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An evaluation of the sulfate resistance of cementitious material accelerated with alkali-free and alkaline admixtures

Laboratory vs. field

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Abstract

A comparison between conventional length change measurements (cement paste, mortar and shotcrete) and ion chromatographic, pH and conductivity measurements (cement paste suspensions) is made in order to find out a relationship between the sulfate resistance of laboratory and field prepared specimens. A correlation between the linear expansion of shotcrete specimens and both the total amount of adsorbed sulfates [ion chromatography (IC) measurements] and the $SO_4^{2-} \Longleftrightarrow OH^-$ exchange (pH and conductivity measurements) within the cement binders is found. Furthermore, a good correlation between the long-term expansion of shotcrete and the short-term expansion of cement paste specimens is observed. On the other hand, no correlation exists between the linear expansion of shotcrete and laboratory mortar specimens. This suggests that the laboratory investigation of the more reactive cementitious material with respect to sulfate ions might be taken as a trustworthy and reproducible evaluation of the sulfate resistance of shotcrete in the field. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The need for laboratory tests providing reproducible and trustworthy information on the sulfate resistance of concrete structures in the field is a matter of considerable concern. The rapid change of materials and working parameters in the field generally require accelerated performance sulfate tests as an on-time response to the changing conditions.

Increasing the sulfate concentration was one of the common methods to accelerate the sulfate resistance tests. However, the change in the attack mechanisms, which might occur under laboratory conditions, does not allow the use of this method to predict the behavior of concrete in the field [1,2]. Other methods such as increasing the reaction surface, raising the temperature, increasing the crystal pressure (wetting–drying cycles) and method combinations were also used [1,3]. The addition of gypsum was also considered, although this accelerating method was not suitable for blended cements [2]. Another method consisted of holding a constant pH of a solution by repeatedly adding acid, although the attacking mechanism appeared to be limited to the gypsum action [4]. High W/C ratios were also used [5,6], but more reproducible results were obtained by low W/C ratios [5].

However, the measurements of the expansion for determining the length change of cementitious material exposed to sulfate solution [2] appears to be the most common method used to predict or evaluate the sulfate resistance. In this case, the expansion is mainly supported by the confined crystal growth of the high voluminous ettringite [7], resulting in expansive pressure [8,9]. Nevertheless, because of the different reaction mechanisms involved, a direct relationship between ettringite amount and expansion has not yet been verified [10–13]. The reaction mechanisms involved apparently depend on the Al_2O_3 content of the cement [12,14] and on the type of the attacking sulfate solution. For structural applications, compressive and flexural strengths were also

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measured. Nevertheless, under particular conditions, the hydrates formed during the attack may fill the pores resulting in an unexpected strength increase [15].

Generally, it appears difficult to provide reliable correlations of the sulfate resistance of field shotcrete on site using laboratory mortars. It also appears that the use of neat cement paste cannot be used as a representative model to extrapolate concrete behavior because of the different effects of the transition zone [16–18]. However, the extension of the transition zone is limited. Moreover, the addition of additives in mortars and concrete, for instance silica fume, indicated the absence of a transition zone, resulting in no microstructural differences compared to the bulk paste [16]. In this latter case, for instance, the use of cement paste to explain the concrete behavior was possible. The use of admixtures such as accelerators strongly influence the bulk chemistry of the cement paste and its susceptibility with respect to sulfate solutions can play a decisive role on the durability of field shotcrete.

2. Experimental

2.1. Binders

An ordinary Portland cement (OPC) "Untervaz" from the Bündner Cement Industry, Untervaz, Switzerland was used. Its chemical and phase composition is indicated in Table 1.

2.2. Admixtures

The admixtures were prepared in the laboratories of SIKA AG, Zurich, Switzerland and consisted of a plasticizer Sikatard 902 based on a sodium carboxylate polysulfonate aqueous solution and accelerating admixtures. The alkali-free accelerators consisted of powdery calcium sulfoaluminate with the addition of powdery $Al_2(SO_4)_3 \cdot 14\ H_2O$ as main components (CSA-SA) and a $Al_2(SO_4)_3 \cdot 14\ H_2O$-based viscous solution (SA). The alkaline accelerator (AR) was composed of a $KAl(OH)_4$ aqueous solution.

Table 1
Chemical and phase composition of the OPC "Untervaz"

Cement I Untervaz chemical composition		Cement I Untervaz phase composition	
CaO	61.7	C_3S	42.8
SiO_2	20.6	C_2S	22.9
Al_2O_3	4.9	C_3A	9.1
Fe_2O_3	2.28	C_4AF	6.9
SO_3	2.70	Free CaO	0.72
MgO	1.90	$CaSO_4$	4.58
Na_2O	0.23	$CaCO_3$	6.65
K_2O	1.15	MgO	1.90
TiO_2	0.24	CA	–
P_2O_5	0.22	C_2AS	–
Mn_2O_3	0.04	$C_{12}A_7$	–
SrO	0.09	CT	–
LOI	4.04	C_4A_3S	–

Table 2
Accelerating admixtures and dosages

Admixture	Dosage (%)
Laboratory (mortar and cement paste)	
Alkali-free accelerator (CSA-SA)	6
Alkali-free accelerator (SA)	8
AR	4.5
Shotcrete	
Alkali-free accelerator (CSA-SA)	6.10
Alkali-free accelerator (SA) A	5.20
Alkali-free accelerator (SA) B	6
AR	6.30

All the dosages are referred to the cement weight. The dosages for the shotcrete are indicative because of the difficulty in maintaining a constant level of concentration during the application.

2.3. Mixing procedure

2.3.1. Laboratory

Cement pastes and mortars were prepared. Aggregates (< 8 mm) were mixed with the OPC Untervaz dry for 1 min. The cement content was 425 kg/m^3. Thereafter, water previously mixed with 1% plasticizer was added and the blends further mixed for 3 min. The accelerating admixtures were then added as depicted in Table 2 and the mixing procedure was stopped after 45 s. In order to simulate similar homogenization conditions as in the field, the CSA-based accelerator was added to the cement. The plasticizer was mixed with water and added to the cementitious powder.

The W/C ratio was held at 0.46, and the water content of the liquid accelerators was considered into the calculations of the total water amount. The mixing water temperature was held at 21 ± 1 °C and the laboratory conditions at 21 ± 1 °C and 65 ± 3% relative humidity.

2.3.2. Field

The W/C ratio for the shotcrete ranged from 0.47 (CSA/SA; AR), 0.48 (SSA-A) to 0.49 (SSA-B) and the aggregate size ranged between 0 and 16 mm. Wet mixing procedure was used.

All the investigated specimens were immersed in deionized water and in 5% Na_2SO_4 solution at 23 °C. The notation "S" before the sample's annotation indicates the difference between sulfate- and water-cured specimens.

2.4. Investigations

2.4.1. Length change

Mortars with sand size < 8 mm and cement pastes were cast in polystyrene 120 × 120 × 120-mm forms. After demoulding (1 day) and storage for 56 days in deionized water at 23 ± 1 °C, each cube was bored to obtain cylindrical specimens with 100-mm length and 50-mm diameter and bolts were glued at the edges. The measurements were performed weekly up to 28 days, then afterwards every 2 weeks up to 6 months (ASTM C 1012-95). The linear expansions was calculated from the difference between sulfate- and water-cured specimens. The shotcrete was sprayed into wood boxes and cylindrical specimens (100 × 50 mm) were bored. Bolts were glued at the edges and measurements were performed up to 546 days.

2.4.2. Ion chromatography (IC)

Cylindrical cement paste specimens prepared as described for the length change measurements were covered with an epoxy resin, cut along the longitudinal side and exposed to the solutions. After 91 days, disks (20-mm thickness) were sawed and the exposed surface was pulverised down to 5 mm (steps of 1 mm each). Suspensions of 0.50-g powder, 40-ml deionized water and 10-ml HCl (0.5 M) were prepared. The filtered solutions were measured with a Metrohm Ion Chromatograph. The working conditions were set at 2000 μl/min at 20 °C and at a pressure of 79 bar. The eluent consisted of a solution of 2-mM phtalic acid/10% acetone/pH 5.0 (NaOH). The dilution was 1:100 and the standard calibration solution had a concentration of 200 μM (SO_4^{2-}). The quantitative method used was a Custom IC-metrodata for windows Metrohm. The total bound sulfates resulted from the differences between the sulfate- and water-cured specimens.

2.4.3. pH

Suspensions (IC measurements) without HCl were measured with an Orion 960 Autochemistry system.

2.4.4. Conductivity

Suspensions (pH measurements) were measured with an auto range CDM 83 conductivity meter.

3. Results and discussion

3.1. Linear expansion and microstructure

The length change of both the shotcrete and the cement paste indicate a correlation with an increased extent of the expansion for the samples accelerated with the CSA-based alkali-free accelerator (Fig. 1, S-CSA/SA) followed by the specimens accelerated with the alkaline (Fig. 1, S-AR) and the sulfate-based alkali-free admixture (Fig. 1, S-SA). A slow expansion followed by onset of rapid expansion is found in particular for the sulfate-based alkali-free accelerated samples. This initial dormant period was also observed in alite paste specimens immersed in 5% Na_2SO4 solutions [22,23]. Nevertheless, the sulfate and aluminate content of the investigated cement paste and accelerator promote the formation of both ettringite and gypsum and shifts the onset of rapid expansion at early stages.

A strong correlation exists between the expansion of cement paste specimens, damage and sulfate susceptibility. In fact, the CSA accelerated specimens show a rapid expansion and a high sulfate penetration down to 5 mm of the exposed profiles (Fig. 4, S-CSA/SA). This results in the almost complete softening and disintegration of the samples. The alkaline accelerated samples indicate a slightly delayed expansion and a main sulfate penetration within the first 2 mm of the profiles (Fig. 4, S-AR), which correlate with cracking and spalling of the surface layer. The samples where the sulfate-based additive was added expand remarkably only after ca. 60 days and show a sulfate penetration within the first 2 mm but to a general lower extent (Fig. 4, S-SA), which correlate with a very slight disruption and cracking. The unaccelerated samples does not show any remarkable damage during the entire investigation period up to 6 months and this correlates with almost no expansion and low sulfate penetration

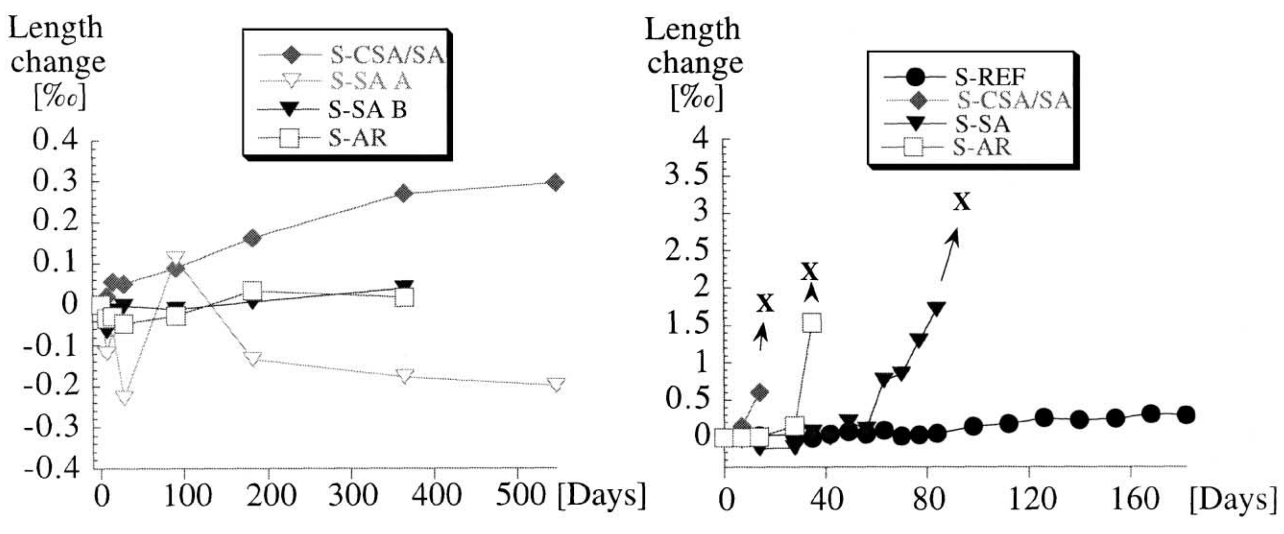

Fig. 1. Shotcrete (left) and cement paste (right) length change over time.

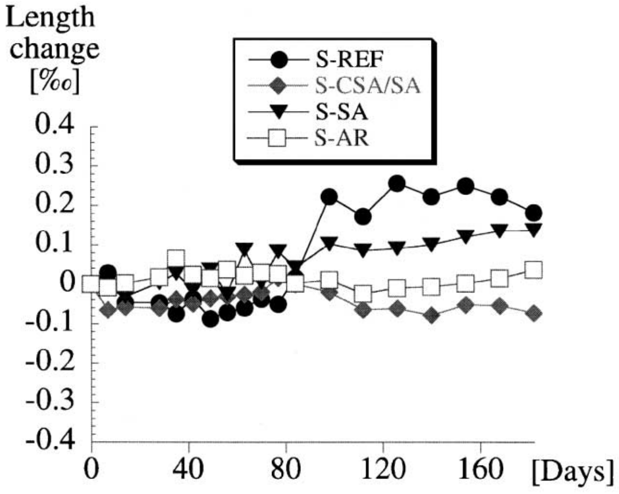

Fig. 2. Mortar length change over time.

values (Fig. 4, S-REF). On the other hand, due to the slow general expansion values of the shotcrete specimens (< 0.5‰), no damage could be observed.

Generally, a poor correlation exists between the linear expansion of the mortar (Fig. 2) and the shotcrete specimens (Fig. 1).

This fact is presumably attributable to the different arrangements of the aggregates and the different mixing procedure. The laboratory mixing procedure appears to strongly influence the microstructural features of the mortars, which in turn exhibit different expansion behavior compared to the shotcrete. It must also be said that the fast setting obtained with the addition of the accelerators does not always allow a proper workability of the mortars, which trap air during the casting. The high porosity may then reduce the expansion as long as ettringite is precipitated within the pores but may cause a sudden increase in the expansion when the pores are filled. In this context, the unaccelerated good workable mortar typically show this effect (Fig. 2, S-REF). Furthermore, measurements of the compressive strength of samples cured in sulfate solutions were reported to indicate unexpected strength increase due to the filling of the pores with hydrates [15].

It is also clear that cement paste and shotcrete do not indicate generally the same microstructural features (Fig. 3).

The inhomogeneous dissolution of the alkali-free accelerator for instance causes enrichment of this admixture within the microstructure. When these admixture-enriched zones come in contact with water or sulfate-rich water at later stages, they react forming high voluminous ettringite and expand. Due to the high compaction attained during the

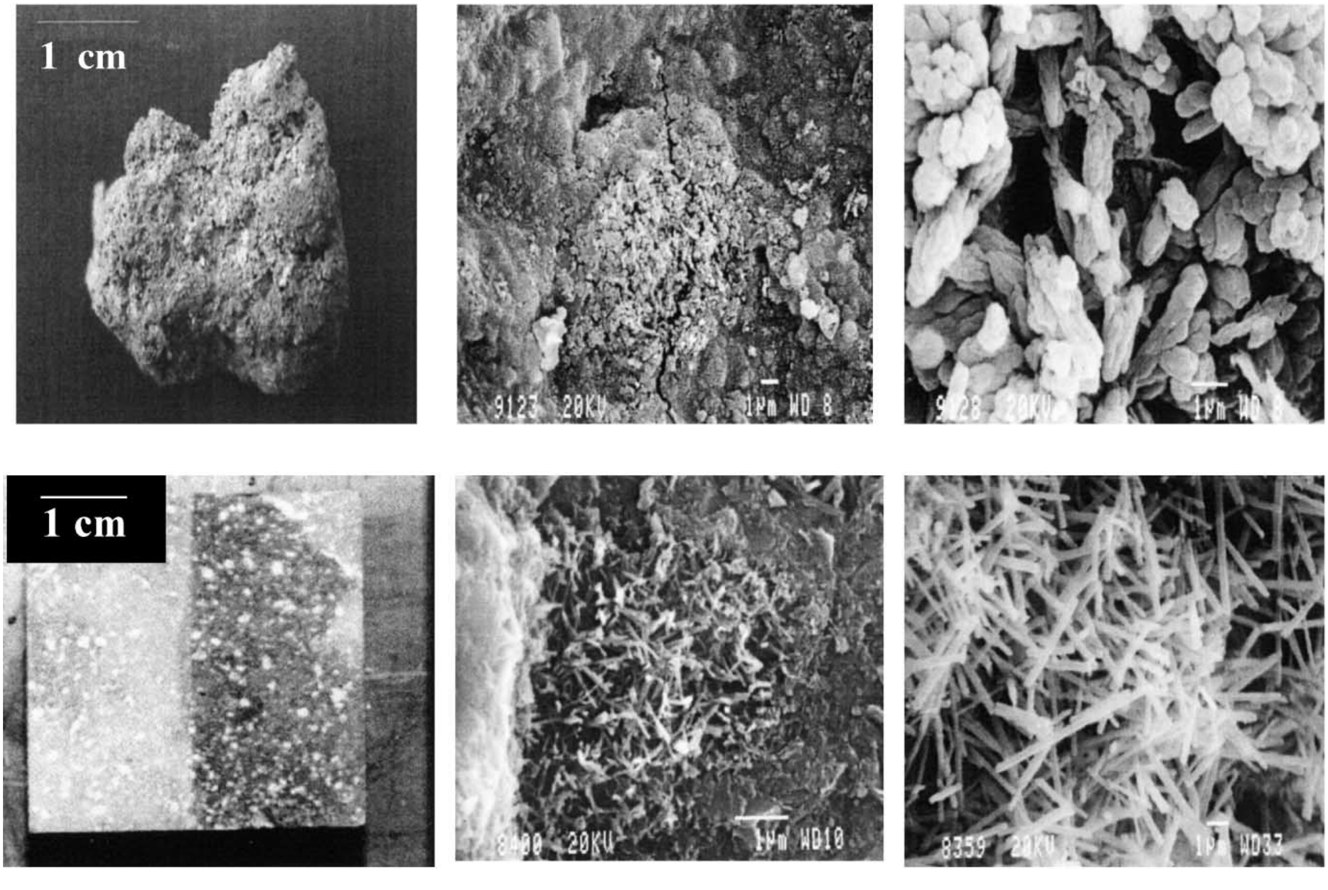

Fig. 3. Microstructural features of shotcrete (above) and cement paste (below) accelerated with the alkali-free accelerator (> 1 month).

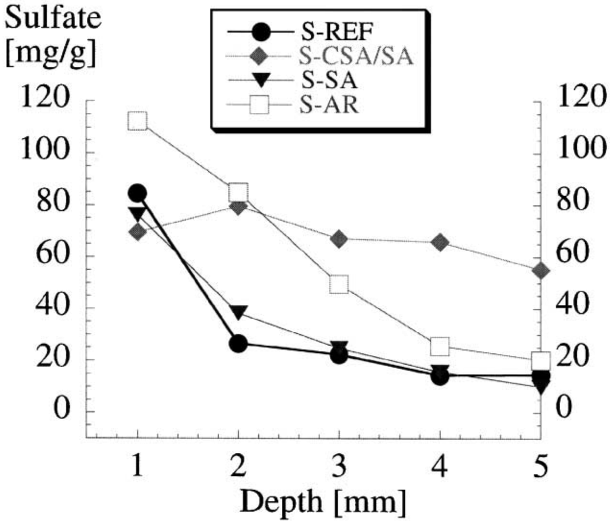

Fig. 4. Sulfate adsorption up to 91 days.

spraying of the shotcrete onto the tunnel walls, the expansion caused the formation of cracks within the microstructure (Fig. 3, above). The lower compaction of the microstructure for the laboratory cement paste, on the contrary, does not allow the formation of cracks (Fig. 3, below). It must also be noticed that the laboratory cement paste show well-crystallized ettringite compared to the one present within shotcrete where a stronger compaction of the microstructure attained during the shotcreting process hinders the crystallization of the ettringite.

Thus, the different mixing procedures and microstructure, such as for instance compaction, aggregate arrangements and cement–paste aggregate interface between laboratory and field samples, do not allow a direct comparison of the sulfate resistance based on similarity of the microstructure. Despite the lack of a relationship between laboratory mortars and shotcrete and the different microstructural features of the latter compared to the cement paste, a correlation is found between the linear expansion of shotcrete and cement paste. This suggests that the investigation of the binder sulfate susceptibility may represent a trustworthy possibility for a reproducible evaluation of the sulfate resistance on the field.

3.2. Evaluation of the binder susceptibility

Despite the diversity in the accelerators homogenization between shotcrete and laboratory cement paste, a general correlation exists between the long-term linear expansion of the shotcrete specimens and the short-term sulfate adsorption of the cement samples. In fact, the addition of the CSA-based alkali-free admixture corresponds to a higher sulfate adsorption along the entire profile (Fig. 4, S-CSA/SA) and to a simultaneous increase in the linear expansion for the shotcrete sample (Fig. 1, S-CSA/SA shotcrete). Conversely, the addition of the alkaline admixture shows a reduced expansion (Fig. 1, S-AR). In this latter case, the main sulfate adsorption takes place only within the first 2 mm of the profile (Fig. 4, S-AR). From 3-mm depth, the sulfate adsorption within the alkaline and the alkali-free admixture almost coincide (Fig. 4, S-AR; S-SA). This fact well correlates with the similar expansion behavior of the respective shotcrete specimens (Fig. 1, SSA-B, S-AR).

Similar features are also observed for the measurements of the $SO_4^{2-} \Longleftrightarrow OH^-$ exchange. The more homogeneous distribution of the alkali-free CSA-based admixture within the cement paste promotes the $SO_4^{2-} \Longleftrightarrow OH^-$

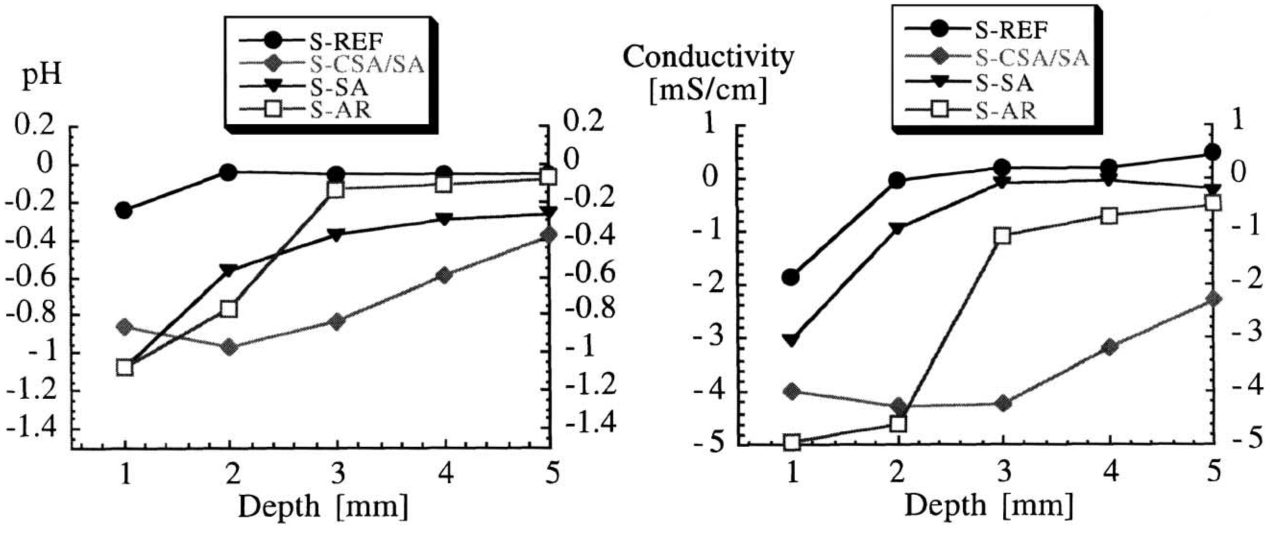

Fig. 5. pH and conductivity up to 91 days.

exchange (Fig. 5, S-CSA/SA). This is related to the prominent linear expansion of the shotcrete samples (Fig. 1, S-CSA/SA). In fact, the increased ion exchange and the subsequent higher sulfate adsorption imply increased reactions with the cementitious phases and increased deleterious physical consequences.

Consequently, the investigation of the reactivity of the cementitious material with respect to sulfate ions appears to give a good qualitative prediction of the sulfate resistance on site. In spite of the general relationship between the W/C and the porosity concerning the sulfate resistance [13,19], the qualitative measurements performed on cement samples show the aluminate and sulfate content and their distribution to be far more important than the structural features regarding the extent of the sulfate attack. The large influence on the rate of sulfate attack caused by the concentration of the solution and the composition of the cement was also described [20]. Hughes [21] also reported that not only the permeability but also the access to susceptible minerals play a decisive role in the sulfate resistance. Despite the fact that the aluminate and sulfate content of the accelerators might increase the rate of the internal sulfate attack, the general faster reactivity of the accelerated cement pastes (< 2–3 months) with respect to sulfate solutions might be used for a short-time qualitative prediction of the durability of shotcrete on site over the years. The measurements of the sulfate susceptibility of the binder give trustworthy reproducible information about the destroying potential. These measurements are independent of the casual structural interactions and arrangements, which may arise with the addition of aggregates. Thus, low permeability shotcrete containing high sulfate susceptible binder appears to be a general negative premise for the sulfate resistance in spite of the low penetration capacity of the sulfate ions. Thus, it appears that a trustworthy correlation of the sulfate resistance between laboratory and field samples is obtained based on the binder–accelerators cement paste chemistry and its susceptibility with respect to sulfate ions rather than on the microstructural features attained.

4. Conclusions

The qualitative investigations (IC, pH and conductivity) of the binder sulfate susceptibility well correlate with the conventional length change measurements of shotcrete specimens.

The measurements of the sulfate susceptibility of the cement paste appears to allow a trustworthy qualitative reproducible prediction of the sulfate resistance of field shotcrete, regardless of the structural interactions and arrangements, which might be caused by the presence of aggregates and different casting procedures. In this case, the laboratory mortars and shotcrete length changes did not correlate.

The fast susceptibility of the accelerated cement paste with respect to sulfates observed with the IC, pH and conductivity tests (< 2–3 months) and the correlation with the shotcrete long-term linear expansion measurements might be used as a “short-time” qualitative prediction for the sulfate resistance of shotcrete over the years.

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