

# Assessment of the Mobility of Toxic Elements in Gold Mine Polluted Land – Column Leaching and Computer Modelling

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## Abstract

Column leaching experiments were designed and used as an alternative rapid screening approach to element mobility assessment for gold mine tailings at the Witwatersrand goldfield in South Africa. Layers from the tailings dump were packed into columns that were designed to allow extraction of leachates from each layer. Extracting solutions used were natural and acidified rainwater. Metals and anions were determined in the leachates. The chemical analytical data and physico-chemical data from field measurements were used for chemometric evaluation of element mobility with principal factor analysis. Results from the partitioned column leaching illustrate much better the complex processes of metals mobility from tailings dump than results from the total column.

**Key words:** tailings dumps, column leaching, ion mobility, chemometrics

## Introduction

Gold mining on the Central Rand (CMR) of the Witwatersrand goldfields has led to the development of South Africa's greatest megalopolis of Johannesburg. Gold was first discovered in the Central Rand in 1886 where it has been mined to depths of 3 km below the surface.

South Africa continues to be the world's largest producer of gold. The combined gold production of the now defunct mines of CMR, all of which ceased operation in the mid 1970s, is 2444 tons of gold mined at an average grade of 8 g/ton. Post-closure history has led to environmental degradation of the area. 81.7% of RSA's solid waste emanates from the mining and metallurgy industries (Environ. and Chemical Consultants, Annual Report, 1998). Many of the tailings dumps in the area have remained undisturbed for almost a century, exposed to oxygenated rainwater. Thus the study of sorption and transport phenomena of heavy metals through tailings dumps is imperative to understand their environmental impact.

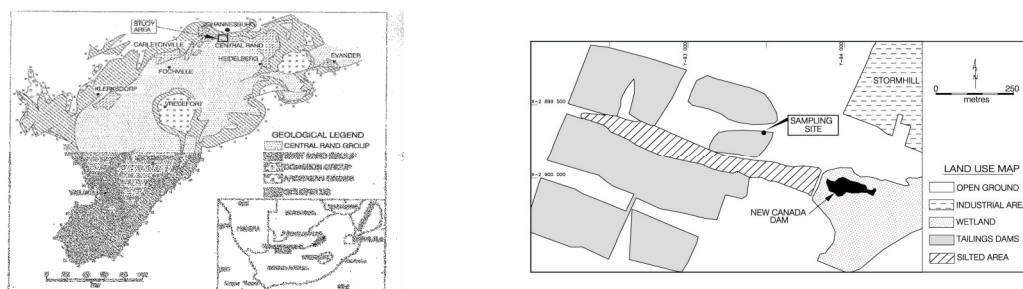
The most common and successfully used sequential extraction procedures, to assess contaminated land, are the EU BCR (Community Bureau of Reference) method and the Tessier method (Davidson et al., 1998). Sequential extraction, with its limitations (does not represent field conditions and the sample matrix is changed by crushing and grinding) provides information for risk assessment since the amounts of metal mobilizable under different environmental conditions can be estimated. Batch or column leaching experiments have recently received much attention (Szakova et al., 1999; Alborés et al., 2000; Anderson et al., 2000; Petersen and Petrie, 2000; Kanungo and Mohapatra, 2000) as a tool to evaluate metal mobility in soil, sediments and slag.

The main advantage of column leaching experiments is that they give information on the current heavy metal mobility. One disadvantage is that they can be time consuming. A compromise must be reached between simulating as closely as possible field conditions and obtaining data on a realistic time scale. The aim of this study was to assess and evaluate the mobility of heavy metals from a gold tailings dump using total and developed partitioned column leaching experiments with rainwater at different acidity and long-term extraction procedures.

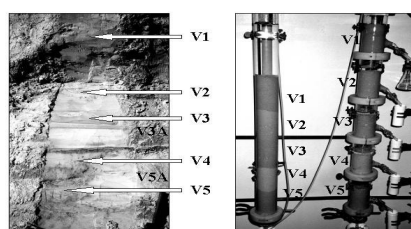
## Description of sampling sites

The regional and detailed settings of the samples studied are shown in Figures 1a and 1b. Sampling was undertaken on the flank of one of two main tailing dumps on CMR (Fig 1b). A 10 cm deep vertical channel was cut through the surficial efflorescence, revealing unaltered layers of tailing dump material. The layers were of the order of a few tens of centimetres thick and displayed greatly varying sulphide (mainly FeS<sub>2</sub>) and heavy metal concentrations (Fig.2a). Layers rich in sulphide and other heavy minerals are represented by numerous thin grey, dark grey to black beds and crust beds.

**Figure 1** a) Major geological features and Goldfields of the Witwatersrand basin, b) Map of existing gold tailing dumps on Central Rand Goldfields showing locality of sampling site.



**Figure.2** a) Layers of tailing dump material, b) Packed columns.



## Methods

### *Column leaching experiments*

The representative set of samples each averaging 30 cm in vertical extent was collected on the side of the tailings dump. In addition, samples of the outermost efflorescence layers were collected, consisting of a light yellow to light grey secondary encrustation and representing products of extreme surficial oxidation.

The samples, were packed sequentially in columns (Fig.2b) at their field moisture content. The experiments were conducted in two glass columns of equivalent length (1m) and with an inner diameter of 85mm. Columns were fitted with porous ceramic plates and delivery stopcocks at the bottom. Each sample (V1-V5) was packed in a 15cm high layer. Column I was designed to perform a total leaching, each sample layer was placed in contact with each other and leachates were collected at the bottom. Column II was partitioned on segments connected to each other by porous ceramic plates and fitted with delivery stopcocks to allow leachates collection along the column. The natural rainwater with a pH 6.8 and acidified rainwater with pH 4.2 were delivered at the top of the columns with a peristaltic pump at a constant rate of 1L over 24 hrs. This flow rate corresponds with a light rain in summer in the Gauteng province in South Africa. This arrangement closely simulated the field settings and allows controlling the transport process in all levels of the column. The aliquots of leachates were taken daily from every column level. The volume of aliquots was 5 mL from each layer which was 2.5 % of the total volume of leaching solution. Leachates were collected daily over a 5 day period.

### *Long term extraction procedure*

Long-term extraction (continuous extraction) was performed on all collected samples including the most exposed surficial efflorescent material, layers (V3a and V5a) for 70 days, in tightly sealed polypropylene bottles. The 5 g of each layer and a fixed 100 ml amount of deionised water were shaken for 20 minutes on a daily basis. Measurements of pH, conductivity and redox potential (ORP) were recorded every 5 days.

## Results and Discussion

The results from the first and second sequential column leaching experiments were used for modelling.

The data for column A are the results from overall effects of physical and chemical processes during movement of leaching solution thorough all five layers. The data for column B are results affected by

physico-chemical properties of each layer and modifications of leaching solution by the above layers. A three-fold increase in the conductivity, iron and sulphate concentration can be observed from the total leaching experiments due to the oxidised pyrite. The mobilities of the anions decrease in the order  $\text{Cl}^- > \text{NO}_3^- > \text{SO}_4^{2-} > \text{PO}_4^{3-}$ . Poor quantification  $\text{PO}_4^{3-}$  was obtained due to its low abundance in the dump material.

All the metals (Ca, Mg, Fe, Mn, Al, Cr, Ni, Co, Zn and Cu) increased in the second leaching. Chemometric evaluation involved principle factor analysis (PFA) (Sharaf et al., 1986; Massart et al., 1998), which reduced the 15 variables ( $\text{PO}_4^{3-}$  was excluded and  $\text{Cl}^-$  since HCl was used to acidify the rainwater) to two factors, for both leaching experiments. A log transformation of the data was performed resulting in a normally distributed data set used in PFA.

For the first column leaching (pH 6.8), the first two factors explained 80% of the total variance of the data. Table 1a shows the factor loadings (varimax normalised). Factor 1 is loaded with conductivity, sulphate and all of the heavy metals. This factor accounts for the major variance that describes the solubility nature of the material. Factor 2, contributing 21 % of the total variance of the data, is loaded with pH, ORP, nitrate and Zn. The high loadings of pH and ORP in this factor account for the redox processes involved in the mobility of species of high leachability in the tailing dump material.

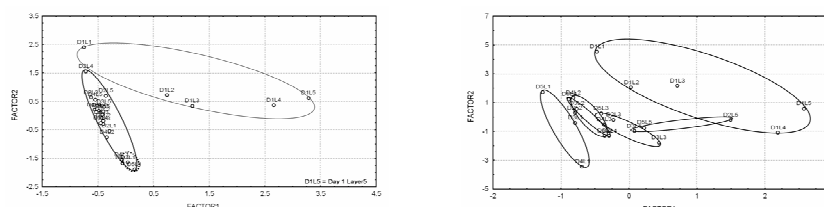
*Table 1 Factor loading for first and second leaching experiments (varimax normalized).*

	Factor 1	Factor 2	Factor 1	Factor 2
PH	-0.39	-0.78	-0.98	-0.17
ORP	0.47	0.71	0.75	0.20
CONDUCT	0.91	0.35	0.94	0.32
NIT	-0.12	0.66	-0.11	0.72
SULPHATE	0.79	0.50	0.90	0.43
CA	0.90	0.10	0.02	0.26
MG	0.79	0.19	0.85	0.00
FE	0.86	0.47	0.90	-0.04
MN	0.91	0.29	0.49	0.76
AL	0.92	0.32	0.70	0.52
CR	0.73	0.37	0.89	0.35
NI	0.95	0.18	0.70	0.53
CO	0.73	0.38	0.81	0.00
ZN	0.57	0.63	0.76	-0.24
CU	0.92	0.01	0.88	0.41
Exp. Var	8.83	3.10	8.77	2.42
Prp. Totl	0.59	0.21	0.58	0.16

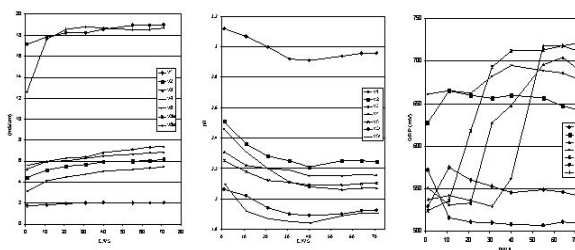
For the second column leaching experiment (pH 4.2), the first two factors explained 74 % of the total variance of the data (Table 1b). Factor 1, which contributes 58 % of the variance of the data, is now loaded with pH and ORP in addition to conductivity, sulphate and all heavy metals with the exception of Ca. This indicates the importance of the redox nature of the layers which becomes more significant at low pH. Factor 2 explains only 16 % of the total variance of the data. The leachates have a pH range of 2.08-3.65. The score plot (Fig. 3) depicts the differences of the first and second leaching experiments. The leachates obtained on the first day (D1) are shown to be extremely different from the rest of the days. Factor 1 accounts for the solubility nature of the tailings material showing a total “wash out” of all soluble species present on the first day. The leachates from the different sample layers cannot be distinguished by the composition of their soluble species or buffering capacity, with the exception of layer 1 (sample V1) which occurs at the lower end of the cluster. It can be concluded that the effect of rainwater with a pH 6.8 shows very similar leaching behaviour on the different layers of material, except on the first day. The score plot for the second column leaching experiment indicates the different leaching behaviour of each layer under the influence of acid rain (Fig. 3b). Again it is found that the first day for all layers involves a dramatic removal of all soluble species. Leachates of layers 1, 2 and 4 shows the same pattern; leachates from layers 3 and 5 roughly the same. It can be concluded that differences in the chemical compositions of the layers of dump material become more defined under acid rain conditions. The importance of the material matrix in controlling metal mobility is evident. Long-term extraction provides a conservative estimate of species leachability and behaviour of tailings dump material over long periods of rainfall over time (Fig. 4 a-c). It is in agreement with the nature of these layers; layers V3 and V5 are with intermediate and heavy mineral content. From the conductivity graph (Fig. 4a), layers V3a and V5a again show extremely different behaviour compared to the other samples. Layer 1 again is extremely different in having the lowest conductivity values. The pH (Fig. 4b) for most of the layers continues to decrease until 40 days, thereafter stabilizing. The efflorescent layers V3a and V5a have the lowest buffering capacity, thereby

producing most acidic leachates. This behaviour could be attributed to dump material having extremely high Al and Fe and low Ca concentrations and the pH value being controlled by the cyclic release of Fe and Al by hydrolysis, as found by Kanungo and Mohapatra (2000). The redox potential (ORP) values obtained from long-term extraction confirm that each layer has a very different oxidizing and reducing nature. A sharp increase in ORP (Fig. 4c) values is noted for layers V3, V3a, V5a after 20, 10 and 30 days respectively. Layers V1, V2, V4 show a similar trend, however layer V2 and V4 have higher ORP values than layer V1. Layer V3a has the most reducing nature and establishes equilibrium quickly, whereas the other layers reach a constant potential after 55-60 days.

**Figure 3** Score plot for a) the first leaching (pH 6.8), b) the second leaching (pH 4.2).



**Figure 4** (a) Conductivity, (b) pH, and (c) redox diagrams for long term batch extractions.



The climatic conditions in South Africa produce a cyclic chemical process. During the dry seasons evaporation and the intense sunlight cause the formation of a hard, white efflorescent crust on the tailings dumps. During the wet season this crust is dissolved and toxic metals are leached into the environment.

## Conclusions

Column leaching experiments can be of value in the assessment of land contamination. A more precise, quicker and more meaningful indication than from BCR sequential extraction is gained on contaminants mobility, which forms a better basis for site risk assessment.

The extrapolation of results from leaching laboratory experiments to real tailings dump environments can be modelled. Column leaching experiments as designed in this study proved to be more useful than total column leaching because much more information can be gained about the variation of the chemical nature of each layer. This outcome further indicates the importance of sampling procedure, which should include the whole profile of the tailings dump, and not only the top or bottom, for continuous monitoring and mobility assessment, which is commonly used. The use of chemometric methods for multivariate analysis of environmental analytical data sets has been successfully applied.

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