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Steam locomotive soot and the formation of thaumasite in shotcrete

M. Romer *

Swiss Federal Laboratories for Materials Testing and Research (EMPA), Laboratory for Concrete and Construction Chemistry, CH-8600 Duebendorf, Switzerland

Abstract

After approximately 40 years the sprayed concrete lining in the Koblenz railway tunnel started to break off from its stonework support. The old masonry showed relicts of a soot layer from the ages of steam locomotive services. Locally small amounts of low mineralised water were running through the tunnel lining. Due to the finding of ettringite at the rear surface of the shotcrete together with soot it was assumed that sulfur from the locally present soot layer was the cause for the shotcrete detachment.

Detailed investigations showed the formation of thaumasite at the concrete interface to its support and up to 15 mm inside the concrete. Thaumasite could be detected filling microcracks and veins parallel to the shotcrete surface. The amount of secondary sulfate minerals and the extent of sulfate uptake are orders of magnitude larger to what could be expected if the sulfur of the soot layer would be present as sulfate.

It is assumed that the finding of thaumasite in cracks and veins is caused by long term interaction with a low mineralised groundwater and is leading toward a complete alteration of the concrete into a mushy material.

Keywords: Soot; Shotcrete; Sulfate attack; Thaumasite

1. Introduction

Combustion of fossil fuels is often associated with emissions of soot, ash and sulfur compounds. A short railway tunnel was constructed around 1900 and lined with limestone masonry. After approximately 50 years of use the railway decided to put a shotcrete lining on the stonework to prevent some problems with ice formation and corroding masonry mortar. Water flow through the tunnel lining has been local and small. Before applying the shotcrete the masonry surface was cleaned and locations with running water have been drained with half pipes. The shotcrete was applied over the whole masonry surface with a thickness of 3–7 cm.

After 40 years, diesel locomotives having replaced steam locomotives, the surface of the shotcrete is again covered with a soot layer and parts of the shotcrete lining have started to detach from their support. Due to the finding of ettringite together with residual soot at the rear surface of the sprayed concrete it was assumed that the soot layer was the cause for concrete deterioration.

We were tasked with clarifying the cause of shotcrete detachment and whether soot or sulfur in soot had been involved in this deterioration process. It was clear from visual inspection that the cleaning process prior to the shotcreting did not remove all soot from the masonry. The role of particulate matter from vehicle exhaust in corrosive processes pertaining to building materials relates to its catalytic sulfation potential [1,2], sulfur itself from the soot not being consumed or transferred into sulfate. Together with the small size of the soot layer and its presumably low sulfur content it is hardly a cause for chemical interaction.

2. Inspection and recovery of samples

After inspection of the deterioration in the tunnel samples of shotcrete were cut or cored from the tunnel lining; larger pieces of shotcrete could be detached from their support next to areas where shotcrete was already broken off (Fig. 1).

The inspection of the tunnel revealed several regions where the shotcrete was either detached and came off its support or where areas of concrete up to several square meters had already broken off. The fracture plane

* Tel.: +41-1-823-41-35; fax: +41-1-823-40-35.
E-mail address: michael.romer@empa.ch (M. Romer).

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Fig. 1. Location 42′154 with larger areas of loose shotcrete (dark due to a soot layer on the surface) and parts of the lining already broken off. Dripping ground water could be sampled on the clean masonry behind the technicians.

Fig. 2. Fracture surface through shotcrete lining showing several contact parallel bright textures in the shotcrete (tunnel surface at the bottom).

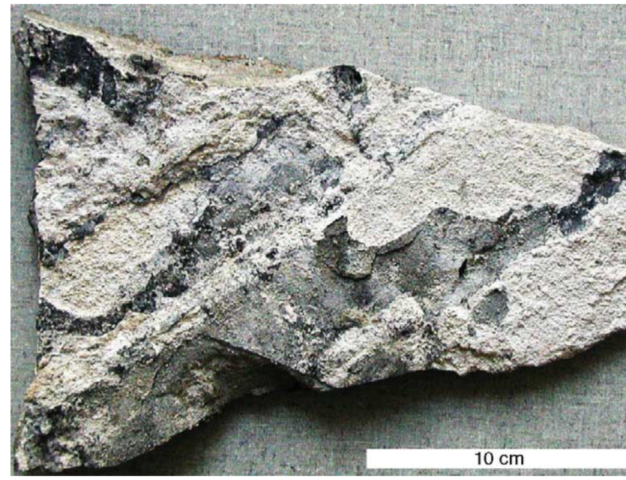

Fig. 3. Rear surface of the lining showing layers of soft, whitish material in the shotcrete and relicts of dark soot representing the original interface of masonry and shotcrete.

Fig. 4. Surface detail of shotcrete interface to stonework with soot relicts (black) next to soft alteration products (whitish) of the concrete.

perpendicular to the lining showed one or more distinct bright layers at the rear of the shotcrete cutting through the concrete in a more or less parallel orientation to the support (Fig. 2) up to 15 mm inside the concrete. The back surface of freshly removed shotcrete samples was partly covered with a soot-like, black layer (Figs. 3 and 4). Within larger layers of whitish material its low strength could be recognised.

The drainage system between shotcrete and masonry consisted of plastic half pipes leading the water to the side of the tunnel vault where it could drop down to the floor on the side of the rail. The obviously low amounts of flowing or dropping water formed finely layered stalagmites (calcite) on the bottom. In a region where a larger piece of shotcrete had broken off long before inspection we were able to collect water which was running sparsely but continuously through the rockwork (Fig. 1).

Samples of this water as well as many samples of shotcrete were further investigated in the laboratory.

3. Results and discussion

3.1. Investigation of chemical and mineralogical compositions

Samples of unchanged shotcrete (reference) and samples of shotcrete with different extent of degradation were dried to constant weight at 50 °C. Loss on ignition was determined by thermogravimetry (1050 °C) and corrected for the content of carbon which was determined by LECO combustion. All other elements were analysed by X-ray fluorescence spectroscopy and calculated together with H_2O and CO_2 as oxides (Table 1).

Table 1
Koblenz tunnel: composition of solid[a] and water samples

Sample	Reference shotcrete	Shotcrete with soft and white layers	Mushy shotcrete		Water [mg/l]
Na_2O	0.3	0.3	0.1	Na^+	12
K_2O	0.6	0.6	0.3	K^+	6
SiO_2	24	18	12		
Al_2O_3	3.6	3.5	2.7		
Fe_2O_3	2.0	1.7	1.3		
CaO	46	42	33	Ca^{2+}	180
MgO	1.1	1.3	1.6	Mg^{2+}	20
SO_3	1.4	2.3	10	SO_4^{2-}	330
CO_2	11	9	12	HCO_3^-	50
H_2O	10	21	27		

Assuming that silica is not exchanged with the environment during alteration of shotcrete into mush, a dilution factor of approximately two is derived. This ratio is lower for calcium, magnesium, sulfate, carbonate and water indicating an uptake of these components relative to their original contents. This is in accordance with the composition of the ground water and the formation of thaumasite as well.

[a] Calculated as oxides in weight%.

Table 2
Mineralogical findings determined by X-ray powder diffraction

Sample	Reference shotcrete	Shotcrete with soft and white layers	Mushy shotcrete
Quartz + feldspar	XXX[a]	XXX	X
Calcite	XX	XX	(X)
Portlandite	X	(X)	–
Ettringite	X	X	?
Thaumasite	–	X	XXX
Gypsum	–	–	X

[a] XXX = main, XX = medium, X = minor, (X) = trace component, ? = uncertain, – = not detected.

Mineralogical compositions of powdered samples were determined by X-ray powder diffraction (Table 2).

Results of chemical and mineralogical compositions are discussed in comparison with the unaltered shotcrete sample. Quartz and feldspar originated from the concrete aggregate and were also present in the mushy material indicating that this mush was altered shotcrete. Reduction of silica in the progressively attacked samples was interpreted as a dilution effect due to the formation of secondary phases rich in crystal water and/or sulfates. Based on the assumption that silica was not exchanged with the environment, calcium, magnesium, sulfate, carbonate and water have been incorporated in the shotcrete during the alteration processes (Table 1). On the basis of mineralogical compounds the amounts of portlandite, calcite and ettringite have been reduced in the system. Whereas in the mushy material thaumasite could clearly be identified by X-ray powder diffraction as mayor compound. The distinction between ettringite and thaumasite in samples with low amounts of secondary sulfate minerals was difficult, maybe not only because of the method but also because of intermediate mineralogical properties of ettringite and thaumasite if present simultaneously. A magnesium containing phase could not be detected in any sample which is attributed to the restricted sensitivity of the analytical techniques used.

3.2. Investigation of microstructure

After drying, the samples for microscopical examination were impregnated with a stained epoxy resin under pressure to allow for the preparation of thin sections. It was assumed from field evidence that the intense formation of subparallel layers of soft and white material was an intermediate stage of the complete alteration of concrete into a mushy material what would be in accordance with the findings of Sibbick and Crammond [3]. Locations of layers in shotcrete are therefore of special interest. Fig. 5 shows a representative sample close to the contact with the tunnel stonework. Portlandite is not present anymore in the hardened cement paste. Swarms of microcracks and larger veins are present in parallel orientation. These are completely filled with a secondary mineral phase identified as thaumasite. On a geometrical basis a net expansion of approximately 10% can be postulated, the orientation of cracks and veins showing this expansion to be unidirectional perpendicular to the stonework support. Aggregate particles show no signs of alteration themselves (siliceous or carbonate) and no specific changes in the interface towards the paste. Mechanisms of concrete deterioration in the Koblenz tunnel together with detailed microstructural data are publishes by Holzer and Romer [4].

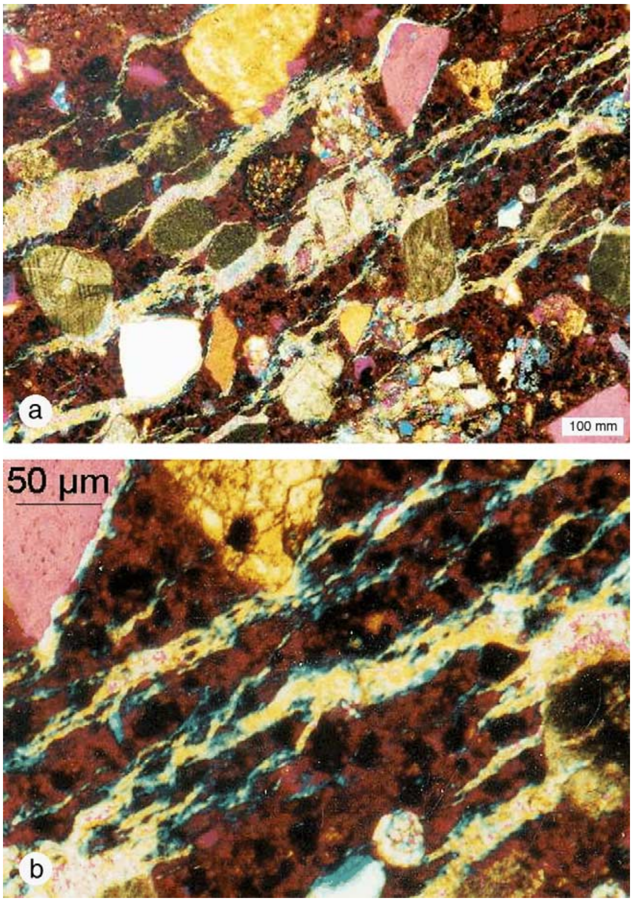

Fig. 5. Thin section (crossed polars) of shotcrete close to the rear surface, orientation perpendicular to the shotcrete lining. The dark colour of the hardened cement paste together with lack of small birefringent components indicates, that the cement paste is leached. Swarms of microcracks have been formed parallel to the shotcrete support and are filled with secondary minerals (thaumasite). Aggregate particles of different mineralogical composition show no sign of alteration.

4. Conclusions

The transformation of hardened cement paste into thaumasite is in accordance with the qualitative chemical and mineralogical findings of the analysed samples and the composition of the interacting ground water. The formation of thaumasite is leading to expansion of the shotcrete, the complete reaction resulting in a volume increase of approximately 100%. The extent and amount of thaumasite formed at and near the interface to the support is related to uptake of sulfate quantities much higher than could be delivered from the thin soot layer on the stonework–shotcrete interface.

The occurrence of larger and also slender cracks next to each other or turning into each other and forming swarms of microcracks indicates a continuous process of crack formation and widening. The fact that all these different generations of microcracks are filled with the same kind of secondary product (thaumasite) leads to the conclusion, that the secondary product is involved in the build-up of stress and the initial formation of the cracks. The formation of finely distributed thaumasite in the matrix of the hardened cement paste is therefore postulated as main deterioration mechanism.

Alteration of hardened cement paste of shotcrete into thaumasite is responsible for the detachment of the shotcrete from its support (stonework tunnel lining). It is concluded that over several decades the contact between shotcrete and weakly mineralised groundwater led to leaching of the hardened cement paste and subsequently to the formation of thaumasite in the shotcrete up to 15 mm from the contact with the support or more precisely with the percolating water.

Acknowledgement

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