# Geochemistry and Mineralogy of Precipitates Formed During Passive Treatment of Acid Mine Drainage in the Ermelo Coalfield, South Africa⊚

N.O. Novhe[1], B. Yibas[1,2], H. Coetzee[1], T Mashalane[1], M. Atanasova[1], V.R.K. Vadapalli[1], C. Wolkersdorfer[3,4]

[1]*Council for Geoscience, 280 Pretoria Rd, Silverton, 0184, South Africa, onovhe@geoscience.org.za*
[2]*Department of Environmental Sciences, College of Agriculture and Environmental Sciences, University of South Africa, Florida Campus, Johannesburg, South Africa*
[3]*SARChI Chair for Mine Water Management, Department of Environmental, Water, and Earth Sciences Tshwane University of Technology Pretoria South Africa*
[4]*Laboratory of Green Chemistry, Lappeenranta University of Technology Mikkeli Finland*

## Abstract

To optimise a passive treatment system for acid mine drainage, this study involved geochemical and mineralogical characterisation of resulting precipitates, using XRF, XRD and geochemical speciation modelling tools. Contaminants are removed as metal sulfides, sulfates and oxy-hydroxide in anaerobic units and as secondary oxides or hydroxides in aerobic units. The mineral phases formed are also responsible for attenuation of other trace elements such as Zn, Ni, Cu, Co, Pb, and REE (such as Ce, La, Nd, Y and Yb) and also control their mobility and fate in the environment. Accumulation of chemical constituents may present an opportunity for metal recovery.

**Keywords:** Anaerobic and aerobic passive treatment systems, XRF, XRD, Mineral phases, PHREEQC geochemical modelling

## Introduction

Passive treatment is considered as a promising long-term solution for the management of polluted mine water in many parts of the world (Hedin et al. 1994; Ziemkiewicz et al. 2001). To contribute towards the development of sustainable mine water management solutions in South Africa, research is on-going to assess the applicability of passive treatment systems, evaluate their performance (to optimise the design criteria), and improve their efficiency and longevity.

Attenuation of contaminants during passive treatment of acid mine drainage is very complex and comprised of a number of reactions that occur under different redox conditions, such as formation and precipitation of metal hydroxides or oxides (due to oxidation reactions), microbial sulfate reduction forming metal sulfides, organic complexation reactions, ion exchange reactions and direct uptake of chemical constituents by living plants (phytoremediation) (Gusek et al. 2009). Some chemical constituents can be removed under both reducing and oxidising conditions (e.g. Fe, As, Al), whereas some can only be removed under oxidising conditions (e.g. Mn) or reducing conditions (e.g. sulfate, U, Co, Zn). Understanding these processes is important for proper design and optimisation of passive treatment systems.

This study involved geochemical and mineralogical characterisation of precipitates formed in a pilot-scale passive treatment plant designed to treat acid mine drainage discharging from an abandoned coal mine. The pilot-scale plant, which was operated for 15 months, successfully neutralised the water and substantially removed contaminants, such as Fe, Al, Co, Zn, Ni, As, Pb, V, and Cu but with minimal $SO_4^{2-}$-reduction.

## Study area and methodology

The pilot plant is situated near Carolina in the Mpumalanga Province, South Africa. Geologically, the area forms part of the Ermelo coalfield. All of the coal seams occur within the Vryheid Formation of the Ecca Group, Karoo Supergroup. Sandstones with subordinate shales represent the bulk of the Vryheid Formation (Bell & Jeremy 2002).

A pilot-scale passive treatment plant consisting of integrated anaerobic and aerobic units was constructed to treat 1440 L of acid mine drainage per day from an abandoned underground coal mine (Fig. 1). The anaerobic unit used is a reducing alkalinity producing system (RAPS), which combines the mechanisms of anaerobic treatment wetlands and anoxic limestone drains, as developed by Kepler and McCleary (1994). Aerobic units consisted of an oxidising pond and a cascading trench. The pilot plant operated for 15 months, with regular monitoring of the water quality. After 12 months of operation, samples of precipitates were collected from the top and bottom of the units, air dried and analysed by means of X-ray fluorescence (XRF) for metal concentrations, as well as X-ray diffraction (XRD) and scanning electron microscopy (SEM) for mineralogical composition. The samples were sent to the Council for Geoscience's laboratory in Pretoria, South Africa, for analysis. To supplement the results obtained, geochemical modelling with PHREEQC code and the PHREEQC database (*Phreeqc.dat*) (Parkhurst and Ap-

pelo 2013) were also used to predict mineral phases that are likely to precipitate. Saturation indices for different mineral phases were determined from the water quality results. Species which are more likely to precipitate were determined using the saturation index (SI), where SI < 1 indicates an undersaturated solution, SI = 1 a saturated solution and SI > 1a supersaturated solution.

## Results and discussions

### Geochemical composition

From the results of the XRF analysis for both top and bottom layers, it can be seen that Fe oxides are dominant, especially in the oxidation pond and at the top of RAPS units (Fig. 2a). The Fe concentration decreases from the top to the bottom layers of the treatment units and this can be attributed to a decrease in oxygen ingress or oxidation rates with depth i.e. 54.46 to 28.52 wt%; 62.48 to 13.09 wt% and 78.10 to 65.08 wt% in the RAPS and oxidising units, respectively. Aluminium (expressed as $Al_2O_3$) is also dominant in the RAPS units, in addition to Fe and it increases with depth and depends on pH, i.e. 0.96 to 37.58 wt% and 11.35 to 18.30 wt%; 0.52–0.82 wt% (wt % expressed as oxides) for RAPS and aerobic units, respectively. Ca is also present in considerable amounts, especially in the RAPS units. Its concentration increases with depth, indicating dissolution of limestone in the RAPS units.

Concentrations of trace metals increase from the top to the bottom of the anaerobic

units i.e. 33 to 8,839 mg/kg; 13 to 1,717 mg/kg; 7.6 to 1,569 and 102 to 118 mg/kg for Zn, Ni, Co and Cu respectively (Figure 2b and 2c). Metals, such as Co, Pb, V, Ni and Zn also precipitate in the aerobic units (oxidation pond). This is likely attributable to sorption/co-precipitation with oxy-hydroxides of Fe. Their concentration also increases with depth (from top to bottom) i.e. <1 to 12 mg/kg; 4.7 to 20 mg/kg, and 34 to 97 mg/kg for Co, Ni and Zn respectively.

Rare earth elements (REE) are also accumulated at the bottom of the RAPS units (Fig 2b). Their concentrations are highest in the first unit (RAPS 1) and slightly decrease in RAPS 2. i.e. Ce: 1035 to 1920 mg/kg, La: 300 to 555 mg/kg, Nd: 373 to 692 mg/kg, Y: 365 to 615 mg/kg, Yb: 31 to 60 mg/kg. These elements substantially accumulated at the bottom of the RAPS units, with minor amounts also accumulated on top of the RAPS2 and in the oxidation unit. The accumulation of REEs seems to depend on the pH and secondary mineral phases that are formed in the system. Al, Fe solid phases (oxides/hydroxides), and sulfate complexes have been reported as excellent sorbents for REE (Zänker et al. 2003, Ayora et al. 2016, Zhao et al. 2007). REEs are essential raw materials for various modern technological developments and are in high demand. Hence, accumulation of REE presents an opportunity for economic recovery, which could be used to help offset the costs of remediation.

## Mineralogical composition

Mineralogical compositions of the precipitates were analysed by means of XRD and SEM (Fig. 3, 4, 5 and 6). Based on XRD, the top layer of RAPS 1 principally consists of goethite (FeOOH) (84.8 wt %), followed by jarosite [$KFe_3 (SO_4)_2(OH)_6$] (8.3 wt %) and hematite (3.32 wt %), whereas the bottom layer consists of gypsum (23.15 wt %), jarosite (10.96 wt %) and sulfur (7.91 wt %). The mineralogical composition has been confirmed by SEM analyses (Fig. 3 and 4). The presence of high concentrations of iron hydroxide on the top layer of RAPS1 is indicative of a high rate of oxidation. The presence of jarosite is indicative of a low pH on top of RAPS1, which is the inlet to the system. However, since this is vertical flow system, the pH increases downwards; hence, the formation of gypsum at the bottom of the unit. Metals, such as Zn and Fe also precipitate as sulfides at the bottom of the RAPS units, which is attributed to microbial sulphate reduction (Fig. 3 and 5).
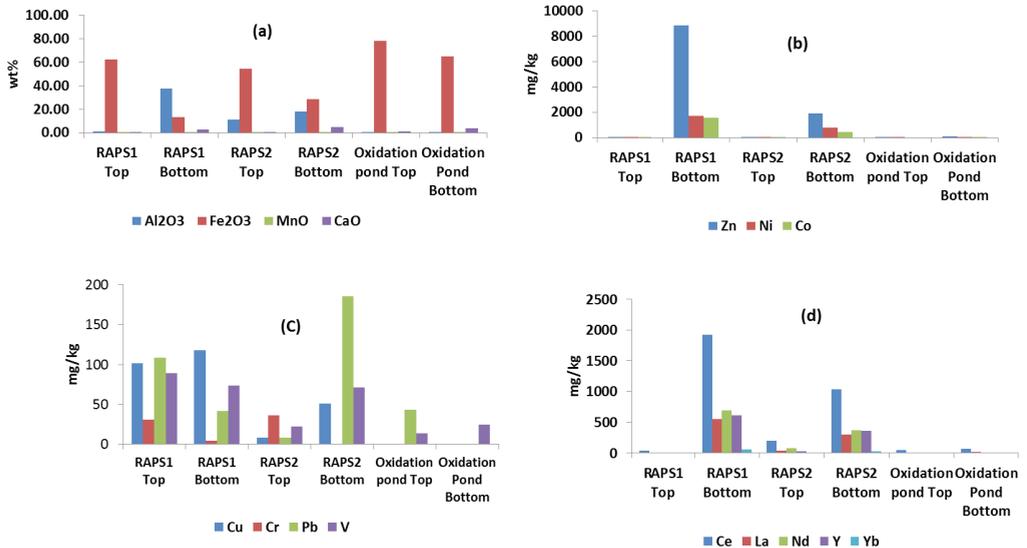


*Figure 2* Major, minor elements as oxides (a) and trace elements composition (b, c and d).

The top layer of RAPS2 principally consists of amorphous contents (100 wt %) or poorly crystalline materials that do not contribute to diffraction peaks. Based on field observations, the top layer of RAPS2 consisted of white to orange slurry-like precipitates. The white is attributed to hydroxides of Al while the orange material is composed of hydroxides of Fe, as confirmed by SEM analyses (Fig. 3, 4 and 5). Gypsum (68.9 wt %) is predominant at the bottom of the RAPS2 unit, where the pH is higher and sometimes occurs as well-developed gypsum crystals (Fig. 6). Goethite is the dominant mineral species in the oxidation pond, especially in the top layer, and this is again attributed to a high rate of oxidation in the pond.

The mineral phases that formed in the passive treatment system are known to be excellent sorbents of trace metals (such as Co, Pb, Cu, Ni, and Zn) and also control their mobility, fate and transport in the environment (Dzombak and Morel 1990, Chapman et al. 1983, Carlson and Schwertmann 1981).
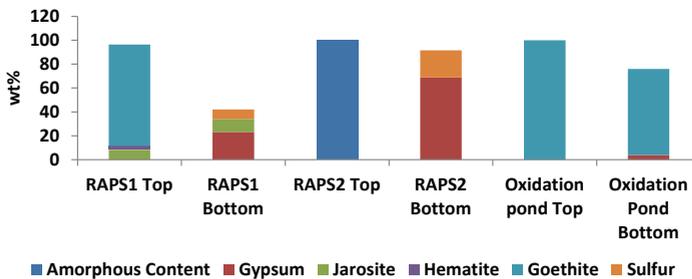


*Figure 3* Mineralogical composition of the precipitates
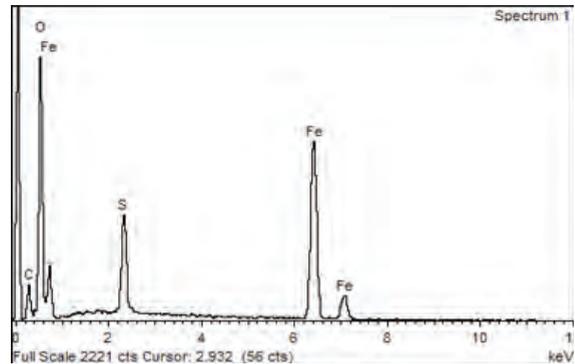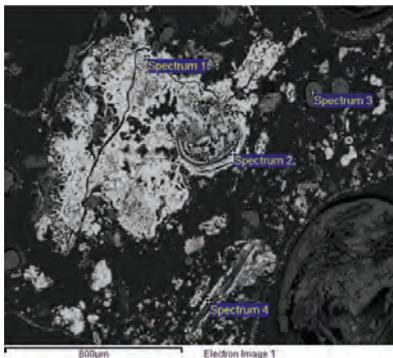


*Figure 4* SEM image for the RAPS1 top layer, showing Fe-oxyhydroxide (Geothite) and Fe sufate (Jarosite) spectra
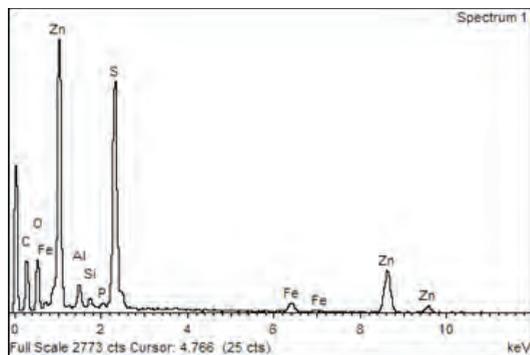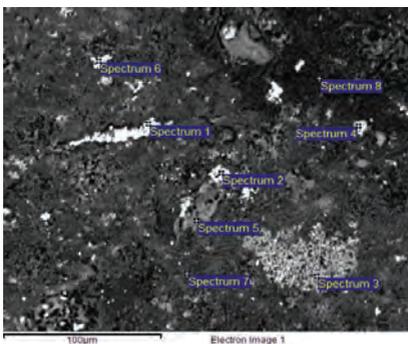


*Figure 5* SEM image for the RAPS1 unit bottom layer, showing ZnS, FeS, Al-oxyhydroxide spectra
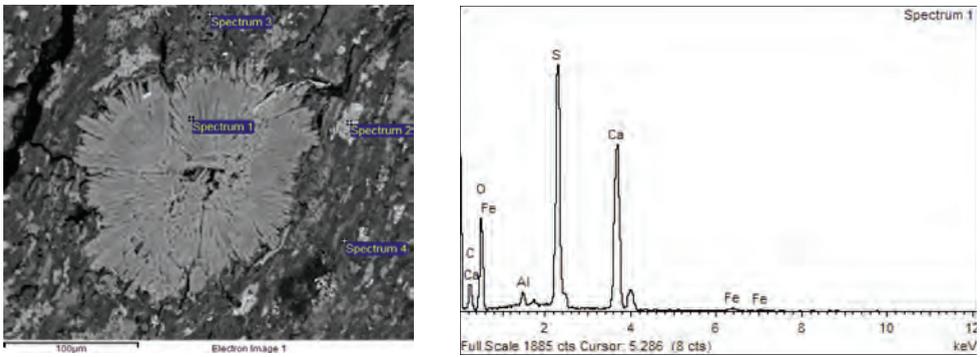
*Figure 6* SEM image for the RAPS2 unit bottom layer and associated spectra.

## Geochemical modelling

Saturation indices of mineral phases were calculated with PHREEQC code for the different treatment units (Fig. 7). The geochemical model confirmed the mineralogical and geochemical composition of the precipitates formed in the treatment units. The feed water or inlet is supersaturated relative to hematite and goethite and slightly saturated relative to jarosite and alunite $(KAl_3(SO_4)_2(OH)_6)$. Their saturation indices increase throughout the treatment units, as the pH of water increases. In addition, the water also becomes supersaturated relative to gypsum $(CaSO_4 \cdot 2H_2O)$ and gibbsite $(Al(OH)_3)$ with increasing pH. Manganese-containing minerals, such as manganite $(MnOOH)$ and pryrolusite, show saturation throughout the treatment units and this justified the minimal reduction of Mn $(MnO_2 \cdot H_2O)$ in the system.

## Conclusions

The study revealed that chemical constituents (e.g. Fe, $SO_4^{2-}$, Al, Mn, Zn, Ni, Cu, Co, Cr, Pb, V, REE) precipitate in the units of the passive treatment system, dependent on various geochemical and biological conditions (such as pH, redox). Contaminants are removed as metal sulfides, sulfates and oxy-hydroxides in anaerobic units and as secondary oxides or hydroxides in aerobic units. The mineral phases formed are also responsible for attenuation of other trace elements such as Zn, Ni, Cu, Co, Pb, REE (e.g. Ce, La, Nd, Y and Yb) due to co-precipitation and control their mobility, fate and transport in the environment.

Accumulation of metals, especially REEs, may present an opportunity for economic metal recovery that can offset the cost of remediation. Sequential extraction is recommended to account for mineral phases responsible for the accumulation of REEs.

The results obtained from this study will enable development of predictive models for the type of precipitates that are likely to form in the passive treatment units, taking into considerations their environmental implications and economic potential. This will also be incorporated in the development of framework for acid mine drainage remediation in South Africa.

## Acknowledgements

## References

Ayora C, Macías F, Torres E, Lozano A, Carrero S, Nieto JM, Pérez-López R, Fernández-Martínez A, Castillo- Miche H (2016) Recovery of Rare Earth Elements and Yttrium from Passive-Remediation Systems of Acid Mine Drainage. Environ. Sci. Technol., 50(15):8255–8262
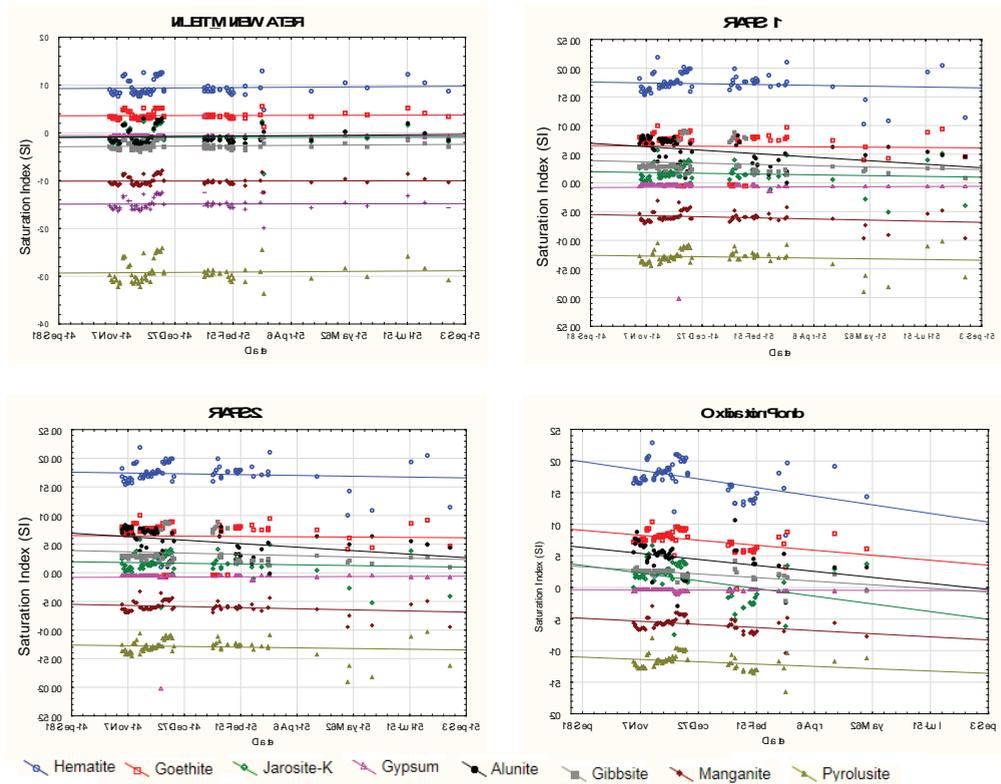
*Figure 7 Saturation indices of mineral phases for different treatment units*

Carlson L, Schwertmann U (1981) Natural ferrihydrites in surface deposits from Finland and their association with silica. Geochim. Cosmochim. Acta 45:421-429

Chapman BM, Jones DR, Jung RF (1983) Processes controlling metal ion attenuation in acid mine drainage streams. Geochim. Cosmochim. Acta 47:1957-1973

Dzombak DA, Morel FMM (1990) Surface complexation modeling – hydrous ferric oxide: New York, Wiley and Sons

Gusek JJ (2009) A Periodic Table of Passive Treatment for Mining Influenced Water. In R. Barnhisel, ed. 2009 National Meeting of the American Society of Mining and Reclamation. 3134 Montavesta Rd., Lexington, KY 40502: ASMR:550–562

Hedin RS, Watzlaf GR, Nairn RW (1994) Passive treatment of acid-mine drainage with limestone. J Environ Qual 23(6):1338-1345

Kepler DA, McCleary EC (1994). Successive Alkalinity Producing Systerm for the treatment of Acid Mine Drainage. In Pittsburgh, PA: International Land Reclamation and Mine Drainage Conference and the third International on the Abatement of Acid Drainage:195–204

Parkhurst DL, Appelo CAJ (2013) Description of Input and Examples for PHREEQC Version 3 – A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. US Geol Surv Tech Methods 6(A43):1-497

Zänker H, Richter W, Hüttig G (2003) Scavenging and immobilization of trace contaminants by colloids in the waters of abandoned ore mines. Colloid Surf. A-Physicochem. Eng. Asp. 217(1–3):21–31

Zhao F, Cong Z, Sun H, Ren D(2007) The geochemistry of rare earth elements (REE) in acid mine drainage from the Sitai coal mine, Shanxi Province, North China. Int. J. Coal Geol. 70(1–3):184–192

Ziemkiewicz P, Skousen J, Simmons J (2001) Cost Benefit Analysis of Passive Treatment Systems. Proceedings, 22nd West Virginia Surface Mine Drainage Task Force Symposium, 3-4 April, Morgantown, WV