# Leachability of Suspended Particles in Mine Water and Risk of Water Contamination

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## ABSTRACT

Water released from underground mine fissures is either pumped at the surface or accumulates in ponds underground. Fine particles of ore suspended in such solutions are susceptible to weathering under environmental conditions or through the effect of indigenous autotrophic microorganisms living in the ore. The leachability of the suspended solids determines the risk of water contamination underground and at the surface as well as the need of a pretreatment process. In this work environmental conditions are partly considered, as aggressive methods are also used for leaching. Water samples collected underground and at the surface of a mine, were filtered and the suspended particles were separated from the solution through filtration and analyzed by SEM-EDS, XRD and XRF. The solid was leached under simulated environmental conditions or ultrasonic acid digestion at various temperatures. The metal mobility test was carried out according to the German standard Norm DIN 19730. The XRD analysis revealed the presence of iron sulfide (pyrite) in underground samples and iron oxides (maghemite and mackinawite) and zeolite in samples collected at the surface, while the SEM-EDS and XRF results showed the presence of trace elements such as chrome, titanium, calcium, zinc, nickel, manganese, lead, copper, cobalt and magnesium. The amount of mobilized metals detected by ICP analysis indicates that the metal could be released from the suspended solids, however, further investigations are required to determine the extent and rate of metal leaching under environmental conditions.

The natural weathering of the suspended solids is possible and this could therefore contribute in the degradation of water quality by decreasing the pH and increasing metal concentration; this implies that pretreatment of mine water is required to mitigate the risk of contamination of water sources.

**Keywords:** Mine water, suspended particles, metal mobility, leachability, underground and surface waters

## INTRODUCTION

Mining of ore as well as recovery of metals and other resources from the ores using mineral processing and hydrometallurgical processes generally results in the accumulation of suspended particle matters (SPM) also referred to as fluid fine mineral tailings. These particles often contain sulfide minerals which, if not properly stored can be oxidized, resulting in the formation of acid mine drainage (AMD), usually containing high concentrations of dissolved potentially toxic elements (PTE) and sulfate ($SO_4^{2-}$). According to several authors (Bird et al., 2008; Fuge et al., 1991; Allan, 1988; Helgen and Davis, 2000; Miller et al., 2007), the release of contaminant metals into the fluvial environment within mining-affected river catchments generally results from (1) acid mine drainage, (2) the release of waste slurries containing solute and particulate-associated metals, (3) dumping of mining and milling waste that is subsequently leached or dispersed downstream. Interaction of ground water and surface water with the suspended particle matters will result in the mobility of the trace elements from the solid phase after a time often determined by environmental conditions. Depending on the hydrogeochemical environment, the dissolution of SPM may give elevated concentrations of the trace elements and create potential contamination of associated ground water and surface water systems. The oxidation of sulfide minerals such as pyrite, chalcopyrite, arsenopyrite and pyrrhotite, will eventually result in the dispersion overtime of large amount of toxic metals into the ecosystem impacting the freshwater resources. From such sources, metal can easily move along the food chain causing genotoxicity among living organisms (Patra et al., 2004).

This study focuses on the investigation of the leachability of suspended particles in water from underground mine fissure and tailing ponds.

## METHODOLOGY

### Sampling

Water was collected from underground mine fissures and from tailings ponds at the surface. Suspended particles were collected from water samples by filtration through filter paper (Whatman 150 mm, Cat No 1440 150). The recovered suspended solid was dried at 50°C in the oven until constant weight.

### Characterization of suspended particles

The suspended solid samples were ground in a mortar and for the determination of the mineralogical phase, they were subjected to X-ray diffraction (XRD) analysis using the Philips model X'Pert pro MPD, at a power of 1.6 kW used at 40 kV; Programmable divergence and anti-scatter slits; primary Soller slits: 0.04 Rad; $2\theta$ range: 4-79.98; step size: 0.017°. The proportion of elements in the suspended solids was determined by X-ray fluorescence (XRF) using the MagiX PRO & SuperQ Version 4 (Panalytical, Netherland); a rhodium(Rh) anode was used in the X-ray tube and operated at 50 kV and current 125 mA; at power level of 4 kW.

### *Scanning Electrom Microscopy (SEM)*

A FEI Quanta 200 ESEM Scanning Electron Microscope, integrated with an Oxford Inca 400 energy dispersive x-ray spectrometer was used for the analysis of the suspended particles.

### Leaching experiments

The suspended solid samples were submitted to batch leaching with three different approaches aiming to test the mobility and rate of release of elements from the three suspended solid samples. The aggressive test using aqua regia aimed to approximate total metals not associated with silicate. In all experiments, about 0.1 g of samples was leached with 10 ml of lixiviant.

### *Leaching with synthetic acid rain*

The Eastern Transvaal Highveld is the area in South Africa where large metal working industries and coal burning power stations are located; in this particular area acid rain can occur at an average pH of 4.2. To simulate the natural lixiviant, synthetic acid rain (SAR) was prepared by diluting the mixture of $H_2SO_4$ and $HNO_3$ to a pH of 4.2; this solution (SAR) was used in batch leaching at room temperature. Leaching was performed with simultaneous shaking on horizontal at a speed of 150 rpm and six shaking periods: 1, 2, 3, 4, 7 and 24 hours; a long term leaching test was performed without shaking over a period of nine weeks (simulation of environmental conditions).

### *Metal mobility test*

The mobility of the elements was measured on the basis of the procedure described in the German Norm DIN 19730 (Deutsche-Norm DIN, 19730, 1997). The suspended solids were leached in deionized water without subsequent change of pH for 2 h at constant shaking speed of 20 rpm and at room temperature (~20°C).

### *Ultrasound assisted acid digestion method*

To maximize the extraction of elements from the suspended solids, the leaching was performed using aquaregia; the mixtures in 250 ml flasks were immersed into the ultrasonic water bath and subjected to ultrasonic energy of 35 KHZ for 20 min. The three temperatures of the ultrasonic water bath considered were 30, 50 and 70°C.

### *ICP analysis*

After the leaching process, the sample from each of the above test was collected into a 50 ml centrifuge tube, then centrifuged at 4000 rpm for 20 min and the supernatant carefully recovered without disturbing the pellet. The metal content of the supernatant was analyzed using the ICP-OES (ICP Expert II, Agilent Technologies 720 ICP-OES).

### Leachability of elements

The leachability of an element was calculated by considering the approximate total metal (expressed in leached amount) and the percentage leached value for the element.

The leached amount was calculated using the following equation:

$$Ca = CL \times VL/S \qquad (1)$$

Where Ca is the leached amount of an element in mg/g; CL is the concentration of an element in the leachate in mg/L; VL is the volume of the leachate in L, S is the mass of the suspended solid in g.

The percentage leached was calculated using the following equation.

$$Cp = Ca/Csp \times 100 \quad (2)$$

Cp is the percentage leached in %; Csp is the total concentration of an element in the suspended solid, estimated by XRF analysis.

## RESULTS AND DISCUSSION

The susceptibility of suspended solids from mine ponds to release metals in the environment is investigated in this study with consideration of natural or environmental conditions impacting on the leachability of metals. **Minerals and elements in the suspended particles**

The chemical characteristic of the suspended particles may determine the rate of reaction with the lixiviant. The mineralogical composition as determined by the XRD showed (Table 1) higher content of pyrite ($FeS_2$) in underground suspended particles (SP). It is assumed that the lower content of pyrite in surface SP is associated with longer exposure to weathering and dissolution of pyrite, hence the presence of iron oxides such as maghemite and mackinawite. The zeolite was identified only in surface samples (B and C), while quartz (SiO2) was abundant in all the SPs.

**Table 1** Mineralogical composition (XRD) of the suspended solids samples

| Sample A | | Sample B | | Sample C | |
|---|---|---|---|---|---|
| **Phase name** | **Wt %** | **Phase name** | **Wt %** | **Phase name** | **Wt %** |
| Pyrite | 12.74 | Silicon Oxide | 17.67 | Calcium silicate | 19.31 |
| Potassium Iron Oxide | 33.55 | Clinoptilolite | 27.46 | Zeolite | 12.59 |
| Silicon Oxide | 26.59 | Mackinawite | 24.42 | Silicon Oxide | 16.86 |
| Magnetite | 27.11 | Maghemite | 30.45 | iron(III) oxide | 24.45 |
| | | | | Iron Sulfide | 26.79 |

Based on the consideration of Price et al. (1997), the above table shows that there will be negligeable clay or carbonate minerals neutralisation potential.

The SEM-EDS analysis (Figure 1) shows the abundance of elements such as Fe, Si, Ti, Cr, Al, K, Mg and S in all the samples which can be correlated to the presence of pyrite and aluminosilicates as revealed by the XRD results; the element composition was confirmed by XRF results in Table 2.

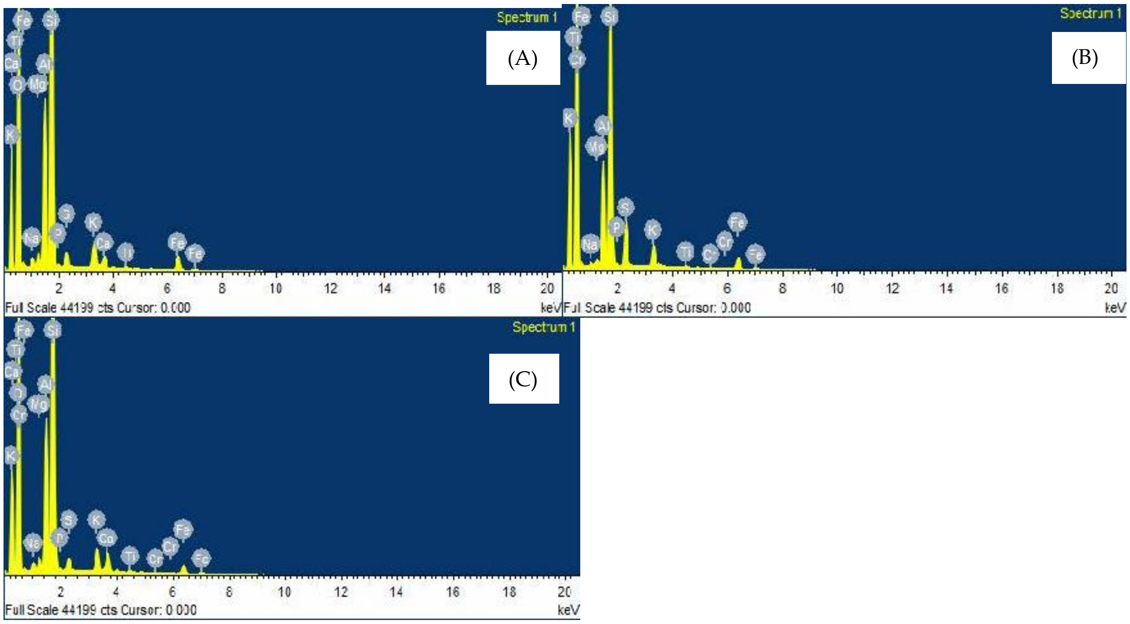

**Figure 1** SEM-EDS analysis of suspended particles

**Table 2** Chemical composition of suspended particles

| **Elements** | **Mass %** | | |
|---|---|---|---|
| | **A** | **B** | **C** |
| $Na_2O$ | 0.24 | 0.82 | 0.94 |
| $MgO$ | 0.37 | 1.65 | 1.73 |
| $Al_2O_3$ | 10.70 | 18.65 | 20.11 |
| $SiO_2$ | 67.50 | 63.56 | 61.40 |
| $P_2O_5$ | 0.07 | 0.06 | 0.06 |
| $SO_3$ | 9.05 | 2.78 | 2.88 |
| $K_2O$ | 3.09 | 2.83 | 3.37 |
| $CaO$ | 0.07 | 4.04 | 2.55 |
| $TiO_2$ | 0.50 | 0.65 | 0.64 |
| $Cr_2O_3$ | 0.24 | 0.17 | 0.19 |
| $MnO$ | 0.02 | 0.07 | 0.06 |
| $Fe_2O_3$ | 7.82 | 4.28 | 5.69 |
| $Co_2O_3$ | nd | 0.01 | 0.01 |
| $NiO$ | 0.03 | 0.03 | 0.03 |
| $CuO$ | 0.01 | 0.01 | 0.02 |
| $ZnO$ | 0.01 | 0.05 | 0.09 |
| $As_2O_3$ | 0.12 | 0.03 | 0.04 |
| $Rb_2O$ | 0.01 | 0.01 | 0.01 |
| $SrO$ | 0.01 | 0.02 | 0.02 |
| $ZrO_2$ | 0.05 | 0.04 | 0.03 |
| $BaO$ | nd | 0.06 | 0.07 |
| $PbO$ | 0.06 | 0.02 | 0.03 |
| $U_3O_8$ | 0.03 | 0.01 | nd |

The Fe enrichment of the SPs is associated with Fe-rich sulfides and Fe oxides as observed with XRD analysis (Table 1) and also reported in the mine residues such as tailings (Hochella et al., 1999; CourtinNomade et al., 2003).

**Mobility of elements under environmental conditions**

The percentages of Al, Fe, Mn, Ni, Sr, Zn and Cr leached from the samples (A, B and C) are plotted in Figures 2a and b which correspond to metal release by long term leaching (simulation of environmental conditions) and mobility test, respectively. It is observed that the metals are easily leached from the SPA which has acidic tendency as revealed by the decrease of pH after nine weeks contributing to dissolution of the mineral. Furthermore the presence of zeolite in surface samples (B and C) reduces the mobility of metals due to its cation exchange and molecular sieving properties; it is reported (Jiwan et al., 2013) that zeolite if often used to reduce the leachability of metals in compost. The long term leaching was carried out without stirring in synthetic acid rain (SAR) which are similar to environmental conditions. The mobility test is carried out at the same pH as the original solution of the SP and could therefore reflect the dissolution likely to occur in mine water at the site; it is observed that (Figure 2B) under such condition all the metals were mobilized from the SPA and only Mn, Sr and Zn from SPB and SPC; overall Fe, Ni, Sr and Zn were found to be the elements with higher leachability.

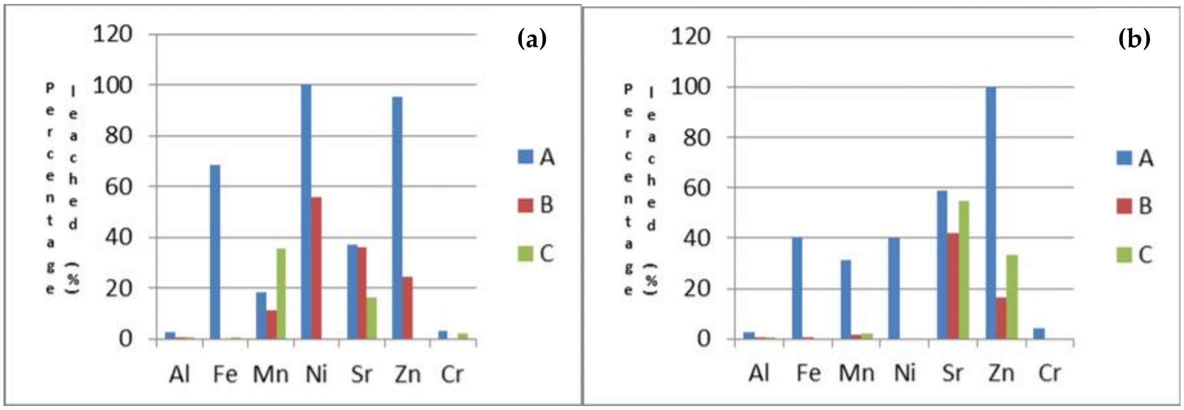

**Figure 2** Percentage leached of metals from suspended particles following (a) long term leaching and (b) mobility test

To better understand the leachability of the element the correlation of their mobility and their concentrations in the SPs was evaluated; as shown in Table 2, the values of the coefficient of determination ($R^2$) were relatively low, implying very little correlation, therefore the mobility of the element is not strictly related to its concentration in the SP, similar results have been reported by Jankowski et al. (2006). Except for Fe and Zn, there was no obvious correlation between mobility of element and the long term leaching; trace elements may exist in different oxidation states in mineral matters and therefore respond differently to leaching (Wadge et al., 1987; Jackson and Miller, 1998).

**Table 2** Correlation between mobility of elements, total concentration of elements and long term leaching

| Elements | Mobility vs Total concentration | Mobility vs long term leaching |
|---|---|---|
| Al | -0.9792 | 0.9304 |
| Fe | 0.834 | 0.9998 |
| Mn | 0.9326 | -0.4852 |
| Ni | -0.8992 | 0.944 |
| Sr | 0.6583 | -0.9435 |
| Zn | 0.74 | 0.99 |
| Cr | 0.9346 | 0.7551 |

This also implies in our study that the dissolution of the metal is mostly dependent on the chemical reactions given the distinctiveness with regard to the mineralogical composition of the samples.

### Leachability of elements from suspended particles

Environmental monitoring often requires the determination of metal content of suspended particles, but most importantly the susceptibility of release by dissolution. Figures 3a, b and c below show the percentage of Al, Fe Mn, Ni, Sr, Zn and Cr released through ultrasonic digestion of SPs. The predominant factor during such leaching approach is the temperature which increased the reactivity between the lixiviant and the SP, but also important in this case, a very aggressive lixiviant namely aqua regia was used to ensure the maximum extraction of the metal from the SPs. This test is basically conducted to detect elements which can be a drainage chemistry concern but is not a direct measure of their threat to the environment (Price et al., 1997). It is observed that irrespective of the temperature, approximately all the metals were extracted from the SPs. The impact of temperature is however noticeable as for metals such Al, Sr and Cr there is significant increase of percentage of metal leached with increase of temperature.

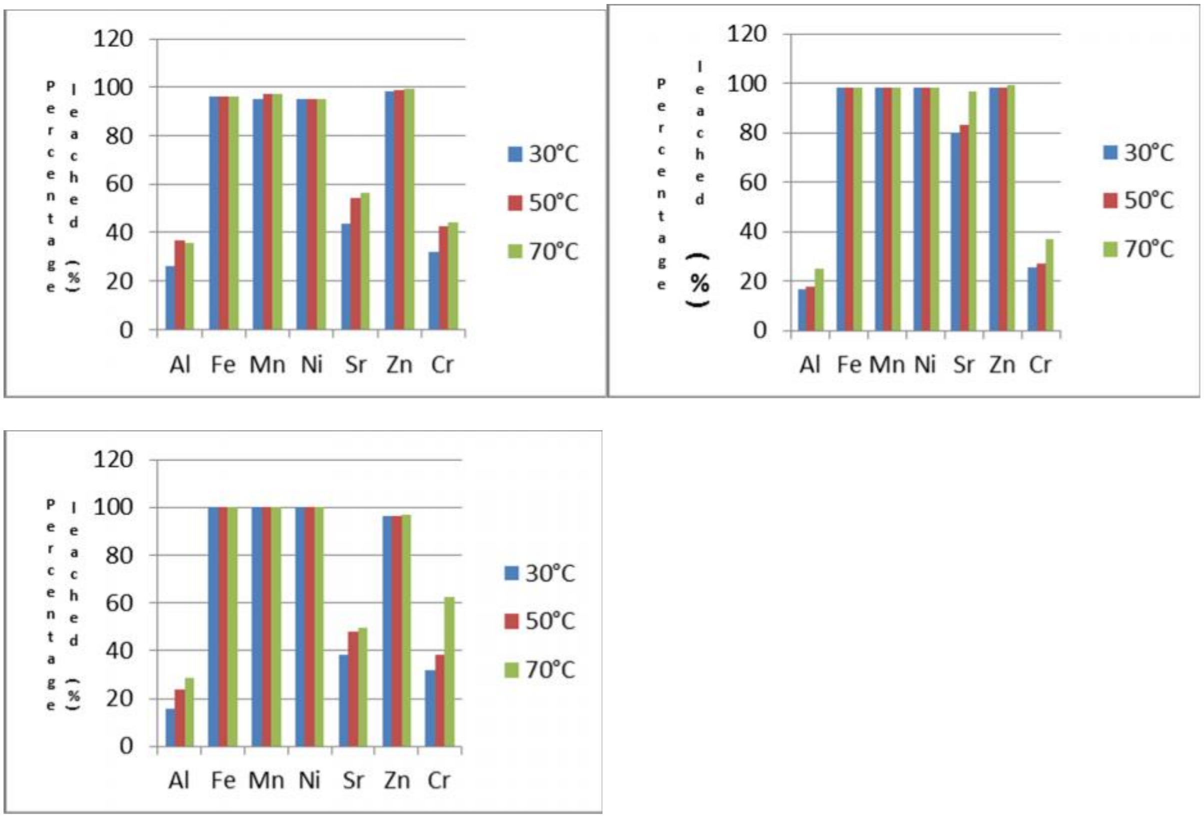

**Figure 3** Percentage leached metals from ultrasonic assisted acid digestion of suspended particles

Maximum recovery close to 100% was achieved in most cases for Fe, Mn, Ni and Zn; Kazi et al. (2000) have also reported similar percentage recovery using ultrasonic acid assisted digestion for the recovery of Cd, Cr, Ni and Pb. This result indicates that weathering of the suspended particles over a relative long period of time will likely result in the release of most of the metals into the environment resulting in the pollution of water sources.

## CONCLUSION

The suspended particles studied contained several metals in relatively high amounts with regard to environmental impact. The suspended particles collected underground were more likely to release the metals, the SP mineralogical propertyy is therefore and important parameter determining the mobility of the metals. The methods of metal extraction considered indicate that these metals will be released at various rates in the water system after short or long period of time. However, environmental conditions being only partly considered, the data could not be used for exact prediction of actual leachability at the mine site.

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## REFERENCES

Allan RJ. 1988. Mining activities as sources of metals and metalloids to the hydrosphere. In: Strigel G. (Ed.), Metals and Metalloids in the Hydrosphere: Impact Through Mining and Industry, and Prevention Technology. UNESCO, Paris, pp. 45 – 67.

Bird G, Brewer PA, Macklin MG, Balteanu D, Serban M, Driga B, Zaharia S. 2008. River system recovery following the Novat-Rosu tailings dam failure, Maramures County, Romania. Applied Geochemistry. 23: 3498 – 3518.

Courtin-Nomade A, Bril H, Neel C, Lenain J-F. 2003. Arsenic in iron cements developed within of a former metalliferous mine-Enguiales, Aveyron, France. Appl. Geochem. 18: 395 – 408.

Fuge R, Laidlaw IMS, Perkins WT, Rogers KP. 1991. The influence of acidic mine and spoil drainage on water quality in the mid-wales area. Environ. Geochem. Health. 13: 70 – 75.

Helgen SO, Davis A. 2000. Quantifying metal contributions from multiple sources to the Clark Fork River, Montana, USA. J. Environ. Forensics. 1: 55 – 62.

Hochella MFJr, Moore JN, Golla U, Putrus A. 1999. A TEM study of samples from acid mine drainage systems: metal-mineral association with implications for transport. Geochim. Cosmochim. Acta. 19/20: 3395 – 3406.

Jackson BP, Miller WP. 1998. Arsenic and selenium speciation in coal fly ash extracts by ion chromatography-inductively coupled plasma mass spectrometry. J. Anal. Atom. Spectrom. 13: 1107-1112.

Jankowski J, Ward CR, French D, Groves S. 2006. Mobility of trace elements from selected Australian fly ashes and its potential impact on aquatic ecosystems. Fuel. 85: 243 – 256.

Kazi TG, Jamali MK, Arain MB, Afridi HI. 2000. Evaluation of an ultrasonic acid digestion procedure for total heavy metals determination in environmental and biological samples. Journal of Hazardous Materials. 161: 1391-1398.

Patra M, Bhowmik N, Bandopadheyay B, Sharma A. 2004. Comparison of mercury, lead and arsenic with respect to genotoxic effects on plant systems and the development of genetic tolerance. Environ. Experimental. Bot. 52: 199 – 223.

Price WA, Morin K, Hutt N. 1997. Guidelines for the prediction of acid rock drainage and metal leaching for mines leaching in British Columbia: Part II. Recommended procedures for static and kinetic testing. Fourth International Conference on Acid Rock Drainage. Vancouver, B.C. Canada. May 31 – June 6, 1997.

Wadge A, Hutton M. 1987. The leachability and chemical speciation of selected trace elements in fly ash from coal combustion and refuse incineration. Environ. Pollution. 48: 85-99.