

Investigation of natural crack healing phenomena on historical masonry mortars

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Cementitious materials have been often observed for many years to have a natural crack healing capability due in part to the re-hydration of previously unhydrated cement within the matrix upon re-submersion in water. However, the natural phenomena such a crack self-healing is very limited, because self-healing capability of crack depends on various environmental conditions. This study aims to clarify the natural healing phenomena of crack in cementitious materials and develop crack self-healing cementitious materials based on the natural healing mechanisms. In this research, secondary phases of newly-formed products in historical masonry mortars were investigated in old bridges in the Netherlands. Moreover, in order to understand the precipitation conditions of calcium salts in the cracks, morphology, the shape and size of re-hydration products in the old mortar and brick, microscopy and SEM (EDS) analysis were also conducted. From these results, modified C-A-S-H phases as well as the formation of calcite were found, which increase the self-healing capability of old masonry mortar by both dissolution and chemical weathering effects of K-feldspar minerals in cracks or pores.

Key words: Crack, Self-healing, Masonry mortars, Re-hydration, Natural healing.

Introduction

Autogenous or self-healing of fine cracks in concrete is often mentioned in literature but there is little quantitative data regarding its mechanism. In the literature until now, [1, 2] the causes of self-healing between cracks are reported to be based on chemical, physical, and mechanical processes.

Recently, several researchers [3, 4] observed the formation of cementitious products such as AFt, AFm and CaCO_3 in cracks and calcium hydroxide crystals in air voids in cracked old masonry, brick and concrete. It was hypothesized that these hydration products had been leached and recrystallized in water that had flown through the crack. However, although it is generally acknowledged that unhydrated cement grains affect the recrystallization of cracked concrete, no detailed examinations have been reported on the healing conditions for this cementitious recrystallization. Therefore, in order to understand natural self-healing phenomena in cracks, it is necessary to look at old concrete structures or historical masonry mortars and bricks.

These centuries-old construction works should have crumbled and collapsed long ago-however, not only did they not collapse but they remain in steady use in European countries. Especially, in the case of old bridges in Amsterdam in the Netherlands, R.V. Hess [5] reported that this was due to the mortar used in

these ancient bridges, which contains a large amount of chalk compared to modern standard materials. Whenever a crack appears the water around the bridge is sucked inside the crack, which for modern concrete is the beginning of the end. However, in these old brick bridges the water dissolves the chalk in the mortar, the chalk flows into the cracks, and then sets again. This is the natural self-healing secret of the Amsterdam bridges. Furthermore, chalk which has more than 60% CaCO_3 can fulfill exactly the same function in conventional concrete. Therefore, a very precise amount of calcium mixed in with the concrete is enough for self-healing design. Nijland et al. also investigated the self-healing phenomena in concrete and masonry mortars utilizing microscopic study [6]. They thought that understanding the naturally-occurring self-healing phenomena may serve as a starting point for the development of purpose-made self-healing lime or cement-bound materials.

As reported in the previous papers, old concrete structures provide a significant clue for the natural healing property in the form of their hydration products. In the case of cementitious recrystallization of cracked concrete, the amount of interstitial phase and its form between cracks is very important for self-healing. It was found that mix-proportion using lime and lime-pozzolana mortars, lime-fired clay pozzolana mortar, and 19th century lime mortar have the potential for self-healing capability by the formation of Ca^{2+} -carbonate, an arrested case of initial self-healing. Some researchers have already reported the formation of 2nd hydration phases between cracks of old masonry mortar [7]; however, in order to design new cementitious

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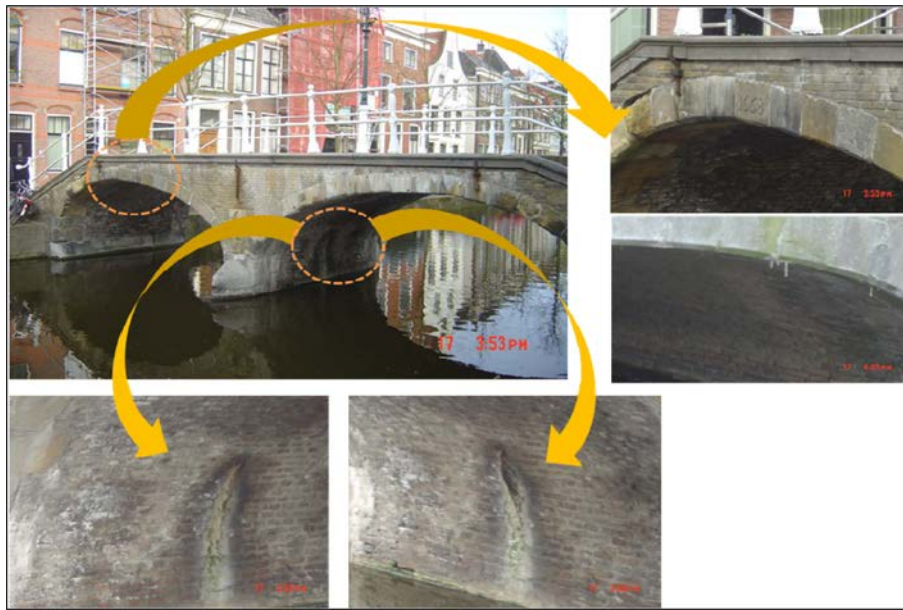


Fig. 1. Formation areas of secondary phases on brick arched Bridge of Delft.

composite materials with self-healing capability, it is necessary to analyze the chemical composition of the original brick, since most precipitation products are based on the dissolution and diffusion of original brick or concrete. Therefore, this field study was conducted beginning in 2007 to investigate this phenomenon. In this research, the natural healing properties of historical masonry mortars and bricks in the Netherlands are investigated and various special factors from these results were used for the design of cementitious composite materials with self-healing capability. [8]

Experimental Program

Survey of brick arched bridges in the Delft city (Netherlands)

The Netherlands is also known as the “low Countries,” with around 25% of the land located below sea level actually [9]. This has led to many researchers studying waterproofing technologies and much of the civil infrastructure has been developed considering water leakage in structures, sealing and crack protection technologies. This field study was conducted in both Amsterdam and Delft. These two areas are located below sea level and have many old bridges which are still in service.

In this research, various brick arched bridges in Delft were investigated in order to obtain a reasonable sample with secondary phases for chemical analysis. It is estimated that they were constructed during the 17th century. In particular, one of these bridges showed a lot of secondary phases on the surface of mortar and bricks as well as in its deteriorated areas, as shown in Fig. 1. As a result, this bridge was selected for sample collection. Furthermore, in order to understand the

precipitation conditions of calcium salts in the cracks, morphology, and the shape and size of re-hydration products in this old mortar and brick, microscopy and SEM(EDS) analysis were conducted.

Estimation of physical properties for secondary phases

Microscopy and SEM with EDS-detector were carried out to investigate morphology and the shape and size of re-hydration products. A JEOL JSM-5600 LV SEM (Scanning Electron Microscopy) and a Keyence VE-7800 for microscopy were used. A JEOL JFC-1200 fine coater was used to gold-coat specimens. X-ray elemental microanalysis with Energy Dispersive X-ray Spectroscopy (EDS) was used in conjunction with the JEOL SEM. Observations were performed at each stop by moving around and following paste/aggregate bond zones and cracks.

Results and Discussion

Microscopy and SEM with EDS-detector were carried out to investigate morphology and the shape and size of re-hydration products, as well as clarify recrystallization.

Fig. 2 shows a sample of secondary products on the surface and in the cracks of the mortar between the old bricks. It was found that white secondary products were formed on the mortar surface. Microscopy analysis is shown in detail in Fig. 3.

The microscopy image shows that most of the cracks were fully filled by newly-formed hydration products. It seems that these are precipitated CaCO_3 composites. However, Fig. 4 shows what appears to be new porosity generated in this system. T. Nijand reported



Fig. 2. Mortar sample with the secondary phases from brick arched bridge.

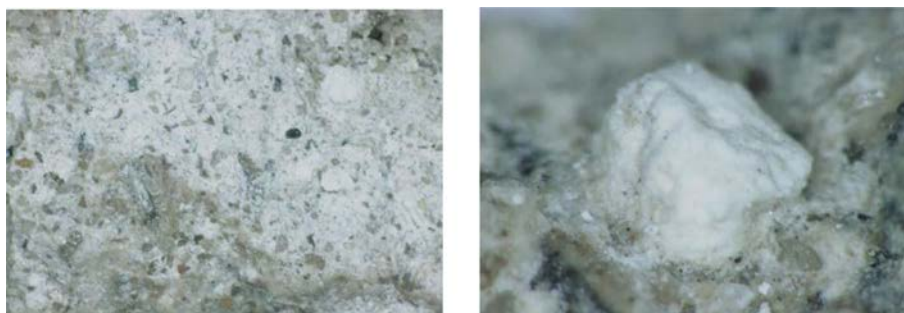


Fig. 3. Microphotograph showing recrystallization of carbonated lime in 17th century mortar.



Fig. 4. Microphotograph showing newly-formed porosity for the supplying Ca^{2+} source.

this phenomenon as follows: when crack self-healing occurs at one location, if the Ca^{2+} source is not enough for the formation of new phases, there is the potential for the generation of new porosity at other locations in order to supply Ca^{2+} source [6]. In other words, formation of secondary phases depends on the Ca^{2+} source conditions. Therefore, the addition of lime for supplying an additional Ca^{2+} source might be considered as one methodology for self-healing.

Fig. 5 shows the X-ray spectra taken from reacted secondary phases on old masonry mortar. X-ray spectra obtained from these phases revealed particular trends in the chemical composition, as formation of Gehlenite phases ($\text{Ca}_2\text{Al}(\text{AlSi})\text{O}_7$) and calcite phases proceeded.

These Gehlenite phases mainly occurred in metamorphosed impure lime stones or in calcium-rich rocks. These phases can be associated with several mineral components such as dolomite, calcite, apatite, augite, olivine, nepheline, leucite, merwinite, merwinite, spurrite, diopside, ferroan spinel, phlogopite, pyrope, grossular, antigorite, pyroxenes, and vesuvianite. In particular, dolomite, calcite and apatite have the potential to occur as secondary phases by the formation of

cementitious recrystallization between cracks; from this analysis, it was found that Gehlenite phases could be formed with these secondary products easily. Furthermore, it means that these compound products have chemical stability in cementitious systems from a durability view point.

Fig. 6 shows X-ray spectra taken from fine aggregate of mortar. There was quite a difference in the chemical composition between modern normal aggregate (SA: silicate aggregate) and the aggregate (ASA: aluminate silicate aggregate, feldspar minerals) used at that time. The aggregate's chemical composition contains a lot of Al_2O_3 ion and Fe_2O_3 as compared with the conventional silicate aggregate. Therefore, it can provide a surplus source of aluminate and silicate for the formation of gehlenite phases with calcite phases in the case of high alkali solution condition through alkali activators or acidic condition.

The chemical weathering effects of K-feldspar were also observed as shown in Fig. 7. Fig. 7(a) shows the X-ray spectra results of conventional silicate aggregate compared with that of transferred phases (b) by chemical weathering. In the case of normal silicate

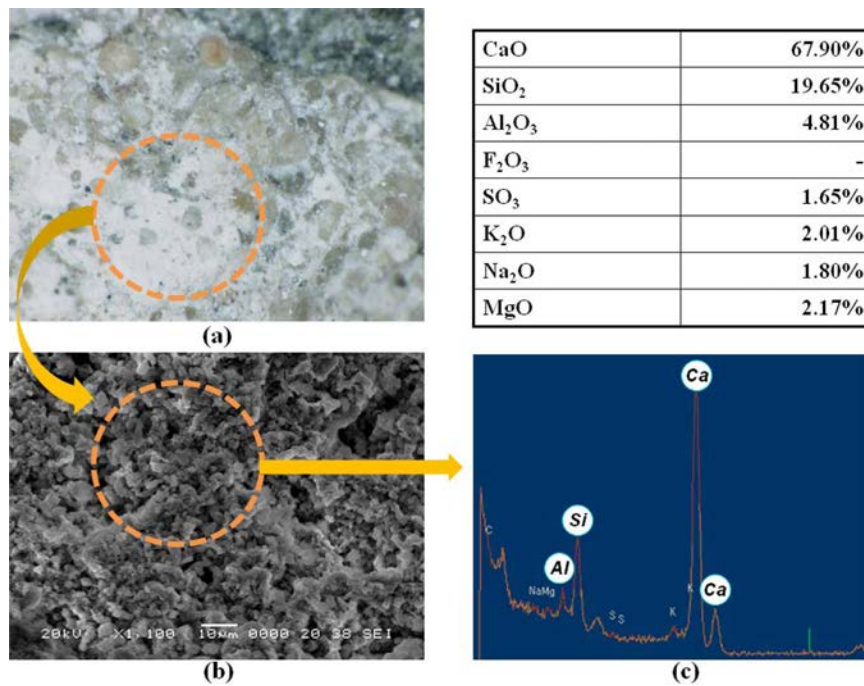


Fig. 5. X-ray spectrum from precipitated products of old masonry mortar.

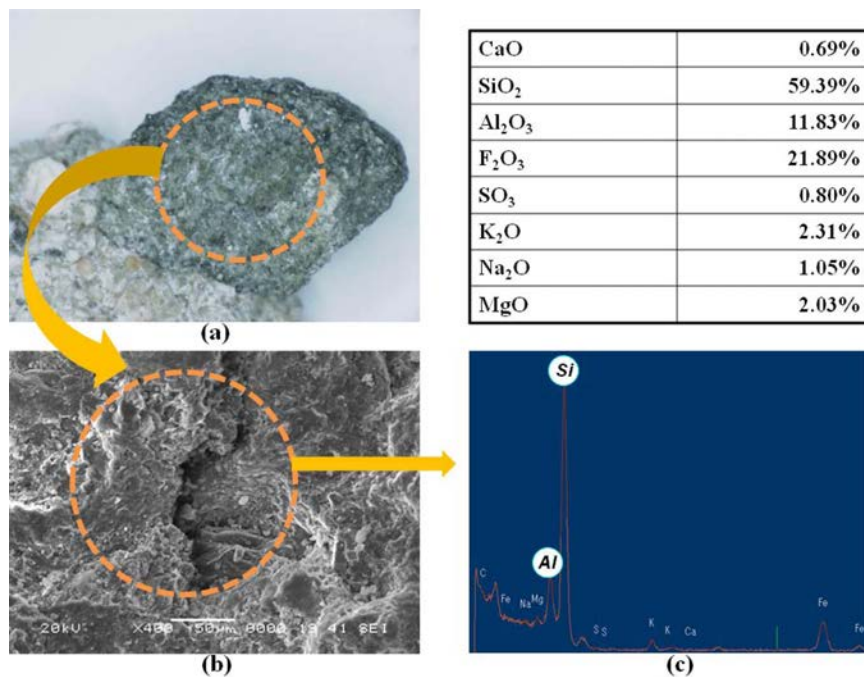


Fig. 6. X-ray spectrum from aggregate of old masonry mortar.

aggregate, if there haven't been any silicate ions diffused near the area, then its morphology will remain clear. However, in case of K-feldspar, it was revealed that the surface of aggregates changed to aluminate silicate phases (Kaolinite phases) over a long time period.

In general, when feldspar minerals react with acidic water, they changed alumina silicate materials (clay minerals) as follows. [10, 11]

- Orthoclase (potash-feldspar)
(K-feldspar) + acidic water (carbonated water) = K⁺ + Kaolinite [a clay mineral]
 $2\text{KAlSi}_3\text{O}_8 + \text{H}_2\text{CO}_3 + 12\text{H}_2\text{O} \rightarrow 2\text{K}^+ + 2\text{HCO}_3^- + 5\text{H}_4\text{SiO}_4 + \text{Al}_2\text{SiO}_5(\text{OH})_4$ [Kaolinite]
 $3\text{KAlSi}_3\text{O}_8 + 2\text{H}_2\text{CO}_3 + 12\text{H}_2\text{O} \rightarrow 2\text{K}^+ + 2\text{HCO}_3^- + 6\text{H}_4\text{SiO}_4 + \text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2$ [Mica]
- Plagioclase (solid solution of NaAlSi₃O₈ and CaAl₂SiO₈)

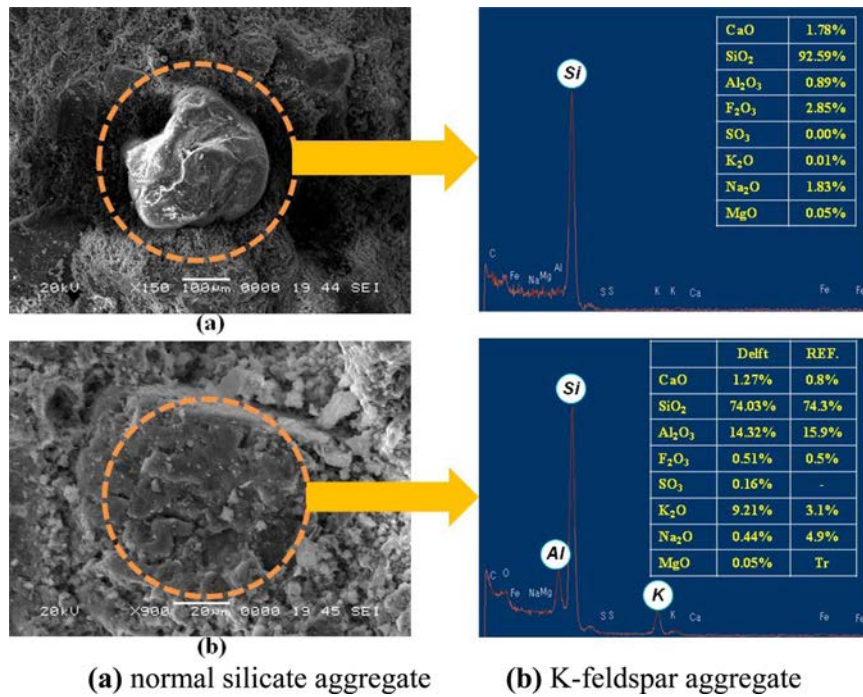


Fig. 7. X-ray spectrum from aggregate of old masonry mortar.

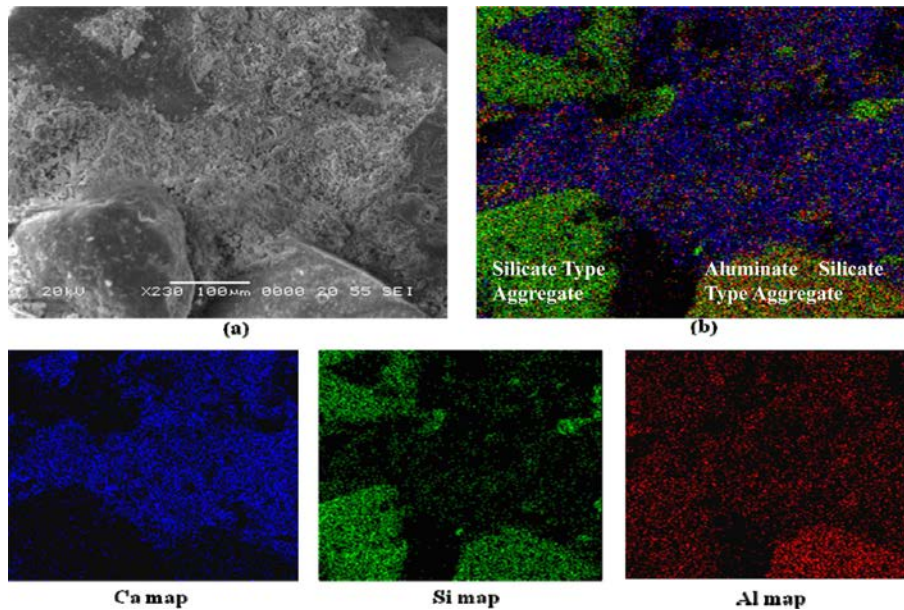
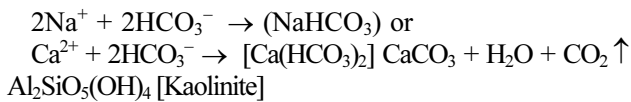
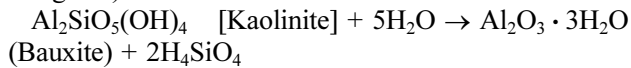


Fig. 8. X-ray mapping results of old masonry mortar.



- Hydrolysis reaction of clay mineral (tropical regions)



And then alumina silicate materials reacted with calcium ions from calcite. Namely, aluminum silicate materials (pozzolanic materials) by the chemical

weathering are easily combined with calcium ions in the high alkali condition of the cement system. Therefore, the C-A-S-H phases easily formed in the cement matrix. In addition, it was found that these aluminate silicate phases from natural status were quite similar to geopolymer structures of aluminate silicate phases. In general, cement pore solution is essentially alkali hydroxides. Therefore, the immediate product is likely to be an amorphous material with K^+ and Na^+ as the dominant cations from feldspars, and it was found that the relatively high potassium contents were

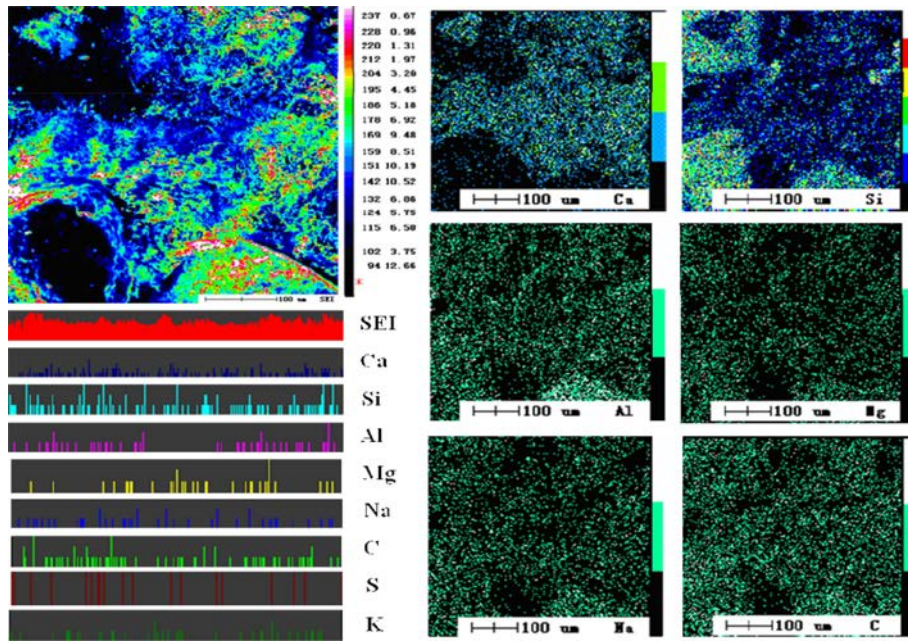


Fig. 9. Diffusion of Al ions from alumina silicate aggregate of old masonry mortar.

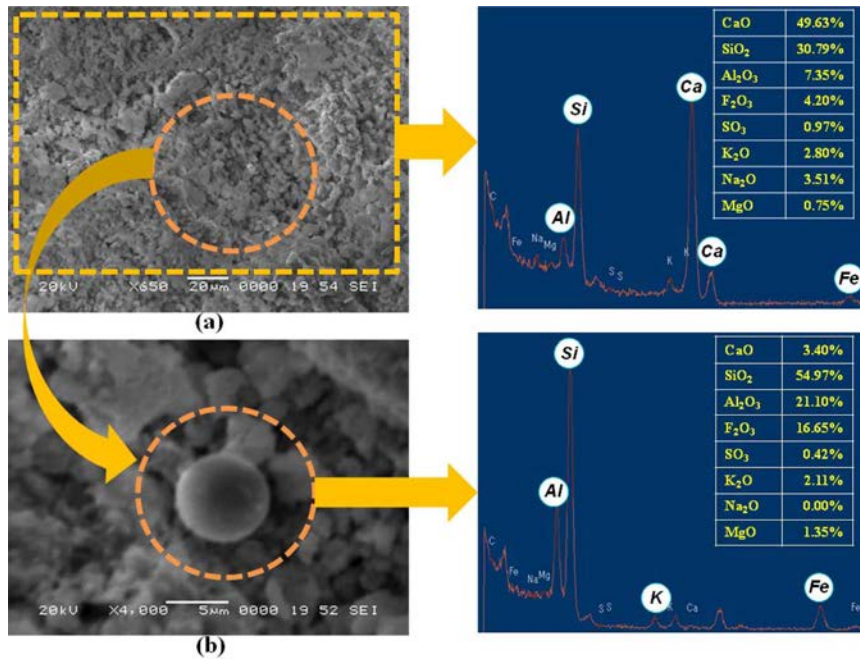


Fig. 10. Formation of modified C-A-S-H phases based on alumina silicate materials by the chemical weathering.

observed in reacting products. In other words, addition of artificial geo-materials might lead to the formation of alumina silicate phases, one of the secondary phases, for self-healing. Fig. 8 and Fig. 9 show the X-ray map and spectra taken from geopolymerized aggregate and cement pastes.

As described above, Fig. 8 clearly shows the existence of two types of aggregates by the X-ray mapping test. It was found that newly-formed hydration products in mortar were diffused from aluminate silicate aggregates by EDS concentration mapping as shown in Fig. 9. In particular, it was revealed that aluminate silicate

aggregates reacted with calcium ions easily, as compared with silicate aggregates. Modified C-A-S-H phases based on alumina silicate materials by the chemical weathering seemed to be produced by a pozzolanic reaction as shown in Fig 10 (a). It appeared that the calcium hydroxide produced by the cement hydration or lime reacted with the pozzolan and produced an additional gel which has a pore-blocking effect. Moreover, unreacted fly ash as the additional geo-materials was also observed, as shown in Fig. 10(b).

Fig. 11 show old masonry mortar deteriorated by sulfate attack. It was observed that the mortar was

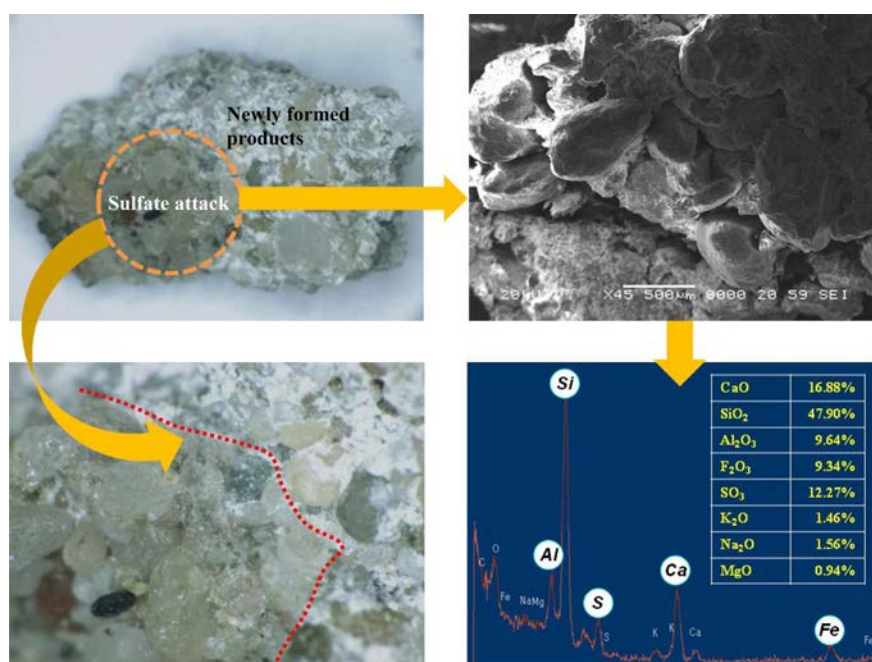


Fig. 11. Deteriorated old masonry mortar by sulfate attack.

attacked by solutions containing sulfate, such as natural or polluted waters, as shown in Fig. 11. It showed that the ratio of sulfate peak height increased due to the sulfate attack. However, an interesting phenomenon was observed: it was found that some areas deteriorated by sulfate attack were self-healed by newly formed products. Therefore, it was found that modified C-A-S-H phases also have the potential to heal mortar deteriorated by sulfate attack.

Finally, it can be concluded that modified C-A-S-H, as well as the formation of calcite, increases the self-healing capability of old masonry mortar and brick by both its dissolution and pozzolanic reactions in cracks or pores.

Conclusions

In this study, the natural healing properties of masonry mortar from historical brick arched bridges in the Netherlands were investigated. Various special factors from these results were suggested for the design of a cementitious composite with self-healing capability.

1) Modified C-A-S-H phases, as well as formation of calcite, increases the self-healing capability of historical masonry mortar by both its dissolution and pozzolanic reactions in cracks or pores. Especially, chemical weathering increases self-healing capability of concrete materials partially.

2) The SEM/EDS analysis results revealed that the chemical stability of newly-formed secondary phases was dependent on the amount of aluminate silicate ions within the cementitious system and its geopolymerization by appropriate alkali-activated conditions. These phases also have the potential to be useful for development of a self-

healing mechanism.

3) It is also desirable to design for the formation of C-A-S-H phases and calcite through cementitious system for the cementitious materials with self-healing capability.

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