

Interpretation of Breakthrough Curves and Permeation Parameters from Sub-Tropical Kaolinite Clayey Soil-AMD Interactions

Emmanuel Emem-Obong Agbenyeku, Edison Muzenda and Innocent Mandla Msibi, *Member, IAENG*

Abstract—Climate change, growth in population and rising pressures on natural resources triggered by mining and similar activities have led to enormous environmental challenges. Acid mine drainage (AMD) from mining operations in South Africa causes severe environmental issues in need of drastic and lasting solutions. Contamination from AMD requires prevention and mitigation measures to address the various significant impacts on human and environmental health. This pressing challenge permitted the study to investigate and analyze the breakthrough curves and permeation parameters of a subtropical kaolinite clay mineral soil interacted with AMD towards determining its buffering efficacy as a natural contaminant barrier for use in sites prone to AMD contamination. Series of AMD permeation through the soil medium was conducted. The results of the study showed that after the percolation of roughly 2.4 pore volumes of 0.01N CaSO₄, a baseline hydraulic conductivity of 2.6×10^{-11} m/s was reached which slightly increased to 3.5×10^{-11} m/s after introducing about 7 pore volumes of AMD. The values fluctuated between 3.3×10^{-11} m/s and 3.4×10^{-11} m/s on continued AMD permeation. However, an average value of 3.35×10^{-11} m/s was recorded on termination of the test after 18 pore volume permeation. 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 can be incorporated into the construction of composite barriers for acid generating containment facilities.

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 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

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Emmanuel Emem-Obong Agbenyeku is a research student at the University of Johannesburg, South Africa (phone: +27 11 559 6396; e-mail: kobitha2003@yahoo.com; emmaa@uj.ac.za).

Edison Muzenda is a Professor of Chemical and Petroleum Engineering and Head of Department of Chemical, Materials and Metallurgical Engineering, College of Engineering and Technology, Botswana International University of Science and Technology, Private Mail Bag 16, Palapye, Botswana, as well as

visiting Professor at the University of Johannesburg, Department of Chemical Engineering, Faculty of Engineering and the Built Environment, Johannesburg, P.O.Box 17011, 2028, South Africa (phone: +27 11 559 6817; e-mail: emuzenda@uj.ac.za; muzendae@biust.ac.bw).

Innocent Mandla Msibi is Group Executive of Innovation and Impact, Water Research Commission, Pretoria; Research and Innovation Division, University of Johannesburg, South Africa (phone: +27 12 330 0344; e-mail: mandlam@wrc.org.za).

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 vital.

Presently, 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 permeation of AMD through kaolinite compacted clayey soil, sampled around the City of Johannesburg (CoJ) where waste is disposed. To assess the impact of contaminant percolation processes on the buffering efficacy and performance of the soil as a lining material, 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 permeation 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 interacted with the sampled subtropical kaolinite clayey sample designated as Soil H being examined for its buffering efficacy towards potential use as natural

earthen lining material (locally available clayey mineral liner) 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 H 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 H 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 H as shown in Fig. 1. The pH of porefluid of the 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 H 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 H (subtropical kaolinite) 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. This outcome was similar to the behaviour displayed by the kaolinite, halloysite and illite/vermiculite mixed layer subtropical clayey soil tested in a previous study. The effluent pH value of Soil H approached equilibrium pH ($\text{pH}_{\text{eff}}/\text{pH}_{\text{inf}} \sim 1$) after 6 pore volumes of AMD permeation.

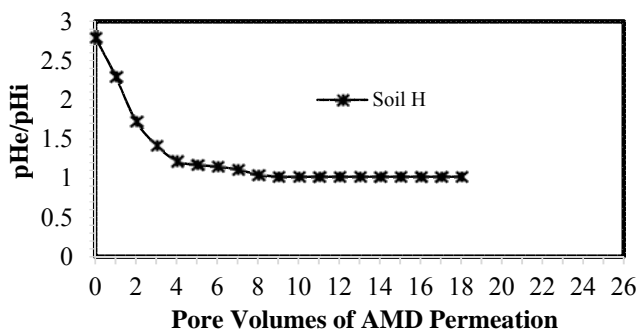


Fig. 1. Effluent breakthrough curve for pH of the tested Soil H

This suggested that Soil H (subtropical kaolinite clayey soil) had a lower soil pH buffering efficacy than kaolinite, halloysite and illite/vermiculite mixed layer and smectite, Fe-chlorite and kaolinite mixed layer tested in previous studies.

C. Electrical Conductivity

Generally, an increase in the relative electrical conductivity of effluent with increasing pore volumes of AMD permeation through the soil was observed. The increase in relative electrical conductivity of the effluents was consequently attributed to the increasing concentrations of ions, particularly aluminium, iron, magnesium, calcium, sodium and potassium in the effluents as a result of AMD permeation through the soil. Fig. 2 shows the relative effluent electrical conductivity (EC_e/EC_i) breakthrough curve obtained from the permeation of Soil H 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.

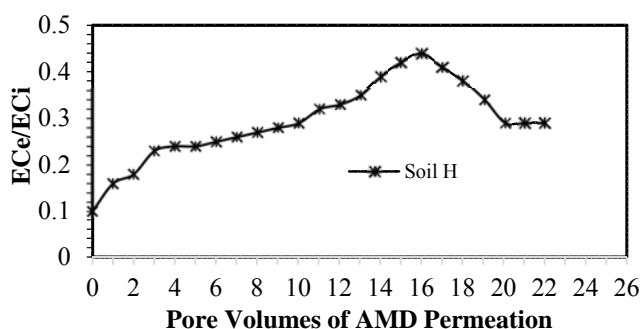


Fig. 2. Effluent breakthrough curve for electrical conductivity of the tested Soil H

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 H as the relative effluent electrical conductivity of 0.5 was not convincingly reached but a value of 0.44 was recorded even after passing 20 pore volumes of AMD. The plausible explanation for this observation may plausibly be the prevalence of ions with lesser equivalent ionic conductivity

than those that were originally existent at the exchange sites after ionic exchange between AMD and the Soil H.

D. Soil H Solute-Solvent Interaction

From Fig. 3a the solute breakthrough curves for calcium, sodium and magnesium in Soil H revealed desorption peaks and the relative effluent concentrations of these species were found to remain below unity even up to 22 pore volumes of AMD permeation. This was an indication that calcium, sodium and magnesium were the main species involved in cation exchange reactions. Calcium, magnesium and sodium were confirmed to be the dominant cations at the exchangeable sites of Soil H from the cation exchange complex (CEC) test results. As presented in a previous study, jarosites (Na,K,H_3O) $Fe_3(SO_4)_2(OH)_6$ were formed in Soil H as a result of AMD permeation which was reported by [27] to be able to integrate solid solution elements such as sodium, calcium and potassium.

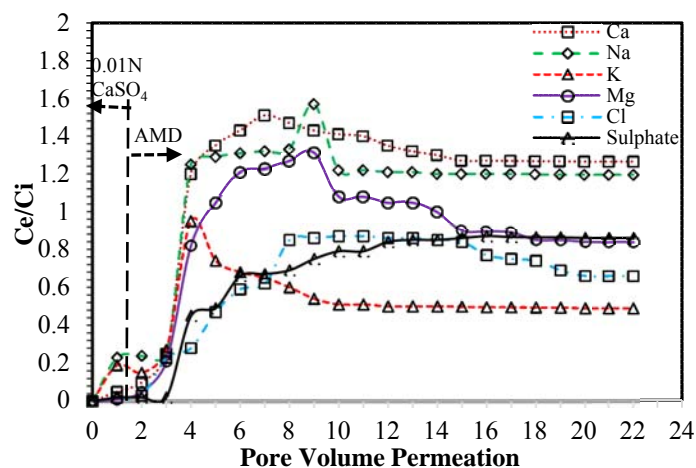


Fig. 3a. Effluent breakthrough curves from Soil H solute-solvent interaction

Consequently, co-precipitation and solid solution substitution of potassium into the jarosites structure are possible mechanisms for removal of potassium from Soil H evident by the reduction of potassium concentration in the effluent as seen in the Fig. 3a. Nevertheless, the relatively higher effluent sodium and calcium concentrations may reasonably be as a result of their participation in exchange reactions. Chloride as seen in Fig. 3a did not achieve a relative effluent concentration unity ($C_e/C_i = 1$) possibly caused by anion exclusion. However as seen in Fig. 3b, the breakthrough curve for copper showed a substantial concentration increase after about 2 pore volumes of AMD permeation. The initial concentrations of iron, manganese and aluminium in Soil H were low but their effluent concentrations eventually surpassed the influent concentrations after about 8 pore volumes of AMD passage.

The effluent concentrations of aluminium and iron species were observed to steadily increase above the influent concentration even after AMD seepage. This can be accounted for by the recorded dissolution of gibbsite ($Al_2O_3 \cdot 3H_2O$) and magnesioferrite ($MgFe_2O_4$) in Soil H caused by AMD attack.

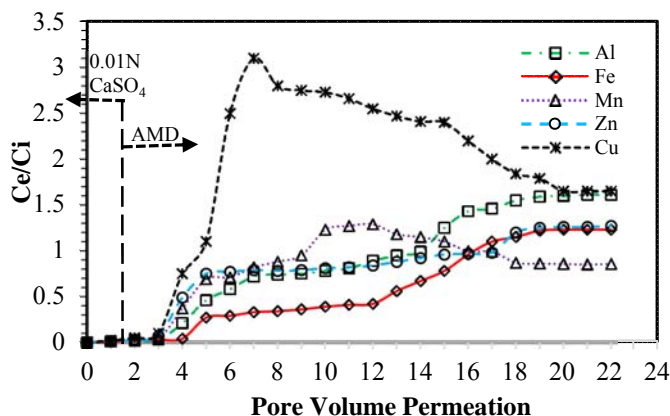


Fig. 3b. Effluent breakthrough curves from Soil H solute-solvent interaction

Additionally, the increased concentration of magnesium, iron and aluminium in Soil H could be a clear indication of the breakdown of the crystal lattice of some clay minerals which led to the release of aluminium and iron. In the case of zinc, the effluent concentration was observed as seen in Fig. 3b to be below the influent concentration even after 22 pore volumes of AMD permeation. Therefore, in consideration of AMD containment based on the buffering efficacy of Soil H under similar solute-solvent interaction (Soil H-AMD permeation), it was generally found out that Soil H was unsuitable for use in this case as a natural barrier lining material.

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 permeated 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 H 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 H	K	47.5	M
	Cl	38.3	M
	SO ₄	14.6	L
	Al	-2.1	N
	Mn	-4.2	N
	Zn	-8.5	N
	Mg	-10.2	N
	Fe	-9.8	N
	Na	-13.5	N
	Ca	-28.1	N
	Cu	-72.5	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 H by AMD as shown in Table II. This observation was however, found to have similar trends with studies by several authors [31], [28] 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 Soil H 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 H	5	2.6	7.5	41.4	187.8	233.5	205.1	8673.5
	10	2.4	7.9	42.5	185.3	231.8	203.6	8679.9
	15	2.5	8.6	43.1	184.9	232.2	202.8	8711.2
		Distribution Coefficient/Dissolution Degree (mL/g) ^{a, b}						
		K	Co	Na	Zn	Ni	Cl	SO ₄
Soil H	5	2.7	1.7	1.6	0.7	1.3	0.3	2.6
	10	3.9	1.4	1.9	0.7	1.3	0.2	2.6
	15	4.2	1.4	1.9	0.6	1.2	0.2	2.5

^a Temperature: $22 \pm 2^\circ\text{C}$; ^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. Generally, the impact of AMD on Soil H 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 and b 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 H obtained from the diffusion tests is shown in Figs. 4a and b.

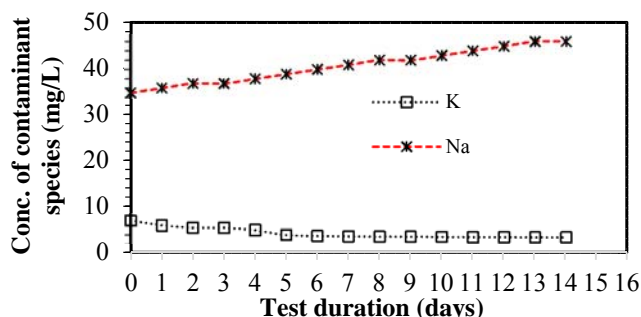


Fig. 4a. Time-dependent chemical species conc. in AMD chamber of Soil H diffusion test

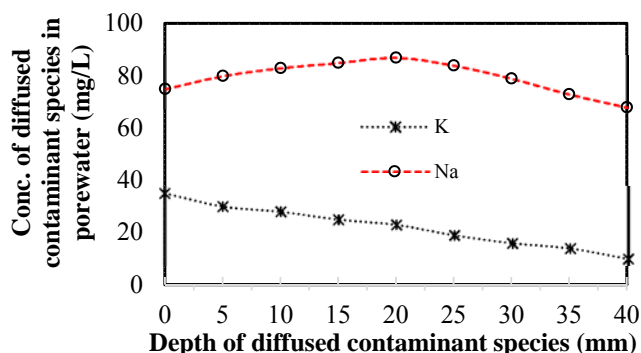


Fig. 4b. Depth-dependent chemical species conc. in porewater of Soil H during diffusion test

Out of the contaminant species monitored during the diffusion tests, results essentially revealed the concentrations of sodium 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 as shown in Fig. 4a. From literature, it was found that [31], [28] obtained similar results. The observed increase in the concentrations of contaminant species in the permeant chamber suggested the release of species from the soil and their reverse diffusion into AMD. Nevertheless, at the end of the diffusion test, sodium concentrations in porewater of Soil H was found to have increased with depth plausibly caused by the release of the specie from the mineral alterations that occurred during the soils-AMD interactions.

IV CONCLUSIONS

The study presented herein, examined the buffering efficacy of Soil H- subtropical kaolinite clayey 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 impacted by mining activities. After 18 pore volumes of AMD permeation through the soil, the measured soil hydraulic conductivity value was 3.35×10^{-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. Moreover, 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 H- kaolinite 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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