

Interpretation of Breakthrough Curves and Seepage Bounds from Kaolinite, Halloysite and Illite/Vermiculite Mixed Layer Sub-Tropical Clayey Soil-AMD Interactions

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Abstract—The insistent climate change, population growth and depletion of natural resources from mining and similar activities have triggered diverse environmental challenges. It has long been established that acid mine drainage (AMD) from mining operations in South Africa constitutes a serious environmental problem which requires dire attention. Contamination from AMD presents a severe risk requiring prevention and mitigation measures for curbing consequential impacts on environmental and human health. This increasing challenge led the study to investigate the breakthrough curves and seepage bounds of a kaolinite, halloysite and illite/vermiculite mixed layer subtropical clayey soil interacted with AMD in ascertaining its mineral buffering efficacy for use as natural contaminant barrier in areas under AMD attack. Sequential prolonged permeation up to 24 pore volume passage of AMD through the soil medium was done. The results of the study indicated that after approximately 2.4 pore volumes of 0.01N CaSO₄, a baseline hydraulic conductivity of 1.3×10^{-11} m/s was obtained for the soil which remained unchanged even after 19 pore volume of AMD seepage through the soil. The value was found to be below the accepted criterion of 1×10^{-9} m/s specified for clay liner construction in South Africa but may as well be considered for use as a natural material in the construction of composite barriers for acid-producing wastes.

Keywords—Contaminants, Seepage, Acid Mine Drainage (AMD), Clayey Soils, Buffers

I. INTRODUCTION

ACID mine drainage (AMD) forms in mining environments when ore and waste materials, containing sulphide minerals such as pyrite, are exposed to water and oxygen. In other words, when some mine tailings from

processed sulphide-rich ores are oxidized, AMD may be generated. In South Africa, studies on AMD formation, transport and impacts particularly in the Witwatersrand have been performed by the Council for Geoscience, on behalf of the Department of Mineral Resources [1]. The disturbance of ore bodies and the transport of large volumes of pyritic material to the surface create conditions highly conducive to the generation of AMD, both owing to the exposure of ore in the underground environment and due to the transport of blasted and/or crushed waste rock and tailings to the surface. In order for pyrite to oxidize, both oxygen and water must be present. Water serves not only as a reactant, but also as a reaction medium and a product transport solvent [2]. The rate of AMD generation in an environment where sulphidic material is exposed to oxygen and water, will be determined by a number of factors. The reactions will proceed rapidly in warm humid environments, while other environmental factors, such as the specific sulphide mineralogy and grain size, and the presence or absence of acid neutralizing minerals, such as carbonates will also influence the rate of AMD production and its eventual environmental impact.

The major source of groundwater contamination by mine tailings have been suggested to be AMD [3]. The environmental impact of AMD as reviewed by [4] include; metal toxicity, sedimentation processes and high acidity, which usually have the potential to cause interrelated negative impacts on terrestrial and aquatic life. Since AMD has potential negative impacts on the environment, efforts are made to either prevent or control its generation and migration. As such, several measures and technologies are available as recorded by [5-7] for mitigating the environmental effects of AMD. These include co-disposal of waste rock and mine tailings and the construction of wetlands, base liners or water covers. Soil covers and liners may also be used as hydraulic barriers for containing AMD leakage at mine sites. When used for this purpose, it is usually pertinent to determine whether the soil liner can buffer contaminants or is compatible with AMD.

Consequently, several studies have been conducted on the compatibility of some soils from temperate regions with AMD [8-10]. However, as earlier pointed out, there is need to investigate the interaction of AMD with tropical/subtropical soils as there is insufficient data and knowledge in this area of AMD-soil compatibility interest whose gap requires bridging. South Africa's mining history has created vast economic

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benefits and still plays an important role in safeguarding the country's stance in the global market. Despite such benefits, mining sector operations as elsewhere in the world, have resulted in serious environmental consequences, notably in respect of poor environmental and water management and, in the case of the gold mines of the Witwatersrand, AMD. Pyrite (FeS_2), sphalerite (ZnS), galena (PbS), arsenopyrite (FeAsS) and occasionally chalcopyrite (CuFeS_2) are associated with gold mineralization in operating gold mines in South Africa [11-13]. As recorded by [7] mining activities and processing from these sulphidic ores have led to several tonnes of mine waste that oxidize and lead to the widespread generation of AMD in and around areas where such operations occur in South Africa.

AMD is known to occur in a number of areas in South Africa, mostly in the Witwatersrand Gold Fields, the country's various Coal Fields and the O'Kiep Copper District. Thus, potable sources of water in mining areas, some of which are densely populated, are severely at risk due to AMD contamination. The key factors which differentiate the developing problem in South Africa from international scenarios is the degree of interconnection of large voids, the sheer scale of the Witwatersrand operations and the fact that many of the problem areas are located in or close to major urban centres. Most mining centres are also covered by the natural habitats of some rare and endangered species. Bioaccumulation of metals from AMD adversely affects flora and fauna in South Africa and this has led to the loss of food sources and elimination of some sensitive species [14], [15]. The surface flow or decant of mine water is also of concern to the environment as the water, in accordance with well-known and researched chemical and geochemical reactions between the mine rock strata, wastes and oxygen, readily becomes acidic, characterized by elevated concentrations of salts, heavy metals and radionuclides. The immediate concern is the threat posed by decanting mine water in the Witwatersrand area, which poses potentially severe environmental and safety impacts on the receiving water environment and associated surface areas [6], [16]. In this light, mitigating the effects of AMD contamination of the South African mine environment is imperative.

Currently, with the sulphidic ore exploitation in South Africa, mine tailings dams and acid water containment ponds are being constructed for the storage of mine waste being generated from mining operations, and assessment of the suitability of local construction materials is therefore essential. In an earlier stage of this study, the chemical and mechanical properties, and the mineralogical composition of the sampled soil, prior and subsequent to AMD percolation were determined and the results were presented. However, the study herein investigates the diffusive and advective migration of AMD through kaolinite, halloysite and illite/vermiculite mixed layer compacted clayey soil, sampled around the City of Johannesburg (CoJ) where waste disposal activities occur. To assess the impact of contaminant migration processes on the buffering efficacy and performance of the respective soils as lining materials, a bespoke device was used to permeate the soil with AMD at low flow rates typical of field conditions. The pH, electrical conductivity and solute breakthrough curves from AMD infusion were examined as well as batch

sorption and diffusion tests. The experimental data here from, forms part of a larger study to characterize a number of solute transfer processes as AMD was interacted with the sampled subtropical kaolinite, halloysite and illite/vermiculite mixed layer designated as Soil A being examined for its buffering efficacy towards potential use as natural earthen lining materials (locally available clayey mineral liners) for the containment of mine waste and associated contaminants.

II. EXPERIMENTAL APPROACH

The contaminant mass transport mechanisms in natural and compacted clayey soils have been extensively studied by several authors from past to recent times [17-24]. Sorption, diffusion and hydraulic conductivity tests were performed to determine retardation factors, effective diffusion coefficients and hydraulic conductivities respectively. Diffusion may be the dominant contaminant transport mechanism in clayey soils and as such, laboratory diffusion testing was carried out as a routine approach in the assessment of the tested clayey samples. The advection-dispersion expression by [25] was used to calculate the one-dimensional solute transport through the homogeneous, isotropic compacted clayey Soil A sample as discussed in a previous study.

III. RESULTS AND DISCUSSION

A. Interpretation of Effluent Breakthrough Curves

The initial AMD composition, soil porewater composition and the cation exchange reactions largely influence the effluent composition. This is resultant of the interactions between cations in AMD and the cations at the soil exchange sites, and the impact of AMD on the crystal lattice of soil minerals. Hence, the effluent pH, electrical conductivity and solute breakthrough curves obtained as a result of AMD seepage through the Soil A medium is generally used to assess the properties and composition of the effluents.

B. pH

The relative effluent pH breakthrough curve indicated an increase in pH of the effluent as against the pH of the influent (AMD) before permeating approximately 4 pore volumes of AMD through the compacted soil as shown in Fig. 1. The pH of porefluid of each natural soil and 0.01N CaSO_4 initially percolated through the soil was greater than the pH of the AMD influent of 2.8. This accounted for the initial increase in effluent pH on percolating the soil with AMD. A sharp decrease in effluent pH after only a few pore volumes of AMD seepage through the Soil A suggested a low acid buffering efficacy. A plausible explanation recorded by [26] states that organic matter and carbonate content of soils, are soil constituents known to possess high pH buffering efficacy. However, the soil used in the study was found to have fairly low organic matter and carbonate content which likely contributed to the poor behaviour as acid buffer. Above 4 pore volumes of AMD flow, the acid buffering efficacy of the soil had neared depletion and as such, effluent pH relative to influent pH approached unity.

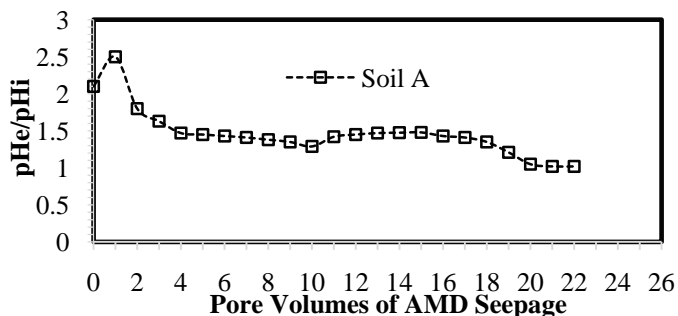


Fig. 1. Effluent breakthrough curve for pH of the tested Soil A

The effluent pH value of the Soil A was seen to increase after only 1 pore volume of AMD seepage beyond which a steep decrease in effluent pH was observed until 4 pore volumes of AMD seepage through the soil. The initial increase in Soil A effluent pH was probably due to mineral alterations caused by the subsequent AMD percolation while approaching equilibrium pH after 20 pore volumes. The considerable increase observed in the effluent pH values after 11 pore volumes of AMD seepage through the Soil A could not be accounted for as this was unclear from the results. However, a similar behaviour was also recorded by several authors [27], [9], [17].

C. Electrical Conductivity

Generally, an increase in the relative electrical conductivity of effluent with increasing pore volumes of AMD seepage through the soil was observed. The increase in relative electrical conductivity of the effluents was consequently ascribed to the increasing concentrations of ions, particularly aluminium, iron, magnesium, calcium, sodium and potassium in the effluents resulting from AMD seepage through the soil. Fig. 2 shows the relative effluent electrical conductivity (EC_e/EC_i) breakthrough curve obtained from the percolation of Soil A with AMD. The relative effluent electrical conductivity breakthrough curve is a weighted contribution from the influent ionic composition and the ions originally present at the soil exchange sites. Thus, the electrical conductivity of a fluid depends on the number and type of ions contained in the fluid.

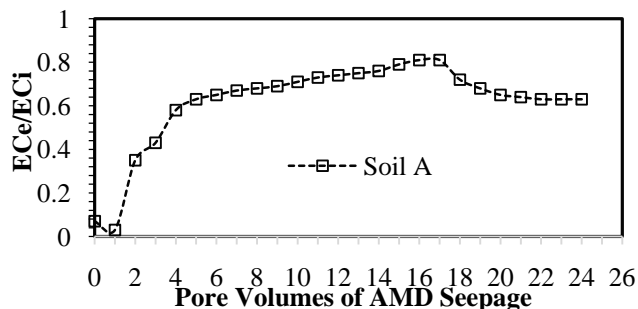


Fig. 2. Effluent breakthrough curve for electrical conductivity of the tested Soil A

Correspondingly, it has been shown that electrical conductivity is an indicator of the ease with which fluid carries an electrical current [28]. Typically, it is expected that close to 1 pore volume of permeant seepage, relative electrical conductivity of 0.5 would be reached as recorded by [29]. This was not the case in Soil A as the relative effluent electrical conductivity value of 0.5 was reached after passing around 4 pore volumes of AMD through the soil. Considering the low seepage rates ensured throughout the study, a decrease in the relative electrical conductivity of Soils A was observed after 19 pore volume of AMD passage. This could not reasonably be accounted for from the composition of effluents as well as from related literature, however, an exception was found in a study by [27] who recorded a similar observation on passage of 15 and 16 pore volumes of AMD through a media of tropical like soils.

D. Soil A Solute-Solvent Interaction

Soil A appeared to have been severely impacted by AMD permeation on termination of the tests. The concentrations of almost all the monitored heavy metals and nominal contaminant species in the effluents from the soil were higher than the influent concentrations as shown in Figs. 3a-c.

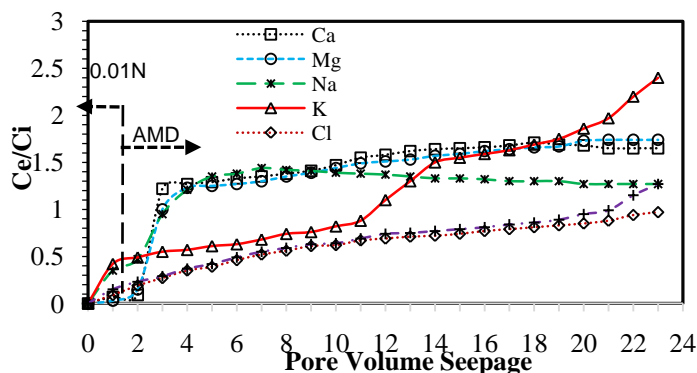


Fig. 3a. Effluent breakthrough curves from Soil A solute-solvent interaction

This indicated the release of species like iron, aluminium, calcium and magnesium due to the dissolution of gibbsite, diaspore ($Al_2O_3 \cdot H_2O$), magnesioferrite and hydroxy apatite ($Ca_5OH(PO_4)_3$) by AMD in Soil A. Furthermore, the concentration of magnesium in the effluent was found to increase and since magnesium occurs chiefly in the octahedral sheets of clay minerals, it suggested the preferential dissolution of the octahedral sheets of the clay minerals existent in Soil A. Also, previous studies on mineralogical and equilibrium speciation studies indicated partial alteration of the illite/vermiculite mixed layer mineral to discrete illite and vermiculite phases after solute-solvent interaction (Soil A-AMD percolation).

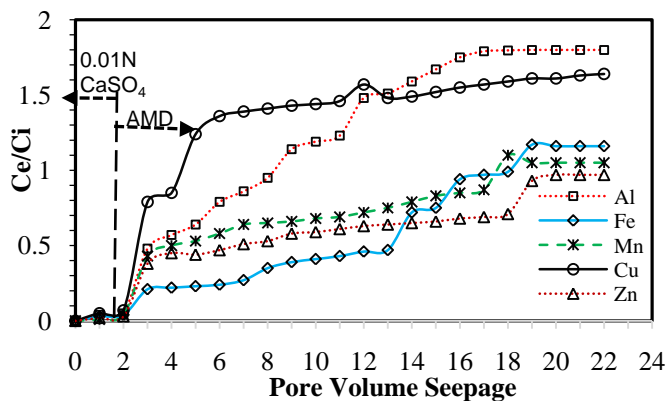


Fig. 3b. Effluent breakthrough curves from Soil A solute-solvent interaction

More so, calcium, magnesium and sodium were the dominant cations in the exchange complex of Soil A as earlier observed. Nonetheless, the observed slight desorption peaks of calcium and sodium shown in Fig. 3a indicated that these were the two species dominantly involved in ion exchange reactions with chemical species existent in the AMD permeant.

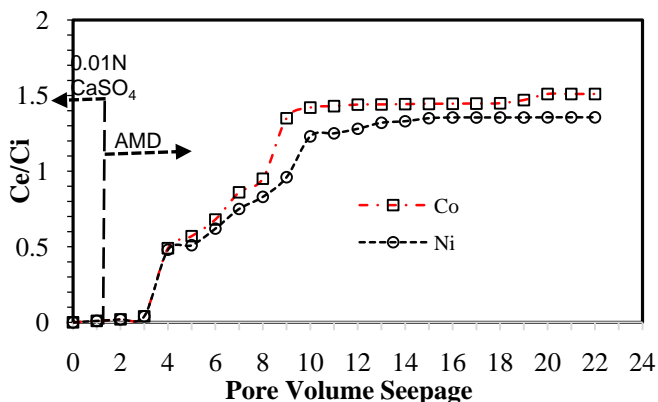


Fig. 3c. Effluent breakthrough curves from Soil A solute-solvent interaction

Therefore, from the effluent solute breakthrough curves there was clear indication that the buffering efficacy of Soil A was low. As such, in a case where AMD of similar composition as used in this study, interacts with a barrier built with Soil A, the integrity of the barrier would be compromised.

E. Contaminant Species Relative Attenuation and Elusion

The procedures outlined by [30] was initiated in determining the relative attenuation number (ATN) for each effluent species representing the relative mobility of the species through the respective compacted soils. The approach entailed calculating the area under the breakthrough curve of each monitored species and expressing the difference between this area and the total area (rectangular area bounded by the initial and final pore volumes of AMD passed and the relative solute concentrations of zero and one) as a percentage of the calculated area under the breakthrough curve of the species. The higher the ATN obtained for a given species present in the effluent the less relatively mobile the species is through the compacted soil while a negative ATN value indicated elution

(desorption) of species from the soil. A qualitative description of the attenuation of species was done using the following classification: $0 < ATN < 30\% \equiv$ low attenuation; $30\% < ATN < 75\% \equiv$ moderate attenuation; while $ATN > 75\% \equiv$ high attenuation. From the tests conducted, Soil A was observed to moderately buffer/attenuate chloride and sulphate from AMD. The ATNs revealed that the exchangeable cations; sodium, calcium and magnesium eluted the soil in various levels into AMD. Table I shows the calculated ATN of each effluent species monitored during soil-AMD percolation tests using the constant-head rigid column hybrid permeameter.

TABLE I
 Relative buffer/attenuation (ATN) of effluent species from soil-AMD interaction tests

Soil Designation	Contaminant Species	ATN*	QAC**
Soil A	Cl	35.7	M
	SO ₄	20.4	L
	Fe	10.3	L
	Zn	4.1	L
	Mn	-0.42	N
	Ni	-0.79	N
	Co	-13.3	N
	Na	-20.2	N
	Al	-27.5	N
	Cu	-28.3	N
	Mg	-37.9	N
	Ca	-51.1	N
	K	-57.4	N

* ATN: Relative Attenuation Number; ** QAC: Qualitative Attenuation Classification- H = High attenuation; M = Moderate attenuation; L = Negative attenuation or Elution

F. Interpretation of Effluent Breakthrough Curves

The results from the dissolution tests indicated that for the soil-AMD interaction time, sodium, nickel, cobalt and sulphate were dissolved from Soil A by AMD as shown in Table II. This observation was however, found to have similar trends with studies by several authors [31], [27] who conducted batch sorption tests using soils from tropical regions under similar conditions with the amounts of cobalt dissolved from the soils by AMD being in ranges of 2.7 to 4.1 mg/L. It was further observed that AMD dissolved zinc from Soils A yet was found to have adsorbed potassium. Generally, small amounts of chloride were either adsorbed or dissolved from the soil over the interaction times of the tests.

TABLE II
 Concentration of contaminant species over the dissolution/batch sorption tests

Sample	Test Period (days)	Concentration of Contaminant Species (mg/L) ^{a, b}						
		K	Co	Na	Zn	Ni	Cl	SO ₄
AMD		4.7	7.5	27.9	161.7	181.3	200.6	5075.4
Soil A	5	2.4	7.8	42.3	192.1	235.5	179.6	8856.6
	10	2.6	9.6	42.7	199.3	239.7	174.4	8859.8
	15	2.7	10.9	43.5	201.7	243.3	173.9	8872.3
		Distribution Coefficient/Dissolution Degree (mL/g) ^{a, b}						
Soil A	5	2.9	1.4	1.7	0.7	1.4	0.4	2.5
	10	2.6	1.7	1.9	0.7	1.5	0.6	2.6
	15	2.8	2.1	2.0	0.9	1.6	0.6	2.7

^a Temperature: 22 ± 2°C; ^b Soil: Solution Ratio (1:4)

Consequently, the most substantially extracted metals by AMD from the soil were cobalt and nickel with the soil observed to adsorb potassium and chloride. Generally, the impact of AMD on Soil A during the batch tests over various interaction times was observed to be closely identical. During the batch tests, equilibrium conditions were attained which was evident from the data in Table II showing the effect of various interaction times on the insignificant amount of contaminant species dissolved from the soil by AMD.

G. Diffusion Tests

Figs. 4a-d presents the time-dependent concentrations of chemical species in the chamber of the AMD solution during the diffusion tests and the depth-dependent species soil porewater concentrations at the end of the tests. The outcomes for Soil A obtained from the diffusion tests is shown in Figs. 4a-d.

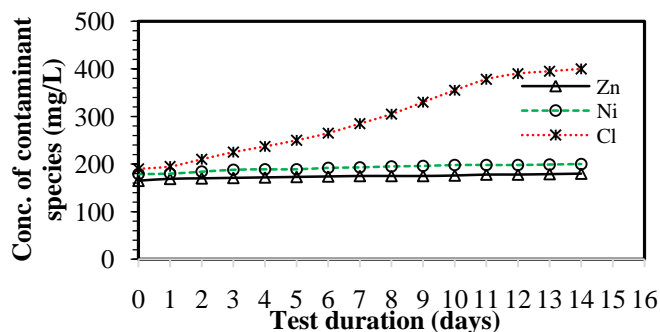


Fig. 4a. Time-dependent chemical species conc. in AMD chamber of Soil A diffusion test

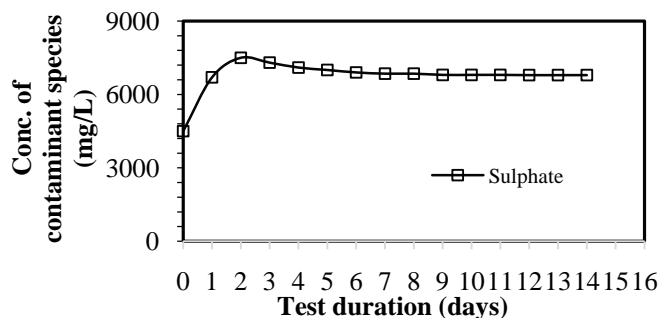


Fig. 4b. Time-dependent chemical species conc. in AMD chamber of Soil A diffusion test

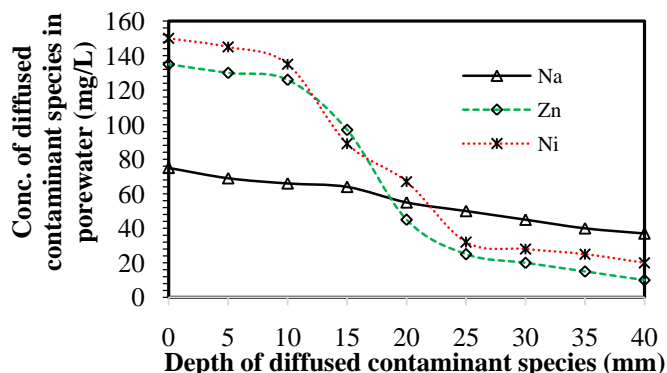


Fig. 4c. Depth-dependent chemical species conc. in porewater of Soil A during diffusion test

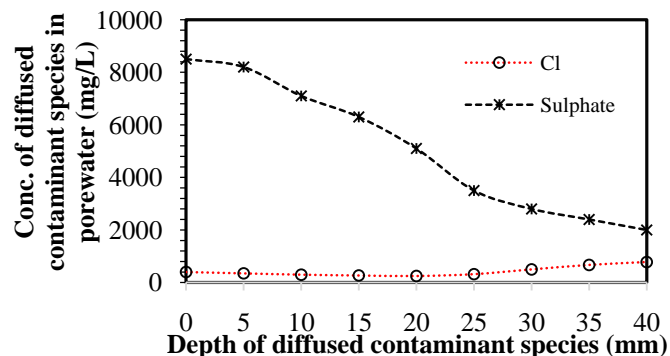


Fig. 4d. Depth-dependent chemical species conc. in porewater of Soil A during diffusion test

Out of the seven contaminant species monitored during the diffusion tests, results essentially revealed the concentrations of sodium, zinc, nickel, cobalt and chloride in the permeant chamber (containing AMD) to increase with respect to time and inclined to reaching equilibrium values towards the end of the diffusion tests.

IV CONCLUSIONS

The study presented herein, examined the buffering efficacy of Soil A- kaolinite, halloysite and illite/vermiculite mixed layer subtropical soil sampled from around the City of Johannesburg (CoJ) towards its efficient and effective use as a natural mineral liner for acid mine drainage (AMD) containment and mitigation in areas affected by mining activities. After at least 19 pore volumes of AMD seepage through the soil, the measured soil hydraulic conductivity value was 1.3×10^{-11} m/s. This final hydraulic conductivity value fall short of the maximum soil hydraulic conductivity acceptance criterion of 1×10^{-9} m/s specified for clay liner construction in South Africa. The pH breakthrough curve revealed that the soil has low buffering efficacy to acids so failed to sufficiently buffer/attenuate potential contaminant species present in AMD. More so, the solute breakthrough curves clearly indicated that the soil was not effective in buffering the heavy metals and the other pollutant species present in AMD. The species concentrations obtained from either the effluents from the hydraulic conductivity tests or the solution and sections of soil samples obtained from dissolution and diffusion tests suggested that the soil-AMD interaction is a complex process. The results of the study suggest that interactions between AMD and the soil plausibly resulted in dissolution of metals from soil grains, desorption of adsorbed contaminant species at the exchangeable sites of the soil and, alteration and dissolution of soil minerals. Therefore, considering the general outcomes of the study, the Soil A-kaolinite, halloysite and illite/vermiculite mixed layer natural subtropical soil was found to be incompatible with AMD and as such, may not be used alone as natural clayey mineral lining materials towards AMD containment disposal.

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REFERENCES

- [1] Coetzee H. Van Tonder D. Wade P. Esterhuysen S. Van Wyk N. Ndengu S. Venter J. Kotoane M. 2007. Acid mine drainage in the Witwatersrand: Department of Minerals and Energy, Pretoria, Council for Geoscience Report No 2007-0260, pp. 81.
- [2] Van Tonder D.M. Coetzee H. Esterhuysen S. Strachan L. Wade P.W. Mudau S. 2009. South Africa's challenges pertaining to mine closure-development and implementation of regional mining and closure strategies. Mine Closure 2009. Proceedings of the fourth international seminar on mine closure. Fourier, A., Tibbett, M., Weiersbye I., and Dye, P., Johannesburg, Australian Centre for Geomechanics.
- [3] Wade P.W. Woodbourne S. Morris W. Vos P. Jarvis N. 2002. Tier 1 risk assessment of radionuclides in selected sediments of the Mooi River, Water Research Commission, WRC Report 1095/1/02, Pretoria: 93 p.
- [4] Coetzee H. Wade P. Winde F. 2006. An assessment of sources, pathways, mechanisms and risks of current and future pollution of water and sediments in the Wonderfontein Spruit Catchment, Water Research Commission, WRC Report No. 1214/1/06, Pretoria: 202 p.
- [5] Vermaak J.J.G. Wates J.A. Bezuidenhout N. Kgwale D. 2004. The evaluation of soil covers used in the rehabilitation of coal mines. Research Report 1002/1/04, Water Research Commission, Pretoria.
- [6] Tutu H. McCarthy T.S. Cukrowska E. 2008. The chemical characteristics of acid mine drainage with particular reference to sources, distribution and remediation: The Witwatersrand Basin, South Africa as a case study. Applied Geochemistry, 23, 3666- 3684.
- [7] International Network for Acid Prevention (INAP) 2009. Global Acid Rock Drainage Guide, <http://www.gardguide.com>.
- [8] Seuntjens P. Mallants D. Simunek J. Patyn J. Jacques D. 2002. Sensitivity analysis of physical and chemical properties affecting field-scale cadmium transport in a heterogeneous soil profile. J. of Hydrol., 264: 185-200.
- [9] Amezaga J.M. Younger P.L. 2006. Mine water management in European Environmental Policy: An Assessment of recent legislative developments. In Barnhisel (ed.) Proceedings of the 7th International Conference on Acid Rock Drainage ICARD, March, 26-30, St. Louis, Missouri.
- [10] Vincenzo C. Antonio C. Alessandro C. 2011. Laboratory-Scale Study on Reactive Contaminant Transport in Soil By Means of One-Dimensional Advective Dispersive Models. Journal of Ag. Eng-Riv. di Ing. Agr. 3: 1-6.
- [11] Hobbs P. Cobbing J. 2007. A hydrogeological assessment of acid mine drainage impacts in the West Rand Basin, Gauteng Province. Report no. CSIR/NRE/WR/ER/2007/0097/C. Council for Scientific and Industrial Research. Pretoria.
- [12] Department of Water Affairs and Forestry, DWAF 2008. Integrated Mine Water Management, Best Practice Guideline H1, Directorate: Resource Protection and Waste, Pretoria, 67 pp.
- [13] Department of Water Affairs DWA 2010. Projects/Programmes, <http://www.dwa.gov.za/projects.aspx> (accessed 29 November 2010).
- [14] Netili K.F. Van Tonder D. Coetzee H. Rust U. Yibas B. 2010. Strategic Water Management Project: Proposed way forward prepared by CGS. Council for Geoscience, Pretoria, 21 pp.
- [15] Lin L. Hansen R.N. 2010. Mine Flooding, Identification of Decant Site and determination of Environmental Critical Level on the Central Rand Gold Field, Council for Geoscience Report Number 2010-0199, Council for Geoscience, Pretoria, 75 pp.
- [16] Yibas B. Pulles W. Nengovhela C. 2010. Kinetic Development of Oxidation Zones in Tailings Dams with specific reference to the Witwatersrand Gold Mine Tailings Dams. Report to the Water Research Commission, WRC Report No. 1554/1/10, 105 pp.
- [17] Celik B. Rowe R.K. Unlu K. 2009. Effect of vadose zone on the steady-state leakage rates from landfill barrier Systems. Journal of Waste Management 29:103-109.
- [18] Nguyen T.B. 2011. Comparison of four composite landfill liner systems considering leakage rate and mass flux. Proceedings of 14th Asian Regional Conference on Soil Mechanics and Geotechnical Engineering, Hong Kong, May 23-27, 2011, 6 p.
- [19] Rowe R.K. 2012. Short- and long-term leakage through composite liners. The 7th Arthur Casagrande Lecture. Proceedings of the 14th Pan-American Conference on Soil Mechanics and Geotechnical Engineering, Toronto, Ont., Oct. 2011. 49:141-169.
- [20] Agbenyeku E.E. Okonta F.N. Ojuri O.O. 2013a. Leachate Flow through Composite Barrier from Defected Geomembrane. 2nd African Regional Conference on Geosynthetics, Accra, Ghana, 18-20 November (CD ROM).
- [21] Agbenyeku E.E. Okonta F.N. Ojuri O.O. 2013b. Evaluation of Empirical Equations for Leachate Migration through Composite Barrier with Defected Geomembrane. 2nd African Regional Conference on Geosynthetics, Accra, Ghana, 18-20 November (CD ROM).
- [22] Agbenyeku E.E. Muzenda E. Msibi I.M. 2014a. "Zeolitic Mineral Liner as Hydraulic and Buffering Material", International Conference on Earth, Environment and Life sciences (EELS-2014) Dec. 23-24, 2014 Dubai (UAE).
- [23] Agbenyeku E.E. Muzenda E. Msibi I.M. 2014b. "Buffering of TOC-Contaminant Using Natural Clay Mineral Liner", International Conference on Earth, Environment and Life sciences (EELS-2014) Dec. 23-24, 2014 Dubai (UAE).
- [24] Agbenyeku E.E. Akinseye S.A. 2015. Leachate Percolation through Failed Geomembrane of a Geo-Composite Soil Barrier World Journal of Environmental Engineering, 2015, Vol. 3, No. 2, 52-57.
- [25] Rowe R.K. Booker J.R. Fraser M.J. 1994. POLLUTEV6 and POLLUTE-GUI. User's guide. Distributed by GAEA Environmental Engineering Ltd., London, ON, Canada.
- [26] Yong R.N. Mohamed A.M.O. Warkentin B.P. 1998. Principles of contaminant transport in soils. Developments in geotechnical engineering. 72. Elsevier Science, Amsterdam, The Netherlands.
- [27] Frempong E. Yanful E. 2007. Tropical Soils-Acid Mine Drainage Interactions: Breakthrough Curves and Some Transport Parameters. Journal of Environ. Eng. 133:7, 733-741.
- [28] Shackelford C.D. Malusis M.A. Mitchell J.M. Stem R.T. 1999. Electrical conductivity breakthrough curves. Journal of Geotechnical and Geoenvironmental Engineering, 125(4):260-270.
- [29] Shackelford C.D. Lee J.M. 2003. The destructive role of diffusion on clay membrane behavior. *Clays and Clay Minerals*, 51(2), 187-197.
- [30] Griffin R.A. Shimp N.F. 1978. "Attenuation of Pollutants in Municipal Landfill Leachate by Clay Minerals", EPA Report No. EPA 600-2/78-157.
- [31] Tsugawa J.K., Boscov M.E.G., Velio K. L., de Olivera E., (2002), Dissolution and reverse diffusion of metals in a compacted lateritic clay. *In Proceedings of the Fourth International Congress on Environmental Geotechnics*, Rio de Janeiro, Brazil, 11-15 August 2002.1. pp. 453-458.