A Model of the Behaviour of Cyanide in a Witwatersrand Sulfidic Au-tailings Environment

Megan Welman-Purchase

Department of Geology, University of the Free State, Bloemfontein, 9301, South Africa, purchasemd@ufs.ac.za

Abstract

Cyanide is one of the main chemicals used in the extraction of Au in mining. It is vital that the cyanide behaviour in tailings dam environments is understood as the speciation controls the release of and persistence in the natural environment. This study has direct consequences for the evaluation of environmental risk when planning new Au-mining operations. In addition, this investigation delves into a possible scenario for the behaviour of cyanide, namely Prussian/Turnbull's blue, which are believed to be stable compounds, which is also reiterated in the modelling produced in this study and may be a solution to environmental contamination.

Keywords: Cyanide speciation, Acid mine drainage, Geochemical modelling

Introduction

Cyanide in the environment can be of either natural or anthropogenic sources (Anning et al. 2019). Natural sources include plants in the form of cyanogenic glycoside (for example almonds) and large quantities from anthropogenic sources include mining, electroplating, vehicle exhaust fumes, sewage, fires (Jaszczak et al. 2017). In the mining environment, cyanide (as NaCN/KCN) is the main compound used in the extraction of Au, which, according to Johnson (2015), is preferred in >90% of mines worldwide. The reaction that occurs in the cyanidation process is known as the Elsner process (Kyle 1997):

$$4Au+8NaCN+O_2+H_2O \rightarrow 4[NaAu(CN)]_2+NaOH \quad (1)$$

$$4Au+8KCN+O_2+H_2O \rightarrow 4[KAu(CN)]_2+KOH \quad (2)$$

The Au compounds produced in equation (1) and (2) are then further processed in the Carbon In Leach (CIL) and Merrill Crowe methods (Acheampong et al. 2010). Even though cyanide is used in low concentrations, as little as 0.5 g.L^{-1} (Rademan and Groot 2012) and the "Best Practice" restriction of cyanide in tailings dams is 0.5 mg.L^{-1} (Bakatula and Tutu 2016), there is a potential for cyanide to leach into the natural environment. Anning et al. (2019) reiterates this by stating that a large percentage of cyanide used in the Au extraction process remains in solution in slurries after the completion of this cyanidation process.

Cyanide can be lethal, especially to aquatic life, yet this is all dependent on the chemical species in which the cyanide occurs. These different species are divided into the following categories: free cyanide (HCN), soluble cyanide (KCN, NaCN), CN_{WAD} (weak acid dissociable cyanide – containing Ni, Zn, Cd, and Cu) and CN_{SAD} (strong acid dissociable cyanide – containing Fe, Co, Ag, and Au) (Zagury et al. 2004). Free cyanide is the most lethal and occurs as a volatile substance, where CN_{WAD} and CN_{SAD} may possibly form free cyanide as they dissociate, where CN_{WAD} dissociates at pH of neutral to slightly acid conditions and CN_{SAD} only dissociates in low pH environments (Zagury et al. 2004).

When cyanide reacts with Fe, stable octahedral aqueous complexes (hexacyanoferrates) form and this includes ferrocyanide$[Fe^{2+}(CN)_6]^{4-}$ and ferri-cyanide $[Fe^{3+}(CN)_6]^{3-}$ (Jambor et al. 2009). When these two compounds further react with Fe^{2+} and Fe^{3+} cations the following compounds may form: Prussian blue $Fe_4[Fe(CN)_6]_3$, Turnbull's blue $Fe_3[Fe(CN)_6]_2$, Prussian brown/green $Fe_2(CN)_6$ and Berlin white $Fe_3(CN)_6$ (Ghosh et al. 1999). Berlin white is only stable in anoxic environments and converts to Prussian blue in oxic environments (Ghosh et al. 1999). Fe-CN compounds are CN$_{SAD}$ compounds and are considered to be among the most stable (Kyle 1997).

This investigation uses PHREEQC, a geochemical modelling software package developed by the USGS, modelling to investigate the possible chemical behaviour and compound formation of cyanide in a gold mine tailings environment, with special reference to Fe-CN compounds, specifically Prussian and Turnbull's blue.

Geological setting

The Witwatersrand was discovered in 1886 in South Africa by George Harrison, who discovered the Au in quartz-pebble conglomerates that outcropped for 45 km (McCarthy 2006). Between 1886 and the 1940s, using drilling and geophysical methods, the Central Rand, East Rand, West Rand, Carletonville and Welkom/Free State goldfields were discovered and developed (McCarthy 2006). These can be viewed in figure 1. This study investigates the tailings of the Free State gold mines where, according to Tucker et al. (2016), the Dreyerskuil, EA, Beatrix, VS5, Basal, Steyn, and Beisa reefs of the Central Rand group are mostly mined. The Beisa reef consists a conglomerate layer that varies from 5 to 150 cm in thickness, the Basal and Steyn are two separate conglomerate layers differing in clast assemblage, the Beatrix is a conglomerate on a disconformity and the VS5 is a conglomerate layer that is sporadically mineralized (McCarthy 2006).

There are currently 5 Au producing mines (Department of Mineral Resources, 2017) of the total of ≈ 17 gold mines (McCarthy 2006) in the Free State goldfields. According to McCarthy (2006) the mines of the Free State goldfields have produced over 7900 t of gold. For arguments sake, if the gold grade of the rocks that were mined for this mentioned gold was 5 g.t^{-1}, then 1580 Mt of waste is produces and discarded of on tailing dams.

Methodology

The modelling in the project used PHREEQC which is a United States Geological Survey project developed by Parkhurst and Appelo (2013). The thermodynamic data of Prussian

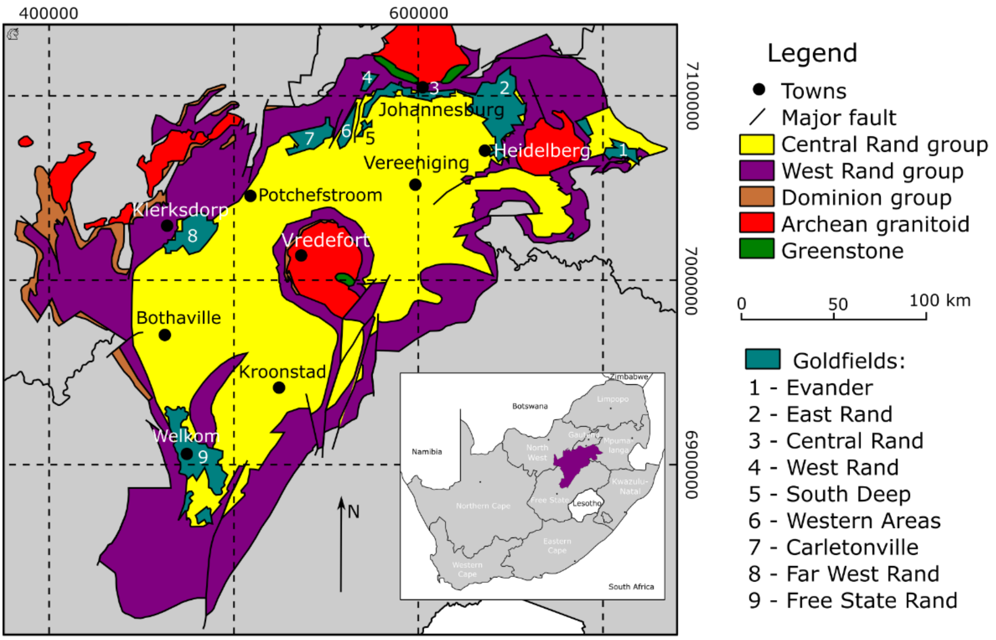

Figure 1 *Map of the Witwatersrand basin displaying the position of the current goldfields in South Africa (Modified after Hansen, 2018 and Frimmel et al., 2005).*

Table 1 QEMSCAN data of a tailings dam in the Free State goldfields (FS01) and a near monomineralic pyrite commercial sample.

Mineral	FS01 *wt%*	Pyrite *wt%*
Quartz	78,61	7,23
Pyrophyllite	7,24	
Mica	6,97	30,19
Chlorite	1,21	
Plagioclase	0,84	
Chloritoid	1,07	
Amphibole	0,21	
Pyroxene/ Olivine	0,43	
Zircon	0,10	
Other silicates	0,19	3,61
Pyrite	2,18	58,97
Other sulfides	0,03	
Fe-oxides	0,26	
Rutile/ Ilmenite	0,19	
Other oxides	0,01	
Dolomite	0,02	
Calcite	0,25	
Ankerite	0,00	
Apatite	0,02	
Alunite	0,05	
Gypsum	0,12	
Total	**100,0**	**100,00**

blue, Prussian brown/green and Turnbull's blue was added to the database of PHREEQC and the values were taken from Wagman et al. (1982). Berlin white was not investigated as it is out of the scope of this study.

The mineralogy used for the speciation model, is Quantitative Evaluation of Minerals by Scanning Electron Microscope (QEMSCAN) data of a tailing sample from one of the dumps of the Free State goldfields, see table 1. The second speciation model was completed using the mineralogy (semi-quantitative results) obtained using X-Ray Diffractometry (XRD) of a natural pyrite sample. The XRD is a Panalytical–Empyrean with a copper side window tube and an X Celerator detector. The geometry of the XRD is Bragg-Brentano and samples are scanned between 3.5° and 70° 2θ at tube settings of 45 kV and 40 mA. The concentration of cyanide added to the speciation models is 0.5 g.L1 after Rademan and Groot (2012). The parameters used for the pH vs pe modelling are as such: cyanide concentration of 0.6 mM was and the Fe content of 0.2327 mM, not in excess, was taken from Ghosh et al. (1999). K (0.4 mM) and NaCl (0.06 mM) are added according to Ghosh et al. (1999) as charge balances.

Results

Prussian/Turnbull's blue did not initially precipitate in the speciation models for both the tailings sample and a pyrite sample at surface conditions. Although a blue substance formed in empirical results (which will be report on in further studies). This led to the investigation into the log K values of Prussian and Turnbull's blue. On altering the log K values, the species formed can be seen in table 2 below, which includes Prussian and Turnbull's blue.

The same log K values were then used to create a pH vs pe diagram, displayed in figure 2 (A). This then led to the investigation of the oxygen fugacity and the effects that O^2 has on the production of ferric and ferrous iron and this effect on the compounds formed. The model can be seen in figure 2 (B).

Discussion

The Fe cation of the hexacyanoferrates determines if the Fe-CN compound is Prussian or Turnbull's blue followed by the Fe cation within this crystallographic structure. Thus, the formation of either of the compounds is dependent on the availability of Fe^{2+} or Fe^{3+} cations in solutions. The FS01 sample mostly consists of silicate minerals and forms Prussian blue and not Turnbull's blue. Contrarily the pyrite sample produces both Fe-CN compounds in the model. A possibility for this is the presence of goethite, hematite and jarosite potentially forming in the model of FS01, which establishes an Fe^{3+} deficient environment. These minerals do not appear in the model of the pyrite sample.

The pH vs pe diagram is similar to the diagram found in Ghosh et al. (1999)

***Table 2** The results of the species models of the tailings dam sample – FS01 and the pyrite sample.*

Minerals	Minerals Chemistry	FS01	Pyrite
Alunite	$KAl_3(OH)_6(SO_4)_2$		x
Anatase	TiO_2	x	
Boehmite	AlO(OH)		x
$CaZrO_3$	$CaZrO_3$	x	
CO_2 (g)	CO_2 (g)	x	
Diaspore	AlO(OH)		x
Goethite	$Fe^{3+}O(OH)$	x	
Hematite	Fe_2O_3	x	
Jarosite	$KFe_3(SO_4)_2(OH)_6$	x	
Jarosite – Na	$NaFe_3(SO_4)_2(OH)_6$	x	
Kaolinite	$Al_2Si_2O_5(OH)_4$		x
Melanterite	$FeSO_4.7H_2O$		x
Nontronite - Ca	$Ca_{0.165}Fe_2Al_{0.33}Si_{3.67}O_{10}(OH)_2.nH_2O$	x	
Nontronite – H	$H_{0.33}Fe_2Al_{0.33}Si_{3.67}O_{10}(OH)_2.nH_2O$	x	
Nontronite – K	$K_{0.33}Fe_2Al_{0.33}Si_{3.67}O_{10}(OH)_2.nH_2O$	x	
Nontronite - Mg	$Mg_{0.165}Fe_2Al_{0.33}Si_{3.67}O_{10}(OH)_2.nH_2O$	x	
Nontronite - Na	$Na_{0.33}Fe_2Al_{0.33}Si_{3.67}O_{10}(OH)_2.nH_2O$	x	
Prussian blue	$Fe_4[Fe(CN)_6]_3$	x	x
Rutile	TiO_2	x	
Turnbull's blue	$Fe_3[Fe(CN)_6]_2$		x

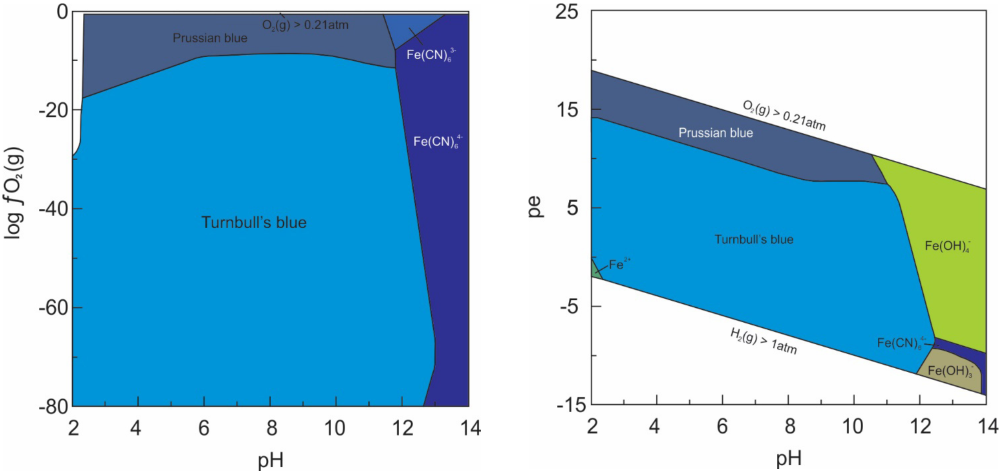

***Figure 2** (A) pH vs pe diagram using the following parameters: cyanide concentration – 0.6 mM, Fe content – 0.2327 mM, K – 0.4 mM and NaCl – 0.06 mM. (B) A pH vs oxygen fugacity diagram of Prussian and Turnbull's blue.*

which was completed using MINEQL+. The diagram in Ghosh et al. (1999) differs in the compounds outside of Prussian and Turnbull's blue compared to figure 2 (A). According to figure 2 (A), Prussian blue is stable between pH ≈ 2 – 11 and pe ≈ 7 – 19. Turnbull's blue is stable (fig. 2A) at pH ≈ 2 – 12.5 and pe ≈ -12 – 15. This is reiterated by Zagury et al. (2004), who suggests that the CNSAD compounds dissociate at low pH levels. In Au mine practices, acid mine drainage is a universal issue and thus should be accounted for and rehabilitated increasing the pH of the tailings dams and thus preserving the stability of the Prussian and/or Turnbull's blue that may form.

During the oxygen fugacity investigation, it was determined that Prussian blue is produced in more oxidizing environments and Turnbull's blue is produced in more reducing conditions. This may be due to the formation of goethite in oxidizing environments.

Conclusions

Cyanide still remains the chemical used to extract Au, even though other options are available. Possibly due to cost effectiveness and the small quantities required for Au extraction. Which reiterates a requirement for studies into the geochemistry and behaviour of cyanide species in the tailings dam environment. This study shows that it is possible for Prussian blue to form and, with an increase in pyrite, Turnbull's blue will form additionally. The stability of these two compounds is a pH from ≈ 2 – 12.5, where dissolution occurs below this and iron-hydroxides form above this area. They also form in both oxidizing and reducing conditions. According to these models, these compounds seems to be great candidates to prevent the release of cyanide into the natural environment. Although further studies are needed, including the altering of cyanide concentration in the modelling and the dissociation of Prussian and Turnbull's blue under UV radiation.

Acknowledgements

The author would like to thank Dr. Robert Hansen for his time, efforts and constant support and Ipakade for their financial support.

References

Acheampong MA, Meulepas RJW, Lens PNL (2010) Removal of heavy-metals and cyanide from gold mine wastewater. J. Chem. Technol. Biotechnol. 85:590–613

Anning C, Wang J, Chen P, Batmunkh I, Lyu X (2019) Determination and detoxification of cyanide in gold mine tailings: A review, Waste Manag. Res. SAGE 37(11):1117-1126.

Bakatula EN, Tutu H (2016) Characterization and speciation modelling of cyanide in effluent from an active slime dam. S. Afr. J. Chem. 69:140-147

Department of Mineral Resources, South Africa (2017) http://www.dmr.gov.za/mineral-policy-promotion/operating-mines/free-state?search=gold – accessed 06 July 2020

Frimmel HE, Groves DI, Kirk J, Ruiz J, Chelsey J, Minter WEL (2005) The Formation and Preservation of the Witwatersrand Goldfields, the World's Largest Gold Province. Econ. Geol. 100th Anniv. Vol. 769–797

Ghosh RS, Dzombak DA, Luthy RG (1999) Equilibrium precipitation and dissolution of iron cyanide solids in water. Environ. Eng. Sci. 16(4):293-313

Hansen RN (2018) Inter-comparison geochemical modelling approaches and implications for environmental risk assessments: A Witwatersrand gold tailings source term characterisation study. Appl. Geochem. Elsevier 95:71-84

Jambor JL, Martin AJ, Gerits (2009) The post-depositional accumulation of metal-rich cyanide phases in submerged tailings deposits. Appl. Geochem. 24:2256-2265

Jaszczak E, Polkowska Z, Narkowicz S, Namieśnik J (2017) Cyanide in the environment – analysis – problems and challenges. Environ. Sci. Pollut. Res. Springer 24:15929-15948

Johnson CA (2015) The fate of cyanide in leach wastes at gold mines: An environmental perspective. Appl. Geochem. Elsevier. 57: 194-205

Kyle JH (1997) Stability of metal-cyanide and hydroxide complexes. World Gold '97 Conference 163-169

McCarthy TS (2006) The Witwatersrand supergroup. In: Johnson MG, Anhaeusser CR and Thomas RJ (Eds.), The Geology of South Africa. Geol. Soc. S. Afr. Johannesburg/Counc. Geosci. PTA. pp 155-186

Parkhurst DL, Appelo CAJ (2013) Description of Input Examples for PHREEQC Version 3 – a Computer Program for Speciation, Batch-reaction, One-dimensional Transport, and Inverse Geochemical Calculations. book 6, chapter A43. US Geological Survey Techniques and Methods 497. available only at. http://pubs.usgs.goc/tm/06/a43/

Rademan L, Groot DR (2012) Cyanidation of reef and surface gold ores. J. S. Afr. Inst. Min. Metall. 112:295-300

Tucker RF, Viljoen RP, Viljoen MJ (2016) A review of the Witwatersrand basin -the world's greatest goldfield. Epis. 39(2):105–133

Wagman DD, Evans WH, Parker VB, Schumm RH, Halow I, Bailey SM, Churney KL, Nuttall RL (1982) The NBS Tables of Chemical Thermodynamic Properties. J. Phys. Chem. Ref. Data, v.11, Suppl. 2

Zagury GJ, Oudjehani K, Deschênes L (2004) Characterization and availability of cyanide in solid mine tailings from gold extraction plants. Sci. Total. Environ. Elsevier 320:211-224