

Modelling the Behaviour of Ferric and Ferrous Iron in a Goldmine Tailings Environment, Free State – South Africa

Megan Welman-Purchase¹, Robert Hansen²

¹Geology Department, University of the Free State, 205 Nelson Mandela drive, Bloemfontein, 9300, South Africa, purchasemd@ufs.ac.za

²Centre for Mineral Biogeochemistry (CMBG), University of the Free State, 205 Nelson Mandela drive, Bloemfontein, 9300, South Africa

Abstract

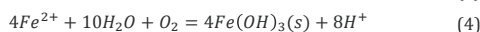
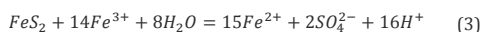
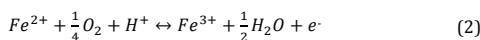
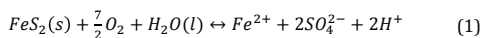
Cyanide has a high affinity for gold and other metals (including iron) attributing to its usage in the goldmine extraction process. After the extraction process, waste material is disposed of onto tailings facilities, where cyanide has previously been found. This study delves into the modelling of the behaviour of iron in a tailings system and the effect that cyanide and iron-cyanide compounds/complexes have on this. Results of this study revealed that jarosite and goethite/ferrihydrate affect the formation of Prussian blue but requires Fe²⁺ in the system to form.

Keywords: Cyanide, ferric/ferrous iron, prussian blue, goethite/ferrihydrate, jarosite

Introduction

Cyanide, that is still widely used worldwide in the gold extraction process, has a high affinity for metals (such as iron and gold) (Bakatula and Tutu 2016, Wang and Forsberg 1990, Zagury *et al.* 2004). A portion of this cyanide is believed to be expelled of onto tailings dams, where iron and aluminium are among the most copious metal cations existing in acid mine drainage (AMD) (Sánchez-España *et al.* 2005).

Iron in this environment, originates from the oxidation of pyrite, according to the equation 1 (Williamson and Rimstidt 1994). In environments where the pH is less than 3, the Fe²⁺ product from equation 1, is further oxidised to Fe³⁺ in equation 2 (Stumm and Lee 1961, Jones *et al.* 2014). Above pH 3, iron- hydroxide minerals form. As the concentration of Fe³⁺ increases, the oxidation of pyrite is further enhanced according to the equation 3 (Williamson and Rimstidt 1994). Contrarily, if the pH of the system is greater than 3, hydroxide minerals form (equation 4) (Jones *et al.* 2014):



Ferrous iron (Fe²⁺) is more soluble than ferric iron (Fe³⁺), remaining in solution at a pH <8, whereas Fe³⁺, seen in the reaction 4, precipitates as a variety of ocherous minerals (pH >3) (Sánchez-España 2007). The distribution of the precipitation of iron species is thus pH dependent. In the environment discussed in this study, not only iron is present but also SO₄²⁻ ions, which strongly affects the complexation of iron (Sánchez-España *et al.* 2005). Thus, the ocherous minerals include jarosite (KFe₃(SO₄)₂(OH)₆ - forms at a pH of ~ 2), schwertmannite (Fe₈O₈(OH)₆.nH₂O - forms at a pH of ~ 2.5-4) and ferrihydrate (Fe(OH)₃ - forms at a pH of > 5). According to Villacís-García *et al.* (2015), goethite forms from an increase in temperature and aging of ferrihydrate.

These matters have been studied, whereas this research focuses on iron and the mineralization of iron-cyanide compounds/complexes and the effect that ocherous minerals mineralization in the goldmine tailings dams have on the formation of iron-cyanide compounds. Specifically on Prussian blue – Fe₄[Fe(CN)₆]₃ and Turnbull's blue – Fe₃[Fe(CN)₆]₂ (Ghosh *et al.* 1999) and possible compounds associated with them.

Geological setting

A large percentage of South Africa's gold is extracted from the Witwatersrand supergroup, which has generated approximately a third of the world's gold to date (Tucker *et al.* 2016). This supergroup comprises successions of sedimentary deposits within the Witwatersrand basin which extends from the north of Johannesburg to south of Welkom (Tucker *et al.* 2016). The goldfields of the Witwatersrand supergroups are the Evander, East Rand, Central Rand, West Rand, South Deep, Western Areas, Carletonville, Far West Rand and Free State Rand goldfields (Frimmel *et al.* 2005). This study involves samples from a tailings dam outside of Welkom in the Free State goldfields.

Post gold extraction, the waste material is discarded on tailings dams, consisting gangue minerals (such as quartz, mica, plagioclase), as well as possible contaminants used in the extraction process (such as cyanide, metals). According to Hansen (2018), the tailings dams display the zones in Figure 1, which are believed to be onion-like, not horizontal. The outer zone is the oxidation zone, adjacent to the transition zone and the core is the reducing zone.

Methods

9 samples were collected from a tailings dam close to Welkom in the Free State goldfields, South Africa. 3 samples were extracted at different depths from 3 different positions on the tailings dams. Samples 1.1 – 2.3 were collected from the top surface of the tailings dam and 3.1 – 3.3 from the side slope. The samples were milled in a carbon steel ring and puck mill, followed by the determination of the loss on ignition (LOI) by weighing

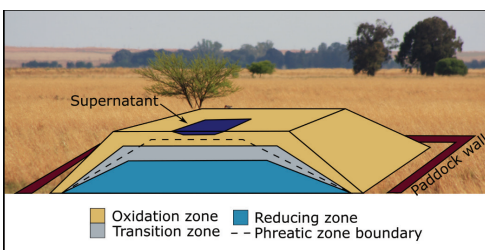


Figure 1 A simplified diagram displaying the geochemical structure of a tailings dam, modified after Hansen (2018).

sample loss after heating a portion of the sample to 950 °C. A fusion disc and pressed pellet (Na₂O only) were produced for each sample to analyse major elements using a Rigaku, Primus IV (4kW generator) X-ray Fluorescence (XRF). Total cyanide of sample 2.1 was determined by X-Lab earth laboratories in Johannesburg. Modelling was completed with PHREEQC, a United States Geological Survey project developed by Parkhurst and Appelo (2013). Parameters used for the modelling were taken from Sánchez-España (2007), where the solution contains 0.1 M of SO₄²⁻ and 0.02 M of Fe³⁺ as a function of pH. In addition to this, the concentration of cyanide found in the tailings sample 2.1 was also added to the solution to model the effects that it may have on the precipitation of other ochreous minerals. Sensitivity analysis was also completed, altering the Fe³⁺, cyanide and oxygen concentrations.

Results

Samples from the tailings dam are fine grained and vary from pale to more orange in colour. This is an indication of the iron present in the samples. A blue staining was found in the sample 2.1, seen in Figure 2, believed to be an iron-cyanide compound. This total sample contained 10 mg.L⁻¹ total cyanide.

The XRF results are displayed in Table 1, where the tailings consist mostly of SiO₂ (85.66 – 88.62 wt%) followed by Al₂O₃ (5.82 – 8.43 wt%). For this study the Fe₂O₃ composition is important, with an average of 2.25 wt%.



Figure 2 Blue staining found on the tailings dam in Welkom, South Africa. This is believed to be an Fe-CN compound and is ~3 cm in length.

Table 1 XRF results of the 9 samples from a tailings dam in the Free State goldfields.

XRF major elements (wt%)	1.1	1.2	1.3	2.1	2.2	2.3	3.1	3.2	3.3
SiO ₂	87.18	87.41	88.62	86.93	86.38	85.66	85.94	85.66	87.46
TiO ₂	0.25	0.28	0.28	0.31	0.35	0.35	0.27	0.26	0.27
Al ₂ O ₃	5.82	6.52	6.39	7.17	7.88	8.43	6.38	6.30	6.40
Fe ₂ O ₃	2.69	1.69	2.27	2.09	2.48	2.54	2.21	2.14	2.15
MgO	1.26	0.40	0.49	0.56	0.41	0.44	0.46	0.44	0.45
MnO	0.02	0.02	0.02	0.04	0.03	0.03	0.02	0.02	0.02
CaO	0.68	0.41	0.41	0.31	0.69	0.43	0.52	0.50	0.51
Na ₂ O	0.28	0.43	0.34	0.54	0.49	0.45	0.31	0.31	0.37
K ₂ O	0.31	0.48	0.52	0.55	0.46	0.52	0.44	0.44	0.43
P ₂ O ₅	0.03	0.02	0.03	0.03	0.03	0.03	0.03	0.02	0.03
LOI	2.01	2.28	2.42	2.53	2.73	2.91	2.44	2.35	2.43
Total	100.53	99.94	101.80	101.05	101.92	101.78	99.02	98.43	100.51

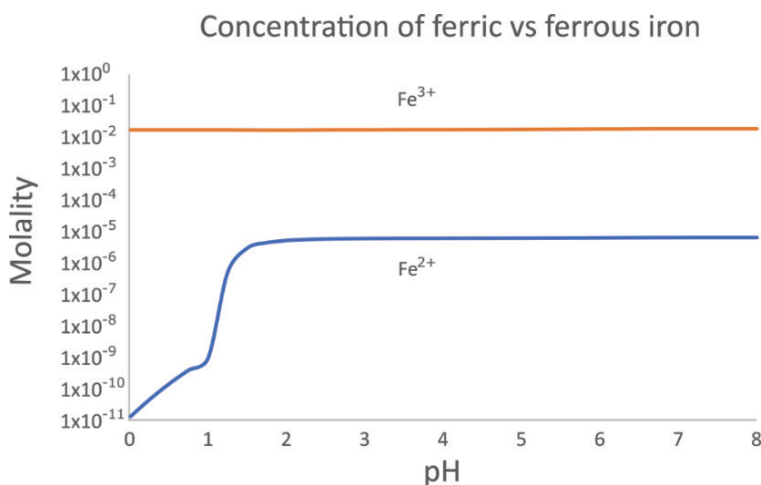
At pH values between 0 and 3, SO₄ compounds form, which correlates with the literature as the conditions where jarosite forms. Above a pH of 3, hydroxide complexes form, where above a pH of 6, ferrihydrite forms. Between a pH of 8 and 14 all compounds decrease to <0.01% and 99.99% of the Fe³⁺ in the modelling produces Fe(OH)₄⁻. Included in Figure 4 is the concentrations of cyanide compounds. This graph reveals that initially HCN is produced, which is consumed as soon as Prussian blue precipitates. At a pH of >4, Turnbull's blue precipitates, consuming a small portion of the production of Prussian blue.

Increasing the Fe³⁺ concentration results in the higher concentrations of the same compounds, exclusive of the concentration

of the iron-cyanide compounds. Contrarily, increasing the cyanide concentration in solution, results in the majority of the formation of Prussian blue. In addition to this, a model was run in a reducing environment, in order to mimic the core of the tailings dam. The only compounds that formed are Turnbull's blue and Fe₂⁺ ions. No ochreous minerals form.

Discussion

The iron-cyanide compounds have previously been found by other authors in tailings samples, namely Bakatula and Tutu (2016) (South Africa – Central Rand goldfields) and Jambor *et al.* (2009) (Balmer lake in Canada - gold mining discharge). These compete for the iron in the system, with minerals such as ferrihydrite and jarosite. All of the

**Figure 3** Modelling results of the oxidation states of iron in solution.

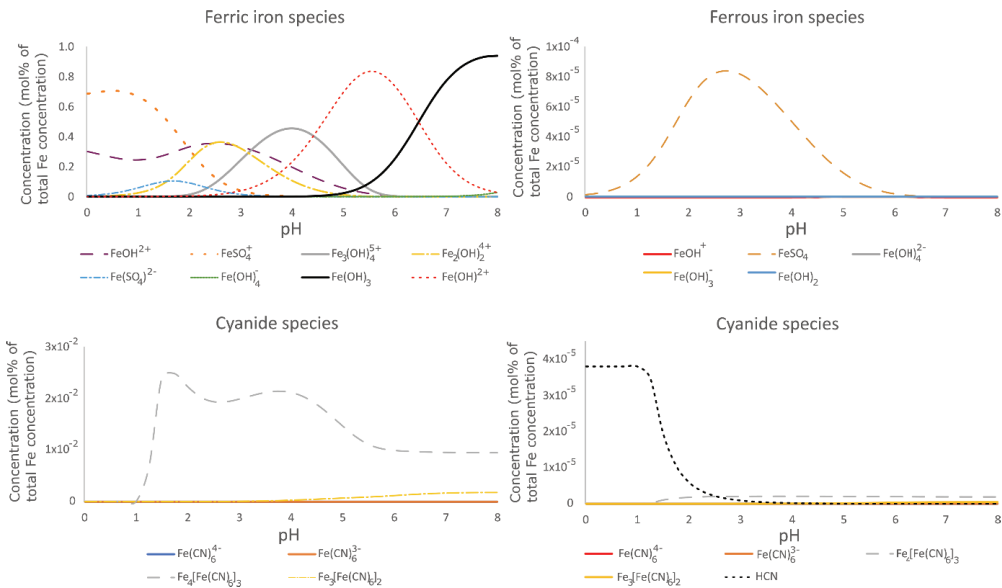


Figure 4 Speciation results of the PHREEQC modelling. 0.02 M ferrous iron, 0.1 M of SO₄²⁻ and 10 mg.L⁻¹ were added to the model in order to compare them to the results in Sánchez-España (2007). Owing to the large discrepancies in the concentration, the results were displayed in separate diagrams.

above-mentioned minerals, including iron-cyanide compounds, require an Fe³⁺ source, additionally Prussian and Turnbull's blue require an Fe²⁺ source. Modelling revealed that the production of jarosite, ferrihydrite and other iron-hydroxide minerals are dependent on the pH and only form in an oxidizing environment. Goethite forms with an increase in temperature or from aging. Comparing these results to the study by Sánchez-España (2007) is displayed in Figure 5, where the largest difference is a shift of all peaks. This may be due to the addition of cyanide or that an additional compound is present in the modelling. Yet further studies will need to be completed to confirm this.

Prussian blue precipitation is dependent

on the presence of both Fe²⁺ and Fe³⁺, and on the redox conditions. The modelling revealed that Prussian blue is the dominant iron-cyanide compound that forms in an oxidizing environment but Turnbull's blue coprecipitates with Prussian blue above a pH of 4. As these compound precipitate, so the concentration of HCN diminishes to 0.04% of the cyanide compounds. In a reducing environment only Turnbull's blue precipitates. Kyle (1997) proposed that producing iron-cyanide compounds could assist in cyanide remediation. Iron-cyanide complexes are CN_{SAD} (strong acid dissociable cyanide compounds) (Zagury *et al.*, 2004), and thus are stable. If these compounds are stable, precipitate spontaneously and prevent

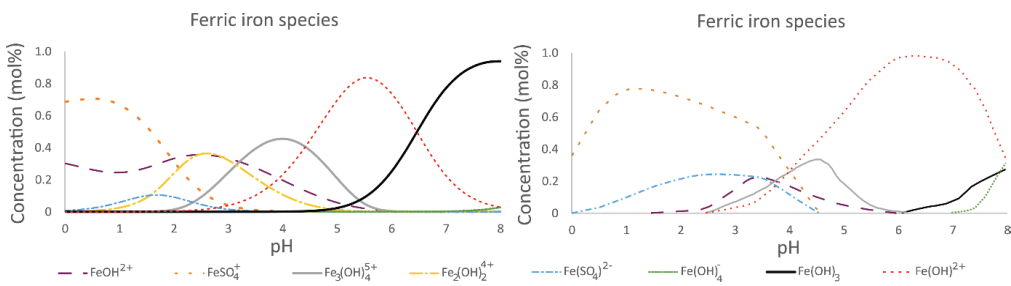


Figure 5 Comparison between the results of this study (left) and the results of Sánchez-España (2007) (right). The results of this study are shifted to the left.

the production of HCN, then they may be a good candidate for remediation.

Conclusions

This study was initiated to understand the behaviour of the different oxidation states of iron, their precipitates and the effect that the addition of cyanide to the system may have using PHREEQC modelling. In order to mimic gold mine tailings environments. It was determined that the precipitation of jarosite, ferrihydrite and other hydroxide minerals, which has been studied previously, is dependent on pH in an oxidizing environment. Fe³⁺ was added to the solution, yet a small portion converts to Fe²⁺, this allows for Prussian blue to form, when the Fe²⁺ concentration decreases as FeSO₄, Fe₂(OH)₂⁴⁺ and Fe(OH)²⁺ form and at a pH higher than 4, Turnbull's blue and Fe(OH)₃ form. Prussian blue also results in the consumption of the cyanide in the system and thus prevents the production of HCN (to less than 0.04%). This study concluded that the precipitation of Prussian blue is affected by the presence of jarosite and goethite/ferrihydrite but requires Fe²⁺ in the system to form.

Acknowledgements

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References

- Bakatula EN and Tutu H (2016) Characterization and speciation modelling of cyanide in effluent from an active slime dam. *S Afr J Chem* 69:140-147
- Frimmel HE, Groves DI, Kirk J, Ruiz J, Chelsey J and Minter WEL (2005) The Formation and Preservation of the Witwatersrand Goldfields, the World's Largest Gold Province. *Econ Geol* 100th Anniversary Volume 769–797
- Ghosh RS, Dzombak DA, Luthy RG and Smith JR (1999) In situ treatment of cyanide-contaminated groundwater by iron cyanide precipitation. *Water Environ Research* 71(6):1272-1228
- Hansen RN (2018) Inter-comparison geochemical modelling approaches and implications for environmental risk assessments: A Witwatersrand gold tailings source term characterisation study. *Applied Geochem*, Elsevier 95:71-84
- Jambor JL, Martin AJ and Gerits (2009) The post-depositional accumulation of metal-rich cyanide phases in submerged tailings deposits. *Applied Geochem* 24:2256-2265
- Jones AM, Griffin PJ, Collins RN and Waite TD (2014) Ferrous iron oxidation under acidic conditions – the effect of ferric oxide surfaces. *Geochim. Cosmochim. Acta* 145, 1–12
- Kyle JH (1997) Stability of metal-cyanide and hydroxide complexes. *World Gold '97 Conference*, 163-169.
- Parkhurst DL and 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, pp. 497, Available only at <http://pubs.usgs.gov/tm/06/a43/>.
- Sánchez-España J (2007) The Behavior of Iron and Aluminum in Acid Mine Drainage: Speciation, Mineralogy, and Environmental Significance. *Thermodynamics, Solubility and Environmental Issues*, Chapter 7
- Sánchez-España J, López Pamo E, Santofimia E, Aduvire O, Reyes J and Baretino D (2005) Acid mine drainage in the Iberian Pyrite Belt (Odiel river watershed, Huelva, SW Spain): Geochemistry, mineralogy and environmental implications. *Applied Geochem* 20(7):1320-1356
- Stumm W and Lee GF (1961) Oxygenation of ferrous iron. *Ind. Eng. Chem.* 53:143–146
- Tucker RF, Viljoen RP and Viljoen MJ (2016) A Review of the Witwatersrand Basin -The World's Greatest Goldfield. *IUGS, Journal of International Geosciences, Episodes* 39(2):105-133
- Villacis-Garcia M, Ugalde-Arztate M, Vaca-Escobar K, Villalobos M, Zanella R and Martínez-Villegas (2015) Laboratory synthesis of goethite and ferrihydrite of controlled particle sizes. *Geológica Mexicana* 67(3):433-446
- Wang X and Forssberg KSE (1990) The chemistry of cyanide-metal complexes in relation to hydrometallurgical processes of precious metals. *Mineral Processing and Extractive Metallurgy Review* 6:81-125
- Williamson MA and Rimstidt JD (1994) The kinetics and electrochemical rate-determining step of aqueous pyrite oxidation. *Geochimica Cosmochimica Acta* 58:5443–5454
- Zagury GJ, Oudjehani K and Deschênes L (2004) Characterization and availability of cyanide in solid mine tailings from gold extraction plants. *Science of the total environ* 320:211-224