Migration parameters and interaction of saline solutions through cement-bentonite cutoffs

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ABSTRACT

The paper discusses the results of an experimental research on hydraulic conductivity, sorption, diffusion and long-term performance of cement-bentonite mixtures in saline sulphate solutions as a function of their composition and curing time. The results show that permeation with solutions of K₂SO₄ can adversely affects the hydraulic performance of cement-bentonite mixtures depending on sulphate concentration and mixture composition. Choosing a very low permeable mixture at brief curing time is essential to limit adverse effects of interaction with SO₄²⁻ on the hydraulic performance. Linear isotherms were found to model sorption of K⁺, with distribution coefficients resulted not to be significantly influenced with curing, allowing testing, usefully and safely, at brief curing. Values of the distribution coefficient in the range of those of cement paste were obtained. On the contrary, diffusion coefficients of K⁺ and of SO₄²⁻ higher than those documented in the literature for cement pastes were found. In designing cut-off walls the results point out the importance of selecting a mixture with very low hydraulic conductivity values at brief curing and of considering its specific diffusion coefficients, as well as interaction and sorption capacity.

Keywords: cement-bentonite, sulphate, potassium, migration, interaction

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 waste landfills with improper or failed barriers. To limit the advective flux a low hydraulic conductivity, k, is mandatory (typically k ≤ 10⁻⁹ m/s), to be maintained for all 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 provided that it does not imply deleterious interaction with the cut-off wall material.

Much literature dealt with hydraulic conductivity of traditional cement-bentonite mixtures (e.g. Manassero et al., 1995; Opdyke and Evans, 2005; Jefferies, 2012), whereas few data and researches are documented about diffusion (Visumdenanukul et al., 2007; Fratalocchi et al., 2013), sorption and chemical interaction (e.g. Jefferis, 2003; Soga and Joshi, 2010; Soga et al., 2013). As a consequence, effective diffusion coefficients of the order of 10⁻¹⁰ m²/s and no sorption capacity are typically assumed in designing self-hardening cut-offs.

The Authors have been performing a research to study the hydraulic performance and migration parameters of traditional and special cement-bentonite mixtures with low hydraulic conductivity already at brief curing (k < 10⁻⁹ m/s at 1-2 months). In particular, the research is aimed at investigating the diffusion coefficient (the diffusive flux is predominant with very low k), sorption and interaction of cement-bentonite mixtures with saline sulphate solutions (potentially dangerous for cementitious mixtures), typically found in soils and groundwaters polluted by fertilizers, or in by-product landfills, marine environment, etc.

The paper is focused on the results concerning mainly the hydraulic performance, interaction and sorption capacity of different cementitious mixtures, as a function of their composition and concentrations of saline sulphate solutions.

2 MATERIALS AND TESTING METHODS

2.1 Mixtures and testing solutions

A traditional cement-bentonite (CB) mixture and two special patented mixtures (Buzzi Unicem S.p.A., Italy) were investigated. The composition of the special mixtures (SA, SB) includes blast furnace slag, Portland cement, activated sodium bentonite and clayey fillers, in different proportions; the solid to water ratio is 0.33.

The CB mixture consists of activated sodium bentonite (bentonite to water ratio = 0.045), slag cement (70% of slag), selected to get low hydraulic conductivity in the short and long term; the cement to water ratio is 0.22. The CB mixture was prepared in the laboratory according to the procedures in ETC8 (1993).

The special mixtures were prepared adding the
ready-made powder to tap water and mixing by a rotary mixer at 5000 rpm for 5 minutes. Both the CB mixture and the special ones match the practical requirements (Table 1). The mixtures were poured in PVC cylindrical moulds (prepared to avoid sample disturbance during extraction, Fratalocchi et al., 2013) and stored under tap water until the curing time of testing.

The testing solutions were tap water for the hydraulic conductivity tests and aqueous solutions of K$_2$SO$_4$, resulted almost neutral (pH in the range of 6.8-7.3, increasing with the concentration of K$_2$SO$_4$).

Table 1. Composition and main properties of the investigated mixtures at the fluid state (Pr. Req. = practice requirement).

| Mixture | solid/water | Marsh viscosity (s) | Bleeding (%) | Unit weight (kn/m$^3$) |
|---------|-------------|---------------------|--------------|-----------------------|
| CB   | 0.27        | 49                  | 1.0          | 11.5                  |
| SA   | 0.33        | 43                  | 1.5          | 11.8                  |
| SB   | 0.33        | 49                  | 0.5          | 11.8                  |
| Pr. Req. | < 60        | ≤ 2                 |              | 11.3–12.2             |

2.2 Testing

The mixtures sorption capacity was analysed by batch-adsorption tests, frequently used to assess the capacity of barrier materials to remove chemicals from solutions. Solutions of K$_2$SO$_4$ at the concentration of 1, 2, 5, 15 and 30 g/l were used. Samples were tested at curing times ranging from 7 days to about 1.5 years.

The cemented nature of the mixtures required a specific preparation of the samples. At a given curing time, each sample was crumbled to pass the 2 mm sieve and tested as such (not dried) to be representative of its actual composition, considering the role of water in reaction and sorption behavior of a cemented material. The ASTM D4646-16 was followed except for the sorbent to solution ratio, equal to 1:10 instead of 1:20, due to technical need. Tests were performed to verify that this choice would not influence the results (§ 3.2). A contact time of at least 48 hours was guaranteed for chemical equilibrium (Fratalocchi et al., 2013). The adsorbed mass, $m_a$, was calculated as the difference between the initial and final mass of solute in solution, the adsorption ratio, $S$, as the ratio between $m_a$ and the dry mass of the sample, $m_d$.

Hydraulic conductivity tests were performed in flexible wall permeameters (effective confining pressure of 40 kPa on average across each sample) with tap water (TW) and K$_2$SO$_4$ solutions at different concentrations. The sample volumetric strains were monitored during each test. Bladder accumulators were used for column testing to store the inlet solution (at constant concentration) and collect the effluent one. Constant head tests were performed under a hydraulic gradient ranging from 25 to about 300 (increased during the same test). The effluent solution was periodically sampled for concentration measures to get the breakthrough curve and check chemical equilibrium through the sample. The number of pore volumes of flow, PV, was calculated assuming porosity equal to 0.5 for the SA and SB samples and 0.6 for the CB one.

3 RESULTS AND DISCUSSION

3.1 Hydraulic conductivity

All the mixtures match the requirement of $k < 1 \times 10^{-8}$ m/s at brief curing (Fig. 1). Due to their higher solid content, SA and SB mixtures exhibit a better hydraulic performance than that of the CB mixture: $k$ values $< 1 \times 10^{-10}$ m/s are reached after just 1 month of curing. Such very low $k$ values at brief curing are fundamental to reduce the risk of negative interaction with the pollutant to be confined, that is, to get a good resistance against chemical attack. Without negative reactions, $k$ values of the order of $10^{-11}$ m/s or lower make the advective flow negligible, even for hydraulic gradients of the order of 10 (or more).

All the mixtures exhibit the typical significant reduction in $k$ with curing, due to the cement hydration which reduces the mixture porosity and the mean size of pores; therefore, increasing cement content not only lowers $k$ at any curing time, but also makes reduction of $k$ faster with time (Fratalocchi and Pasqualini, 2007).

To analyse the different decreasing gradient of $k$ with curing (Fig.1), the equation proposed by Fratalocchi (1996) and ICE et al. (1999), validated for several types of mixtures until about 1 year of curing (Fratalocchi and Pasqualini, 2007), can be used:

$$k = k(t/t_r)^\alpha$$

(1)

where $k$, is the $k$ value at a given curing time, $t_r$, and $\alpha$ [-] expresses the reduction of $k$ with curing, that was found to depend on the cement type and the cement/water ratio (Fratalocchi and Pasqualini, 2007). The $\alpha$ values resulting by fitting the measured $k$ value with time for the mixtures investigated (Fig. 1) reveal a higher cement content in the special mixtures (Fig. 2) respect to the CB one. The SB mixture is supposed to have a bentonite or clayey filler content greater than SA since it is less permeable (Fig. 1).

Fig. 1. Hydraulic conductivity in water measured on the mixtures investigated and fitted by eq. (1) with $t_r = 1$ day.
3.2 Sorption

Sorption is here considered as the overall mechanism removing contaminant from solution, including cation exchange, precipitation, adsorption and in general any binding between solutes and the solid matrix.

With reference to the solid to water ratio used in the present study (1:10 for most of tests), the batch tests repeated on the same sample with the solid:water ratio = 1:20 (ASTM D4646-16) demonstrated that there is no difference on the sorption capacity (Fig. 3), confirming the reliability of testing with the solid:water ratio = 1:10, more convenient from a practical point of view.

It is important to point out that, for CB mixtures, the sorption isotherms of K\(^+\) and SO\(_4\)\(^2-\) from batch tests were found to be in good agreement with the sorption isotherms by column tests (Fratalocchi et al., 2013) which better simulate the in situ migration conditions.

Fig. 4 shows the batch test results of sorption of K\(^+\) by the mixtures at different curing times. The potassium sorption is always well modelled by a linear isotherm:

\[
S = k_d C
\]  
(4)

with: \(S\) = equilibrium solute concentration [ML\(^{-3}\)], \(k_d\) = distribution coefficient [L\(^3\)M\(^{-1}\)]. The linear isotherm was found to well reproduces sorption of K\(^+\) on cement pastes, too (e.g. Hong and Glasser, 1999), with \(k_d\) values of 0.5 – 6.0 ml/g, depending on the Ca/Si ratio in the cement. The \(k_d\) values of the tested mixtures result in the range of about 3.5-5.5 ml/g corresponding to Ca/Si ratios typical of blended cements, such as the slag cement of the mixtures investigated. As for cement pastes, the main sorption mechanism of K\(^+\) on the mixtures can be considered at the CSH and/or CASH phases. Sorption of K\(^+\) by bentonite is negligible: considering its mass (< 20% of the total solid mass), cation exchange capacity (supposed = 70 meq/100g), even if only K\(^+\) is adsorbed, the K\(^+\) mass adsorbed by the bentonite results less than 10% of the overall K\(^+\) mass absorbed by the mixture.

Fig. 5 compares the \(k_d\) values of the three mixtures as a function of curing time. For the CB mixture, the potassium sorption capacity tends to slightly increase with curing, consistently with the sorption mechanisms related to the CSH and CASH phases documented for cement pastes (e.g. Hong and Glasser, 1999). The potassium sorption capacity of SA and SB mixtures is not appreciably influenced by curing and is higher than that of the CB mixture at brief and medium times of curing. The greater cement to water ratio of the special mixtures is likely the reason for this performance.

The \(k_d\) trend with curing time in Fig. 5 demonstrates that for all the mixture investigated sorption capacity can be determined at brief curing to safely analyze the potassium migration through a cut-off wall. Simulations of migration through a cut-off made of the different mixtures investigated (Fratalocchi et al., 2019) showed the importance of considering the sorption capacity to optimize the design of a cut-off wall.

Fig. 2. Coefficient of reduction of k with time (\(\alpha\) in eq. 1) vs cement/water ratio for IIIB slag cements (slag content 66-80%).

Fig. 3. Batch sorption tests on the special mixtures SA and SB for different solid:water ratio and curing times (in the legends).
Sorption of SO$_4^{2-}$ can be assumed to be related only to cement and essentially due to gypsum formation:

$$\text{Ca(OH)}_2 + \text{SO}_4^{2-} + 2\text{H}_2\text{O} \rightarrow \text{CaSO}_4\cdot 2\text{H}_2\text{O} + 2\text{OH}^- \quad (2)$$

and to reactions mainly involving gypsum, tricalcium aluminate, tricalcium aluminate monosulphate or the hydrated phases of tricalcium aluminate, e.g. C$_3$AH$_6$ (H=H$_2$O), that give rise to ettringite:

$$\text{C}_3\text{AH}_6 + 3\text{Ca}^{2+} + 3\text{SO}_4^{2-} + 26\text{H}_2\text{O} \rightarrow >\text{C}_3\text{A}.3\text{CaSO}_4.32\text{H}_2\text{O} \quad (3)$$

Fig. 6 shows the sulphate batch test results at different curing times fitted by the Freundlich isotherm:

$$S = k_f C^\varepsilon \quad (5)$$

where $k_f$ [L$^3$M$^{-1}$] and $\varepsilon$ [-] are constant. For the CB mixture, sorption of SO$_4^{2-}$ decreases with curing, due to the decrease in porosity and in the mean void size of the mixtures (sorption sites tend to be less accessible with curing; Fratalocchi et al., 2013). For the same reason, sorption of SO$_4^{2-}$ by the special mixtures results lower than that of the CB mixture and independent of the curing time (Fig. 6). The low sulphate sorption of the special mixtures means that minor interaction occurs with sulphate, as confirmed by the column test results discussed in the following.

### 3.3 Hydraulic performance with sulphate solutions

A deleterious effect on the $k$ values of the mixtures was expected due to the high sulphate concentrations investigated ($K_2\text{SO}_4$, $C = 5$ to 30 g/l), according to eq. 2 and subsequent deleterious reactions producing ettringite (eq. 3). Fig. 7 shows the results on samples of the CB mixture permeated with $K_2\text{SO}_4$ solutions at $C = 5$ g/l and 27.5 g/l. With the most concentrated solution, the mixture initially exhibits a fast decrease of $k$, with values that are one order of magnitude lower than those in water; after ~2 months of curing (~1.5 PV), $k$ rapidly increases to values of the order of $10^{-8}$ m/s.
The CB sample permeated with the K$_2$SO$_4$ solution at $C = 5$ g/l results in a $k$ trend with curing that is qualitatively like that with $C = 27.5$ g/l: an initial decreasing trend, but here with a lower reduction gradient of $k$ with time, followed by an increasing trend. The minimum $k$ value (the same in both tests, $2 \times 10^{-10}$ m/s) is reached at longer curing, after ~17 PV. In both tests, the increase in $k$ corresponds to the increase in the effluent sulphate concentration (Fig. 8).

The results in Fig. 7 can be explained considering the progressive interaction mechanisms through the samples, as discussed in Fratalocchi et al., 2013: the initial dissociation of Ca(OH)$_2$ (confirmed by the pH of the effluent solution = 12-12.4) and precipitation of gypsum cause pores clogging that contributes to the decreasing in $k$ with time. Clogging effect becomes negligible as expansive reactions start (and ettringite is produced), 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 (Fratalocchi et al., 2013).

The breakthrough curves of potassium and sulphate in Fig. 8 show a higher retardation of SO$_4^{2-}$ relative to K$^+$, due to the reactions to form gypsum and ettringite. The delay of the sulphate breakthrough curve respect to the K$^+$ one is more noteworthy in the case of the lower inlet concentration because the mixture-sulphate interaction has not yet significantly changed the sample macrostructure.

Due to the fissuring produced by the sulphate-mixture interaction, the evaluation of the effective diffusion coefficient, $D^*$, could be properly done only for potassium at the lowest concentration, for which no significant microstructure modifications can be supposed in correspondence of the K$^+$ breakthrough curve as the hydraulic conductivity values were close to those with water (Fig. 7). The K$^+$ experimental breakthrough curve was fitted by the POLLUTE.v7 program able to solve the one-dimensional contaminant migration equation with time varying properties. Details on assumptions for modeling (boundary conditions, flow rates and parameters) are given in...
Fratalocchi et al. (2013). The best fitting curve was obtained with: \( k_d = 4 \text{ ml/g} \), \( \alpha_L = 0.1 \cdot L \) (\( L \) = sample thickness) and \( D^* = 2 \times 10^{-10} \text{ m}^2/\text{s} \) (Fig. 9). Values of \( D^* \) of the order of \( 10^{-11} \text{ m}^2/\text{s} \), typical for diffusion of K\(^+\) through cement pastes (e.g. Alonso et al., 2001), was not found to give a good fitting. The reasons can be found in the greater porosity of a CB mixture compared with a cement paste and the presence of bentonite for which values of \( D^* \) for K\(^+\) are documented of the same order of magnitude (e.g. Malusis et al., 2013).

As observed on the CB sample permeated with the highest concentrated solution (Fig. 7), also for the special mixtures a more rapid decrease in \( k \) occurs than in the case of water (Fig. 9). Also in these mixtures a progressive clogging effect due to gypsum formation is supposed to occur, with possible increase of \( k \) at longer curing. To this regard, since the sulphate content at the effluent starts to increase before the increase in \( k \) (Fig. 8), it is important to point out that in the tests of Fig. 9 the effluent concentration of K\(_2\)SO\(_4\) resulted always zero. Since an increase in \( k \) could occur at longer times, the column tests on the SA and SB samples with the K\(_2\)SO\(_4\) concentration of 30 g/l are still going on, also to get the breakthrough curve for \( D^* \) evaluation.

Both samples of the special mixtures permeated with the K\(_2\)SO\(_4\) solution at \( C = 15 \text{ g/l} \) were dismantled and cut, to continue the test on the portion of the sample close to the inlet line, in order to increase the PV with time and verify in a shorter time any increase in the \( k \) value (tests just started). Both parts of the two samples appeared intact in color and consistency, without any trace of deleterious interaction. The remaining parts of the samples, analysed by X-ray diffraction, resulted identical to the composition of the sample of the corresponding mixture stored in water for the same curing time. No ettringite was detected. These observations, consistent with the effluent concentration equal to zero and absence of volume change, confirm the absence of interaction in the down-flow part of the samples and will be very useful in interpreting the future test results of the re-permeated sample portions.

From a practical point of view, the result points out that values of \( D^* \) of cement pastes cannot be used for CB mixtures because they can give unsafe prediction of potassium migration.

With reference to the performance of the special mixtures, Fig. 9 shows the \( k \) values with curing time of samples of SA and SB mixtures, permeated with K\(_2\)SO\(_4\) solution at \( C = 15 \text{ g/l} \) and 30 g/l, together with the relevant \( k \) values in water. The excellent performance of both mixtures in water is maintained with the solutions, notwithstanding the high SO\(_4^{2-}\) concentrations. The very low \( k \) values of the mixtures at brief curing (\( 10^{-9} - 10^{-10} \text{ m/s at 30 days} \)) strongly reduced the pore volumes of flow through the samples. As a consequence, under high hydraulic gradients for about one year, only 0.5 PV and 0.4 PV passed through the SA and SB samples, respectively, permeated with the saline solution at \( C = 30 \text{ g/l} \). No appreciable change in volume of the samples was measured during the tests, confirming none or negligible negative interaction with sulphate.

![Fig. 8. CB mixture: hydraulic conductivity and breakthrough curves with K\(_2\)SO\(_4\) solutions at the concentration of 5 g/l (a) and 27.5 g/l (b) (Fratalocchi et al., 2013).](image)

![Fig. 9. Hydraulic conductivity vs curing time of the SA and SB mixtures permeated with tap water (TW) and with K\(_2\)SO\(_4\) solutions at the concentration of 15 g/l and 30 g/l.](image)
4 CONCLUSIONS

The results allow to state that permeation with aqueous solutions of K$_2$SO$_4$ can adversely affects the hydraulic performance of cement-bentonite mixtures depending on sulphate concentration and mixture composition. Interaction with sulphate was found to give an initial decrease in the hydraulic conductivity, with values that can be lower than those in water, followed by an increase in $k$, that occurs after a number of $PV$ that is lower the higher the sulphate concentration in solution and that depends on the mixture composition. Gypsum formation (causing pore clogging) and ettringite formation (causing swelling and fissuring) are the main responsible for these trends, respectively. From a practical point of view this means that the evaluation of hydraulic performance of a mixture in the design phase requires permeation testing times to be determined on the basis of the cut-off hydraulic boundary conditions and the possible pollutant flow rate through the cut-off, otherwise unsafe results can be obtained.

The choice of a mixture having a very low hydraulic conductivity at brief curing is fundamental to reduce adverse effects on $k$ due to interaction with sulphate. In particular, the two special mixtures investigated showed no interaction with sulphate, resulting in very low $k$ values even after about one year of continuous permeation, under very high hydraulic gradients, with solution of sulphate at the inlet constant concentration of 15.2 g/l. The higher resistance of the special mixtures against sulphate attack was confirmed by the batch sorption test results, which showed a sorption capacity, i.e. reaction with sulphate, lower than that of the traditional CB mixture investigated.

For the three mixtures investigated, sorption of K$^+$ was found to be significant and well described by a linear isotherm for any curing time. The distribution coefficients resulted not to be appreciably influenced (or slightly increasing) by curing, allowing testing, usefully and safely, at brief curing times. Values of the distribution coefficient in the range of those documented in the literature of cement pastes were always obtained.

The Freundlich isotherm was found to model sorption of sulphates. Sorption (interaction) of sulphate by the CB mixture tends to decrease with curing, whereas no significant variation was detected for the special mixtures. This means that the curing time can be beneficial for durability since a mixture can become less reactive to sulphate, depending on its composition. This implies that batch sorption tests performed at brief curing give safe results both for SO$_4^{2-}$ and K$^+$.

The diffusion coefficient of K$^+$ through the CB mixture, $D^* = 2 \times 10^{-10}$ m$^2$/s, is of one order of magnitude greater than the values documented for cement pastes; therefore, using $D^*$ values taken from the literature of cement pastes may lead to unsafe prediction of potassium migration through CB mixtures.

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 considering its specific diffusion coefficient and sorption capacity.

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