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Cyanide and cyanide complexes in the goldmine polluted land in the East and Central Rand Goldfields, South Africa

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DECLARATION

I declare that this dissertation is my own, unaided work. It is being submitted for the Degree of Master of Science in the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination in any other University.

_____

Signature of Candidate

This----------Day of----------2009

ABSTRACT

The use of cyanide in gold extraction is of concern when it is not properly managed from the extraction process to the management of wastes. The distribution and fate of cyanide in the environment upon release from the tailings dumps depends on its physical-chemical speciation.

This study presents results of distribution, speciation and fate of cyanide in selected compartments, namely: tailings, sediments and water systems in gold mine polluted land.

Sampling of tailings in a facility that is being rehabilitated was done in 2006 and 2007 to assess the impact of AMD on cyanide release over that period. Deposition of materials in the tailings dams stopped in 2004. The results revealed that the pH of the tailings decreased between 2006 and 2007. Elevated concentrations of CN_{free}, SCN^- and CNO^- were observed for 2007 compared to 2006. Most cyanide species had degraded as a result, primarily, of decrease in pH due to generation of AMD, also the oxidation of CN_{free} and the reaction with active sulphur species such as S_2O_3.

The decrease of cyanide total (CN_T) with time is a consequence of natural attenuation of cyanides in tailings which may be attributed to physical-chemical and microbiological mechanisms.

Cyanide and its metal complexes were found to be unstable following generation of AMD in the dump over a period of one year. The dissociation of metal-cyanide complexes when the pH drops, releases CN_{free} which is either volatilised as HCN(g) or transported in solution with the contamination plume or converted to SCN^- ,CNO^- and NH_4^+.

However, in most of cases high concentrations of metal-cyanide complexes were found even at low pH values of the tailings suggesting that these complexes are very stable. This was substantiated by the geochemical modelling which predicted the predominance of iron-cyanide complexes in tailings at low pH.

Cyanide released from cyanide complexes flows into the central pond of the tailings facility and partly leaches into the groundwater.

Salt crusts were observed along the capillary fringe of the central pond as well as around other water bodies considered in the study. These crusts were found to contain elevated concentrations of heavy metals (e.g. 12940 mg kg^{-1} Fe and 186.1 mg kg^{-1} Co) and cyanide (e.g. 118.4 mg kg^{-1} CN_T, 14.36 mg kg^{-1} CN_{WAD} and 100.2 mg kg^{-1} CN_{SAD}). This obviously has implications of secondary pollution as these crusts tend to be very soluble in water thus leading to the release of heavy metals and cyanide into water systems during rainfall.

Characterization of cyanide was also done in drainage water from an active slimes dam where deposition from a reprocessing plant takes place. The slimes dam had drainage pipes and a solution trench around it that drained away excess water. Low concentration of CN_T was obtained in pipe water from the pipe with low pH values (2 - 4) whilst this concentration was high in water from the trench with high pH values (5 -7). Copper and iron complexes were the most abundant. High concentrations of SCN^- and CNO^- were obtained as result of conversion of CN_{free} as explained previously.

Salt crusts collected around the dam presented low pH (3) and high conductivity, the evidence of high metals content. High concentrations (198.4 mg kg^{-1}) of CN_T were obtained in the crusts with predominance of CN_{SAD} (Fe and Co). The bluish-green colour of the crusts and the elevated concentrations of CN_{SAD} as well as those for iron could suggest the presence of Prussian blue.

Analysis of the wetland sediments showed the transport of cyanide from the tailings dumps to the wetland through the streams.

An enrichment of cyanide was observed in the sediment with the enrichment factor of 3 for CN_T with predominance of strong complexes (Fe and Co). The sediment is rich in organic matter and cyanide is known to bind strongly with organic matter. Although other possible sources (e.g. bacterial or microbial sources) could have contributed to the enrichment of cyanide in sediment, this was not investigated.

Cyanide can be transported from the tailings dams to natural streams and other surface water bodies through groundwater. A natural stream within a reprocessing area was considered as a water system and cyanide in it was characterised. Three clusters were observed: water collected upstream with high pH, water from downstream with low pH (4) and the groundwater with low pH (3). Low concentrations of CN_{free} were obtained downstream. This could be due by the lost of CN_{free} by volatilization due acidic pH conditions. CN_T was found to be lower downstream than upstream with the predominance of CN_{WAD}. CN_T concentrations were high at the seepage point, where the groundwater discharges to the surface. These concentrations were similar to those obtained in the groundwater.

Copper and iron complexes were dominant in the surface and groundwater and this was substantiated by modelling results as well.

SCN^- was not detected in surface water as it is highly soluble in water and then leaches in the groundwater. The concentrations of CNO^- were the same up and downstream.

The results obtained from the study revealed that concentration of CN_{free} in most water bodies exceeded stipulated limits by bodies such as WHO, USEPA and UE. For instance, concentrations of up to 0.304 mg l^{-1} of CN_{free} were obtained in some instances to compare with limits of 0.07 mg l^{-1} by WHO, 0.02 mg l^{-1} by DWAF/South Africa.

Additional studies should be done to find out the impact of organic matter (e.g. humic and fulvic acids) on the fate of cyanide. Various natural attenuation mechanisms of cyanide in tailings dams should be investigated. An assessment of the phytoremediation program vis-à-vis cyanide cyclisation is recommended and a monitoring of groundwater (borehole water) quality is required.

DEDICATION

To Mado Bakatula, my twin sister and Prof. Fidele Lungungu, my mentor, I cannot express in words how grateful I am for having you in life.

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ABBREVIATIONS

CN_{free} Cyanide free

CN_{WAD} Cyanide weak acid dissociable

CN_{SAD} Cyanide strong acid dissociable

CN_{T} Cyanide total

AMD Acid mine drainage

ISE Ion selective electrode

CEC Cation exchange capacity

TSF Tailings storage facility

ppm Part per million

ORP Oxidation-reduction potential

Eh Redox potential

Ec Electrical conductivity

IUPAC International Union of Pure and Applied Chemistry

UNEP United Nations Environment Programme

USGS United States Geological Survey

AMIRA Australian Mineral Industries Research Association

ICMI International Cyanide Management Institute

UNEP United Nations Environment Programme

WHO World Heath Organisation

DWAF Department of Water Affairs and Forestry/ South Africa