DIFFUSION OF CHLORIDES IN CRACKED STRAIN-HARDENING CEMENT-BASED COMPOSITES (SHCC)

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Abstract
Strain-hardening cement-based composites (SHCC) are high-performance fiber-reinforced composites with promising durability properties due to their considerably enhanced crack control under tensile load conditions. The knowledge of the transport properties of such composites in cracked state are crucial for estimating their durability characteristics. In the project at hand, chloride diffusion tests were performed and their results were related to crack widths and crack distances in SHCC specimens under investigation. SHCC specimens were first subjected to uniaxial tension under deformation-controlled loading regime in order to achieve formation of multiple cracks. Optical investigations provided a basis for evaluating the crack pattern. Eventually the cracked specimens were exposed to chloride solutions. Qualitative and quantitative chloride evaluations were conducted and discussed with particular respect to the recorded crack pattern. The results obtained within the project for chloride diffusion in cracked and crack-free areas enlarge the basis for assessing durability characteristics of SHCC and for further developing existing durability concepts and approaches.
Keywords: crack distribution, chloride diffusion, SHCC, durability

1. INTRODUCTION
Strain-hardening cement-based composite (SHCC) was developed at the beginning of the 1990s by Victor C. Li [1] under the name of ECC (Engineered cementitious composites). Both terms refer to the same material. Due to its strain-hardening tensile behaviour, SHCC was originally used as a repair material applied in thin layers to cover cracked members of reinforced concrete. Such layer impedes the penetration by harmful substances through narrow cracks typical for SHCC and herewith ensures a more resistant and durable member. SHCC has been continuously used in rehabilitation of reinforced concrete structures or as a replacement for concrete in reinforced concrete members [2] [3]. Therefore, the performance of SHCC with respect to the protection of reinforcement plays a crucial role in the research on this material [3] [4]. The characteristic stress-strain diagram of SHCC in

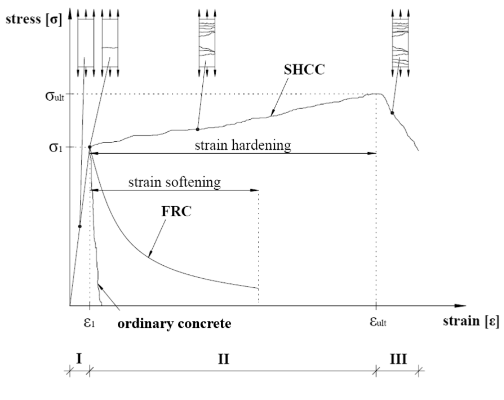


Figure 1: Typical stress-strain behaviour and crack pattern of SHCC under uniaxial tensile loading.

comparison to conventional fibre-reinforced concrete (FRC) and ordinary concrete are shown in Fig. 1

To investigate the durability behavior properly a broad range of tests for the various environmental factors must be performed. Due to the promising tensile strain characteristics SHCC is very suitable to be used together with steel reinforcement as presented by Fisher et al. [5], the durability investigations need to consider not only the deterioration of SHCC as such but also the corrosion protection of the steel reinforcement. A reinforced SHCC member is subjected to a variety of aggressive environmental factors. Damage processes are thereby often initiated by a pollutant which is carried into the component by liquids, especially water. Such ingress is accelerated by cracks and increases with growing crack widths. Since a long time crack width regulating proofs are used for this reason in standards for the serviceability design. Since SHCC has significantly lower crack widths as ordinary concrete, it is considered a promising material with respect to durability [6]. Water is mostly acting as a carrier for harmful pollutants, e.g. in connection with chlorides and sulfates, it is reasonable to perform permeability tests on cracked construction components. In the project at hand, a series of experiments were performed to enlarge the data base for the durability related properties of SHCC. The main focus was on the behaviour of SHCC with respect to liquid-based, durability-influencing transport mechanisms. Special attention was directed to the crack width effect on the transport of chlorides. While a variety of transport processes may occur usually in combinations (cf. Fig. 2), this paper focusses on the diffusion-based process only. To separate this process from other ones, a complete water saturation of the specimens under investigation must be attained before starting actual diffusion tests. The experiments were based on a broad experience collected at the Institute of Construction Materials of the TU Dresden [7] [8] [9] [10].The data base developed will be the basis in further research to assess the crack-related material behaviour and to verify the durability concept for SHCC presented by Altmann [11] [9].

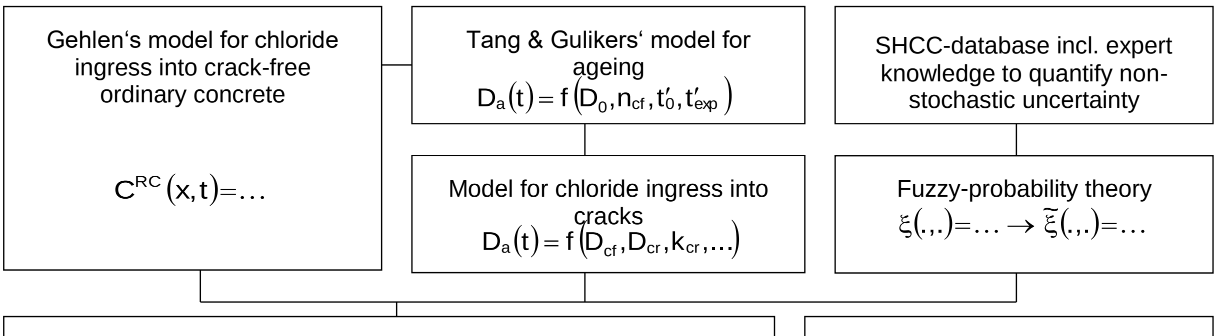


Figure 2: Schematic model for chloride ingress according to Altmann [9]

2. EXPERIMENTAL PROGRAMM

To evaluate effect of the crack width on the chloride diffusion in SHCC a series of experiments were designed and performed. The experiments were based on a mechanical preloading to generate multiple crack patterns. For this purpose, dumbbell shaped specimens were produced and subjected to monotonic, uniaxial tensile loading after 28 days to achieve the SHCC typical cracking pattern. Subsequently, the specimens were cut, coated and subjected to concentrated different saline solutions with various exposure times. To ensure a good comparability between the results of this project with former findings, in particular those from Altmann [9], the recommendations derived from his work served as basis for the experimental setup and evaluation procedure.

2.1 Materials and specimen preparation

The SHCC mixture under investigation was developed at the Institute of Construction Materials, TU Dresden and yielded already promising results in earlier studies. The mixture composition is given in Table 1. It has a fibre content of 2.0% by volume, the fibres are made of polyvinyl alcohol (PVA) and have a length of 12 mm and a diameter of 40 µm. The mixing was performed following the procedure described by Jun [12].

Table 1: Composition of SHCC under investigation [13]

Cement	CEM I 42,5 R-HS	505	kg/m³
Coal fly ash	Powerment HKV / Kreament alt	621	kg/m³
Water	H_2O	398	kg/m³
Aggregate	Sand 0,06-0,2	536	kg/m³
Add1	FM GlenAce 30	10	kg/m³
Add2	UW-Comp	3	kg/m³
Fibre	PVA	26	kg/m³

2.2 Uniaxial tensile loading

After taking the specimens out of the water tank, they were wrapped in foil at the mid-section. Both dumbbell shaped ends were briefly dried and subsequently glued in the universal testing machine Instron by means of a two-component adhesive, see also Fig. 3.

All 15 specimens were subjected to the uniaxial tension at the age of 28 to 30 days. The loading was performed under deformation-controlled low-cyclic tension regime with a loading speed of 0.01 mm/s and 0.25 mm increase in deformation per cycle, which corresponds to a strain increase by 0.1% per cycle, cf. Fig. 4. The deformations were measured by two inductive displacement transducers fixed to the respective opposite sides of the specimen. The final state of damage was determined by 1% residual strain after unloading. After tensile loading, each specimen was cut in two bars with the dimensions of 250 mm x 48 mm x 60 mm.

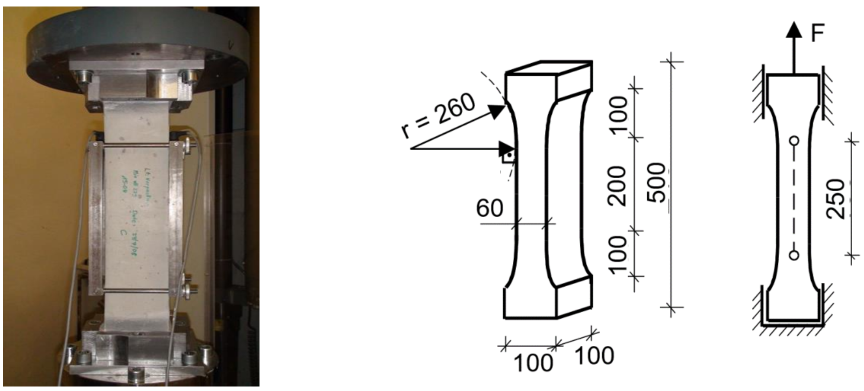


Figure 3: Uniaxial tensile loading: (a) test setup and (b) geometry of the specimen

2.3 Crack evaluation and quantification

The crack pattern of each specimen was recorded directly after the cutting works using a high resolution scanner (3600 dpi). This resolution enables pictures with a pixel size of 7.06 µm by 7.06 µm. On this bases, cracks could be theoretically observed starting by a crack width of 14.1 µm. The crack widths and crack distances were evaluated using image editing software and counted specifically along one central axis, according to the recommendations of JSCE (Japan Society of Civil Engineering) [14] (Fig. 5).

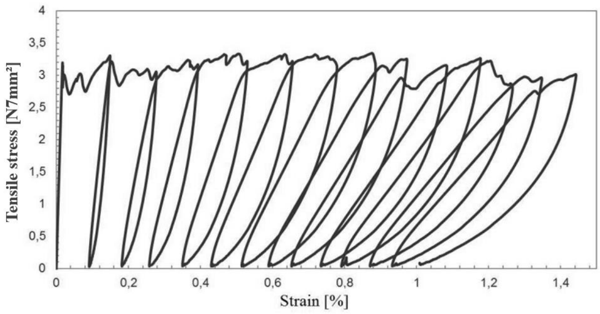
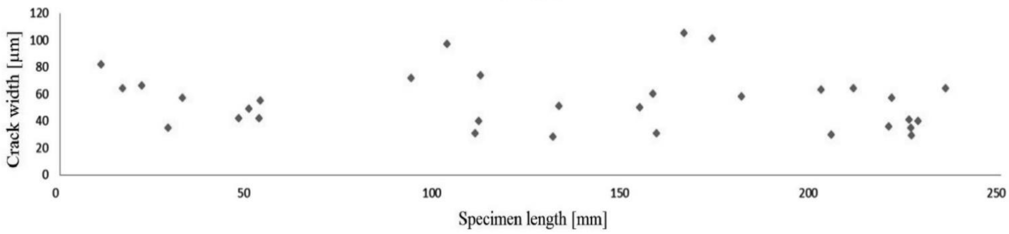


Figure 4: Stress-strain curve of deformation-controlled low-cyclic tensile loading of the specimens

(a)



(b)

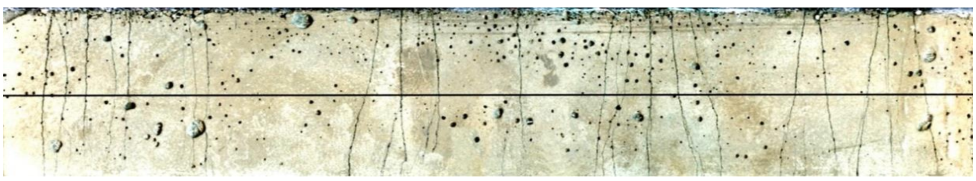


Figure 5: (a) Crack width distribution along the length of a specimen after tensile loading and (b) corresponding specimen with line at which crack measurements were performed

(a) b)

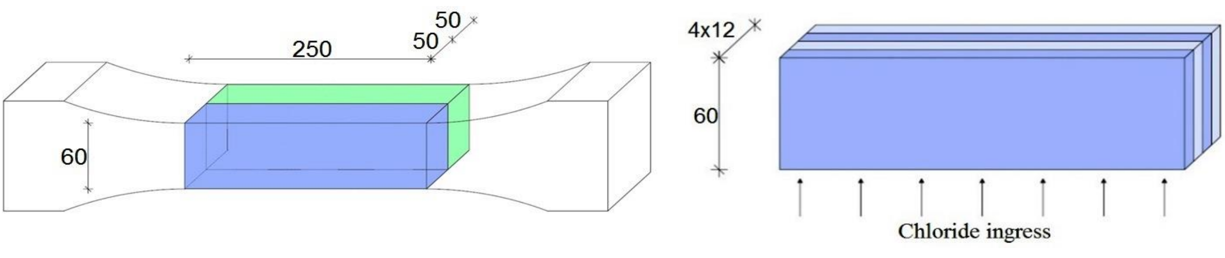


Figure 6: Specimen with cutting regime before chloride penetration

2.4 Chloride diffusion test

Different concentrated sodium chloride solutions were produced. One solution was prepared according to NT BUILD 443 with a sodium chloride concentration of 165g/l. The second solution with a concentration of 30g/l [15] [9]. Both sodium chloride solutions were stored at 20°C and fully sealed to minimize evaporation effects. The cracked and non-cracked specimens were subjected to the different chloride solutions and different exposure from 3 to 7 days as shown in Fig. 7. Complete water saturation was ensured by an aluminum butyl coating which prevented specimen from evaporation.

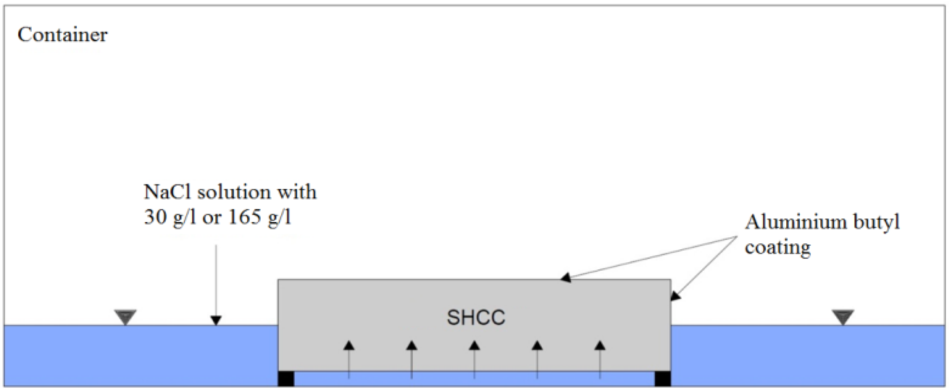
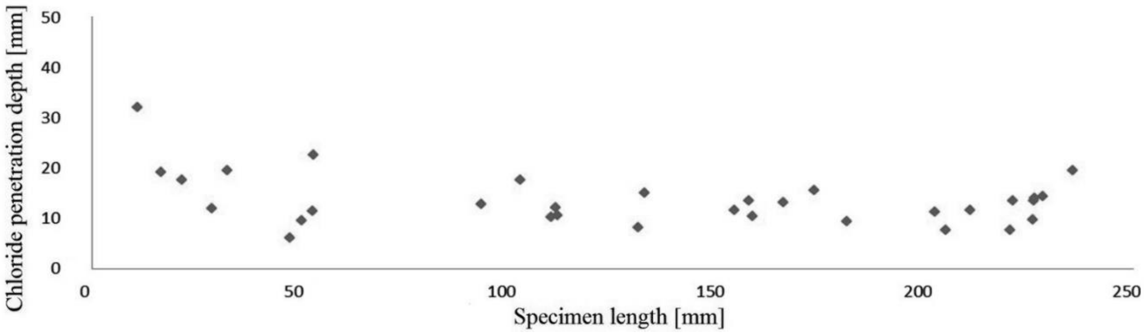


Figure 7: Test setup for chloride ingress experiments



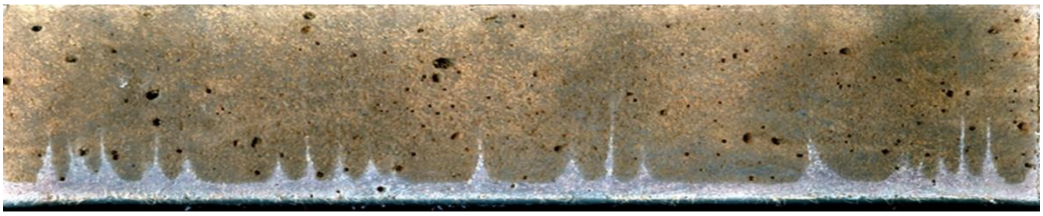


Figure 8: (a) Chloride penetration depths and (b) appearance of chloride ingress on a slice surface upon spaying AgNO3 solution

2.5 Silver nitrate test

After removing the samples from sodium solution the silver nitrate test was conducted, in which a 0.1 M $AgNO_3$ solution was used [15]. Silver nitrate reacts on a freshly fractured surface with unbound chlorides to silver chloride which can be seen on the surface due to its silver-gray reaction product. The visual analysis of the colour change enables qualitative evaluation of chloride ingress in cement based materials, cf. Fig. 8b. Due to high fibre content of SHCC and subsequently it high ductility, it was not possible to split SHCC specimens to produce fresh fracture surfaces, the way it is usually done for concrete or mortar. Instead, all specimens were cut, which led to four slices of approximately 10 mm thickness (cf. Fig. 6). Subsequently, silver nitrate solution was sprayed on each surface. Half an hour later silver nitrate was sprayed for the second time. After drying each surface was scanned and the chloride penetration depth measured as shown in Fig. 8 and afterwards related to the crack width.

2.6 Quantitative chloride determination

While the silver nitrate test only provides qualitative statements for chloride ingress, the quantitative analysis of chloride concentration was performed following the recommendations described in NT BUILD 443 by abrade thin layers of each specimen. For chloride concentration investigation the crack-free specimens which were subjected to 28 days exposure in sodium solution were used exclusively. A minimum of 6 layers of each specimen were abraded to define the particular chloride concentration for this layer. The thickness of each abraded layer was 1 mm to 2 mm. In order to conduct the chemical analysis for the test material, the powdered material was given in 18% diluted nitric acid (HNO3). The filtrate was afterwards investigated by using a photometer which provided the exact chlorid concentration per layer.

3. EXPERIMENTAL RESULTS

3.1 Crack evaluation

Crack width distributions were evaluated combining all specimens investigated and grouped by their widths, while for each group a range of 0.01 mm was set. Fig. 9 shows the empirical density function for crack widths. This probability density function shows a similarity to a lognormal distribution as described by Wang et al. [17]. However, a precise statistical description of this function was not scope of this project.

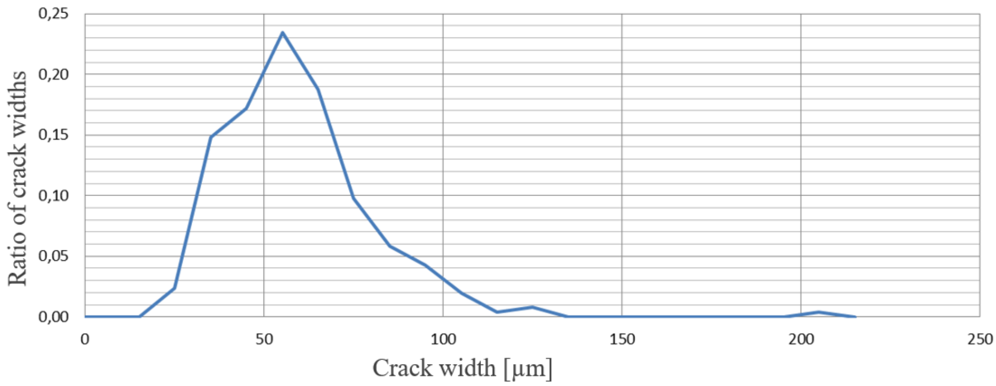


Figure 9: Empirical density function of crack widths

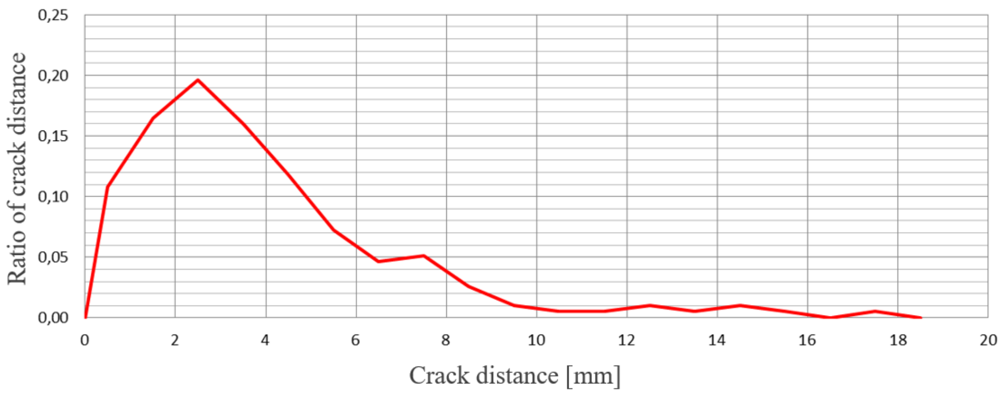


Figure 10: Empirical density function of crack proximity

Evaluating the crack distances turned out to be more challenging due to the fact that they are only relevant and harmful with respect to durability in situations of mutual crack influence of two neighboring cracks. For this reason a general statement regarding specific distances relevant from the durability perspective would be to uncertain. Within the framework of this project the evaluation of crack distances was conducted after the chloride tests. The measurements were performed for all specimens but only the distances which appeared to clearly accelerate the chloride transport were taken into consideration.

3.2 Qualitative chloride evaluation

After analysing the chloride penetration depth every crack was related to certain amount of chloride penetrated into SHCC. None accelerated chloride ingress could be observed in non-cracked areas. Based on this founding, the authors assume that for crack widths below 25 µm no acceleration of chloride diffusion occurs measurable by the applied techniques. The chloride penetration increases with increasing crack width and chloride concentration gradient. The conducted silver nitrate tests however only enable finding free, unbound chlorides in SHCC and give no indication on physically and chemically bounded chlorides. This must be considered when evaluating the mechanisms compromising durability. In particular so, knowing that chloride binding is a reversible process and that already bounded chlorides can easily be released again with increasing solution concentration or as a result of another chemical deterioration process. As mentioned before also the crack distances plays a significant role on the chloride penetration depths. Thus, Fig. 12 relates chloride penetration to specific crack distances. As expected the chloride ingress increases with growing crack width and decreases with growing crack distance.

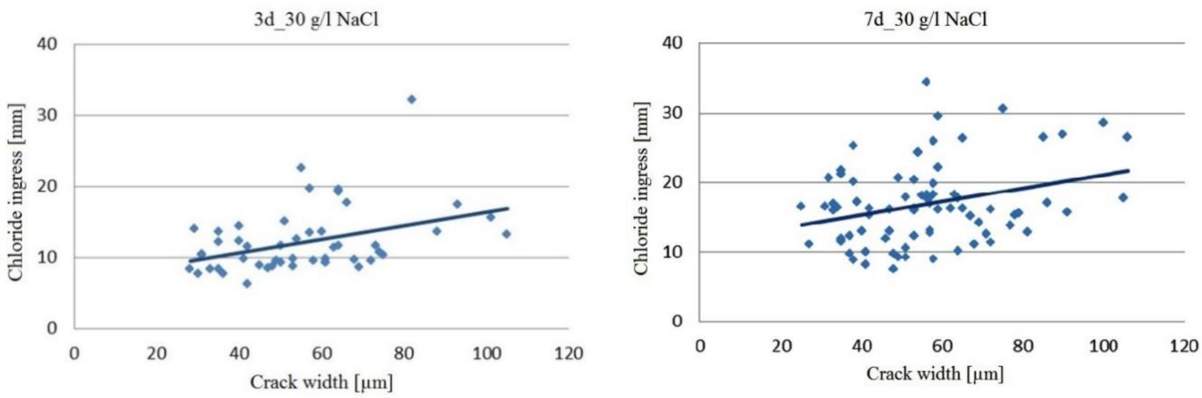


Figure 11: Evaluation of chloride ingress in relation to crack widths for different exposure times and concentration of NaCl solution: 3d with 30g/l NaCl (left) and 7d with 30g/l (right)

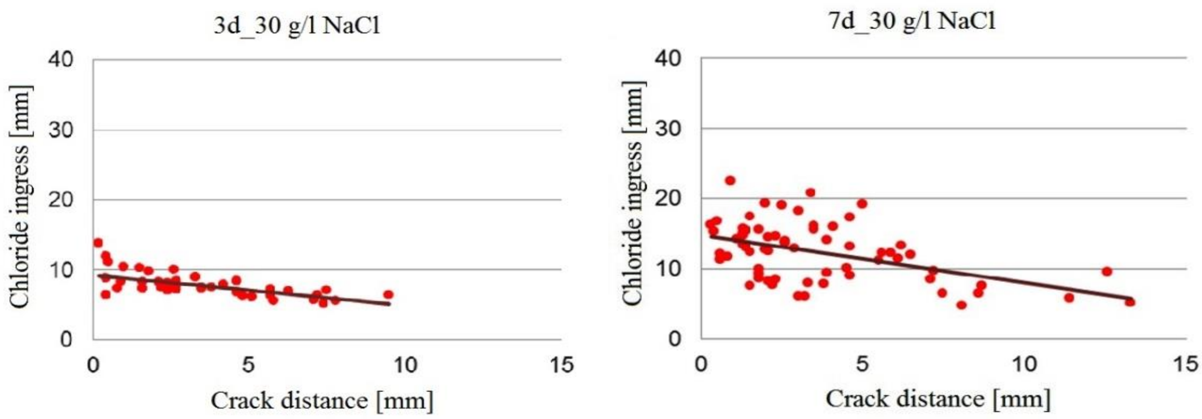


Figure 12 : Evaluation of chloride ingress in relation to crack proximity for different exposure times and concentration of NaCl solution: (a) 3 d and 30 g/l NaCl, (b) 7 d and 30 g/l NaCl, (c) 3d and 165 g/l NaCl

3.3 Quantitative chloride evaluation

The quantitative chloride evaluation was performed on un-cracked specimens. It must be kept in mind that the quantitative chloride evaluation considers bound and unbound chlorides, while the qualitative one captures the unbound chlorides only. The quantitative analysis provided various chloride profiles over penetration depth, see Fig. 13. The results obtained from the photometer tests gave the chloride concentration per mass of SHCC.

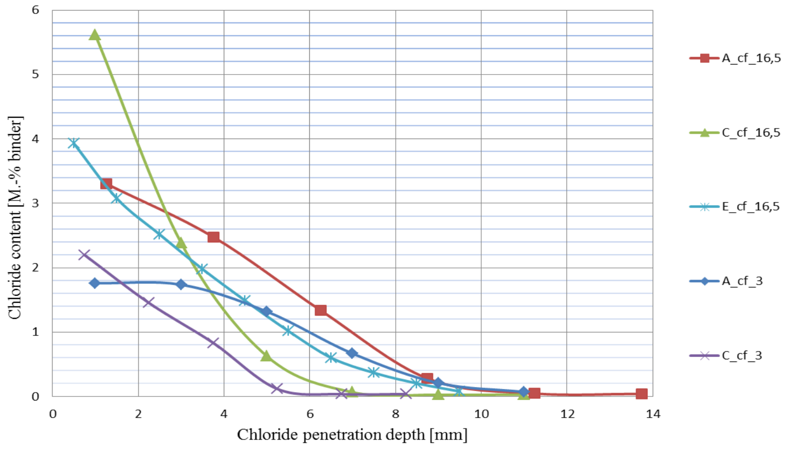


Figure 13: Chloride profiles, chloride content is given in mass % of binder

4. SUMMARY AND CONCLUSIONS

Chloride diffusion tests were performed no non-cracked and cracked specimens made of SHCC. First, crack width distributions were assessed showing that the most crack widths were in the range between 50 µm and 60 µm, while 96% of all cracks evaluated had widths below 100 µm. The smallest crack distance recorded was 200 µm, the most crack distances in multiple crack patterns amounted between 2 mm and 3 mm. In the investigation at hand, 95% of all crack distances leading to noticeable acceleration of chloride diffusion were under 10 mm. Based on the qualitative chloride profiles as observed in the silver nitrate test, it could assured that beside diffusion no noticeable other transport processes took place. It was found that the specimen dimension chosen for the experimental investigations were suitable for chloride exposures upto 14 days. Chloride diffusion tests on cracked material have shown to be an order of magnitude faster process compared to chloride diffusion in crack-free regions.

The qualitative tests yielded to no accelerated chloride diffusion in crack-free regions. Thus, it can be assumed that crack widths below 25 µm do not course any acceleration of diffusion. Referring also to similar findings by Djerbi et al. [18] a certain lower limit of crack width can be suggested to be set at 25 µm postulating that more narrow cracks do not contribute significantly to the higher ingress of chlorides by diffusion processes. It should be however underlined that the silver nitrate test only considers free, unbound chlorides. The quantitative tests, however, consider both bound and unbound chlorides [16]. This must be taken into account when relating a certain chloride concentration to the moment of colour changing in the silver nitrate test. Within the framework of this project specific magnitudes of chloride binding capacity, surface chloride concentration and diffusion coefficient were calculated. Based on this data further investigations can be conducted to verify particular durability concepts [19]. The described experimental approach provides suitable procedure to achieve information on durability indicators and to lower uncertainties that come along with handling new materials.

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