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Field performance of concrete exposed to sulphate and low pH conditions from natural and industrial sources

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ABSTRACT

Laboratory investigations have been used to derive a high number of important details on sulphate attack on hardened concrete, but are not able to forecast the performance of this material under field conditions. In order to obtain reliable information on the long term behaviour of concrete, a survey is presented that looks at sulphate and sulphide containing environments in a particular region in mid-Europe. Twenty concrete structures have been sampled and analyzed.

The classical idea of sulphate attack considering the migration of sulphate ions from ground or river water into concrete with subsequent phase transformation and damage has not been confirmed. This kind of exposure was found to be rare and no serious deterioration has been observed in connection with it. However, concrete is liable to be destroyed when in contact with sulphide bearing environments or if intimately mixed with gypsum. Disintegration and serious expansion requiring immediate repair has been observed. Information on all investigated structures are presented in this article and in more detail in a separate report.

1. Introduction

Concrete is a material that is used for many purposes in construction without the need of maintenance during the life time of the structure. However, it can be damaged by a number of chemical reactions that are often due to the ingress of certain reactive species in the microstructure. Such reactions are carbonation, chloride induced steel corrosion and sulphate attack, among others. Attack from an aggressive species is considered during concrete production by selecting cements that exhibit superior resistance in the relevant exposition.

Research into performance and durability of hydraulic limes and cements has a long tradition, starting in the 18th and 19th century with investigations reported by Blezard [1]. A high number of research programs have been conducted in the 20th century, acquiring knowledge on the nature of sulphate attack mechanisms. Monographs and review articles on this issue are available [2–7] and design of concrete exposed to sulphate attack is supported by standards and guidelines.

Upon the contact of concrete with sulphate containing environments, a diffusion of sulphate and potentially of other ions in the hardened cement paste takes place. Some of the phases in the microstructure are sensitive to an interaction with sulphate. Calcium hydroxide reacts with sulphate ions to gypsum, AFm phases are converted to ettringite, and C–S–H is potentially transformed into thaumasite. All of these reactions induce a modification of the microstructure of the hardened cement paste. Most often, expansion and micro-cracking are observed, although softening and disintegration have been reported as well. In order to avoid these deterioration processes, mix design properties such as water/cement-ratio and cement content are modified and sulphate-resisting cements or binders are used. Susceptibility is reduced by restricting the amount of the clinker phase C_3A in the cement and by adding mineral admixtures such as blast furnace slag and coal fly ash. These information and many other details have been derived from the results of a great number of experimental investigations carried out under laboratory conditions. Experimental investigation in laboratories benefit from the fact that the test conditions can be carefully controlled whereas real field situations are much more complex. It has been proved difficult to compare the outcome of laboratory scaled investigations with experiences of the performance of hardened concrete under field conditions. This is mainly due to the limited number of studies addressing field situations. Most of the latter have been focused on the cause of damage in a special case [8–24,34], whereas more general studies are rare. Information related to the distribution of sulphur bearing environments and the performance of concrete in these conditions would be helpful to identify correlations and differences between lab and field behaviour. Only a few publications are available on this topic. A systematic survey of concrete structures in the UK damaged by the thaumasite form of sulphate

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attack (TSA) has been reported recently [5]. The performance of concrete is currently being tested in situ by exposing a number of different concretes to the aggressive environment that has been identified in the aforementioned study [25]. Information on the distribution of sulphate containing environments is hardly available [5,26,27]. Field concretes exposed to sulphate have been studied by SEM [28].

The current study has been set up in order to add supplementary data on the nature and distribution of sulphate and sulphide containing environments in a specific area in mid-Europe. Twenty structures exposed to these environments have been examined by visual inspection and core drilling of hardened concrete followed by testing of the obtained samples with different analytical techniques. Information on the long term performance of the structures under examination have been derived from strength data and the depth of the damaged surface layer. The obtained data can be used to discuss the relevance of laboratory investigations with respect to kind and frequency of different types of expositions, correlation of attack mechanisms between laboratory and field, extent of damage, and other questions.

The investigations reported in this paper are restricted to a special region in Germany with a broad range of sulphate related expositions. However, the spectrum is not exclusive and other conditions can be met elsewhere. Most relevant are aride soils and sulphide containing clays that are not abundant in the region under discussion.

2. Laboratory examination and testing

Most of the concretes investigated in this study have been sampled by core drilling (diameter 100 mm). These samples were tested with respect to compressive strength, carbonation depth (phenolphthalein test) and phase transformation. The latter comprised SEM on polished sections and fracture surfaces, thin section light microscopy and qualitative XRD. The chemical composition of the aggressive environments has been analyzed by wet methods and ICP–OES. Data on the original composition of the concrete was included in the evaluation where available.

3. Results

Thuringia is a region in Germany, mid-Europe, with about 2 million inhabitants residing on about 16,000 km^2. A few small mountains with a maximum altitude of approximately 1000 m are located in this region. Ores and other resources have been exploited by mining for more than 500 years. Due to its geographic history, marine evaporates such as gypsum and rock salt are at or close to the earth crust in some places. The climate is humid with a medium temperature of approximately 8 °C and a medium rainfall of 400–500 mm per year.

The classical model of sulphate attack relies on the idea that sulphate ions migrate from an aggressive environment into concrete leading to phase transformation and structural damage. The extent of deterioration depends on the sulphate ion concentration itself and the kind and concentration of accompanying ions. Subsequently, exposition classes depending on the sulphate ion concentration in the water have been introduced in standards for the production of concrete, and measures are suggested to increase the resistance of the material. Most prominent are the decrease of the water/cement-ratio and the use of more resistant cement types. However, standards and guidelines are developing over time and differ between nations.

This study discusses the nature and distribution of sulphate related environments in a special region and the performance of concrete in these conditions. Classification of the exposure types is different from the one suggested by the currently valid standard EN 206. The following grouping in five classes has been found appropriate. Exposition types 1–3 consider attack by dissolved sulphur species in combination with different accompanying ions, types 4 and 5 are relevant for environments containing undissolved sulphur bearing minerals.

- Type 1: Mobile water may contain sulphate ions due to the dissolution of other minerals such as gypsum, and exposition class 1 considers elevated sulphate ion concentrations at a neutral pH in the absence of harmful accompanying ions.
- Type 2: In contact with pyrite, increased sulphate ion concentrations in connection with low pH values in mobile water may lead to a faster progress of deterioration.
- Type 3: This class includes highly concentrated brines with a salt content ranging from 50 to approximately 300 g salt/kg solution. Such brines are found in the vicinity of stockpiles and waste tips from salt mining.
- Type 4: A direct contact of hardened concrete with sulphate containing soil and rock is discussed in this exposition class.
- Type 5: Rock and soil with reduced sulphur in the form of sulphide is considered in class 5. Relevant minerals are pyrite, markasite, and pyrrhotite.

For each exposition type, occurrence details are discussed in combination with results from the examination of concrete structures that were exposed to this particular environment.

3.1. Elevated sulphate concentration in mobile water

Concrete structures in contact with mobile water such as bridges and dams are mostly located on rivers. The sulphate ion concentration of most rivers in the region under consideration is monitored by local authorities. Depending on rainfall, the sulphate concentration rises and falls over the course of the year. There is a tendency to lower sulphate ion concentrations in wet seasons due to a dilution with rainwater. An example presented in Fig. 1 shows data collected over 6 years from one particular sampling point. There is also a second variation of sulphate ion concentration between different sampling points on the same river.

The number of rivers falling in three categories with differing sulphate ion concentrations is presented in Fig. 2. A majority of test sites indicate sulphate ion concentrations never exceeding 400 mg/l. In contrast to this, a medium sulphate concentration of approximately 600 mg/l is encountered for only a few very small rivers. Both categories correspond to exposition class XA0 or the lower range of XA1 according to EN 206. It is unlikely that such low sulphate ion concentrations are able to damage hardened concrete and subsequently only three bridges exposed to low sulphate ion

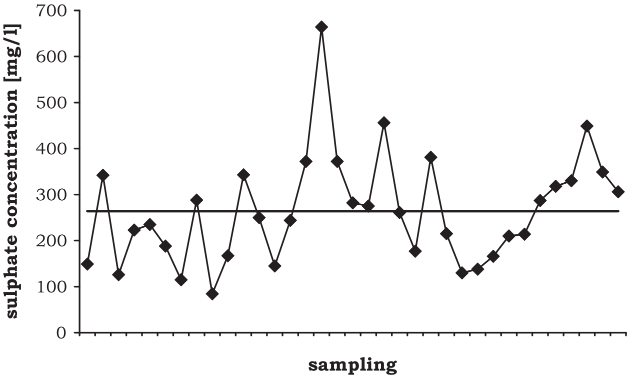

Fig. 1. Variation of sulphate ion concentration in a particular river over time (mean value is indicated by the horizontal line).

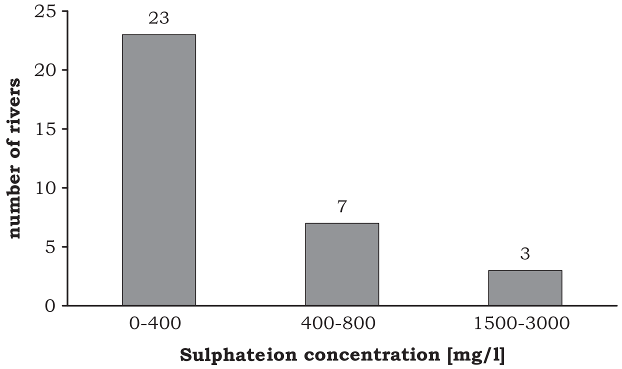

Fig. 2. Number of rivers falling in three categories with different sulphate ion concentration.

concentrations were examined (structures 1–3). As indicated in Fig. 2, three small rivers were found to contain a much higher sulphate level constantly over the year. Relevant concrete structures were found on two of these three rivers with medium sulphate ion concentrations between 1500 and 3000 mg/l. These two bridges were sampled and analyzed (structures 4 and 5). Both are located in an area of mining and the high sulphate levels are due to accidents in the mining sewage systems. Sulphate ion concentrations in these rivers are constantly high despite the fact that mining has been abandoned in the respective areas. It can be assumed that there is a contamination of the river bed itself, and the release of sulphate and other ions proceeds rather slowly.

Two additional structures exposed to moderate sulphate ion concentrations, but not considered in Fig. 2, have also been investigated (structures 6 and 7).

Results of the experimental investigations are reported in detail in a separate publication [29]. The present paper provides a short description of all structures, summarized in Table 1 and conclusions drawn from the results.

3.1.1. Structure 1

The foundation of a bridge had been in contact for 13 years with river water having sulphate ion concentrations of approximately 600 mg/l (XA1). A very low compressive strength of 9 MPa was measured for the concrete and attributed to a high porosity of the material (Fig. 3). Apparently, it had not been properly compacted when the concrete was placed. Attack by sulphate ions and carbon dioxide on a low quality Portland cement concrete had resulted in carbonation and formation of ettringite. These phase transformations were observed in an approximately 11 mm surface layer.

3.1.2. Structure 2

A small bridge built using precast concrete elements was exposed for 16 years to a very low sulphate ion concentration (400 mg/l, XA1). The material did not show any signs of sulphate attack such as ettringite formation. A carbonation depth of approximately 3 mm was measured in the Portland cement concrete (45 MPa).

3.1.3. Structure 3

A very small river in an area with gypsum soils was found to have high variation in sulphate ion concentration depending on the rainfall in the particular region (XA2). The river runs through a water channel under a bridge when crossing a road. Concrete made from Portland cement with coal fly ash (28 MPa) showed severe micro-cracking, ettringite formation and carbonation in the first 3 mm. Minor micro-cracking and reduced phase transformation was evident between 3 and 10 mm depth.

None of the three bridges exposed to low sulphate ion concentrations showed serious signs of sulphate attack.

Other structures exposed to sulphate ion concentrations between 1000 and 2500 mg/l showed signs of deterioration depending on the application of a surface protection system and combination with frost attack.

3.1.4. Structure 4

The foundation of a river bridge had been in contact with sulphate containing water (2000 mg/l) for a period of 12 years (XA2). A high strength (>70 MPa) was measured below the surface of the concrete that was affected by micro-cracking due to the formation of ettringite, thaumasite, gypsum, and Friedel's salt (Fig. 4). Deterioration was found to be intense in the first 10 mm, whereas only minor phase transformations were present in a depth between 10 and 20 mm. The concrete had been produced from Portland cement with a small amount of coal fly ash.

3.1.5. Structure 5

Exposed for approximately 35 years to a slightly higher sulphate ion concentration (2500 mg/l, XA2) than structure 4, virtually no sulphate related deterioration was evident in a concrete from slag cement (CEM III). The concrete of a bridge foundation (68 MPa) was protected by a bituminous coating that showed only minor signs of delamination. Formation of ettringite in pores, voids and the microstructure itself had led to micro-cracking (up to 30 μm) in the first 4 mm. Minor deterioration was evident between 4 and 7 mm. The carbonation depth was highly variable, locally up to 10 mm.

3.1.6. Structure 6

A deep underground mine for the exploitation of iron ore and pyrite was subjected to water penetration from the surrounding rock. This water is highly aggressive due to the oxidation of pyrite still present in the mine. It is subducted and processed in order to prevent contact with rivers and poisoning of their fauna. The ground slab of a mining waste water processing basin was in poor condition after exposure to sulphate attack for 25 years. Damaged concrete was removed and a protective coating applied. This 3–4 cm thick layer of slag cement mortar (CEM III) showed only minor signs of attack after 15 years of contact with water of moderate sulphate ion concentration (up to 1000 mg/l, XA2). Approximately 5 mm of the mortar was damaged by ettringite formation, excessive micro-cracking (Fig. 5), and carbonation. The core of the material and the ground slab itself were in good condition (43 MPa). However, upper parts of the basin walls were exposed to frost–thaw-cycles and seriously damaged by this form of attack. Thaumasite was identified in samples from the deteriorated concrete.

3.1.7. Structure 7

A small water reservoir for irrigation purpose had been erected in a soil containing a high amount of gypsum. Dissolution of gypsum led to sulphate concentrations of approximately 1000 mg/l in the water thus attacking the concrete of the dam and the abstraction channel (XA2). The 33 year old slag cement concrete (CEM III) in the outflow channel was protected by a 7 cm floor screed against the combined attack by frost, sulphates and water abrasion. About 1 cm of the screed mortar was already lost and 2 cm were seriously affected by phase transformation (ettringite, thaumasite, calcite, ASR gel) and micro-cracking. The concrete of the walls and the underlying floor was protected by a bituminous coating and thus not affected (81 MPa).

3.2. Elevated sulphate ion concentrations in mobile water at reduced pH

Colliery spoil from lignite mining may contain sulphides such as pyrite. Some of the open pits have been flooded after exploitation and a number of small and medium sized lakes exist now in

Table 1
Summary of all experimental investigations including concrete mix details where available (structures appearing in bold exhibited serious damage due to sulphate exposure).

No.	Description	Age (years)	Cement	w/c	Specified 28-day strength (MPa)	Exposition	Observation
Elevated sulphate concentration in mobile water							
1	Road bridge Kölleda	13	CEM I	0.48	25	$SO_4^{2-} = 0.6$ g/l	Low strength, high porosity, not compacted
2	Road bridge Buttstedt	16	CEM I	No data available	35	$SO_4^{2-} = 0.4$ g/l	High strength, sulphate attack not confirmed
3	Road bridge Wickerode	15	CEM I + coal fly ash	No data available	No data available	$SO_4^{2-} = 0.8$ g/l	High porosity, phase transformations up to 1 cm
4	Road bridge Gera 1	12	310 kg/m^3 CEM I + 40 kg/m^3 coal fly ash	0.50	25	$SO_4^{2-} = 2.0$ g/l	High strength, phase transformations up to 2 cm
5	Road bridge Gera 2	35	CEM III	No data available	No data available	$SO_4^{2-} = 2.5$ g/l	High strength, bituminous coating, phase transformations up to 1 cm
6	Concrete basin Elbingerode	15	CEM III	No data available	No data available	$SO_4^{2-} = 1.0$ g/l	Phase transformations up to 1 cm, deterioration when exposed to frost
7	Outflow channel Dachwig	33	450 kg/m^3 CEM III	0.44	22.5	$SO_4^{2-} = 1.0$ g/l	1 cm already lost, phase transformations in further 2 cm
Elevated sulphate concentration in mobile water at reduced pH							
8	Water channel Cospuden	3	350 kg/m^3 CEM III + coal fly ash	0.48	37	$SO_4^{2-} = 1.0$ g/l pH = neutral	High strength, phase transformations up to 0.5 cm
9	Bridge Barbarakanal	6	360 kg/m^3 CEM I	0.48	35	$SO_4^{2-} = 0.3$ g/l pH = 4.0	High strength, acid attack, phase transformations
10	Concrete basin Restloch 29	2	390 kg/m^3 CEM III + 30 kg/m^3 coal fly ash	0.45	45	$SO_4^{2-} = 0.4$ g/l pH = 3.3	High strength, acid attack, phase transformations
Concrete in contact with concentrated salt brines							
11	**Sewage manhole Menteroda**	6	CEM I (SRPC)	No data available	No data available	$SO_4^{2-} = 14$ g/l in brine	low strength, concrete completely deteriorated
12	Concrete basin Bischofferode	7	CEM III + coal fly ash	No data available	35	$SO_4^{2-} = 7.4$ g/l in brine	high strength, phase transformations up to 2 cm, chloride attack
Concrete in gypsum containing soil							
13	Bridge Rottleberode	47	CEM III	No data available	No data available	$SO_4^{2-} = 3$ g/kg (soil)	Concrete destruction not due to sulphate attack, phase transformations up to 1 cm
14	Radio mast Vogelsberg	10	CEM III + coal fly ash	No data available	25	$SO_4^{2-} = 3$ g/kg (soil)	High strength, phase transformations up to 2 mm
15	Power transmission line Nordhausen	44	CEM I	No data available	No data available	No sulphate attack	Low strength, carbonation
16	**Soil stabilization Leinefelde**	1	CEM I + Lime	–	–	15% gypsum in claystone	Formation of ettringite and thaumasite, up to 15–25 cm expansion
Concrete in contact with soil and rock containing sulphides							
17	**Tunnel Lössau**	30	CEM II, CEM III	No data available	22.5	$S^{2-} = 0.1$ wt.%	CEM II shotcrete disintegrated in some spots, minor problems with CEM III concrete
18	**Tunnel Leibis/Lichte**	10	350 kg/m^3 CEM I	0.50	25	Pyrite in rock	Shotcrete completely disintegrated in some spots
19	**Tunnel Breitenbachtalsperre**	42	300 kg/m^3 CEM I, CEM III	0.50	22.5	$S^{2-} = 0.1$ wt.%	CEM I shotcrete disintegrated, CEM III shotcrete unaffected
20	**Water channel**	2–4	CEM I (SRPC)	No data available	No data available	Up to 6 wt.% pyrite	Shotcrete completely disintegrated in some spots

regions of lignite mining. Oxidation of sulphides is able to generate high sulphate ion concentrations and low pH-values in the lake water. Three structures exposed to different conditions have been tested. Despite their relative youth (2–6 years), serious deterioration due to acid attack was evident at low pH. All three sites are located outside the core region considered in this study.

3.2.1. Structure 8

The ground slab of a water channel made from slag cement (CEM III) did not show any visual signs of deterioration after being exposed to sulphate attack for a period of three years. A sulphate ion concentration of 900 mg/l and a neutral pH (6.9) have been found by chemical analysis (XA2). Approximately 5 mm of the dense, good quality concrete (48 MPa) were affected by carbonation, ettringite formation and micro-cracking. There was no significant deterioration or phase transformation below this surface layer.

3.2.2. Structure 9

Evidence for acid attack was found on the supporting wall of a 6 year old bridge exposed to pH = 4.0 and $SO_4^{2-} = 350$ mg/l (>XA3). Dissolution of the hardened cement paste up to a depth of 5 mm resulted in exposure of aggregate particles. Formation of ettringite was evident in the matrix below the dissolved layer. The core of the Portland cement concrete was unaffected and maintains a high strength (55 MPa).

3.2.3. Structure 10

Contaminated water (pH = 3.3, $SO_4^{2-} = 350$ mg/l, >XA3) is transported via pressure pipes. It is pumped from a small concrete basin

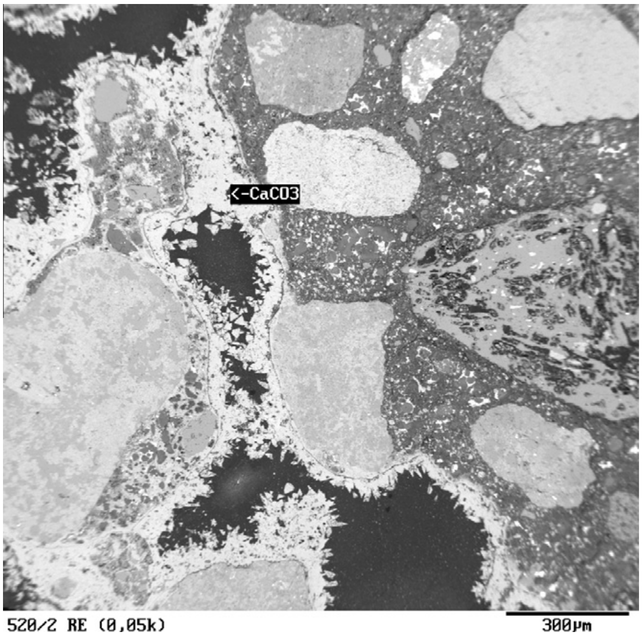

Fig. 3. SEM micrograph indicating the formation of calcium carbonate in the pores of a low quality, low strength Portland cement concrete (structure 1).

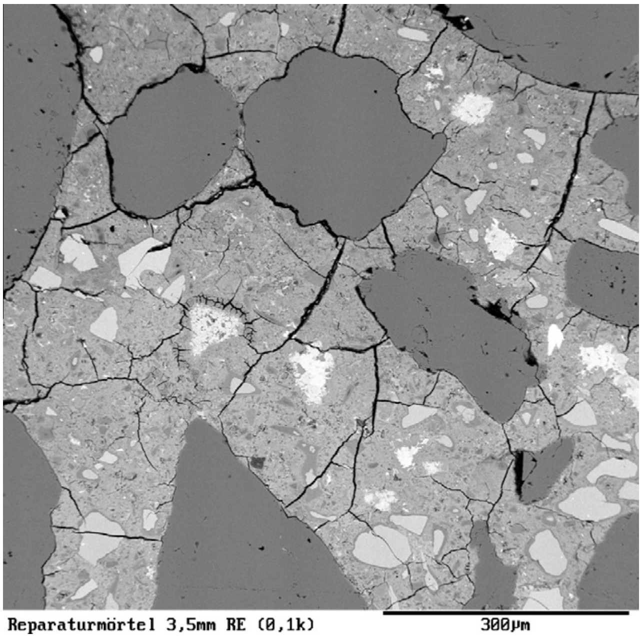

Fig. 5. Massive formation of micro-cracks in a 5 mm surface layer of a mortar exposed to moderate sulphate attack for 15 years (structure 6).

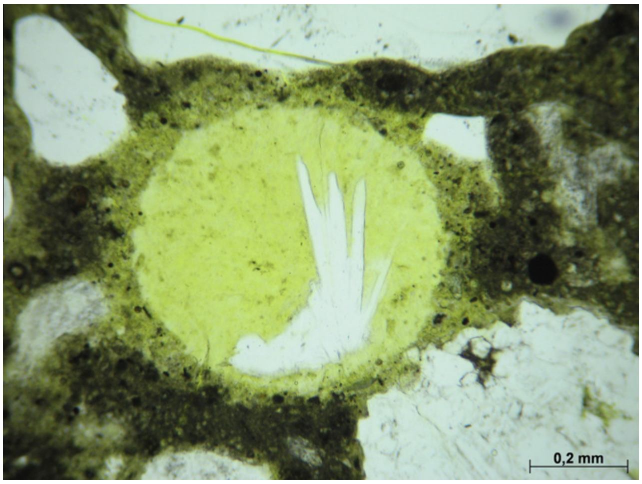

Fig. 4. Secondary phases in a circular void detected by light microscopy in a concrete exposed to $SO_4^{2-} = 2000$ mg/l for 12 years (structure 4).

made using slag cement (CEM III) and a small amount of coal fly ash. Dissolution of hardened cement paste, formation of ettringite and hematite were detected after 2 years of acid and sulphate attack. A 6 mm surface layer of the high quality concrete (43 MPa) showed signs of deterioration after this relatively short period of time.

3.3. Concrete in contact with concentrated salt brines

Underground salt mining for the production of fertilizer started at the end of the 19th century in the region of investigation, but hardly any mine is currently being exploited. However, spoil piles with dimensions up to 100 Mio. t are still present at the abandoned exploitation sites. The spoil consists mainly of alkali and earth alkali chlorides and sulphates. Rain water penetrating the mining waste dumps dissolves these salts, and ionic concentrations of 100–300 g salt/l can be found that also include very high sulphate ion concentrations. A contact of these brines with river and ground water is prevented by collecting the aggressive salt brines in drainage systems and transporting them back to the mines. Parts of the drainage and transport systems have been made from concrete.

3.3.1. Structure 11

The ground slab of a sewage manhole made from sulphate-resisting Portland cement (SRPC) was seriously damaged after 6 years contact with a highly concentrated salt brine (>XA3). Chemical reactions of the hardened cement paste with chloride (163,000 mg/l), sulphate (14,000 mg/l), and magnesium (660 mg/l) ions resulted in the formation of gypsum, thaumasite and brucite (Fig. 6). These phase transformations were accompanied by salt crystallisation (halite), carbonation, formation of massive cracks

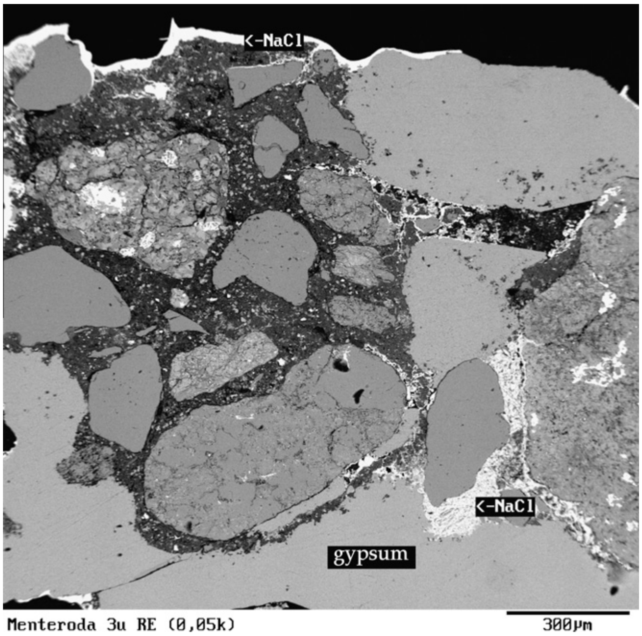

Fig. 6. Transformation of the cementitious matrix in secondary phases upon contact of concrete with a concentrated brine (structure 11).

and strength loss (14 MPa). Considering the high degree of salt contamination of the concrete, it can be assumed that the material had already been penetrated by salt solution during construction.

3.3.2. Structure 12

A concrete basin for the collection and storage of salt brine (Cl^- = 93,000 mg/l, $SO_4^{2-} = 7,400$ mg/l, Mg^{2+} = 1,700 mg/l, >XA3) was inspected after being in service for a period of 7 years. The slag cement concrete (CEM III) with a strength of approximately 70 MPa was in good condition according to visual and microscopic examination. A 20 mm surface layer showed minor phase transformation including formation of calcite, magnesium silicate hydrate, Friedel's salt and ettringite. However, a high chloride concentration has been observed and it can be expected that chloride induced reinforcement corrosion will shorten the service life of the concrete.

3.4. Concrete in gypsum containing soil

The investigated region is rich in gypsum sediments deposited in Zechstein and Triassic. A schematic map indicates the distribution of gypsum/anhydrite deposits and gypsum containing soils (Fig. 7). Some of these areas have been explored in order to find concrete structures that are in direct contact with gypsum. It has been proven difficult to identify such structures, as most areas marked grey in Fig. 7 are low in population with a limited number of buildings and structures. However, foundations of a bridge, a radio mast, and a high voltage transmission line have been selected and tested (structures 13–15).

A different kind of interaction takes place when gypsum containing soil is stabilized by cement–lime binders. Gypsum and clay minerals from the soil are able to react with calcium hydroxide and C–S–H supplied by the hydrating binder. The formation of ettringite and thaumasite by this reaction led to serious heave of a motor highway (structure 16).

3.4.1. Structure 13

A small bridge in a plaster production plant has been investigated after 47 years of service. Foundations and supporting walls of the bridge are in contact with river water and gypsum dust from the production and transport processes in the plant (XA1). One of the supporting walls showed serious cracks and a low strength (21 MPa). This has been attributed to a low concrete quality during production because ettringite formation, carbonation and micro-cracking were restricted to a 10 mm surface layer. The opposite wall had been produced using a concrete with a higher quality. Subsequently, a higher strength (38 MPa) and no macro-cracks were found in this wall. Slag cement (CEM III) was identified in both concretes.

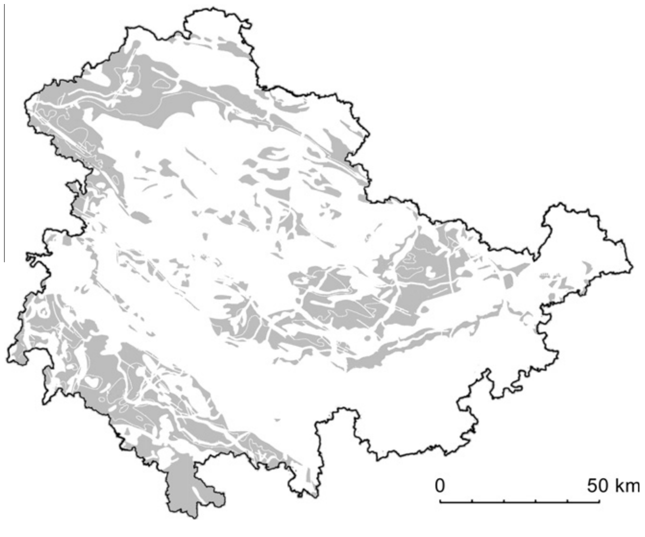

Fig. 7. Schematic map indicating areas (shaded grey) in the core region with soils that potentially contain gypsum.

3.4.2. Structure 14

A high quality concrete of the foundation of a radio mast did not show any signs of damage. A high strength (84 MPa) and the absence of micro-cracks, carbonation and ettringite formation below a 2 mm surface layer were attributed to the fact that the site was relatively dry. Contact with gypsum containing soil for 10 years (XA1) in the absence of water was not able to induce sulphate attack in the concrete made from slag cement under addition of coal fly ash.

3.4.3. Structure 15

The foundation of a steel tower of a high voltage transmission line has been tested. Despite indications from geological information that the concrete is situated in a gypsum containing soil, no sulphate has been detected when analyzing the soil (XA0). The approximately 45 year old Portland cement concrete was of low quality (14 MPa) but did not suffer from sulphate related phase transformation.

3.4.4. Structure 16

Soil stabilization had been carried out when building a new highway in a gypsum rich area. A reinforced concrete slab (30 cm) was placed between stabilized soil and bituminous pavement in order to prevent deformations such as settlement and sinkhole formation related to washing out of gypsum from the soil. Settlement has not been observed but serious expansion (up to 15 cm after 1 year, up to 25 cm after 2 years). The claystone containing approximately 15 wt.% gypsum had reacted with the cement–lime binder to ettringite (up to 6 wt.%) and thaumasite (up to 13 wt.%) in spots where a high amount of water was available. Similar processes have been observed when recycled concrete waste containing gypsum is used for road subbases [14,30–33], after application of gypsum–lime plasters in cold and wet conditions [5], during restoration of gypsum masonry with cement, and in other incidents where gypsum and cement are intensively intermixed.

3.5. Concrete in contact with soil and rock containing sulphides

Damage of concrete due to oxidising sulphides has been widely reported [5,8,13,19,23]. Oxidation of pyrite, markasite, pyrrhotite and other minerals liberates sulphate ions initiating sulphate attack that is accelerated by a combination with acid attack. A few small mountains are located in the investigated region with rock containing sulphide in some sites whereas sulphides are not abundant in soils. Four tunnel linings have been selected for sampling, one of these is located outside the investigated region.

3.5.1. Structure 17

A tunnel for water transport had been constructed by using shotcrete for the ceiling and the upper parts of the walls, whereas mixed-in-place concrete was used for the lower parts of the walls. The shotcrete was found to be seriously affected after 30 years service. Pyrite oxidation had led to sulphate attack on the 3–10 cm thick concrete layer. Combination with carbonation caused the transformation of all cementitious phases into calcite, gypsum and thaumasite. The concrete had lost adhesion to the rock and had fallen apart in some spots. The lower parts of the walls had been constructed using mixed-in-place concrete (20–30 cm). Diffusion of oxygen through this slag cement (CEM III) walls was restricted, due to better quality and higher thickness of the concrete. Thus only a reduced amount of sulphuric acid had been liberated by pyrite oxidation. Approximately 1–3 cm of the concrete was affected by minor micro-cracking and ettringite formation.

3.5.2. Structure 18

Slate containing a high amount of pyrite had led to total disintegration of a Portland cement shotcrete tunnel lining in some sites. After 10 years of service, the soft concrete mud consisted mainly of thaumasite and calcite. Phase transformation and softening started at the concrete–rock interface.

3.5.3. Structure 19

A tunnel in another region was in contact with rock having a sulphide concentration of approximately 0.1 wt.%. Reinforced concrete had been applied in two layers using different cement types. A Portland cement concrete was in direct contact to the rock but had completely disintegrated in places with high water migration. The water had even washed most of the cement phases away leaving an empty shell filled with the concrete aggregates. The second concrete layer was made from slag cement. It had no direct contact to the aggressive rock and showed superior performance.

3.5.4. Structure 20

Local damages in the shotcrete lining of an underground water channel were visible after only 3 years. The 10–40 cm thick Portland cement concrete had been directly applied on a rock with up to 6 wt.% pyrite. Oxidation of pyrite led to the formation of thaumasite, ettringite, gypsum and brucite in the concrete (Fig. 8). The extent of damage proved to be a function of nature of aggregate, thickness of concrete, pyrite concentration in the rock, access of water, and application of rock anchors. A number of different Portland cements also including sulphate-resisting Portland cement had been applied, all being sensitive to sulphate attack.

4. Discussion

Altogether, 20 structures have been sampled and analyzed. Considering this data and information on the distribution of sulphate related exposition sites allows a discussion of the performance of concrete exposed to sulphate attack under field conditions.

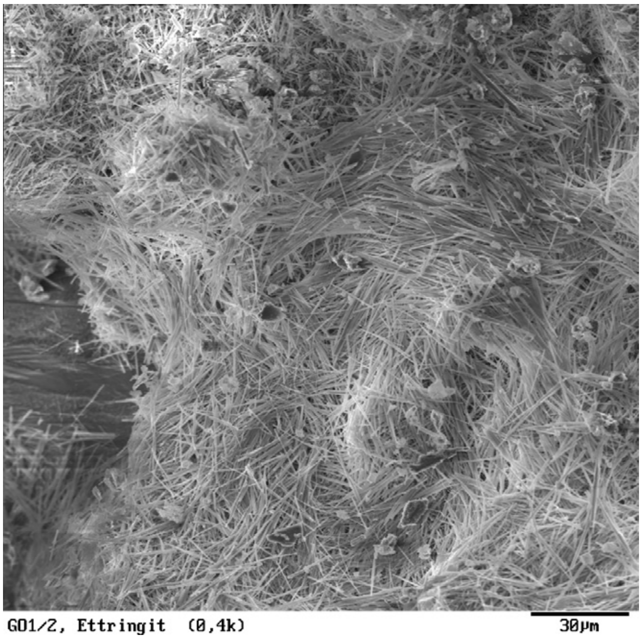

Fig. 8. Massive deposits of ettringite in shotcrete applied to a rock containing a high amount of pyrite (structure 20).

Six out of 20 structures (bold in Table 1) showed serious damage and demand immediate repair (11, 16–20). Most of them showed disintegration due to TSA (16–20). Thaumasite formation (TF) was identified in samples 1, 3, 4, 7, 11, and 14.

The development of concretes with only minor damage was estimated. Data referring to age of the structure and corroded surface layer has been used to estimate the thickness of the deteriorated zone after an assumed life-time of 100 years [29]. These computations rely on a simple root-time-law. Most concretes contain steel reinforcement which is likely to corrode if the concrete cover is seriously affected by sulphate attack. It has been assumed that concrete structures will be damaged if the computed thickness of the damaged surface layer is higher than 5 cm, which is a suggested concrete cover for reinforcement in hydraulic engineering structures in Germany. Evaluation of the results indicates that most structures will not show structural damages within their lifetime (1–3, 5–10, 13–15). It is expected that in two concretes the corroded or chloride penetrated layer will be thicker than 5 cm after 100 years (4, 12). However, the method of extrapolation is liable to show deviations from the true behaviour. It can be derived that structures 4 and 12 should be controlled again in order to avoid reinforcement corrosion.

The classical concept of sulphate attack suggesting that ions naturally present in unpolluted river or ground water are able to migrate into concrete and may cause phase transformation and damage has not been validated in this study. Only negligible sulphate ion concentrations have been found in uncontaminated rivers. However, anthropogenic activities had occasionally led to an increase of sulphate ion concentration in some small rivers. Concrete exposed to such rivers showed minor damages at the microscopic level such as phase transformation and micro-cracking in the first mm and cm (structures 1–7). Only one of these structures may exhibit significant signs of damage if the attack is not controlled by additional measures (structure 4).

Similar results have been obtained for soils containing gypsum. Only a limited number of exposed buildings have been identified with marginal consequences such as carbonation, micro-cracking and ettringite formation (structures 13–15). However, the presence of gypsum is able to impair the durability of stabilized soils, road subbases from recycled concrete and other construction elements where hydrated cement phases are in close contact with gypsum (structure 16).

Serious damage requiring renovation has been identified in cases where hardened concrete was in direct contact with rock containing sulphides such as pyrite (structures 17–20). This behaviour has been reported before for sulphide bearing soils and rocks.

Concentrated brines from industrial and mining processes containing high sulphate ion concentrations may affect the performance of concrete. Beside the formation of ettringite, thaumasite, Friedel's salt and gypsum, chloride induced reinforcement corrosion is potentially able to shorten the expected lifetime of the structure.

A discussion of the impact of cement type on performance is difficult because the structures were widely varying with respect to environment, concrete quality and age. 10 concretes out of 22 have been produced using slag cement. No serious damage has been detected after exposure to sulphate attack under field conditions. Portland cement and blended cements have been identified in 12 concretes in some instances as SRPC in others in combination with coal fly ash. All damages reported in this study were encountered with these cements which indicates a lower resistance to sulphate attack. However, it has to be kept in mind that Portland cements have been used in very aggressive environments such as sulphide bearing rock. The selection of cement type plays only a secondary role when compared to the impact of the environment. Portland limestone cement has not been identified in the concretes under investigation and subsequently no conclusions about its performance under field conditions can be drawn from the present study.

It has been found even more difficult to access the impact of concrete quality on durability because the structures in this survey were much different with respect to age, exposure, and quality.

5. Conclusions

The following conclusions were drawn from a survey of sulphate related expositions and the performance of concrete in these conditions:

- It is confirmed that sulphate attack on concrete is a phenomenon that can potentially lead to failure of this material within a relatively short period of time.
- The number of damaged structures is very low. Most often, it is related to a contact of concrete with soil or rock containing sulphide. Also, a close contact with gypsum may lead to failure. These exposition types are not regularly implemented in standards and guidelines for the production of concrete.
- TSA has been observed in most of the seriously damaged structures. The expansion induced by the formation of ettringite has damaged one structure (stabilization of gypsum containing soil with cement).
- Contact with sulphate containing river or ground water is rarely observed and the corrosion reactions are restricted to a surface layer. The absence of serious deterioration under these conditions may be due to the fact that such environments are considered in most standards.
- Sulphate attack is accelerated by low pH values in the water due to a combination with leaching induced by acid attack.
- The data obtained in this study tends to confirm conclusions that blast furnace slag cement performs better in sulphate rich environments than Portland cement.

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References

[1] Blezard RG. The history of calcareous cements. In: Hewlett PC, editor. Lea's chemistry of cement and concrete. London: Arnold; 1998. p. 1–23.
[2] Taylor HFW. Cement chemistry. London: Thomas-Telford; 1997.
[3] Marchand J, Skalny JP, editor. Materials Science of concrete: sulphate attack mechanisms. Westerville: American Ceramic Society, 1999.
[4] Skalny J, Marchand J, Odler I. Sulfate attack on concrete. London: Spon Press; 2002.
[5] Department of Environment, Transport and Regions. The thaumasite form of sulfate attack: risks, diagnosis, remedial works and guidance on new construction. Report of the Thaumasite Expert Group. London: DETR, 1999.
[6] Eglinton M. Resistance of concrete to destructive agents. In: Hewlett PC, editor. Lea's chemistry of cement and concrete. London: Arnold; 1998. p. 299–342.
[7] Mehta PK, Monteiro PJM. Concrete-microstructure, properties, and materials. New York: McGraw-Hill; 1993.
[8] Baronio G, Berra M. Concrete deterioration with the formation of thaumasite – analysis of the causes. II Cemento 1986;83(3):169–84.
[9] Bickley JA. The repair of arctic structures damaged by thaumasite. Cem Concr Comp 1999;21(2):155–8.
[10] Brown PW, Badger S. The distributions of bound sulfates and chlorides in concrete subjected to mixed NaCl, $MgSO_4$, Na_2SO_4 attack. Cem Concr Res 2000;30(10):1535–42.
[11] Eden MA. The laboratory investigation of concrete affected by TSA in the UK. Cem Concr Comp 2003;25(8):847–50.
[12] Erlin B, Stark DC. Identification and occurrence of thaumasite in concrete. Highway Res Rec 1965;113:108–13.
[13] Freyburg E, Berninger AM. Field experiences in concrete deterioration by thaumasite formation, possibilities and problems in thaumasite analysis. In: Proceedings of the first international conference on thaumasite in cementitious materials, Garston, UK, 19–21.6. 2002, paper 35.
[14] Gouda GR, Roy DM, Sarkar A. Thaumasite in deteriorated soil-cements. Cem Concr Res 1975;5(5):519–22.
[15] Harboe EM. Longtime studies and field experiences with sulfate attack. In: George Verbeck symposium on sulfate attack on concrete (ACI Special publication, 77). Detroit: American Concrete Institute; 1982. p. 1–20.
[16] Hurst WD. Experiences in the Winnipeg area with sulphate-resisting cement concrete. In: Swenson EG, editor. Performance of concrete – a symposium in honour of Thorbergur Thorvaldson. Toronto: University of Toronto Press; 1968. p. 125–34.
[17] Kalousek GL, Porter LC, Harboe EM. Past, present, and potential developments of sulphate-resisting concretes. J Test Eval 1976;4(5):347–54.
[18] Lukas W. Betonzerstörung durch SO_3 – Angriff unter Bildung von Thaumasit und Woodfordit. Cem Concr Res 1975;5(5):503–7.
[19] Bellmann F, Röck R, Stark J. Thaumasite damage in a shotcrete tunnel lining. Cem Int 2005;3(5):102–9.
[20] Mather B. Field and laboratory studies of the sulphate resistance of concrete. In: Swenson EG, editor. Performance of concrete – a symposium in honour of Thorbergur Thorvaldson. Toronto: University of Toronto Press; 1968. p. 68–76.
[21] Verbeck GJ. Field and laboratory studies of sulphate resistance of concrete. In: Swenson EG, editor. Performance of concrete – a symposium in honour of Thorbergur Thorvaldson. Toronto: University of Toronto Press; 1968. p. 113–24.
[22] Oberholster RE. Deterioration of mortar, plaster and concrete: South African laboratory and field case studies. In: Proceedings of the first international conference on thaumasite in cementitious materials, Garston, UK, 19–21.6. 2002, paper 42.
[23] Romer M, Holzer L, Pfiffner M. Swiss tunnel structures: concrete damage by formation of thaumasite. In: Proceedings of the first international conference on thaumasite in cementitious materials, Garston, UK, 19.-21.6. 2002, paper 39.
[24] Stark D. Longtime study of concrete durability in sulfate soils. In: George Verbeck symposium on sulfate attack on concrete (ACI Special publication, 77). Detroit: American Concrete Institute; 1982. p. 21–40.
[25] Crammond NJ, Collett GW, Longworth TI. Thaumasite field trial at Shipston on Stour: 3-year preliminary assessment of buried concretes. Cem Concr Comp 2003;25(8):1035–43.
[26] Lea FM. Some studies on the performance of concrete structures in sulphate-bearing environments. In: Swenson EG, editor. Performance of concrete – a symposium in honour of Thorbergur Thorvaldson. Toronto: University of Toronto Press; 1968. p. 56–65.
[27] Czerewko MA, Cripps JC, Reid JM, Duffell CG. Sulfur species in geological materials–sources and quantification. Cem Concr Comp 2003;25(7):657–71.
[28] Diamond S, Lee RJ. Microstructural alterations associated with sulfate attack in permeable concretes. In: Marchand J, Skalny J, editors. Materials science of concrete – special volume: sulfate attack mechanisms. Westerville: American Ceramic Society; 1999. p. 123–73.
[29] Bellmann F, Erfurt W, Stark J. Gefährdungspotential der betonschädigenden Thaumasitbildung. Weimar: Bauhaus Universität Weimar; 2010.
[30] Sarkar SL, Little DN. Microstructural investigation of severe distress in a crushed concrete base. Cem Concr Res 1998;28(3):401–10.
[31] Schlorholtz S, Demirel T. Quick lime–gypsum interactions in stabilized soil bases for concrete highways. Cem Concr Res 1984;14(4):529–32.
[32] Wild S, Kinuthia JM, Jones GI, Higgins DD. Suppression of swelling associated with ettringite formation in lime stabilized sulphate bearing clay soils by partial substitution of lime with ground granulated blastfurnace slag (GGBS). Eng Geol 1999;51(4):257–77.
[33] Yong RN, Ouhadi VR. Experimental study on instability of bases on natural and lime/cement-stabilized clayey soils. Appl Clay Sci 2007;35(3/4):238–49.
[34] Leemann A, Loser R. Analysis of concrete in a vertical ventilation shaft exposed to sulfate-containing groundwater for 45 years. Cem Concr Comp 2011;33(1):74–83.