FACTORS AFFECTING DEF AND ASR IN THE CONCRETE DAM AT **VRANÉ NAD VLTAVOU**

Šárka Šachlová¹, Zdeněk Pertold², Aneta Šťastná³, Tomáš Míčka⁴

¹Charles University in Prague, Faculty of Science, Institute of Geochemistry, Mineralogy and Mineral Resources, Albertov 6, 128 43, Prague 2, Czech Republic

²Charles University in Prague, Faculty of Science, Institute of Geochemistry, Mineralogy and Mineral Resources, Albertov 6, 128 43, Prague 2, Czech Republic

³Charles University in Prague, Faculty of Science, Institute of Geochemistry, Mineralogy and Mineral Resources,

Albertov 6, 128 43, Prague 2, Czech Republic

⁴Pontex Ltd., Březová 1658, 147 00, Prague 4, Czech Republic

Abstract

Two degradation mechanisms, delayed ettringite formation (DEF) as well as the alkali-silica reaction (ASR), were investigated in the concrete dam at Vrané nad Vltavou, CZE with an aim to: (1) find those aggregates causing the degradation of the concrete; (2) define those parts of the concrete most affected by the degradation; and (3) correlate the water attack with the extent of degradation. The following methods were used: measurement of residual expansion of the concrete (following the CSN 72 1179 standard), optical microscopy, petrographic image analysis, and scanning electron microscopy combined with energy dispersive spectrometer (SEM/EDS). Eight different sampling points were selected according to the cracks observed on the concrete's surface. DEF was found to be the most important degradation mechanism in the concrete samples; ASR and calcite-rich rims are regarded as minor. Influence of freezing/thawing degradation is also possible. The highest residual expansion was measured on one concrete sample periodically washed by water (this sample taken from an area one meter above the water level). The same sample shows the highest content of ettringite and microcracks, as well as minor contents of calcite-rich rims and alkali-silica gels. All samples that were taken below the water level as well as samples without any contact with water, showed lower contents of ettringite and microcracks, and very low (or no) contents of alkali-silica gels. The highest degree of degradation by DEF, freezing/thawing and ASR is explained by the following factors: (1) position of sampling points one meter above the water level; and (2) coarse, as well as fine aggregates that are mainly composed of acid volcanic rocks (alkaline rhyolite, tuff and tuffite).

Keywords: DEF, ASR, concrete dam, microscopy.

1. INTRODUCTION

The solidification of cement paste containing gypsum particles is always associated with ettringite formation (e.g., [1] and [2]). This reaction, also called early ettringite formation (EEF), occurs in the plastic stage of a cement mixture, and does not produce any stress or damaging disruption in the concrete construction. Secondary ettringite formation (SEF), also called delayed ettringite formation (DEF), differs in many aspects. It originates later, in concretes several months or years old when in the rigid hardened stage, and produces cracking in concrete structures (e.g., [1] and [3]). Thus, only DEF can be connected with a damaging sulphate attack [1 - 4]. Sulphur content, the high permeability of concrete, and exposure to water are regarded to be the most important factors affecting DEF. The source of the sulphur can be internal (e.g., a high content of sulphur in aggregates or cement paste) or external (from water or soil). Cracking and spalling are the main indicators of DEF macroscopically visible on the concrete surface. Thus, DEF can easily be mistaken for the alkali-aggregate reaction, which displays similar macroscopic indicators. On the microscale, both reactions (DEF and AAR) are indicated by microcracks and dissolution of the cement paste. The

reactions can be distinguished due to the presence of secondary ettringite or alkali-silica gels in the concrete (e.g., [1], [5], [6]).

The aim of our study was to determine the degradation mechanism in the concrete dam at Vrané nad Vltavou. It was necessary to distinguish whether the concrete was damaged by AAR, as was suggested by the "in situ" inspection, or if other degradation mechanisms were active.

2. EXPERIMENTAL PROCEDURE

2.1 Sampling

The concrete dam located at Vrané nad Vltavou is situated on the Vltava river, 15 km south of Prague. The dam was constructed in 1930-1936 as a part of the first water power station on the Vltava river and is exploited since 1936 till present. Concrete drill cores were taken from eight different sampling points, selected according to the number of cracks observed on the concrete's surface (Fig. 1). Two drill cores were taken from pillars 1 and 2 situated 0.5 meter below the water level. Another two drill cores were taken from the concrete wall one meter above the water level. Four other samples came from the pillar and bridge of the dam, which are not washed by water.

2.2 Concrete Prism Test

Residual expansion was measured on the concrete samples following the CSN 72 1179 standard [7] in the laboratory of the Road and Motorway Directorate of the Czech Republic by J. Hromádko and A. Procházková. Concrete prisms of the size $40 \times 40 \times 200$ (resp. 300) mm were cut from concrete drill cores, and maintained at a temperature of $38\pm2^{\circ}$ C and 99% humidity. The residual expansion was periodically measured over 497 days.



Fig 1: Location of the sampling points V7, V8, V9 (above) and V14 (bellow).

2.3 Microscopic Techniques

Unpolished thin sections of the size 25×25 mm were prepared from each drill core. A Leica DMLP polarising microscope (Laboratory of microscopic techniques, Charles University in Prague) was employed in this study. The main indicators of the degradation mechanisms were located according to the presence of degradation products (secondary ettringite, alkali-silica gels, calcite-rich rims). Afterwards, the thin sections were polished with the aim of describing the petrographic characteristics of the aggregates. Representative areas of the thin sections were documented using an Olympus digital camera. Scanning electron microscopy with an energy dispersive spectrometer (SEM/EDS analysis) was conducted at the Laboratory of Electron Microscopy and Microanalysis (Charles University in Prague; operators R. Procházka and L. Nosál). The measurements were performed on a Cambridge Cam Scan S4 instrument with an energy dispersive analytical system (Oxford Instruments LINK ISIS 300) under the following conditions: beam current 3 nA, accelerating voltage 20 kV. For the routine quantitative calibration, a SPI Supplies 53 Minerals Standard set #02753-AB was used.

The petrographic image analysis (PIA) was performed on the microphotographs obtained by polarising microscope using SigmaScan Pro v. 5.0.0 [8]. The PIA procedure consisted of five different steps: (1) image digitizing, (2) image acquisition, (3) image pre-processing, (4) measurement, and (5) data analysis. Manual outlining of individual measured objects (mineral grains and/or microcracks) by an operator (an experienced petrographer) allowed for their discrimination from the image background and from surrounding grains. More details connected to PIA can be obtained elsewhere (e.g., [9 - 11]). The length of the microcracks and the area of the coarse and fine aggregates were measured. The number of analysed objects (including aggregates and microcracks) varied between 250 and 800 per sample. In the last step, the length of the microcracks (in mm) was recalculated into the specific length of the microcracks (in mm / mm2); and the total area (in mm2) of the aggregate types were recalculated into the percentage area.

3. RESULTS

3.1 Residual Expansion of Concrete Prisms

The residual expansion of concrete prisms (%) were calculated from the changes in length of prism specimens, measured periodically for 497 days. All expansion curves (Fig. 2) show an increasing residual expansion during the first two months of testing (expansion reaches values from 0.016 - 0.046%). Most expansion values stagnate for the next four months. Only one expansion value decreases slightly (sample No. VR6). During the final 10 months, all expansion values slightly increase or stagnate. Maximum expansion (0.044%) was measured for sample No. VR5. The remainder of the samples show lowered expansion (0.024 - 0.036%). According to the classification of concrete (e.g., [11]), only sample No. VR5 could be classified as "critical", exceeding the limit of 0.040% after 12 months. The rest of the samples are classified as not critical.



3.2 Composition of Concrete Prisms

According to the microscopic investigation, the concrete samples were composed of coarse (diameter > 2 mm) and fine (diameter < 2 mm) aggregates, cement paste, pore voids, microcracks, and degradation products (alkali-silica gels, ettringite, microcracks, and calcite-rich rims). The coarse aggregates studied exhibit a relatively wide range, both in their petrographic type as well as in their proportions, with respect to the other phases (Tab. 1 and Tab. 2).

Table 1: Proportion of coarse aggregates (> 2 mm) to the total volume of concrete samples A. – aggregates, c.p. - cement paste, deg. p. – degradation products, v. - voids. All

values in vol. %.					
Sample no.	VR1	VR2	VR5	VR6	
Coarse a.	60.8	59.1	59.4	59.6	
C.p., fine a., voids and deg. products	39.2	40.9	40.6	40.4	
Total	100.0	100.0	100.0	100.0	
Sample no.	VR7	VR9	VR13	VR14	
Coarse a.	60.8	59.8	59.2	60.6	
C.p., fine a., voids and deg. products	39.2	40.2	40.9	39.4	
Total	100.0	100.0	100.0	100.0	

Table 2: Composition of coarse aggregates (> 2 mm) .Q-f – quartz-feldspar, tuffitic rocks – tuf, porphyric tuf, tuffitic greywacke, greywacke, All values in vol %

Sample no.	VR1	VR2	VR5	VR6
Quartz	2.1	1.0	2.0	0.0
Feldspar	3.4	9.0	0.0	0.0
Q-f agg., granitoid	8.4	6.7	8.5	10.3
Volcanic rock types	0.0	2.5	0.4	0.0
Granulite	0.0	0.0	0.0	0.0
Amphibolite	0.3	0.0	0.5	0.0

Sandstone	0.5	0.0	0.0	1.4
Schist	5.4	7.2	8.1	2.1
Tuffitic rocks	40.7	32.7	39.9	45.9
Sample no.	VR7	VR9	VR13	VR14
Quartz	0.0	10.3	1.8	0.0
Feldspar	0.0	0.0	0.0	0.0
Q-f agg., granitoid	39.3	18.2	16.3	27.8
Volcanic rock types	0.0	0.0	0.0	0.0
Granulite	0.0	0.0	2.1	0.0
Amphibolite	0.0	0.3	0.0	5.2
Sandstone	1.4	0.0	0.0	0.8
Schist	4.6	2.5	26.2	10.5
Tuffitic rocks	15.4	28.5	12.7	16.3

Tuffitic rocks (including tuff, porphyric tuff, and tuffitic greywacke) represent the most common rock types in six out of eight investigated samples. Their volume varies between 12.7 and 45.9 vol.%. Tuffitic rocks are mainly composed of a very fine-grained tuffitic matrix (grain size < 10 μ m) surrounding clasts of feldspar, quartz, and/or lithic fragments. Their source area is regarded in the local SE part of the Barrandien Neoproterozoic complex.

Granitoids (including granite and granodiorite), together with quartz-feldspar aggregates, are the second most frequent type of aggregates in the concrete samples. Their volumes varied between 6.7 and 39.3 vol.%. These aggregates are coarse grained (grain size mostly > 0.3 mm) and composed of quartz, plagioclase, K-feldspar, amphibole, and mica.

Schists (including phyllite, mica schist, and green schist) are the most common rock types in sample No. VR13 (26.2 vol.%). They are less common in the remainder of the samples (2.1 - 10.5 vol.%). Their structure is very fine grained with a sub parallel texture and minor quartz veins. Amphibolite, granulite, sandstone, and mafic volcanic rocks are less common, forming a maximum of 5.2 vol.% of the samples investigated.

3.3 Indicators of Concrete Degradation

According to the shape of the cracks visible on the concrete surface, as well as their intensity and position within the structure, the ASR (AAR) was suggested as the degradation mechanism. The microcracks were assessed as the most important micro-indicator of concrete degradation observed in all of the investigated samples. Three types of microcracks were observed: (1) microcracks intruding aggregates, (2) microcracks intruding the cement paste, and (3) microcracks intruding the aggregate-cement paste boundaries. The highest value for the specific length of microcracks was measured in sample No. VR5 (0.16 mm/mm2, Tab. 3). The microcracks are interconnected, forming a network of microcracks. Their thickness varied between 50 µm and 2 mm. They were less common in sample Nos. VR7, VR9, VR13, and VR14 (0.07 mm/mm2).

Table 3 Residual expansion of concrete prisms (RE), specific length of microcracks (SLM), the presence of DEF, carbonation (C) and ASR and description of contact of concrete samples with water due to the position in concrete

S.No.	RE (%)	SLM (mm/mm 2)	DEF	ASR	С	Water contact
VR1	0.027	0.12	++	-	+	permanent
VR2	0.026	0.10	++	+/-	+	permanent
VR5	0.048	0.16	++	-	+	partial
VR6	0.037	0.13	++	+	+	partial
VR7	0.026	0.07	-	-	-	none
VR9	0.017	0.07	-	-	-	none
VR13	0.023	0.07	+	-	-	none
VR14	0.028	0.07	+	-	-	none

The microscopic investigation was focused on the identification of alkali-silica gels and ettringite as well as on the detailed description of microcracks. Several microcracks were found sub parallel to the concrete surface and/or propagating round the margins of aggregates. Both these characteristics indicate additional influence of freezing/thawing degradation.

Alkali-silica gels were only identified in samples VR5 and VR2, in the form of small drops filling pore voids. Their extremely small volume, and their presence limited to only two of the investigated samples, eliminated the ASR as the main degradation mechanism according to our analysis.

In contrast, ettringite was assessed to be very common in six out of eight samples investigated. Typical needle-like crystals of ettringite, as well as massive ettringite (Fig. 3), fill pore voids and microcracks. In some cases, ettringitefilled microcracks are surrounded by calcite rich rims. This only confirms the fact, that DEF is the major degradation mechanism in investigated samples. Freezing/thawing, carbonation and ASR are assessed to be minor.





Fig 3 (above) Massive ettringite (Ett.(m)) and needle-like crystals of ettringite (Ett.) situated allong the contact of greywacke with cement paste (CP). (bellow) Microcrack filled by ettringite (Mc.- ett.) intruding cement paste (CP) and greywacke. SEM/EDS method, sample Nos. VR1 and VR5.

4. DISCUSSION

4.1 Influence of Water Level

Eight different sampling points were selected, based on macroscopic inspection of cracks observed on the surface of concrete dam. The position of concrete samples affected their exposure to water. Two were permanently in contact with water (sample Nos. VR1 and VR2), another two samples were periodically washed by water (sample Nos. VR5 and VR6), with another four samples unaffected by water in the reservoir (sample Nos. VR7, VR9, VR13, and VR14). One concrete sample (sample No. VR5), which was periodically washed by water, showed the highest values of residual expansion as well as the highest value of the specific length of microcracks, plus the presence of DEF, ASR, and/or carbonation (see Tab. 3). In contrast, the lowest values of the specific length of microcracks, low degree of DEF, no signs of ASR and carbonation, and low residual expansion were observed in connection with samples not in contact with the reservoir water.

Several authors [1, 12, 13] have suggested that periodic wetting and drying of concrete samples as one of the most important factors affecting the origin of DEF. Periodic wetting and drying and its association with temperature changes (the effects of sunshine and shade), is also important factor influencing concrete degradation due to freezing/thawing (e.g. [14 - 15]).

4.2 Influence of Aggregates

A weak correlation can be seen between the residual expansion and the total content of tuffitic greywacke (resp. tuffitic greywacke + schist, Fig. 4). The ASR of greywacke, schist, and tuffitic rock types is mostly connected to the presence of a matrix containing very fine-grained quartz and amorphous SiO2-rich phases [5, 10, 16 - 17].

The degree of DEF can be connected to sulphur-rich minerals contained in the aggregates. Sulphur can be released into the pore solution and form secondary ettringite [1, 18 - 20]. Sulphur-rich minerals are rare in the investigated samples. Only a few grains of sulphides were observed in aggregates using SEM/EDS methods. The very low content of sulphides eliminates the aggregates as the main source of sulphur.

We suggested the following mechanism of concrete degradation: (1) high humidity and high alkali-silica reactivity of aggregates cause ASR as well as the origin of alkali-silica gels and microcracks; (2) formation of alkali-silica gels reduces the content of alkalis and decreases pH values of the cement paste and pore solutions; (3) the sulphur leached in the pore solutions is consumed by newly formed secondary ettringite; and (4) secondary ettringite fills the previously formed micro-cracks, pore voids, and micro-cavities. This mechanism has previously been confirmed by several authors [1, 19]. In that manner, ASR can be accepted as a precursor of DEF.

Ettringite is stable at lower pH than portlandite, i.e., between 12.5 and 10 [21]. According to Terai et al. [22] it forms above a Ca/Al ratio of 1.5, and above a pH of 9.86. Its origin and stability in some parts of the Vrané dam concrete was very likely enabled by the combination of: 1) decrease of alkali content in the pore solutions due to the formation of alkali silica gels, and 2) by periodic washing out of the alkalis by the dam's water.



Volume of tuffitic greywacke and schist (vol. %)



5. CONCLUSIONS

The origin of concrete degradation was recognised by the combining of the measurements of residual expansion of concrete prisms with the microscopic characterisation of the concrete samples. DEF is the main mechanism responsible for deterioration of concrete samples; freezing/thawing, ASR and carbonisation are minor. Concrete deterioration proceeded in several steps:

- The ASR originated due to the presence of alkalireactive aggregates (tuffitic greywackes and schists), highly alkaline conditions in cement, and high humidity. The alkali-silica gels expanded, producing the initial stages of concrete deterioration, and forming a system of microcracks and cavities.
- The content of alkalis in the cement was reduced by the formation of alkali-silica gels, plus decreasing pH values of the cement paste and pore solutions.
- The secondary ettringite originated filling the previously-formed microcracks, pore voids, and cavities causing later stages of the concrete degradation.
- Carbonation is expected to be active in the late stages, following the system of microcracks which originated prior.

Permanent or periodic contact with water increases the humidity in the concrete, and causes temperature changes. Both of these factors support the origin of DEF, freezing/thawing and ASR.

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BIOGRAPHIES



Šárka Šachlová, Ph.D. graduated from the Faculty of Science, Charles University in Prague, in 2008. She focuses on concrete and mortar-based materials and aggregate testing (e.g. microscopic techniques, chemical

leaching, degradation processes).



Zdeněk Pertold, professor emeritus Faculty of Science, Charles University. During the last years interested in regionally metamorphosed skarns of the Bohemian Massif, and in ASR



Aneta Šťastná, Ph.D. graduated from the Faculty of Science, Charles University in Prague, in 2008. She focuses on building materials (microscopic techniques, stable isotopes, mortar bar test etc.).



Ing. Tomáš Míčka graduated from the Faculty of Civil Engineering Czech technical University in Prague, Structural and Transportation Engineering, in 1989. These days he is manager of the diagnostic centre company Pontex Ltd.