ENVIRONMENTAL AND HEALTH IMPACTS OF MINING IN AFRICA

Edited by Benjamin Mapani and Bohdan Kribek
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**PROCEEDINGS ENVIRONMENTAL AND HEALTH IMPACTS OF MINING IN AFRICA**

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PREFACE AND EDITORIAL COMMENTS

A large amount of information about the contamination of mining sites in different parts of the world has been gathered by carrying out systematic geochemical sampling and analysis. This has led to an improved understanding of cause and effect that has provided the impetus for new environmental legislation and strategies for remediation in many developed countries. As the demand for mineral resources and fossil fuels continues to grow worldwide, the impact of mining will be an increasingly important concern in the field of environmental science.

In Africa, because of economic pressures and slower evolution of environmental awareness, local communities have been particularly exposed to the detrimental effects of contamination arising from mining and its effects on public health, agriculture and the environment. In addition, the legacy of mining has left thousands of sites in Africa contaminated by mining and associated mine dumps such as tailings and slag material.

On the other hand, the number of studies focused on the impacts of mining and mineral processing on the environment and human health in Africa have increased significantly during the last decade. However, these studies tended to be concentrated on the effects of mining and mineral processing at national levels and in specific mining districts without taking into account the overall impact on larger hydrological and environmental domains across the continent. Consequently, there is sufficient scope for sharing the knowledge of monitoring methods and for developing a common approach to the management and interpretation of geochemical data taking into account the geology, topography, climate, vegetation and hydrology and hydrogeology of different regions of Africa. Therefore, the IGCP/SIDA project No. 594 entitled ASSESSMENT OF THE IMPACT OF MINING AND MINERAL PROCESSING ON THE ENVIRONMENT AND HUMAN HEALTH IN AFRICA was proposed to the International Geological Correlation Programme (IGCP) Board in 2010, and approved by the Board in 2011. This project has been designed (1) to correlate and integrate the results of multidisciplinary studies carried out in contaminated sites and areas using the best contemporary procedures for statistical analysis, management and compilation of the geochemical data; (2) to strengthen the capacity of African institutions in environmental geochemistry by cooperation with foreign experts and organizations, (3) to raise public awareness of the impacts of mining on the environment and human health and, (4) to facilitate cooperation among geoscientists and medical scientists. In 2011, the Inaugural Workshop of the IGCP/SIDA 594 was held in Kitwe, Zambia, where a decision was taken to present the first results achieved so far to be presented at this Annual Meeting at Windhoek.

Extended abstracts given in this Volume of Proceedings are to be presented in oral form or as posters at the Windhoek Meeting. We believe that the results of this meeting will contribute to a better cooperation between African and European countries in the field of environmental science.

On behalf of the Organizing Committee of Inaugural Workshop we wish to thank all the institutions which participated in preparation and organization of this Annual Meeting.

Our thanks are also directed to all experts who will participate at the Annual Workshop in Windhoek and who intend to present their papers of which extended abstracts are given in this Volume of Proceedings. It is a very pleasant duty to thank all the reviewers for their valuable comments on submitted papers. Special thanks are due to Vladimir Majer, Jan Kribek and Jaroslav Hak for having revised the English and proofreading of abstracts text. The Volume would not have been published without a great effort of the Editorial and Publishing Department of the Czech Geological Survey. We would also like to thank the efforts of our host, the Geological Survey of Namibia, especially Dr Gabi Schneider and Miss Rosina Leonard for logistical and secretarial duties. The University of Namibia, Geology Department is acknowledged for its support in providing transport and financial administration.

In conclusion, it is a great pleasure of the Organizing Committee to wish all the participants at the Annual Workshop a pleasant stay at Windhoek.

Windhoek and Prague, June 20th, 2012

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Biosorption of metals from gold mine wastewaters by *Penicillium simplicissimum* immobilized on zeolite: Kinetic, equilibrium and thermodynamic studies

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Abstract. A biosorbent based on zeolite and *Penicillium simplicissimum* (heat-killed fungal biomass) was developed for the clean up of metals from gold mine wastewaters. With an initial concentration of 500 mg L⁻¹ at pH 3–4 for a single component system, 99% adsorption was observed for: Cu²⁺, Co²⁺, Cr⁶⁺, Fe³⁺, Ni²⁺, Zn²⁺, Hg²⁺. Immobilisation of fungi on zeolite yielded higher biomass, showing the potential of this study towards remediation of polluted mine sites. Desorption results showed that the adsorbent could be reusable.

Keywords. Biosorbent, *Penicillium simplicissimum*, heavy metals, wastewaters, acid mine drainage, chemisorption

1 Introduction

Wastes generated by the mining industry contain high concentrations of metals and metalloids which can be mobilised, resulting in leaching into groundwater and surface water. Most of these heavy metals are highly toxic and are not biodegradable: As such, they must be removed from the polluted streams in order to meet increasingly stringent environmental quality standards. Conventional chemical and some physical methods are often expensive, generating toxic and non eco-friendly products. At times, these are ineffective when the metal concentration is very high. Such methods include: ion exchange, adsorption on charcoal and activated carbon, chemical precipitation, reverse osmosis and solvent extraction (Ahluwalia 2007).

Biosorption has been used with success in the last decades because of its advantages which are: ecofriendly nature, reusability of biomaterial, short operation time, selectivity for specific metals of interest, no production of secondary compounds which might be toxic, low operating cost (Tobin et al. 1984). Several adsorbents have been developed and used world-wide for the removal of pollutants from wastewaters but the challenge of achieving high adsorption efficiencies still remains as well as the development of cheaper materials for the adsorption of heavy metals from polluted sites.

In this study, a biosorbent based on zeolite and *Penicillium simplicissimum* was developed to clean up heavy metals from gold mine wastewaters. Several chemical processes may be involved in biosorption, including adsorption, ion exchange, co-ordination and covalent bonding. The main chemical groups in biomass which are able to uptake metals are hydroxyl, thiol, carboxyl, phosphate and amino groups (Quintillas et al. 2009). Zeolite was selected as a support material in this study due to its capacity for immobilizing microorganisms and its large surface area.

2 Materials and methods

2.1 Fungal biomass preparation

*Penicillium simplicissimum* (originally isolated from gold mine tailings) was maintained on the following solid media: 39 g L⁻¹ Potato Dextrose Agar (PDA) and 50 g L⁻¹ Malt Extract Agar (MEA). For experimental purposes, cultures were grown at 25°C in liquid medium at pH 4, comprising the following: (NH₄)₂SO₄, KCl, MgSO₄.7H₂O, EDTA-Fe, ZnSO₄.7H₂O, MnSO₄.H₂O, CaCl₂.2H₂O, K₂HPO₄, yeast, glucose in 1 L of sterilised deionised water. Zeolite (1 g) was added into the medium, and the mixture was inoculated after autoclaving. All chemicals used were from Merck. The Zeolite used in this work, purchased from Sigma Aldrich (South Africa), was in a powder form with 150 Å of pore diameter. The immobilized biomass was separated from the broth by filtration and washed with deionised water.

2.2 Biosorption studies

Batch biosorption assays were carried out in heat-killed biomass for Co, Cu, Fe, Hg, Cr, Ni, U and Zn metals (single and multi components). The effects of initial metal concentrations were assessed at pH 3 in the range 50–500 mg L⁻¹ while the contact time was in the range 0–180 min. The process was monitored at temperatures between 25 and 60°C. A ratio of 1 g biomass: 50 mL metal solution was used. The concentration of metal ions remaining in solution was analyzed using the multi-element Genesis Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) (Spectro, Germany). Langmuir and Freundlich isotherms were used to fit the experimental data (Guangyu et al. 2003).

It is well known that the Langmuir model is usually used with an ideal assumption of a monolayer adsorption surface (Langmuir 1918). The Freundlich model is appropriate for the description of multilayer adsorption with interaction between adsorbed molecules (Freundlich 1906). If the value of n is between 1 and 10, this refers to a beneficial isotherm.

Kinetics of metal ion sorption governs the rate, which
determines the residence time and it is one of the important characteristics defining the efficiency of an adsorbent (Krishnan et al. 2003).

2.3 Data analysis

In order to compare the validity of each model, the normalized standard deviation (Δq(%) was calculated using the following equation:

\[
\Delta q(\%) = 100 \sqrt{\frac{\sum_{i=1}^{n} \left( \frac{q_{exp} - q_{calc}}{q_{exp}} \right)^2}{n - 1}}
\]

where: \( q_{exp} \) is the experimental metal ion uptake, \( q_{calc} \) the calculated amount of metal ions adsorbed and \( n \) is the number of experimental data. Curve Expert 1.37 free ware program was used in all calculations with the confidence level set at 95%.

2.4 Desorption studies

Batch desorption tests of metals (regeneration of the biosorbent) was conducted using different concentrations of HNO₃ (0.5–7 mol L⁻¹). The mixture was agitated in 250 mL bottles at 150 rpm for 12 h using a mechanical automated shaker. The solution was then filtered using a Whatman No. 41 filter paper. The concentration of the metal ions in the filtrate was measured using the ICP-OES. The desorption efficiency was calculated using the following equation:

\[
\text{Desorption efficiency} = \left( \frac{\text{Amount of metal ions desorbed (mg/L)}}{\text{Amount of metal ions adsorbed (mg/L)}} \right) \times 100\%
\]

3 Results and discussion

3.1 Characterization of the biomass

The growth of the fungus showed a 10-fold increase in biomass when immobilized on zeolite (600 mg g⁻¹) at pH 4 (Fig. 1). Maximum biomass was obtained 5 days after inoculation at pH 4. Infrared spectra of the biomass in the range of 500–4000 cm⁻¹ confirmed the presence of functional groups with lone pairs of electron that are available to bind to the positively divalent metal ions. These include: hydroxyl, carbonyl, carboxyl, amide, amine, imidazole, phosphate groups.

The results obtained for the CEC and the elemental analysis of the biomass are given in (Tab. 1). The % of C was high in the biomass; these results confirm the presence of organic compounds released by the fungi as revealed by with the IR spectra (not shown in this paper).

<table>
<thead>
<tr>
<th></th>
<th>C (%)</th>
<th>H (%)</th>
<th>N (%)</th>
<th>S (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zeolite-Fungi</td>
<td>0.388</td>
<td>2.295</td>
<td>0.254</td>
<td>0.102</td>
</tr>
<tr>
<td>Natural zeolite</td>
<td>0.219</td>
<td>2.209</td>
<td>0.193</td>
<td>0.090</td>
</tr>
</tbody>
</table>

3.2 The effect of pH

The effect of pH on the adsorption of heavy metals on the natural zeolite and the zeolite-fungi was studied in the pH range 2 to 7. The results are shown in Figures 2 and 3. The results showed an increase in adsorption capacity with the zeolite - fungi (40–50 mg/g) compare to the natural zeolite (2–10 mg/g). The adsorption rate of metal ions studied on zeolite-fungi was constant for the all range of pH. This high adsorption capacity for the metals indicates that adsorption of these metals is independent of the change in pH. This adsorbent is effective in the removal of metals at low pH values, which makes it an effective adsorbent in the remediation of acid mine drainage.

3.3 Biosorption isotherms

Adsorption constants of Langmuir and Freundlich equation and correlation coefficient (R²) were calculated and are represented in Table 2. The high adsorption capacity was obtained with Cr (III) (525 mmol kg⁻¹). The decreasing sequence of uptake values by the biosorbent is Cr(III) > Cu(II) > Co(II) > Fe(II) > Zn(II) > Ni(II) > U(VI) > Hg(II). The correlation coefficients show that the biosorption process is better defined by Freundlich demonstrating the heterogeneous character of the adsorption surface of the biomass. Only Ni and Co have high correlation coefficients for the Langmuir model, implying a monolayer coverage process. The good fit of Freundlich isotherm to an adsorption system means there is almost no limit to the amount adsorbed.

The magnitude of the Freundlich parameters Kf gives the quantitative information on the relative adsorption affinity towards the adsorbed cation. The value of 1/n less than unity is an indication that significant adsorption
Figure 2. Plots of the adsorption capacity versus pH on natural zeolite of heavy metals in single component solutions, $C_i = 100 \text{ mg L}^{-1}$.

Figure 3. Plots of the adsorption capacity versus pH on zeolite-fungi of heavy metals in multi-component solutions, $C_i = 100 \text{ mg L}^{-1}$.

Table 2. Langmuir and Freundlich constants and correlation coefficients.

<table>
<thead>
<tr>
<th>Metal ions</th>
<th>Langmuir parameters</th>
<th>Freundlich parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$q_{\text{max}}$ (mol/kg)</td>
<td>$b \times 10^3$ (L/mg)</td>
</tr>
<tr>
<td>$^{1}\text{Cu}^{2+}$</td>
<td>0.483</td>
<td>86.17</td>
</tr>
<tr>
<td>$^{2}\text{Co}^{2+}$</td>
<td>0.427</td>
<td>58.75</td>
</tr>
<tr>
<td>$^{3}\text{Cr}^{3+}$</td>
<td>0.525</td>
<td>12.26</td>
</tr>
<tr>
<td>$^{4}\text{Fe}^{3+}$</td>
<td>0.421</td>
<td>69.76</td>
</tr>
<tr>
<td>$^{5}\text{Hg}^{2+}$</td>
<td>0.128</td>
<td>43.47</td>
</tr>
<tr>
<td>$^{6}\text{Ni}^{2+}$</td>
<td>0.268</td>
<td>37.85</td>
</tr>
<tr>
<td>$^{7}\text{UO}_{2}^{2+}$</td>
<td>0.169</td>
<td>22.03</td>
</tr>
<tr>
<td>$^{8}\text{Zn}^{2+}$</td>
<td>0.298</td>
<td>41.42</td>
</tr>
</tbody>
</table>

Detection limit (mg l$^{-1}$): $1.741 \times 10^{-4}; 2.105 \times 10^{-4}; 3.20 \times 10^{-4}; 4.118 \times 10^{-4}; 5.265 \times 10^{-4}; 6.88 \times 10^{-4}; 7.52 \times 10^{-2}; 8.45 \times 10^{-4}$

Table 3. Kinetic models at 298 K and pH 3; $R^2$ - Correlation coefficient.

<table>
<thead>
<tr>
<th>Metal ions</th>
<th>Pseudo first-order parameters</th>
<th>Pseudo second-order parameters</th>
<th>Intraparticle diffusion parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$q_e$ [mg g$^{-1}$ min$^{-1}$]</td>
<td>$R^2$</td>
<td>$q_e$</td>
</tr>
<tr>
<td>$\text{Cu}^{2+}$</td>
<td>0.022</td>
<td>0.075</td>
<td>0.715</td>
</tr>
<tr>
<td>$\text{Co}^{2+}$</td>
<td>0.014</td>
<td>0.072</td>
<td>0.618</td>
</tr>
<tr>
<td>$\text{Cr}^{3+}$</td>
<td>0.034</td>
<td>0.065</td>
<td>0.794</td>
</tr>
<tr>
<td>$\text{Fe}^{3+}$</td>
<td>0.012</td>
<td>0.011</td>
<td>0.466</td>
</tr>
<tr>
<td>$\text{Hg}^{2+}$</td>
<td>0.072</td>
<td>0.029</td>
<td>0.751</td>
</tr>
<tr>
<td>$\text{Ni}^{2+}$</td>
<td>0.002</td>
<td>0.02</td>
<td>0.507</td>
</tr>
<tr>
<td>$\text{UO}_{2}^{2+}$</td>
<td>0.033</td>
<td>0.019</td>
<td>0.846</td>
</tr>
<tr>
<td>$\text{Zn}^{2+}$</td>
<td>0.005</td>
<td>0.014</td>
<td>0.625</td>
</tr>
</tbody>
</table>
takess place at low concentration but the increase in the amount adsorbed with concentration becomes less significant at higher concentrations and vice versa (Teng and Hsieh 1998).

3.4 Biosorption kinetics

The estimated model and related statistics parameters are reported in Table 3. Based on the linear regression ($R^2 > 0.99$) values of the metal ions, it is observed that the sorption of the metals studied followed the pseudo second-order kinetic model except for U. The biosorption of U followed the intraparticle diffusion model rather than the pseudo second-order. The pseudo second-order is based on the assumption that sorption follows a second order mechanism, with chemisorption as the rate limiting step. Adsorption at such low pH regimes shows potential for the remediation of acid mine drainage (AMD) impacted water.

3.5 Thermodynamics of biosorption

Activation energy (Eₐ), standard Gibbs' free energy ($ΔG^o$) and enthalpy change ($ΔH^o$) calculated from the experimental data are given in Table 4). The equilibrium regime is defined by the distribution coefficient $K_d$ (L mol⁻¹) calculated as:

$$K_d = \frac{C_o - C_e}{C_e} \cdot \frac{V}{M} \quad (3)$$

where: $C_o$ and $C_e$ (mol L⁻¹) represent the initial concentration and equilibrium concentration, respectively, and $V/M$ (L kg⁻¹) is the ratio of the solution volume to the mass of adsorbent. The experimental data obtained at different temperatures were used in calculating the thermodynamic parameters $E_a$, $ΔG^o$ and $ΔH^o$ using the following equations:

$$ΔG^o = -R.T.\ln K_d \quad (4)$$

$$\ln K_d = \frac{1}{T}\left(ΔS^o + ΔH^o/T\right) \quad (5)$$

The negative values of the standard free energy change, $ΔG^o$, imply that the biosorption process was spontaneous. These results validate the feasibility of the biosorption. The positive values obtained for $ΔH^o$, except for Fe and Co, demonstrate that the biosorption process was exothermic. This indicates that higher temperature led to a decrease in biosorption. The rate of biosorption also decreases with an increase of temperature. The values of activation energy (Eₐ) obtained in Table 4 show that most of these metals adsorb onto the biosorbent by chemisorption (40 < $E_a$ < 800 kJ mol⁻¹) reaction, with the exception of Cu, Co and Ni which adsorb by a physisorption (5 < $E_a$ < 40 kJ mol⁻¹) type of reaction (Nollet et al. 2003). Most of the metals studied have negative values for activation energy which could be attributed to their preference to bind to low energy active sites.

2.6 Desorption

The results for the effect of nitric acid in the removal of metals are presented in Figure 4.

Desorption studies help to elucidate the nature of adsorption and recycling of the spent adsorbent and the metal ions. The desorption results showed an optimum desorption (> 90%) at about 1 mol L⁻¹ HNO₃ for the metals studied except for U⁶⁺ with 60% desorption. Uranium metal ion forms strong complex with the phosphate group of the biosorbent. Sodium carbonate solution may be used to remove the uranium; it is well known that carbonate ions have high affinity for the uranyl ion, therefore the energy formation of uranyl carbonate complex is greater than the uranyl phosphate complex. Further experiments have to be done with the sodium carbonate to remove the uranium from the biosorbent.

3 Conclusions

The biosorbent displayed good adsorption of metals even at low pH values and as such can be used efficiently in areas contaminated by AMD with high metals concentration. The metal loaded in the biomass can potentially be desorbed in order to regenerate the biosorbent and possibly reclaim valuable metals. Adsorption kinetics is important in establishing the time zones and effective lifetime of adsorbents and shed information on the need for regeneration. Thermodynamic results are essential in determining the surface-metal reaction mechanisms.

Acknowledgements

The authors express their thanks to the National Research Foundation of South Africa, Anglogold Ashanti and THRIP for funding this project. Similar work has already been published in the Proceedings of the 13th International Mine Water Association Symposium, Aachen, Germany, 4-11 September 2011, pp 271-276 (ISBN 978-3-00-035543-1).

References


**Table 3.** Different parameters $E_a$, $\Delta G^\circ$ and $\Delta H^\circ$ calculated from the adsorption rates.

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>$\Delta E_a$(kJ/mol)</th>
<th>$\Delta H^\circ$(kJ/mol)</th>
<th>25°C</th>
<th>30°C</th>
<th>40°C</th>
<th>60°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co$^{2+}$</td>
<td>17.49</td>
<td>104.4</td>
<td>-18.66</td>
<td>-19.31</td>
<td>-17.09</td>
<td>-19.29</td>
</tr>
<tr>
<td>Cr$^{3+}$</td>
<td>-80.57</td>
<td>-481.0</td>
<td>-6.232</td>
<td>-6.019</td>
<td>-22.78</td>
<td>-16.58</td>
</tr>
<tr>
<td>Cu$^{2+}$</td>
<td>-6.424</td>
<td>-38.32</td>
<td>-1.513</td>
<td>-0.436</td>
<td>-1.833</td>
<td>-2.484</td>
</tr>
<tr>
<td>Fe$^{3+}$</td>
<td>109.9</td>
<td>651.1</td>
<td>-25.96</td>
<td>-21.64</td>
<td>-22.24</td>
<td>-16.89</td>
</tr>
<tr>
<td>Hg$^{2+}$</td>
<td>-75.84</td>
<td>-452.4</td>
<td>0.986</td>
<td>0.795</td>
<td>5.200</td>
<td>7.767</td>
</tr>
<tr>
<td>Ni$^{2+}$</td>
<td>-27.91</td>
<td>-166.6</td>
<td>-5.860</td>
<td>-5.768</td>
<td>-6.896</td>
<td>9.978</td>
</tr>
<tr>
<td>UO$_2^{2+}$</td>
<td>-120.4</td>
<td>-718.9</td>
<td>-5.689</td>
<td>-6.342</td>
<td>-12.75</td>
<td>-20.64</td>
</tr>
<tr>
<td>Zn$^{2+}$</td>
<td>-113.2</td>
<td>-675.7</td>
<td>-7.373</td>
<td>-19.65</td>
<td>-19.47</td>
<td>-21.72</td>
</tr>
</tbody>
</table>

**Figure 4.** Desorption of metal with HNO$_3$ solution.
Pathways of exposure to cobalt in populations living in Katanga, D.R. Congo

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Abstract. In order to determine the main pathways of human exposure to metals, especially cobalt, urinary concentrations of metals measured in adults and children living in various locations of Katanga were related to estimated intakes of metals, based on concentrations measured in drinking water, food items and dust. Contamination of locally grown vegetables and locally caught fish represent significant sources of exposure to cobalt, with the contribution of contaminated dust also being substantial, especially for children.

Keywords. Cobalt, vegetables, fish, dust, water, Katanga, DR Congo

1 Introduction

The population of Southern Katanga is substantially exposed to several metals or metalloids, with subjects living within 3 km of mines or metal smelters having significantly higher urinary concentrations of As, Cd, Co, Cu, Pb and U, than those living farther away (Banza et al. 2009). In this follow-up study we investigated further the pathways of exposure to Co, with a focus on the contribution of dietary sources.

2 Methods

We studied subjects living in urban areas polluted by copper/cobalt processing plants [Lubumbashi (Tshamilemba, Kabecha), Likasi (Shituru, Panda)], in a rural area close to a copper/cobalt mine (Shamitumba), in villages (Shinangwa, Kibangu, Kansalabwe) close to Lake Changalele, which receives effluents from the Likasi industry, as well as control subjects from two villages in southern Katanga (Kidimudilo, Misisi-Sando) and two villages outside southern Katanga (vicinity of Kamina and Mbuji Mayi).

In the various locations, we obtained urine samples from male and female adults and children, as well as samples of drinking water, outdoor and indoor dust, locally grown vegetables and/or purchased food, locally caught fish, and chickens. Food questionnaires were administered to assess the type and quantity of food consumed. The concentrations of metals (and metalloids) in the samples were analyzed by ICP-MS. The dietary intake of Co was estimated separately for adults and children, based on Co concentrations measured in food items and the food questionnaire. The intake of Co from other sources was estimated based on existing models.

3 Results

As previously reported for part of the studied population (Banza et al. 2011), the urinary Co concentrations were lowest in the control populations, intermediate in those living close to Lake Changalele and highest in those living close to the industrial sources of pollution. The same was true for Co in outdoor or indoor dust.

Average concentrations of Co (µg/g dry weight) were substantially higher in food items obtained from the polluted than from the control and lakeside areas: 0.4 vs 0.05 µg Co/g for maize flour, 12 vs 1.5 µg Co/g for cassava leaves, 6.7 vs 1.1 µg Co/g for sweet potato leaves, 46 vs 1.2 µg Co/g for other leafy vegetables, 22 vs 0.84 µg Co/g in beans, 22 vs 0.58 ppm µg Co/g in fruit vegetables. Concentrations of cobalt were higher in fish caught in Lake Changalele than in control fish.

A linear positive correlation was found between the estimated dietary intake of Co and the urinary concentration of Co up to 20 µg Co/g creatinine. Above this value, urinary Co leveled off with increasing Co intake, potentially because of lower bioavailability of Co in dust and/or overestimated dust ingestion. In adults, cereal flour and vegetables contributed almost equally and exclusively (~90%) to the intake of Co in control areas, whereas fish contributed substantially (~25%) in Lakeside areas, and vegetables and dust contributed proportionately more in polluted areas. The same was true for children, but with larger contributions of dust.
4 Conclusions

These analyses confirm that subjects living close to the sources of industrial pollution in Katanga have high concentrations of metals in their urine. Both diet and contaminated dust were found to contribute to the intake of Co. Contamination of locally grown vegetables and locally caught fish represent significant sources of exposure to Co. The contribution of dust may also be substantial in adults and even more so in children.

These data should help designing policies to prevent excessive exposure to Co and other pollutant metals in Katanga.

References


The Impact of Gold Mining on Mercury Pollution in the Witwatersrand Basin, South Africa

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Abstract. Gold mining in the Witwatersrand basin, SA contains the biggest and richest gold mines in the world. Mercury occurs in some gold-bearing ores, was used for gold recoveries till 1915 and is still used in artisanal mining. Presently some old gold tailings dumps are reprocessed releasing Hg to the environment. The purpose of this work was to assess the Hg pollution in the West Rand areas with long history of gold mining. High Hg concentrations were found in surface water (0.01–220.63 ng IHg L⁻¹ and 0.04–2.12 ng MHg L⁻¹) and sediments (46–2090 ng IHg g⁻¹ and 2–5 ng MHg g⁻¹). Field parameters demonstrated a typical case of acid mine drainage (high EH, EC and the pH as low as 3).

High Hg concentrations found in this study suggest that post-gold-mining operations may be important contributors to the pollution of stream draining the mining site and affect the nearby game reserve and Cradle of Humankind. Organic matter and sulfur contents together with redox potential and pH appear to be important contributing factors to the methylation process. Methylation of Hg is occurring in the water system and allow MHg to enter the food web.

Keywords. Gold mining, mercury pollution, Witwatersrand, South Africa

1 Introduction

Gold mining on the West Wits Line, which also includes the West Rand region, contains the biggest and richest mines in the entire Witwatersrand Basin. Mercury, which occurs in some gold-bearing ores, was also used for gold recoveries by amalgamation till 1915 and is still used in illegal artisanal mining. Presently some old gold tailings dumps are reprocessed. Consequences of these activities are the release of Hg to the environment. It was reported that the Hg emissions in South Africa are second only to China (Pacyna et al. 2005); now revised to the forth – sixth place but without proof. This is mainly due to coal combustion and gold mining.

Risk assessment of Hg pollution in South Africa is based on total element concentrations. Unfortunately, the determination of total Hg is not sufficient to understand its transport and fate in the environment. It is necessary to evaluate Hg speciation, and characterize potential sources, pathways, receptors and sinks in order to implement mitigation strategies and minimize risk.

The purpose of this work was to carry out a quantitative assessment of Hg pollution in areas suspected to have elevated concentrations of total Hg due to a long history of gold mining activities and to investigate the Hg distribution, transport and fate in the study areas.

2 Materials and methods

Water, soil and sediment (surficial and bulk) samples were collected during a sampling campaign conducted in the late dry season in old boreholes and the receiving stream, wetlands and dams in a closed mining site located on the West Rand and through the Krugersdorp game reserve to the Cradle of Humankind.

Samples were prepared using the methodology of Rodriguez Martin-Doimeadios et al. (2003), and Hg species, inorganic Hg (IHg) and methylmercury (MHg), were determined by Isotope Dilution Gas Chromatography Inductively Coupled Plasma Mass Spectrometry (ID-GC-ICP-MS). Analyses were validated using a certified reference material (IAEA405).

3 Results and discussion

3.1 Mercury species in water and sediment

High Hg concentrations were found in surface water (0.01–220.63 ng IHg L⁻¹ and 0.04–2.12 ng MHg L⁻¹) and sediments (46–2090 ng IHg g⁻¹ and 2–5 ng MHg g⁻¹) (Figure 1). Mercury enrichment was observed in bulk sediment reaching 3900 ng IHg g⁻¹ and 83 ng MHg g⁻¹ at 20 cm depth.

Field parameters measurements in water samples have demonstrated a typical case of acid mine drainage with high redox potential (0.3 to 0.6 V), high electrical conductivity (3.9 to 5.3 mS cm⁻¹), high electrical conductivity (3.9 to 5.3 mS cm⁻¹) and the pH dropping as low as 3.

Figure 1 IHg and MHg concentrations in surficial sediments (0–2 cm depth).
3.2 Factors controlling mercury methylation

MHg in sediment profiles correlated carbon, sulfur (sulfate) and some heavy metals distribution. The production of MHg in the old borehole appeared to occur at deeper layer under reductive conditions, high pH and in the presence of elevated IHg concentration (Figure 2).

4 Conclusions

High Hg concentrations found in this study suggest that post-gold-mining operations may be important contributors of Hg to the stream draining the minim and affect the nearby game reserve and precious Cradle of Humankind site. Mercury enrichment in bulk sediments also confirms the long-term pollution of the site. Organic matter and sulfur contents together with redox potential and pH appear to be important contributing factors to the methylation of Hg. The study also showed that methylation of Hg is occurring in the water system, which allow MHg to enter the food web.

Acknowledgements

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Advances in mitigation and rehabilitation technology in major and abandoned mines in Sub-Saharan Africa

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Abstract

Mine rehabilitation involves the minimisation and mitigation of the environmental effects of modern mining. Today, mining legislation in most Sub-Saharan African mining countries dictates that mine closure requires the return of land to a viable post-mining use, such as agriculture. The increasing scientific methods now being applied to rehabilitation are bringing about an improved level of performance, in response, largely to this legislation. This review illustrates how implementation of best practices in coal and metal mines (mitigating acid mine drainage (AMD); revegetation) and development of more energy-efficient technologies are allowing the mining sector in Sub-Saharan African countries to contribute significantly towards the maintenance of environmental integrity and sustainable development.

Keywords: mitigation, rehabilitation, AMD, revegetation, energy use, Sub-Saharan Africa

1 Introduction

To contribute effectively to sustainable development, the mining industry must develop, and consistently apply, sound environmental management practices to minimise on- and off-site environmental impacts through proper mitigation and rehabilitation procedures. In Sub-Saharan Africa such work has significantly increased since the beginning of the 1990’s, largely due to the recognition of national legislation processes, general technological advancement, and the efforts of governments in supporting the mining industry. Effective mitigation techniques for active mines may require new approaches to mine design, improved methods of mine backfill, better design and analysis of ground support systems and early identification of potential failure modes. In the case of abandoned mines, major impacts may include – acid mine drainage (AMD), loss of productive land, visual effects, surface and groundwater pollution, soil contamination, siltation, contamination of aquatic sediments and fauna, and so on.

In this paper, an illustration is given of how advances in technology have led to a better understanding of these impacts, and how technological improvements in mitigation strategies and sustainable rehabilitation, have been attained in the fields of AMD, revegetation, phytostabilisation and the optimisation of energy use.

2 Acid mine drainage

Acid mine drainage, refers to the outflow of acidic water from metal mines or coal mines. It is a well-known and almost pervasive problem at abandoned mines in Sub-Saharan Africa (Fig. 1), especially ones that have

Figure 1. AMD from an old metalliferous mine, South Africa.

sulphide mineralization. Acid mine drainage begins with the exposure of iron sulphide materials to air and water. The exposed, relatively insoluble sulphide materials are converted to soluble sulphuric acid and to iron compounds by oxidation.

A general equation for this process is:

\[2\text{FeS}_2(s) + 7\text{O}_2(g) + 2\text{H}_2\text{O}(l) = 2\text{Fe}^{2+}(aq) + 4\text{SO}_4^{2-}(aq) + 4\text{H}^+(aq)\]

The sulphuric acid, in turn, dissolves other metals including toxic metals and radionuclides from the rocks with which it interacts. This may result in acute and chronic toxicity to both human users and the environment (aquatic life; corrosive effects of acid on infrastructure and equipment; and so on), and will generally render water unfit for most purposes. For example, in the West Rand, near Krugersdorp in South Africa, the decant of AMD has had a devastating effect on the ecology in the areas immediately downstream of the decant, and has degraded streams and groundwater which feed the ‘Cradle of Humankind’ World Heritage Site.

2.1 Treatment of acid mine drainage

The treatment of AMD requires the integrated implementation of a range of measures. Such measures include active water treatment such as at the plant at eMalahleni (Mpumalanga Province, South Africa), and at the Water Utilities Corporation (Botswana); passive water treatment systems (e.g., constructed wetlands), controlled placement of acid-generating mine waste, and prevention of water ingress into mine voids, and of AMD loss from mine voids.
In Sub-Saharan Africa, many of the more sophisticated methods for AMD treatment are already available or are being developed; these range from using microbes to building faux-wetlands to ion exchange technology to remove sulphur, heavy metals, and increase pH, allowing water to be discharged and/or used for human consumption. Other AMD solutions that are being developed include reverse osmosis (Fig. 2) and integrated algae pond systems. Many of these solutions demonstrate how chemicals with economic value, such as sulphur and potassium nitrate, could be extracted from AMD. Passive water treatment systems, typically wetlands, operate without chemical amendments and without motorized or mechanized assistance. In contrast active water treatment systems (Fig. 3) are highly engineered water treatment facilities commonly employing chemical amendment of acid mine water to achieve a water quality standard specified in a discharge permit.

Two other exciting developments apart from current treatment methods are worthy of mention. The first relates to the GYP-CIX process, which uses the well-known cation and anion exchange resins to absorb from the AMD, cations (e.g. Ca²⁺) and anions (SO₄²⁻) by exchanging them for hydrogen and hydroxide ions, respectively. This reduces gypsum level, and also TDS and corrosion potential. When the resins are fully loaded with the pollutants, they have to be regenerated with an acid and an alkali, respectively. Additionally a pure gypsum product, the result of both cationic and anionic exchange and can be sold commercially thus offsetting treatment costs. The reactions occur by mechanisms such as:

Cation Regeneration:
\[ R=Ca^{2+} + H_2SO_4 = 2 R=H^+ + CaSO_4 \]

Anion Regeneration:
\[ R=SO_4^{2-} + Ca(OH)_2 + CaSO_4 \]  \begin{equation} \text{Bowell 2000} \end{equation}

Some of the mines in South Africa on their own account have established treatment plants that utilise these reactions to treat AMD more satisfactorily than the more conventional methods, e.g. at the Western Areas Gold Mine in Johannesburg, South Africa. Another novel technology for addressing AMD, recently described by Professor Alison Lewis (University of Cape Town) (pers. comm.), involves making water out of waste through eutectic ice crystallisation. Eutectic freeze crystallisation basically takes contaminated water and freezes it to a point where water can be recovered in the form of ice and also pure usable salts. Because of the density differences, the ice floats and the salt sinks, and the two can be separated. The water that is recovered is pure and immediately drinkable. The most environmentally effective of these techniques to date, are considered to be internal neutralisation methods, water-covers and biological/natural degradation processes.

Finally, Hesketh et al. (2010) describe an improved, integrated approach to tailings management and AMD mitigation, whereby conventional tailings are separated with the use of floatation into a largely benign tailings stream and a sulphide-rich product. These authors (Hesketh et al. 2010) outline the key features of this conceptual approach and partly demonstrate it for the case of porphyry-type copper sulphide tailings. The significance of this approach, they (Hesketh et al. 2010) pointed out, is that it provides a basis for the identification of opportunities for the development of new process designs incorporating waste management systems for mitigating AMD in a manner consistent with the principles of cleaner production and sustainable development.

While the effectiveness of the different technologies varies, one common thread runs through: they all take time, money and commitment – qualities that are often wanting from the mining industry and government. Practical examples of acid mine drainage mitigation success are the eMalahleni water treatment project (Fig. 2) and the Brugspruit mine water treatment plant in Witbank, South Africa, where polluted mine water is no longer viewed as a major problem but as a valuable water resource. Commissioned in 2007, the eMalahleni plant treats and coverts acid mine water into drinkable water. With reverse osmosis as the main component and...
a combination of available technologies, the eMalahleni municipality receives over 16 million litres of clean water per day and has resulted in 99 percent potable water recovery from surface and underground mine water.

3 Revegetation

Techniques for regenerating indigenous tree species cover are being used to develop practical and cost-effective strategy in revegetation (e.g., van den Berg et al., 2011). In the process of vegetative rehabilitation, the normal ecological succession using low-cost techniques should be initiated, so that the environment can enrich itself naturally in terms of biodiversity.

Vetiver grass (Vetiveria zizanioides L.) (recently reclassified as Chrysopogon zizanioides), is the main component of all ‘Vetiver Grass Systems’ based bioengineering and conservation applications. The grass is unique and can be used in the tropics and semi-tropics, and areas where there are hot summers, and winters where there are no permanently frozen soil conditions. With its unique morphological and physiological characteristics, Vetiver has been widely known for its effectiveness in erosion and sediment control, and is highly tolerant to extreme soil conditions including heavy metal contaminants. Rehabilitation trials have been conducted at several mines in South Africa, including Kimberlite fines at Cullinan mine (east of Pretoria), and at Premier (near Cullinan mine) (Truong 1999). It is highly effective in the rehabilitation of mining waste, particularly contaminated tailings.

3.1 Advantages of Vetiver

Vetiver grass has a number of favourable ecological characteristics, including its resistance to drought and high levels of flooding, as well as a high level of tolerance to soil salinity, sodicity and acid sulphate. The roots of the grass have an average tensile strength of 75 MPa and can improve the shear strength of soil by between 30 percent and 40 percent.

Vetiver is marketed by Hydromulch (Pty) Ltd., a company that has established a Vetiver Grass Nursery on its farm situated 20 km north of the Oliver Tambo International Airport in Johannesburg. The company is able to supply Vetiver Grass slips/plants to any destination worldwide, but in particular to African countries, to whose mining industries it has offered specialist environmental rehabilitation and erosion control services, and has played an integral part in the rehabilitation of opencast mines. Through the development of its own specific equipment, products, methods of hydraulic seeding and vegetation restoration to establish vegetation on degraded lands, often in hostile climatic or soil conditions, the company has become a significant player in its field.

3.2 Hydroseeding

Hydroseeding is the fastest, most cost effective method of seeding vegetation, land rehabilitation and erosion control practices. Hydroseeding is the process of combining seed, mulch, fertilizer, tackifiers, and optional soil amendments with water to mix in a HydroSeeder™ tank to form a thick slurry. This slurry is applied with pressure via hose or tower onto the soil to create an ideal environment for seed germination and turf development. Vegetation establishes quickly providing a uniform cover for erosion control.

The vegetation quality that hydroseeding affords is much healthier, greener, and lasts longer because all ameliorants, fertilizers and organic material may be applied with the hydroseeding slurry. The root system is grown deep in the soil and experiences less shock in foreign soil.

Hydromulch Pty (Ltd.) has been contracted by most mining consortiums to apply a substantial vegetative cover to many rehabilitated opencast mines to prevent erosion and restore the area’s vegetation to its natural state. The company has helped pioneer the landscape, soil reclamation and erosion control industry through its years of experience on projects in the Southern African Development Community (SADEC) countries.

Other successful contracts have also been completed in countries such as Tanzania, Zambia, Uganda, Kenya, Benin, Guinea, Madagascar and the West Indies.

4 Phytoremediation

4.1 Phytostabilisation

Metal hyperaccumulator plants are in the focus of research in recent decades due mainly to their applicability in phytoremediation techniques; but there are also many other potential applications for these plants. For example, attention has been given to establishing metal-tolerant plants on mine dumps in South Africa (Reilly and Reilly 1973). Metal hyperaccumulators are characterized by the ability to accumulate very high concentrations of certain elements from the soil in which they grow, far in excess of normal physiological requirements (if any), and far in excess of the levels found in the majority of other species tolerant of metalliferous soils. Selection of a variety of perennial grasses, shrubs, and trees for revegetation of mine tailings is important for phytostabilisation. Berkheya coddii Roessler (Asteraceae) (Fig. 4), an endemic herbaceous and perennial nickel-accumulating plant grows on Ni enriched ultramafic soils in South Africa. Phytoremediation/phytomanagement makes use of specially selected or engineered plants to improve trace element contaminated sites by immobilisation of the trace elements (phytostabilisation), or their extraction (phytorextraction). One of the main advantages of phytoremediation is that of its relatively low cost compared to other remedial methods such as excavation.
With its goal to reduce its energy use by 15 percent by 2015, coal miner Exxaro (South Africa) has built green housing for its employees through the company’s eco-friendly housing project, in Lephalale, Limpopo. This is in line with the DEM’s ‘Energy Efficiency Accord’ for the industrial and mining sectors (Sikhakhane 2011).

### 6 Legislation

Current best practice attempts to avoid negative impacts and, where necessary, to restore impacted environments to their pre-mining state, are essential steps to be followed by all stakeholders in the mining industry, if this industry is to contribute significantly towards sustainable development in any country. The present situation indicates that this message is now being carried through. But why has the situation changed so rapidly in a positive way? The answer is: “Legislation”. The environmental awareness campaign mounted in the late 60’s, first in the USA, e.g., USEPA; The Clean Water Act; Environmental Impact Assessment requirements, has been followed through to the rest of the world.

Mining legislation in most mature African mining countries dictates that mine closure requires the return of land to a viable post-mining use, such as agriculture. It is not even sufficient to simply physically reclaim mined lands anymore as the socio-economic impacts of the closure must be assessed and managed.

Like most of the other mining countries on the continent, South Africa has over the past decade been enforcing legislation that requires mining companies to undertake environmental remediation when mines are decommissioned. This is informed by policies aimed at sustainable use and management of the environment.

The South African legislation governing mine closure, particularly the Mineral and Petroleum Resources Development Act (28 of 2002), requires rigorous mitigation of both biophysical and socio-economic impacts. For example local legislation requires all manganese operations to keep all exposures longer than an 8 hour per day below 1 mg/m$^3$ – responsible companies are working towards levels of 0.2 mg/m$^3$.

However, in most cases, enforcement and implementation of these legislations are still difficult, because of the limited capacity of the relevant authorities. However, as Petja et al. (2008) have shown, the use of freely available Landsat images in the context of the asbestos environment can be used to address some monitoring problems experienced after the closure of various mines. For example, by studying the reflective properties of the variables (vegetation species) used for environmental remediation, a better understanding of the type of positive environmental change can be gained from satellite images. Earth observation therefore can be an important supplement to the limited field monitoring capacity for observing the dynamics of mining environments in the post-closure phase.

### 7 Conclusions

Local environmental impact of Africa’s mines, many of which are located in remote areas, has been a topic of concern to environmentalists for many years – and
mining companies have worked hard on technological innovations, to address burning issues such as land scarification, AMD and water quality. Successful closure must consider medium to long term post-mining land use and, critically, land capability. Effective mitigation may require new approaches to min design, so as to have minimal impact on water quality, for instance. Current best practice attempts to avoid negative impacts and, where necessary, to restore impacted environments. These developments are the result of increasing adherence to legislative protocols by mining stakeholders, brought about largely by massive public and government pressure on the industry. The increasingly scientific methods applied to impact mitigation and rehabilitation ensures a continually improving level of performance.

This paper describes AMD generation and its associated technical issues. Despite the fact that research and development in African metal-and coal mines have led to significant advances in the treatment of AMD, through active treatment systems such as neutralisation using limestone, sulphate removal using sulphate-reducing technology and mine water desalination technology, there is still a need for further technical research and innovation in developing cost-effective treatment processes for the range of AMD waters. Many treatment processes give rise to new large waste streams (such as brines or gypsum).

Of all the methods to minimise on- and off site environmental impacts, revegetation is the most documented and widely used because it is most practical and economic, though it is often slow due to the hostile conditions such as toxicity of heavy metals (Troung, 1999). Ultimately, an integrated approach to closure planning is required whereby joint action of stakeholders - mining companies, Government and communities - assume responsibility for long-term sustainability of closed mines. However, the situation is still not yet ideal, and much more needs to be done to minimise the impacts.

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Environmental impact of ore smelting: the African and European experience

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Abstract. The presentation will cover our research activities in areas affected by non-ferrous metal smelting in Europe (Czech Republic) and Africa (Zambia, Namibia). The aspects related to production, mineralogy and chemistry of waste materials (slags, fly ashes) will be demonstrated in view of their environmental stability. Data from laboratory leaching experiments of various smelting wastes coupled to speciation-solubility modelling and investigation of in-situ weathering products will be presented and described in context with possible contaminant mobility in waste disposal sites and smelter-affected soil systems.

Keywords. Metals and metalloids, non-ferrous metal smelting, mineral wastes, soil pollution, Czech Republic, Zambia, Namibia

1 Introduction
Non-ferrous metals smelting activities represent one of the most important point sources of metals and metalloids in the environment. Key factors are mainly the production and dumping of waste materials (slags, fly ashes) and pollution of soils in the vicinity of the smelters via atmospheric deposition. Since 2000, our research group has been involved in numerous projects dealing with highly-polluted environmental systems in the vicinity of smelting factories. The aim of the present paper is to summarize the key findings related to smelting waste stability and their effect on the adjacent environments (soils) and to demonstrate possible environment-friendly ways for their management and disposal.

2 Materials and Methods
We examined a number of smelting sites in the following countries: Czech Republic (Pribram, primary and secondary Pb smelting), Namibia (Tsumeb, Cu-Pb-As smelting), Zambia (Copperbelt – Nkana, Mufulira, Chambishi, Cu-(Co) smelting). Waste materials (slags, fly ash) were sampled on dumps in the vicinity of the smelting complexes and/or directly in the smelting process. In addition, topsoils and soil profiles were sampled around all the smelters. For the mineralogical and chemical investigation we used numerous analytical techniques: XRD, HRTEM/EDS/SAED SEM/EDS, EPMA, ICP-OES, ICP-MS. Long-term and pH-static laboratory leaching tests were conducted according to various methods (e.g. EN 12457, EN 14497, TCLP). The mobility and bioavailability of smelter-derived pollution in soils were studied using sequential extraction procedures (SEP), Pb isotopic tracing and various bioaccessibility extraction tests.

3 Lead smelting (Pribram, Czech Republic)
Pribram (Czech Republic) is one of the famous European localities, where Ag-bearing polymetallic ores have been mined and processed since the Middle Ages. The ore smelting left enormous amounts of waste products deposited on the dumps (1.8 Mt of slags) exposed to weathering (Ettler et al. 2001). Investigation of their natural alteration features indicated that numerous geochemical/mineralogical mechanisms leading to Pb attenuation occur under oxidizing dumping scenario (Ettler et al. 2001; Ettler et al. 2003). However, a covering of slag dumps with a soil layer could lead to an accelerated release of metals/metalloids due to extensive complexation with organic ligand (low-molecular-weight organic acids, humic substances) present in the soil pore water (Ettler et al. 2004a). Figure 1 shows the Pb leachability from these two slags as a function of time and confirms that higher amounts of Pb are released from the primary Pb slag. A comparison of leaching data with regulatory limits for non-hazardous and hazardous waste according to EU criteria indicates that in a long-term perspective, only primary Pb slag can be considered as hazardous material. In contrast, the modern slag from car-battery processing is relatively stable. In this case, the released amounts of Pb are low even after long-term interaction with water (Figure 1).

Figure 1. Release of Pb from two types of Pb smelting slags obtained by batch leaching experiments at L/S of 10 L/kg in deionized water and comparison with regulatory concentration limits for non-hazardous and hazardous waste defined for the 24-h leaching tests EN 12457.

Even worse situation can be observed for Zn, where the concentrations released from primary Pb slag exceed the regulatory limit for hazardous waste (i.e. 200 mg/kg) approximately ten times after 1 year of leaching and...
more than forty times after 12 years of leaching.

Another aspect is related to the stability of the Pb smelter fly ash in aqueous and soil environments (Ettler et al. 2005a). Whereas fly ash from primary Pb smelting is composed mainly of sulphates/oxides, fly ash from secondary Pb smelting (car battery processing) is also composed of highly soluble chlorides (Ettler et al. 2005b; Ettler et al. 2008). When the fly ash is deposited in soils, Pb becomes extremely mobile and can vertically migrate downward in the soil profile as also confirmed by Pb isotopic tracing (Ettler et al., 2004b).

3 Smelting in Namibian and Zambia sites

Extensive mining and processing of ores in Namibia and Zambia left huge amounts of wastes potentially affecting surrounding environments (e.g., 200 kt of slag in Tsumeb; 20 Mt of slag in Kitwe-Nkana). The leaching experiments conducted on the Tsumeb slags indicated high risk of As and Sb release. In particular arsenates forming efflorescence secondary minerals on the slag surfaces can be dissolved during the rainy season and significant amounts of As and related Pb/Cu can be flushed into the environment around the slag dumps (Ettler et al. 2009). The formation of highly soluble metal-bearing secondary phases on the surfaces of copper slags in the Zambian Copperbelt can lead to similar effects (Vitkova et al. 2010). Moreover, the grinding of slag material, which is at the Tsumeb site subsequently deposited on the tailing pond (to lower the wind dispersal of mine waste) leads to its higher chemical reactivity and increases the risk of metal/metalloid release. Similarly, the formation of fine slag dust before the slag reprocessing (Kitwe-Nkana) is partly responsible for the contamination of surrounding soils. Although the slag particles have significantly lower solubility than the fly ash deposited in soils, the metal leachability is two orders of magnitude higher under acidic conditions corresponding to soil pH (4–5) (Vitkova et al. 2011). As a result, even production of waste materials in smelters is significantly affecting agro-environmental systems and can have influence on the contaminant bioaccessibility to plants and humans (Ettler et al. 2011; Ettler et al. 2012).

4 Conclusions

Waste materials from non-ferrous metal smelting are complex materials, which need to be studied using the combination of mineralogical and chemical methods to assess adequately their harmful properties. In particular the solid speciation is strongly affecting the release of metals and metalloids from these waste materials under specific disposal scenarios. For any evaluation of the smelting waste recycling potential and their environment-friendly management (solidification or stabilization), the local context must also be considered.

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Mobility and bioaccessibility of inorganic contaminants in soils in the vicinity of copper smelters, Copperbelt, Zambia

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Abstract. In this paper we examined the spatial and vertical distribution of metals (Co, Cu, Pb, Zn) and As in Oxisols in the vicinity of the Nkana smelter. The Pb isotopic tracing and sequential extraction procedure indicated that some contaminants can be vertically mobile in the soil profiles (e.g. calculated penetration rate of Pb was 1.36 cm/y). In contrast to mining area, the bioaccessibility determined using simulated gastric conditions was significantly higher in the smelting area (up to 100% of total Pb and As). Thus, a severe health risk related to topsoil ingestion should be taken into account especially in smelting areas.

Keywords. Metals and metalloids, soil pollution, mobility, bioaccessibility, smelting, mining, Copperbelt, Zambia

1 Introduction

Non-ferrous metals smelting activities represent one of the most important point sources of metal/metalloid pollution of soils via atmospheric deposition. So far, relatively few studies have been focused on ecosystems (soils, water, air, biota) polluted by mining/smelting industries in developing countries in Africa. Based on a previous screening study focusing on the central-northern part of the Zambian Copperbelt (Kříbek et al. 2010), we investigated in detail the soil contamination around the Nkana smelter at Kitwe, one of the hot spots of metal/metalloid contamination in this region. This paper is focused on the spatial distribution of As, Co, Cu, Pb and Zn in topsoils around the Nkana smelter coupled to Pb isotopic tracing of the degree of contamination and detailed investigation of the vertical mobility of inorganic contaminants in these highly polluted soils using chemical fractionation and Pb isotopic methods. In addition, a comparison of gastric bioaccessibilities of metals/metalloids in soils from smelting and mining areas (Kitwe, Chingola) in the Copperbelt has been performed.

2 Materials and Methods

A total of 196 topsoil samples (A horizon, depth 0-5 cm) were collected to cover the 32-km²-large zone in the vicinity of the Nkana copper smelter, Copperbelt, Zambia and a 110-cm-deep soil profile (Oxisol) was sampled within the highly polluted zone close to the smelter stack to investigate in detail the vertical mobility of contaminants. To evaluate possible risks related to soil ingestion and metal/metalloid gastric bioaccessibility, 52 topsoils from the mining area (Chingola) and 55 topsoils from the smelting area (Nkana-Kitwe) were also collected. Total contaminant (As, Co, Cu, Pb, Zn) concentrations were determined in bulk soil digests using ICP techniques (ICP-OES, ICP-MS). The chemical fractionation of the studied contaminants was studied using a BCR sequential extraction procedure. Lead isotopic composition of soils and possible sources of pollution (slags, smelter dust) were measured using ICP-MS (206Pb/207Pb isotopic ratio was used) (Ettler et al. 2011). The Simple Bioaccessibility Extraction Test (SBET) using the extraction fluid containing 0.4 M glycine, adjusted to pH 1.5 ± 0.05 by reagent grade HCl and L/S ratio of 100 was used to simulate the gastric accessibility of metals in topsoils (Ettler et al. 2012).

3 Results and Discussion

The spatial distribution of the major contaminants indicated the highest contamination NW of the smelter stack, corresponding to the prevailing wind direction in the area. The highest metal/metalloid concentrations in the topsoils were: 255 mg/kg As, 606 mg/kg Co, 27410 mg/kg Cu, 480 mg/kg Pb and 450 mg/kg Zn. Lead isotopes helped to differentiate the extent of metallic pollution and indicated the mixing of three major pollution sources (given as 206Pb/207Pb ratios): smelting activities (1.19-1.28), petrol combustion (1.07 –1.09) and regional background (deep soil horizons, ca. 1.35). Investigation of the soil profile indicated that the contamination is mostly located in the uppermost soil horizons enriched in organic matter (< 10 cm). Based on SEP, the isotopic composition and knowledge of smelter activities in the area, it was predicted that anthropogenic Pb (corresponding to a concentration of 1 mg/kg, i.e. ca. 1.5% of total Pb) exhibited downward migration in the soil profile with estimated penetration rate of 1.36 cm/yr (Figure 1). Copper, being substantially bound in the exchangeable fraction, also showed significant mobility in the profile (Ettler et al. 2011). Higher bioaccessibilities of contaminants were observed for As and Pb, attaining 100% of the total metal/metalloid concentration, especially in topsoils from the hotspots close to the smelter area (Figure 2). In contrast, the maximum bioaccessibilities of As and Pb in the mining area were 84% and 81%, respectively. The ranges, mean and median bioaccessibilities of Co, Cu and Zn were similar for the two areas.
The maximum bioaccessibilities of Co, Cu and Zn were 58–65%, 80–83% and 79–83%, respectively. The obtained data indicate that a severe health risk related to topsoil ingestion should be taken into account, especially in smelting areas. The calculated amounts of ingested metals (assuming the soil ingestion rate of 100 mg/day and a child weighting 10 kg) exceeding tolerable daily intake (TDI) values calculated from the human-toxicity maximum permissible levels (Baars et al. 2001). The risk was mainly related to Cu (TDI = 1400 µg/day) and Co (TDI = 14 µg/day) (Ettler et al. 2012).

4 Conclusions

Soils in the vicinity of the Nkana copper smelter and Chingola copper mine (Copperbelt, Zambia) were highly polluted by As and metals. The spatial distribution of As, Co, Cu, Pb and Zn were mostly affected by the prevailing wind direction and the highest concentrations were detected downwind (NW) of the smelter. The sequential extractions indicated that a number of metals (mainly Cu) can be mobile in the soil profile. According to the gastric bioaccessibility investigation, the ecotoxicological risks related to soil ingestion were mainly important for Cu and Co.

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Contaminant Mobilisation by Fluid-Rock Interaction and Related Transport Mechanisms in Platinum Tailings

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Abstract. Contaminant release and transport in platinum tailings are poorly studied in literature. This study serves to characterise these processes. The tailings facility is located in Steelpoort, Mpumalanga, South Africa on Critical Zone rocks of the Rustenburg Layered Suite in The Bushveld Igneous Complex. Samples were collected by hand auger- and direct push probe drilling. The samples were analysed using XRD, XRF, ABA, NAG, Reflected Light Microscopy, Acid Leaching Tests and ICP scans. The flow through the tailings, underlying vadose zone and fractured rock aquifer was characterised using permeameter- and pumping tests. Analyses-, test- and modelling results showed that alteration mineral phases formed within ten years in the tailings material. Elevated major cation and anion concentrations were found in the fluid discharging from the tailings as well as the in groundwater. However discharge from the tailings was predicted to take place at 0.7 m per decade into the underlying vadose zone with fracture flow in the aquifer ranging from 0.46-0.026 m/d. Contaminant migration into the Steelpoort River is inhibited by the Dwarsriver Fault. Therefore, groundwater is considered to be the major receptor in the system and groundwater users may be negatively impacted by increasing groundwater salinity and major ion concentrations.

Keywords. Platinum tailings, fluid-rock interaction, geochemistry, unsaturated flow, contaminant transport, fractured aquifer, receptor, Steelpoort

1 Introduction

The transport mechanisms and liberation of contaminants in platinum tailings storage facilities (TSF’s) are poorly studied and rarely documented. Previously published studies have focussed mainly on gold-, copper-, zinc and lead tailings such as Moncur et al. (2004). This study highlights the importance of platinum TSF’s as contaminant producers due to mineral dissolution and oxidation.

The tailings facility investigated, is located in Steelpoort, Mpumalanga, South Africa. The local geology comprises of Critical Zone rocks of the Rustenburg Layered Suite of the Bushveld Igneous Complex. This zone formed some time after the intrusion of the Bushveld Complex, the largest layered mafic intrusion in the world, and is comprised of gabbro-norite, pyroxenite, anorthosite and diorite rocks (Cawthorn et al. 2004). The UG2 reef is generally mined in this area for platinum group elements and ferrochrome, and is one of the chromitite reefs that divide the critical zone into upper and lower zones. In the study area, the Dwarsriver thrust fault system cross-cuts the Critical Zone (Hartzer 1995).

The area receives high rainfall during the summer months providing enough water, along with mineral processing effluent, for fluid-rock dissolution reactions Stimmie et al. (2001).

The tailings facility has been operational since 2008 at the start of the mining operation, providing relatively fresh material to analyse as well as material that has been altered and neo-mineralised to make predictions on the mineralogical evolution.

The tailings material in this TSF is rich in mafic minerals that include sulphides, oxides and silicates. Plagioclase, pyroxene and spinel groups were found to be the most abundant minerals contained in the local pyroxenite and anorthosite rocks.

2 Methodology

2.1 Sampling

The tailings material was sampled using hand auger drilling as an initial probing phase. This was followed by direct push drilling down to the original soil profile, in order to provide a complete record of all tailings disposal cycles. The final direct push sampling frequency provided a continuous sample of the entire profile in the TSF, preserving the original material distribution, mineralogy, redox conditions and fluid content in undisturbed samples that were preserved in sealed PVC tubes.

2.2 Analyses and Models

The samples were chemically analysed using methods such as X-Ray Diffraction, X-Ray Fluorescence, Reflected Light Microscopy, Acid- Base Accounting, Net Acid Generation Potential, Acid Leaching and Inductively Coupled Plasma Scans. Hydraulic testing was also performed on the samples and at the TSF in the form of falling-head permeameter tests and pumping tests respectively.

Utilising all the data gathered from these analyses and tests, geochemical and unsaturated flow models were calculated for the tailings and underlying natural vadose zone.

3 Discussion

The following minerals were identified in the analyses of the tailings: anthophyllite, chlorite, chromite, enstatite, muscovite, anorthite, talc, tremolite, diopside, lizardite, chalcopyrite and biotite as illustrated in Figure 1.
The dominant ions contained in mineral solid phases are Si, Al, Fe, Cr, Mg and Ca.

Reflected light microscopy results indicate that chalcopyrite and pyrite are the only sulphide minerals present in the tailings material.

The main leachable contaminants that may be released from the tailings material were found to be Ca, Mg, Na, Si with SO₄ and Cl leachable in lesser amounts as well as trace amounts of heavy metals. This may also explain the acid base accounting results which show a slightly lowered pH, but an elevated, positive neutralisation potential ratio which may, in the long term, cause more alkaline drainage.

Figure 1. Abundances in weight% of each mineral found in each sampling run in the tailings material down to soil level.

These analyses were used to calibrate a geochemical flow-through model. The model was used to predict short term drainage compositions, neo-mineralised phases and pH conditions. The model predicted elevated pH, Na, Ca, Mg, SO₄ and Cl levels in the groundwater as indicated by Figure 2, as well as low temperature hydrothermal precipitates and smectite group clay minerals as alteration products in the tailings material as indicated by Figure 3.

Figure 2. Chemical components released into tailings fluids over a 100 year flow period.

The inductively coupled plasma scans show an elevated pH in TSF toedrain fluids, corresponding to predicted pH values in groundwater by the geochemical model, with a more neutral pH further away from the facility in the aquifer. This may be facilitated if acidic chemical species accumulate in the system. Groundwater ICP scans also show elevated SO₄, Cl, Ca, Mg and Na concentrations, which were successfully predicted by the model, especially with respect to Na, SO₄ and Cl values as indicated by Figure 4.

Figure 3. Neo-mineralised alteration phases forming over a 100 year flow period.

Figure 4. Chemical component concentrations in sampled groundwater as indicated by ICP scans.

Minor clay minerals were also a component found in XRD results, which were used as indicator phases, corresponding with the model.

The permeameter tests provided an arithmetic average for the saturated hydraulic conductivity of the tailings material in the order of 10⁻⁴ m/d equating to 0.1 m/y. This was used in a numerical, unsaturated flow model along with gravimetric fluid content of the material. The model predicted an unsaturated hydraulic conductivity ranging between 10⁻⁸ and 10⁻³ m/y for the tailings material (M1), as well as an unsaturated hydraulic conductivity ranging between 10⁻⁸ and 10⁻⁵ m/y for the underlying soil material (M2), depending on degree of saturation as indicated by Figure 5. The flux of fluid from the foot of the tailings is predicted as approximately 0.7 m every ten years as a maximum discharge as indicated by Figure 6.
The transport of the contamination in the underlying fractured rock aquifer was characterised using pumping test data. The fractured and faulted rock underlying the TSF was found to be structurally inhomogeneous, according to drill log data received from the mine. Therefore, due to the anisotropic nature of the aquifer, markedly different hydraulic conductivity values were obtained for the different tests. The pump tested borehole closest to the tailings facility provided a fracture hydraulic conductivity value of 0.46m/d if estimated with the Gringarten method, while the pump tested borehole closest to the river has an estimated value of 0.026m/d, an order of magnitude lower, if the same method is used.

**Figure 5.** Unsaturated hydraulic conductivities for the tailings- (M1) and soil material (M2) at different moisture contents.

**Figure 6.** Predicted fluid flux from the bottom of the tailings into the natural vadose zone.

The hydrochemistry of the groundwater as measured by the ICP scans is also indicative of this lowered flow rate with contaminant concentrations increasing with distance from the tailings, which indicates an accumulation of chemical components as the groundwater becomes more stagnant. The pumping test conducted on the borehole closest to the river, also indicates a no flow boundary condition.

All these factors may be attributed to the Dwars river fault system which runs parallel to the Steelpoort River and may act as a barrier for contaminant transport to the river, protecting this receptor from excessive contaminant loading.

### 4 Conclusions

The tailings can be considered a point source contaminator, producing metals, sulphates and chlorides as well as alkaline drainage through fluid-rock chemical interaction. Some contaminants may be precipitated in the form of secondary minerals in the form of late stage phyllosilicates, alkaline drainage precipitates and clay minerals.

However, the movement and discharge of contaminants occurs at a rate of 0.7 metres of flow per decade in unsaturated conditions and at an even slower rate through the underlying vadose zone, when unsaturated. At aquifer level, contamination moves rapidly through fracture flow in the igneous rocks, but slows down and accumulates to a degree at a no flow boundary in the form of a major thrust fault system.

Therefore, the nearby river may be impacted far less than expected. However, an accumulation of the major cations and anions as well as trace heavy metals may take place in the aquifer at the thrust fault boundary.

Therefore, the Steelpoort River should not be discarded as a potential receptor, but more focus should be directed to the underlying fractured aquifer. The accumulation and continuous, slow input of chemical species may add to the salinity of the groundwater, degrading its quality and may eventually impact on the health and environment of local groundwater users.

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### References


Metals and arsenic in cassava: Indicators of contamination in the Zambian Copperbelt mining district

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Abstract. The contents of metals and arsenic in the leaves and tubers of cassava (Manihot esculenta) growing on uncontaminated and contaminated soils of the Zambian Copperbelt mining district have been analyzed. The contents of copper (Cu) in cassava leaves growing on contaminated soils reach as much as 612 mg kg⁻¹ Cu (total dry weight [dw]). The contents of copper in leaves growing on uncontaminated soils are much lower (up to 252 mg kg⁻¹ Cu respectively). The contents of cobalt (Co), arsenic (As) and zinc (Zn) in leaves of cassava growing on contaminated soils are higher compared with uncontaminated areas, while the contents of lead (Pb) do not differ significantly. Even in strongly contaminated areas, the contents of copper in the leaves and tubers of cassava do not exceed the daily maximum tolerance limit of 0.5 mg kg⁻¹ human body weight (HBW) established by the Joint FAO/WHO Expert Committee on Food Additives (JECFA). The highest tolerable weekly intake of 0.015 mg kg⁻¹ HBW for arsenic are exceeded slightly in a few samples. Therefore, dietary exposure to metals and arsenic through the consumption of these vegetable crops has been identified as a low risk to human health. Nevertheless, as the surfaces of cassava leaves are strongly contaminated by metalliferous dust in the polluted areas, there is still a significant risk of ingesting dangerous levels of copper, lead and arsenic if dishes are prepared with poorly washed foliage.

Keywords. Cassava, Metals, Arsenic, Contamination, Copperbelt, Zambia

1 Introduction

The Zambian Copperbelt region has been strongly affected by mining and processing of copper and cobalt ores (Kříbek et al. 2007, 2010). The area is also characterized by cultivation of cassava which represents a substantial part of food intake of the local population, particularly in the countryside.

This extended abstract presents (1) data on the contents of metals and arsenic in cassava particularly in its leaves and tubers that are used for preparation of meals, growing in contaminated and uncontaminated areas of the Copperbelt mining district, (2) contents of the given elements in studied crop and how they correlate with those contained in soils of contaminated and uncontaminated areas, and finally (3) an assessment of whether food prepared from cassava growing in contaminated areas endangers the health of the local population. Particular attention was paid to surface contamination of leaves caused by dust fallout on aboveground parts of cassava in the neighborhood of smelters.

2 Materials and methods

2.1 Sampling

Samples of cassava were collected mostly during the cool and dry seasons in the years 2005 to 2009. The sampling sites for the soil and vegetation were selected so as to cover both contaminated and uncontaminated areas. Soil samples were taken to a depth of approximately 10 cm, close to the roots. Altogether 54 samples of cassava leaves and 50 samples of cassava tubers and 71 soil samples were collected.

The soil samples were air-dried at and after homogenization; half of each sample was passed through a clean polyethylene (PE) 0.25-mm mesh screen using a USGS sieving set. For chemical analyses, soil samples were oven-dried at 105 °C and pulverized in an agate ball mill to <0.063 mm mesh. Plant parts were thoroughly washed with tap and distilled water, cut to pieces and dried.

2.1 Soil and plant analyses

The pseudo-total digests of soil samples were obtained by a standardized aqua regia extraction protocol in accordance with the ISO 11466 procedure (International Organization for Standardization, 1995). All reagents were declared pro analyti, and all solutions were prepared with double-distilled water. Standard working solutions were prepared from original certified stock solutions (MERCK) concentration 1000 mg L⁻¹ in 1% supra pure HNO₃. Co, Cu, Fe, Pb and Zn were determined using Flame Atomic Absorption Spectroscopy (FAAS, Perkin Elmer 4000 Spectrometer). Arsenic was determined using Hydride-Generation
Atomic Absorption Spectrometry (HGAAS, Perkin Elmer 503 equipment).

Approximately 1-g aliquots of the plant parts were burned down in a muffle oven. A temperature program from 25°C to 550°C was employed with a temperature increase of 2°C/min, and then kept constant at 550°C for 2 hrs. The amount of resulting ash was weighed and the metals were analytically determined in HNO₃ and HCl at 5:1 (v/v) leachate. As and metals were analyzed in leachate as described previously. The detection limit was 1mg kg⁻¹ for Cu and Zn, 0.5 mg kg⁻¹ for Co and Pb and 0.04 mg kg⁻¹ for As. Due to the requirements for precision in As and metals analyses, standards CRM 1575a pine needles and CRM 1515 apple leaves were used for plant samples. Relative errors determined using reference materials were ±9.9% for Cu, ±11.8% for Co, 11.4% for Zn and ±14.6 for Pb. The relative error for As was higher (±28%) due to a low concentration of this element in CRMs (0.038 and 0.039 mg kg⁻¹, respectively).

3 Results and discussion

3.1 Sources of contamination

The main sources of soil contamination in the studied area include the dust fallout from smelters and also dust wind-blown from dry parts of tailings ponds. Although the Copperbelt ores are chiefly extracted for high amounts of other metals and metalloids. Consequently, during the smelting process, apart from major copper and cobalt, some other compounds are also emitted into the air, particularly volatile elements such as As, Pb, and Zn.

3.2 Delimitation of uncontaminated and contaminated areas

Because of the very variable lithological and geochemical character of the bedrock and soils in the studied area, it is very difficult to distinguish contaminated from uncontaminated areas in the Copperbelt mining district. Since the uppermost part of the soil horizon is mostly affected by dust fallout, an enrichment index (EI) was used to distinguish between contaminated and uncontaminated areas. This index is based on the average ratio of the actual and median content of the given contaminants (As, Co, Cu, mercury [Hg], Pb and Zn in topsoil):

\[ EI = \left( \frac{As}{m_{As}} + \frac{Co}{m_{Co}} + \frac{Cu}{m_{Cu}} + \frac{Hg}{m_{Hg}} + \frac{Pb}{m_{Pb}} + \frac{Zn}{m_{Zn}} \right)^{0.5} \]

The enrichment index (EI) actually shows a higher-than-median or lower-than-median average content of the six elements and to a large extent it also reflects the enrichment of topsoil from anthropogenic sources (Kříbek et al. 2010). A total of 719 data on topsoil acquired in the years 2004–2007 (Kříbek et al. 2007) in the studied area were used for calculation of the enrichment index. It is evident from the contour map of

EI values (Fig. 1) that areas with EI higher than 1 are restricted to the mining and ore processing areas of Kitwe, Mufulira and Chingola and downwind, in a north-westerly direction. According to the EI value calculated for the sampling site at which cassava was collected, it was possible to classify these crops as belonging either to the uncontaminated area (EI<1) or the contaminated area (EI>1).

Figure 1. Map of sampling sites of cassava collected in the studied area of the Zambian Copperbelt. Contaminated (EI>1) and uncontaminated (EI<1) areas and the major sources of contamination are marked.

3.3 Contents of metals and arsenic in uncontaminated and contaminated soils

The basic statistical data, i.e. minimum, maximum and median analytical values, values of the 15%, 25%, 75% and 95% percentiles for the selected elements in soils in the uncontaminated area (EI<1) and the contaminated area (EI>1) of the Copperbelt are given in Table 1.

The median values for Cu, Co and Fe are much higher in soils of the contaminated area, but also the median values of As and Zn were found to be enhanced. On the other hand, the median values for Pb are very low in soils of both the uncontaminated and the contaminated areas, whereas maximum contents of Pb were found to be even higher in soils from the uncontaminated area. The dispersion of values, particularly those for Cu, Co and Zn in uncontaminated soils are in general much lower when compared with those in contaminated soils.