = CaSO_4 \cdot 2H_2O$ (Anhydrite) (Gypsum)	2.09 (20 °C)	2.41 (0 °C) to 2.22 (100 °C)
$Na_2SO_4 + 10H_2O = Na_2SO_4 \cdot 10H_2O$ (Thenardite) (Mirabilite)	47.6 (0 °C) to 427 (100 °C)	110 (0 °C) to 927 (30 °C)
$Na_2CO_3 \cdot H_2O + 9H_2O = Na_2CO_3 \cdot 10H_2O$ (Thermonatrite) (Natron)	330 (0 °C) to 521 (100 °C)	215.2 (0 °C) to 4210 (100 °C)
$Na_2CO_3 \cdot H_2O + 6H_2O = Na_2CO_3 \cdot 7H_2O$ (Thermonatrite) (7-hydrate)	330 (0 °C) to 521 (100 °C)	169 (0 °C) to 339 (35 °C)
$MgSO_4 \cdot H_2O + 6H_2O = MgSO_4 \cdot 7H_2O$ (Kieserite) (Epsomite)	684 (100 °C)	710 (20 °C) to 910 (40 °C)

reaction product, mirabilite (220 cm^3). That is because Haynes, O'Neil, and Mehta considered the volume of water in their calculations. According to Hime,[7] water does not need any extra space because it comes to the reaction site through the capillary pores. We agree with Hime. This reaction, and other similar reactions—many of which are reported to cause distress in concrete—result in final products that have volumes less than the total volume of the reactants (that is, salt plus water).

Table 2 gives some examples of hydration reactions, molar volumes of the solid reactants, and their hydration products—in each case, the hydration products occupy significantly greater volumes than the solid volumes of the reactants. In SHD, it is the greater solid volume of the final hydration product, rather than the solid volume of the initial salt, that causes the distress. Available water for the reactions enters the concrete via spaces such as microcracks and interconnected capillary pores.

The solubilities of the solid reactants are probably important, as demonstrated by the high solubility of thenardite (Table 1), which Hime et al.[3] mentioned as a requirement for SHD. The stress created by a single cyclic change of thenardite to mirabilite is probably relatively small because of their high solubilities wherein some of the thenardite may return to solution and precipitate elsewhere—it is the cyclic stresses that probably eventually cause fatigue to the concrete. The low solubilities of free lime, periclase, and their hydroxides (Table 1) probably account for the extremely high stresses created by their hydration transformations.

Hydration of free lime and magnesia

The reactions of free lime (CaO, hard-burned lime) and magnesia (MgO, periclase) with water result in the formation of epizet ($Ca(OH)_2$, strained calcium hydroxide) and brucite ($Mg(OH)_2$, magnesium hydroxide), with respective solid volume increases of 91.7 and 119.6% (Table 1). In the hydration of free lime, the sum of the molar volumes of CaO and H_2O is 35.25 cm^3, and the molar volume of their reaction product, epizet, is 33.07 cm^3. In the hydration of periclase to brucite, the sum of the molar volumes of MgO and H_2O is 29.25 cm^3, and the molar volume of their reaction product, brucite, is 24.71 cm^3. The molar volumes of the hydration products thus are smaller than the reactants. Epizet and brucite, however, are about twice the size of free lime and periclase—it is the increase in particle size that causes the distress to hardened concrete.

The hydration reactions are topochemical, that is, they occur in place at the surface of the anhydrous particles (Fig. 5), so that the hydroxides formed at the reaction surfaces are forced away by new hydroxide products as the reactions progress. If there is encasement around the reacting particles, stresses are created that can eventually cause microcracking (Fig. 6),[8] macrocracking, and popouts (Fig. 7), which provide relief of the stress. The magnitude of that stress can be small (Fig. 6)[8] or large (Fig. 8).

The hydration of free lime and periclase are not examples of SHD because they are not salts. They have much lower solubilities than the typical sodium sulfate or carbonate salts of SHD (Table 1), and their reactions are irreversible.

Sources of free lime and periclase that have caused distress to concrete in the past include portland cement (Fig. 6), dolomite refractory brick contamination (Fig. 7), steel-making slag used as aggregate (Fig. 8) (including magnesium wustite, (Fe,MgO) and "burnt" limestone contamination from stone used to bank furnace fires.[9]

TABLE 2:

HYDRATION REACTIONS THAT CAUSE DISTRESS IN CONCRETE DUE TO INCREASES IN SOLID VOLUME (DATA FROM *CRC HANDBOOK OF CHEMISTRY AND PHYSICS*, 1995)

Hydration reactions	Molar volumes (cm^3/mole)		Decrease in reaction volume, %	Increase in solid volume, %
	Solid reactant	Solid product		
$CaO + H_2O = Ca(OH)_2$ (Free Lime) (Epizet)	17.25	33.07	–6.2	+91.7
$MgO + H_2O = Mg(OH)_2$ (Periclase) (Brucite)	11.25	24.71	–15.5	+119.6
$CaSO_4 + 2H_2O = CaSO_4 \cdot 2H_2O$ (Anhydrite) (Gypsum)	45.99	74.21	–9.5	+61.3
$Na_2SO_4 + 10H_2O = Na_2SO_4 \cdot 10H_2O$ (Thenardite) (Mirabilite)	53	220	–5.6	+315.1
$Na_2CO_3 \cdot H_2O + 9H_2O = Na_2CO_3 \cdot 10H_2O$ (Thermonatrite) (Natron)	55.11	198.7	–8.5	+260.5
$Na_2CO_3 \cdot H_2O + 6H_2O = Na_2CO_3 \cdot 7H_2O$ (Thermonatrite) (7-hydrate)	55.11	153.7	–5.8	+178.9
$MgSO_4 \cdot H_2O + 6H_2O = MgSO_4 \cdot 7H_2O$ (Kieserite) (Epsomite)	56.7	146.71	–10.9	+158.7

Hydration of kleinite

As mentioned previously, Alexander Klein invented anhydrous calcium sulfoaluminate (kleinite) to cause controlled expansion of concrete, and developed and patented Type K expansive cement. ASTM C 845[1] and ACI 223-98[10] specify the industry standards for Type K cement and its design use. Expansion results from the reaction of kleinite, calcium sulfate, calcium hydroxide (from portland cement paste and free lime), and water, which forms ettringite. Also contributing to the chemical reactions and the expansion (to some extent) is the free lime that is invariably present in kleinite.

The volume increase as kleinite forms ettringite is very large, so limiting the amount of sulfate and kleinite in the cement controls expansion. The physical reactions that cause the expansions are similar to the free lime-epizet and periclase-brucite reactions; that is, the reactions are topochemical (Fig. 9).

Laumontite-leonhardite transitions (zeolites)

ASTM C 294[11] mentions the reversible reactions of laumontite and leonhardite as contributors to concrete distress because of their volume changes upon wetting and drying. Leonhardite is a family of several dehydrated forms of laumontite produced by drying.[12] The general formula for laumontite is $Ca_4[(AlO_2)_8 \cdot (SiO_2)_{16}] \cdot 16\text{-}18H_2O$—leonhardite has the same formula except it can have 12 or 14 H_2O (sodium and potassium can substitute for some of the calcium). Differences in the solid volumes of the hydration products are difficult to determine because of the lack of density data for the several forms of leonhardite. Based upon calculations using unit cell dimensions, however, the change in solid volume is in the range of 3 to 6%, depending on its hydration state

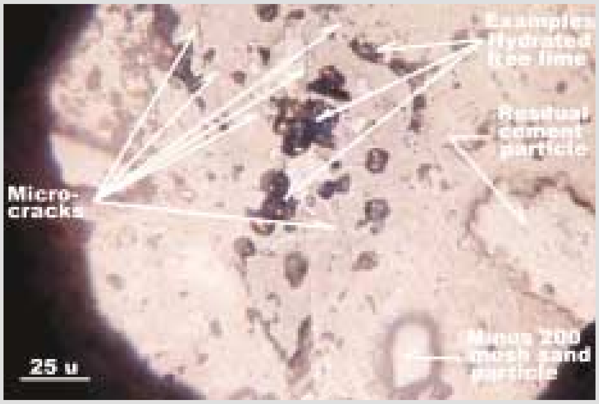

Fig. 6: Polished section showing hydration of free lime to hydrated free lime (epizet) and attendant microcracks

Fig. 7: Twelve in. (300 mm) popout caused by hydration of free lime and periclase from 1 in. (25 mm) sized refractory brick contamination. The offensive particle is within the circle

Fig. 8: "Thrust faults" in an asphalt shoulder flanking a concrete pavement expanding laterally due to electric furnace slag aggregate that contained free lime and periclase in an econo-crete subbase (concrete lean in portland cement)

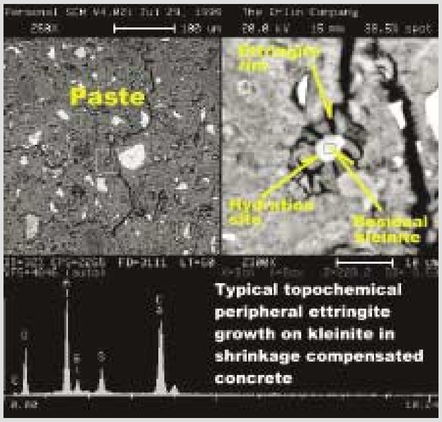

Fig. 9: Electron micrographs of topochemical formation of ettringite on kleinite in a shrinkage-compensated concrete. The right micrograph is of the boxed area in the left micrograph. The x-ray spectrum is of the small, boxed area in residual kleinite in the right micrograph (arrow). Hydration always occurs at the surface of the kleinite

Fig. 10: Surface scaling due to cyclic conversion of laumontite to leonhardite at a location exposed to periodic water spray from sprinklers

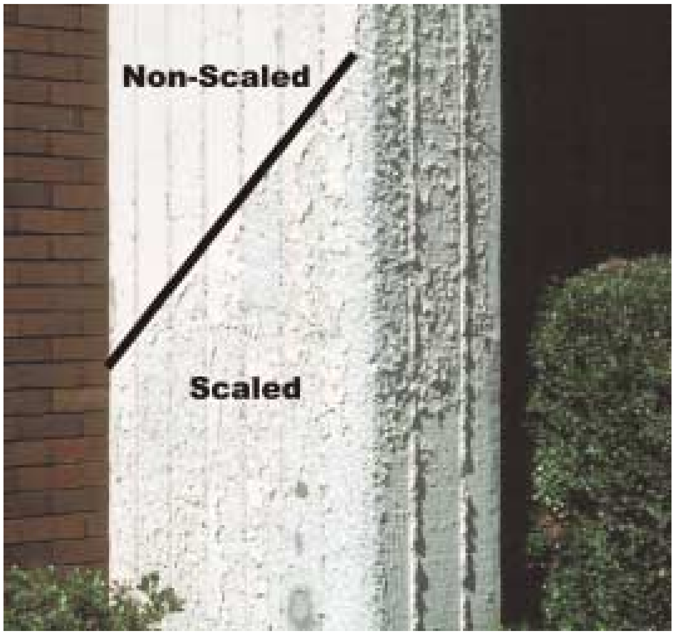

Fig. 11: Surface scaling due to cyclic conversion of laumontite to leonhardite at a location exposed to periodic water spray from sprinklers

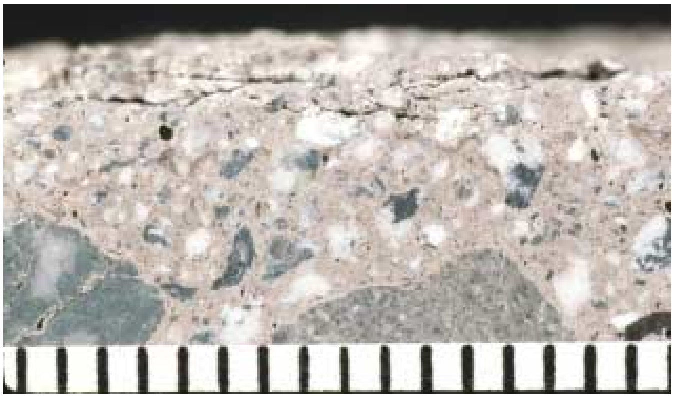

Fig. 12: Cracks oriented subparallel to the surface—formed due to cyclic conversion of laumontite to leonhardite. The scale is in 1/16 in. (1 mm) increments

and calcium-alkali ratio. Although the volume changes are not as large as those that occur with the SHD salts, free lime, periclase, and their hydrates, they are sufficient to cause popouts and scaling.

Figure 10 and 11 illustrate concrete surface distress caused by cyclic laumontite-leonhardite conversions. Figure 12 shows a cross section of a core from a surface-deteriorated concrete.

Zeolites are usually the alteration products of feldspars, and in the case of altered granite, the zeolites are associated with other rock components such as quartz, unaltered feldspars, mafic minerals, and mica. The laumontite-leonhardite transformations cause particles that are present to crumble and turn into powder. In turn, concrete flanking the crumbling particles cracks. Because the wetting and drying occurs at the concrete surface (which is in contact with ambient temperature and moisture), thermal and moisture fronts move in and out of the surface region of the concrete. This causes cyclic transformations of laumontite to leonhardite so that distress occurs in line (parallel) to the front—hence, the distress occurs as scales, a look-alike to scaling due to cyclic freezing.

The probable physical mechanism causing damage by the cyclic, and relatively small, volume changes is a wetting and drying hysteresis resulting from failure of leonhardite crystals, after rehydration, to return to the exact spatial position they occupied before dehydration. The resulting "jacking," or "ratchet," effect accumulates, resulting in a progressive increase in bulk particle volume. The jacking or ratchet effect indicates a net positive increase in length or volume of a material by repeated heating and cooling, or wetting and drying, that lengthens and shortens the material, but it never goes back to its original length or volume. Reference 13 describes a similar jacking phenomenon due to thermal hysteresis for fine-grained marble.

EPILOGUE

According to ACI 201.2R-01,[14] Section 2.3, Physical Salt Attack, to help mitigate deterioration one must: (a) minimize water ingress and contact to concrete; (b) use a maximum water-cement ratio of 0.45 along with a pozzolan; and (c) use vapor barriers and drain water away from the concrete.

To avoid damage to concrete due to free lime and periclase: (1) use portland cements (ASTM C 150),[15] blended cements (ASTM C 595),[16] and hydraulic cements (ASTM C 1157)[17] that meet maximum autoclave expansion requirements of 0.80%; (2) do not incorporate steel-making slag in concrete; and (3) do not contaminate concrete with materials that contain free lime, periclase, and potentially expansive salts. To mitigate damage due to laumontite-leonhardite, don't use aggregates that contain them.

Maybe, someday, the destructive forces of these reactions can be better accommodated, avoided, or turned around to benefit our industry (as Alexander Klein did with ettringite and the Japanese did with epizet). In the cases of kleinite and epizet, may the force be with you—otherwise, may the force not be with you.

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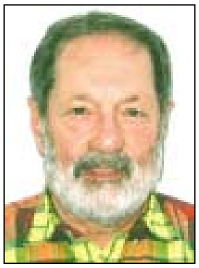

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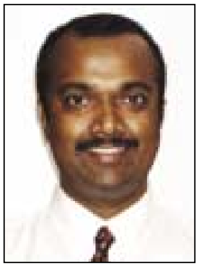

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