

Technical Paper

Sorption and hydraulic performance of cement-bentonite cutoffs in saline sulphatic solutions

Evelina Fratolocchi^{*}, Jonathan Domizi, Mirko Felici, Francesco Mazzieri

Università Politecnica Delle Marche, Ancona, Italy

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Abstract

The paper discusses the results of an experimental research on the short and long term hydraulic performance and sorption of cement-bentonite mixtures in saline sulphate solutions. Batch tests at different curing times and permeation tests were performed on three cement-bentonite mixtures with solutions of K_2SO_4 . The results show that permeation can adversely affect the hydraulic performance of cement-bentonite mixtures depending on the sulphate concentration and mixture composition and that the choice of a very low permeable mixture is essential to limit adverse effects of interaction with SO_4^{2-} on the hydraulic performance.

Sorption of K^+ was found to be significant, well described by a linear isotherm in a wide range of concentration and nearly constant with curing. Sorption of SO_4^{2-} was found to decrease with mixture porosity. Since sorption of SO_4^{2-} means negative interaction, batch tests were found to be useful for a rapid estimation of possible negative effect of SO_4^{2-} on the hydraulic behaviour in the long term, when selecting a mixture in the design phase.

All the results point out the importance of selecting a mixture to be used for cut-off walls with a low hydraulic conductivity already at brief curing and of carefully considering interaction with solute pollutants and sorption capacity.

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1. Introduction

Cement-bentonite cut-off walls are typically used to isolate polluted sites when remediation technologies cannot provide enough reduction of soil and/or groundwater contamination or in the case of waste landfills with improper or failed barriers. To limit the advective flux of contaminants a low hydraulic conductivity, k , is mandatory (typically $k \leq 10^{-9}$ m/s), to be maintained for the lifetime of the wall. Low effective diffusion coefficients are also required to reduce the diffusive flux and sorption capacity is a desirable property to retard pollutant migration pro-

vided that it does not imply a deleterious interaction with the cut-off wall material.

Extensive literature dealt with the hydraulic conductivity of traditional cement-bentonite mixtures (Jefferis, 1981; Manassero et al., 1995; and many others) and with intrinsic factors affecting k (composition, types of cement and bentonite, e.g., Fratolocchi and Pasqualini, 1998; 2007; Opdyke and Evans, 2005; Jefferis, 2012). It is currently well known that cement-bentonite mixtures exhibit a significant reduction of k with time (one or two orders of magnitude) within the first year of curing, due to the cement hydration processes, and that with a proper selection of components and dosages k values lower than 10^{-9} m/s can be reached within a few months of curing.

On the contrary, limited data and research studies are documented in the literature about the chemical compati-

^{*} Corresponding author at: via Brece Bianche 12, 60131 Ancona, Italy.
E-mail address: e.fratolocchi@univpm.it (E. Fratolocchi).

bility, interaction and durability of cement-bentonite mixtures as well as about diffusion and sorption capacity with solute pollutants.

As far as interaction and long term performance of cement-bentonite mixtures are concerned, Jefferis (2003) and Fratolocchi et al. (2005; 2006) describe case histories of composite CB cut-off walls to isolate acidic leachates (pH = 2.8 and pH = 2, respectively) with high concentrations of metals and sulphates (these last ones of the order of g/l). In both cases, a reduction in hydraulic conductivity followed by an increase with time was observed, due to the combined progressive effects of cement hydration, precipitation of gypsum, calcium carbonate and insoluble magnesium salts, dissolution of cement hydrated products and formation of secondary ettringite, resulting in final expansion and cracking. Similar effects in terms of k trends with curing time were observed by Fratolocchi et al. (2013; 2020) on cement-bentonite mixtures permeated with saline sulphatic solutions. In particular, the higher the sulphate concentration, the fastest the increase in k and the shorter the curing time at which the increase of k starts, hydraulic conditions being equal. A correlation was proposed by Fratolocchi et al. (2013; 2019) linking the number of pore volumes of flow at which the increase in k occurs and the sulphate concentration, that can be useful from the practical point of view to estimate a cut-off wall durability on the basis of the expected flow rate through it.

A coupled impact of contaminant exposure and curing time was also demonstrated for saline sulphate solutions by immersion tests on samples of various curing (Soga et al., 2013) and by permeation tests conducted with organic solutions (ethanol) on young and long-cured samples of a cement-bentonite mixture (Manassero et al., 1995; Fratolocchi and Pasqualini, 2007). In particular, the permeation tests performed with almost pure ethanol (able to inhibit the cement hydration) resulted in constant k values with curing, thus demonstrating that the cement hydration processes are responsible for the typical reduction of k with time of cement-bentonite mixtures.

Very few data are available in the literature on migration parameters of solute pollutants through cement-bentonite mixtures. Column tests with low concentrated chloride solutions (Visudmedanukul et al., 2007) and sulphate solutions (Fratolocchi et al., 2013) gave effective diffusion coefficients of those anions of the order of 10^{-10} m²/s. The same range of values of the diffusion coefficient is documented in Fratolocchi et al. (2013; 2020) with reference to potassium. For designing cement-bentonite mixtures cut-off walls, the diffusion coefficient of most solutes is usually assumed in this range, in analogy with saturated clayey soils (Mitchell and Soga, 2005). Referring to sorption capacity, the only research studies specifically devoted to sorption of solute pollutants in cement-bentonite mixtures are those by Fratolocchi et al. (2013; 2020). This research, recently extended and thorough with further investigations, is detailed and discussed in the present paper.

The current lack of data on sorption capacity of cement-bentonite mixtures leads to refer to the literature of cement pastes, which however have cement/water ratios much higher than cement-bentonite mixtures, or to assume no sorption capacity in designing self-hardening cut-off walls. This assumption can be too conservative in case of significant sorption, or it can result in unsafe design when sorption implies interaction mechanisms that can worsen the hydraulic performance in the long term.

The present paper is focused on the short and long term hydraulic performance and the sorption capacity of traditional and special cement-bentonite mixtures permeated or in contact with saline sulphate solutions. Results concerning their hydraulic conductivity trend with curing, both in water and with saline solutions of potassium sulphate, as well as their sorption capacity with the same solutions are illustrated and discussed considering the interaction between the solutes and the solid phases. The type of saline solutions has been chosen because it is known from literature of cementitious materials that sulphates are potentially dangerous and because they can be representative of groundwaters polluted by fertilizers, landfill leachates or of the marine environment. Moreover, both sulphate and potassium are typically used as tracers to promptly detect leachate migration out of waste landfills with compacted clay as the bottom and sidewall barrier because of their high mobility through them (null or negligible sorption). The knowledge of sulphate and potassium mobility and interaction with cement-bentonite mixtures is therefore important when cement-bentonite cut-off walls are used to isolate uncontrolled landfills.

2. Materials and testing methods

2.1. Mixtures and sample preparation

A traditional cement-bentonite (CB) mixture and two special patented cement-bentonite mixtures were investigated. The CB mixture consists of tap water, an activated sodium bentonite (liquid limit = 520%, plasticity index = 430%; cation exchange capacity, CEC = 75 me q/100 g) and a blast furnace slag cement (average diameter of grains, $D_{50} \sim 15$ μ m; Blaine specific surface area ~ 3400 cm²/g; density = 3.13 g/cm³) made by about 30% ordinary Portland cement and 70% of slag. The mixture was prepared with a bentonite/water ratio = 0.045 and cement/water ratio = 0.22. The cement type was selected because it is known to give good performance in terms of hydraulic conductivity of cement-bentonite mixtures in the short and long term (Opdyke and Evans, 2005; Fratolocchi and Pasqualini, 2007) and to confer a good resistance against sulphate attack to the mixtures (provided that its Al₂O₃ content is lower than 15%, as in the cement of concern). The chemical composition of the CB mixture components is given in Table 1.

The two special mixtures, named SA and SB, consist of tap water and a ready-made powder containing blast fur-

Table 1
Chemical composition of the solid components of the investigated mixtures (percentages by weight).

SA and SB				CB	
	cement	slag	bentonite + filler*	slag cement	bentonite
CaO	68.0	45.9	5.8	47.8	2.0
SiO ₂	17.2	32.9	59.6	30.6	58.0
Al ₂ O ₃	3.8	9.7	18.2	7.8	17.1
Fe ₂ O ₃	3.3	0.9	7.0	1.8	5.3
MgO	1.4	6.6	2.8	5.3	5.7
SO ₃	4.2	2.1	0.8	1.5	0.8
TiO ₂	0.3	0.8	0.9	0.4	0.6
K ₂ O	0.9	0.4	1.9	0.5	0.5
Na ₂ O	0.5	0.2	2.2	0.3	4.3

* average composition (different types of filler).

nace slag, Portland cement, activated sodium bentonite and clayey fillers. The types and dosages of the constituents of the ready-made powders to prepare the SA and SB mixtures are the same except for the type of fillers. The Blaine specific surface area of the slag + cement is about 4000 cm²/g. Table 1 shows the chemical composition of the solid components of the SA and SB special mixtures. No other data on the composition and dosages are available since they are patented products. Further information has been derived from the slurry characteristics and from the results of hydraulic conductivity tests.

Both special mixtures were prepared with a solid/water ratio = 0.33. The resulting (cement + slag)/water ratio is in the range of 0.20–0.24 (as stated by the manufacturer).

The CB mixture was prepared in the laboratory by a two-stage process according to the procedures recommended by ETC8, 1993 and ICE et al. (1999). Starting from 3 l of tap water, the bentonite powder was added and thoroughly mixed with a high shear rotary mixer at 1500 rpm for 5 min. The bentonite mud was allowed a minimum of 8 h to hydrate. It was then remixed before and during the cement addition and a further mixing time of 5 min was kept at the same speed.

The special mixtures were prepared in one step by adding the ready-made powder to tap water while mixing, by a special high shear rotary mixer at 5000 rpm for 3 min (procedure set up by the special mixtures' manufacturer).

The main characteristics of all the mixtures at the fluid state were determined immediately after mixing to verify their suitability for practical use. The measures were always performed after each mixing. The unit weight was measured by a mud balance (ASTM D4380-12) whereas the viscosity was indirectly evaluated by the run-out time through the Marsh funnel, according to procedure recommended by API (2009). The bleeding was measured using a 1000 ml graduate glass cylinder with accuracy of 0.5%, after leaving the mixture to stand undisturbed for 24 h from filling.

The mixtures were poured in cylindrical PVC moulds (internal diameter = 7.1 cm or 10.0 cm, height = 11 cm) purposely prepared to avoid sample disturbance during

extraction (Fratolocchi et al., 2013) and submerged in tap water until testing.

At the desired testing time, each sample was extracted from the mould and only the upper portion in contact with water was cut to get a flat horizontal surface. The final thickness of each sample was chosen depending on the purpose of the test (as detailed in § 2.4).

2.2. Testing solutions

The hydraulic conductivity in water was measured using potable tap water, as recommended by ASTM D5884-16a to limit chemical changes in pore water and interactions with the solid phase. The average concentrations of the main ions in the potable tap water were: Ca²⁺ = 86 mg/l, Mg²⁺ = 13 mg/l, Na⁺ = 15 mg/l; K⁺ = 1 mg/l, SO₄²⁻ = 88 mg/l, Cl⁻ = 29 mg/l. The water was slightly alkaline (pH = 7.7–7.8) and its electrical conductivity was in the range of 0.5–0.6 mS/cm.

The hydraulic conductivity tests were also performed with aqueous solutions of K₂SO₄ at different concentrations, prepared by dissolving the anhydrous salt in distilled water (DW) in different proportions. The K₂SO₄ concentrations of the solutions used to permeate the mixtures are shown in Table 2. All the solutions resulted almost neutral (pH in the range of 6.8–7.3, increasing with the concentration of K₂SO₄). The unit weight of each sulphate solution used in the hydraulic conductivity tests was always considered in calculation of the hydraulic heads across the samples.

Potassium sulphate solutions were also used to perform batch tests on samples of the three mixtures. In these tests, for each mixture, the maximum K₂SO₄ concentration was equal to the maximum concentration of the permeation tests, i.e., 30 g/l for the special mixtures and 95 g/l for the CB mixture. The minimum K₂SO₄ concentration was always equal to 1 g/l.

2.3. Sorption tests

The sorption capacity of the mixtures was analysed by batch adsorption tests according to the procedures for fine

Table 2

Water content, w , and dry unit weight, γ_d , measured on the samples for permeation tests and K_2SO_4 concentrations of the permeant solutions (TW = tap water).

mixture	Curing time (days)	Permeant solution	w (%)	γ_d (kN/m ³)
CB	14	TW	305	2.8
	16	K_2SO_4 , C = 5 g/l	296	2.9
	14	K_2SO_4 , C = 27.5 g/l	302	2.9
	16	K_2SO_4 , C = 50 g/l	301	2.8
	14	K_2SO_4 , C = 75 g/l	303	2.8
SA	17	K_2SO_4 , C = 95 g/l	300	2.8
	21	TW	251	3.4
	22	K_2SO_4 , C = 15 g/l	251	3.4
SB	20	K_2SO_4 , C = 30 g/l	253	3.3
	21	TW	251	3.3
	22	K_2SO_4 , C = 15 g/l	252	3.3
	20	K_2SO_4 , C = 30 g/l	254	3.3

grained soils (US EPA, 1992; ASTM D4646-16). This type of test is frequently used, mainly for its simplicity, to assess the capacity of barrier materials to remove chemical constituents from solutions. In the present research, the aim of batch testing was also to assess and compare the reactivity of the different mixtures with a given solute, as a function of their curing time. The curing time was always intended as the time elapsed from the mixing until the beginning of the batch test.

Samples of the three mixtures were tested, after curing underwater, at curing times ranging from 7 days to about 1.5 years.

The cemented nature of the mixtures as well as their high water content required a specific procedure to prepare the specimens for batch testing. After a given curing time, a sample of each of the three mixtures was crumbled to pass the 2 mm sieve. The mixture “grains” resulted completely retained at the 0.075 mm sieve, with a percentage of passing through the 0.425 mm sieve lower than 5% (Fig. 1); therefore, a grain size of a medium sand (as defined by the Unified Soil Classification System, ASTM D2487-17) was obtained. The material was no further crumbled to avoid significant reduction in the water content. Few minutes were sufficient to obtain enough material for 5 specimens of 20 g each and for 2 measurements of the water content (about 50 g each), according to ASTM D2216.

Batch tests were performed on the specimens as such (not dried) in order to be representative of their actual state

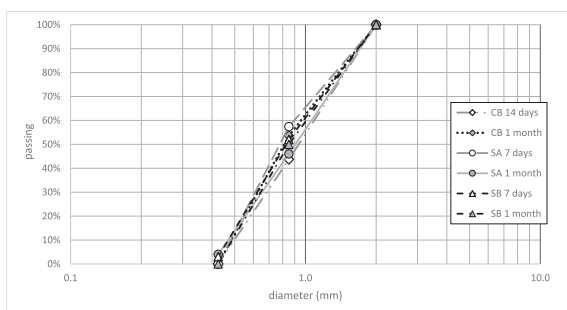


Fig. 1. Grain size distributions of samples for batch testing.

and composition, considering the role of water in the reaction and sorption behaviour of cemented materials.

Each specimen was poured in high-density polyethylene bottles (compatible with the nature of the solutes under investigation). The solution was then added to the container in an amount necessary to yield a 1:10 sorbent-to-solution ratio, instead of the 1:20 ratio required by the ASTM procedure, due to a technical need (dimensions of the bottles compatible with the rotary mixer). However, tests were performed on purpose to verify that the sorbent-to-solution ratios did not influence the results (Fratolocchi et al., 2020). Each container was placed on the rotary mixer and agitated continuously at 30 rpm at controlled temperature ($20^\circ \pm 2^\circ C$). All the batch tests were performed with a contact time of at least 48 h, that was found to be enough to reach chemical equilibrium in the case of cement-bentonite mixtures (Fratolocchi et al., 2013) as well as for cement pastes (e.g., Hong and Glasser, 1999). After decantation, the solution was filtered through a 0.45- μm pore size membrane and stored in a refrigerator until analysed.

The retained mass, m_a , was calculated as the difference between the initial and final mass of solute in solution and the sorption ratio, S , as the ratio between m_a and the dry mass of the sample, m_s .

The sorption capacity of the CB mixture was also evaluated from 5 hydraulic conductivity tests conducted with K_2SO_4 solutions at the inlet constant concentrations, $C_0 = 95$ g/l, 75 g/l, 50 g/l, 27.5 g/l and 5 g/l (Fratolocchi et al., 2013; 2020). For each test, after the effluent concentration, C , of both K^+ and SO_4^{2-} resulted equal to the inlet one (this occurred only in the tests performed on samples of the CB mixture), the mass of K^+ or SO_4^{2-} adsorbed by the sample, m_a , was calculated as follows:

$$m_a = m_{in} - m_{out} - m_p \quad (1)$$

where m_{in} is the total mass of solute (K^+ or SO_4^{2-}) entered into the sample, m_{out} is the total mass of solute collected in the effluent solution (both evaluated by periodic sampling to measure C_0 and C during the test) and m_p is the mass of solute in the interstitial pores of the sample. The

mass m_p was calculated considering the interstitial solute concentration equal to C_0 (since $C/C_0 = 1$) and the sample porosity = 0.6. As for the batch tests, S was assessed as the ratio between m_a and m_s for each of the 5 tests, at the equilibrium concentration equal to C_0 .

2.4. Permeation tests

Hydraulic conductivity tests with potable tap water (TW) and with K_2SO_4 solutions at different concentrations were performed on samples of the mixtures permeated after a curing time ranging from 14 to 22 days of submersion in water. In the hydraulic conductivity tests with the K_2SO_4 solutions, the inlet concentration was kept constant and the effluent concentrations of K^+ and SO_4^{2-} were measured with time.

The hydraulic conductivity tests with water and with the K_2SO_4 solutions were conducted for at least 5 months to a maximum of about 2 years of continuous permeation, to assess the k trend with curing time and the mixture long-term performance (Fratolocchi et al., 2013; 2020).

The thickness of the samples for the hydraulic conductivity tests in water was in the range of 7.0–9.5 cm. In the case of the hydraulic conductivity tests with the potassium sulphate solutions, the samples were prepared with a different thickness (in the range of 2.0–7.2 cm) considering the concentration of the permeant solution. In particular, the samples to be permeated with the solutions at the lowest K_2SO_4 concentrations had a thickness of 2.0 to 5.1 cm in order to increase the number of pore volumes of flow (PV) per unit time and to make evident the effect of any interaction on the k values in a reasonable duration of testing. The number of pore volumes of flow was evaluated assuming total porosity values equal to 0.5 for the special mixtures and 0.6 for the CB mixture.

Flexible wall permeameters were used for all the permeation tests, under an effective confining pressure of 40 kPa on average across the sample. The sample volumetric strains were monitored during each test by measuring the change in the water volume of the permeameter cell. Bladder accumulators were installed along the inlet and outlet lines to store the inlet solution (kept at constant concentration by periodical replacing) and to collect the effluent one. Constant head tests were performed under a hydraulic gradient, i , which was changed in steps during each test from 25 to a maximum of almost 300, depending on the hydraulic conductivity. In particular, high i values were necessary to get accurate measures of the volume of flow in a reasonable time when the k values were lower than 10^{-10} m/s. The increase in the hydraulic gradient was imposed, without changing the cell pressure, by increasing the inlet water pressure and reducing the effluent one in order to keep the average water pressure constant (i.e., the average effective confining pressure of 40 kPa). In all the k tests the maximum effective stress at the effluent base of the specimens always resulted not greater than 65 kPa and the minimum effective pressure at the influent base was not lower

than 15 kPa. These changes of stress levels along the specimens during the tests were considered not to significantly alter the sample porosity and homogeneity because they were applied on samples after some months of permeation (i.e., curing), when their compressive stiffness is very high due to cement hydration processes. Indeed, no significant volume changes were detected on the samples. Similar results were found by Jefferis (1981) on cement-bentonite mixtures permeated under hydraulic gradients of the order of hundreds.

Notwithstanding the high hydraulic gradients, the small thicknesses of the samples and the long duration of the hydraulic conductivity tests, in all the tests performed with the K_2SO_4 solutions on the SA and SB samples the relative effluent concentrations of both K^+ and SO_4^{2-} resulted much lower than 1.

2.5. Chemical and microstructural analyses

The chemical analyses of the testing solutions were performed by ion exchange chromatography (Dionex ICS-1000). The solutions at concentrations greater than about 60 ppm were diluted.

The interaction mechanisms were investigated by means of X-Ray Diffractometry, XRD (BRUKER D8 ADVANCE), Scanning Electron Microscopy, SEM (FESEM ZEISS SUPRA 40) with Energy Dispersive X-ray Spectrometry, EDS. The specimens for XRD analyses were prepared after air drying. The specimens for SEM observations (and EDS analyses), of a volume of about $0.5\text{--}1\text{ cm}^3$, were taken by breaking off little pieces from the sample, without cutting, in order to limit change in the microstructure morphology. They were air dried and then gilded or graphitized. After air drying the specimens did not show fissuring or apparent variation in volume.

3. Results and discussion

3.1. Slurry properties

Table 3 shows the average, minimum and maximum values of Marsh viscosity, bleeding and unit weight measured at the fluid state on the mixtures investigated. All of them fully match the usual practice requirements (ICE et al., 1999) in terms of density, workability and volumetric performance.

The slurry properties of the SA and SB mixtures allowed assumptions on their relative composition. The same solid content of the special mixtures is confirmed by the same unit weight, which is obviously higher than that of the CB mixture. Since the bleeding value of the SB mixture is lower than that of SA, a higher total clayey fraction, i.e., higher activity of the fillers can be supposed for the SB mixture respect to the SA one. In fact, the role of the colloid component in a cement-bentonite mixture is maintaining the cement particles in suspension until setting and it is well known that the higher the bentonite/cement ratio, the lower

Table 3

Solid content and average values of properties at the fluid state of the investigated mixtures (minimum and maximum measured values in brackets).

Mixture	solid/water	Marsh viscosity (s)	Bleeding (%)	Unit weight (kN/m ³)
CB	0.265	49 (47–50)	1.0 (1.0–1.5)	11.5
SA	0.33	43 (42–44)	1.5 (1.0–1.5)	11.8
SB	0.33	49 (48–49)	0.5 (0–0.5)	11.8
Practice requirement		< 60	≤ 2	11.3 – 12.2

the bleed water (e.g., Jepsen and Place, 1985). The value of the Marsh viscosity of the SB mixture, higher than that of the SA one, is coherent with a higher clayey fraction.

3.2. Water content and dry density

The water content, w , measured on all the samples of the batch and permeation tests are shown in Fig. 2 as a function of the curing time at the beginning of testing, i.e., after curing in water. A decrease in the water content with curing is evident for all the mixtures investigated mainly during the first month of curing and is appreciable for months. This result is consistent with the cement hydration process, which goes on for months or years and is more rapid during the first months of curing. The reduction of w demonstrates that the mixtures' total porosity decreases with curing. The special mixtures show the same w trend with curing (differences of their w in the range of 0–3%), which is coherent with their equal cement content, and a lower water content than the CB mixture, curing time being equal, due to their higher solid content. Correspondingly, the values of the dry unit weight, γ_d , of the special mixtures resulted always greater than those of the CB mixture (Table 2).

3.3. Hydraulic conductivity in water

Fig. 3 shows the hydraulic conductivity values in water measured on the same sample for each of the three mixtures investigated, as a function of curing time. All of them reach k values lower than 10^{-9} m/s at brief curing, as required for a barrier material. Both SA and SB mixtures show a better hydraulic performance than that of the CB

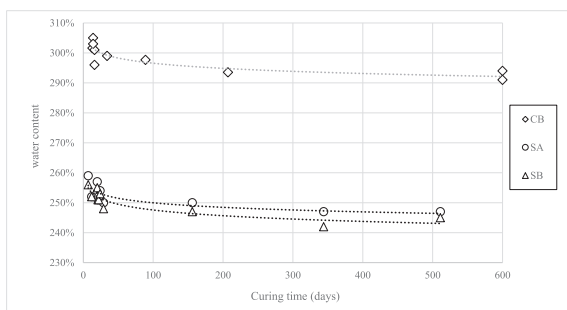


Fig. 2. Water contents measured on the samples for the batch and permeation tests (after curing in water).

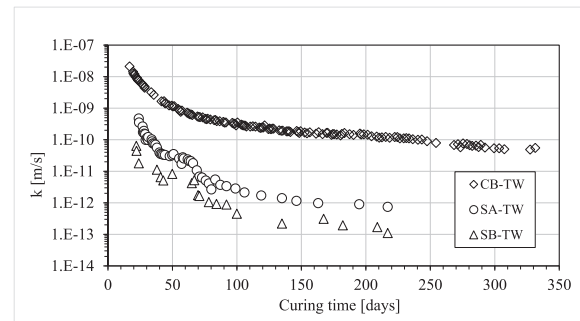


Fig. 3. Hydraulic conductivity values in tap water (TW) measured on the CB, SA and SB mixtures (Fratolocchi et al., 2020).

mixture due to their higher solid content. In particular, $k < 1 \times 10^{-10}$ m/s is reached after just 1 month of curing.

The three mixtures exhibit a significant reduction in k with curing, as typically occurs for this kind of materials due to the cement hydration process which cause a decrease in the mixture porosity (evidenced by the reduction in the water content with curing, see Fig. 2) as well as a decrease in the mean size of pores, as documented in Fratolocchi and Pasqualini (2007). In particular, the cement hydration process results in an increase in the solid volume at the expense of the volume of voids (a cement particle doubles its volume when fully hydrated); moreover, growth of needle-shaped crystals, due to the slag hydration, too, gives rise to a sort of “net meshes thickening” with progressive reduction of the area available for flux.

The lower k values of the SB mixture than the SA, at any curing time, are consistent with its higher clayey content, as supposed from its characteristics at the fluid state. Both the quantity and quality of the solid components are responsible for the better hydraulic performance of the special mixtures in comparison with the CB.

3.4. Sorption and interaction

In the present study, sorption is considered as an overall mechanism able to remove solute contaminants from a given solution, independently on the nature of the reaction between the solutes and the solid phase (e.g. cation exchange) or the physical reaction occurring due to changes in chemical equilibrium (e.g. precipitation).

With reference to the solid to water ratio used in the present study (1:10 for most of tests), batch tests were also performed on the same samples with the solid:water ratio = 1:20 (Fratolocchi et al., 2020). The comparison

between the series of tests demonstrated that there is no difference on the sorption capacity, confirming the reliability of testing with the solid:water ratio = 1:10, more convenient from a practical point of view.

3.4.1. Potassium

Fig. 4 shows the batch test results on the CB mixture related to sorption of K^+ at different curing times, starting from 2 weeks to about 1.5 years. A significant sorption

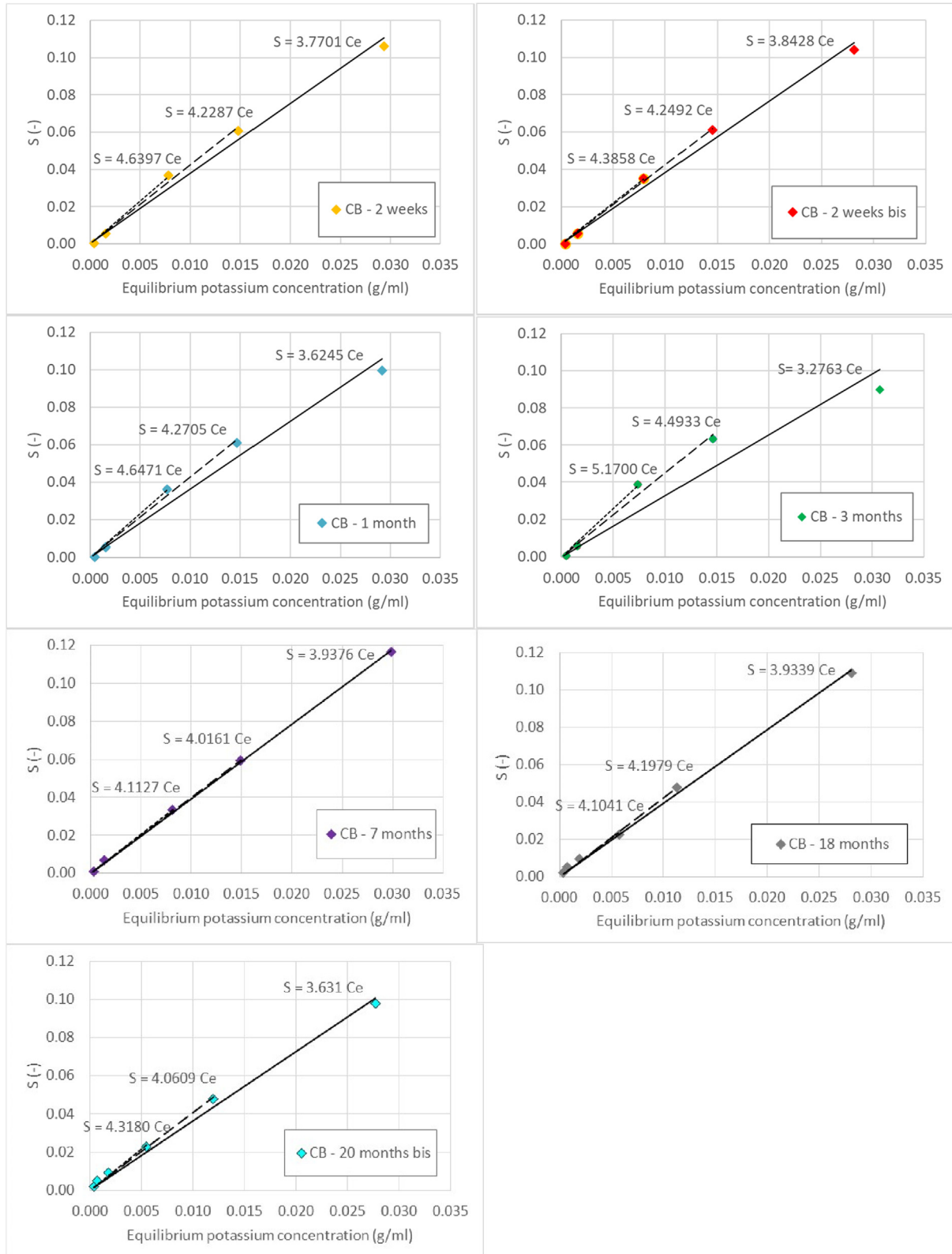


Fig. 4. CB mixture: potassium sorption isotherms at different curing times and for different concentration ranges.

increase is evident for any curing time with increasing potassium concentration in solution, notwithstanding the wide range of concentration investigated. As typically occurs in reactive materials, the sorption capacity is a function of the concentration with a concave down trend.

For each curing time, sorption of potassium has been modelled, for different ranges of concentration, by a linear isotherm:

$$S = k_d C_e \quad (2)$$

where C_e is the equilibrium solute concentration [ML^{-3}] and k_d is the distribution coefficient [L^3M^{-1}].

In particular, the ranges of the equilibrium concentration (ΔC) from zero to almost 0.01 g/ml (ΔC_1), 0.015 g/ml (ΔC_2) or 0.03 g/ml (ΔC_3) have been selected as representative of a small, medium or wide concentration range, respectively. In these ranges the experimental results have been fitted by Eq. (2), in order to quantify the influence of ΔC on the distribution coefficient and to analyse the reliability of modelling sorption in a wide range of concentrations by a linear isotherm, the simplest and most convenient isotherm from a practical point of view.

Before examining the results it is necessary to point out that for the curing of 2 weeks the batch tests were duplicated. They gave very close results (Fig. 4). In particular, the values of k_d differ of 5.6%, 0.5% and 1.9% for ΔC_1 , ΔC_2 and ΔC_3 , respectively. Moreover, by comparing the results of the tests performed at 18 and 20 months of curing (when the cement hydration process is practically ended) the k_d values differs of a maximum of 8.0%. It is important also to consider that the batch tests performed at the same curing time on the same CB mixture with solid to water ratios of 1:10 and 1:20 (documented in Fratolocchi et al., 2020) gave practically coincident results.

The k_d values obtained by fitting with Eq. (2) the results of each test in the three different ΔC are plotted in Fig. 5 as a function of the curing time of the mixture. The results from the batch tests performed on the same mixture with the solid to solution ratio of 1:20 (documented in Fratolocchi et al., 2020) are included. All the k_d values result in the range of 3.3–5.2 ml/g and demonstrate an appreciable sorption capacity of the CB mixture. For the

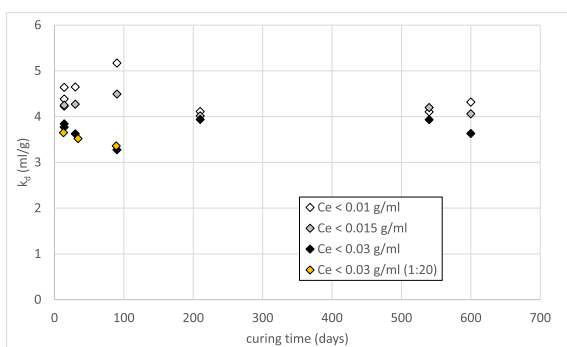


Fig. 5. CB mixture: distribution coefficient of potassium vs curing time as a function of the range of the equilibrium concentration, C_e .

same mixture, Fratolocchi et al. (2013) found similar values of k_d (3.2–3.9 ml/g) with solutions of KOH.

The k_d value always decreases with increasing concentration, but the reduction is rather limited. In particular, within the first 3 months of curing, the values of k_d obtained on the widest ΔC are from 12% to 36% lower than those related to the smallest ΔC . From Fig. 5 it is also evident that the differences of k_d due to the range of concentration decrease with curing: at curing times of several months, the reduction of k_d with increasing ΔC is of 4%. Finally, it can be noted that for each range of concentration k_d is almost constant with curing: specifically, with reference to the k_d values at 14 days of curing, k_{d-14} , the values at all the investigated curing time are in the range of $[0.02 \div 0.11] \cdot k_{d-14}$ in the case of the smallest ΔC and in the range of $[-0.13 \div 0.04] \cdot k_{d-14}$ for the widest concentration range. To this regard it is important to point out that the differences of the k_d values resulting from the 2 tests performed at the same curing (2 weeks) (Fig. 4) differ from 3% to 4% depending on ΔC . Even if this is a single comparison, it can give an idea that the order of magnitude of variation of k_d due to testing is expected of the unit percentages. Therefore, the results obtained on the CB mixtures allow to consider that if the potassium distribution coefficient is determined at brief curing and assumed constant with curing, the error is limited and can be acceptable.

The same analysis of the results has been performed with reference to the batch tests on the special mixtures, considering the two ranges of concentrations $\Delta C_1 = 0-0.01$ g/l and $\Delta C_2 = 0-0.015$ g/l (on the base of the available results on the SA and SB mixtures). These ranges are equal to the first two ΔC chosen for the CB mixture. Some examples are given in Fig. 6, whereas all the obtained k_d values are reported in Fig. 7. As found for the CB mixture, also the special mixtures show a significant sorption increase for any curing time with increasing potassium concentration and a sorption capacity depending on the concentration with a concave down trend (Fig. 6).

The k_d values of all the mixtures obtained for the same concentration intervals are compared in Fig. 7 as a function of the curing time. It is evident that the potassium sorption capacity of the special mixtures is very similar and appreciably greater than the CB mixture, ΔC being equal.

The reduction of the k_d values with increasing ΔC is in the range of 8%–23% for the SA mixture and of 5%–15% for the SB depending on the curing time; such reductions are in the same range of those obtained for the CB mixture.

The variation of k_d with curing has been quantified also for the special mixtures with reference to the k_{d-14} value: for the SA k_d results in the range of $[-0.11 \div 0.02] \cdot k_{d-14}$ in the case of ΔC_1 and in the range of $[-0.06 \div 0.08] \cdot k_{d-14}$ for ΔC_2 ; for the SB the k_d values are in the range of $[-0.12 \div 0.05] \cdot k_{d-14}$ in the case of ΔC_1 and in the range of $[-0.12 \div 0.05] \cdot k_{d-14}$ for ΔC_2 . As for the CB mixture, also for the special mixtures the potassium distribution coefficient can be assumed constant with curing.

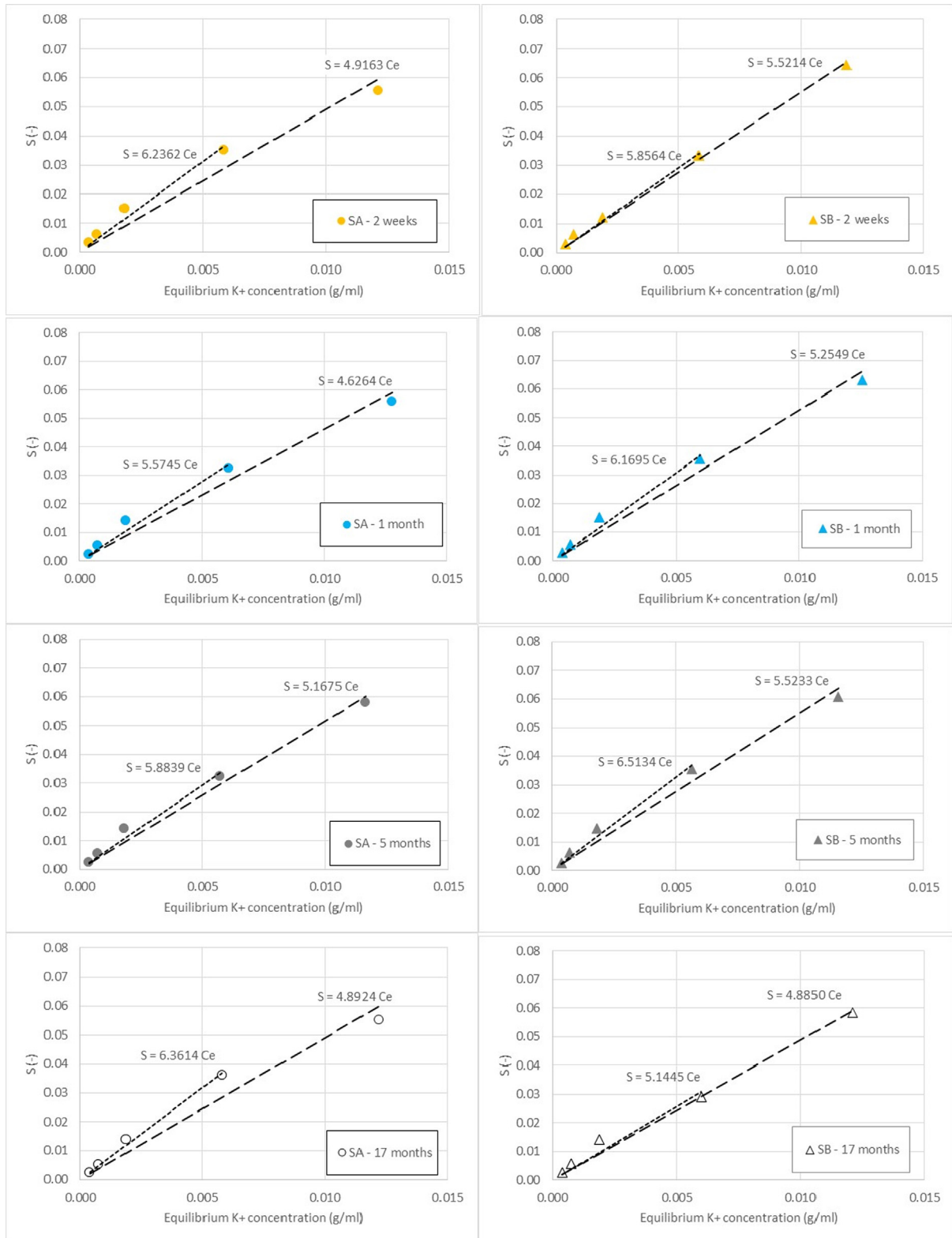


Fig. 6. SA and SB mixtures: potassium sorption isotherms with reference to different concentration ranges, obtained from some of the batch tests at different curing times.

From a practical point of view, the results obtained from all the mixtures demonstrates that the potassium sorption capacity can be usefully and reliably determined

on mixtures at brief curing, i.e. in the design phase, to assess potassium migration through cut-offs. Moreover, migration of K^+ can be modelled with a constant k_d value

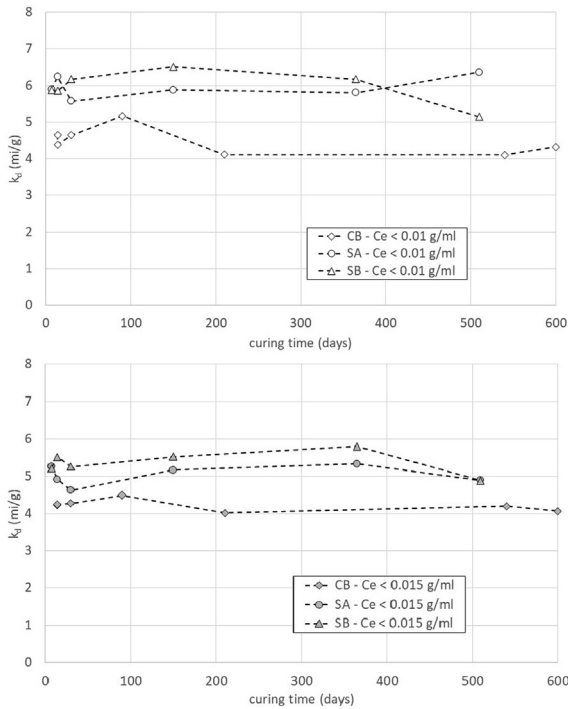


Fig. 7. Comparison of the K^+ distribution coefficients of the mixtures vs curing time as a function of the range of the equilibrium concentration, C_e .

notwithstanding the influence of curing on the advective and diffusive flow through a cement bentonite cut-off wall.

Questions may arise on the representativeness of batch tests in evaluating the actual sorption capacity of mixtures since the testing conditions are very different from those during migration of solutes through a cut-off wall. To this purpose, the results of the batch tests on the CB mixture have been compared with those obtained from the permeation tests (more representative of actual migration conditions) performed with solutions of K_2SO_4 at different constant inlet concentrations (documented in Fratolocchi et al., 2013; 2020), in which a relative effluent concentration, $C/C_0 = 1$ was obtained of both K^+ and SO_4^{2-} before the end of each test. The comparison could not be done for the special mixtures since C/C_0 of K^+ and SO_4^{2-} during the permeation tests resulted much lower than 1 notwithstanding the long duration of testing and high hydraulic gradients (§ 2.4).

Fig. 8 shows the comparison between sorption of K^+ from the permeation tests and from the batch tests performed from 2 weeks (which is about the curing time at the beginning of the permeation tests) to 7 months of curing, that is about the maximum curing of the samples when C/C_0 of K^+ resulted equal to 1 (Fratolocchi and Pasqualini, 2007; Fratolocchi et al., 2013; 2020). It can be noted that within the concentration interval ΔC_3 the different tests give similar results. At the two higher concentrations (data only from permeation tests) sorption is lower than the extrapolated values from batch tests. To analyse the results it is necessary to take into consideration that on the sam-

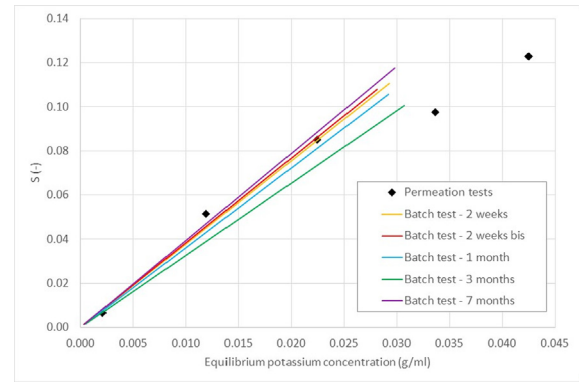


Fig. 8. CB mixture: comparison between sorption of Potassium from batch tests and permeation tests.

ples permeated with the two highest concentrations of K_2SO_4 the potassium relative effluent concentration equal to 1 was obtained when fissuring occurred in a large part of the samples as a consequence of expansive reactions due to sulphate (as discussed in § 3.3.2 and 3.4), whereas, in the case of the lower concentration, $C/C_0 = 1$ was obtained long before fissuring, as shown in Fig. 9. The preferential flow through the fissures implies a non-uniform contact with the whole sample and therefore a lower sorption in the permeation tests than in the batch tests at the highest concentrations. Therefore, it cannot be excluded that the sorption capacity of K^+ from permeation tests can be equal to that from the batch tests at the highest concentrations when fissuring does not occur. On the basis of the similar results obtained from batch and permeation tests at the lower concentrations, the solid-liquid ratio could have a negligible influence on sorption of potassium, in agreement with the same sorption isotherms obtained for the 1:10 and 1:20 solid to water ratios (Fratolocchi et al., 2020). Moreover, since the equilibrium concentration in batch tests is reached within 48 h (Fratolocchi et al., 2013), and considering the much longer

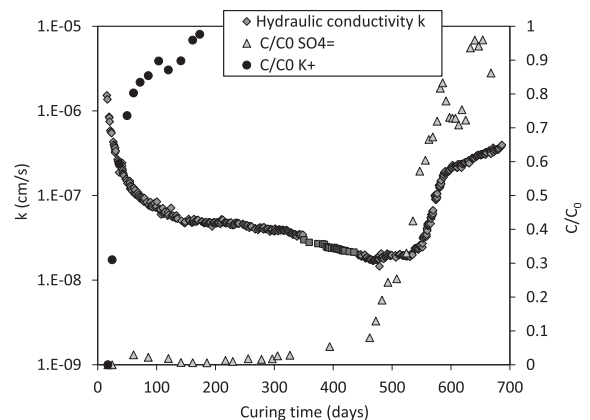


Fig. 9. CB mixture permeated with the solution of K_2SO_4 at $C = 5$ g/l: hydraulic conductivity trend with curing time and breakthrough curves of K^+ and SO_4^{2-} (Fratolocchi et al., 2013).

duration of the permeation tests before and after $C/C_0 = 1$ (e.g., more than 1 year in the test of Fig. 9) it is reasonable to consider that the sorption kinetics did not play a significant role.

The mechanisms of sorption of potassium in the mixtures can be analysed distinguishing the role of bentonite and cement in the mixtures. With reference to bentonite, its sorption capacity of K^+ can be assessed as negligible for the following reasons. The bentonite mass of the three mixtures investigated is lower than 20% of the total dry solid mass. The cation exchange capacity of the bentonite of the CB mixture is equal to 75 meq/100 g and the same value can be assumed for the bentonite of the special mixtures since both of them contain activated bentonite. Even if the bentonite did not absorb any other cation than K^+ , the mass of absorbed K^+ results <10% of the overall K^+ mass absorbed by each mixture. The actual sorption of K^+ by bentonite is certainly lower considering its greater affinity to Ca^{++} , largely available in the pore water of any cement-bentonite mixture due to dissociation of $Ca(OH)_2$. Moreover, studies from the literature (Evans et al., 2021), showed that bentonite clay minerals dissolve in slag-CB slurries and that bentonite is virtually absent in the hardened slag-CB material. Therefore, sorption of potassium in the mixtures can be analysed considering only the role of hydrated cement constituents.

Research on binding of alkali into cement pastes demonstrated that sorption of potassium correlated with the Ca/Si ratio of C-S-H: decreasing Ca/Si increases the overall sorption capacity, although some results exhibited considerable scatter (Stade, 1989; Thomas et al., 2011). In particular, Hong and Glasser (1999) performed sorption tests on C-S-H and aqueous solutions of KOH with a maximum potassium concentration 0.3 M (11.7 g/l, similar to that used in the batch tests on the mixtures) and found essentially straight-line sorption isotherms and distribution coefficients that increase with decreasing Ca/Si ratio (Fig. 10), expressed as molar ratio. The trend of the distribution coefficient values confirms that the low Ca/Si ratio C-S-H, characteristic of blended cements (such as the slag

cement used in the mixtures) binds alkali better than high ratio C-S-H of the ordinary Portland cements.

The k_d values obtained on the investigated mixtures can be compared with those in the literature starting from the chemical composition of the cements of the three mixtures. From the data in Table 1, values of the Ca/Si molar ratio equal to 1.8 and 1.7 result for the special mixtures and the CB mixture, respectively (supposing a slag content of 80% in the special mixtures). If compared with the results by Hong and Glasser (1999), the k_d values of the investigated mixtures ($k_d = 3.5$ – 5.5 ml/g) are significantly higher than those corresponding to Ca/Si ratios of 1.7–1.8 ($k_d = 0.5$ – 1 ml/g), as shown in Fig. 10. To this purpose, it is necessary to consider that, as pointed out by Hong and Glasser (1999), the presence of inhomogeneities in the C-S-H “real” pastes, in which local regions having low Ca/Si ratios are expected, can significantly contribute to the overall sorption. Moreover, further research by Hong and Glasser (2002) on alkali sorption by C-A-S-H gels revealed that introduction of Al into C-S-H markedly enhances potassium binding (more than twice). The higher sorption capacity of the special mixtures than the CB one could be due to a greater Al content (i.e., a higher slag content) than the CB.

Finally, it is necessary to observe that the results by Hong and Glasser (1999) in Fig. 10 are expressed as a function of the initial K^+ concentration in solution and not with reference to the equilibrium concentration (higher values of k_d are obtained in this last case).

Of the hypotheses presented in the literature to explain alkali binding (Taylor, 1987; Stade, 1989), binding occurring at the relatively acidic silanol (Si-OH) sites have been proved to be the most coherent with the experimental results. The concentration and acidity of silanol groups increase as the Ca/Si ratio of C-S-H decreases, especially when $Ca/Si < 1.5$ (Hong and Glasser, 1999) and when solid solution of Al in C-S-H increases.

To investigate the presence of potassium compounds, XRD analyses were performed on some samples after batch tests, both as such and after air drying. The results (some of which are in Fig. 11) did not reveal any potassium compounds.

Therefore, on the basis of what has been discussed, the results and potassium sorption mechanisms obtained on the mixtures investigated can be considered consistent with those documented in the literature of cement pastes. As for the cement pastes, the sorption mechanism of K^+ on the mixtures can be mainly considered to occur at the CSH and/or CASH phases (VDZ, 2005).

Simulations of potassium migration through a cut-off wall made of the mixtures investigated (Fratolocchi et al., 2019) showed the importance of considering the sorption capacity of a mixture for optimizing cut-off wall design.

3.4.2. Sulphate

Fig. 12 shows the results of all the batch test on the CB and special mixtures with reference to SO_4^{2-} . The Fre-

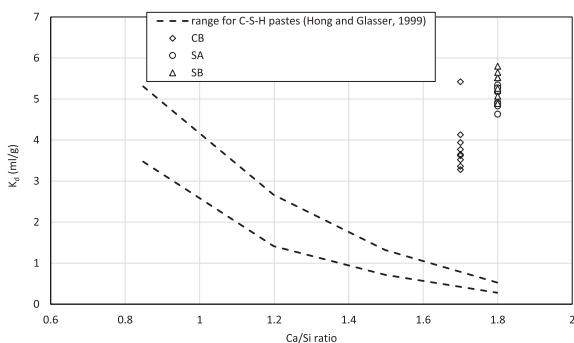


Fig. 10. Distribution coefficient of K^+ as a function of the calcium to silicon molar ratio of the mixtures investigated and of C-S-H pastes (range of values from Hong and Glasser, 1999).

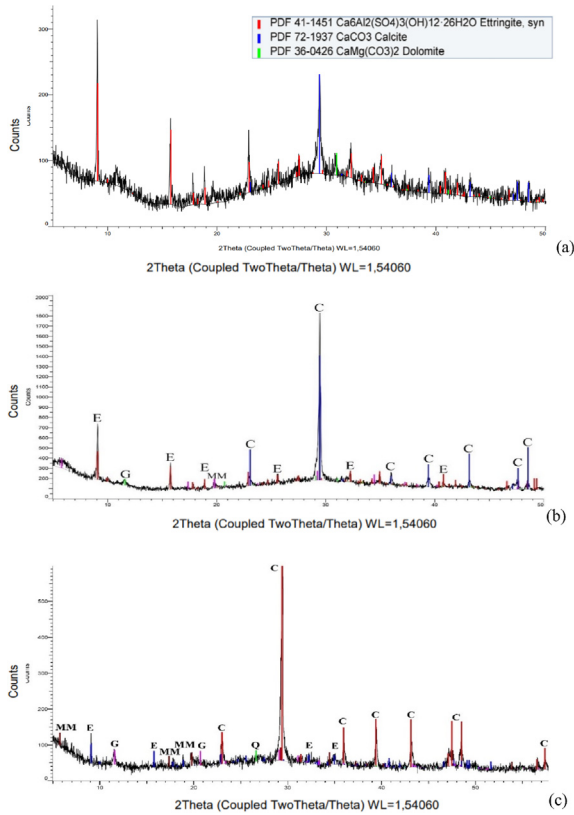


Fig. 11. XRD diffractograms of mixture samples after batch testing with K_2SO_4 solution at the concentration of 30 g/l: (a) CB, curing time = 2 weeks; (b) SA, curing time = 1 month; (c) SB, curing time = 1 month (C = calcite; E = ettringite; G = gypsum; MM = montmorillonite; Q = quartz).

undlich isotherm (widely used in environmental soil chemistry) was found to give the best fitting for all the tests:

$$S = k_f C^{\epsilon} \quad (3)$$

where $k_f [L^3 M^{-1}]$ and $\epsilon [-]$ are constant.

For the CB mixture, sorption of SO_4^{2-} tends to appreciably decrease with curing (Fig. 12.a) whereas in the case of the special mixtures the curing time does not significantly modify their sorption capacity (Fig. 12.b and 12.c). The special mixtures also show SO_4^{2-} sorption ratios systematically lower than the CB, ΔC being equal. For example, at the equilibrium concentration of 10 g/l, the CB sorption ratio is in the range of 0.11–0.19 depending on curing, whereas it is 0.07–0.09 for the special mixtures.

To discuss the results in Fig. 12 it is necessary to consider that sorption of SO_4^{2-} in the mixtures is due to the interaction with the hydrated cement products. Indeed, bentonite is not expected to adsorb SO_4^{2-} under neutral or alkaline pH conditions (as in the case of the interstitial water of cement-bentonite mixtures) due to predominantly negative surface charges, resulting in anion repulsion. Batch-type adsorption tests on a commercial-grade bentonite and a sulfate concentration of 1250 mg/l (Darbi et al., 2003) showed that bentonite did not show any adsorption capacity for sulfate.

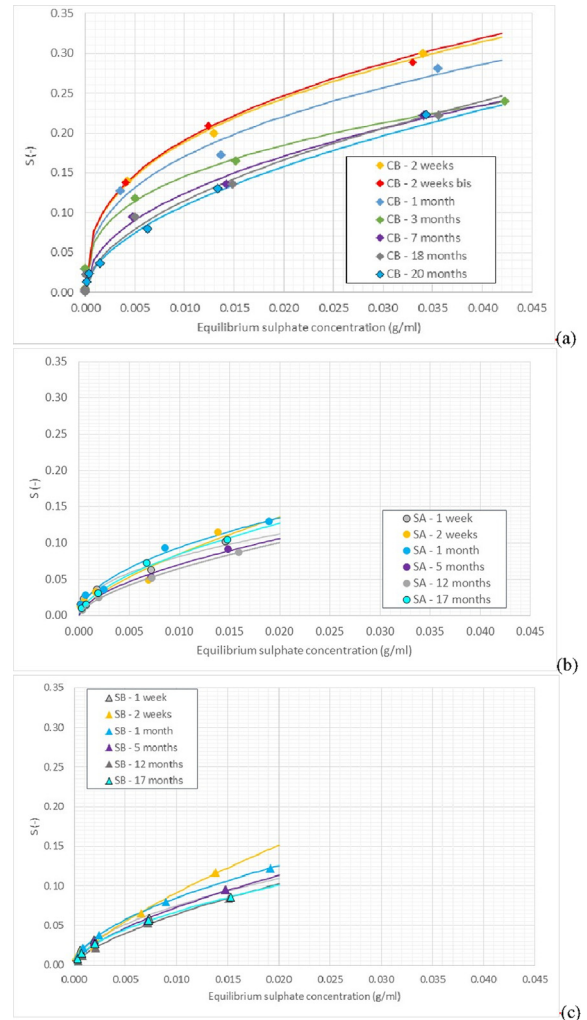
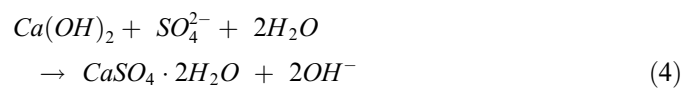


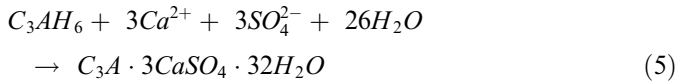
Fig. 12. Sulphate sorption isotherms from batch tests on the mixtures investigated at different curing times (Fratolocchi et al., 2020, with integrations).

There is a large volume of literature on the theoretical mechanisms of sulfate attack, combined with experimental evaluations on cement pastes (e.g. Hewlett, 2003). Even if there are many questions concerning the complex characteristics of cement and their effects on sulfate attack (e.g. Skalný and Pierce, 1999), all the studies mainly relate tricalcium aluminate content of the cement and the concentration of sulfates in the exposure solution to the external sulfate attack. Sulfate initially reacts with the calcium hydroxide to form gypsum:



After the gypsum formation, different reactions occur mainly involving gypsum, tricalcium aluminate (C_3A , where C = CaO, A = Al_2O_3), tricalcium aluminate mono-

sulphate ($C_3A \cdot CaSO_4 \cdot 12H_2O$) or the hydrated phases of tricalcium aluminate, e.g. C_3AH_6 (where $H = H_2O$), that give rise to ettringite, e.g.:



Gypsum and/or ettringite formation were confirmed by XRD analyses performed on some of the samples of the three mixtures after batch testing (Fig. 11). On the basis of the wide literature on interaction between sulphates and cement pastes, many intrinsic and chemical-environmental factors can affect the development of reactions and formation of gypsum and ettringite. Since the chemical and environmental conditions in batch tests were the same (type and concentrations of solutions, time and way of contact, temperature), the different behaviour of the mixtures investigated can be ascribed to their different composition (quality and quantity of cement) and porosity.

Both special mixtures show a lower sorption of SO_4^{2-} (i.e. less interaction with SO_4^{2-}) than the CB mixture (Fig. 12). The reason can be ascribed to a cement content that can be lower than that in the CB mixture and/or a different chemical composition of the cement and slag. In particular, the lower reactivity of the SA and SB mixtures with sulphate cannot be attributed to a content of Al_2O_3 in their cement lower than that of the CB mixture because this is incompatible with the chemical composition of their cement and slag (Table 1). Substitution of C_4AF for C_3A in the cement of the special mixtures can be supposed since it is known that this results in decreased susceptibility to sulfate attack and a much stronger negative correlation with expansions (Hewlett, 2003).

The reduction of reactivity with curing of the CB mixture (Fig. 12.a) suggests that the porosity of a mixture plays a role in reaction with sulphate, as in the case of cement pastes (e.g. Roy, 1986). It is important to remind that the batch tests were performed on “grains” of mixture of the size 0.4 mm–2 mm (Fig. 1). Inside the mixture “grains” interaction sites become less accessible with curing since the porosity decreases due to the development of the hydrated cement products during curing.

The lower reactivity of the special mixtures than the CB one can be at least partly due to their lower porosity. In particular, the SA and SB mixture have a total porosity lower than that of the CB mixture due to their higher solid/water ratio, as also shown by the difference of their water contents (Fig. 2). Such a difference is very significant considering the typical narrow range of porosity for cement-bentonite mixtures. Moreover, the effective porosity of the special mixtures is lower than that of the CB mixture as proved by their lower hydraulic conductivity in water (Fig. 3).

As for sorption of potassium, the results of sorption of sulphate from batch tests have been compared with those from the permeation tests on samples of the CB mixture performed with different constant inlet concentrations of

K_2SO_4 (Fratolocchi and Pasqualini, 2007; Fratolocchi et al., 2013; 2020).

The sulphate equilibrium concentration can be considered equal to the inlet concentration since at the end of all the tests the effluent concentration resulted equal to the inlet one. Fig. 13 shows the comparison between the results of sorption of sulphate obtained from the batch and the permeation tests. To analyse these results it is necessary to point out that in all the permeation tests the sulphate equilibrium concentration (i.e., $C/C_0 = 1$) was observed after a large increase in k (1–2 orders of magnitude, e.g., Fig. 9) due to fissuring created by the reaction of the samples with the sulfate itself, as a consequence of the expansive formation of ettringite (Fratolocchi et al., 2013). The net of fissures developed across the samples during the permeation with sulphate resulted in preferential paths of different lengths, direction and opening. In any case, the preferential flow of sulphate through these paths implies a non-uniform contact with the whole sample and therefore a lower sorption of sulphate per unit mass of solid.

Another important factor to consider is that in the permeation tests sorption of sulphate (i.e., reaction with the sample) is progressive through the sample and that in the meantime the sample curing increases. Therefore, the results from permeation and batch tests can be compared considering, on average, the curing time of the samples at the beginning of the permeation tests (about 2 weeks, see Table 2) and the curing time at which $C/C_0 = 1$. In the case of the highest concentrations, $C/C_0 = 1$ occurred after few months of permeation, i.e., of curing (Fratolocchi and Pasqualini, 2007; Fratolocchi et al., 2020), whereas for the lowest one it happened at a curing time of almost 2 years (Fig. 9). From Fig. 13 it is evident that the influence of fissuring in reducing the sulphate sorption is significant since, in the case of the highest concentrations, sorption from permeation tests is always lower than sorption from the batch tests in the range of 2 weeks – 3 months of curing. In the case of the lowest concentration, sorption of sulphate from the column test is in the range of sorption from the batch isotherms at 2 weeks and at 20 months and the

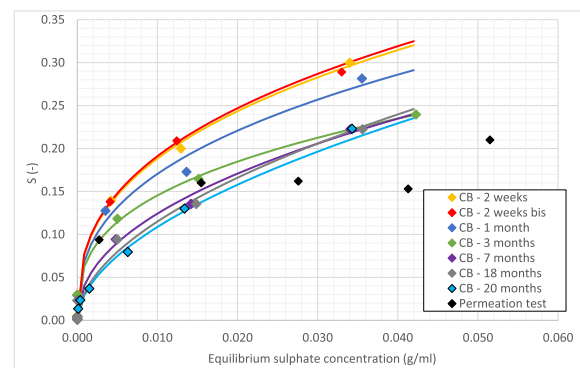


Fig. 13. CB mixture: comparison between sorption of sulphate from batch tests and permeation tests.

effect of fissuring is not detectable. Further research is necessary to confirm sorption of sulphate from permeation tests at low concentrations and to investigate reaction kinetics of sulphates through cement-bentonite mixtures. However, on the basis of the results in Fig. 12 and Fig. 13, it is evident that the batch tests, when performed at brief curing time, can be conveniently used in design practice to assess the reactivity of a mixture in sulphate solutions and compare different cement bentonite mixture in order to select the less reactive one, on which the long-term permeation test can be performed.

3.5. Hydraulic conductivity with potassium sulphate solutions

The sorption behaviour of the investigated mixtures with sulphate is consistent with the results of the permeation tests performed on the mixtures with the K_2SO_4 solutions at different concentrations. As documented and

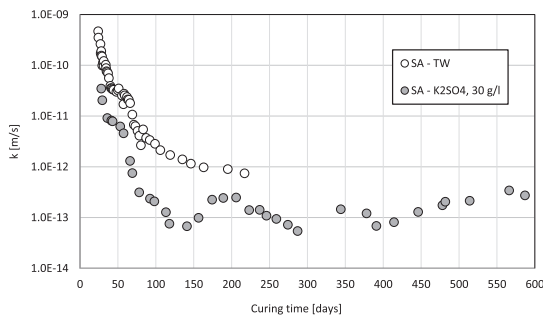


Fig. 14. Hydraulic conductivity vs curing time of the SA mixture permeated with tap water (TW) and with K_2SO_4 solution at the concentration of 30 g/l.

discussed in Fratolocchi et al. (2013; 2020), in the case of the CB mixture, interaction with sulphate was found to give an initial decrease in k , with values that can be lower than those in water, followed by an increase in k (e.g., Fig. 9), that occurs after a number of pore volumes that is lower the higher the sulphate concentration in solution. Gypsum formation (causing pore clogging) and the subsequent ettringite formation (causing swelling and fissuring) are the main responsible for the k trends. Clogging effect becomes negligible as ettringite is produced and expansive reactions start, with a consequent inversion of the k trend with time. The expansive reactions and ettringite were confirmed by the sample volume increase (7–10%), by diffuse small fissuring observed on the sample and by X-ray diffractometries (Fratolocchi et al., 2013).

With reference to the performance of the special mixtures, it was found that their excellent performance in water is maintained with the K_2SO_4 solutions, notwithstanding the high SO_4^{2-} concentration, due to the very low k values of the mixtures at brief curing which strongly reduced the pore volumes of flow through the samples (Fratolocchi et al., 2013; 2020).

Fig. 14 shows the results of the permeation tests on samples of the SA mixture with tap water and with the K_2SO_4 solution at the inlet constant concentration of 30 g/l. The values of k are plotted as a function of curing time to take into consideration the effect of the cement hydration as the permeation with the K_2SO_4 solution goes on.

A fluctuating trend of k with time is observed with k values that are significantly lower than the k values measured in water and tend to them in the long term. This test has been dismantled after almost 600 days of permeation when

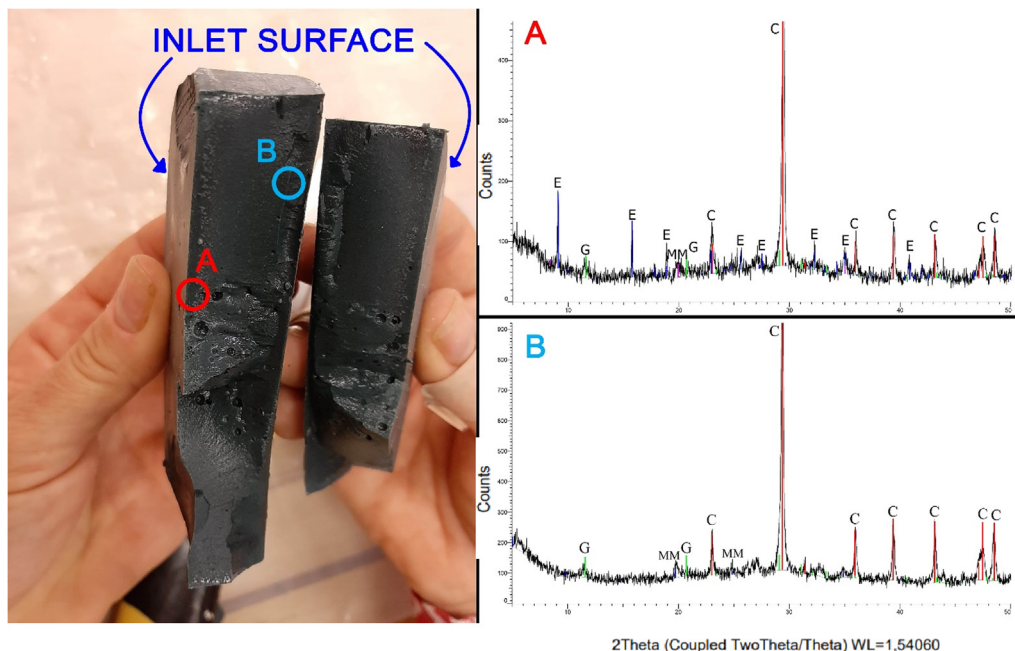


Fig. 15. Image of the SA sample dismantled after permeation with the solution of K_2SO_4 at $C = 30$ g/l (Fig. 14) and XRD diffractograms on portions of the sample taken close to the inlet and effluent surfaces (C = calcite; E = ettringite; G = gypsum; MM = montmorillonite).

the relative effluent concentration was about 0.05 for both ions and the number of pore volumes of flow was 0.6, to analyse the micro and macrostructure of the sample. The sample appeared intact in color and consistency, without any visual trace of deleterious interaction (Fig. 15). Small portions of the sample were taken close to the inlet and the effluent surfaces for XRD analyses and SEM observations.

The XRD analyses revealed the presence of gypsum and ettringite in the portions close to the inlet surface, whereas only gypsum was detected close to the effluent surface (Fig. 15). The SEM observations show that ettringite crystals are found at fissures (Fig. 16) and that fissures are of dimension < 1 mm.

The k trend with time of the sample of concern and the results of XRD and SEM analyses confirm that, as for the CB mixture permeated with a solution of similar concentration of K_2SO_4 (Fratalocchi et al., 2013; 2020), the inter-

action mechanisms in the SA mixture are progressive through the sample: the dissociation of calcium hydroxide (confirmed by $pH \sim 12$ measured in the effluent) and the consequent precipitation of gypsum (Eq. (4)) clog the mixture pores and contribute to the reduction of the hydraulic conductivity with time. The effect of clogging on k tends to decrease as ettringite crystals are produced through the sample due to a progressive fissuring. The fluctuating trend of k may be ascribed to the growth of ettringite crystals which reduce the effective porosity of the fissures created by themselves. Unlike the CB mixture (Fratalocchi et al., 2020), such expansive reaction is not able to definitely invert the hydraulic conductivity trend with time due to the very low k values of the SA mixture (which implies very low pore volumes of flow). Further investigations are ongoing to understand the influence of the mixture composition and strength characteristics on the development of ettringite crystals and on their effect on k .

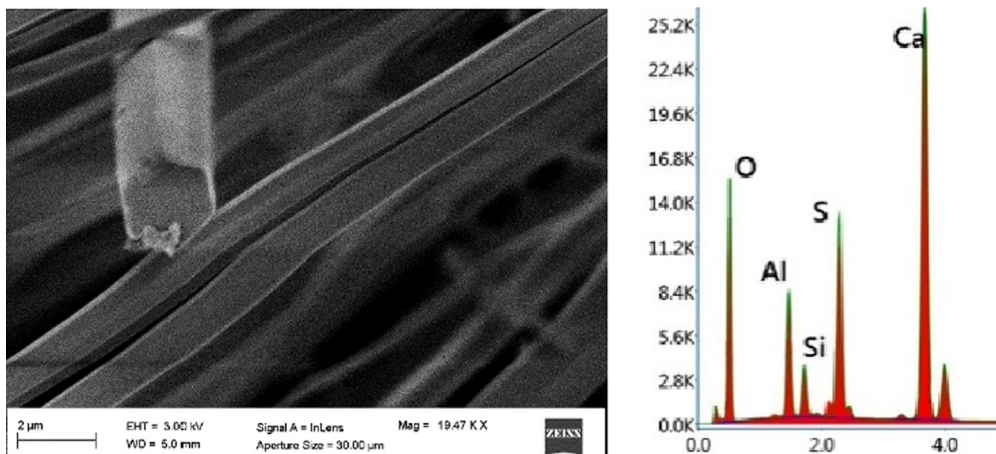
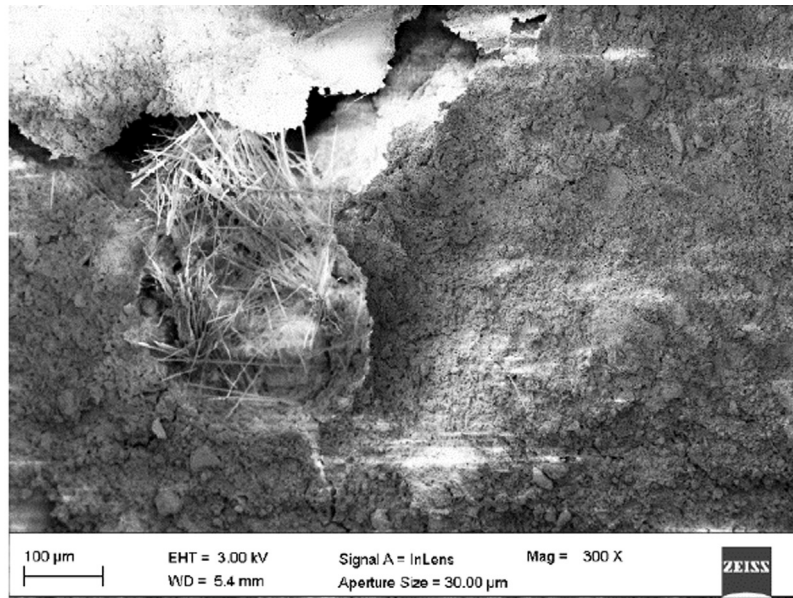


Fig. 16. SEM images with detail of an ettringite crystal in the portion of the SA sample taken close to the inlet surface (point A in Fig. 15) after almost 600 days of permeation with the solution of K_2SO_4 at $C = 30$ g/l.

4. Conclusions

The results discussed in the present paper allow to conclude that permeation of cement-bentonite mixtures with aqueous sulphate solutions can adversely affect their hydraulic performance depending on sulphate concentration and mixture composition. Interaction with sulphate was found to give an initial decrease in the hydraulic conductivity, with k values that can be significantly lower than those in water, followed by increasing k . Permeation with sulphate solutions results in a progressive formation of gypsum, causing pore clogging, and ettringite able to produce swelling and fissuring depending on the mixture composition and porosity. Both reactions are the responsible for the k trend with time. From a practical point of view this means that the hydraulic performance of a mixture in the design phase of a cut-off wall subjected to a sulphatic groundwater cannot be determined by permeation tests performed on the basis of the possible pollutant flow rate through the cut-off because unsafe results can be obtained. The flow rate should be increased for the reaction front to fully migrate through the sample even if long term permeation tests can still be necessary, depending on the sulphate concentration and the mixture composition.

The mixture composition was found to be fundamental to retard the effect of the negative interaction with sulphate on the hydraulic conductivity: the lower the mixture porosity and therefore the hydraulic conductivity at brief curing (i.e., the higher the solid/water ratio in the mixture), the better the hydraulic performance in sulphate solutions.

With reference to the solutions investigated, sorption isotherms of K^+ from batch tests (with the specific preparation procedure set-up for cement-bentonite samples) were found in good agreement with those resulting from mass balance of permeation tests (which better simulate the in-situ migration conditions), up to equilibrium concentrations of about 20 g/l.

Sorption of K^+ was found to be significant and modellable by a linear isotherm within a range of equilibrium concentrations of at least 15 g/l. The k_d values resulted nearly constant with curing and dependent on the chemical composition of the cement in the mixture. The k_d values of the traditional CB mixture resulted in the range of about 4–5 ml/g for curing times ranging from 14 days to 1.5 year. The k_d values of the special mixtures resulted of 20–35% higher than that of the traditional mixture. From a practical point of view, the results concerning sorption of K^+ demonstrate that: a) sorption should be considered in analyzing migration of K^+ through cement-bentonite cut-off; b) sorption can be conveniently modelled by a linear isotherm; c) k_d can be usefully determined by batch tests performed at brief curing; d) a constant value can be assumed with time to model migration in column testing or through cutoffs.

Sorption of SO_4^{2-} resulted due to the formation of gypsum and ettringite as a consequence of the reaction with the cement hydrated products. It was found to significantly increase with the sulphate concentration in solution, with a

concave down trend, up to concentrations of the order of tens of g/l.

Sorption of sulphate, dependent on the chemical composition of the cement in the mixtures, was found to decrease with the mixture porosity, concentration of sulphate in solution being equal. Since sorption of SO_4^{2-} means negative interaction in terms of hydraulic conductivity, the results from batch tests, performed at brief curing time, turned out to be useful in design practice to assess the reactivity of different cement-bentonite mixtures in order to select the less reactive one, on which the permeation test will be performed.

All the results point out the importance of selecting a mixture to be used for cut-off walls with a low hydraulic conductivity already at brief curing and of carefully considering its sorption capacity.

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