Effect of strong acid on some geotechnical properties of fine-grained soils

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ABSTRACT
Results of an experimental program to study the changes in the liquid limit, the compressibility and the hydraulic conductivity of two fine-grained soils from Fort McMurray oil sands region when exposed to sulphuric acid of pH 1, 0, and -1 are presented. The exposure to sulphuric acid was achieved using diffusive transport at 20 kPa, 100 kPa, and 500 kPa confining stresses. Volume changes in the clay were observed to be less than 1.5% for diffusive exposure to pH -1. Increases in hydraulic conductivity were found to be one half to over an order of magnitude for samples at 20 kPa and 100 kPa confining stresses while samples at 500 kPa confining stress displayed no such increase in hydraulic conductivity.

RÉSUMÉ
Les résultats d'un programme expérimental pour étudier les changements dans la limite liquide, la compressibilité et la conductivité hydraulique de deux sols à grains fins de la région des sables pétrolifères de Fort McMurray résultant d'un exposé à des acides sulfuriques de pH 1, 0 et -1 sont présentés. L'exposition à l'acide sulfurique a été accomplie en utilisant le transport diffusif à des contraintes de confinement de 20 kPa, 100 kPa et 500 kPa. Les changements de volume dans l'argile ont été moins de 1.5 % pour l'exposition diffusive à pH -1. Les augmentations dans la conductivité hydraulique ont variés d'environ la moitié jusqu'à un ordre de grandeur pour les échantillons soumis à des contraintes de confinement de 20 kPa et 100 kPa, alors que les échantillons soumis à la contrainte de confinement de 500 kPa n'ont montré aucune telle augmentation dans la conductivité hydraulique.

1 INTRODUCTION

Fine-grained soils are extensively used in industry as a means of containing industrial pollutants such as brine and acid mine drainage (AMD). These barriers can be prepared in a variety of different ways, such as slurry placement and kneading compaction. The swelling characteristics of bentonite-rich fine-grained soils are particularly useful as containment barriers constructed using a mixture of bentonite and natural soils swell upon saturation, resulting in tightening of void space and reduction in permeability of the barrier. Such barriers are being used for the storage of sulphur blocks at Fort McMurray oil sands region. It has been observed that oxidation of sulphur at this site has the potential of generating sulphuric acid solutions with pH less than 1.

Previous studies on the interaction between fine-grained soils and acid solutions (e.g. Lentz et al. 1985, Ruhl and Daniel 1997, Kashir and Yanful 2000, 2001) have focused on mild acid solutions. These studies have formed the basis for understanding the change in geotechnical properties of fine-grained soil when exposed to acid solutions. There is a strong need, however, to study the response of fine-grained soils when exposed to strong (pH < 1) acid solutions. Of particular interest are the changes in the liquid and plastic limits, the compressibility, the hydraulic conductivity and the shear strength of fine-grained soils after diffusive exposure to strong acid solutions. It is also important to study the effect of confining stress during exposure to strong acid solutions on the above-mentioned geotechnical properties.

This paper presents the results of an experimental study undertaken at University of Saskatchewan to study changes in the liquid and plastic limits, the compressibility and the hydraulic conductivity of two fine-grained soils from Fort McMurray oil sands region when exposed diffusively to sulphuric acid solutions of pH 1, 0, and -1.

2 LITERATURE REVIEW

Permeability testing on clay soils subjected to mild acid solutions was carried out by Lentz et al. (1985), Ruhl and Daniel (1997), Kashir and Yanful (2000, 2001).

Lentz et al. (1985) measured changes in hydraulic conductivity of clays that were subjected to hydrochloric acid solutions of pH 1, 3, and 5. A flexible wall triaxial test was performed on kaolin, kaolin-bentonite mixture, and magnesium bentonite. The authors found that the hydraulic conductivity of the different clays remained unchanged after acidic flow equivalent to six times the pore volume had permeated the samples. One reason for this observation could be that the acidic solutions were passed through the soil under high hydraulic gradient, which did not allow sufficient time for the completion of clay-acid reactions.

Ruhl and Daniel (1997) observed that the permeability of bentonite samples changed when these samples were permeated with hydrochloric acid solution of ph 1. The authors' experiment was conducted at confining stresses of only 35 kPa on the sample. The authors found that a contaminant-resistant bentonite layer had higher permeability than the original bentonite layer when permeated with acid solution. The authors also observed that soil samples permeated directly with acid solutions showed greater increase in permeability compared with soil samples that were hydrated prior to permeation with acid solutions. In fact, samples of soils that were hydrated showed a reduction in permeability when permeated with acid solutions.

Kashir and Yanful (2000) used a mixture of 6% (by weight) bentonite and a natural soil from London, Ontario and subjected it to AMD solution at 0 kPa, 50 kPa, and 120 kPa confining stresses. The authors noted negligible change in the hydraulic conductivity of the samples after infiltrating them with AMD.

Kashir and Yanful (2001) used an AMD solution of pH 2.5 containing several different metals to permeate through bentonite. The testing was performed at confining stresses ranging from 0 kPa to 50 kPa. High hydraulic gradients of 20 to 500 were used in order to complete the tests in a reasonable amount of time and to obtain an understanding of the long-term behaviour. Metal concentrations and pH of the effluent material were measured after each passing of approximately two pore volumes of the permeant. The authors found that the hydraulic conductivity of the soil increased by about one order of magnitude at 30kPa and 50kPa confining stresses. At zero confining stress, the hydraulic conductivity increased rapidly by about 1.5 orders of magnitude, indicating that fracturing occurred within the sample. Increases in hydraulic conductivity were attributed to the development of macropores in the bentonite and the reduction in the diffuse double layer thickness. The pH of the effluent in the test was close to the pH of the influent after permeation equivalent to three pore volumes had occurred, indicating the point where the majority of buffering compounds in the soil were dissolved in solution and the buffering capacity of the soil was exhausted.

3 MATERIALS AND METHODOLOGY

3.1 Soils

Two different fine-grained soils were tested:

- Cretaceous clay from the Fort McMurray oil sands region (denoted by Kc); and,
- Estuarine clay also from the Fort McMurray oil sands region (denoted by Km).

Additionally, a few tests were conducted on a commercially available bentonite (BARA-KADE® sodium bentonite; denoted by BK). The Kc soil comprised approximately 1% sand, 41% silt, and 68% clay and contained a mixture of quartz, smectite, illite, kaolinite and chlorite. The Km soil comprised approximately 4% sand, 47% silt, and 51% clay and was predominantly composed of quartz, illite and kaolinite. Table 1 gives a summary of mineral composition of the Kc, Km and BK soils.

Samples of the Kc and the Km soils were first ground and then sieved through ASTM sieve #200 (75 micron opening size). Fraction of soil retained on the sieve was ground a second time and sieved again using the #200 sieve. The fraction of each soil passing the #200 sieve was used to prepare samples for compressibility and hydraulic conductivity measurements. Such samples were prepared by standard proctor compaction at moisture contents approximately two percentage points wet of optimum (dry density 1860 kg/m^3).

Table 1. Mineral composition of the Kc, Km, and BK soils

Mineral	Percent (by weight)		
	Kc	Km	BK
Quartz	15.7	6.2	3.5
Plagioclase	0.0	0.8	5.2
Siderite	0.0	2.8	0.0
Dolomite	0.0	0.0	0.0
Smectite	25.9	0.5	79.4
Illite	25.8	23.0	0.0
Kaolinite	24.2	66.2	0.0
Chlorite	8.4	0.6	0.0
Cristobalite	0.0	0.0	11.8

3.2 Consolidometer

The changes in the compressibility and the hydraulic conductivity of soil samples during diffusive exposure to sulphuric acid solution were measured using a rigid-wall consolidometer and falling head permeability apparatus connected to the base plate of the consolidometer. Since the consolidometer would be subjected to strong sulphuric acid solutions of pH as low as -1, it was necessary to make the walls of the consolidometer as corrosion resistant as possible.

Consolidometers are normally fabricated from stainless steel, which is prone to corrosion in strongly acidic environment. Uhlig (1948) found that the corrosion rate for austenitic stainless steel 18-8 (304) when subjected to 10% (by mass) sulphuric acid solution at room temperature was 0.079 inches per year whereas testing done at 15°C using 40% sulphuric acid solution (pH close to – 3) gave corrosion rates of less than 0.08 inches per year. It was noted, however, that the corrosion rates were substantially greater than 0.08 inches per year at higher temperatures. Uhlig (1948) observed that the addition of molybdenum to stainless steel increased its corrosion resistance substantially. He found that the corrosion rate for austenitic stainless steel 18-8 (316) containing 2% molybdenum was an order of magnitude lower than that for austenitic stainless steel 18-8 (304). It was decided, therefore, to fabricate the consolidometers using austenitic stainless steel 18-8 (316). To increase the corrosion resistance further, the walls of the consolidometers were coated with polytetraflouroethylene (PTFE; Teflon®). Figure 1 shows a typical consolidometer used in the present study.

Similarly, 3-mm-thick hydrophilic porous PTFE disks were used instead of the usual sintered brass porous disks at the top and the bottom ends of the consolidometer. In order to make sure that the compressibility of the PTFE disks was not going to be an issue, several PTFE disks were subjected to cyclic vertical loading at stress levels higher than those expected during the testing. The elastic modulus of the PTFE disks was around 20 MPa, which is significantly greater than the expected range of elastic modulus for soil. The compressibility of PTFE disks was, therefore, not considered to be problematic.

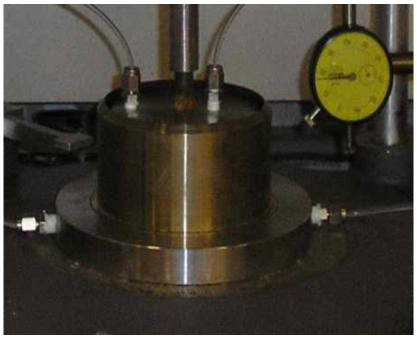


Figure 1. A typical consolidometer used in the present study

3.3 Diffusive Permeation

The soil samples were subjected to diffusive permeation of various sulphuric acid solutions with pH ranging from 7 to -1 and measurements of the liquid and plastic limits, the compressibility and the hydraulic conductivity were carried out. The BK soil was only tested for its liquid and plastic limits.

Samples were tested at three different confining stresses: 20 kPa, 100 kPa, and 500 kPa. The highest confining stress corresponds approximately to the vertical stress applied on the liner by the full height of the sulphur blocks. Samples were exposed to sulphuric acid solutions with pH 7, 1, 0, and –1 by allowing diffusion from a reservoir connected to the top and the bottom porous disks. Figure 3 gives an overview of the testing program.

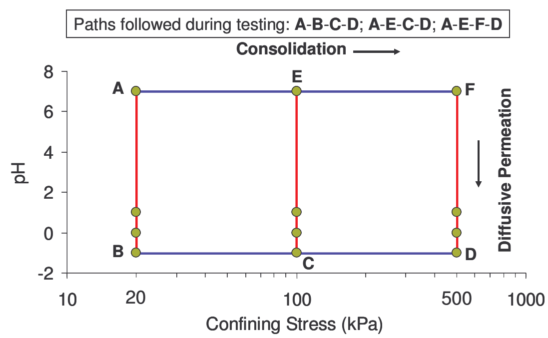


Figure 2. Overview of the testing program

4 RESULTS

4.1 Mineral Dissolution Effect

To gain some insight into how mineral dissolution may have an effect on soil properties, the liquid limit changes with exposure to various pH concentrations for a two-week period were plotted against aluminium dissolution for twelve-month batch test results completed by Shaw (2008) as shown in Figure 2. It can be inferred from Figure 1 that pH of 1 is the point where aluminium dissolution seems to increase substantially. This is also the point where the liquid limit of the BK soil decreases substantially. It is hypothesized that pH of 1 is the point where mineral dissolution starts to have dramatic effects on the geotechnical properties of soils that contain a high percentage of smectite.

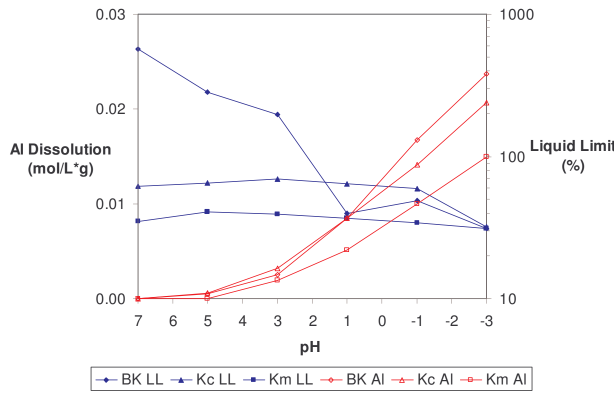


Figure 3. Variation of aluminium dissolution and liquid limit with pH of sulphuric acid solution

4.2 Hydraulic Conductivity

Hydraulic conductivity values obtained from falling head permeability tests were corrected for the viscosity and the density of sulphuric acid based on the data given by Rhodes and Barbour (1923). Figure 3 shows the corrected hydraulic conductivity (k) values for the Km and the Kc soils, obtained at different pH values and at three different confining stresses. In case of both the Km and the Kc soils, for the 20 kPa and 100 kPa confining stresses, k at pH of 1 is consistently higher than k at pH of 7 whereas for the 500 kPa confining stress, the value of k are virtually identical for pH of 7 and 1.

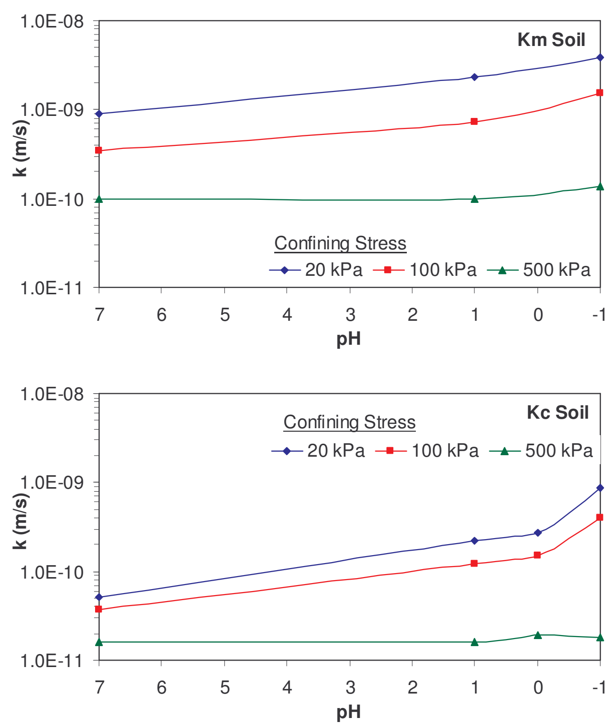
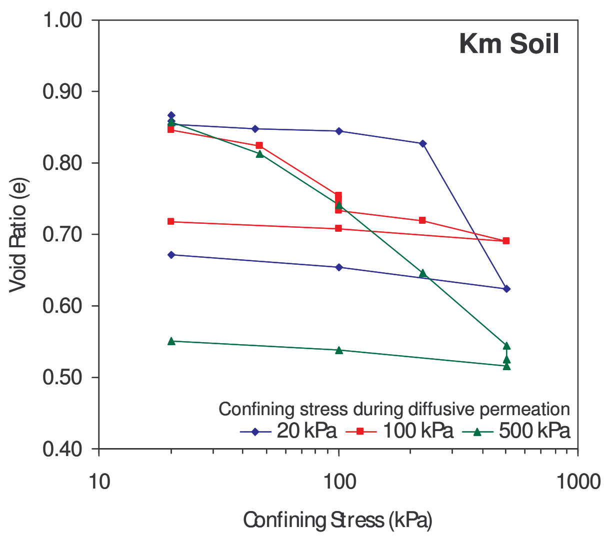


Figure 4. Variation of hydraulic conductivity (k; corrected for viscosity and density of pore fluid) with pH of sulphuric acid solution

At 20 kPa and 100 kPa confining stresses, the increase in k as the pH changes from 1 to –1 is more pronounced for the Kc soil than for the Km soil. For the Kc soil, most of the increase in k occurs when pH goes from 0 to –1. At 500 kPa confining stress, there is only a small increase in k for both the Km and the Kc soils as the pH changes from 1 to –1. For the Kc soil, k decreases slightly at 500 kPa confining stress when pH changes from 0 to –1. One plausible reason for the decrease in k values could be the precipitation of dissolved salts.

4.3 Compressibility

The samples were subjected to diffusive permeation of sulphuric acid solution from the top and bottom of the sample each time the pore fluid pH was to be lowered. Figure 5 shows the results of these tests presented in terms of void ratio vs. log of effective stress plots.



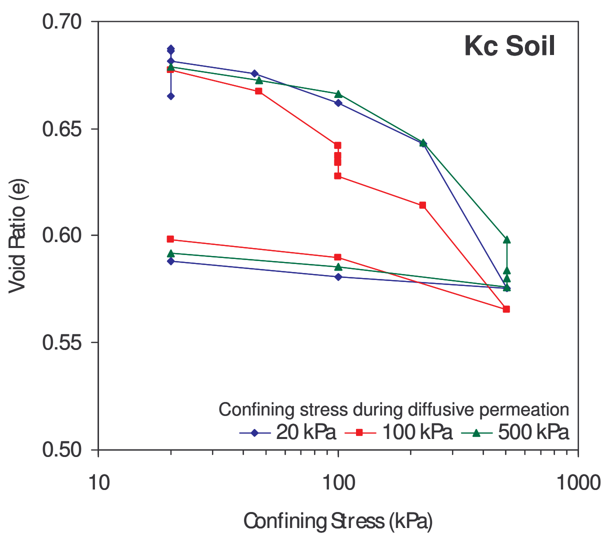


Figure 5. Change of void ratio during diffusive permeation of sulphuric acid solution and subsequent consolidation

In the case of Km soil, the sample at 20 kPa confining stress expanded when subjected to permeation using sulphuric acid solution of pH 1. Permeations using sulphuric acid solutions of other pH values caused contraction in the clay. When pH was changed from 7 to –1, total volume change values were 0.3%, 0.8%, and 1.4% for samples at 20 kPa, 100 kPa, and 500 kPa confining stresses, respectively. For the samples at 20 kPa and 100 kPa confining stress, there also appears to be an increase in the preconsolidation pressure when the samples are consolidated under mechanical loading after coming to equilibrium with pH -1 solution of sulphuric acid.

In the case of Kc soil, the sample subjected to diffusive permeation at 20 kPa confining stress expanded whereas the samples subjected to diffusive permeation at 100 kPa and 500 kPa confining stresses contracted. When pH was changed from 7 to -1, total volume change values for Km soil samples were 1.0%, 0.9%, and 1.0% at 20 kPa, 100 kPa and 500 kPa confining stress, respectively. Samples of Kc soil do not show increase in preconsolidation pressure when consolidated under mechanical loading after coming to equilibrium with pH -1 solution of sulphuric acid.

5 DISCUSSION

Kashir and Yanful (2001) attributed the increase in hydraulic conductivity of bentonite during AMD permeation to the development of macropores and the reduction in the diffuse double layer. This is the same mechanism that Yang (1990), Yang and Barbour (1992) and Barbour and Yang (1993) attributed to the cause of osmotic consolidation and hydraulic conductivity increase in clay samples exposed to brine solutions.

The testing completed by Kashir and Yanful (2001) shows changes in clay mineralogy even though the samples were subjected to the AMD for a fraction of the amount of time that would occur in the field for comparable flow volumes with a pH of only 2.5. Shaw (2008) found smectite minerals were more susceptible to dissolution than that of illite of kaolinite in the Km, Kc, and BK clays. Dissolution increased significantly below a pH of 3. These soils show increased changes in the liquid limit with a higher smectite soil fraction. This could suggest a combination of reduction in the thickness of diffuse double layer and dissolution causing the changes in liquid limit.

The Kc soil displayed an increase in hydraulic conductivity of over one orders of magnitude for samples at 20 kPa and 100 kPa confining stress. The Km soil displayed an increase of approximately one-half orders of magnitude. This result fits with the previous theory as the smectite present in the Kc is expected to be more susceptible to the diffuse double layer effect and mineral dissolution. There is almost no change in hydraulic conductivity for the Km and Kc exposed to sulphuric acid at 500 kPa suggesting increases in hydraulic conductivity can be minimized with confining stress.

Changes in soil volume can be attributed to the reduction of the diffuse double layer and possibly mineralogical dissolution. Volumetric changes due to acid exposure down to pH -1 were found to be less than 1.5%

for all samples tested. There was no noticeable change in compressibility of the Kc soil after exposure to pH -1; however, the Km soil displayed an apparent increase in preconsolidation pressure. It is thought that the difference in these two results stems from the Km taken to pH -3 for a short period of time but then later returned to pH -1 due to unacceptably high corrosion rates and subsequent hydrogen production within the apparatus.

6 CONCLUSIONS

Volume changes for the Km and Kc soils tested were found to be less than 1.5% of total volume when subjected to diffusive permeation using sulphuric acid solutions of pH 7 to -1. Increases in hydraulic conductivity values were over one orders of magnitude and approximately one half an order of magnitude for samples with confining stress of 20 kPa and 100 kPa for the Kc and Km soils, respectively. This result suggests that increased susceptibility of the Kc soil to mineralogical dissolution causes a slightly higher increase in hydraulic conductivity. The hydraulic conductivity did not change significantly when the soils were exposed to the acid at 500 kPa confining stress.

The changes in geotechnical properties of fine-grained soils exposed to strong sulphuric acid solutions can be attributed to changes in the thickness of the diffuse double layer and mineralogical dissolution. This causes expansion of inter-aggregate macropores, resulting in higher hydraulic conductivity values. These macropores may be expanded further by mineral dissolution occurring in the clay. Adequate confining stresses on the sample can minimize the expansion of these macropores.

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