Damage Mineral Transformation of Greywacke Aggregate in SMA 11 and AC 11 Wearing Courses Used in A1 Motorway Pavement in Silesia Poland

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Abstract. The paper covers the issues of mineral transformations in the natural aggregate made of greywacke rock used in A1 Motorway asphalt wearing courses (SMA 11 and AC 11) under hypergenic conditions (connected with external environment factors), typical for pavements. The results of these transformations have an appearance of rusty efflorescences on surfaces, which denote destruction process of some grains of the aggregate. This process can next initiate local damage to the wearing course. The research was focused on the experimental tests and mineralogical studies aimed at greywacke grains isolated from A1 Motorway pavement. Experimental tests in laboratory conditions allowed to simulate the process leading to arising of the efflorescences, which finally adopted an evaporite form. Precipitates recreated in laboratory conditions, acquired for mineralogical research, were similarly coloured to those observed on the pavements. Mineralogical studies – performed using optical microscopy, X-ray methods and a scanning electron microscope (SEM), for grains which were the sources of rusty efflorescences and the received precipitates – allowed to identify minerals involved in the transformations (primary minerals) and the minerals subsequently produced (secondary minerals). The most important primary mineral involved in the process leading to arising of efflorescences was pyrite, while the most important secondary minerals were gypsum, halotrichite and copiapite. What was noticed was that mechanism of mineral transformations leading to creation of hydrated sulphates on the surface and in the pores of the grains can be accompanied by the exudation process. The work is closed by short description of the proposal procedure according to PN-EN 1744-1 method modified for pavements applications, which allows to predict the tendency of natural aggregates to the mineral transformations. The modification involves activation of aggregate susceptible to mineral transformation using different than standard lime water factor which can imitate accurately hypergenic conditions typical for pavements.

1. Introduction

In the years 2010 - 2016 at the Silesian University of Technology a research was conducted on the phenomenon of rusty efflorescences occurring on the surface of some wearing courses made of mineral-asphalt mixtures. The phenomenon has become a subject of concern of road managers as it...
may have a negative impact on the durability of the surface, as the discovery was made on newly built roads. The carried out laboratory results and field tests enabled to debunk the current prevailing view, that the only sources of efflorescences are metallurgical slags or other metallic impurities present in the mineral-asphalt aggregate. In the analyzed cases, the sources of efflorescences were the mineral components of natural aggregates made of: amphibolite, dolomite, limestone, gabbro and hornfels [1], [2], [3]. Moreover, there is a known case of efflorescence presence coming from granite aggregate [4]. The following study takes into consideration the efflorescence occurring on the wearing courses of the A1 motorway pavement in Silesia, carried out in 2017, based on greywacke aggregate, which hasn’t shown the mentioned changes in this respect so far. It should be noted that as demonstrated in [2], the tendency to form efflorescences can’t be predicted using the applicable test procedures included in the standards [5] and [6].

The efflorescences observed on wearing courses made of stone mastic asphalt SMA 11 and asphalt concrete AC 11 formed multitudinous rusty spots with diameters ranging from several to several tens of mm (figure 1). Typically, in the individual efflorescence focal point a single grain of aggregate could be identified as a source of pigmentation. Some of the efflorescences were responsible for initiating local damage to the wearing course (figure 2). Basing on the graphical analysis (figure 3, 4), it was found that locally the efflorescence covered approx. 16% of the wearing course surface.

Figure 1. Brownish efflorescences coming up from under horizontal marking (due to centimetres rule below)

Figure 2. Local damage of AC wearing course (blister) in focal point of efflorescence

Figure 3. About 9 m² area of AC wearing course stricken with brownish efflorescences

Figure 4. Graphic analysis of total area of efflorescences (16.3 %) on the photographed fragment of the surface
At the stage of technical documentation analysis by taking into account laboratory prescriptions it was found that the basic mineral component used in the wear courses was greywacke aggregate from Jakubčovice quarry (Czech Republic). In case of AC 11 aggregate, the greywacke in the form of crushed sand 0/2 and grit 2/5, 4/8, 8/11 accounted for 93.0% of the mineral mixture, while in case of SMA 11 the total share of greywacke was 88.5% of mineral mixture. In both cases, the mineral mixture was supplemented by limestone (calcium carbonate) mineral filler. The courses of SMA 11 (main roadway of the motorway) and AC 11 (service roads) were made in 2011.

2. Research methodology

The source of the analyzed greywacke aggregate was the core sample taken from the service road pavement. The core was obtained in accordance with the standard [7] using a drilling machine equipped with a $\phi=100$ mm drilling crown, allowing to cover at least one single focal point in the form of aggregate grain. In the next stage, the wear courses, were mechanically separated from the collected sample, which were heated in order to separate the grains constituting the efflorescence focal points.

The grains were cleaned of asphalt with the use of tetrachloroethene solvent (chemical formula: C$_2$Cl$_4$) for mineral-asphalt extraction. The prepared grains, after being placed on Petri dishes, were treated with distilled water to reinitiate mineral transformations leading to the same efflorescence as on the wearing course. Performing the test on the laboratory dishes, after one to several cycles of evaporation at room temperature (22 ÷ 25°C), the precipitates with the same colours were obtained with the ones observed on the road pavement (figure 5).

![Figure 5. Laboratory sample - evaporate in the form of a rusty-brown precipitate of secondary products of greywacke mineral components transformations caused by the influence of distilled water](image)

In order to carry out the intended mineralogical tests, microscopic sample for transmitted (thin section) and reflected light (polished section) research were made out of obtained aggregate grain samples. Microscopic observations in the transmitted light of the precipitates obtained as a result of the experiment were carried out directly on the dishes. The mentioned tests were performed on ZEISS Axioskop and Axioplan polarized light microscopes.

The chemical composition of the precipitate mineral components was determined using the Hitachi SEM SU3500 scanning microscope with variable pressure, cooperating with the X-ray spectrometer with EDS UltraDry energy dispersion of Thermo Scientific NORAN System 7. Observations in the electron microscope also determined the crystal morphology at 5 - 30000x magnification. The X-ray microanalysis was performed with the following parameters: accelerating voltage - 15 keV (where 1 eV = 1,6021766208(98) × 10$^{-19}$ J), working distance (WD) - 10 mm, pressure - 30 Pa, vacuum - variable. The tests were carried out in micro-areas on the precipitate observing directly on the dishes.
In addition, the X-ray diffraction phase identification method with the HZG-4 diffractometer, equipped with a nickel filter copper lamp at 30 kV and amperage of 20 mA was carried out for the dish sample precipitate.

3. Results and discussions

3.1. Mineral composition of greywacke rock in microscopic studies

The aggregate grain collected from the efflorescence focus point was identified as a well-sorted, fine-grained sandstone in grey colour with shades of beige. In microscopic view at transmitted light, sharp-edged grains, matrix binder, fully porous, compacted structure, unordered, only in some places poorly marked parallel arrangement of muscovite plates were found.

The mineral composition was dominated by quartz, but also by the presence of feldspar in a smaller amount. Multitudinous muscovite plaques of various sizes between the quartz grains and feldspars were seen. (figure 6, figure 7). The presence of heavy minerals, including garnet, zircon and titanite, was also observed.

The presence of opaque minerals was found in the greywacke sample. Some of them were sharp-edged, had cubic shaped habits, others were more irregular, sometimes shining brownish edges occurred. In their vicinity, the brown colour of the rock was often seen, which indicates the presence of iron oxides or hydroxides, which can be pyrite oxidation products (figure 8). The performed research in reflected light allowed to identify these minerals as iron sulphides - pyrite (figure 9, figure 10), as well as hematite and ilmenite (figure 11, figure 12).
Figure 8. Photomicrograph (transmitted light) of greywacke grain. Aggregation of cubic crystals of opaque minerals in the center and brown coloured products of pyrite oxidation to the left, 1 polar, magn. 200x

Figure 9. Photomicrograph (reflected light) of greywacke within pyrite crystal in the center, 1 polar, magn. 200x

Figure 10. Photomicrograph (reflected light) of greywacke within pyrite crystal in the center, crossed polars, magn. 200x

Figure 11. Photomicrograph (reflected light) of greywacke within ilmenite crystal in the center, 1 polar, magn. 200x

Figure 12. Photomicrograph (reflected light) of greywacke within ilmenite crystal in the center, crossed polars, magn. 200x
3.2. Mineral composition of precipitates in SEM research

In the precipitate analysis by electron scanning microscope, the fibrous halotrichite and Fe-halotrichite crystals (figure 13, figure 14) containing Mg$^{2+}$ consecutive substitutions and most frequently parted by gypsum (table 1) were identified. There were also Mg-copiapite crystals found accompanying halotrichite, with a characteristic tabular habit (figure 14). The following contained consecutive Al and Ca substitutions.

![Figure 13. SEM photomicrograph of precipitate - fibrous crystals of Fe-halotrichite (points 1-2) and halotrichite (points 3-6) parted by gypsum](image)

![Figure 14. SEM photomicrograph of precipitate - fibrous crystals of halotrichite (points 1-5) and tabular crystals of copiapite (point 6) parted by gypsum](image)

Table 1. Chemical composition of halotrichite (without H$_2$O) with gypsum (%mas.) and copiapite (figure 14, point 6).

| Measuring point | Al$_2$O$_3$ | FeO | MgO | CaO | SO$_3$ | Total | Reference |
|----------------|------------|-----|-----|-----|--------|--------|-----------|
| 1              | 5.61       | 29.50 | 0.58 | 4.23 | 60.08  | 100.00 | Figure 13 |
| 2              | 9.44       | 23.66 | 0.64 | 2.32 | 63.94  | 100.00 |           |
| 3              | 13.92      | 20.23 | 0.92 | 2.27 | 62.66  | 100.00 |           |
| 4              | 15.47      | 18.77 | 1.13 | 2.79 | 61.84  | 100.00 |           |
| 5              | 13.09      | 20.46 | 0.88 | 3.05 | 62.52  | 100.00 |           |
| 6              | 17.45      | 16.18 | 1.44 | 2.05 | 62.88  | 100.00 |           |
| 1              | 14.39      | 19.41 | 1.09 | 1.71 | 63.40  | 100.00 | Figure 14 |
| 2              | 12.99      | 22.38 | 0.96 | 1.50 | 62.17  | 100.00 |           |
| 3              | 13.68      | 18.92 | 1.02 | 1.34 | 65.04  | 100.00 |           |
| 4              | 11.03      | 19.93 | 1.05 | 1.41 | 66.58  | 100.00 |           |
| 5              | 14.19      | 20.21 | 1.15 | 1.66 | 62.79  | 100.00 |           |
| 6              | 0.80       | 37.34 | 4.44 | 1.51 | 55.91  | 100.00 |           |

An important component of the precipitate is gypsum, crystallizing in characteristic tabular or elongated columnar shapes. Gypsum crystals are often covered with very small halotrichite agglomerates (figure 15), which is supported by the chemical composition of the studied micro-areas (table 2).

Copiapite not only accompanies halotrichite, but also creates its own aggregates (figure 16). The chemical composition of the investigated copiapite micro-areas indicates (table 3) that this mineral group is represented mainly by the variety magnesiocopiapite, which contains Al, Zn and Ca additives, as there are known varieties such as aluminocopiapite, zincocopiapite and calcioopiapite.
3.3. Mineral composition of precipitates in X-Ray Diffraction (XRD) studies

In the precipitate, by using XRD method, a mineral from the mica group - phlogopite KMg$_3$(AlSi$_3$O$_{10}$)(OH)$_2$ was identified, which is supported by the presence of its basic reflections on the diffractogram (10.19 and 3.39Å) (figure 17). Phlogopite belongs to primary minerals, and the presence in the precipitate was caused by its mechanical chipping from the greywacke grain during the experiment on the dish. Similarly, the presence of 3.23Å reflexes should be explained, which is the main reflection of feldspar. A small share of phlogopite and feldspars resulted in their single reflexes on the diffractogram.

The diffractogram also identified significantly weaker, but clearly visible reflections from secondary minerals formed during the experiment. The reflections of gypsum were the most apparent, whereas copiapite and halotrichite were slightly lower. The low reflection intensity is probably caused by the small amount of the obtained precipitate.
3.4. Hypergenic conditions typical of road pavements

Already in the 1950s, the attention was directed towards harmful effect of the active iron sulphides present in the aggregate, which were decomposed in the strongly alkaline environment of cement concrete. In the subsequent years, methods for detecting the aggregate tendency to create efflorescence [8], [9], [10] were developed to eliminate aggregates in cement concrete applications. The method [10] currently functions within the standard [6], which involves a 30-minute immersion of the aggregate in a saturated aqueous solution of calcium hydroxide. In case of iron sulphide a light green, gelatinous precipitate of iron II sulphate is seen within the first 5 minutes, which then turns into brown iron III hydroxide. Considering the low efficiency of the method [1] and the fact that the wearing courses of asphalt mixtures are not exposed to the influence of alkaline environment, a search for another factor that better imitates road-type hypergenic conditions was initiated. The nature of the hypergenic environment typical of road surfaces in Silesia is mainly affected by the pH of rainwater. The road pavement is subjected to the influence of rainwater, having a variable chemical nature ranging from neutral (pH 7) to acidic (pH 3.5) [1]. Acidification of rainwater is related to the presence of sulphates, chlorides and nitrates, as well as strong mineral acids such as sulfuric acid and nitric acid. An additional factor decreasing the pH of water on the surface of wearing courses may be simple carboxylic acids formed in the aging process of asphalt [11]. Another component of rainwater with an acidic reaction is H$_2$O$_2$ hydrogen peroxide [12], [13]. [14]. The acidic character of the hypergenic road surface environment was of fundamental importance when modifying the research method originally developed for aggregates for cement concrete applications (alkaline environment).

3.5. Modification proposal to EN 1744-1 standard method

Experimental tests carried out on the greywacke aggregate confirmed the full effectiveness of 5% aqueous hydrogen peroxide H$_2$O$_2$ being a provoking factor of mineralogical transformation of aggregate components, the result of which are brownish efflorescences. The H$_2$O$_2$ solution was one of 6 factors of diverse chemical nature used in 2010-2015 during experimental research conducted on various natural aggregates susceptible to chemical transformations under the influence of hypergenic factors. The same tests showed poor effectiveness of the strongly alkaline Ca(OH)$_2$ calcium hydroxide solution in initiating the transformation of aggregate mineral components, the use of which is provided.
for in the standard [5]. The use of Ca(OH)₂ is intended to reflect the strongly alkaline environment of aggregates in cement concrete, which also promotes the degradation of sulphides present in the aggregate. The standard method, based on a 30-minute immersion of the aggregate in the limewater, turns out to be highly unreliable in predicting the aggregate susceptibility to mineral transformations occurring on the surface of wearing courses. The applied modification involves placing a sample of aggregate on a Petri dish with 5% H₂O₂ solution in an amount that evaporates at room temperature after 24 hours, giving more precise results. Thus, determining the presence of a brown precipitate on the bottom of the dish is a qualitatively positive test result. Such result clearly indicates the susceptibility of aggregates to mineral transformations, which was also confirmed by research on the greywacke aggregate in question.

4. Conclusions
In the performed analysis, the occurrence of rusty efflorescences was caused by the decomposition of iron sulphide -FeS₂ pyrite present in the aggregate. Pyrite, which oxides easily in the acidic hypergenic environment was a source of iron and sulfur for secondary minerals that were identified as precipitate components. The secondary minerals identified in the study were hydrated sulphates: CaSO₄·2H₂O gypsum, FeAl₂(SO₄)₆·22H₂O halotrichite and (Fe,Mg)Fe₄(SO₄)₆(OH)₂·20H₂O copiapite. Primarily responsible for brownish color of precipitate is iron hydroxide Fe(OH)₃ accompanying oxidation and hydrolysis of pyrite, which arises in the reaction chain [15]:

\[
\begin{align*}
2\text{FeS}_2 + 2\text{H}_2\text{O} + 7\text{O}_2 & \rightarrow 2\text{FeSO}_4 + 2\text{H}_2\text{SO}_4 \\
12\text{FeSO}_4 + 3\text{O}_2 + 2\text{H}_2\text{O} & \rightarrow 4\text{Fe}_2(\text{SO}_4)_3 + 2\text{Fe}_2(\text{OH})_6 \\
\text{Fe}_2(\text{SO}_4)_3 + 6\text{H}_2\text{O} & \rightarrow 2\text{Fe(OH)}_3 + 3\text{H}_2\text{SO}_4
\end{align*}
\]

The sulfuric acid formed during pyrite decomposition facilitates lixiviation of elements such as aluminium, magnesium or calcium from primary minerals more resistant to weathering. The primary source of aluminium and calcium present in the composition of secondary minerals was the feldspar identified in greywacke, while magnesium (also aluminium) could have originated from phlogopite. It should be noted that initial crystallizing hydrated sulphates are characterized by significantly larger molar volumes in relation to the primary minerals providing the components for their formation. Thus, the described mineral transformations are conducive to exudation classified as physical weathering processes. Exudation plays an important role in destroying of the aggregate grains in which the described changes occur. The total disintegration of the aggregate grain structure can cause local damage to the wearing course of the asphalt mixture.

The conducted experimental research confirmed the relationship between mineral transformations leading to the formation of brownish efflorescences and hypergenic conditions typical of road pavements. In case of greywacke, the aggregates containing pyrite, but also in other aggregates containing mainly iron sulphides, the formation of secondary minerals takes place in a slightly acidic environment. The observations confirmed the need to modify the standard method [5], so that it is possible to effectively predict the aggregate susceptibility to mineral transformations in the environment typical of asphalt road pavements.

The aggregate susceptibility to weathering according to the mechanism described above should be considered as undesirable, also in case of aggregates used in mineral-asphalt mixtures as potentially threatening the pavement lifespan. A positive result of the aggregate test according to the proposed method should exclude the possibility of using aggregate in asphalt mixtures dedicated to wearing courses.

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