

Mineral efflorescent crusts as sources of pollution in gold mining environments in the Witwatersrand Basin

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Abstract Mineral efflorescence crusts on the soil surface are diagnostic of acid mine drainage (AMD). This study highlights the potential impacts of mineral efflorescent crusts on water quality in the Witwatersrand Basin. Characterisation of the crusts has shown that they consist of various sulphate secondary minerals, a fingerprint of the ore composition and local geochemistry. Most crusts have high acidity and contain significantly high metal concentrations. Some of the crusts contain an unusually high concentration of cyanide and its evolution species e.g. thiocyanate, cyanate and ammonium. Geochemical vectors were used to explore the influence of sulphate salts on pH and conductivity.

Key Words acid mine drainage, efflorescent crusts, cyanide, geochemical vectors

Introduction

Efflorescent crusts are minerals that are known to precipitate from ion-rich solutions or brines and have been exposed and dehydrated by the atmosphere. Efflorescent crusts are not unique to AMD as they are also formed by the capillary evaporation of groundwater brines from pans and sabkhas. In mine tailings, the water table below the dumps is usually elevated and feeds ponds where the surface intersects the water table. This phenomenon as well as capillary evaporation leads to the formation of multi-coloured efflorescent crusts (Naicker 2003). These crusts are easily dissolved and are not preserved past the first thunderstorms at the start of the wet season (Sutton 2008).

Remote sensing images taken across the Witwatersrand Basin in 2003 gave a snapshot of the primary minerals and secondary minerals that are characteristic of the mining wastes in this region (Sutton 2008). The most prominent primary minerals identified were pyrophyllite ($\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$), muscovite ($\text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{OH},\text{F})_2$) and pyrite (FeS_2). The combination of these minerals is characteristic of late hydrothermal, greenschist facies metamorphism that occurred within the gold-bearing Central Rand Group (McCarthy 2006). Secondary minerals identified include copiapite ($\text{Fe}^{2+}\text{Fe}^{3+}_4(\text{SO}_4)_6(\text{OH})_2 \cdot 2\text{OH}_2\text{O}$) and jarosite ($\text{KFe}^{3+}(\text{SO}_4)_2(\text{OH})_6$) which are derived from weathering of sulphides.

This study aimed at exploring the pollution potential of efflorescent crusts on receiving waters. Their pollutant load contribution and impact on pH were studied. In most cases, the crusts are dissolved and washed off into streams and wetlands but in other cases they dissolve and the leachates drain into and remain in ponds and puddles. In

these features, continuous dissolution and precipitation of these salt crusts is observed.

Materials and methods

Samples of efflorescent crusts were collected from various sites across the East and Central Rand goldfields. The sites varied from stream banks, capillary fringes around tailings ponds and solution trenches around tailings dumps.

The samples were collected into polypropylene containers and were dried at 40 °C in an oven. The crusts were dissolved in deionised water and filtered to remove grit prior to analysis.

A water sample was collected at a pond in an abandoned tailings footprint. The sample was collected into an acid-washed polypropylene container and field measurements conducted using a multi-line field meter. The sample was filtered using a 0.45 µm cellulose nitrate filter paper and was stored at 4 °C prior to analysis.

Analysis of the liquid samples for sulphates and metals was done using ion chromatography and inductively coupled plasma optical emission spectroscopy (ICP-OES), respectively. The samples (except for the pond water) were analysed for CN^- , CNO^- and SCN^- according to standard methods (Clesceri *et al.* 1989). Metal-cyanide complexes were determined by reversed-phase ion interaction high performance liquid chromatography with UV detection (Haddad and Kalambaheti 1991).

Results and Discussion

Two samples of crusts (F1 and F2) were collected at an abandoned tailings footprint. The results for the analyses are presented in Table 1.

Elevated concentrations of metals and sulphates were observed. The results essentially

Table 1 Metal and sulphate concentrations in crusts from an abandoned footprint

Component (mg kg ⁻¹)	F1	F2
Al	28503	28147
Ca	182	145
Co	586	2755
Cu	70,9	626
Fe	5090	2484
Mg	42,9	41,8
Mn	919	1526
Ni	1711	963
Zn	1677	1074
SO ₄ ²⁻	96523	96759

point to the capacity of crusts to store pollutants. Physically, the crusts showed different colourations with F1 having a brownish colour and F2 having a pinkish colour. This could be attributed to elevated concentrations of Fe in F1 compared to F2 and Co and Mn in F2 than in F1.

The potential effect of the dissolution of F1 on receiving waters is shown in Figure 1. The trend showed an increase in electrical conductivity and a decrease in pH with an increase in dissolved crusts. This would be expected from the concentrations in Table 1. The evolution of the resulting waters depends on a number of processes as depicted by the different geochemical vectors (Fig. 2). The evaporation of this water would take the

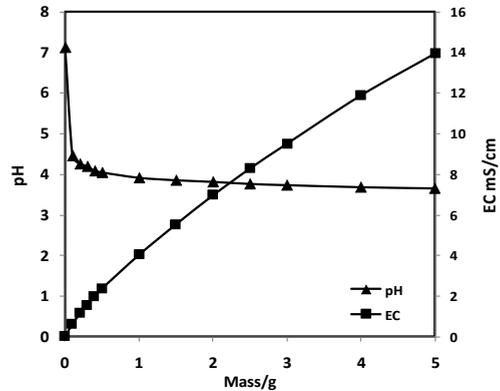


Figure 1 Potential effect of crusts on receiving waters (dissolution in 100 mL of deionised water)

path shown for evaporation of water containing acidic salts. If gypsum-containing salts are dissolved, the path will likely be that of increasing pH and electrical conductivity. Dilution is the most common process once the salt-laden waters enter larger water systems such as streams and dams. The dilution path is generally an opposite of evaporation.

The results for the composition of the footprint pond water are presented in Table 2. The results bear semblance to the aspects discussed above regarding dissolution and dilution. The pH

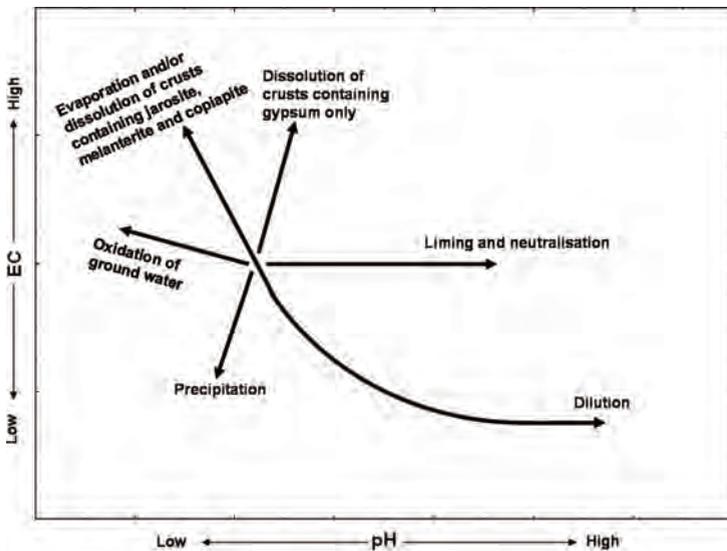


Figure 2 Geochemical vectors for the evolution of water (Tutu et al.2008)

Table 2 Composition of footprint pond water

pH	Temp °C	Eh V	EC μS cm ⁻¹	Al mg l ⁻¹	Au mg l ⁻¹	Ca mg l ⁻¹	Co mg l ⁻¹	Cu mg l ⁻¹	Fe mg l ⁻¹	K mg l ⁻¹	Mg mg l ⁻¹	Mn mg l ⁻¹	Ni mg l ⁻¹	Zn mg l ⁻¹	SO ₄ ²⁻ mg l ⁻¹
1,5	18,9	0,4	3138	34,7	2,5	274,5	2,83	0,5	2,5	57,2	159	43,7	4,27	7,636	1671

Table 3 Cyanide-complexes in crusts

Component (mg kg ⁻¹)	T1	T2	T3
Cu(CN) ₃ ²⁻	15.17	52.38	37.59
Fe(CN) ₆ ³⁻	55.24	67.19	85.99
Ni(CN) ₄ ²⁻	35.16	16.02	27.74

showed that acid-containing salts had been dissolved. A notable gold content could also be observed which would be expected of this site as there were tailings reprocessing activities prior to the abandonment of the footprint.

The presence of other components in the crusts, namely cyanide-complexes was also investigated. The samples studied were collected from a capillary fringe on top of an active slimes dam. The results are presented in Table 3.

The table shows the metal-cyanide complexes which were identified in the crusts. These can be potential sources of free cyanide during dissolution.

Conclusion

Efflorescent crusts have been shown to be evaporation barriers and storage features for various pollutants. Their potential impact on receiving waters has been explored, with various crusts (i.e. acid-containing, circum-neutral, etc) being shown to impact the receiving waters differently. While dilution effects are essential in depressing pollutant concentrations particularly during flush flooding, these effects are not observed in instances where the leachates from dissolved crusts are contained in ponds. Rather, in such instances

the solutions are likely to undergo cycles of precipitation and dissolution. This renders the crusts potent sources of secondary pollution.

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References

- Clesceri S, Greenberg E, Rhodes R (1989). Standard methods for the examination of water and wastewater, 17th edition, 22–45.
- Haddad PR, Kalambaheti C (1991). Advances in ion chromatography: speciation of μL^{-1} levels of metallo-cyanides using ion-interaction chromatography. *Anal. Chim. Acta*, 250:21.
- McCarthy TS (2006). The Witwatersrand Supergroup—The Geology of South Africa. Geological Society of South Africa, 155–185.
- Naicker K, Cukrowska EM, McCarthy TS (2003). Acid mine drainage arising from gold mining activities in Johannesburg, South Africa and environs. *Journal of Environmental Pollution*. 122: 29–40.
- Sutton M (2008). Use of remote sensing and GIS in a risk assessment of gold and uranium mine residue deposits and identification of vulnerable land use (MSc Research Report, University of the Witwatersrand).
- Tutu H, McCarthy TS, Cukrowska EM (2008). The chemical characteristics of acid mine drainage with particular reference to sources, distribution and remediation: the Witwatersrand Basin, South Africa, as a case study. *Applied Geochemistry*. 23: 3666–3684.

