

Swiss tunnel structures: concrete damage by formation of thaumasite

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Abstract

The severity of concrete deterioration is related to the risk of failure of the construction and to the costs of repair. Severe conditions may also be related to interactions with water regarded as weakly aggressive, although these processes are slow and long periods of time are needed for heavy deterioration.

We often encounter thaumasite in concrete exposed to ground water with high as well as with low sulfate contents. Thaumasite may form relatively thin layers near the concrete surface in contact with the water as well as larger continuous volumes of completely altered concrete.

Based on the description of macro- and microscopic textures and the chemical alterations, a succession of corrosive reactions is postulated. It seems that natural ground water conditions in the Swiss Alps preferentially lead to a sulfate attack with the formation of thaumasite rather than the formation of ettringite. The consequences of these findings are discussed for underground constructions, properties of concrete used as well as for performance testing regarding sulfate attack.

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1. Introduction

Modern concrete materials are generally characterised by durability qualities. Regarding actual tunnel projects in Switzerland service periods without major repairs of up to 100 years are requested. Ground water is therefore of major importance also concerning maintenance of the drainage system [1,2].

However, under certain circumstances the interaction with water may lead to serious chemical alterations of concrete which shorten the service life of buildings. In the case of tunnels and other underground constructions the costs for renovations are extremely high. In order to initiate protective countermeasures against corrosive damages it is important to understand the deterioration processes.

Although concrete corrosion has many different faces, there are some general phenomena, which are observed in most field studies of deteriorated concrete. Thaumasite is a quite common finding and is increasingly discussed in literature as a special form of sulfate attack [3–11]. Low temperatures and delivery of car-

bonate are of special concern in field investigations as well as in laboratory studies [12,13].

In this study we investigate the underlying mechanisms of short and long term concrete–water interactions in selected tunnel structures which lead to these deterioration phenomena. Based on the description of macro- and microscopic textures and the chemical alterations, a succession of corrosive reactions can be postulated. The reactions include leaching and dissolution, transportation, (re)precipitation and formation of new products. Thereby it is important to note that physical parameters like permeability or inhomogeneities are at least as important as chemical parameters like the composition of the paste, pH-values and composition of the interacting water or the pore solution. Tunnel structures have to be regarded as complex systems in that all these parameters may vary over time or distance.

2. Examples of concrete deterioration in Swiss tunnels: field evidence

On the basis of reports [14–17] and an inquiry with Swiss road authorities several tunnel projects have been chosen for our study. The composition of the ground water, the age and the kind of construction as well as the

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kind and degree of damage have been criteria for the selection of objects for detailed investigation.

2.1. Evidence of interaction with ground water in general

Elevated water saturation of concrete with or without efflorescence is often associated with pathways (joints, cracks) through the concrete component. The formation of homogeneous layers of secondary minerals on the surface of concrete could only be observed with relatively thin shotcrete and sodium sulfate hydrates. Surface scaling of concrete due to the crystallisation of salt near the surface is rare in tunnels (maybe due to high levels of humidity). In most cases water is moving along local and permeable inhomogeneities through the concrete. Low flows of water are accompanied by formation of calcite and/or water soluble salts on the surface of the concrete close to the intersection. Larger flows of water are frequently escorted by biofilms on the concrete surface and water soluble salts may form in the lateral drying region of the wet concrete. Under biofilms the concrete surface may show phenomena of cement paste dissolution and erosion.

In contrast to these surface phenomena the back of underground constructions is much less accessible for investigation but more susceptible for interactions. On the surface of concrete in contact with ground water we find the evidence of aggressive components of this water. In a simplified view two processes may be distinguished: First components of the hardened cement paste get dissolved and leached away by the ground water. Second components of the ground water (like magnesium or sulfate) may form stable compounds with constituents of the pore solution or the cement paste. Only dilute concentrations of water soluble reactive components (like magnesium or sulfate) may be transported together with pore solution through the concrete, as a consequence this process is followed by substantial leaching. Potassium, sodium and chloride may get transported in higher concentrations, therefore accompanied by leaching to a relatively lower degree.

Phenomena on the inner surface of tunnel linings may or may not give indications of severe deterioration processes regarding interactions with ground water. Detailed examination of localities in the concrete with high permeabilities (pathway for ground water) may deliver indirect evidence of corrosive interactions on the outer surface of the concrete exposed to ground water.

The condition of the drainage system may also give indications of water–concrete interaction. Even if many natural ground waters show the tendency for precipitating themselves, the extensive formation of solid deposits in cavities and pipes of the drainage system is likely to result from chemical interactions with cementitious building materials indicating that the original water was therefore aggressive to concrete.

2.2. Laboratory investigations of field concrete

Samples of shotcrete or massive concrete have been cored carefully in locations showing representative deterioration phenomena as well as at positions without any evidence of deterioration serving as reference samples. After cutting and drying, fractions of the material were chosen for microscopical or analytical investigation. After a macroscopical description of the sections through the whole region of interest, locations have been selected for further investigation under the light microscope and/or in the scanning electron microscope. The preparation of thin sections was based on epoxy resin impregnated samples. To determine the uptake or change in concentration of chemical components, element mappings have been performed on impregnated and polished samples, whereas qualitative identification of solid phases were obtained by energy dispersive X-ray spectroscopy (EDS) of untreated but broken samples in the environmental scanning electron microscope (ESEM). Samples of efflorescence or portions of chemically reacted paste in concrete have been analysed by X-ray diffraction (XRD) to identify the chemical compounds, especially the mineralogical nature of sulfate containing solids.

3. Results and discussion

3.1. Leaching of concrete, definition of zones

Chemical compositions of natural ground waters are quite different from a representative pore solution leading to mass transfer interactions between the ground water and the saturated cement paste [18–20]. Percolating ground water along pathways through concrete is efficiently leaching alkalis and portlandite, leading to a “leaching zone” characterised by the reduction of portlandite while calcium silicate hydrate (C–S–H) phases are still present (Fig. 1).

During further leaching all portlandite is removed and the pH-value is getting reduced rapidly. C–S–H phases are not stable anymore and start to dissolve [21], leading to a “corrosion zone” consisting of a S–H residue (Fig. 2). During these leaching processes the density of the hardened cement paste is reduced accompanied by microcracking and therefore increasing permeability properties.

3.2. Occurrence of secondary sulfate minerals in field concrete

In relation to the interaction of ground water in tunnel concrete the formation of sulfate-containing minerals was dominated by thaumasite. Ettringite was detected only in minor proportions together with

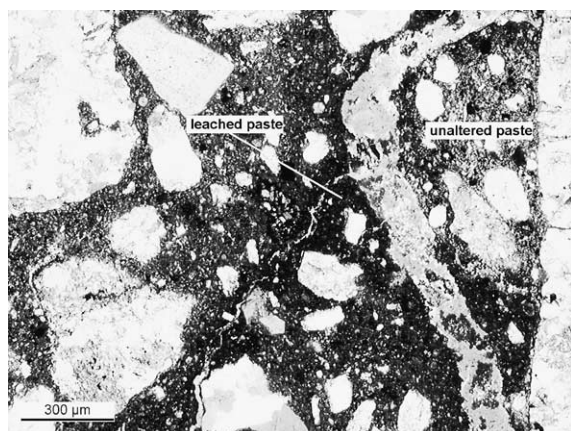


Fig. 1. Sample of 2-year-old shotcrete (thin section, crossed polars) of Gotschna-Tunnel: the hardened cement paste in contact with the cracks shows discoloration which is related to the reduction of portlandite compared to unaltered paste, therefore representing the leaching zone. The sample was cored close to a water outlet, the water contains in mg/l: sodium 415, bicarbonate 630, sulfate 540 and calcium, magnesium and potassium less than 5 mg/l each.

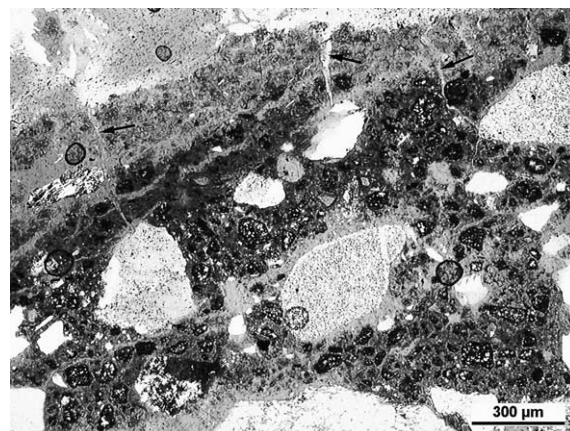


Fig. 3. Sample of shotcrete (thin section, crossed polars) of Bauen-Tunnel: the hardened cement paste shows a gradient of leaching and corrosion with effect from top left. In areas of complete corrosion of all calcium containing constituents of the paste small amounts of thaumasite are formed along contacts and secondary cracks (arrows).

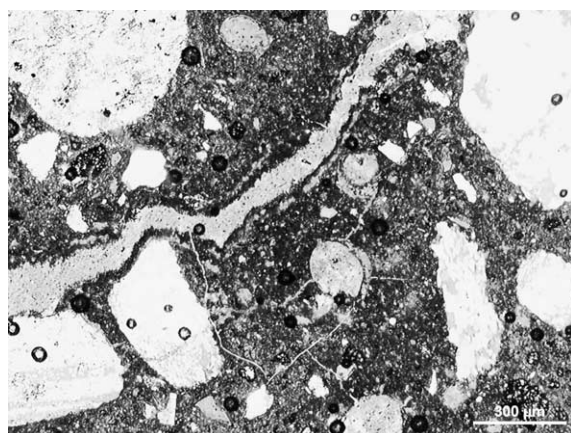


Fig. 2. Sample of 30-year-old shotcrete (thin section, crossed polars) of Bauen-Tunnel: the hardened cement paste in contact with the crack is completely amorphous, representing the corrosion zone. The alteration product in addition is affected by smaller cracks perpendicular and parallel to the larger crack. The water in contact with this shotcrete could not be analysed. In the nearby Seelisberg tunnel ground water was analysed to contain in mg/l sodium 1200, potassium 15, magnesium 14, calcium 47, sulfate 300, bicarbonate 118 and chloride 1700.

thaumasite in cement paste with minor degrees of chemical alterations. Ettringite could otherwise be detected as recrystallised needles in air voids surrounded by unaltered paste which is interpreted as a ordinary consequence of high degrees of water saturation over longer periods of time [22]. Thaumasite in contrast is associated with a different kind of chemically altered or deteriorated concrete.

Thaumasite in the corrosion zone is characterised as partial replacements of S–H phases initiating from crack

surfaces (Fig. 3). Only small amounts of thaumasite have been detected and often signs of surface erosion were present indicating very low mechanical resistance of S–H and thaumasite layer and increased flow rates of percolating water.

In the leaching zone thaumasite is formed at the expense of C–S–H phases. Substantial or almost complete volume fractions of the hardened paste may get changed into thaumasite with only aggregates and few relicts of leached paste left. Formation of thaumasite in the leaching zone is accompanied by contact parallel cracks (Fig. 4).

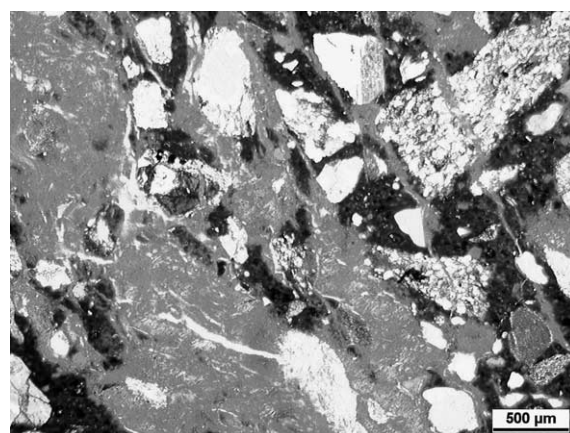


Fig. 4. Sample of shotcrete (thin section, crossed polars) of Bauen-Tunnel: relicts of hardened cement paste shown in dark grey which indicates the loss of portlandite. The sample shows extensive cracking parallel to the contact of the shotcrete (to the bottom left). Cracks and larger veins are filled with fibrous aggregates of thaumasite (light grey colour). In the field of view significantly more than 50% of the original paste is altered into thaumasite.

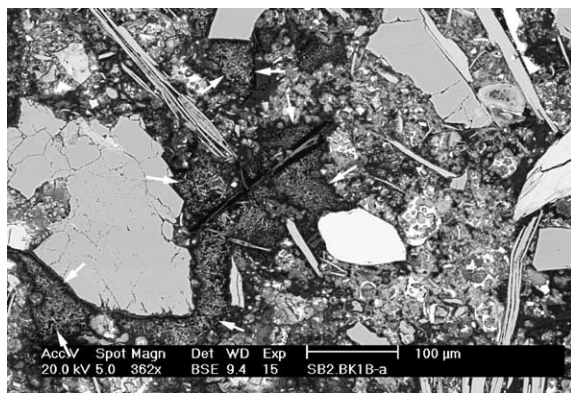


Fig. 5. This concrete sample originates from the contact with the rock support of the San Bernardino tunnel (service gallery) whereas within half a meter distance the concrete is completely altered into a mush-like material as shown in Fig. 6. Larger areas of white or grey colour represent mineral aggregate (quartz, feldspar and mica) as well as clinker relicts. Hydrated cement paste shows darker grey levels and granular texture. The polished sample shows several distinct regions of fibrous paste (border marked with arrows) within the concrete matrix, this fibrous paste consists of thaumasite and subordinate ettringite. The nearby ground water was analysed to contain in mg/l calcium 270, magnesium 270, bicarbonate 200 and sulfate 1900. The original concrete was produced with sulfate resistant cement.

Thaumasite may also be found in more or less sound cement paste. This phenomenon is restricted to concrete in close contact to ground water. Starting from regions with slightly increased porosities, hardened cement paste may be replaced by thaumasite and subordinate ettringite (Fig. 5). The transition is quite sharp between altered parts and unchanged regions of paste. It seems as if local uptake of dissolved carbonate and sulfate without much leaching may lead to the formation of thaumasite while the pH value is unaffected. It may be assumed that the formation of larger amounts of these sulfate containing minerals after a certain degree leads to expansion of the concrete. This would be accompanied by extensive cracking and an acceleration of mass transfer. In the end this mechanism could produce the phenomenon of local but complete paste deterioration characterised by the formation of mush containing the original aggregates of the concrete (Fig. 6). This stage corresponds to zone 4 of Sibbick and Crammond [9] which is the last zone in the degradation sequence, whereas the zones two and three are very well comparable to the leaching zone proposed here.

Crammond and Halliwell [13] and other studies showed the role of limestone aggregates and fillers in delivering the carbonate for the thaumasite reaction. In our investigations all concrete contained preferentially siliceous aggregates and we observed no indications of dissolution or alteration of limestone aggregates. In these cases and in regard to the chemical composition of the corresponding groundwater, it is likely that the percolating water is the source for the carbonate in the thaumasite reaction.



Fig. 6. Portion of the base of the tunnel lining with the drain channel to the left. Large volumes of concrete have been altered into a soft mush like or crumbly material depending on the degree of water saturation. The concrete deterioration is limited locally to volumes of several dm³ and was triggered by permeable pathways through the concrete. Some years after construction of the tunnel the drainage system collapsed, the pressure of the ground water increased and percolating water was forced to penetrate the unprotected concrete lining of the tunnel.

4. Proposed mechanisms of thaumasite formation

From the literature, thaumasite may be formed in two different ways [23,24]. The direct formation at the expense of C–S–H-phases is related to large amounts of thaumasite in that cement paste normally consists of over 70% calcium silicate hydrate [25]. To react all silicon from the cement in the paste, calcium has to be added in addition and together with sulfate and carbonate. The alteration of more than 20% of the cement paste into thaumasite is followed by a more or less complete loss of cohesion of the concrete [23].

The indirect formation of thaumasite is related to exchange of aluminium by silicon as well as water and sulfate by carbonate in the crystal structure of ettringite already present [26]. Stable compositions in-between ettringite and thaumasite may exist under different conditions but miscibility gaps in the thaumasite–ettringite solid solution exist as well [27].

The different kind of occurrences of thaumasite in field concrete as shown here gives evidence of more complex ways of thaumasite formation which are somehow related to the nature of the altered paste in contact with thaumasite.

4.1. *In situ* formation of thaumasite

In situ is meant to be direct or indirect formation of thaumasite in cement paste hardly affected otherwise. The detection of secondary sulfate minerals leads to the assumption, that diffusion and uptake of sulfate and carbonate lead to the formation of ettringite and

thaumasite in succession or in parallel when in contact with a high pH pore solution. The local dominance of thaumasite in such circumstances implies the consumption of C–S–H and portlandite (Fig. 5). Maybe the concentration of carbonate in the pore solution compared to the concentration of sulfate plays a major factor in determining the stability of thaumasite. The role of alkalis or other ions like magnesium in stabilising thaumasite is not known well.

4.2. Formation of thaumasite in the corrosion zone

On the basis of field evidence we postulate that thaumasite is formed in the corrosion zone by long term interaction of cement paste with ground water with low concentrations of calcium, sulfate and carbonate. Over the first period of this interaction the cement paste is leached, the concentrations of sulfate, carbonate and calcium in the percolating water still being too low for the formation of ettringite or calcite. The formation of ettringite may also be prevented as a consequence of pH reduction. In a second period the destabilisation of C–S–H is increasing the chemical activity of silicon in the system as a reaction partner for the formation of thaumasite. The small amounts of the later in the corrosion zone of field concrete indicates a small window for the chemical composition of percolating water leading to intense leaching (corrosion) and the formation of thaumasite.

4.3. Formation of thaumasite in the leaching zone

The pattern of contact parallel layers of thaumasite in contact with portlandite-depleted paste and the presence of small cracks filled with thaumasite in this paste is the result of the volume increase due to the alteration of leached paste into thaumasite. Surface parallel cracks in leached paste may be the precursors of more extensive alterations leading to dense thaumasite layers. The chemical environment of the underlying processes is reducing the pH of the paste by mobilising portlandite and on the other hand delivering sulfate, carbonate and calcium as reactants for the thaumasite reaction. Calcium may partly originate from leaching processes of cement paste nearby. Compared with the thaumasite formation in the corrosion zone, calcium concentrations might be higher in the leaching zone. Maybe sulfate and carbonate concentrations in the percolating water next to the leaching zone are also higher than those in the corrosion zone.

Low flowing ground waters will be affected in the concentration of their chemical constituents by the chemical interaction with concrete and by the loss of water due to suction and evaporation. Therefore phenomena of water interaction in thin walled concrete may

vary over short distances due to differences in flow rate and amount of evaporation.

5. Conclusions

In all investigated tunnel structures with concrete in contact with ground water, the processes of leaching and the formation of sulfate minerals, predominantly thaumasite, have been detected. As a consequence thaumasite may be a very common finding in a large number of underground constructions [27].

In our view a number of chemical parameters are controlling the course of concrete deterioration, low temperature not being a prerequisite for the formation of thaumasite as mentioned frequently in literature [12,28]. For instance in the San Bernardino tunnel in regions with thaumasite-related concrete, deterioration the temperature was always above 20 °C.

The severity of concrete deterioration due to these chemical interactions is dependent on a large number of parameters like

- the chemical composition and amount of ground water (incl. flow rate and pressure);
- the thickness of the concrete and the bulk quality in respect to porosity and permeability;
- the nature and distribution of pathways through the concrete (like joints, cracks, interfaces).

The concentration of sulfate in the ground water as well as the use of cement with low contents of aluminium seem to be less important. In the case of tunnel linings consisting only of shotcrete the contact with low amounts of weakly mineralised ground water was leading to partial break downs of the concrete due to the formation of thaumasite on the back of the lining over 20–30 years [15]. Severe conditions may therefore be related to ground water not considered as aggressive by current standards.

5.1. Consequences for the underground construction

The adhesion of shotcrete linings may be affected by small amounts of interactions on the interface. In this regard not only water described as “aggressive” corresponding to regulations have to be considered but also water with a wide range of chemical compositions. Shotcrete linings are rather thin and inhomogeneous regarding the distribution of porosity. Therefore shotcrete is quite often found to be substantially affected by ground water whereas the deterioration in ordinary concrete is mostly restricted to primary inhomogeneities like joints, cracks or regions with poor compaction.

Interaction of water and cementitious materials may affect the chemical composition and stability of the

ground water as well and lead to severe amounts of precipitation and finally blocking of the drainage system. Depending on details of the construction and on potentials of water–concrete interactions the design of underground constructions therefore has to consider the accessibility of the drainage system for maintenance operations or measures to prevent formation of sinter crusts. Regarding only service life of structural concrete in underground constructions the best solution would be to keep the concrete dry. Attempting this by application of sealing, the service life of the sealant itself also needs to be considered.

5.2. Consequences for the concrete composition

Application of sulfate resistant cement as a consequence of high levels of sulfate in the water as recommended by the respective regulations is not an absolute prevention to sulfate damage. This is related to the presented occurrences of thaumasite under different conditions which itself is not dependent on the presence of aluminium in the system.

The only countermeasure against sulfate attack is the placement of concrete with low water permeability (high density). The workmanship in the production of such concrete as well as in the placement and aftercare are crucial for the bulk properties of the concrete components as well as for tight joints between them.

It might therefore be beneficial to use a well known concrete system with optimised admixtures to get correct workability and optimum density at a maximum level of homogeneity throughout the concrete component. Using a somehow dictated cement in replacement of a experienced constituent may lead to troubles in production and application of the concrete and therefore promote chemical interactions.

5.3. Consequences for performance tests

The role of thaumasite in relation to sulfate-induced damages in concrete structures might be underestimated so far due to difficulties in its identification and differentiation from ettringite. In contrast to the findings of this report the deterioration of laboratory samples in sulfate performance tests is related to the formation of ettringite.

It has to be assumed that the underlying mechanisms of these performance tests and those leading to deterioration involving thaumasite in real underground concrete are different. To be able to find countermeasures against effects of natural ground waters containing sulfate new solutions have to be elaborated to correctly optimise the performance of concrete. These new tests probably have to put weight on leaching as well as on sulfate attack considering water compositions with sulfate and carbonate and maybe also with a blend of ca-

tions. The task of a “thaumasite performance test” is demanding and will take some time especially because one set of parameters has to be established to take into account different representative conditions of real situations.

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References

- [1] Wegmüller M, Chabot JD. Einflüsse des Bergwassers auf die Dauerhaftigkeit von Bauwerken. Institut für Bauplanung und Baubetrieb IBB, ETH Zürich, 1997. p. 132.
- [2] Wegmüller MC. Einflüsse des Bergwassers auf Tiefbau/Tunnelbau. Stäubli AG, Zürich, 2001. p. 215.
- [3] St. John DA, Poole AB, Sims I. Concrete Petrography—A handbook of investigative techniques. London: Arnold Verlag; 1998.
- [4] Mehta PK. Mechanism of sulfate attack on Portland cement concrete—another look. *Cement Concrete Res* 1983;13:401–6.
- [5] Lawrence CD. Sulfate attack on concrete. *Mag Concrete Res* 1990;42(153):249–64.
- [6] Cohen MD, Mather B. Sulfate attack on concrete—research needs. *ACI Mater J* 1991;88(1):62–9.
- [7] Mehta PK. Sulfate attack on concrete—A critical review. In: Skalny J, editor. *Materials Science in Concrete III*. American Ceramic Society; 1993. p. 105–30.
- [8] Hime WG, Mather B. Sulfate attack, or is it? *Cement Concrete Res* 1999;29:789–91.
- [9] Sibbick RG, Crammond NJ. Microscopical investigation into recent field examples of the thaumasite form of sulfate attack (TSA). In: *Proceedings of the 8th Euroseminar on Microscopy Applied to Building Materials*, Athens, Greece, 2001. p. 261–9.
- [10] Hagelia P, Sibbick RG, Crammond NJ, Grønhaug A, Larsen CK. Thaumasite and subsequent secondary calcite deposition in sprayed concretes in contact with sulfate bearing alum shale, Oslo, Norway. In: *Proceedings of the 8th Euroseminar on Microscopy Applied to Building Materials*, Athens, Greece, 2001. p. 131–8.
- [11] Santhanam M, Cohen MD, Olek J. Sulfate attack research—whither now? *Cement Concrete Res* 2001;31:845–51.
- [12] Bickley JA, Hemmings RT, Hooton RD, Balinsky J. Thaumasite related deterioration of concrete structures. In: *Proceedings of Concrete Technology: Past, Present and Future ACI SP: 144–8*, 1995. p. 159–75.
- [13] Crammond NJ, Halliwell MA. Assessment of conditions required for the thaumasite form of sulfate attack. In: Scrivener KL, Young JF, editors. *Mechanisms of Chemical Degradation of Cement-Based Systems*, London, 1997. p. 193–200.
- [14] Romer M, Lienemann P. Versalzung und Korrosion von Spritzbeton (Sicherheitsstollen des Gotthard-Strassentunnels). *Chimia* 1998;52:197–201.
- [15] Romer M. Chemische Interaktion von Bergwasser mit Beton. In: Löw A, Wyss R, editors. *Vorerkundung und Prognose der Basistunnels am Gotthard und am Lötschberg*, Tagungsband zum Symposium Geologie AlpTransit. Rotterdam, Zürich: AA. Balkema; 1999. p. 279–89.
- [16] Holzer L, Romer M. Corrosion of concrete: assessing the mechanisms. In: Pietersen HS, Larbi JA, Janssen HA, editors.

- 7th Euroseminar on Microscopy Applied to Building Materials. Technical University of Delft, The Netherlands, Faculty of Civil Engineering and Geosciences, Delft, NL, 1999. p. 67–79.
- [17] Romer M, Holzer L, Pfiffner M. Interaction of water with concrete: Deterioration Mechanisms. Consec' 01. Vancouver, 2001. p. 1075–82.
- [18] Diamond S. Concrete pore solutions. *Cement Concrete Res* 1981;11:383–92.
- [19] Trägårdh J, Lagerblad B. Leaching of 90-year old concrete mortar in contact with stagnant water. Stockholm, Sweden: SKB Swedish Nuclear Fuel and Waste Management Co; 1998.
- [20] Andac M, Glasser FP. Long-term leaching mechanisms of Portland cement-stabilized municipal solid waste fly ash in carbonated water. *Cement Concrete Res* 1999;29:179–86.
- [21] Steinour HH. C–S–H-stability and pore solution chemistry. 3rd ISCC 1954:261–70.
- [22] Famy C, Taylor HFW. Ettringite in hydration of Portland cement concrete and its occurrence in mature concretes. *ACI Mater J* 2001;98:350–6.
- [23] Bensted J. Mechanism of thaumasite sulphate attack in cements, mortars and concretes. *ZKG Int Zem Kalk Gips* 2000;53:704–9.
- [24] Grijalvo JA, Blanco-Varela MT, Maroto FP, Sanchez AP, Moreno TV. Thaumasite formation in hydraulic mortars and concretes. In: Malhotra VM, editor. *Durability of Concrete, Proceedings of 5th International Conference*, vol. II, Barcelona, Spain, 2000. p. 1173–92.
- [25] Diamond S. Cement paste microstructure. Hydraulic cement pastes: their structure and properties—an overview at several levels. Cement and Concrete Association, Slough, UK, Sheffield, 1976. p. 2–30.
- [26] Stark J, Wicht B. *Dauerhaftigkeit von Beton*. Finger-Institut für Baustoffkunde FIB, Weimar, 1995.
- [27] Barnett SJ, Macphree DE, Crammond NJ. Solid solutions between thaumasite and ettringite and their role in sulfate attack. *Concrete Sci Eng* 2001;3:209–15.
- [28] Hartshorn SA, Sharp JH, Swamy RN. Thaumasite formation in Portland-limestone cement pastes. *Cement Concrete Res* 1999;29:1331–40.