Characterisation of cyanide in gold-mine tailings of the Witwatersrand

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Abstract

The use of cyanide in gold extraction has resulted in the persistence of this pollutant in the tailings and water systems in the Witwatersrand Goldfields.

This study presents results of the study of distribution and speciation of cyanide in a representative gold tailings dump. Cyanide and its metal complexes were found to be unstable following generation of AMD in the dump over a period of one year, resulting in the formation of thiocyanates and cyanates.

Key words: cyanide, thiocyanates, acid mine drainage, Witwatersrand

Introduction

The disturbance and exposure of the mine waste dumps to weathering elements provide a potential source of pollution mainly in the form of acid mine drainage (AMD). Heavy metals and other pollutants including cyanides tend to be leached to surface and ground water systems.

Cyanides in gold effluent can be classified into four categories: (i) free cyanide (HCN, CN^-); (ii) readily soluble (e.g. NaCN, KCN, $Ca(CN)_2$; (iii) weak acid dissociable cyanides (CN_{WAD}) which are relatively unstable complexes composed of cyanide and transition metals (including Cd, Cu, Ni and Zn) and which dissociate under neutral or mildly acidic conditions; and (iv) strong acid dissociable cyanide (CN_{SAD}) strong complexes with metals such as Fe, Co, Ag, and Au that are dissociable under extreme acidic conditions (Meeussen *et al.*, 1992; Zagury *et al.*, 2003).

The mobility of soluble cyanide species in soil is governed by precipitation-dissolution, as well as adsorption-desorption reactions with the soil matrix. Biodegradation reactions and changes in solution chemistry will also influence cyanide speciation and hence transport.

In this study, cyanide in a gold tailings dump in Johannesburg was characterised as free, CN_{WAD}, CN_{SAD} and CN_T. Deposition of waste slurry has been discontinued and the dump is being prepared for phytoremediation. As such, the dump presents a suitable case in studying the chemical evolution of cyanide and its complexes over a period of time.

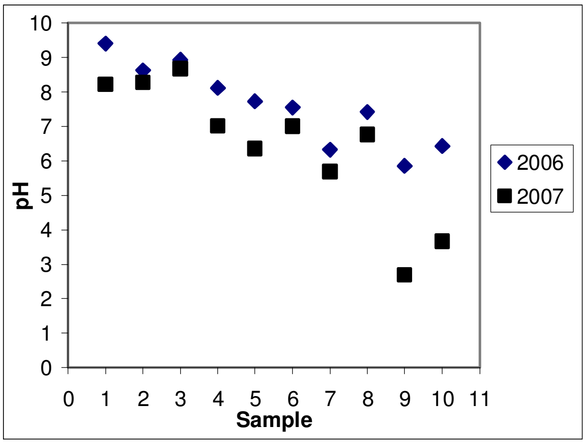
Methods

Samples were collected along a transect in the dump at depths of 0-20 cm and 20-40 cm at each drill core using an auger. A water sample and sediment sample were collected from the central pond. Sampling was done in December 2006 (summer) and in July 2007 (winter). The field parameters, namely pH, redox potential (Eh), electrical conductivity (EC) and temperature were measured in the samples. The samples were placed in polypropylene containers and stored in the refrigerator at 4^oC prior to preparation and analysis. The cyanide and cyanide complexes were analysed according to standard methods (Clesceri *et al.*, 1989).

Results and discussion

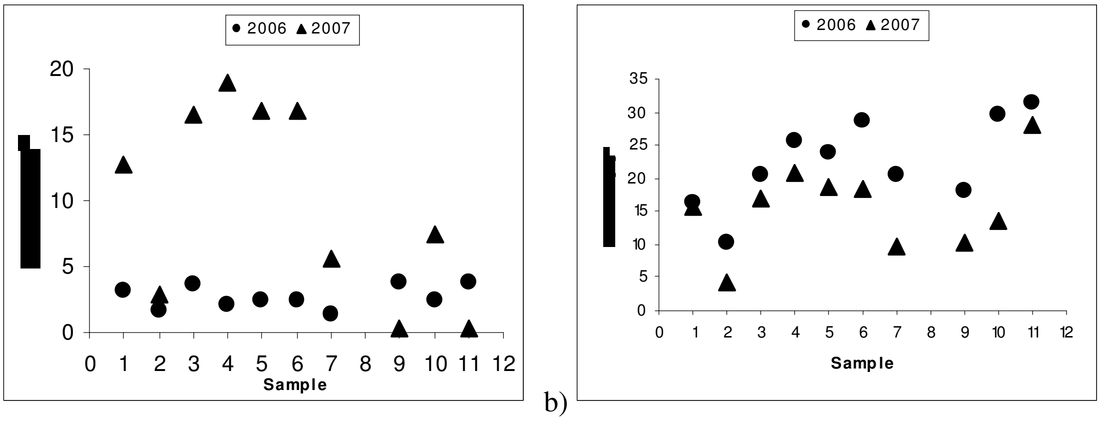
The pH values for the two sampling periods (2006 and 2007) are presented in Fig. 1. The samples were collected along a transect (from 1, close to the pond to 11, close to the edge of the dump). The trend shows a decrease in pH within the year. This could be attributed to the generation of AMD which is accelerated by the discontinuation of disposal of fresh tailings (of higher pH). The results for the concentrations of cyanide species according to the sampling period are shown in Figure 2. The trend generally shows an increase in CN_{free} concentrations for samples close to the pond for 2007. Samples farther from the pond displayed lower CN_{free} concentrations. This could be due to release of CN_{free} from CN_{WAD} as pH values decrease. Further decrease in pH (as in samples towards the edge of the dump) may be causing CN_{free} loss as the volatile HCN.

***Figure 1** pH values of the tailings for 2006 and 2007*



Total cyanides are higher for the 2006 samples, leading to a corresponding trend being observed for CN_{WAD} and CN_{SAD}. This could be attributed to that during deposition of tailings pH values are high and cyanide complexes are stable. As pH decreases, the complexes begin to dissociate releasing CN_{free}. Thiocyanate (SCN) concentrations (Fig. 2e) are observed to be higher in 2007 than 2006. This observation is consistent with that by Plumlee *et al.* (1995) that relatively high concentrations of thiocyanate may persist in the presence of acidic solutions. This could be due to the interaction of CN_{free} with sulphates, both of which are released with a decrease in pH of the tailings. CN_{free} reacts with forms of sulfur in mining effluents, such as sulfur, sulphates, thiosulfates, or sulfide ions, to produce thiocyanates, SCN^- (Gagnon *et al.*, 2004). Thiocyanate also combines with metals to form metal-thiocyanate complexes. Cyanate (CNO^-) concentrations do not seem to differ significantly in the two periods. This could be due to exposure to exposure of CN^- to similar oxidation conditions (largely atmospheric oxygen).

***Figure 2** (a) CN_{free}; (b) CN_{WAD}; (c) CN_{SAD}; (d) CN_T; (e) SCN and (f) CNO^- in tailings collected in 2006 and 2007*



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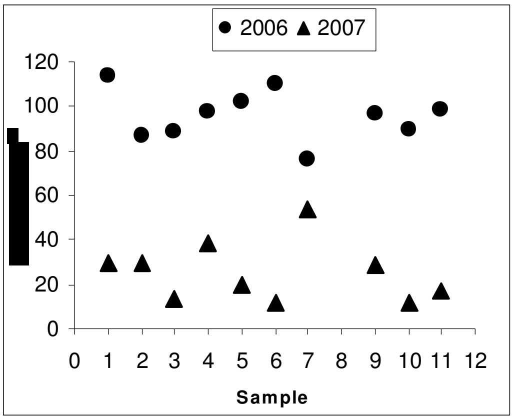

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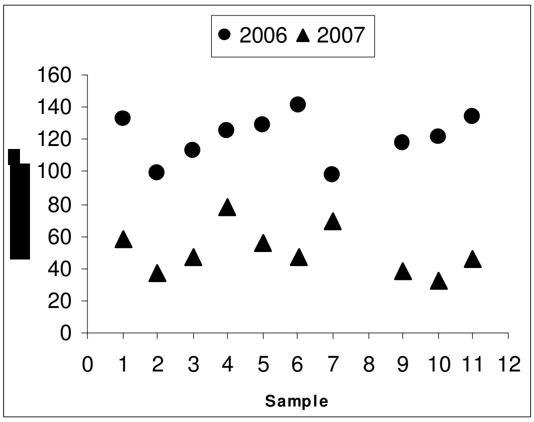

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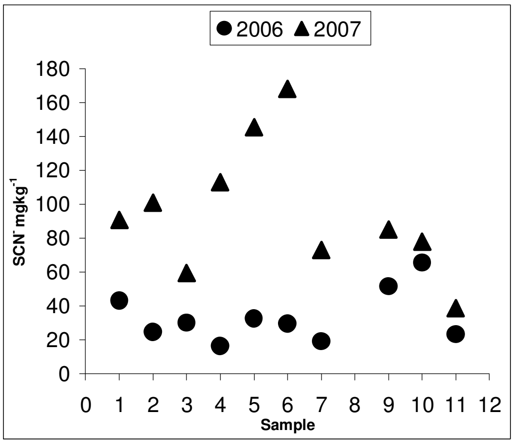

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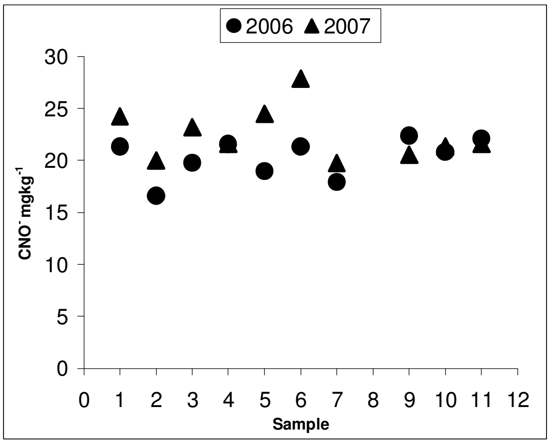

f)

Conclusion

Characterisation of cyanide in a tailings dump has revealed that on contact with AMD, cyanide evolves to form other cyano-species including thiocyanate and cyanate. The stability of cyanide complexes such as CN_{WAD} and CN_{SAD} depends strongly on the extent of acid generation. Acid generation was observed to be high towards the edge of the dump and decreasing towards the central pond.

Acknowledgements

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