

# Chemical alterations in three clayey soils from percolation and interaction with acid mine drainage (AMD)

Agbenyeku Emem-Obong Emmanuel<sup>a</sup>, Muzenda Edison<sup>a,b</sup>, Msibi Mandla Innocent<sup>c,d</sup>

<sup>a</sup>Department of Chemical Engineering, University of Johannesburg, Johannesburg, South Africa

<sup>b</sup>Department of Chemical, Materials and Metallurgical Engineering, Botswana International University of Science and Technology, Palapye, Botswana

<sup>c</sup>Research and Innovation Division, University of Johannesburg, Johannesburg, South Africa

<sup>d</sup>Innovation and Impact, Water Research Commission, Pretoria, South Africa

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**Abstract**-The issues of acid mine drainage (AMD) from mining activities is not a new phenomenon to the present day developing South Africa as well as in most developed countries around the globe. However, the persistent rise in environmental contamination in South Africa is drastically attracting massive concerns. Vital concerns of AMD in South Africa still remain the threat to soil, surface, subsurface and ground water reserves among others, which consequentially impact human and environmental health. This insistent challenge has given rise to the need for investigating the buffering efficacy of clayey mineral soils for use as natural contaminant barriers to contaminant species from AMD. Therefore, the study presented herein, was channeled towards assessing the chemical alterations in three clayey soils from permeation and interaction with AMD via successive protracted percolation up to 18-25 pore volume passage of AMD through the respective soil medium. The final hydraulic conductivity measured, ranged between  $1.3 \times 10^{-11}$  m/s and  $1.5 \times 10^{-11}$  m/s. The obtained pH, electrical conductivity and solute breakthrough curves indicated the soils had low acid-buffering efficacies. Chemical species such as Na, Co and  $\text{SO}_4^{2-}$  were highly dissolved due to attack on the soil grains by AMD. Chemical species were also released from the soils including the dissolution of metals and desorption of chemical species from AMD attack. As such, the study revealed that the buffering efficacies of the respective tested clayey soils to AMD chemical contaminants were generally ineffective.

## INTRODUCTION

As reported by Coetzee et al., (2007) acid mine drainage (AMD) occurs in sulphide-bearing mine waste due to the oxidation of iron sulphides, especially pyrite ( $\text{FeS}_2$ ), pyrrhotite ( $\text{FeS}$ ) and marcasite ( $\text{FeS}_2$ ) leading to the creation of several soluble hydrous iron sulphates, the generation of acidity and subsequent leaching of metals. AMD have several negative human and environmental impacts (Gray, 1997; Manzano et al., 1999; Wates and Rykaart, 1999; Vermaak et al., 2004) which may be alleviated by lining possible acid-generating waste rock or mine tailings impoundments with clayey or composite clayey liners. For the competent performance of these liners, it is important that their properties are not compromised over time when exposed to AMD. As such, assessment of the chemical interaction and compatibility of clay/clayey liners with aggressive AMD is a pertinent consideration in the proper management of potentially acid generating mine waste (Hobbs and Cobbing, 2007). These AMD-soil interactive/compatibility studies may involve percolation/hydraulic conductivity testing, contaminant migration analysis and determination of soil chemical alterations. Although, some studies on the interaction of soils from temperate regions with AMD have been conducted (e.g., Yanful et al., 1995; Kashir and Yanful, 2000; Kashir and Yanful, 2001) there still remains however, insufficient data on the interactive outcomes/compatibility of soils from tropical and subtropical regions with AMD. More to this, sufficient outcomes of chemical studies were not reported in most of these works which nonetheless, paved way for this study to bridge that gap in knowledge. Notwithstanding, it is known that the chemical composition, texture and crystal structure of a mineral may influence its stability, the type and severity of the environment to which it is exposed could also accelerate its alteration (Coetzee et al., 2002). AMD usually has high acidity and is rich in sulphate and potentially toxic elements and heavy metals.

For instance, acid attack of clay/clayey soils can lead to chemical alteration and the release of cations and toxic elements, thereby influencing several physical, biological and chemical processes occurring in the geological media. These include pH variation in natural waters and metal mobility (Kalinowski and Schweda, 1996; Lin and Hansen, 2010), ground water flow and contaminant migration mechanisms (Welch and Ullman, 1996; Coetzee et al., 2006) and the availability of essential soil micronutrients (Hamer et al., 2003; International Network for Acid Prevention-INAP, 2009). In the long run, aquifer porosity and permeability, ground water and soil quality may be adversely

affected. Similarly, AMD could lead to soil acidification and potentially minimise soil fertility through the depletion of vital micronutrients. These have consequential impacts for most of the agrarian economies in the tropics and subtropics as it has been recorded by Hartemink (2004) that one-third of the soils in the world occur in the tropics which supports more than 75% of the world's population.

It is therefore imperative that the soil chemical alteration from the interactions between AMD and these clayey soils is understood towards the efficient management of AMD and related contaminated soils. AMD attack on clays could also affect the soil-electrolyte system; as a decrease in ion concentration or valency of the medium forming the absorbed layer (counter ion of clay) could trigger an increase in electric repulsive forces between the clay particles (Mitchell, 1993; Iwata, 1995). These upsurges in repulsive forces can result in swelling and dispersion of the clay particles, which in turn may increase hydraulic conductivity if adequate confining pressures are not imposed on the compacted clay/clayey lining system. Consequently, clay surface charge characteristics have an impact on hydraulic conductivity. As most tropical soils contain kaolinite, iron and aluminium hydroxides that have variable (pH-dependent) charge characteristics (Mendoca et al., 2002), the pH of the permeating fluid can have an impact on their hydraulic conductivity. In this study however, the physicochemical compositions as well as the mechanical properties of three subtropical clayey soils as relates to the buffering efficacy of the soils were determined. A bespoke constant flow rigid wall permeameter device was used to percolate compacted samples of the respective clayey soils with several pore volumes of AMD. The chemical alterations of the soils after AMD permeation were assessed using x-ray diffraction and chemical analyses in order to ascertain their contaminant buffering efficacy or potential value for use as clay liners in aggressive chemical waste containment facilities. In view of the overall objective of evaluating the contaminant buffering ability of the soils for use as liners in mine tailings dams and effluent ponds, the impact of the permeant on the hydraulic conductivity of the clayey soils after interaction with AMD were also evaluated.

## MATERIALS AND METHODS

### Materials

Three different natural clayey soil samples were harvested from different active waste disposal sites around the City of Johannesburg (CoJ) for this investigation. Samples of the three subtropical clayey soils were designated as Soil A, Soil H and Soil K for the purpose of the study. Sufficient volumes of AMD were not available throughout the study due to restrictions on access and transportation of mine and other forms of industrial and hazardous wastes. As such, these difficulties in obtaining AMD from operating mines during the study period led to the laboratory generation of AMD. This was achieved by mixing potential acid-generating mine waste rock and acidic slurred mine tailings collected from two different mines in a plastic bucket. The mixture was submerged in acid mine water and thoroughly mixed with a constant temperature circulator. Pictorial views of the active waste disposal sampling sites where the respective natural clayey soils (A, H and K) were collected are shown in Figures 1a-c. The soils from the respective sites were collected at points sufficiently remote from the actual dump ground to guarantee a certain degree of purity.



a) Soil A sampling site

b) Soil H sampling area

c) Soil K sampling site

Figure 1: Respective soils samples collected remotely distant from the actual dump space (site recon., 2014)

Soil sample A was harvested as reddish brown lean clay at a depth of 0.4-1.2 m. Soil sample H was also reddish brown and was sampled at a depth of 0.6-1.5 m as elastic silt. While Soil sample K was obtained as fat clay of yellowish brown colour at a depth of 0.3-1.3 m. As noted decades ago by Brammer (1962) and Ahn (1970) the reddish brown

colour is suggestive of the presence of non-hydrated iron oxide, perhaps hematite ( $\text{Fe}_2\text{O}_3$ ) in the soil whereas, the yellow colour may suggest the relative presence of goethite over hematite.

### **Material Characteristic Properties**

The index mechanical and standard Proctor compaction tests were performed on the respective soils using standard methods in conformance to American Society for Testing and Materials (ASTM) 420-D 5779 (ASTM, 2002). However, in determining the Atterberg limits, the samples were mixed with water or AMD to an appropriate consistency at their existing moisture contents. The prepared samples were then covered with plastic wraps and left to stand for 48 hours to ensure equilibration (so the clay paste became more uniformly saturated) prior testing. The total organic matter content of the soils were determined by way of the Walkley-Black method as described by Walkley and Black (1934). The Chittick apparatus was used to determine the carbonate content as per Dreimanis (1962). The glycol retention procedure was used to determine the specific surface of the <#200 mesh air-dried soil samples in accordance to Martin (1955). The cation exchange complex (CEC) of the soils was determined with 1N ammonium acetate ( $\text{NH}_4\text{CH}_3\text{COO}$ ) as the extracting solution for exchangeable bases while 1N barium acetate ( $\text{Ba}(\text{CH}_3\text{COO})_2$ ) was used for exchangeable acidity. According to the procedures by the US Department of Agriculture (USDA, 1996) the soil samples were analysed for pH in 1:1, soil: water and 1:2, soil: 0.01M  $\text{CaCl}_2$  suspensions by weight. The pH test was performed with a mini pH/ion meter (Beckman Century TM SS-1) probe that was calibrated with standard buffer solutions of pH 4, pH 7 and pH 10. The oxide and trace element composition of the soils were determined using x-ray fluorescence spectrometer (XRF) while loss on ignition (LOI) of the soils was determined by calcination. Analyses were carried out with an analytical Magi'X Pro version wavelength dispersive XRF spectrometer operation system. Before the analysis, 1.0 g powdered soil sample was measured and calcined at approximately 1000°C in an electric furnace for 2 hours. On cooling to room temperature in a desiccator for 1 hour, the sample was reweighed and the weight difference was calculated as the LOI. About 0.5 g of the calcined sample was then mixed with 6.5 g of the flux (50% lithium tetraborate and 50% lithium metaborate) and fused with an automatic fluxer at approximately 1000°C for 15 minutes before casting into a 30 mm disk for analysis.

The soil pore fluid composition and effluents from the hydraulic conductivity tests, metals and cations present in the AMD used in the study was determined using inductively coupled plasma-atomic emission spectroscopy (ICP-AES). Ion chromatography was used to analyse sulphate and chloride. Also, the procedures required the laboratory preparation of a 1:10 suspension of the respective pulverised soil types in distilled water. The fluid was then separated from the solid by centrifugation spinning process and chemical analyses were subsequently carried out on the separated solid. The tests revealed the amount of soluble ions present in the samples per 100 g of soil. The analyses involved the determination of heavy metals (Zn, Cu, Pb and Fe), cations (Na, K, Ca and Mg), anions ( $\text{CO}_3$ ,  $\text{HCO}_3$  and Cl), pH and electrical conductivity. The Atomic Absorption Spectrophotometry was then carried out in the analysis of the heavy metals. The Beckman Century TM SS-1 mini pH/ion meter probe used to measure the pH of soil samples was also used to measure the pH of water samples. The specific electrical conductivity of the water samples was determined with a 1202 Model Electro-phoretic mass-transport analyser.

### **Laboratory Hydraulic Conductivity Testing**

Effectively evaluating the impact of AMD permeant on the chemical compositions of the respective soils and their hydraulic conductivity, required several pore volumes of permeant flow at equitably low seepage rates. This was basically to prevent wash off of fines as well as afford the permeant a longer dwelling time to interact with the soil structure and pore fluid. From long ago to recent times, flow pump systems have been utilised to speedily determine hydraulic conductivity by generating very low but accurate seepage rates of permeant which results in realistically low hydraulic gradients across compacted soil specimens in real time (Kashir and Yanful, 1997; Foose et al., 2001; Bouazza et al., 2002; Barroso, 2005; Barroso et al., 2006). In the present study however, a simple bespoke constant-flow rigid wall permeameter called a Modular Consolidometer-Percolation Column Hybrid device for clay barrier-permeant interaction/compatibility studies was used. A schematic representation of the modular rigid wall laboratory hydraulic conductivity testing equipment is shown in Figure 2. The modular device comprises of three main components: (1) the bottom part called the buffering chamber; which contained the lightly compacted soil layers acting as the natural earth and buffering layers below the liner system with an outlet to trap effluent (2) the perforated mid-block called the sample holder; carried the designed liner system (25 mm natural soil as CCL alone) which sits on the buffering chamber- 225 mm thick, and (3) the upper portion above the CCL liner system; functioned as the permeant chamber with an inlet for permeant infusion.

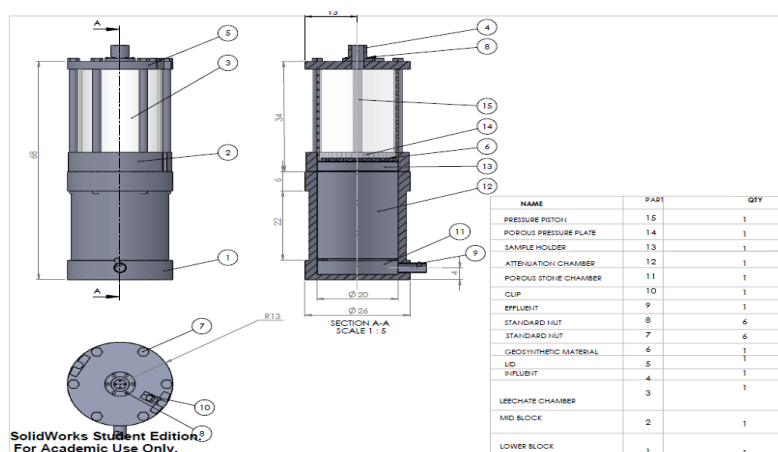


Figure 2: Schematic view of the small-scale modular consolidometer-percolation column hybrid device used for the series of hydraulic conductivity and compatibility studies

Since AMD is a potentially corrosive permeant, the reservoir was constructed as a transparent rigid cylindrical cell with high strength, corrosion resistance and of polymethyl (methacrylate) called acrylic glass or plexiglass that allowed for visual observation during testing; while the lower sections (i.e., the pressure pad, sample holder and buffering chamber) were constructed of polished anodised aluminium (to resist corrosive attacks and scarring during or after testing, assemblage or dismantling processes). Furthermore, O-rings, gasket corks and silicon sealants were used to prevent leakages, escape of corrosive vapours into the laboratory-work environment and maintain pressure-tight seals between the top, mid and bottom sections of the device. Approximately 25 mm of compacted soil (at about 2% above the optimum moisture content) was used in the percolation studies. The respective samples required saturating to the pore fluid and in accordance to Frempong and Yanful (2006) soils other than very soft clays have pore pressure coefficients (B-values) at full saturation significantly less than 1.0. Similarly, a B-value of 0.91 was gotten in the pore pressure reaction test thus, considering the compacted soil to be adequately saturated. Thereafter, the sample was lightly rammed in layers into the mid-block and the buffering chamber. The entire assemblage was set and a consolidation pressure of 25 kPa as was done by Barroso et al., (2006) was applied to the soil (CCL in the mid-block) from a hydraulic frame through a piston rod resting on a perforated pressure plate after which it was successively permeated with at least 1.5-2 pore volumes of 0.01N CaSO<sub>4</sub> and 18-25 pore volumes of AMD at flow rates of  $6.1 \times 10^{-7}$  mL/s -  $6.5 \times 10^{-6}$  mL/s.

## RESULTS AND DISCUSSION

### Acid Mine Drainage (AMD)

The chemical composition of the AMD used in this study is summarised in Table 1. As anticipated, the AMD had a low pH, high electrical conductivity and contained elevated levels of sulphate and dissolved heavy metals. As recorded by Coetzee et al., (2007) failure of a soil liner to buffer the migration of various toxic elements and metals (contaminant species) present in AMD into soil and ground water reserves can lead to consequential impacts on the ecosystem (human and environmental health).

Table 1: Summary of the properties of AMD initiated in the study

Parameter	Value (mg/L)
pH (pH units)	2.8
Electrical conductivity @ 25°C, $\mu$ S/cm	7253
Sulphate	5150
Iron	635
Calcium	318
Magnesium	285
Chloride	200
Nitrate	185
Silica	140
Nickel	180
Zinc	160
Aluminium	135

Manganese	65
Silicon	72
Sodium	35.7
Cobalt	7
Potassium	5.63
Copper	1.98
Lead	0.79
Vanadium	0.73
Phosphorous	0.58
Arsenic	0.45
Cadmium	0.37
Chromium	0.26
Barium	0.04
Zircon	<0.01

## Natural Soils

### *Mechanical Soil Characterisations*

The high air-dry moisture content of Soil A (4.7%) suggests the presence of an active clay mineral in the soil. However, all three sampled soils were found to contain substantial fine fractions above 50% passing the No. 200 sieve. The measured specific gravities of solids were gotten in the range of 2.62 - 2.79 which suggests the existence of metal oxides (Hemsi et al., 2002; Frempong and Yanful, 2006) in these sub-tropical soils. In accordance to the Unified Soil Classification System (USCS) the soils were classified as inorganic clays of relative plasticity. Soil A had liquid limit of 47 which by the classification rule is considered low as it is lesser than 50. The limits of Soil A plotted in the hatched zone on the plasticity chart which further classifies it as lean clay-CL. Soils H and K had higher liquid limit values above 50. Soil H however, had its limit plotted below the "A" line on the plasticity chart which classified it as an elastic silt-MH. While Soil K had plotted limits above the "A" line on the plasticity chart, classifying it as fat clay-CH. The volumetric shrinkages of 30.7, 10.5, 3.4% were obtained for Soils A, H and K respectively. Soil A had a relatively high volumetric shrinkage as against Soils H and K with moderate and low volumetric shrinkages respectively. The maximum Proctor dry unit weights in ranges of 15.15 and 17.33 kN/m<sup>3</sup> achieved on compacting the soils suggest they can provide adequate compacted strength as bottom liners for waste containment. Fine gravelly material with narrow range particle size passing the 19.0 mm (3/4") but retained on the 9.5 mm (3/8") sieve openings were specially selected, washed, oven dried and used as porous stone to serve as filter to the drainage path in the experimental setup of this study. Table 2 presents the mechanical characteristics of the natural untreated soils.

Table 2: Mechanical index properties of the studied natural untreated soils

Properties	ASTM Test Designation	Soil A	Soil H	Soil K
Natural Water Content (%)	D 2216	20	32	27
Water Content (Air-dry soil) (%)	D 2216	4.7	1.3	1.4
Optimum Water Content (%)	D 698	16.2	15.4	15.7
Liquid Limit	D 4318	47	61	55
Plastic Limit	D 4318	25	36	31
Plasticity Index	D 4318	22	25	24
Volumetric Shrinkage, Vs (%) @ w = OWC + 2%	D 4318	30.7	10.5	3.4
USCS*	D 2487	CL/lean clay	MH/elastic silt	CH/fat clay
Specific Gravity	D 854	2.77	2.79	2.62
Dry Unit Weight (kN/m <sup>3</sup> )	D 698	15.15	16.37	17.33
Wet Unit Weight (kN/m <sup>3</sup> )	D 698	17.7	18.9	20.1
Void Ratio	-	0.79	0.67	0.48
Porosity	-	0.44	0.40	0.32

\*Unified Soil Classification System

### *Soil Chemical Composition*

Soil A had a pH of 4.9 while Soil H had a pH of 5.2 describing both as strongly acidic in accordance to Frempong and Yanful (2006). Notwithstanding, with Soil K being close to neutral, it had a pH of 6.8. Out of the total oxide composition of the soils, silica and sesquioxides of iron and aluminium accounted for about 81%. With a silica: sesquioxide ratio greater than 2.0, Soils A and K are non-lateritic (as per BRRI/Lyon Associates, 1971); however, Soil H is lateritic as its ratio is in a range of 1.73-2.0. Table 3 summarises the results of the chemical tests performed on the natural and untreated soils. The high losses on ignition (LOI) of the soils suggest that generally, the amount of structural water, organics, carbonate, sulphate and chloride present in the clays is high. The glycol retention value and

the cation exchange complex (CEC) of Soil K were higher than those of Soils A and H as seen in Table 3. This is plausibly due to the presence of smectite in Soil K and the relatively higher total organic matter content of the soil.

Table 3: Comparison of some chemical properties of the soils after soil-AMD interactions

Properties	Soil A	Soil H	Soil K
pH in water (soil: water; 1:1)	4.9 (3.2)	5.2 (3.8)	6.8 (4.6)
pH in 0.01M CaCl <sub>2</sub> (soil: solution; 1:2)	4.5 (3.2)	4.8 (3.8)	6.4 (4.6)
Total Organic Matter (%)	1.2 (0.61)	1.5 (0.81)	1.8 (1.3)
Carbonates (%)	3.5 (0.55)	2.9 (0.97)	4.7 (1.96)
Glycol Retention (mg/g of clay)	25.3 (23.1)	28.7 (11.2)	87.4 (58.2)
Cation Exchange Complex CEC, (meq/100 g)	5.2 (21.3)	4.4 (11.9)	36.7 (28.6)
<b>Major Oxides (%)</b>			
SiO <sub>2</sub>	65.5 (63.9)	58.4 (59.6)	61.3 (56.3)
Al <sub>2</sub> O <sub>3</sub>	16.8 (17.7)	22.6 (23.8)	14.3 (13.2)
Fe <sub>2</sub> O <sub>3</sub>	4.1 (4.9)	9.3 (9.8)	7.7 (7.2)
TiO <sub>2</sub>	0.7 (0.7)	1.7 (1.3)	1.5 (1.1)
K <sub>2</sub> O	0.9 (0.95)	0.15 (0.13)	0.29 (0.25)
MgO	0.4 (0.5)	0.24 (0.24)	0.75 (0.72)
CaO	0.08 (0.11)	0.13 (0.15)	2.25 (2.17)
MnO	0.03 (0.04)	0.06 (0.06)	0.20 (0.16)
Na <sub>2</sub> O and P <sub>2</sub> O <sub>5</sub>	<0.03 (<0.05)	<0.09 (<0.07)	0.79 (0.53)
Silica: Sesquioxide Ratio	3.1 (2.88)	1.86 (1.84)	2.87 (2.85)
SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	3.5 (3.4)	2.7 (2.5)	4.5 (4.5)
SiO <sub>2</sub> /Fe <sub>2</sub> O <sub>3</sub>	16.2 (14.7)	6.45 (6.3)	8.1 (7.5)
Loss On Ignition LOI (%)	8.5 (8.3)	12.5 (11.3)	13.2 (16.8)
<b>Trace Element Concentration (µg/g)</b>			
Vanadium	145 (153)	154 (147)	179 (183)
Chromium	157 (177)	88 (95)	122 (131)
Zinc	53 (152)	42 (137)	65 (331)
Nickel	45 (188)	42 (163)	40 (427)
Copper	21 (14)	27 (6)	42 (13)
Lead	12 (13)	16 (22)	24 (23)
Arsenic	4	6	3
Cobalt	82	11	40
<b>Anions, ppm</b>			
Chloride	11	485	104
Sulphate	44	335	220
Nitrate	42	95	10

( ) Value after percolation/interaction with AMD

### Soil Hydraulic Conductivity

On permeation with approximately 2.4 pore volumes of 0.01N CaSO<sub>4</sub>, a baseline hydraulic conductivity of  $1.3 \times 10^{-11}$  m/s was obtained for Soil A. It was however, discovered that after passing almost 19 pore volumes of AMD through Soil A, the hydraulic conductivity remained basically unaffected. The impact of permeants on the hydraulic conductivity of Soil A is shown in Figure 3. While in Figure 4, the variation in the hydraulic conductivity of Soil H when permeated with AMD is presented. Here, the baseline hydraulic conductivity was  $2.6 \times 10^{-11}$  m/s but was found to slightly increase to  $3.5 \times 10^{-11}$  m/s after introducing about 7 pore volumes of AMD. On continued percolation with AMD, the hydraulic conductivity was seen to fluctuate between  $3.3 \times 10^{-11}$  m/s and  $3.4 \times 10^{-11}$  m/s owing to an average value of  $3.35 \times 10^{-11}$  m/s after 18 pore volumes of permeation. The hydraulic conductivity of Soil K was found to slightly increase from the baseline value of  $8.2 \times 10^{-12}$  m/s when percolated with 0.01N CaSO<sub>4</sub> to roughly  $9.1 \times 10^{-12}$  m/s after permeation with nearly 2 pore volumes of AMD. Nevertheless, after passing 23 pore volumes of AMD, the hydraulic conductivity was seen to increase by nearly half an order of magnitude ( $8.2 \times 10^{-12}$  m/s to  $1.5 \times 10^{-11}$  m/s). Figure 5 shows the difference of the hydraulic conductivity of Soil K when percolated with 0.01N CaSO<sub>4</sub> and AMD. From the results, there is clear indication of an increase of less than one quarter of an order of magnitude over the baseline hydraulic conductivity of  $2.6 \times 10^{-11}$  m/s at the end of the percolation exercise, which was considered a fair outcome. Studies by Omid et al., (1995), Bouazza et al., (2002), Barroso et al., (2006), Frempong and Yanful (2006) revealed that soils with volumetric shrinkage beyond 11% are vulnerable to excessive hydraulic conductivity alterations caused by wet-dry loadings. A plausibly explanation for the increase in hydraulic conductivity of Soil K to closely half an order of magnitude may be as a result of volume changes caused by the AMD, leading to the increase in pore volume of Soil K. On the contrary, the alterations in Soils A and H respectively did not seem to have unfavorably impacted their hydraulic conductivities when percolated with AMD.

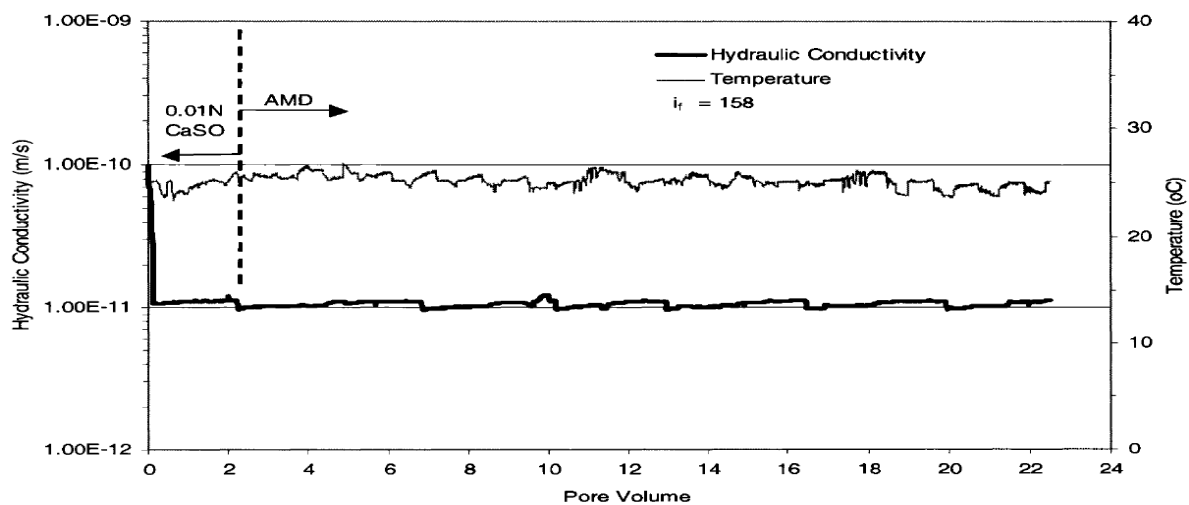


Figure 3: Hydraulic conductivity variation of Soil A on percolation/interaction with AMD

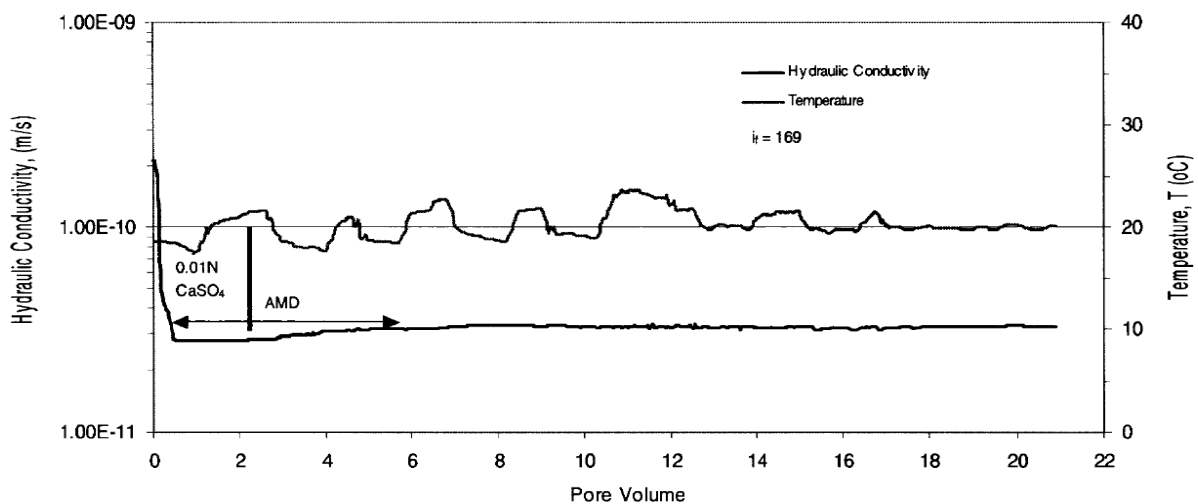


Figure 4: Hydraulic conductivity variation of Soil H on percolation/interaction with AMD

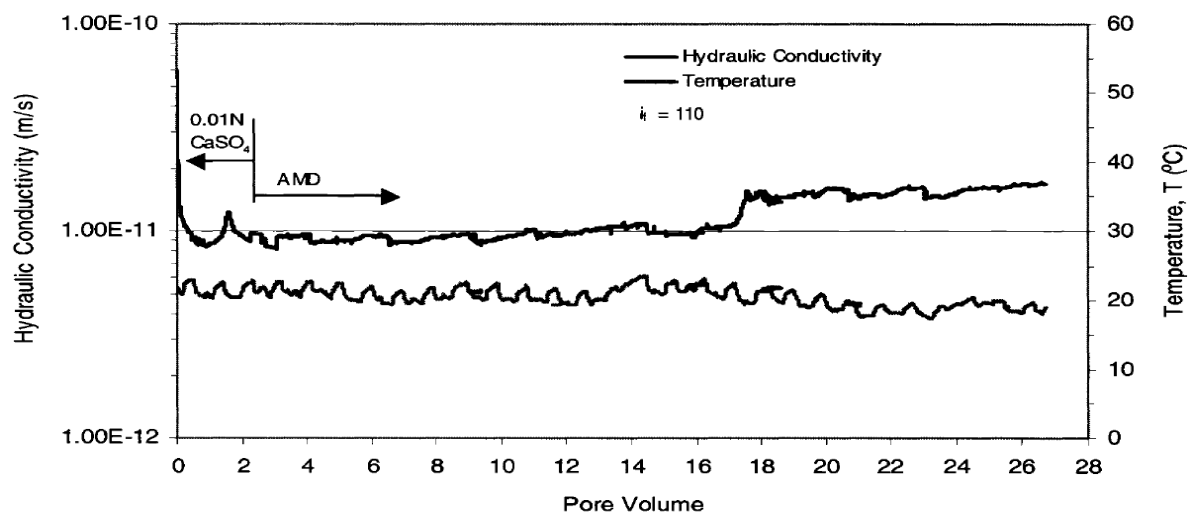


Figure 5: Hydraulic conductivity variation of Soil K on percolation/interaction with AMD

### Interpretation of Effluent Chemistry

According to Mitchell (1993) the distance between the negatively charged clay particle surface and the centre of the mass of diffuse double layer,  $1/k$ , may be associated to the thickness of the double layer. Also, a study by Kashir and Yanful (2001) have shown that the ionic strength,  $I$ , of effluents from compacted clays permeated with AMD could be associated to  $k$ , as expressed in equation 1.

$$k = 3.28\sqrt{I} \text{ (nm}^{-1}\text{)} \quad (1)$$

Where,

$1/k$  = Thickness of diffuse double layer; and

$I$  = Ionic strength.

From the present study, the ionic strength of the effluents sampled during the hydraulic conductivity tests was computed using *MINTEQA2* with the corresponding  $k$  values being calculated. Figure 6 shows the difference of the diffuse double layer thickness surrounding the clay particles in each compacted soil during AMD percolation. An insubstantial reduction in the double layer thickness appeared to have occurred in the respective soils after about 4 pore volumes of AMD permeation. More so, the level of double layer contraction was inconsistent with the corresponding increases in the hydraulic conductivity of the soils recorded. As such, it becomes tricky to consider the double layer contraction as responsible for the observed alterations in hydraulic conductivity of the soils.

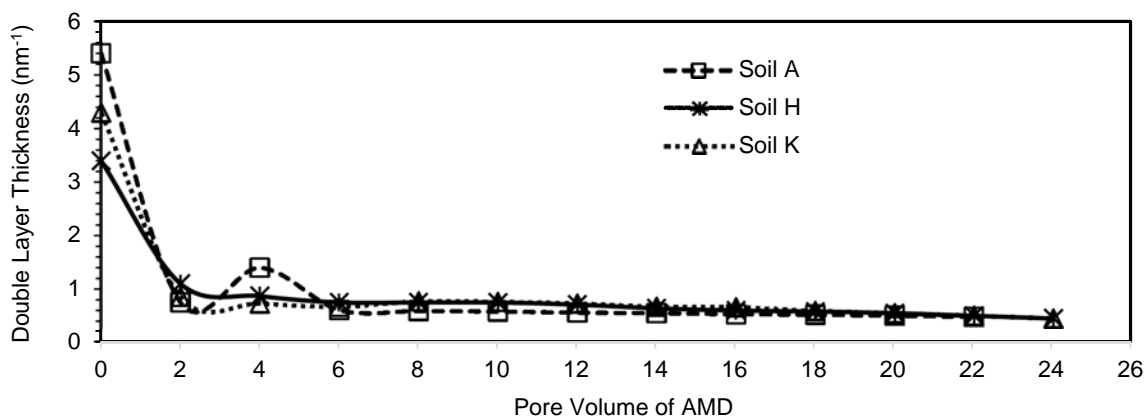


Figure 6: Difference of double layer thickness of clay with pore volume of percolated AMD

### Chemical Constituents of Soil Percolated with AMD

#### *pH*

Results of the soils chemical tests before and when percolated with AMD are shown in Table 3. The Table 3 facilitates the discussion herein, such that prior percolation with AMD, the pH values with 0.01M CaCl<sub>2</sub> were seen to be lesser than the values with distilled water for the respective soils. As noted by Mendoca et al., (2002) this difference between the pH determined with salt solution and distilled water, point to the presence of negative charges on the soil surfaces in their natural states. At the end of AMD infusion, the pH values of the soils were found to have lessened to a range of 3.2 - 4.6 as seen in Table 3 and the results were similar to pH determinations made with 0.01M CaCl<sub>2</sub> and distilled water. This suggests that cations in AMD perhaps neutralised the exchangeable anions i.e., hydroxides, chlorides, sulphates and nitrates originally existing on the mineral surfaces of the soils. Similarly, the lowering of the pH signifies soil acidification by AMD, which on progression could result in the diminution of essential soil micronutrients such as copper, aluminium and zinc, as well as lead to the devastation of agrarian land/soil, and contamination of ground and surface water reserves thereby, adversely impacting human and environmental health.

#### *Glycol Retention and Cation Exchange Complex (CEC)*

Glycol retention is a measure of the specific surface of the soil. The glycol retention values of the respective soils were reduced with AMD infiltration. From Table 3, it can be seen that the most noteworthy alterations occurred in Soils K and H respectively. The glycol retention reduction and subsequently, specific surface of the respective soils



is plausibly due to the reduction in organic matter content plus the mineral transformations that occurred in the soils. Consequently, at the end of AMD infiltration, the cation exchange complex (CEC) of Soil H was found to increase from 4.4 to 11.9 meq/100 g while that of Soil A increased from 5.2 to 21.3 meq/100 g. However, a reduction in the CEC was recorded for Soil K from 36.7 to 28.6 meq/100 g. It is important to recognise that both Soils H and A contained mixed layer vermiculites which correlates with the outcomes by Frempong and Yanful (2006). Post-permeation mineralogical studies are presented in succeeding papers which reveal that the soil-AMD interaction caused dehydroxylation of the hydroxy-interlayered vermiculite thereby, creating the existence of vermiculite as a distinct phase in the soils. As vermiculite would have a higher CEC than its mixed layer varieties, alteration of hydroxy-interlayered vermiculite and illite/vermiculite tend to have added to the increased CEC in Soils H and A observed at the termination of AMD permeation. This outcome also conforms with those of Sucha et al., (2001), Frempong and Yanful (2006) who reported an increase in CEC resulting from the presence of smectite as a separate phase owing to the dissolution of the illite-smectite interlayer on weathering in a natural environment. Sposito (1989) noted that CEC results from specific surface and surface charge density and as the specific surface of each of the soils was lowered by AMD (as indicated by the glycol retention values) the increase in CEC of Soils H and A suggested substantial increases occurred in their surface charge densities. On the contrary, Soil K tended to have experienced a reduction in its surface charge density subsequent to AMD percolation. Furthermore, Soil K contained smectite and the reduction in soil CEC following AMD permeation could have been partly due to the structural alteration of smectite as structural dissolution has been observed by Sucha et al., (2001) to contribute to the reduction of CEC of naturally weathered montmorillonite.

Table 4 present the influences of exchangeable cations and exchangeable acidity to CEC, prior and subsequent to AMD percolation. The outcomes reveal that the substantial increase in exchangeable base cations, particularly calcium and magnesium, added to the significant increase in the CEC of Soil A after permeation with AMD. Nonetheless, the increase in exchangeable acidity was considered to be fair. Conversely, Soils H and K revealed a substantial increase in exchangeable acidity and a fair to significant reduction in exchangeable base cations after AMD permeation. The net decrease in CEC of Soil K subsequent to AMD permeation was reasonably due to the fact that the decrease in exchangeable base cations, particularly calcium and magnesium, was much more substantial than the increase in exchangeable acidity.

Table 4: Effects of exchangeable cations and exchangeable acidity to CEC, prior and subsequent to AMD percolation

Soil	Exchangeable Base Cation (meq/100 g)				Exchangeable Acidity (meq/100 g)	CEC (meq/100 g)	
	Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Total		
Soil A	0.28	0.06	1.81	0.40	2.55	2.65	5.2
MSW landfill leachate infused- Soil A	1.19	0.64	5.55	9.76	17.14	4.16	21.3
Soil H	0.25	0.08	2.30	0.47	3.10	1.30	4.4
MSW landfill leachate infused- Soil H	0.24	0.06	1.80	0.93	3.03	8.87	11.9
Soil K	1.2	0.24	16.7	19.2	34.50	2.20	36.7
MSW landfill leachate infused- Soil K	0.31	0.14	9.66	7.10	17.21	11.39	28.6

### *Oxides and Trace Elements*

Minimal alterations in the major oxide compositions of the soils subsequent to AMD percolation were mainly observed as presented in Table 3. Due to the high acidity of AMD, it was expected to attack the octahedral and tetrahedral sheets thereby, causing the release of silicon, aluminium and iron and hence, leading to a reduction in SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> after permeation. In contrast to this expectation, the percentage of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> increased subsequent to permeation, plausibly due to the high amounts of silicon, aluminium and iron initially existent in the permeant. From the post-permeation soil oxide composition of the respective soils as shown in Table 3, it can be seen that AMD permeation led to the removal of Si, Al and Fe only from Soil K although, the quantities (expressed as SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub>) were moderate. Soil A also experienced a decrease in both the silica: iron oxide and the silica: sesquioxide ratios. It was observed that the difference in LOI of Soil A prior and subsequent to permeation with AMD was moderate. However, the 11.3% LOI of Soil H after AMD permeation was lower than the pre-permeation value of

12.5%. Also, there was an increase in LOI of the natural Soil K from 13.2% to 16.8% after interaction with AMD. The relatively high LOI of these soils possess that the total amount of structural water, organic matter, carbonate, sulphate and chloride present in the soils is high. Outside copper, which showed decreases in concentration after permeation, the other trace metal concentrations in the respective soils increased after permeation, with noteworthy alterations occurring in zinc and nickel. The increased concentration was possibly due to adsorption of these metals from AMD. As such, these subtropical soils function as operative sinks for the zinc and nickel present in AMD, partially because of the presence of iron oxides. This behavioral pattern is similar to that observed by Schwartzman and Taylor (1977) stating that iron oxides function capably as sinks for trace elements and for some anions, may be due to their chemical nature and generally high specific surface area. Although, it is indistinct why copper behaved differently even though, the post-permeation chemical test results revealed that the AMD caused alterations in the variable charge properties of these subtropical soils due to the composite effects of changes in the adsorption or desorption of non-exchangeable cations, composition of exchangeable ions, soil pH and organic matter reduction.

### CONCLUDING REMARKS

The compositions and properties of three subtropical soils sampled from respective active disposal sites around the City of Johannesburg (CoJ) were studied together with the chemical alterations that occurred when percolated with AMD. The effect of AMD on the soils hydraulic conductivity was also assessed. The reduction in organic matter content and mineral alterations that occurred in the soils resulted in the decrease of glycol retention values in the respective soils due to AMD percolation. The pH values of the soils were observed to have reduced at the termination of the test. Furthermore, it was noticed that AMD led to at least 55% increase in the CEC of Soils A and H due to structural changes within the soils (these changes are further reported in detail in succeeding studies). On the contrary, about 40% decrease in the CEC of Soil K containing smectite was observed. This was plausibly due to the structural alteration of the mineral. Variations in LOI of the respective soils subsequent to AMD percolation was recorded. This could possibly be ascribed to the composite effect of soil compositional changes, mainly with regard to mineralogy, structural water, carbonate contents and organic matter. On passing 18-25 pore volumes of AMD through the soils, the hydraulic conductivities of the soils remained almost unchanged from the baseline values with the exception of Soil K, which showed nearly half an order of magnitude increase from  $8.2 \times 10^{-12}$  to  $1.5 \times 10^{-11}$  m/s. As for the trace metals, outside copper which decreased in concentration subsequent to AMD permeation, the other trace metal concentrations in the respective soils were seen to have increased after permeation. Also, substantial changes were observed to have occurred in zinc and nickel, probably due to adsorption and desorption and as such, from AMD permeation the subtropical soils appeared to be active sinks for zinc and nickel. The study revealed that the buffering efficacies of the respective tested clayey soils to AMD chemical species were generally ineffective. As such, it is not advisable for the respective tested soils to be utilised alone in the construction of chemical barrier liners in acid producing waste mine containment facilities, as this may lead to consequential impacts on human and environmental health over time.

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