Soil Quality in the Basin of Mine Effluents and the Potential of Alleviation of Metal Dispersion

E. Fosso-Kankeu[1*], R. Kaitano[1], F. Waanders[1]and A.F. Mulaba-Bafubiandi[2]

1 School of Chemical and Minerals Engineering, Faculty of Engineering, North West University, Potchefstroom Campus, Potchefstroom, South Africa, [*]e-mail: 24838616@nwu.ac.za;
2Minerals Processing and Technology Research Center, Department of Metallurgy, School of Mining, Metallurgy and Chemical Engineering, Faculty of Engineering and the Built Environment, University of Johannesburg, PO Box 17011, Doornfontein 2028, Johannesburg, South Africa

Abstract   The soils along the basin ofmine effluent were investigated for their role in the mitigation of the pollution of river water in the residential areas around Potchefstroom in South Africa.The results showed that the soils were mainly semi-permeable soil (K from 5.96×10^{-6} to 1.26×10^{-5} m/s) and the cation exchange potential (CEC) values(19.3 to 38.5 cmol/kg)were indicative of the presence of clays in the soils. Investigation of the adsorption potential of soils showed that they had higher affinity for Cu compared to Ni and Zn, and bottom soils were better adsorbents than the top soils. Clayey material in soils along the mine effluent basin enhances interaction with metals, contributing to the mitigation of water pollution.
Keywords metal retention, mine effluent, soil permeability, clay,cation exchange capacity

Introduction

The mobility of metals in surface water or in the soil is often dependent on the adsorption potential and the permeability of the soil (Shakelford and Daniel, 1991; Jungnickel et al., 2004). The physical and chemical nature of the soil is therefore an important factor controlling the dispersion of metals in the environment. It is reported that clay components of the soil play an important role in the sorption of metals or metal ions from environmental water sources (Antoniadis and McKinley, 2003). The reversible or irreversible fixation of metals ions on the soil components has been described by a migration term which includes advective and diffuse transport as well as a retardation term (Roehl and Czurda, 1998). Clay minerals have different geochemical behaviors and may undergo different physical and chemical responses to environmental conditions. The transport of solute and the cations exchange capacity of the clays will therefore depend of the rock-leachate in a given soil (Cuevas et al. 2009). The mineral component of soil is divided into silt, sand and clay, with clay materials belonging mainly to the phyllosilicates class. The formation of clay materials in soil depends on transformation mechanisms and neo-formation processes; it is therefore evident that the content of the soils will differ with environmental exposure related to the geographical area. The potential of the soil in a river basin to retard metal migration intothe ground water, or the transportation to other surface water sources must be investigated with particular attention to the nature of the specific soil. Metal retention in the soil can be affected by chemical interaction between the charged groups of the soil and the metals or by physical interaction, as metal migration through the soil is also determined by the soil permeability.

In this study the main focus is on the investigation of the physical and chemical characteristics of environmental soils likely to contribute to the remediation of metal dispersion in surface water.

Methodology

a- Sampling of environmental water and soils

Water samples were collected from effluents around obsolete mines near residential areas of the North West Province in South Africa. Soils in the same basin were collected at the

surface and at a depth of 1 m below the surface. The soils were extracted as block and loose samples for permeability test and mineralogical analysis, respectively.

b-Characterization of environmental soils

XRD and XRF analyses

Loose soil samples were dried at 100 ℃ for 24 hours in a oven (Digital Oven 700 L, model code 385). The dried samples were then crushed using a mortar and pestle to obtain a powder and subsequently sieve screened to retain a particle size of less than 75 micron.

The recovered powder samples were analyzed by X-ray diffractometer (XRD) and X-ray fluorometer(XRF) techniques.

Permeability test

The undisturbed soil was carefully cut in a mold and soaked for 48 hours till saturation. The saturated soil in the mold was then introduced into the permeameter. The falling head apparatus had a stand pipe of 4 mm diameter, which constituted the manometer. The water was allowed to flow in the manometer and a stop watch was started giving the time for water to flow from level 1 to level 2, which was recorded. The experiment was repeated three times and the average of readings in close agreement was considered for the calculation of the permeability according to the following formula:

$$K = \frac{aL}{At} \ln \frac{h_1}{h_2} \quad (1)$$

Where K is the coefficient of permeability, a is the cross sectional area of the stand pipe, L is the length of the soil sample, A is the cross sectional area of the soil, h_1 is the hydraulic head across the sample at the beginning of the experiment, h_2 is the hydraulic across the sample at the end of the experiment

Cation exchange capacity test

The determination of the cation exchange capacity of the soil samples was done through a modified method, or the $BaCl_2$-compulsive exchange procedure (Gillman and Sumpter, 1986) using 1 M of NH_4Cl in replacement of $BaCl_2$.

c- Metal adsorption experiments

The dried soil samples, of particle size <75 microns, were exposed to metals in a batch system. A mass of 0.1 g of soil was mixed in 100 ml solution of Cu and Zn at initial concentration of 5, 10, 15 and 20 mg/L. The mixture was stirred at 160 rpm on a shaker for 5 hours at room temperature (~25 ℃); after exposure the mixture was centrifuged for 5 min at 10000 rpm, and then the residual metal in the supernatant was measured using an atomic adsorption spectrophotometer (AAS). The adsorption capacity was determined using the following equation:

$$q_e = \frac{C_0 - C_e}{m} \times V \quad (2)$$

Where: q_e is adsorption capacity (mg/g), C_0 is the initial concentration of metal (mg/L), C_e is the concentration of metal at equilibrium (mg/L), V is the volume of the solution (L) and m is the mass of adsorbent (g)

Results and discussion
Mineralogical composition of soils in effluent basin

The XRD analysis showed that the soil samples mainly consisted of aluminosilicate minerals with a dominance of phyllosilicates which included muscovite, bentonite, montmorillonite and illite. This result clearly indicated that there was a considerable amount of clayey materials in the soil essentially downstream of the mine areas (points 7, 8 and 9). Major trace metals identified by XRF analysis included Zn, Cu, Ni and Co, relatively abundant in soils around mine areas (points 1 and 2).

Water quality in the effluents

The analysis of water in the effluents was done to determine what major metal pollutants in the mine effluents were transported in the surface water in the residential areas. As shown in Table 1 nickel and zinc were present in relatively high concentrations in the mine effluents, but there was a significant decrease of these concentrations in water downstream, below recommended values for drinking water use (SABS, 2005).

Physico-chemical characteristic of soils

The physico-chemical properties of the soil samples were determined by the permeability and CEC tests. It was observed (table 2) that the soils with a relatively high content of clay minerals (points 7, 8 and 9) had a very low permeability ($K < 10^{-4}$ m/s), while the soils around the mine areas (points 1, 2 and 6) had a relatively higher permeability ($K \sim 1 \times 10^{-1}$ m/s). The CEC values were generally between 19 and 48 cmol/kg, which is to a large extent also indicative of claying soils. There were no major differences among the physico-chemical properties of the top and bottom soils, although the CEC values tend to increase in the bottom soils at sampling points 6, 7, 8 and 9; different trend was observed at sampling points 1 and 2 where the soils have been disturbed by mining activities.

Table 1   Concentrations of selected elements in mine effluents

Sampling points	Elements concentration mg/L									
	Na	Mg	Fe	Co	Ca	Al	Si	Ni	Zn	Cu
1	132.1	186	nd	nd	206.04	86.4	175.7	2.42	4.46	nd
2	131.04	485.4	nd	nd	1028	35.58	156.7	2.56	5.607	nd
3	132.2	250.4	nd	nd	181.8	21.6	161.3	2.43	4.965	nd
4	130.5	112	nd	nd	168.17	nd	170.7	0.35	0.27	nd
5	131.6	87.4	nd	nd	169.6	nd	173.03	nd	0.402	0.2
6	131.14	92	nd	nd	171.35	nd	167.9	0.5	0.36	nd
7	206.7	45.09	1.442	0.013	111.6	1.439	na	0.008	0.171	nd
8	197.1	53.46	0.420	nd	138.9	0.082	na	0.019	0.096	nd
9	162.6	64.38	11.71	nd	140	15.06	na	0.028	0.178	nd
MAL (mg/L)	0.2-0.4	70-100	0.2-2	0.5-1	150-300	0.3-0.5	nav	0.15-0.35	5 - 10	1 - 2

nd: not detected, na: not analyzed, nav: not available, MAL: maximum allowable limit (SABS, 2005)

Table 2   Permeability and CEC values of top and bottom soils

Sampling points	Sample types			
	Top soil		Bottom soil	
	Permeability (m/s)	CEC (cmol/kg)	Permeability (m/s)	CEC (cmol/kg)
1	5.784×10^{-1}	37.81	1.542×10^{-1}	13.81
2	1.2	21.71	na	22.65
6	5.702×10^{-1}	30.86	1.02	48.23
7	1.294×10^{-5}	19.3	6.108×10^{-6}	34.32
8	6.469×10^{-6}	21.13	7.188×10^{-6}	38.5
9	8.06×10^{-6}	25.723	7.188×10^{-6}	35

Metal adsorption potential of soils

The metal adsorption capacity of soil indicates its ability to reduce the mobility of metal ions in the effluent. The main metal ions observed in the mine effluents were exposed to powdered dried soils in a batch system, to estimate the possible interaction. Results in table 3 show that the soil samples from sampling points 7, 8 and 9 had a higher adsorption capacity compared to the soil samples from the mine area. The soils had a higher affinity for copper than nickel and zinc. The adsorption capacity of the bottom soils was higher than for the top soils.

Table 3 *Adsorption capacity of top and bottom soils*

Sampling points	Adsorption capacity (mg/g)					
	Top soil			Bottom soil		
	Cu	Ni	Zn	Cu	Ni	Zn
1	2.0302	1.5929	0.0000	2.4215	1.9730	0.0839
2	3.8515	1.8033	0.0000	3.6846	1.4974	0.0000
6	8.0450	3.0901	1.7723	9.2118	4.8350	3.5411
7	17.0081	3.5654	5.0376	19.8845	7.0922	11.4323
8	14.5404	4.0340	4.6615	19.6250	6.6929	9.9608
9	13.9350	2.9908	3.7840	18.6574	3.9756	9.6111

Discussion

The presence of clay minerals in soils may affect both the vertical and the horizontal mobility of the metals in the effluent by reducing the permeability and increasing the CEC values. The higher permeability of soils in the mine areas may be due to the disturbance of the soil during mining activity but mostly to the lower content in clay minerals. In this study the soil samples were collected only up to 1 m depth, which makes it difficult to predict the vertical mobility of metals up to the water table; however, with stagnant water in the ponds around the mine areas, the abundance of acid rain water and the higher content of metals in the soil, such properties (low clay content and higher permeability) of the soils are conducive to potential contamination of ground water in relatively short period of time (Bhattacharya et al. 2012).

The impact of the soil properties on the retention of metals was confirmed by the determination of the adsorption capacity of the different soils. The soil samples around the mining area with lower clay content had a lower adsorption capacity (< 4 mg Cu/g soil, < 2 mg Ni/g soil and < 1 mg Zn/g soil) compared to other soils with a higher clay content (up to 19.9 mg Cu/g soil, 7.1 mg Ni/g soil and 11.4 mg Zn/g soil). A similar trend was observed among the top and the bottom soils, the latter having a higher adsorption capacity. Although the lower adsorption capacity of soils around mine areas may be ascribed to a lower content of clay minerals, it is important to mention that the higher concentration of metals may play a role of poisoning, competing with absorbates for binding sites on soils' surface (Sheikhhosseini et al. 2013). The implication on surface water was the high concentration in water of metals (nickel and zinc) with lower binding affinity to soils 1 and 2 at mine sites, and a decrease of the concentration of these metals in water downstream where soils (7, 8 and 9) had higher binding capacity.the progressive reduction of metal concentration in non-diluted water downstream was partly ascribed to the adsorption capacity of the soils, and it therefore ensues that the soils in the effluent basin may have played a considerable role in the alleviation of the concentration of nickel and zinc in water.Although,the surface water at points 4 and 6 downstream still content relatively high concentration of nickel above the value (< 0.15 mg/L for Ni) recommended by the South African National Standard (SABS, 2005), the concentration of zinc was within acceptable range (< 5 mg/L for Zn) in downstream effluent.

Conclusion

The cost implication of waste water treatment is often a limitation factor to the commitment of some companies to abide to environmental regulation, therefore discharging effluents with abnormal concentrations of metals into the water system. The ability of the receiving basin in the mining areas near Potchefstroom (South Africa) to naturally mitigate the level of metal pollutants was determined to estimate the risk of pollution of surface water, impairment of

ecosystem and human risk. The clay content of the soil was found to improve the metal adsorption capacity and reduce the permeability of the soil. This may have contributed to an improvement of water quality along the effluent basin, resulting in less polluted water in the residential areas. However, the extent to which the soil contributes to the mitigation of metal dispersion is not estimated since parameters such as flow and seasonality have not been considered.

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