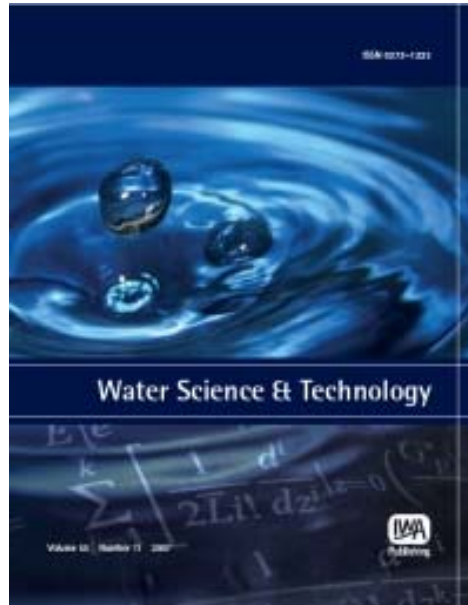


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Geochemical modelling of the evolution and fate of metal pollutants arising from an abandoned gold mine tailings facility in Johannesburg

B. P. C. Camden-Smith and H. Tutu

ABSTRACT

Analytical techniques were combined with geochemical modelling to study the release mechanisms of pollutants from an abandoned gold mining tailings storage facility near Johannesburg. Inverse modelling of sampled tailings pond water and experimental single extractions using various solutions indicated which combination of naturally occurring leaching solutions were likely to give rise to the observed pond water quality. The potential fate of metals in the pond was predicted by modelling the formation of efflorescent crusts and adsorption onto hydrated iron oxide minerals.

Key words | forward modelling, inverse modelling, single extractions

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INTRODUCTION

Gold production from the Witwatersrand gold fields in South Africa has been on a long-term decline since its peak in the 1970s. Despite the decrease in mining activity, the environmental impacts resulting from flooding of abandoned mines and tailings storage facilities continue.

Acidic water is generated as a result of oxidation of residual pyrite and other sulphide minerals in the tailings ores. This has been exacerbated by tailings reprocessing activities that are currently underway in most of the mining areas, as the tailings tend to be exposed to water and oxygen, the key features for acid generation (Salomons 1995). Metals, sulphate and cyanide have been reported to emanate from tailings in these areas (Naicker *et al.* 2003; Tutu *et al.* 2008; Bakatula *et al.* 2012).

Quantifying the total metal content of a sample of waste will verify the presence and abundance of a potential pollutant but does not indicate the bioavailability or mobility in water resources of the pollutant (Rao *et al.* 2008). The mobility of pollutants from mine drainage is dependent on four major factors, namely: the occurrence of the contaminant, a sufficient abundance of the contaminant, the reactivity of the contaminant and the presence of a hydrological flow path (Nordstrom 2011). By focusing on the first three factors, this study was conducted with the aim of predicting the potential release and fate of metals from an abandoned gold mine facility into the water systems in the vicinity by

using a combination of analytical techniques and geochemical modelling.

MATERIALS AND METHODS

Figure 1 is a diagrammatic outline of the study site. Leaching of the tailings occurs when rainwater or shallow groundwater enters the tailings storage facility (TSF). The flow pathways of the plumes are represented by arrows.

Three water samples were collected from a pond adjacent to the TSF. Field measurements included temperature, pH, oxidation-reduction potential (Eh), dissolved oxygen and conductivity. Fractions of the samples were filtered using Prima Pes 0.45, 0.22 and 0.1 μm filter paper in order to determine whether or not a potential colloidal dispersion of the analytes was present. Six samples of different coloured efflorescent crust were collected from the sides of the TSF and the dry edge of the pond. The mineralogy of the crusts was determined using powder X-ray diffraction (PXRD). PXRD was carried out using a Bruker D2 Phaser desktop diffractometer with a cobalt X-ray source and a LynxEye 1-D detector. Samples of yellow oxidised and grey unoxidised tailings material were collected from the same site as the crusts, then air dried and stored in a cool, dark place.

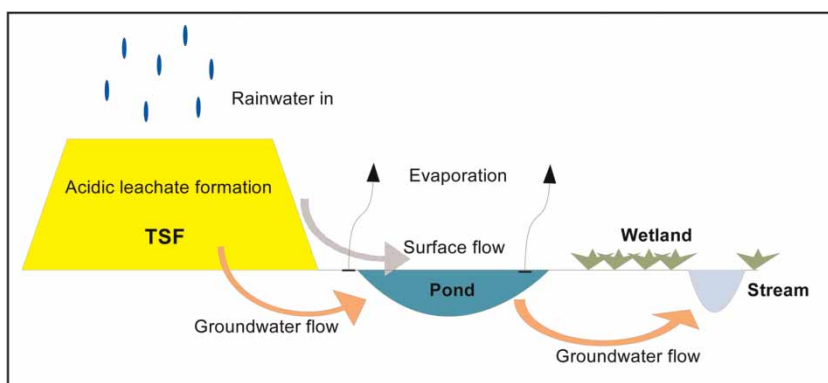


Figure 1 | Conceptual model of predicted water flow in the study site.

Single extraction and batch leaching experiments were conducted on oxidised and unoxidised tailings material with a variety of leaching solutions. The choice of the leaching solutions was based on the likely environmental reactions that could mobilise pollutants within this case study. Deionised water and artificial rainwater dissolve minerals that are readily water soluble. A calcium chloride leaching solution is expected to extract the exchangeable fraction as well as the water-soluble fraction. It has been shown to be a suitable solution to predict the available fraction of material available for plant uptake (Rao *et al.* 2008). Sodium carbonate and sulphuric acid solutions extract the base and acid soluble fractions respectively. Sulphuric acid is generated during the oxidation of pyrite and this acidic solution could leach surrounding material. EDTA solution leaches elements that are organically bound or that can be solubilized through complexation. A 20:1 ratio of leaching solution to solid material was used. This is the same leaching ratio as used by the USGS Field Leach Test and USEPA Method 1312, synthetic precipitation leaching procedure leach test (Hageman 2007).

Therefore 20 g of air-dried sample was weighed into 500 mL wide-mouthed plastic bottles and leached with 400 mL of leaching solutions. Each leaching experiment was prepared in triplicate. The bottles were shaken on an elliptical shaker for 24 hours and filtered using Prima PES 0.45 μm filter paper. Measurements of pH, Eh, temperature and conductivity were taken before and after leaching. Leachates and water samples were analysed in triplicate (with analytical uncertainty within 5%) using chemically suppressed anion chromatography (IC) and inductively coupled plasma-optical emission spectroscopy (ICP-OES).

The PHREEQC interactive geochemical modelling code (Charlton *et al.* 1997; Parkhurst & Appelo 1999) was used to

construct inverse and forward geochemical models. Inverse geochemical modelling uses mass balance equations to identify which precipitation and dissolution reactions could have occurred to produce a final solution from an initial solution or combination of initial solutions. Inverse modelling provides several possible models that allow for the transformation of initial solutions into final solutions. These models are then inspected and unfeasible models discarded. Inverse geochemical modelling was used to correlate laboratory-based batch leaching studies with pond field samples. Leachates emanating from the tailings precipitate minerals and the resulting leachates collect in the tailings pond. Evaporation of the pond water concentrates the analytes.

The potential fate of pollutants was modelled using forward modelling. Two temporary sinks for the metal pollutants were considered, namely efflorescent crust formation and adsorption onto iron surfaces. It was supposed that 1, 3, 5 and 10 g of hydrated iron oxide are added to 1 L aliquots of pond water. These amounts were chosen based on the expected concentrations of iron oxide. Other possible sinks include the complexation by organic material or precipitation due to pH changes during mixing with fresh water. The extensive Lawrence Livermore National Laboratory (llnl) database was used for inverse and forward modelling involving the addition of hydrated iron oxide to the system. A comparison of the common databases was conducted during the evaporation modelling. The modelling used was based on the assumption of thermodynamic stability and local equilibrium, that is, that the leachates represent equilibrium between solids and solutions (Bethke 1996). In constructing inverse models, the multiple precision solver function of PHREEQC was employed with the multiple precision tolerance and censor multiple precision variables set to 10^{-12} and 10^{-14} .

RESULTS AND DISCUSSION

Pond water results

The average pH of the pond water samples was 3.70 ± 0.02 at a temperature of 15.7 ± 1.5 °C. The pond water samples contained a high concentration of aluminium as well as manganese, nickel, cobalt, copper, iron and uranium (Figure 2). Dissolved oxygen content was 8.0 ± 0.6 mg L⁻¹ and Eh was 618 ± 10 mV. Sulphate concentration was $3,550 \pm 340$ mg L⁻¹ and chloride concentration was 85 ± 33 mg L⁻¹. Aluminium content is known to have a strong dependence on the pore size of filter paper used as colloidal aluminium particles could dominate an analysis in which there is actually a low portion of dissolved aluminium (Zhu & Anderson 2002). There did not appear to be a major dependence of the aluminium concentration on filter paper size.

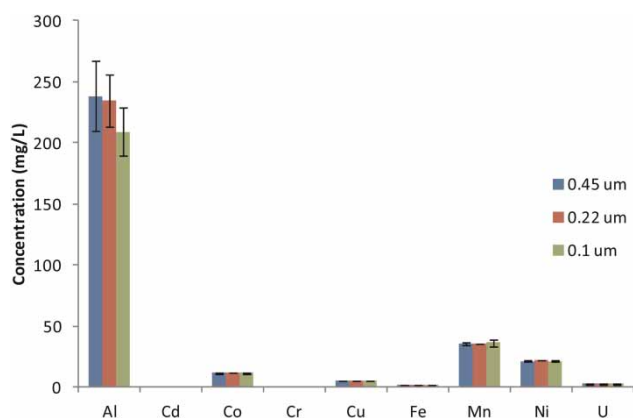


Figure 2 | ICP-OES results of samples from tailings pond water.

Batch leaching results

The leaching results for select metals followed one of two patterns (Figure 3). The ICP-OES results showed that more aluminium was leached from the oxidised tailings than from unoxidised tailings (Figure 3). The form of aluminium in the unoxidised tailings is most likely a partially soluble or insoluble aluminosilicate whereas aluminium in the weathered, oxidised tailings could be from the abundant soluble sulphate crusts that were present. Copper (maximum of 18 mg kg⁻¹ using EDTA leach) and chromium (maximum of 0.2 mg kg⁻¹ using H₂SO₄ leach) had similar leaching schemes to aluminium. In general, more cobalt (maximum of 16.8 mg⁻¹ in artificial rainwater), manganese (Figure 3) and nickel (maximum of 41 mg kg⁻¹ in artificial rainwater) were leached from the unoxidised tailings than from oxidised tailings (Figure 3). Iron also followed a similar pattern to manganese, except that there was a marked increase in the amount of iron leached using the EDTA solution. For the sulphuric acid–unoxidised tailings leach, 597 mg kg⁻¹ of iron was leached compared to 1,787 mg kg⁻¹ leached using EDTA. Iron was the only metal that exhibited such an increase in mobilisation with the EDTA solution.

Figure 4 shows the results of the artificial rainwater batch leaching for major elements. The original pH of the rainwater leaching solution was 4.5. The pH of the solutions after leaching of the oxidised material was 3.59 ± 0.05 and that of solutions of unoxidised material was 3.87 ± 0.10 . The sulphate released was 7.2 ± 2.7 mg per gram of oxidised material and 3.6 ± 0.9 mg per gram of unoxidised material. The Eh of the solutions before and after leaching did not change significantly.

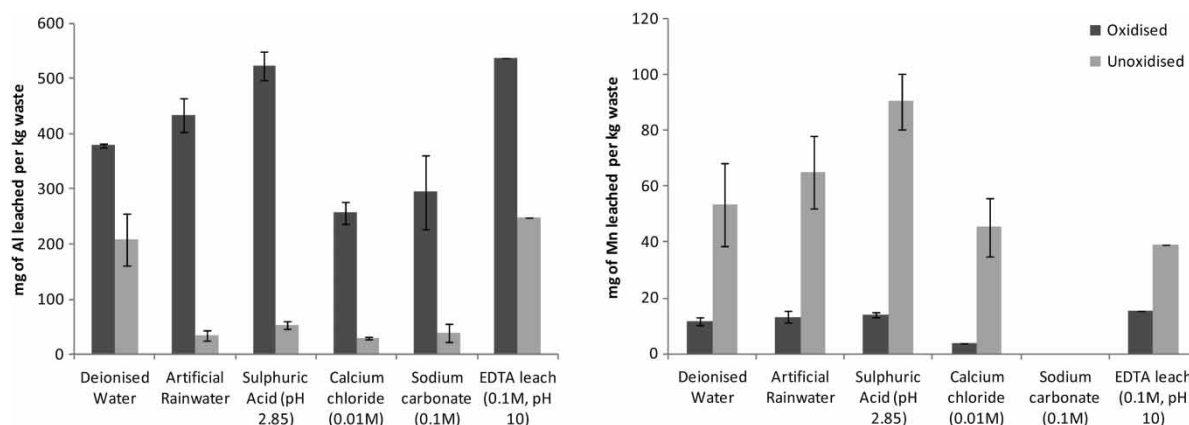


Figure 3 | Aluminium (similar to chromium and copper schemes) and manganese (similar to cobalt, iron and nickel) results from leaching experiments.

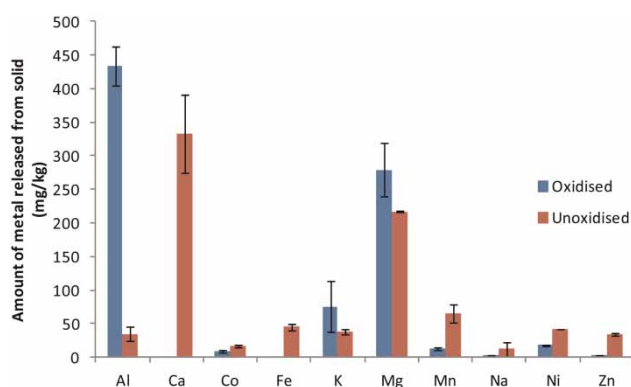


Figure 4 | Major metals released from tailings material using artificial rainwater leaching.

Modelling results and discussion

Inverse modelling was used to predict which leachates could contribute to the tailings pond water. PXRD revealed that the crusts consisted of a series of sulphate minerals, predominantly alunogen ($\text{Al}_2(\text{SO}_4)_3 \cdot 17\text{H}_2\text{O}$) as well as coquimbite

($\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$), epsomite ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$), pickeringite ($\text{MgAl}_2(\text{SO}_4)_4 \cdot 22\text{H}_2\text{O}$) and magnesiocopiapite ($\text{MgFe}_4(\text{SO}_4)_6(\text{OH})_2 \cdot 20\text{H}_2\text{O}$). The mixed-metal sulphate crusts are not present in the common PHREEQC databases. A series of single-metal hydrated sulphate salts were defined as phases. Where the hydrated crusts were not available, the anhydrous forms were specified. Quartz was set as a phase to balance the silica concentration. The models did not converge unless a hydroxide-bearing phase was specified. Therefore, jarosite ($\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$), sodium jarosite ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) and goethite (FeOOH) were defined. Sulphate was set as a charge balance for the solutions. A selection of the possible mass balance models is presented in Table 1. This compilation is in no way extensive, but illustrates how models generated using inverse modelling can vary. Calcium chloride, sodium carbonate and EDTA leaches were not used in the models. The sodium carbonate leach is a basic leach that could be expected to represent some form of acid neutralisation remediation. The TSF was partially removed and when operations ceased, the site was

Table 1 | Inverse models for the transformation of laboratory leachates into sampled tailings pond water

Model	Leaching solutions	Ratio of initial solution(s) to final solution	Minerals precipitated (moles)	Minerals dissolved (moles)
1	Deionised water on oxidised tailings	308,400:1	CuSO ₄ ·5H ₂ O (1.4) MgSO ₄ ·7H ₂ O (154) CaSO ₄ ·2H ₂ O (56) CoSO ₄ ·6H ₂ O (2.1) Quartz (0.4) MnSO ₄ (3.3) NiSO ₄ (4.1) Al ₂ (SO ₄) ₃ ·6H ₂ O (108) KFe ₃ (SO ₄) ₂ (OH) ₆ (2.5) Fe ₂ (SO ₄) ₃ (10)	Goethite (27) NaFe ₃ (SO ₄) ₂ (OH) ₆ (0.001)
2	Rainwater on oxidised tailings and rainwater on unoxidised tailings	2.7:0.8:1	CaSO ₄ ·2H ₂ O (0.00023) Fe ₂ (SO ₄) ₃ (0.00015)	CuSO ₄ ·5H ₂ O (0.000073) MgSO ₄ ·7H ₂ O (0.0074) CoSO ₄ ·6H ₂ O (0.00016) Quartz (0.000014) MnSO ₄ (0.00057) NiSO ₄ (0.00030) Al ₂ (SO ₄) ₃ ·6H ₂ O (0.0033) KFe ₃ (SO ₄) ₂ (OH) ₆ (0.00010) Na ₂ SO ₄ ·10H ₂ O (0.00064)
3	Rainwater on oxidised tailings and sulphuric acid on unoxidised tailings	22:0.04:1	MgSO ₄ ·7H ₂ O (0.0033) Al ₂ (SO ₄) ₃ ·6H ₂ O (0.0044) KFe ₃ (SO ₄) ₂ (OH) ₆ (0.0017) Fe ₂ (SO ₄) ₃ (0.00073)	Quartz (0.000012) MnSO ₄ (0.00038) Goethite (0.003) NaFe ₃ (SO ₄) ₂ (OH) ₆ (0.0012)

abandoned and no remediation of the TSF was conducted. There is no vegetation growing on the TSF and as such complexation of metals by organic ligands (simulated by the EDTA leach) is not expected.

Ideally, the models would only precipitated minerals. However, it was necessary to allow for the dissolution of some minerals. These minerals could possibly represent material that was not leached due to kinetic constraints. For example, the pond water could contain a greater proportion of iron compared to the leachates because the contact time between the solution and material might be greater inside the TSF compared to the 24 hours in the laboratory, and more oxidation of pyrite would be expected to occur. Model 1 requires the smallest selection of additional minerals (only goethite and sodium jarosite) in order to yield the pond water. However, it is clear that model 1 is an unfeasible model as it would require the evaporation of over 300,000 L of leachate to yield 1 L of pond water. The model that is most likely to be of relevance to the system under study is model 3. The minerals predicted to precipitate correlate to the efflorescent material that was sampled from the site. The predicted aluminium sulphate, iron (III) sulphate and magnesium sulphate minerals correlate with the observed alunogen, coquimbite and epsomite respectively. The water content of the predicted and observed minerals differ due to the absence of the observed minerals in the available databases. This model agrees with the conceptual model of the system (Figure 1). Rainwater would interact with the surface of the tailings material (oxidised material) and run off into the pond would occur. Rainwater that infiltrated the tailings would be acidified by sulphuric acid released during the oxidation of pyrite and this solution would leach unoxidised material.

There was extensive efflorescent crust material present around the tailings. The pond water was sampled towards the end of its evaporation sequence. Evaporation modelling of the remaining pond water was used to predict which minerals would form next. The forward evaporation modelling was carried out in two steps, namely examining saturation indices and mineral precipitation, both of which form the basis of ongoing experimental work. The importance of this exercise is to assess the potential partitioning of pollutants in various precipitates during evaporation. This is also intended to complement PXRD analysis, particularly in instances where it may not be possible to determine some of the minerals analytically.

In the first step, water evaporation was simulated using an incremental forward reaction model in which the reactant was negative H_2O and no additional phases were defined. The resulting saturation indices were assessed.

Ideally, a mineral should begin as undersaturated and become progressively more saturated during the course of evaporation. Minerals may be saturated at the start of the evaporation sequence. In such cases, their precipitation could be kinetically hindered but it should also be considered that their precipitation from an aqueous solution at atmospheric pressure is unlikely (for example, the precipitation of silicate minerals). Four of the common databases that come as standard with the software were used in this modelling, namely phreec.dat (updated in 2010), wateq4f.dat (updated in 2005), llnl.dat (updated in 2010) and minteq.v4.dat (updated in 2006). There is variation between the minerals available in the databases and their saturation indices. The phreec.dat is not as extensive as the other databases and the model has fewer minerals of interest. The wateq4f model gave similar results to the minteq.v4 model. Celestite (SrSO_4) and chalcedony (SiO_2) followed the ideal saturation index pattern in all of the models. For the llnl database, sodium jarosite ($\text{NaFe}_3(\text{SO}_4)_2(\text{OH})_6$) also followed this pattern. Barite and MnHPO_4 were consistently close to saturation and could have been precipitating from the solution during sampling.

In the second step of evaporation modelling, the minerals of interest were selected as equilibrium phases. When they became oversaturated, the mineral was allowed to precipitate out of solution. The pH might be affected and this could cause a change in the saturation indices of other minerals. Therefore, the saturation indices were inspected once more in case additional minerals needed to be defined as phases. Minerals that were defined as equilibrium phases in the llnl model were barite, chalcedony, sodium jarosite and MnHPO_4 . The precipitation sequence of these minerals is shown in Figure 5. The minerals defined using the minteq.

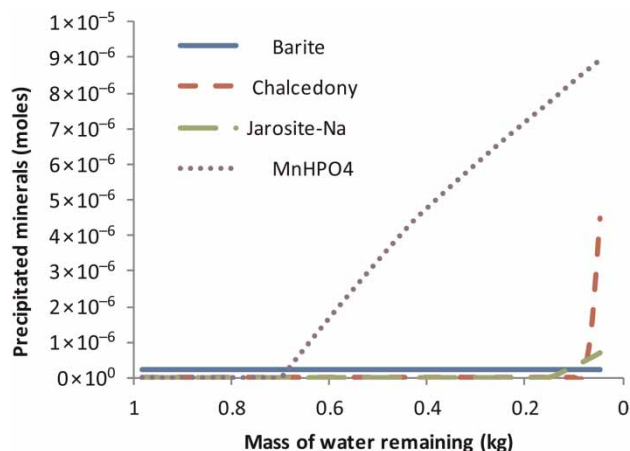


Figure 5 | Evaporation-precipitation model of pond water (llnl.dat).

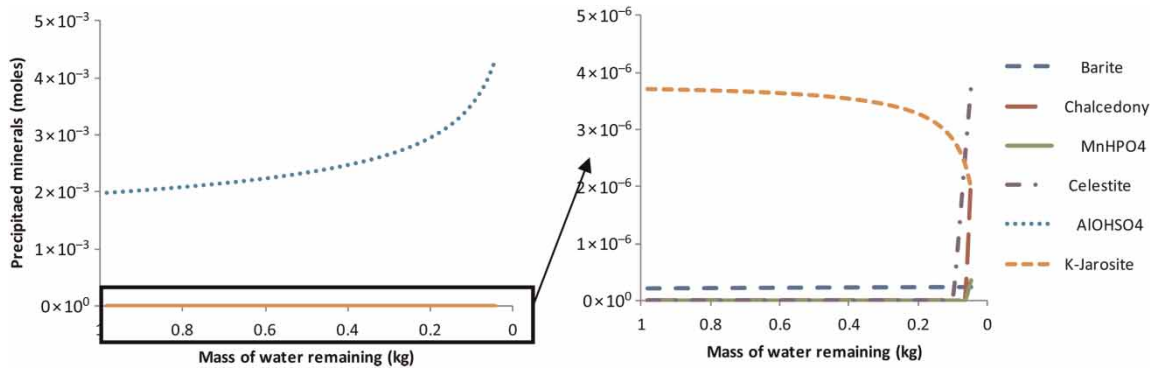


Figure 6 | Evaporation-precipitation model of pond water (Minteq.v4.dat).

v4.dat model were barite, chalcedony, celestite, MnHPO_4 , $\text{Al}(\text{OH})(\text{SO}_4)$ and potassium jarosite (Figure 6). The initial saturation indices for MnHPO_4 for both methods are similar; the point at which the mineral is predicted to precipitate is different. For the *l1n1.dat* model, the mineral begins to precipitate when there is 69% water remaining whereas for the *minteq.v4.dat* model, the mineral precipitates much later in the evaporation sequence with 5% water remaining. Chalcedony follows the same path in both models. The precipitation of $\text{Al}(\text{OH})(\text{SO}_4)$ in the *minteq.v4.dat* model decreases the water pH. The final pH in this model is 2.15 compared to a pH of 2.95 in the *l1n1.dat* model. The differences in pH and the relative abundance of the species HPO_4^{2-} is likely to be the cause of the discrepancy between the two models.

Iron oxide deposits occur naturally in soil and are also associated with areas affected by acid mine drainage. Modelling of adsorption onto hydrated iron oxide surfaces was undertaken assuming the following: a surface area of $600 \text{ m}^2 \text{ g}^{-1}$, 0.2 mol of weak binding sites per mole of HFO and 0.005 mol of strong binding sites per mole of HFO (Dzombak & Morel 1990). The predicted results are summarised in Table 2. The initial pH of the pond water was 3.70. The majority of strong and weak binding

sites is occupied by the H^+ cation. For example, after the 3 g addition of HFO, 92% of strong sites and 57% of weak sites are occupied by H^+ , 7% of strong sites occupied by Cu^{2+} and 42% of weak sites occupied by SO_4^{2-} . The binding of H^+ causes the pH of the contact solution to increase. Strong sites would typically form very strong (irreversible) surface complexes. A weak to moderate desorption mechanism of adsorbed ions would most likely affect the weak sites. A stronger desorption agent would be required to desorb the copper from the strong sites. For instance, 0.5 M acetic acid or 0.05 M lead nitrate solutions could be used to desorb the copper from strong sites, although oxalate, dithionite, citrate, bicarbonate and 0.1 M hydroxylamine hydrochloride are more commonly used to attack the iron oxide sorbed fraction (Rao *et al.* 2008).

CONCLUSIONS

Geochemical modelling combined with analytical techniques can be used to study the evolution and fate of pollutants released through acid mine drainage. In this paper, the use of inverse modelling showed that the combined leaching of oxidised material with rainwater and the leaching of unoxidised material with sulphuric acid followed by evaporation gives a final solution similar to that sampled from a tailings pond. Further, precipitation of minerals with a similar composition to that of the observed efflorescent minerals was simulated. Forward modelling of the evaporation of pond water showed that although efflorescent material is expected to temporarily store pollutants, the extent of this sink is not adequately described by the modelling. Co-precipitation is not accounted for by this modelling and the results are largely influenced by the presence of minerals and their associated thermodynamic data in the

Table 2 | Final results of addition of HFO to pond water

	1 g HFO	3 g HFO	5 g HFO	10 g HFO
pH	3.79	3.95	4.07	4.11
Cadmium removed (%)	0	0.03	0.07	0.19
Copper removed (%)	1.4	7.7	18.6	36.0
Iron removed (%)	0.01	0.05	0.13	0.33
Manganese removed (%)	0	0	0.01	0.02
Zinc removed (%)	0.02	0.1	0.27	0.66

databases. The introduction of hydrated iron oxide surfaces into the tailings pond water increases pH and removes copper from the solution by strongly binding it. Iron oxides are present in soils and iron oxyhydroxides are often associated with acid mine drainage. The adsorption of metals onto these surfaces is a form of natural remediation of acid mine drainage.

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