Pergamon

Cement and Concrete Research 30 (2000) 669–671

CEMENT AND CONCRETE RESEARCH

Discussion

A discussion of the paper "Crystallisation in pores" by G.W. Scherer[☆]

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Received 19 November 1999

Dr. Scherer, in this very interesting paper, has extensively reviewed the crystallisation processes in pores, the growth of crystallisation pressure, and the consequent degradation of the host porous matrix. Dr. Scherer also showed that the concept of the crystallisation pressure could be used, without any discrimination, to explain damages of stone and masonry due to efflorescence as well as damages to mortar and concrete as a result of ice formation in them. Dr. Scherer stated that "gross damage is not expected until the crystals propagate through the pore space" and the filled pore space contains a strength-limiting flaw. In my discussion of this interesting paper, I shall distinguish between damages due to salt efflorescence in stone and masonry and ice formation in a porous matrix. The reasons for this distinction will be obvious from the discussion. However, before I start my discussion, I would like to state my position clearly. I agree with Dr. Scherer that under appropriate conditions, the crystal growth pressure could be very aggressive to a host porous matrix. I have done this since 1964 [1–5].

1. Damage due to efflorescence

1.1. Other accompanying processes

Any damage to stones or masonry units with visible signs of efflorescence is generally attributed to salt crystallisation. The destructive pressure is attributed either to a crystal growth or a volume increase with the formation of a hydrated crystal from its anhydrous precursor. However, in many instances, other processes play important parts in this breakdown. For example, marble cladding plates from many sources, but not all, undergo progressive bending and strength loss over the years without any sign of efflorescence or any other chemical attack. Laboratory experiments show that similar bending and strength loss could be simulated by wetting the marble plates with water and drying them from one side only [6]. This breakdown is a growing problem in the European countries where marble cladding is fashionable. I understand that this is also a problem in some parts of the USA. Efflorescence is always associated with wetting by and drying of a salt solution in a porous matrix. A marble sample weakened by the action of wetting–drying of water could be damaged by a pressure that would be unable to cause any damage otherwise. There is another more destructive process for marble and masonry. This is the formation of $Na_2CO_3 \cdot H_2O$ from $CaCO_3$ and evaporating NaCl solution at temperatures above about 35°C. This reaction occurs naturally on the limestone shores of Egyptian salt lakes. Observation of this formation by the French scientists, accompanying Napoleon to Egypt, started the study of chemical equilibrium. In marble samples, this attack starts at the inter-particle contact surfaces where calcium carbonate is under stress; this formation causes a loss of strength. Furthermore, moist $Na_2CO_3 \cdot H_2O$ forms $Na_2CO_3 \cdot 10H_2O$ below 35.4°C. The formation of $Na_2CO_3 \cdot 10H_2O$ causes further breakdown of the porous matrix. The phase diagram of the Na_2CO_3–H_2O system has many similarities with that of Na_2SO_4–H_2O system. Chemical analyses of water extracts from more than 100 broken down stones or masonry units showed the presence of mixtures of sulfate, chloride, and carbonate of alkali metals (mainly sodium) in them but never alkali chloride alone. In the cases of cement-based materials, other damage-causing processes like sulfate or carbonate attack or even alkali–silica reaction invariably occur. Obviously, the breakdowns generally attributed to efflorescence may not be due to crystal efflorescence only. However, efflorescence breakdown of properly burnt clay products like brick can only be due to salt crystallisation. The situation can also be simulated by subjecting brick samples to the ASTM C88 test method.

1.2. The nature of breakdown

Examinations of the naturally occurring efflorescing samples show that the surfaces of the samples are covered

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[☆] Cem Concr Res 29 (8) (1999) 1347–1358.

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PII: S0008-8846(00)00224-6

with powders of broken down host matrices. The powdery material seldom contains grains bigger than about 0.5 mm. The removal of the powdery material by brushing and subsequent scratching of the freshly exposed surface with a hard needle reveals a soft layer of a couple of millimeters thickness. Below this soft layer, the material appears to be uniformly strong. Thus, the breakdown process reduces the host matrix to a powdery material only near the outer surfaces. The damage is progressive and not catastrophic. The nature of this breakdown will be contrasted with that of samples damaged due to ice formation.

From the phenomenological analysis of the breakdown process, the following three scenarios could be visualized below.

(a) All the necessary strength controlling critical flaws are within a couple of millimeters thick layer. The spacing of the critical flaws must be such that the matrix breaks down into a less than 0.5-mm-sized powder. This means that any 0.5 × 0.5-mm area in any arbitrary plane in the sample must have at least one critical sized flaw.

(b) Once a breakdown occurs at a critical flaw, it creates new critical flaws of the required density to produce powdery degradation products.

(c) Crystallisation within surface pores does not require critical flaws to cause a local damage. Another view will be that the local crystal growth pressure is working on local sub-critical flaws. The spacing of the pores determines the size of the powder. These local damages in their turn produce new sub-critical flaws. The damage patterns of Pyrex test tubes during crystallisation of melts of sodium thiosulfate or $Na_2SO_4 \cdot 10H_2O$ are consistent with this scenario [2,5]. Pores at the surface may be likened to micro-test tubes. To break down thin, wedge-shaped, inter-pore walls around a larger pore does not require much pressure and this process will create new sub-critical flaws to nearby pore walls. This self-sustaining, progressive breakdown will naturally produce fine powder. This is consistent with the damage patterns of field observations.

The above scenarios are not totally exclusive of each other. Dr. Scherer's comments will be of much interest.

1.3. Can crystallisation of NaCl cause any damage?

In discussing Eq. (18) of his paper, Dr. Scherer expressed the opinion that a 2-fold supersaturation of NaCl ($C/C_o = 2$) could easily be produced during evaporation. In mid-1980s, I tried to developed a test method similar to ASTM C88 using saturated NaCl solution. ASTM C88 test method uses a saturated solution of sodium sulfate. Sodium sulfate has a number of disadvantages. It is aggressive to concrete samples and waste drains, near room temperature its solubility varies much with slight changes in storage temperature, etc. A saturated NaCl solution avoids all these disadvantages. I subjected brick samples to ASTM C88 test method using both saturated NaCl and Na_2SO_4 solutions. Brick samples in saturated sodium sulfate solution started to form small pop-outs after about eight cycles; these pop-outs were not as small as in natural weathering. These pop-outs formed after oven-dried brick samples were re-submerged in the saturated sodium sulfate solution, i.e. when $Na_2SO_4 \cdot 10H_2O$ formed. Brick samples in saturated NaCl solution did not show any sign of damage even after 20 cycles when the experiment was stopped. Discussions with other workers revealed that they have a similar experience with NaCl solution. Subsidiary experiments showed that shortly after the samples were placed in the drying oven, they were encrusted with crystals and the rate of water evaporation dropped sharply. This happened for samples stored both in sodium sulfate and NaCl solutions. Experimenting with evaporating NaCl solution in beakers at about 60°C, I could get at best 1.1-fold supersaturation until floating crystals formed and then the supersaturation dropped to about 1.05-fold. It appears that a transient high supersaturation may be obtained until NaCl crystallisation starts. This has to be contrasted with Na_2SO_4 solution where persistent metastable supersaturation occurs even in the presence of crystals [2,5]. From this, I inferred that crust formation on the drying brick samples hindered high supersaturation in the bricks stored in NaCl solution. I would be interested to know what drying regime Dr. Scherer used to get a 2-fold supersaturation of NaCl.

2. Damage due to ice formation

2.1. Some general observations on the strength of ice in porous matrix, the achievable degree of super-cooling, etc.

In a recent review article, I have drawn attention to the fact that ice formed in a siliceous porous matrix is much stronger than ice formed from bulk water [7]. For example, a clay paste containing 20–30% water when frozen can have compressive strength as high as 60 MPa [8]. Normalization to 100% water gives a compressive strength of about 200 MPa for ice in the clay matrix. Strengths of frozen samples increase with decreasing temperature. Similarly, the mean flexural strength of Portland cement mortar bars, which are stored at 20°C, is about 3 MPa whereas that of the companion bars at −18°C is about 10 MPa [9]. The stress–strain curves of both the unfrozen and frozen bars show that the descending branches are so curved that "no K_{ic} values are available" to any one of the samples. Of course, one can always assume a safe K_{ic} value for civil engineering calculations. In evaluating the damage-causing pressure, one has to use mechanical characteristics of the frozen matrix. An average concrete, which has been cooled to about −20°C, needs a bursting pressure of about 10 MPa and a corresponding super-cooling of about 8–10°C of water to cause any breakdown [10]. For a sample cooled to a lower temperature, a higher degree of super-cooling is necessary.

Field measurements show that a substantial structure seldom cools at a rate more than about 3–4°C per hour. Similarly, the achievable super-cooling seldom exceeds −2°C to −3°C; this is mainly due to ice nucleation by snow and ice on the outer surfaces and the slow rate of outdoor cooling. High cooling rates and high degree of super-cooling, reported in research journals, are available to small samples only. In this connection, one should keep in mind that ice is a very good insulating material and that ice formed on the outer surface of a structure protects it from fast cooling.

2.2. The nature of breakdown due to the formation of ice in a porous matrix

Saturated consolidated porous materials like concrete or limestone nodules do not break down to powders due to ice formation. These materials break down into a small number of large pieces. Photographic evidence for this has been shown in Ref. [11]. Phenomenological analyses of many such frost-fractured limestone nodules indicate that the damage-causing pressure must have been generated near the centroids of these nodules. Analyses of reported pictures of frost-damaged concrete samples, as well as field experiences, indicate that the damage-causing pressure develop deep inside these samples. A priori, one would expect that the crystal growth pressure can develop anywhere in the volume of the sample as it happens in the case of efflorescence. This difference between the frost and efflorescence damages needs an explanation. The often referred crystal growth pressure mechanism does not explain the above difference. It would be of much interest to know Dr. Scherer's opinion on this point.

3. Pressure generation within water entrapped in ice

Dr. Scherer has not considered the possibility of frost damage due to a pressure generation within unfrozen water entrapped in ice. The entrapment of still unfrozen water within the ice layer is quite a widespread phenomenon. It occurs during the freezing of meat, etc. in a deep-freezer, in water-filled drinking troughs for animals, wet sand piles, in improperly protected municipal water pipes. It has been shown that in all these cases, still unfrozen water is under high compression and the encasing ice layer is in tension [11,12]. The measured super-cooling was about −2°C. Visage [13] reported generation of compressive pressure up to about 7.6 MPa within 7–10-mm-sized water drops during freezing. A simple analysis of freezing process has indicated that the compressive pressure in water increases with the initial volume of water such encased and decreasing temperature [7]. Very recently, such compressive pressure generation of about 500 atm (about 50 MPa) has been reported [14]. Very few porous materials are capable of withstanding the corresponding high tensile stress. This mode of pressure generation does not need a large super-cooling. This mechanism of frost damage is consistent with the breakage patterns of field observations.

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