

Deterioration of mortar caused by the formation of thaumasite on the limestone cladding of some Slovenian railway tunnels

Jerneja Strupi Šuput ^{a,*}, Ana Mladenovič ^a, Lidija Černilogar ^b, Vlado Olenšek ^b

^a Slovenian National Building and Civil Engineering Institute, Ljubljana, Slovenia

^b TKK Factory of Chemical Products, Srprenica, Slovenia

Abstract

The cause of degradation of the non-shrinking cement mortar used in repair works in some Slovenian railway tunnels was studied. This cement mortar was used to fill in the joints between the individual worked limestone blocks of the tunnel walls. The damage to the mortar appeared one to three years after the repair works had been performed. The results of preliminary investigations showed that the degradation of the mortar was due to the formation of thaumasite. The carbonate ions came from the limestone cladding and from the water, whereas it is assumed that the pollution of the limestone cladding with soot from the furnaces of former steam locomotives, as well as from the fumes of modern diesel engines, is the main source of the sulfate ions, which produced the thin layer of gypsum on the limestone. Understandably, the limestone cladding had not been cleaned sufficiently to remove the old layers of soot and gypsum.

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1. Introduction

In recent years, when it has been necessary to repoint the mortar joints of the stone claddings of railway tunnels, greater use has been made of special, factory-prepared repair materials instead of the previously more commonly used Portland-cement based mortars. The reason for this change is to be found in the fact that such factory-prepared materials are easier to prepare and apply, and also have superior physical and mechanical properties. They can be applied by machine and contain additives which prevent mortar shrinkage. They also need smaller quantities of water for preparation, they are less permeable, and they achieve higher final strengths.

However, in a number of railway tunnels in Slovenia where repair works have been carried out—mostly dewatering using various drainage systems, and the re-pointing, using the above-described repair materials, of stone claddings made of different types of limestone—unexpected damage has been observed to the repaired areas. On the basis of results obtained in laboratory tests it has been found that what is involved is the formation

of thaumasite. The main characteristics and probably damage mechanism are described in the paper.

2. Field investigations

In the first stage of the investigations, five railway tunnels, located in two different parts of Slovenia, were inspected, and their materials sampled. Two were located in south-eastern Slovenia (Semič, Peščenik), whereas three were in south-western Slovenia (Jurgovski, Ležeški and Križiški). Both of these geographical regions have similar geomorphological and geological characteristics—they are located on the Karst in hard, dense, Cretaceous limestones [1,2]. However, with respect to their engineering geology characteristics, these limestones can be classified as permeable and liable to the formation of caverns. This means that in these areas it is necessary to take into account potential water currents and trickling, depending on the time of year and the quantity of precipitation. The water which penetrates through the ground contains a lot of Ca^{2+} and Mg^{2+} ions, which can participate in the sulfate reactions. The water also contains dissolved CO_2 , which is hydrolyzed into a weak acid and accelerates the dissolving of calcite from the limestone claddings.

* Corresponding author.

No records are available regarding the hydrological and microclimatic conditions in the investigated tunnels throughout the year. However, to a certain extent it is possible to draw conclusions about these conditions on the basis of measurements which were performed at the time of sampling, while at the same time taking into account the general, continental climatic conditions in the above-mentioned parts of Slovenia.

The investigated tunnels have lengths of between 300 and 2000 m [3]. At the time when the samples were taken, there was a rather untypical dry period of autumnal weather. In the first two tunnels, Semič and Peščenik, the air temperature was between 2.5 and 3.5 °C, and the relative humidity was greater than 90%. Water occurred randomly at various locations of the walls and roof of the tunnels in the form of percolation, dripping and bedewing. The air temperature in the other three tunnels (Križiški, Jurgovski, and Ležeški) was in the range between 3.5 and 5 °C, with relative humidities greater than 80%. At the time when samples were taken, there was no visible percolation of water from the walls of the tunnels, but there were local damp areas.

The cut stones which are used for cladding the tunnels are made of grey, dense limestones, and their average size is 40×40×40 cm. The stone appears to have been obtained locally and contains only a small amount, i.e. a few percent, of impurities, usually in the form of quartz and clay minerals. In the Jurgovski and Ležeški tunnels, some sections of the tunnel are lined with bricks.

The walls of the investigated railway tunnels, which are more than 150 years old, are heavily polluted. On the surface of the limestone blocks there is a layer of gypsum, on top of which there are layers of soot, iron particles and other smut. Before the repair works were carried out, the surface of the tunnel walls was cleaned using water, but the quality of this cleaning process is open to doubt since, due to the difficult operating conditions (time and space limitations due to railway traffic) only the surface pollution was removed, whereas the layer of gypsum remained on the stones of the claddings.

From the available technical documentation it follows that the mortar used to repair the tunnels consisted of one part, by weight, of binder, and three parts, by weight, of quartz aggregate of size 0–3 mm, with small quantities of special additives. The binder was based on Portland cement, but it contained a shrinkage-compensating component, with the chemical composition $3\text{CaO} \cdot 3\text{Al}_2\text{O}_3 \cdot \text{CaSO}_4$. This component amounted to 10% by weight of the Portland cement.

The ready-mixed repair mortar was applied by machine. According to the requirements of the design documents, this mortar should have been applied to the joints between the cladding stones to a thickness of between 2 and 5 cm. However, taking into account the appearance of the repaired surfaces it appears that the

mortar did not have satisfactory consistency and therefore had a tendency to run down the surface of the limestone blocks (see Fig. 1).

On the walls of the tunnels various types of damage were observed such as the swelling and flaking away of the mortar from the surfaces of the stone and the mortar joints. It is clear that the reaction has taken place on the inner side, at the jointing areas between the stone cladding and repair mortar or mortar joints and repair mortar. At these locations the repair mortar, which in its hardened state is usually of a dark grey colour, has changed into a soft, white mushy powder (see Fig. 2). At those locations where there is greater dampness, a light-grey mud, often in kidney-shaped clumps, can be observed.

During the period of time which passed between the execution of the repair works and the taking of samples of the failed repair mortar, a period of time which varied between one and three years, a layer of dirt, which was the consequence of railway traffic, was deposited on the external surface of the mortar.

3. The results of laboratory analyses

Samples were taken at selected damaged locations in the tunnels. In the laboratory tests emphasis was placed on the whitish soft products on the internal side of the failed repair mortar. The external black polluted surface of this mortar was also analysed. For the purposes of laboratory analysis the XRD method was used with a Philips–Norelco diffractometer, using $\text{CuK}\alpha$ radiation, as well as SEM analysis using a JEOL 5500 microscope with a low vacuum mode. Semiquantitative chemical analysis of selected areas of the samples was performed by means of EDS, using INCA software.



Fig. 1. Inappropriate consistency and application of repair mortar covering. It can be seen that the layer of repair mortar covers not only the joints but also the limestone blocks. Development of the reaction is best seen in the lower left corner of the figure.

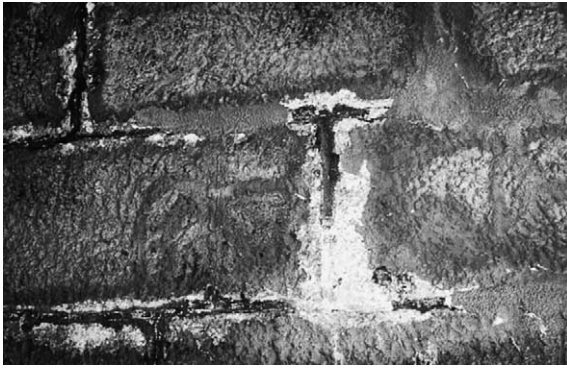


Fig. 2. Degradation products of the repair mortar. On the dry sites, a white mushy powder can be seen.

3.1. Results of the analysis of the white mushy powder from the inner side of the mortar

Using XRD, thaumasite was identified as the main decomposition crystalline product. Clear peaks were observed at 19.5, 23.4, 26.0 and 28.0, 2θ , which make possible differentiation between the otherwise identical ettringite and thaumasite. Also present were calcite as the result of carbonation of the portlandite, as well as quartz, which comes from the aggregate.

On the SEM images it is possible to see what the failed repair mortar looks like. From a typical image (see Fig. 3) it is clear that the preserved minerals of portlandite are surrounded by masses of thaumasite needles. The second way in which thaumasite occurs is in the form of roundish agglomerations, up to 0.4 mm in size, as can be seen from Fig. 4. In Fig. 5, which shows a magnified region of the previous image, fine white acicular crystals of thaumasite, with dimensions of up to maximum 5 μm length and 1–2 μm width, can be seen well. The spectrum of the semiquantitative chemical analysis of the crystals is presented in Fig. 6.

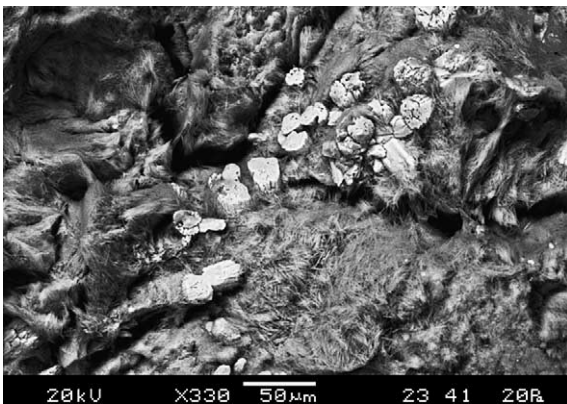


Fig. 3. SEM image of sulfate-attacked inner layer of the repair mortar, showing portlandite crystals surrounded by masses of thaumasite needles.

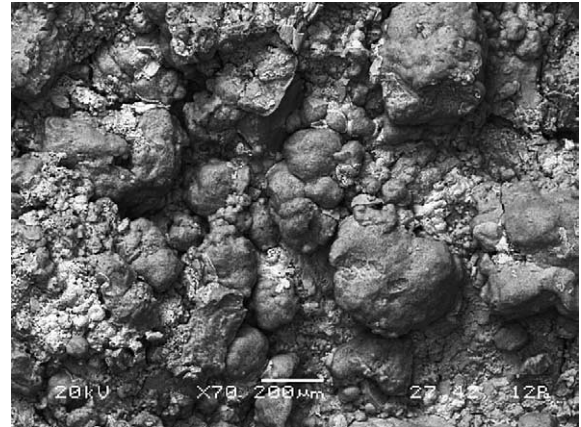


Fig. 4. SEM image of thaumasite in roundish agglomerations.

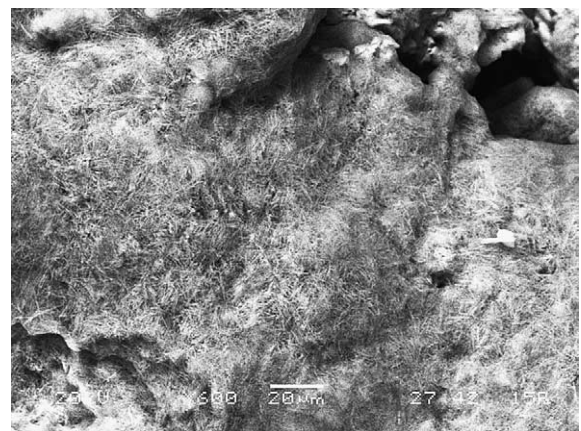


Fig. 5. SEM image of the thaumasite shown in Fig. 4, at a higher magnification.

3.2. Analysis of the external black side of the mortar

The images obtained using SEM analysis showed a large number of particles, containing iron, some carbon, and mostly a lot of well crystallized gypsum in the form of monoclinic crystals (see Fig. 7).

4. Discussion

The formation of thaumasite requires the presence of sulfate and carbonate ions, and is associated with wet and cold conditions [4]. The environmental conditions in the investigated tunnels are wet and very cold, especially in the Winter, and the regions where the tunnels are located have the most severe climatic conditions in all of Slovenia.

On the basis of the results obtained by means of the field investigations and laboratory analyses, it follows that the failure mechanism of the repair mortar was, in the case of all five investigated tunnels, the same. Among the reaction products of the decomposed, failed repair

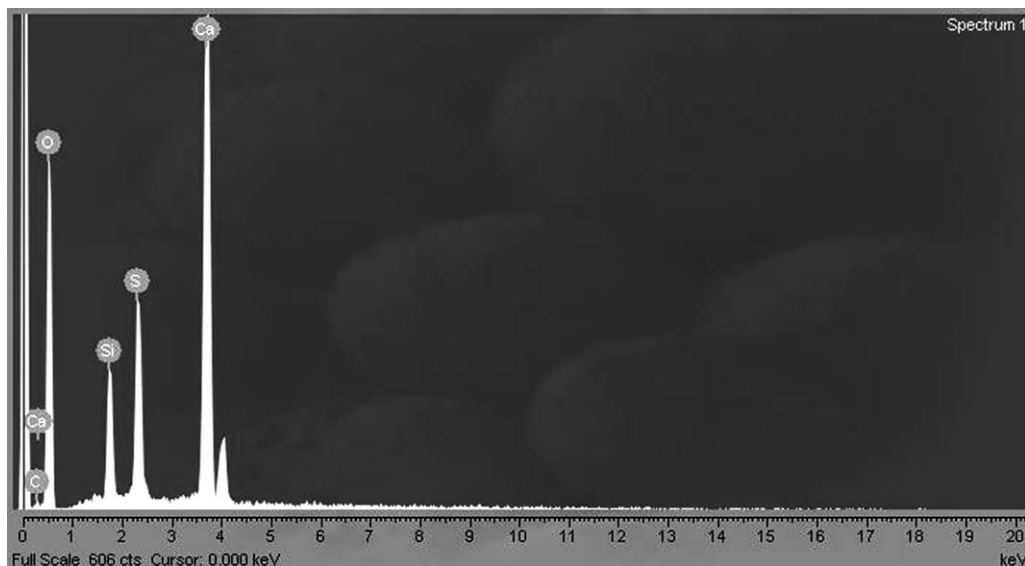


Fig. 6. Spectrum corresponding to the semiquantitative analysis of the fine acicular crystals.

mortar, thaumasite predominates, followed by gypsum and, mainly in the pores of the mortar, some ettringite.

The reaction cores for the formation of thaumasite are on the internal side of the repair mortar, so that the formation of thaumasite spreads from the inner to the outer surface. As the sulfate attack began to affect the whole mass of the repair mortar, the latter began to swell, flake and fall away in the shape of soft white particles without any cohesion. For the time being there are not many places where the reaction with the formation of thaumasite has included the whole depth of the repair mortar. On the outside surface, the changes showing the failure of the repair mortar and the sulfate attack are visible in the form of secondary gypsum. This phenomenon, as such, does not indicate the larger-scale destruction of the repair mortar.

Clearly, if thaumasite is to occur, all necessary conditions, i.e. sources and the environment, have to be fulfilled [5,6]. In the case described in this paper, the

source of sulfate ions is the sulfur, which in the form of SO_2 has occurred in the past due to the burning of fuel in the furnaces of steam locomotives, and in recent decades due to the fumes produced by diesel locomotives. The source of the calcium and carbonate ions is the stone cladding made of limestone, together with the ground water from the local catchment area. A sufficient quantity of water for the transport of the reactants and the occurrence of thaumasite is available, with a high air humidity and the presence of ground water. The temperatures in the tunnels were, in the Autumn–Winter period, between 0 and 5 °C, whereas in the Summer the temperatures were somewhat higher, up to 8 °C.

The formation of ettringite and thaumasite in the investigated Slovenian railway tunnels was caused, not only by the general climatic conditions, but also by the composition of the repair mortar. According to Nagataki and Gomi [7], during the hydration of the shrinkage-compensating component $3\text{CaO} \cdot 3\text{Al}_2\text{O}_3 \cdot \text{CaSO}_4$ (which was used in the repair mortar for the investigated tunnels) in the presence of gypsum and water, ettringite occurs, which could, under favourable conditions, undergo transformation to thaumasite by the Woodfordite Route, i.e. by the substitution of Al^{3+} ions by Si^{4+} in the presence of CO_3^{2-} [6]. In the given case, the unsatisfactory consistency of the repair mortar used must certainly have accelerated this reaction.

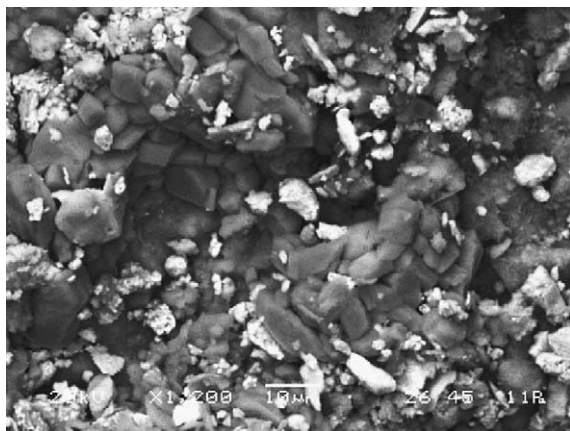


Fig. 7. SEM image of the outer layer of the degraded repair mortar. Monoclinic crystals of gypsum can be observed.

5. Conclusions

The reason for the failure of the non-shrinking repair mortar, which has been used in recent years to repair the mortar joints between the stone blocks of the claddings of several Slovenian railway tunnels, is the formation of

thaumasite. On the one hand the formation of thaumasite is made possible due to the environmental conditions and pollution, whereas another reason for the failure of the repair mortar lies in its unsatisfactory consistency and its chemical composition. The extent of the reaction could be reduced if the water/binder ratio were to be reduced, since this would impede the ingress of water and extraneous ions.

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