Effect of cement-zeolite grouts on the durability of stabilised clays

Effet des mortiers Béton-zéolite sur la durabilité des argiles stabilisés

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ABSTRACT

Although cement-based grouts are widely used in geotechnical and geoenvironmental engineering applications, e.g. for the stabilisation of soft soils, their performance can be adversely affected by exposure to aggressive chemicals. The use of zeolites, which are alumino-silicates with rigid hollow structures, has recently been suggested as a means of enhancing the durability of cement-based grouts especially for sulphate attack. As a result, an experimental study was carried out to verify the potential improvements in the behaviour of cement-based grouts containing zeolites in various aggressive environments. This paper focuses on the durability of soft clays stabilised with cement-bentonite and cement-zeolite grouts and addresses the diversity in their behaviour. The aggressive environments applied included sulphate and acid solutions and freeze/thaw cycles. The impact of the aggressive environment is assessed using the unconfined compressive strength (UCS). The results showed a clear difference in behaviour between the cement-zeolite and cement-bentonite grouts with the former significantly outperforming the latter in their resistance to both sulphate and acid solutions, although the latter still maintained its superior resistance to freeze-thaw cycling. The strength was also generally much higher due to the pozzolanic nature of zeolite and hence also enhanced the UCS compared to cement grouts alone.

RÉSUMÉ

Bien que les mortiers à base –béton soient largement utilisés dans les applications de génie géotechnique et de l'environnement, par exemple pour la stabilisation des sols mous, leur comportement peut être grandement touché par l'exposition aux éléments chimiques agressifs. L'utilisation de zéolite, silicate-alumine avec des structures creuses rigides, a récemment été proposée comme moyen d'augmenter la durabilité des mortiers à base de ciment particulièrement contre l'attaque des sulfates. De là, une étude expérimentale a été menée pour vérifier les améliorations et leur étendues sur le comportement des mortiers à base béton contenant des zéolites dans les différents environnements agressifs. Cet article va se concentrer sur la durabilité des argiles molles stabilisées avec les mortiers béton-bentonite et béton-zéolite et adresse les variations dans leur comportements. Les environnements agressifs comprennent des solutions de sulfate et acide, et des cycles gel-fonte. L'impact de l'environment agressif a été déterminé en utilisant la force de compression libre. Les résultats ont indiqué une nette différence de comportement entre le béton-zéolite et les mortiers béton-bentonite. D'une part le mélange béton-zéolite a significativement mieux résisté aux solutions sulfate et acide (que le mélange béton-bentonite), d'autre part le mélange béton-bentonite a gardé sa résistance supérieure aux cycles gel-fonte. La solidité a généralement été encore plus élevée dû à la nature pozzolonique du zéolite, ce qui signifie qu'il a aussi relevé la force de compression libre en comparaison des mortiers béton seul.

Keywords : Soil Stabilisation, Durability, Zeolite, soft clay

1 INTRODUCTION

Ground improvement by in-situ mixing of clays with wet binders has become a vital technology used in a wide range of geotechnical and geoenvironmental engineering application. The main objectives of mixing a binder with soft clays are to enhance their mechanical properties, e.g. strength, permeability, and to improve their durability by significantly reducing the voids and binding the particles together (Probaha, 2000). The mechanical properties and durability of the stabilised clay are directly dependant on the binder type, its quantity and the mineralogical properties of the clay itself (DGSSS, 2001 and Porbaha, 2000). Cement-based grouts in general and cement-bentonite in particular are the most commonly used grouts for soil stabilisation purposes. However, the use of cement-bentonite grouts, particularly in the presence of extreme aggressive conditions, raises major concerns over their long-term behaviour. It has been documented that the behaviour of cement-bentonite grouts as well as clays stabilised with cement-based grouts can be significantly damaged by the presence of certain chemicals in the soils especially sulphate solutions (Sherwood 1957, Roy et al., 2003, Jefferis 1992 and Garvin & Hayles 1999).

Recently, the use of natural zeolites as partial or total replacement of bentonite in cement-bentonite suspensions for enhancing durability has been advocated in studies such as those conducted by Janotka & Stevula (1998). Zeolites are alumino-silicates similar to clay; however they have a rigid three-dimensional tetrahedral structural framework which is open containing channels and cavities in which cations and water molecules are located (Dyer, 1988), as shown in the schematic diagram in Figure 1. Janotka & Stevula (1998) found that in a 10% sodium sulphate solution, total collapse of the cement-bentonite suspension occurred in 1 month whilst no disintegration took place in the cement-zeolite suspension after 1 year. More recently, Janotka et al. (2003) investigated the resistance of Portland-pozzolan to sulphate attack. The resistance of cement with a zeolite content of 35% and 50% was compared with that of pure cement. Samples were immersed in 5% Na_2SO_4 solution and in reference water for 365 and 720

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days. They were then tested using physical, mechanical and chemical techniques. It was found that blending Portland cement with natural zeolite was useful for enhancing the sulphate resistance of cement. The sulphate resistance of mortar blended with 35% zeolite was greater than that of Portland cement. This was accounted to a significant reduction of sulphate ions binding into the cement matrix and the decreased quantities of CaO^- containing hydration products capable of reacting with the sulphate solution. The incorporation of zeolite as part of cement-based grouts used in soil stabilisation is novel.

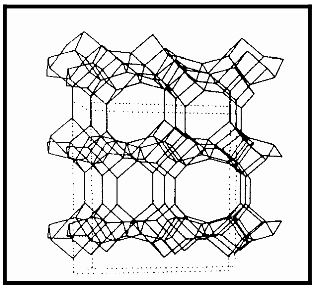


Figure 1. A schematic diagram of the structure of the zeolite Clinoptilolite (Dyer, 1988).

Therefore, an experimental study was carried out to verify the improvements in the behaviour of clays stabilised using cement-based grouts which incorporate zeolite in various aggressive environments. Different cement-based grouts using both zeolite and bentonite were used to stabilise medium stiff and soft clays. The improvement was assessed using the unconfined compressive strength (UCS). The improvement of the mechanical properties of the stabilised clays due to the presence of zeolite in the grout, in the absence of aggressive environments, was discussed elsewhere (Osman & Al-Tabbaa, 2006). This paper will mainly focus on the performance of the stabilised clays in the aggressive environments. Full details of the work presented here can be found in Osman, 2007.

2 EXPERIMENTAL WORK

Polywhite China clay was used to produce a model clay employed in the research and had liquid and plastic limits of 51% and 30% respectively. Two different moisture contents of 50% and 100% were used to produce a medium stiff and very soft clay respectively. Another model clay, more representative of a natural clay, was also modelled using 60% kaolin clay and 40% silt (using silica flour) with a moisture content of 50%. The liquid and plastic limits of this model clay were 40% and 28% respectively. The cement used was Portland cement (PC) (conforming to BS 12) supplied by Rugby cement. The zeolite used was a Clinoptilolite (using Bulgarian Beli Plast). Both natural sodium bentonite (NaB) and calcium Bentonite (CaB) were used. The chemical composition of these materials is shown in Table 1.

Table 1. Chemical composition of the raw materials used.

	PC	*NaB*	*Silt*	*Zeolite*	*CaB*
SiO_2	20	63.6	99.3	65.8	57.0
Al_2O_3	5	21.4	0.34	10.9	23.0
Fe_2O_3	3.7	3.8	0.08	1.6	2.2
Na_2O	0.7	2.7	<0.05	0.8	4.8
CaO	63.3	0.6	<0.02	2.9	1.2
MgO	-	2.0	<0.05	1.1	2.3
K_2O	-	0.3	0.04	3.4	1.2
SO_3	3.0	-		-	-
H_2O	-	-		13.2	-
LOI	-	5.5		-	8.0

Five different grouts were utilised, the details of which are summarised in Table 2. Grout 1 consisted of cement alone. Grouts 2 and 3 are cement-CaB grouts in two different ratios containing 90% and 50% cement respectively. Grout 4 is a cement-NaB grout with the same ratio as grout 2 and grout 5 is a cement-zeolite mix with the same ratio as grout 3. For all those grouts, the water:solid grout ratio used was 1:1. Those grouts were selected based on previous related study on the grouts alone (Osman, 2003). The Marshal Funnel results for these grouts showed similar viscosity of around 33 seconds except for grout 3, which was more viscous. The aggressive environments imposed on the stabilised clay included: sodium sulphate solution (5% w/w Na_2SO_4), sulphuric acid solution (0.5% w/w H_2SO_4) and up to 12 freeze/thaw cycles (freezing temperature of 0° C using the ASTM method D560-96).

Table 2. The constituents of the grouts used.

Grout No	*Grout type*	*Solids*	
1	Cement	100%	
2	Cement-CaB (1)	90% cement	10% CaB
3	Cement-CaB (2)	50% cement	50% CaB
4	Cement-NaB	90% cement	10% NaB
5	Cement-zeolite	50% cement	50% Zeolite

The grouts were mixed with the clay soils in a high power food mixer to produce ten different clay-grout mixes as detailed in Table 3. Most of the mixes were prepared for the 50% water content kaolin clay. Two different soil:grout ratios of 1.5:1 and 3:1 were used. The mixes were then placed in plastic moulds, 50 mm in diameter and 100 mm high. The treated soil specimens were then placed in curing tanks at 20°C and 95% relative humidity. Once the samples developed a sufficient strength, at ~2 weeks, the specimens were demoulded. The control samples which were not subjected to any aggressive environments were tested at 28, 60 and 90 days. The other samples were at 28 days subjected to the aggressive environments. The physical integrity of the mixes while in the aggressive environments was monitored and the samples were removed just before sufficient deterioration occurred which would have prevented their testing. Hence, in some cases, the samples were tested at different ages depending on the duration they survived in the environments. The samples were tested for strength, permeability and microstructure. Duplicate samples were used for the permeability and triplicate samples for the UCS tests. As appropriate, these samples, or parts of these samples, were then placed in their initial environment again to observe further deterioration.

Table 3. The clay-grout mixes.

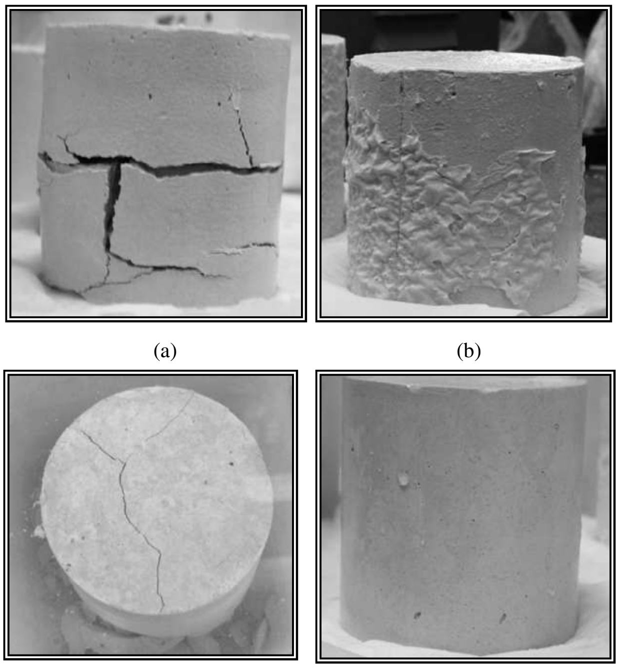
Mix	*Clay composition*	w_c *(%)*	*Grout type*	*Soil:grout ratio*
1	Kaolin	50	Cement	1.5:1
2				3:1
3			Cement-CaB (1)	1.5:1
4				3:1
5			Cement-CaB (2)	1.5:1
6			Cement-NaB	1.5:1
7			Zeolite-cement	1.5:1
8	Kaolin	100	Cement-CaB (1)	3:1
9			Zeolite-cement	3:1
10	Kaolin clay & silt	50	Cement	1.5:1

3 RESULTS AND DISCUSSION

The following sub-sections discuss some of the results obtained for the clay-grout mixes detailed in Table 3.

3.1 *Visual inspection*

The clays stabilised with either cement alone or cement-bentonite were, in general, significantly damaged by the aggressive chemicals with the mode of attack being different for each chemical. The sulphuric acid solutions discoloured, bleached and softened the samples by leaching the hydration products, whilst sodium sulphate solutions produced expansion and cracking. The degree of attack was mainly dependent on the mix proportions, type of grout used and the duration of the exposure. The samples were also vulnerable to freeze/thaw cycles. The attack appeared in the form of surface pop-outs, similar to the effect of freeze/thaw on concrete. Figures 2(a)-(c) show typical photographs after the exposure to the various aggressive environments. On the other hand, mixes 7 and 9, containing zeolite, performed significantly better in the sodium sulphate and acid solutions and all samples remained intact as shown in Figure 2(d) with no signs of cracking or expansion.



(a) (b) (c) (d)

Figure 2. Photographs of some of the mixes: (a) Mix 3 after 55 days in sodium sulphate solution, (b) Mix 8 after 5 days in sulphuric acid solution, (c) Mix 2 after 9 cycles of freeze/thaw cycles and (d) Mix 7 after 1.5 years in sodium sulphate solution

3.2 *Unconfined compressive strength*

The results of mixes 1, 5 and 7 are presented in this section to illustrate the effect of the various aggressive environments on clays stabilised with cement, cement-bentonite and cement-zeolite grouts. Figure 3 shows the results obtained from mix 1 samples subjected to the environments together with the control samples tested at 28, 60 and 90 days. The figure shows reductions in the UCS for samples subjected to the different aggressive environments and in particular the sodium sulphate solution, which led to a UCS decrease of almost 55% after 18 days. Alternatively, the sulphuric acid solution caused a reduction in the UCS of 17% after 18 days. The UCS reduced by around 23% after 7 cycles of freeze/thaw.

Figure 4 presents the UCS results of mix 5 for the three environments along with the control samples. A considerable decrease, of about ten fold in the UCS for the mix subjected to sodium sulphate solution is seen. Mix 5 was found to be the most vulnerable mix to sulphate attack of all the 50% water content stabilised kaolin clay mixes. This can be accounted to two factors: the first is the low cement content in the mix samples thus providing limited tolerance to sulphate attack, and the second factor is the high calcium bentonite content. A reduction of around 40% in the UCS can also be seen in the figure after just 4 days in the sulphuric acid solution, thus suggesting the likelihood of a rapid damage occurring to the mix. On the other hand, following three freeze/thaw cycles, the UCS of mix 5 was not affected. The slight increase in strength could be attributed to the high bentonite content that is resistant to the effects of freeze/thaw cycling.

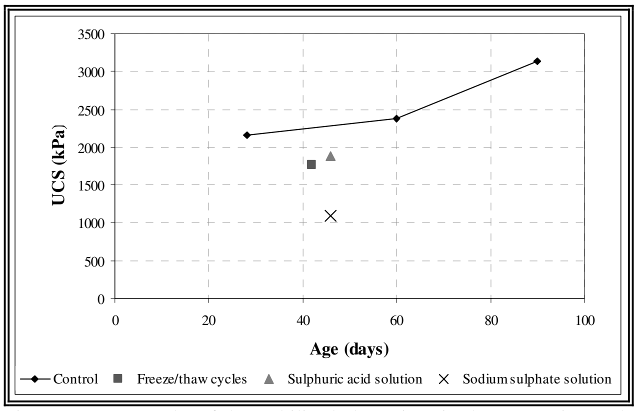


Figure 3. UCS results of the stabilised clay mix 1 in the aggressive and control environments

The UCS results of mix 7 are shown in Figure 5. The UCS of the samples tested after 90 days of exposure to the sodium sulphate solution showed no reduction in strength. These results can be attributed to the presence of zeolite in the soil-cementitious grout mix. As a pozzolanic material, the zeolite consumes the $Ca(OH)_2$ formed during the cement hydration to produce cement-like hydration products. It is known that $Ca(OH)_2$ is essential for expansion reactions (Mitchell, 1986). Therefore, the addition of zeolite reduced the amount of $Ca(OH)_2$ available and thus the amount of expansion that could take place. A further contributing factor is the fact that zeolites have an open structural framework and contain a series of channels and cavities in which cations and water molecules are located. It is possible that the zeolite structure was able to accommodate the ettringite needles formed during the sulphate attack within the cavities, and so prevented the material from expanding.

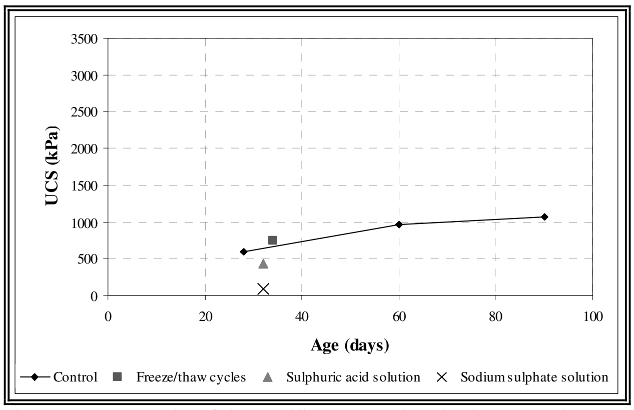


Figure 4. UCS results of the stabilised clay mix 5 in the aggressive and control environments

The UCS results for the sulphuric acid solution and freeze/thaw cycles show little deviation from the results of the control samples although freeze/thaw samples showed around 16% reduction. The reason for the good performance of the mix in the acidic solution could be justified by the fact that pozzolanic materials are expected to be more durable to acid attack, given that calcium oxide is involved in a less soluble form (Portland Cement Association, 2006 and Hewlett, 1998). These results are also concur with those obtained by Janotka et al. (2003) where it was identified that zeolite sand neutralises acidic solution and thus reduces the detrimental attack on the alkaline cement paste. While both mixes 5 and 7 contained the same cement content, mix 5 included calcium bentonite and in mix 7 the bentonite was replaced by zeolite. It was evident that mix 7 performed much better than mix 5 in both the sodium sulphate and sulphuric acid solutions. This is attributed to the presence of the zeolite. Conversely, the performance of mix 7 in the freeze/thaw cycles was worse than that of mix 5.

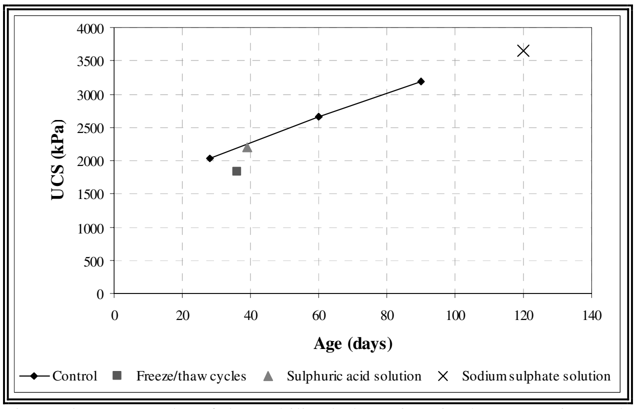


Figure 5. UCS results of the stabilised clay mix 7 in the aggressive and control environments

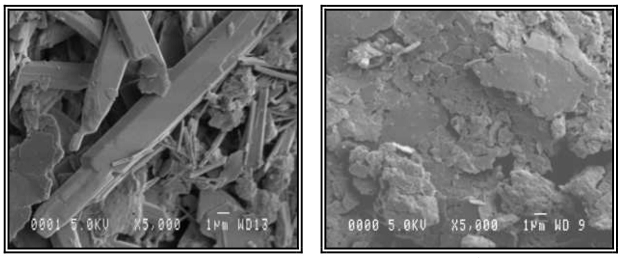
3.3 *SEM*

Generally, the observations of SEM images obtained for the stabilised clays were in strong agreement with the strength variations. Typical SEM micrographs from the outer surface of mixes 2 and 9 subjected to the sulphuric acid solution are shown in Figures 6 (a) and (b) respectively. Figure 6(a) shows that the sample of mix 2 subjected to the sulphuric acid solution had a significant amount of gypsum crystals (one of the sulphate attack reaction products). The figure indicates the abundance, and the large size, of the gypsum. Alternatively, samples of mix 9 (Figure 6(b)) showed no signs of attack and the surface seemed to be conventionally coherent and hydrating. This image agrees with the UCS and permeability results. The microstructural analyses were, in general, found to be valuable as tools o support the UCS and permeability results.

4 CONCLUSIONS

From the investigation carried out on the clays stabilised with cement, cement-bentonite and cement-zeolite, the following conclusions can be made:

- clays stabilised with cement grouts are susceptible to sodium sulphate solution, sulphuric acid solution and freeze/thaw cycles. In the case of sulphate attack, the sulphate ions enter into chemical reactions leading to the destruction of cement hydration products while the acid selectively leaches out those elements of the cement matrix which are dissolved by the very low pH, and consequently increases the porosity of the samples.
- the incorporation of both types of bentonite in cement-based grouts reduces the stabilised clay's resistance to sulphate attack and acid attack. This can be attributed to the high shrink-swell potential of the bentonite, leading to more cracking when subjected to sulphate attack.
- it can be suggested that bentonites in general, and sodium bentonite in particular, are resistant to the effects of freeze/thaw cycles



(a) (b)

Figure 6. SEM micrographs of samples subjected to sulphuric acid solution (a) stabilised mix 2 (8 days) (b) stabilised mix 9(46 days)

- the replacement of half the cement content with zeolite significantly enhanced sulphate resistance of the mix. No signs of cracking appeared on the samples for durations of up to 1.5 years. As a pozzolanic material, zeolite consumes the $Ca(OH)_2$ formed during cement hydration to produce cement-like hydration products. The addition of zeolite reduces the levels of available $Ca(OH)_2$, essential for expansion reactions, and consequently the amount of expansion that takes place.

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