

Microscopic observations of sites and forms of ettringite in the microstructure of deteriorated concrete

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Extended Abstract

Determination of delayed ettringite formation (DEF) in hardened concrete relying simply on identification of ettringite by electron microscopy or powder X-ray diffractometry can be imperfect because of a high risk of overlooking other possible deterioration phenomena. Presence of ettringite can be easily misunderstood as an indication of DEF while the actual cause of deterioration is ASR. In this study microstructural observation was carried out on concrete samples with cracks caused in the absence of external sulfate attack, using petrological methods under polarizing and electron microscopes. The samples were a floor slab with high concentration of SO₃ (No. 1), a parapet placed around a dam lake (No. 2), a prestressed concrete (PC) pole with vertical cracks (No. 3), and a precast concrete product (No. 4).

Excluding the precast concrete product (No. 4), all of the floor slab (No. 1), the parapet (No. 2) and the PC pole (No. 3) had ASR cracks extending from aggregate particles into the cement paste. Ettringite formation was confirmed in all of the four samples, but none of them had been exposed to external sulfate attack.

No cracks were found in the SO₃ rich area in the floor slab (No. 1). Considering the depth of carbonation, it was likely that sulfate ions were formed during decomposition of ettringite in the carbonation area, eluted into the pore solution, carried to the inside due to concentration diffusion and concentrated there, then used to form ettringite. Therefore, the main cause of the deterioration is thought to be ASR.

The cause of the cracks in the parapet (No. 2) exposed to cold weather was ASR. The scaling of the mortar cover can be attributed to frost attack. One reason is the absence of entrained air voids in the cement paste. The sample, which had been exposed to freezing and thawing actions during the winter, had laminar cracks parallel to the surface where scaling was found. These suggested that the ettringite did not contribute to formation of cracks, but precipitated from the soluble components which had leached into the cracks due to the freezing and thawing actions. In deteriorated concretes the formation of ettringite is promoted by the migration of the soluble sulfates from inside the concrete toward the external surface.

There was a concern of DEF for the PC pole (No. 3) which had been steam cured at high temperatures. However, observation showed no characteristic findings of DEF, i.e. gaps between aggregate particles and the cement paste, and web-like cracks in the cement paste. The cracks filled only with ASR products were likely to have occurred due to a large tensile stress acting on the concrete surface as a result of ASR expansion of concrete. Formation of ettringite was found in cracks that were obviously attributable to ASR, which suggested no association with expansion. Replacement of ASR gel by ettringite, leaving a texture of original ASR gel within cracks, has been reported. One of the possible factors of ettringite formation was considered to be the high SO₃ concentration which was originally high due to the high cement content in the concrete mix proportions and further increased in the inside by the centrifugal casting. The other possible factor was the water which could enter from the ASR cracks and promoted re-formation of ettringite.

The precast concrete product (No. 4) had been used in an area with no influence of freezing and thawing actions, and thus frost attack was excluded from possible causes. Ettringite was found all over the concrete sample, which also excluded the possibility of the concentration diffusion carrying the SO₃ from the carbonation area. The precast concrete product could have been steam cured during the manufacturing process, and the polarizing and electron microscopic observations revealed the presence of gaps between aggregate particles and the cement paste, as well as fine cracks in the cement paste,

and both of which were found filled with ettringite. Consequently, DEF was highly likely to be the cause of deterioration.

Another observation by the same methods was carried out on a concrete specimen with cracks after exposure to fly ash (with addition of CaCl_2 and water), in order to determine the deterioration causes and demonstrate the importance of petrological approach. The result that cracks and scaling were found along the circumference near the surface of the specimen. Needle-like crystals of the 3-1-15 crystalline phase were found to be present in the cracks. No ASR was confirmed.

Ettringite and the 3-1-15 crystalline phase are double salts which are formed in concrete containing $\text{Ca}(\text{OH})_2$, and both can cause deterioration of the concrete. Similar to ASR, formation of $3\text{CaO}\cdot\text{CaCl}_2\cdot 15\text{H}_2\text{O}$ directly causes volumetric expansion and concrete deterioration, and the substance causing the expansion can be clearly observed. By contrast, in DEF which occurs upon supply of moisture after exposure to elevated temperatures, concrete expansion is caused by secondary ettringite which is formed in the cement paste. The secondary ettringite is so fine and unstable that it cannot be observed in the magnification ranges of polarizing or electron microscopes. What is actually observed microscopically is considered to be the ettringite that has formed by solution and re-precipitation in cracks or gaps between aggregate particles and cement paste caused by expansion of cement paste, and trace of which is the determining factor of DEF in the microstructure observation. Therefore, it is inappropriate to make judgement on DEF, without microstructural observation, based only on detection of ettringite by electron microscopy and EDS analysis in a microscopic area of concrete or by powder X-ray diffractometry using finely ground samples. The microstructure observation in a wider view by polarizing microscopy is essential to determination of concrete deterioration causes, and its combined use with electron microscopy and EDS analysis is important for examining fine cracks and locating and assaying the products.

It has been known that factors that contribute to stable formation of ettringite include temperatures and alkali ion concentration, and that ettringite decomposes to produce monosulfate at elevated temperatures and at high alkali ion concentrations. For the estimation of ettringite formation factors, it is necessary to make comprehensive consideration with the depth of carbonation, concrete mix proportions, curing conditions and various environmental conditions taken into account.

In this study, causes of deterioration of several samples concrete with cracks, produced under no external sulfate attack and exhibiting ettringite formation in the texture were determined. Authors claim the microstructure observation by polarizing microscopy as an essential step to determination of concrete deterioration causes, and its combined use with electron microscopy and EDS analysis, that is important for examining fine cracks and locating and assaying the products. They find also important in determining DEF, take into account the occurrence of previous damage due to ASR and frost attack.

Keywords: *alkali-silica reaction; delayed ettringite formation; electron microscope; ettringite; polarizing microscope.*

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