Long term performance of cement-bentonite cut-offs in saline and acidic solutions

Perméabilité à long terme des parois ciment-bentonite en solutions acides et salines

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ABSTRACT: The paper presents the results of a research aimed at evaluating and predicting the long term performance of CB mixtures in terms of hydraulic conductivity, k. A low k value is the necessary (even if not sufficient) requirement for a cut-off wall to isolate polluted sites. Aqueous sulphate solutions of different nature (acidic, saline) and concentrations were used as permeants in column tests performed for long time (one year or more) in order that full effects of physical and chemical reactions may occur. Results of these tests are here analysed mainly with the aim to find a criterion to predict how long a cement-bentonite cut-off wall can keep a proper hydraulic performance.

RÉSUMÉ: L'article présente les résultats d'une recherche ayant pour objectifs l'évaluation et la prévision de la perméabilité (k) à long terme des mélanges ciment-bentonite (CB). Une perméabilité faible est une condition nécessaire (bien que non suffisante) pour jouer le rôle d'écran de confinement sur les sites pollués. On a utilisé des solutions aqueuses de sulfates de différents natures (acide, saline) et concentrations dans des essais d'infiltration de longue durée (une année voire plus), pour s'assurer du développement complet des interactions chimiques and physiques. Les résultats de ces essais sont analysés avec l'objectif principal de trouver un critère pour prévoir les performances hydrauliques à long terme des parois en ciment-bentonite.

KEYWORDS: cut-off, acid, sulphate, cement-bentonite

1 INTRODUCTION

Few data are available in literature on the long term performance and durability of cement-bentonite (CB) cut-off walls (e.g. Jefferis 1992, 1993; Jefferis and Fernandez 2000; Fratalocchi et al. 2006, 2010) although this kind of vertical barriers (single or composite with geomembrane sheets) is frequently used to isolate polluted soils and groundwater (e.g. Manassero et al. 1995).

The authors are being performing a research aimed at evaluating and predicting the long term performance of CB mixtures in terms of hydraulic conductivity, k. A low k value is indeed the necessary (even if not sufficient) requirement for a cut-off wall to isolate polluted sites. Aqueous sulphate solutions of different nature (acidic, saline) and concentrations were used as permeants in column tests performed for long time (one year or more) in order that full effects of physical and chemical reactions may occur. Results of these tests are here analysed mainly with the aim to find a criterion to predict how long a cement-bentonite cut-off wall can keep a proper hydraulic conductivity.

2 MATERIALS AND TESTING METHODS

The CB mixture was selected in order to get a good hydraulic performance when permeated with water. To this purpose blast furnace slag cement was chosen (70% slag) as well as Na-bentonite (activated) and a special additive. The mix design is: cement/water = 0.22, bentonite/water = 0.0456, additive = 2 l/m^3 of mixture. Details on the mixing and sampling procedures are given in Fratalocchi et al. (2010). Typical values of density (11.4 kN/m^3), Marsh viscosity (50 s) and bleeding (1.0%) were obtained on the mixture at the fluid state, according to the practice requirements.

After a curing time of 10-14 days, each sample was permeated with a different saline or acidic solution of K_2SO_4 or H_2SO_4. Details of the permeant solutions are given in Table 1. The thickness of all the samples was in the range of 3.0-5.7 cm except two samples permeated with the same less concentrated acidic solution (sample A was 9.0 thick, sample B was 2.2 thick).

Flexible wall permeameters with bladder accumulators were used in order to control the effective confining pressure (40 kPa), the sample volumetric strains and to collect the effluent liquid. Constant head test were performed at hydraulic gradient, i, ranging from 25 to 100. Samples of the effluent liquid were periodically taken for concentration measurements to get the breakthrough curve (Fratalocchi et al. 2010; Brianzoni 2012) and to know the starting time at which the pore liquid fully consists of the inlet liquid. Permeation was kept for long time (months up to almost 2 years) in order to verify the long term performance.

Table 1. Main data of the permeant solutions

Solution	SO_4^{2-} (mg/l)	pH
K_2SO_4 (5.0)	2756	6.8
K_2SO_4 (27.5)	15159	7.0
K_2SO_4 (50)	27562	7.3
K_2SO_4 (95)	52368	8.0
H_2SO_4 (1.0)	9789	1.0
H_2SO_4 (1.5)	1176	1.5
H_2SO_4 (2.0)	310	2.0

3 RESULTS

Figure 1 shows the hydraulic conductivity trend over time of the mixture permeated with the salt solutions of K_2SO_4 at different concentrations together with the k trend of the same mixture permeated with water. With reference to the performance in water, the mixture shows the decrease of k with time typical of the well selected CB mixtures: k values of the order of 10^{-8} cm/s can be reached just after two months of curing. The reduction of k is significant during the first year of curing.

As far as the hydraulic conductivity with the salt solutions is concerned, each sample shows an initial decrease in the k value (no effluent SO_4^{2-} concentration were detected in this period), followed by an increasing hydraulic conductivity. Finally an almost constant trend of hydraulic conductivity with curing time occurs with the effluent SO_4^{2-} concentration that was measured to be equal to the inlet one. From Figure 2 it is also evident that the rate of reduction or increase of k with time depends on the permeant concentration: the higher the concentration, the faster the reduction and the successive increase in the k value with time, as well as the shorter the curing time at which the inversion of the k trend occurs. The reduction in the hydraulic conductivity exibited by the mixture during the first month of curing is equal or even higher than that of the mixture permeated with water. Significant (increasing) concentrations of SO_4^{2-} were measured at the effluent only when the k values increase with time; this transient phase lasted when the k values starts to be constant with time (Fratalocchi et al. 2010; Brianzoni, 2012).

In order to explain the results of Figure 1 it is necessary to consider the reactions occurring between sulphates and cementitious materials. Sulphate attack initially develops from the reation between SO_4^{2-} and both calcium hydroxite, $Ca(OH)_2$, and (partially) calcium hydro-silicate, C-S-H, with the consequent precipitation of gypsum ($CaSO_4 2H_2O$) and release of OH^-. The subsequent (damaging) reactions take place between the sulphate and the hydrated calcium alluminate or calcium alluminate monosulphate hydrate (Bensted 1995; Gollop and Taylor, 1992, 1995) to produce ettringite with a consequent expansion.

All the aforesaid interaction mechanisms are progressive through the sample with curing time: the initial gypsum precipitation into the pores (reaction confirmed by the high pH values measued at the effluent, pH = 12-12.4) causes clogging of pores and contributes to the reduction of the hydraulic conductivity with time. This contribution tends to reduce and become negligible as the ettringite starts to form along the reaction front; such an expansive reaction is able to progressively invert the hydraulic conductivity trend with time up to a rapid increase. The expansive reaction of ettringite was confirmed by the increase in volume on the samples equal to 7-10% (Fratalocchi and Pasqualini 2007) and by a net of diffuse fissures observed on the samples at the end of the tests. The fissures give rise to preferential pathways that are responsible of the overall constant value of k (2-3 x 10^{-6} cm/s) at the end of the interaction mechanisms.

Samples of the same mixtures were permeated also with three aqueous solutions of sulphuric acid at different pH (Table 1). Two samples of different thickness (sample A and B) were permeated with the same H_2SO_4 solution (pH = 2.0) in order to evaluate the interaction effect taking into consideration different curing time. Figure 2 shows the hydraulic conductivity trends over time of all the samples. It is evident that the hydraulic conductivity trends versus time are similar to those measured on the samples permeated with the salt solutions. The main chemical reactions are indeed the same, with the addition of the dissolution of the cement hydration products (mainly calcium hydroxide and C-S-H) by the acidic solutions. SO_4^{2-} being equal, the increase in hydraulic conductivity tends to be faster when the mixture is permeated with the acidic solution. This is evident if we compare the k trend of the samples permeated with the salt solution at concentration of SO_4^{2-} of 2756 mg/l and the acidic solution of 1176 mg/l: both samples show a fast decrease followed by an increase of hydraulic conductivity but with the acidic solution the increase in k starts after about 250 days of curing whereas the increase of k occurs much more later (about 520 days) when the CB mixture is permeated with the saline solution, notwithstanding the lower concentration of SO_4^{2-}.

Considering the chemical reactions occurring between the different solutions and the mixture, it is necessary to point out that the overall hydraulic conductivity trend measured on the samples in Figures 1 and 2 depend on the sample thickness and on the flow rate through them. Therefore, in order to define how long the mixture is able to keep a good performance, the curing time cannot be considered as a reference parameter. To this purpose, the pore volume of flow, PV, is an appropriate parameter. Different criteria can be adopted to establish a satisfactory hydraulic performance for the CB mixture: for example, hydraulic conductivity lower than a maximum allowable value, or k lower than the k value measured with water, etc.; among them, the number of pore volumes of flow until k is decreasing, PV*, can be appropriate for the following reasons:

- at brief curing, both for K_2SO_4 and H_2SO_4, whatever concentration, the reduction of k with time is equal or lower than that with water;
- in the long term, if there is no inversion of the k trend with time, low k values can be reached;
- it is not necessary to establish a target k value (that would be related to a particular curing time);
- an increasing k trend with time does not imply a bad performance at least immediately; therefore, the criterion is on the safe side.

Therefore, the number of pore volumes of flow at which the k value stops decreasing (named "critical pore volumes", PV*) was assumed as the reference value for the mixture good performance. This value (calculated assuming a porosity of the mixture equal to 0.6) was related to the concentration of SO_4^{2-} for the different salt and acidic solutions, as shown in Figure 3. Referring to the samples permeated with the acidic solution at pH = 2.0, only the thin one (sample B) showed a stop in decreasing of k after about 49 PV (500 days of curing) whereas the other one (sample A) still shows a decreasing k with time after 850 days of curing (at this time only 4 PV permeated the sample). Therefore, data of sample A could not be considered in Figure 3.

Figure 3 shows that PV* decreases as the sulphate ion concentration increases; the relation is well represented by a bilogarithmic correlation. In particular, for concentrations of the order of g/l or more, that is, in aggressive conditions, the critical number of pore volumes assumes the same trend for both the solutions (saline and acidic). For concentrations of SO_4^{2-} lower than 1 mg/l, data are currently available only for the H_2SO_4 solution; the critical PV* should be lower for the H_2SO_4 solution than that of the salt solution considering its combined deleterious effect due to ettringite formation and dissolution of cement hydration products. Data are necessary to confirm this hypothesis.

Even assuming the criterion of good performance as the PV value until the k trend over time be not increasing (instead of decreasing), the data in Figure 3 would be practically the same except for the data with the lowest concentration of SO_4^{2-} which would have a PV* slightly higher (equal to about 57). It is important to point out that a little increase in PV* means a significant longer lasting for the mixture when the k value is low.

The results in Figure 3 can be useful from the practical point of

view to estimate the durability of a cement-bentonite cut-off wall on the basis of the flow rate through it (i.e. on the basis of the hydraulic boundary conditions and assuming, safely, the minimum hydraulic conductivity value measured at brief curing). Since a high value of PV* results in case of low concentration of SO_4, this means that a good long term performance can be always expected because the hydraulic conductivity values after few months of curing are sufficiently low so that very few pore volumes of flow can pass through a cut-off wall in case of typical hydraulic heads of the order of units.
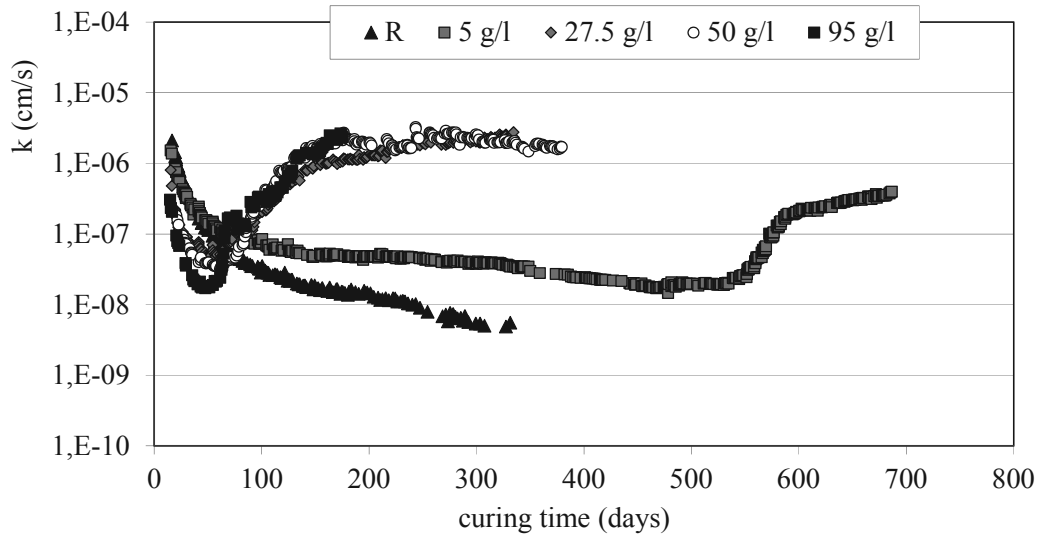

Figure 1. Hydraulic conductivity trend with curing time of the sample of the CB mixture permeated with water (R) and with solutions of K_2SO_4 at different concentrations (in the legend)
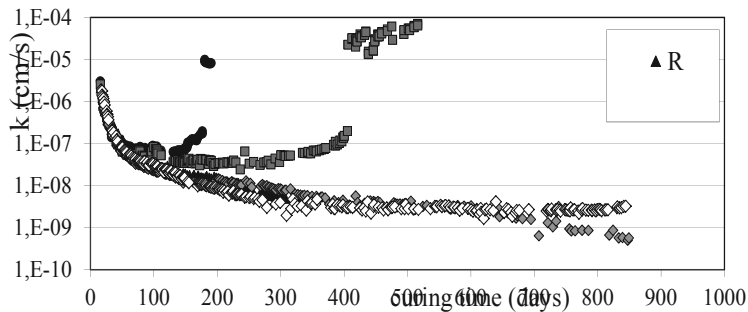

Figure 2. Hydraulic conductivity trend with curing time of the sample of the CB mixture permeated with water (R) and with solutions of H_2SO_4 at different pH (in the legend)
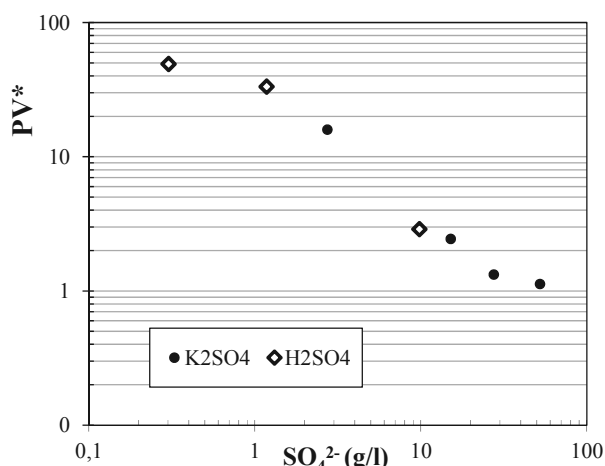
Figure 3. Critical number of pore volumes, PV*, as a function of the SO_4^{2-} concentration in sulphuric acid and potassium sulphate solutions.

4 CONCLUSIONS

On the basis of the available results it is possible to state that aqueous solutions of H_2SO_4 and K_2SO_4 may adversely affect the hydraulic performance of CB mixture depending on SO_4^{2-} concentration and pH. At concentration of the order of g/l or more, both solutions produce an initial decrease in the k value, followed by an increase and finally an almost constant trend of hydraulic conductivity with curing time. Swelling and a dense net of fixtures were detected on the samples after permeation mainly due to ettringite formation, both in samples permeated with the acidic and saline solutions.

The number of pore volumes of flow at which the change in the k trend occurs is greater the higher the SO_4^{2-} concentration. The PV at which this change of trend occurs (PV*) does not seem to be affected by the pH when SO_4^{2-} concentration exceeds 1 g/l.

A correlation between PV* and SO_4^{2-} concentration was found 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. This criterion is on the safe side because it is based on the PV related to the requirement of decreasing k with time: a constant or increasing k with time does not necessarily imply a bad performance, at least immediately. Moreover, the chemical conditions adopted in the tests are not expected to occur continuously in the field if a pumping system is provided so that there is an advective flow of groundwater and not of pollutant across the barrier.

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