Investigation of phosphatic-vermiculite-heavy metal interaction and the implication to pollution of Solati River in Limpopo Province, South Africa

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Abstract

A phosphate mine in Limpopo Province of South Africa disposes of substantial phosphate-vermiculite sludge as a by-product. This study investigated the implication of phosphate-vermiculite interaction with heavy trace metals to pollution of a nearby river, evaluating the possibility of using the phosphate-vermiculite mix as a sink and possible agent of reduction of metal solubility.

Analytical data of Zn, Cd and Pb were compiled using three sets of samples; namely from the aqueous phase by conventional grab sampling for total concentrations, data from diffusive gradient in thin-films (DGTs) for bioavailable concentration and total concentration from stream sediments (solid phase). The samples from the three different methods were analysed for trace metals using IC and ICPMS whereas samples of phosphatic-vermiculite admixture were characterized using XRD, XRF, as well as physical and physico-chemical properties of the phosphate-vermiculite material.

The results show that the phosphatic-vermiculite mixture aided by liming and subsequent pH buffering of the mine waste tailings materials causes most trace metals to be adsorbed and effectively immobilized onto the solid phase. Furthermore, the result confirms the relatively low level of bioavailable trace metals in the surface water and groundwater samples taken from the area.

The findings of the investigation are beneficial in pollution remediation efforts as potentially applying phosphatic-vermiculite by-products to significantly reduce migration of hazardous soluble trace metals by *in situ* immobilization from polluting surface and groundwater resources.

Key words: **p**hosphatic vermiculite; XRD; XRF; pH; DGT; bioavailable

Introduction

Mining has been practiced in South Africa for over a century leaving more than 6000 tailings dams, 4800 abandoned mine sites and generating roughly six billion tons of mine waste (Mengistu et al., 2012). The majority of the mines are exploiting precious metals especially. Several mine waste dumps are generated from gold mines and most previous pollution related research and development mainly focused on assessing environmental impacts of discharges emanating from the mines. Considerable efforts were made to eliminate, reduce and contain precious metal mine generated pollutants mainly on the basis of conventional pumping and treatment technologies, which obviously consumes considerable finance to setup and operate requiring expensive energy, manufactured inputs, regular maintenance and skilled personnel. The majority of economically mined phosphate deposits are associated with hazardous trace and radioactive metals, which imply that mine residue deposits from such mines have considerable potential of generating discharges contaminated with these metals (Khater and Al-Sewidan, 2008).

In situ immobilization of heavy metals using phosphate mine residues and apatite is a relatively new technology providing cost-effective contaminant remediation. The immobilization of metals on site at the contaminant source using cheaply available mine residues is getting more attention as remediation of heavy metals from ground water, sediments and soil is capital intensive and expensive to install, operate or run. More importantly, previous remediation experience shows that complete clean-up of metals is technically impossible due to current limited knowledge of subsurface processes and the complexity of individual metal and suites of metals exhibiting different solubility, sorption and complexation behaviours (Singh et al., 2001). It is economically beneficial and technically more feasible than other comparable methods that metals can be immobilized *in situ* before the highly cocktail of soluble metals migrate into the ecosystem undergoing not-thoroughly understood complex geochemical and biochemical changes. Currently, the method is widely applied to the relatively non redox metals while the more highly redox sensitive ones can be dealt with once a basic understanding of the technology is firmly established. Metals most effectively stabilized by this treatment are lead, zinc, copper, cadmium, nickel, uranium, barium, caesium, strontium, plutonium, thorium, and other lanthanides and actinides (Basta and McGowen, 2004).

It has also been found that some metals such as lead can enter the apatite mineral structure during precipitation as lead-apatite, or by exchange processes with the major cation by the trace metal. Therefore, metals complexed and sequestered with phosphate residue and apatite base minerals have high chemical stability owing to the apatite base minerals being stable under a wide range of pH and temperature and therefore forming not readily soluble complexes (Kovach and Zartman, 1981; Shaw and Wasserburg, 1985; Keto and Jacobsen, 1987).

The results of previous and ongoing work demonstrates that treatment of contaminated soil and groundwater by vermiculite clays and apatite base admixtures has the potential to be the most cost effective and widely applicable remediation strategy for metals and radionuclides in the future. The fundamental theoretical concepts and laboratory based investigations were performed providing the basis to conduct on pilot scale and large scale application of the method by various studies; (Skinner and Burnharn, 1968; Altschuler et al., 1967; Chen et al., 1997a, b; Ruby et al., 1994; Xu and Schwartz, 1994; Stanforth and Chowdhury, 1994; Ma et al., 1993; Adepoju et al, 1986; Koeppenkastrop and DeCarlo, 1988, 1990; McArthur, 1985).

Site Information

One major phosphate mine operates in Limpopo Province, northeast of South Africa producing nearly 2.6 million tons of concentrated phosphate out of roughly 35 million tons of ore material (Figure 1). There are two major tailings dams, two open pits of few km in width and 50 m and 20 m in depth, two waste rock dumps of which one is for magnetite by-product, and one return water dam. The two open pits necessitate dewatering of the local aquifer of an unknown volume of water, which iss used for processing. The mine uses roughly 20 ML/day of water of which approximately 12 MlL/day is being recycled (personal comm., May 15, 2012). The phosphorites in the area were formed under oxic, shallow-water conditions where microbial populations assimilated phosphorus primarily from seawater and mediated precipitation of calcium fluroapatite during early digenesis at the sediment-water interface. Lime is extensively applied to buffer the pH of seepage water from tailings, and waste rock dumps. There is one downstream mine which extracts vermiculite, Cu as and Mn, a fertilizer company is situated on the upstream side.

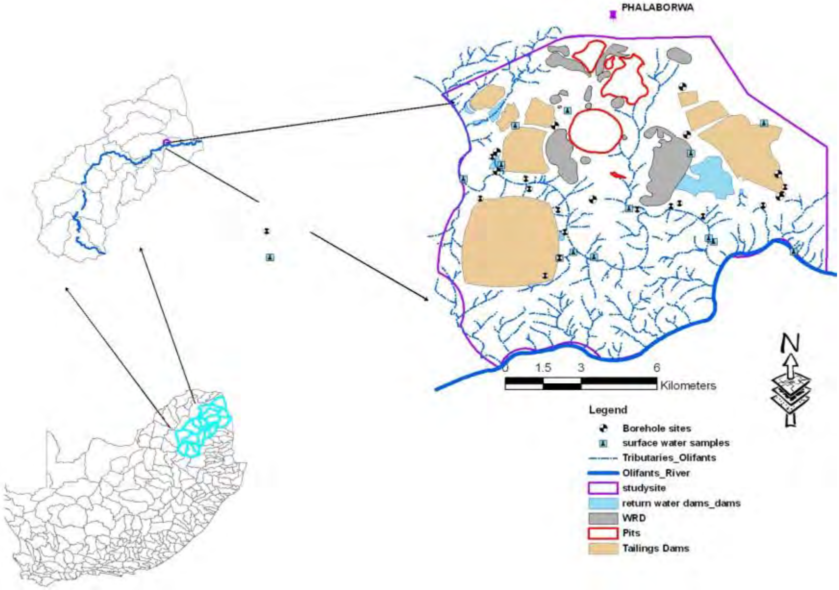


Figure 1 *Location map of the study site in North-eastern South Africa*

Geology of the area is dominated by Archean gneiss locally known as Makhutwi gneiss intruded by alkali complex of syenite composition locally named as Phalabora Formation, which actually hosts the phosphate, Cu, vermiculite, and Mn mines in the area. The southern portion of the area is covered by scattered Archean greenstone and quartzite units, known as the Gravelot formation (Figure 2). The area is dissected by younger dolerite dykes, which are offset mainly by NE-SW faults. The major tributary river is Solati River, which flows southeast to merge with the SW-NE flowing Olifants River. Undulating landform dominates the area punctuated by quartzite ridges especially in the southeast of the study area bordering the Olifants River. The major aquifer in the area is the fractured and weathered gneiss however the perched aquifer is created due to the considerable seepage of waste water from the mining operations, and especially adjoining return water dams and tailings dams.

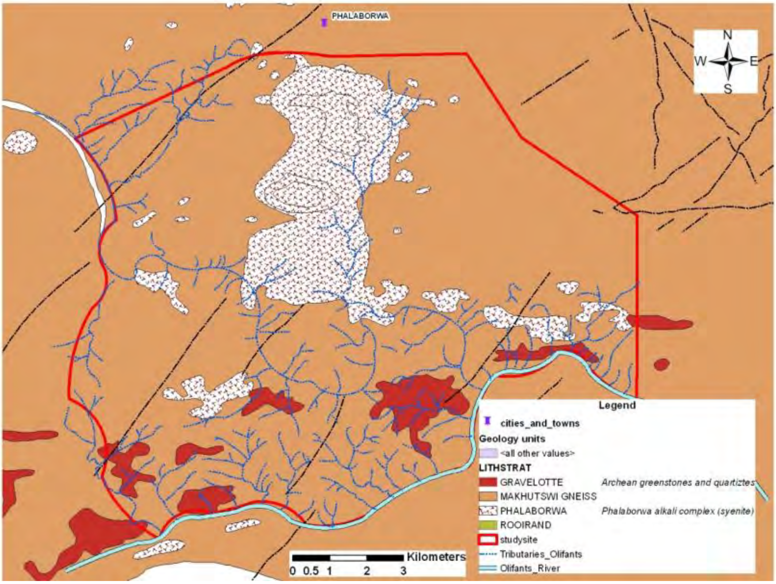


***Figure 2** Simplified geology map of the area.*

Methods

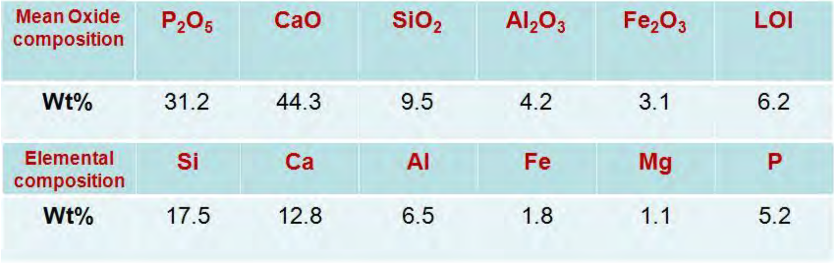
Column Leaching Experiment

Two 3 cm diameter, 5 cm long core sample holders were each packed with 40 g of dry contaminated soils for the traditional soil column experiments. Cores of the contaminated soils were run as untreated cores. Leachates were analyzed by ICP/MS on both unfiltered portions and portions filtered to 0.45 µm. Filtering had no effect on the results.

Characterization of Phosphatic Clay

Moisture content of clay samples from the phosphate admixture averages around 6 wt% whereas the rocks are enriched in P_2O_5 with a rough weight percentage of 30 wt%, with CaO and MnO. Strong correlation between CaO and P_2O_5 indicates that apatite is the major form of phosphate. A number of heavy metal elements and trace elements including Cr, V, Ni, Cu, and Cd, were measured and were interpreted to be in the phosphate minerals, largely apatite. Mean oxide compositions (wt %) are 31. % P_2O_5, 44 % CaO, 9.5 % SiO_2, 4 % Al2O3, 3 % Fe_2O_3, 6 % LOI (loss of ignition) and trace amounts of K_2O, Na_2O, MnO, MgO and TiO_2 (Table 1). Analytical data of the mine tailings show that the purification process which includes floatation and thickening of the ore slurry leads to the enrichment of certain metals (Cr, Cu, Ni, V, Zn, Ba, Sr, Fe, and Al) due to their association with the clay minerals, whereas Cd and U are enriched in the purified apatite-rich product.

Table 1 *Mean oxide and elemental composition of the phosphatic-vermiculite mixture*



Mean Oxide composition	P_2O_5	CaO	SiO_2	Al_2O_3	Fe_2O_3	LOI
Wt%	31.2	44.3	9.5	4.2	3.1	6.2
Elemental composition	**Si**	**Ca**	**Al**	**Fe**	**Mg**	**P**
Wt%	17.5	12.8	6.5	1.8	1.1	5.2

The phosphatic-vermiculite material used in this study was obtained from a phosphate, copper and vermiculite mining Company, in Limpopo Province of South Africa. The elemental composition of phosphatic clay expressed in average mass percentage (% w/w) is Si 17.5%, Ca 12.8%, Al 6.5%, Fe 1.8%, Mg 1 %, and P 5 % (Table 1). Relatively high contents of Al, Si, Ca, and P reflect the presence of apatite and phylosillicates as major constituents. Phosphatic-clay mineralogy was determined both prior to and after various aqueous metal treatments using XRD in conjunction with standard cation-saturation procedures for identification of expandable phyllosilicates. X-ray diffraction analyses were conducted on a computer-controlled X-ray diffractometer equipped with stepping motor and graphite crystal monochromator. Scans were conducted from 2 to 60° at a rate of 2°θ per min. Particle morphology of phosphatic-clay was assessed by SEM and elemental spectra for individual particles using energy-dispersive X-ray spectroscopy (EDS) during SEM observations. The apatite and phyllosilicates (i.e., especially smectite) were identified as major phosphatic clay components with high potential to reduce the mobility and bio-availability of heavy metals in contaminated aqueous environment.

Results and Discussion

A total of six sediment samples taken from streams, Selati River, trenches, waste rock dumps and tailings materials from plant areas were analysed for various major, minor and trace metals as well as anions. The analytical data of sediment extract shows that Zn, Pb and Cd were found in noticeable concentrations in the order of 100, 10 and 0.005 mg/l respectively (Figure 3). It is interesting to observe that among the 21 surface water samples scattered from upstream sites to downstream area, the concentration diminished rapidly from around 60 % below detection limit in upstream sites to 100 % below detection values in the downstream samples (Figure 4).

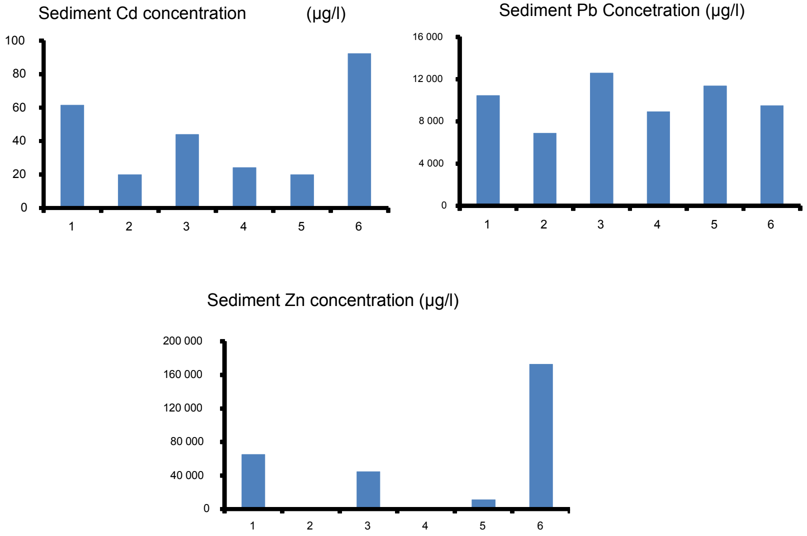


Figure 3 Analytical data of leachate extracted from phosphatic-vermculite sediment.

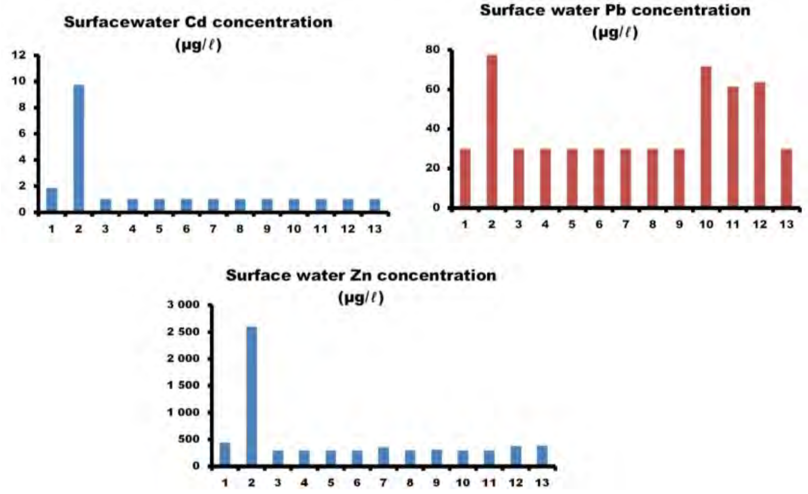


Figure 4 Analytical data of surface waters.

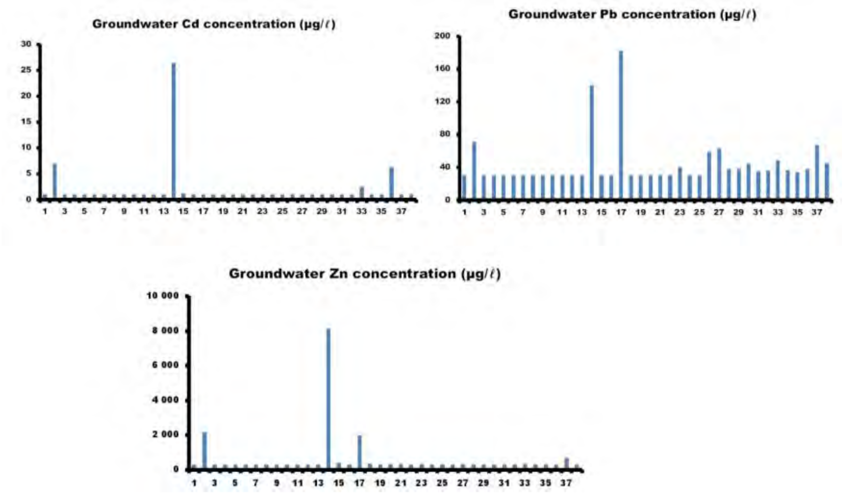


***Figure 5** Analytical data of groundwater samples.*

However, 45 groundwater samples scattered within the three sampling sites indicate a rather mixed immobilization trend in that concentrations range from roughly 80% below detection limit in the upstream sites to down to 30% below detection limit in the downstream sites (Figure 5). Trace metals which include Zn, Pb and Cd in surface waters are all below the detection limit in downstream areas slightly increasing toward upstream mines. The metal distribution between the aqueous phase and the solid phase, which is a mixture of vermiculite and phosphate base minerals clearly demonstrate that the three trace metals are evidently immobilized onto the solid phase and the trend becomes stronger in the downstream sites (Figure 6).

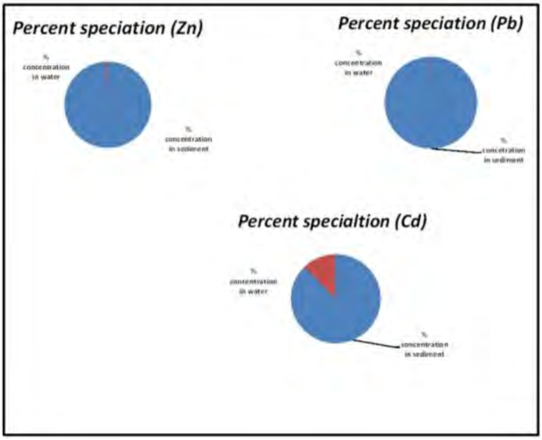


***Figure 6** Comparison of Pb, Zn and Cd in the phosphatic-vermiculite sediment versus in groundwater and surface water samples.*

The analytical data shows that there is a strong positive correlation between the abundance of phosphatic-vermiculite waste material and the low level of the metals in the surface and groundwater samples. The result confirms earlier laboratory and field investigations that the phosphatic-vermiculite mixture accounts for >75% of the Pb, Cd and Zn pool compared to the equivalent aqueous phase. Extensive lime application in the area buffers the pH to circum-neutral, which is enhancing adsorption of most metals (Mengistu et al., 2005). The geochemistry of the three metals (Pb, Cd, Zn) is in such a way that in almost many circumstances, the metals exist as un-complexed cations, which actually the strengths the argument of adsorption on the phosphatic-vermiculite sediment.

Surface water analytical data also displays that F and SO4 concentrations exceed the SANS drinking water guideline value in > 60% of the cases where the groundwater samples exceedances range from 32% to 86% of the cases. The extreme concentration of the two anion highlights that the net negative surface charge of the phosphatic-vermiculite mix is not involved in adsorption process but it also underscores that the high supply of the anions by the mining operation in the area.

Therefore, there is enough evidence to argue that unintended disposal of phosphatic sediments and vermiculite waste in the area is playing a major role as a metal sink and can be investigated in more detail if the mine waste can be properly used as metal immobilizer.

Conclusions

Two mines and a fertilizer plant in the area causes substantial negative environmental impact regardless of the efforts that were made to reduce and control groundwater and surface water pollution. Mine waste, which is a mixture of phosphate and vermiculite, generated and were disposed of in several water courses and areas. The unintentional disposition in the area actually immobilizes some trace metals (Pb, Cd and Zn) among others and contributes to extremely low level in downstream aquifer and surface waters.

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