Microstructural Changes in Self-Compacting Concrete by Sulphuric Acid Attack

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Abstract
Five different Self-Compacting Concrete (SCC) compositions, composed of three different types of mineral additions (limestone powder, quartz powder and fly ash) and two types of cement (CEM I 52.5 R HES and CEM III/A 42.5 N LA), were exposed to a continuous immersion in a H_2SO_4-solution (pH ~ 1.7) for 26 weeks. Rate of attack was estimated by means of mass variation versus time. Microstructural degradation was investigated using polarising light microscope and scanning electron microscope. SCC containing CEM I and limestone powder gives better resistance to sulphuric acid attack compared to the traditionally vibrated concrete (TC) and SCC compositions with fly ash and quartz powder due to the buffering effect of calcium carbonate ($CaCO_3$) under acidic conditions. The extent of damage is greater in SCC incorporating CEM I-fly ash, CEM I-quartz powder and CEM III/A-limestone powder despite the presence of $CaCO_3$ in the latter. With the inward movement of the acid attack from the surface, two distinct zones are observed. The outmost attacked zone indicates severe erosion due to decalcification of hydrated phases under low pH and contains gypsum crystals formed extensively in the form of small or large inclusions. This is followed by a transition zone acting as the border which separates the attack zone from the relatively sound part of the concrete. Gypsum has been found to be the only reaction product formed independently of the type of mineral addition, type of cement and water-to-cement ratio. Despite densification of the pore structure of SCC by incorporating fly ash and quartz powder to achieve lower permeability for sulphate ions, low resistance to acid attack has been established. This is due to the negative consequences of pore densification creating less space to accommodate stresses induced by the growth of relatively large gypsum crystals. The fact that SCC with CEM I and limestone powder having higher porosity indicates better performance under sulphuric acid conditions, points to a combined role of pore structure and chemical effect of the mineral addition on the ultimate resistance of SCC to sulphuric acid attack. Contrary to the general statement that durability of concrete is improved with reduced permeability, this aspect can induce negative consequences under sulphuric acid conditions.

Originality
Incorporation of high contents of mineral additions in SCC reduces the porosity of concrete resulting in a refinement of the pore structure. Generally it can be stated that a denser pore structure reduces the permeability of concrete increasing its durability. Despite these positive aspects, pore structure refinement in SCC with fly ash and SCC with quartz powder results in low resistance to sulphuric acid attack while SCC with limestone powder with a higher porosity shows a better performance. Physical (pore structure of concrete) and chemical effects (chemical composition of mineral addition) seem to play a combined role in the ultimate behaviour of SCC under sulphuric acid conditions.

Chief contributions
Many scientific papers deal with durability issues of SCC induced by external sulphate attack but the essential knowledge on the durability of SCC to sulphuric acid attack is generally ignored and few researches are available. The introduction of SCC urges new questions related to the behaviour of powder-rich concrete mixtures in sulphuric acid environments. This paper provides results of a dedicated research on the influence of SCC compositions, being the type of mineral addition, type of cement and powder fraction, on the resistance of SCC to sulphuric acid attack. Microstructural investigations combined with mass variations, analytical methods and porosity will provide additional insights on the degradation of SCC under sulphuric acid environments and will contribute to a better understanding of the implications involved in design and construction of durable concrete structures.

Keywords: *self-compacting concrete, sulphuric acid attack, mass variation, microstructure, porosity*

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Introduction

Self-compacting concrete (SCC) is a special type of concrete that readily flows and consolidates under its own weight due to its mix design incorporating high-range water-reducing admixtures and viscosity modifying agents or relatively high volume fractions of powders (cement and mineral additions such as limestone powder, fly ash, silica fume, etc.). As the incorporation of a high powder content modifies its microstructure, pore size distribution and permeability, eventually the ultimate durability properties of powder type SCC will be different from that of traditionally vibrated concrete (TC).

One of the crucial durability issues that threatens the life cycle performance of concrete structures is the sulphuric acid attack leading to severe degradation. Sulphuric acid as a chief component in groundwater, wastewaters, sewage systems, backfills, microbiological actions etc. can severely concrete elements such as foundations, floors, basement walls and sewage pipe systems. The effect of sulphuric acid attack is more detrimental than that of external sulphate attack by sulphate salts due to two important aspects: the reaction with sulphate ions and the dissolution effect caused by hydrogen ions at low pH. Sulphuric acid first reacts with portlandite in the concrete matrix, resulting in the formation of gypsum that causes cracking and spalling of surface layers due to the volume expansion (up to a factor of 2). In a second step, gypsum may further react with calcium aluminate leading to the formation of ettringite which has higher volume (up to a factor of 7) than that of gypsum, thus resulting in more micro- and macro-cracking. At low pH levels (≤ 11.5-12) ettringite is not stable and decomposes to form gypsum. Under severe acidic conditions the hydrated cementitious matrix is decomposed with the decalcification of the calcium silicate hydrates (C-S-H). This eventually leads to the disintegration of concrete and strength loss.

Although the use of SCC is growing in numerous concrete applications in many countries such as in Belgium, the fundamental knowledge on its performance to sulphuric acid attack is very limited in the literature (Monteny *et al.*, 2000, Monteny *et al.*, 2003, Bassuoni and Nehdi, 2007, Dinakar *et al.*, 2008, Girardi *et al.*, 2010). Studies were mostly concentrated on external sulphate attack rather than sulphuric acid attack (Trägårdh and Bellmann, 2007). Compared to TC, SCC has a higher volume fraction of powder (cement and mineral addition) acting as the paste volume with cementitious properties. This makes SCC more vulnerable to deterioration in an acid sulphate environment because the prevailing low pH conditions lead to direct attack on the hydrated phases, specifically C-S-H. Thaumasite formation (reaction between C-S-H, carbonates and sulphates) in the presence of limestone is less pronounced under acidic conditions while it is promoted under alkaline conditions containing sulphate salts (Zhou *et al.*, 2006). Even though concretes with low permeability show better sulphate resistance, the performance of SCC with a denser microstructure (due to lower water-to-powder ratio and mineral addition) under sulphuric acid conditions is not straightforward. It may significantly depend on the type of mineral addition used but the role of mineral addition incorporated in SCC under acidic conditions is ambiguous. It is well established that SCC with limestone powder shows better resistance to sulphuric acid attack (Bassuoni and Nehdi, 2007). However, the performance of SCC incorporating pozzolanic materials such as fly ash or silica fume under sulphuric acid attack is contradictory. Therefore, in-depth research is needed on the durability aspects of SCC containing different types of mineral addition under aggressive sulphuric acid environments for a better understanding of the implications involved in design and construction of durable structures.

In this study, the resistance of various SCC mixtures to sulphuric acid attack is investigated. The main variables are the type of mineral addition, the type of cement and water-to-powder ratio. An effort is made to understand the degradation mechanism from mass variations and microstructural investigations, and to explore the possible relationships in-between.

The SCC mixtures studied in this paper are based on the powder type SCC, using high powder content with readily available materials in Belgium. Ground limestone powder is the most commonly used mineral addition in Belgian precast (and on-site) SCC production. In addition, fly ash and quartz powder which are also used as mineral addition for the SCC production in Europe, are studied. In this way, SCC mixtures with different compositional and microstructural properties are obtained to investigate their durability performance under sulphuric acid attack.

Experimental program

1. Materials and concrete compositions

In total, six different concrete compositions were studied: five SCC and one traditionally vibrated concrete (TC). The compositions of the concrete mixtures are given in Table 1. The SCC mixtures were prepared using CEM I 52.5 R HES (High Early Strength OPC) and limestone powder (SCC-lst), quartz powder (SCC-qz) or fly ash (SCC-fa) at the same mass fractions. One SCC mixture (SCC-lst-c) was prepared using a different type of cement, CEM III/A 42.5 N LA (Slag Cement). The same water-to-cement (W/C) and cement-to-powder (C/P) ratios were considered. These two parameters were altered for the last SCC mixture (SCC-lst-p) by replacing part of the cement (CEM I) by limestone powder, resulted in higher W/C and lower C/P. The gravel and the sand used are natural siliceous materials. To improve the flowability of the SCC mixtures at constant W/C and W/P, a polycarboxylate-ether based high-range water-reducing admixture was used.

Table 1: Composition of the concrete mixtures.

Materials (kg/m³)	**TC**	**SCC-lst**	**SCC-qtz**	**SCC-fa**	**SCC-lst-c**	**SCC-lst-p**
Gravel 4/14	1225	698	698	698	698	698
Sand 0/5	640	853	853	853	853	853
CEM I 52.5 R HES	360	360	360	360	-	300
CEM III/A 42.5 N LA	-	-	-	-	360	-
Limestone powder	-	240	-	-	240	300
Quartz powder	-	-	240	-	-	-
Fly ash	-	-	-	240	-	-
Water	165	165	165	165	165	165
Superplasticizer	-	4.50	5.00	6.75	3.50	3.75
W/C (water/cement)	0.46	0.46	0.46	0.46	0.46	0.55
C/P (cement/powder)	1	0.6	0.6	0.6	0.6	0.5
W/P (water/powder)	0.46	0.28	0.28	0.28	0.28	0.28

2. Sulphuric acid attack

An accelerated test procedure was used to assess the compositional and microstructural parameters of SCC on the resistance to sulphuric acid environment. At the age of 28 days, cores (∅ = 80 mm, h = 80 mm) were drilled from each cast concrete specimens and were immersed continuously in a sulphuric acid solution (1.5 g H_2SO_4 per litre water) at a constant pH of ~1.7 and at temperature 20°C up to 26 weeks. During the first 6 weeks of immersion, the mass variation of the specimens was determined every week, followed by mass measurements every two weeks. In this way, rate of attack was estimated by means of mass variation versus time.

3. Analytical techniques and microstructural investigations

Thermogravimetric analysis (TGA) and X-ray diffraction (XRD) analysis were used to identify the nature of the hydrated phases in the SCC mixtures. In order to determine the reaction product formed after acid attack, the damaged part at the outer zone of the concrete specimens was scraped out and characterized by XRD. TGA was carried out using a Netzsch STA 409 PC DSC-TGA system in static N_2 atmosphere (at 20-1000°C; heating rate 10°C/min). XRD was performed using a Philips Analytical X-ray diffractometer (CuKα radiation; 5-60 º2θ measuring range; 0.02 º2θ/s; 1.25 s/step).
To perform microstructural investigations, polished thin sections were prepared after double impregnation with epoxy resin containing yellow fluorescent dye. Petrographic examinations were carried out using polarizing light microscopy and fluorescence light microscopy. Microstructural investigations were further performed using a scanning electron microscope (SEM, FEG XL30) on carbon-coated thin sections. Additionally, the pore structure and the porosity of the concrete specimens before exposure to acid attack were identified using mercury intrusion porosimetry (MIP).

Results and discussion

Results of MIP on unexposed concrete specimens are given in Figure 1. When compared to TC, all SCC mixtures containing high powder amounts show reduction in the volume of capillary pores (0.1-100 μm), eventually leading to a reduction in the total porosity up to 17%. A shift from capillary pores towards gel pores (< 0.1 μm) is observed except for SCC-lst-c. Replacement of limestone powder by the same mass fraction of quartz powder or fly ash has resulted in higher volumes of the latter two due to their lower specific gravity. As a result, a denser microstructure is formed in SCC with quartz powder (SCC-qtz) and in SCC with fly ash (SCC-fa) when compared to that of SCC with limestone powder (SCC-lst). In addition, pozzolanic reaction taking place between fly ash and portlandite, forming secondary hydration products, plays a role in the densification in the pore structure of SCC-fa.

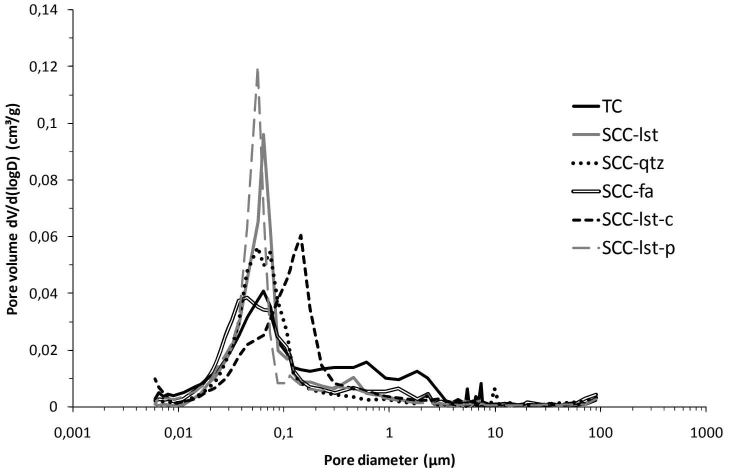


Figure 1: Pore volume of the unexposed concrete specimens.

Figure 2 shows the mass variation of the concrete specimens with time during acid attack. The initial mass gain is due to the formation of the reaction products. This is followed by mass loss induced by the damaging effect of sulphuric acid on the hydrated cement matrix leading to decalcification of C-S-H. We would expect that the physical effect of densification of the pore structure by mineral additions would improve the resistance of SCC to sulphuric acid attack because reduced pore size decreases the diffusion of the sulphate ions into the concrete. However, destructive effect of sulphuric acid leading to decalcification of C-S-H plays a major role here. Only SCC-lst shows the lowest mass variation at a lower degradation rate referring to a higher resistance despite the presence of portlandite. This is because limestone powder has the chemical role of neutralizing the acid in the matrix, and creating a buffer zone leading to a slower rate of degradation (Bassuoni and Nehdi, 2007).

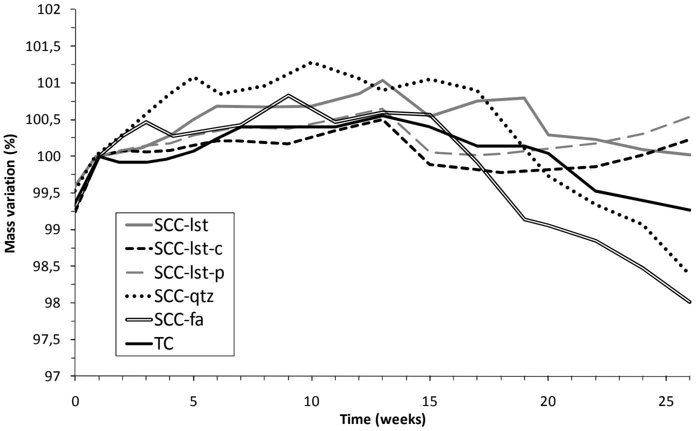


Figure 2: Mass variation in SCC mixtures and TC during continuous immersion in sulphuric acid solution.

XRD analyses of the damaged zone reveal the presence of only gypsum formed after sulphuric acid attack (Figure 3). Ettringite was not detected due to low pH. Quartz powder and fly ash were partially leached out from the damaged zone while the depletion of limestone powder is much more severe. Traces of gypsum and ettringite are not established in the core of the specimens, characterized typically by C-S-H, AFm and portlandite in XRD and TGA.

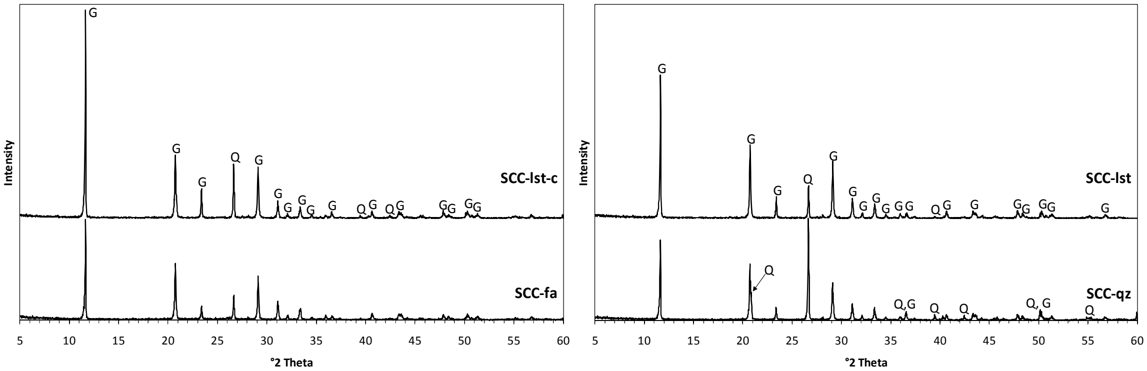
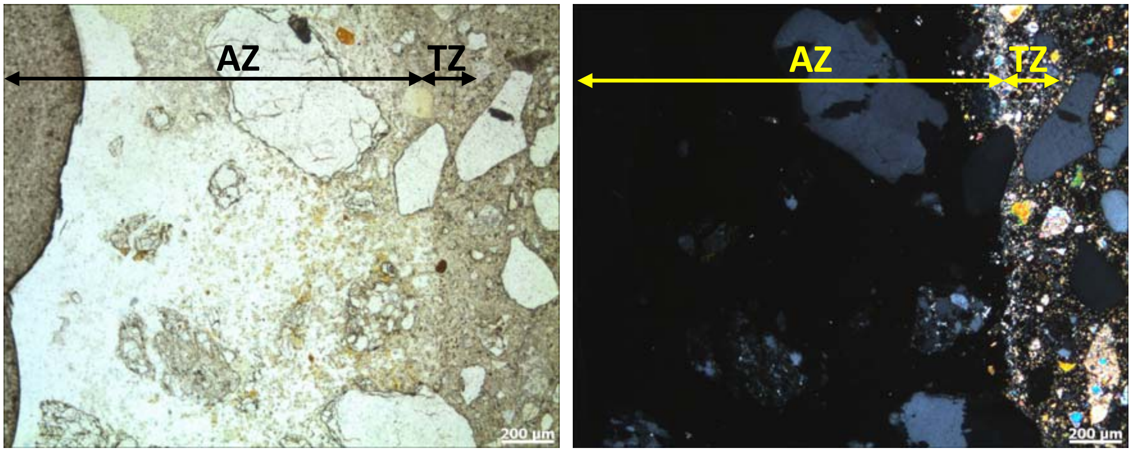
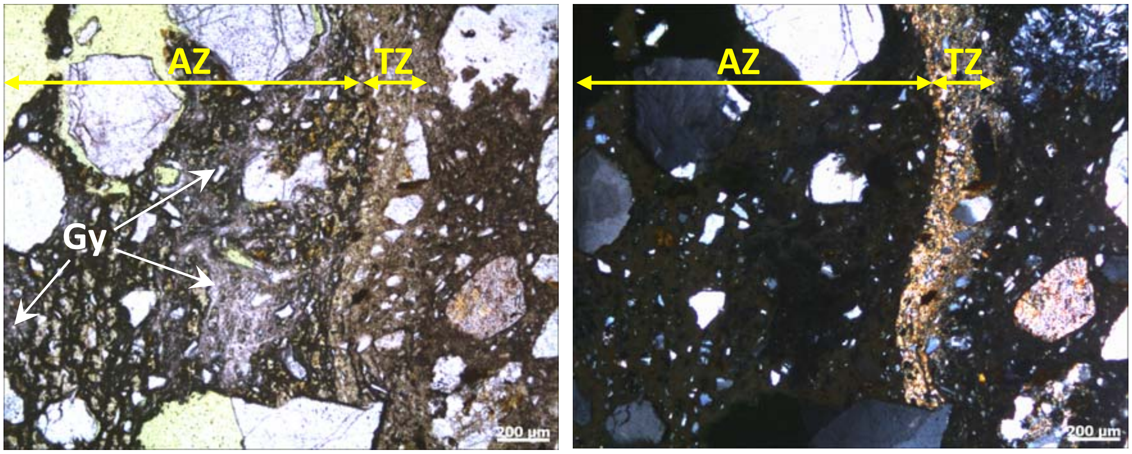


Figure 3: XRD patterns of the attacked zone of the SCC specimens (G: gypsum; Q: quartz).

Microscopic investigations indicate that the sulphuric acid attack has induced severe erosion at the outer edge of the SCC specimens at a depth being typically in the order of a millimetre (Figure 4). The core of the specimens is relatively sound despite the presence of portlandite because of the reduced pore size making the diffusion of the sulphate ions into the concrete more difficult. With the inward movement of the reaction from the surface, two distinct zones are observed. There exists an outermost zone, i.e. attacked zone, containing gypsum crystals dominantly in the form of small or large inclusions (Figure 4). Large gypsum crystals were preferentially formed around the aggregates due to the higher porosity of the interfacial transition zone (ITZ) (Figure 5). Beyond ITZ gypsum crystals are present in the form of veins running along the matrix in the attacked zone. The chemical reactions in this zone were accompanied by the detachment of aggregates, formation of microcracks at the surrounding matrix of gypsum crystals, and leaching of portlandite and limestone particles. Fly ash and quartz particles are still observed in this attacked zone of SCC-fa and SCC-qtz respectively (Figure 5). There exists a second zone beyond the attacked zone, which is the transition zone between the attacked zone and the unattacked zone looking relatively sound except for microcracks (Figures 4-5). However, under polarized microscopy and SEM we have observed partial depletion of portlandite and limestone powder, and the presence of microcracks in this unattacked zone. The transition zone is characterized by a dense skin of calcium carbonate with a thickness of 10-30 µm, acting as the border in-between the attacked and unattacked zones. The formation of calcium carbonate is possibly due to carbonation of depleted portlandite during weight measurements.



SCC-lst



SCC-qtz

Figure 4: Polarizing light microscopic images of SCC-lst and SCC-qtz with parallel polarising (left) and crossed polarising (right) show the extent of damage induced by chemical attack of sulphuric acid (AZ: attacked zone; TZ: transition zone; Gy: gypsum)

SCC with quartz powder (SCC-qtz) and fly ash (SCC-fa) with a very dense pore structure show the greatest mass variation at a higher degradation rate (Figure 2). These two concrete compositions also indicate gypsum formation to a large extent. Since the formation of gypsum requires the presence of free portlandite, the addition of fly ash would lower its amount by pozzolanic reaction. TGA analysis has shown that only 2.2% portlandite was present in SCC-fa before exposure to sulphuric acid solution but gypsum was extensively formed. These results indicate that fixation of portlandite and densification of the pore structure seem to be ineffective to prevent the degradation mechanism. The densification of the pore structure by adding fly ash and quartz powder creates a negative effect to accommodate expansive reaction product of gypsum because finer pores provide less space for crystal growth leading to higher internal stresses and eventual microcracks to be further filled with gypsum. We have also observed microcracks in the unattacked zone of SCC-fa up to 2 mm beyond the transition zone while the depth of microcracks in SCC-lst is less than 0.5 mm (Figure 5). Similarly, concrete with silica fume having a dense pore structure has been reported to exhibit low resistance to sulphuric acid attack due to the densification of the pore structure (Monteny *et al.*, 2003).

SCC-lst-c (CEM III/A) and SCC-lst-p (CEM I, C/P = 0.5) suffer from larger extent of acid attack, resulting in greater damage of the matrix and the detachment of the aggregates. These two SCC mixtures have also indicated a different trend in the mass variation with a second attack-phase after 15 weeks, resulting in a second mass gain with further formation of gypsum. This is attributed to the lower cement content in SCC-lst-p and the type of cement in SCC-lst-c. Blast-furnace slag cements with a minimum slag content of 66 wt% (CEM III/B) show good sulphate resistance (Trägårdh and Bellmann, 2007, Monteny *et al.*, 2003). However, CEM III/A incorporated in SCC-lst-c has a slag content lower than that value, making this concrete mixture more vulnerable to sulphuric acid attack.

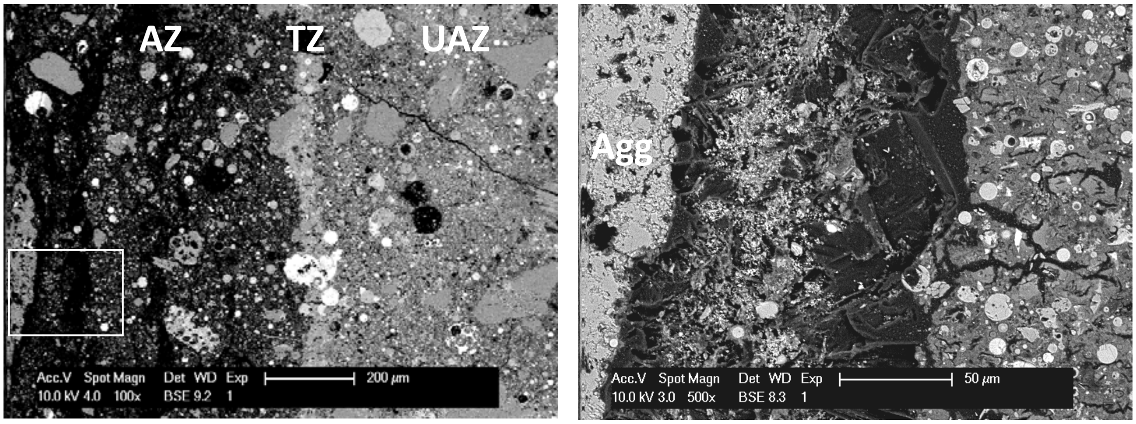


Figure 5: SEM micrographs showing a dense transition zone (TZ) between attacked zone (AZ) and unattacked zone (UAZ) (left image), and gypsum crystals surrounding an aggregate (Agg) at the ITZ (right image as highlighted within a square in the left image) in SCC-fa.

Conclusions

SCC with CEM I and limestone powder has indicated a rather good resistance to sulphuric acid attack due to the buffering effect of $CaCO_3$. Damage is more pronounced in SCC incorporating fly ash, quartz powder or CEM III/A. Independent from the type of mineral addition and type of cement, gypsum is the only product formed after sulphuric acid attack. Despite densification of the pore structure of SCC by fly ash and quartz powder to achieve lower permeability, low resistance to acid attack has been established. This is due to the negative consequences of pore densification creating less space to accommodate stresses induced by the growth of large gypsum crystals.

References

- Bassuoni, M.T., Nehdi, M.L., 2007. Resistance of self-consolidating concrete to sulfuric acid attack with consecutive pH reduction. *Cement and Concrete Research*, 37 (7), 1070-1084.
- Dinakar, P., Babu, K.G., Santhanam, M., 2008. Durability properties of high volume fly ash self compacting concretes. *Cement and Concrete Composites*, 30 (10), 880-886.
- Girardi, F., Vaona, W., Di Maggio, R., 2010. Resistance of different types of concretes to cyclic sulfuric acid and sodium sulfate attack. *Cement and Concrete Composites*, 32 (8), 595-602.
- Monteny, J., Vincke, E., Beeldens, A., De Belie, N., Taerwe, L., Van Gemert, D., Verstraete W., 2000. Chemical, microbiological, and in situ test methods for biogenic sulfuric acid corrosion of concrete. *Cement and Concrete Research*, 30 (4), 623-634.
- Monteny, J., De Belie, N., Taerwe, L., 2003. Resistance of different types of concrete mixtures to sulfuric acid. *Materials and Structures* 36 (258), 242-249.
- Trägårdh, J., Bellmann, F., 2007. Sulphate attack. In Durability of Self-Compacting Concrete, State-of-the-art report of RILEM Technical Committee 205-DSC, RILEM Report 38, RILEM Publications S.A.R.L., 89-118.
- Zhou, Q., Hill, J., Byars, E.A., Cripps, J.C., Lynsdale, C.J., Sharp, J.H., 2006. The role of pH in thaumasite sulfate attack. *Cement and Concrete Research*, 36 (1), 160-170.