Modelling the Hydrogeochemistry of Decommissioned Opencast Coal Mines

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Abstract

Water quality improvement in underground mines after the initial flush can render these mines as potential water supplies. However, in certain settings, opencast mining is often preferred. With the prospect of an initial flush in backfilled opencast mines, it is essential to study the initial flush in this setting as these mines may also show water supply potential.

Previous work focused on idealised curve fitting to existing mine water chemistry data, analytical calculations, simplified geochemical modelling and numerical transport models. The study presented here combines components of each to predict the initial flush from backfilled opencast mines. An additional component is the calibration of geochemical- and numerical flow and transport modelling data, with existing groundwater monitoring- and laboratory analysis data. A statistically defined mineral assemblage, based on analysis data, is used as input to geochemical models and calibrated using leaching test data. Leaching test data is further compared to speciation calculations and mine water analysis data to ensure representative laboratory data. Long term geochemical modelling results are then used as input to transport models, which are calibrated against groundwater monitoring data.

The study presents a calibrated modelling approach which shows that calibration can provide realistic estimates which is supported by existing work, showing the duration of the initial flush in underground mines to be a few decades. The calculated duration of the initial flush in this study ranged between 20 and 100 years. Results obtained are considered to be more representative than static estimates and can aid in the improvement of rehabilitation techniques and the management of post-mining groundwater quality, with calculated concentrations calibrated up to a 1% error range.

Key words: Mine water, Opencast mining, Hydrogeochemistry, Modelling

Introduction

Various authors have conducted research on the prediction of the initial flush from abandoned underground mines (Appelo and Postma 2005; Banks 1994; Gzyl and Banks 2007; Younger 2000; Younger 2001; Younger and Robins 2002). Calculation of a "first flush", as it was called by Whitehead and Jeffrey (1995), in backfilled, decommissioned opencast collieries, has not been established, even though the extent of this is likely to exceed the temporal magnitude of its underground counterpart. This is attributed to higher reactive mineral surface areas, slower groundwater flow rates and partly the absence of stable mine water stratification found in underground mines (Younger and Sapsford 2004). With mass opencast closure becoming a reality in the future of South Africa (Vermeulen and Usher 2005), the need for a more advanced conceptualisation is evident. Acid-base accounting, which is especially employed in Mpumalanga, South Africa where most of the country's coal reserves are mined (Pinetown et al. 2007), cannot be viewed as a reliable tool to predict temporal ARD variations. Unfortunately, this is occasionally the case with this indicator test (Younger and Sapsford 2004).

This study focusses on the development of a conceptual model approach to numerical geochemical modelling of the initial flush from decommissioned opencast mines. The need for such a study is highlighted by a directive issued to a mine near Carolina, Mpumalanga which required the quantification of the initial flush from its opencast mines as well as the acid rock drainage (ARD) potential of its backfill material.

Methods

An improved understanding of the mine site's hydrogeology, mineralogy and geochemistry was required to address the quantification of the initial flush using a conceptual model based approach. To obtain this information, a review of previous studies and available monitoring data was performed along with sampling of backfill material on site. The material generated on site was sampled from overburden dumps and backfilled opencast mining areas (Figure 1) using a hand auger.
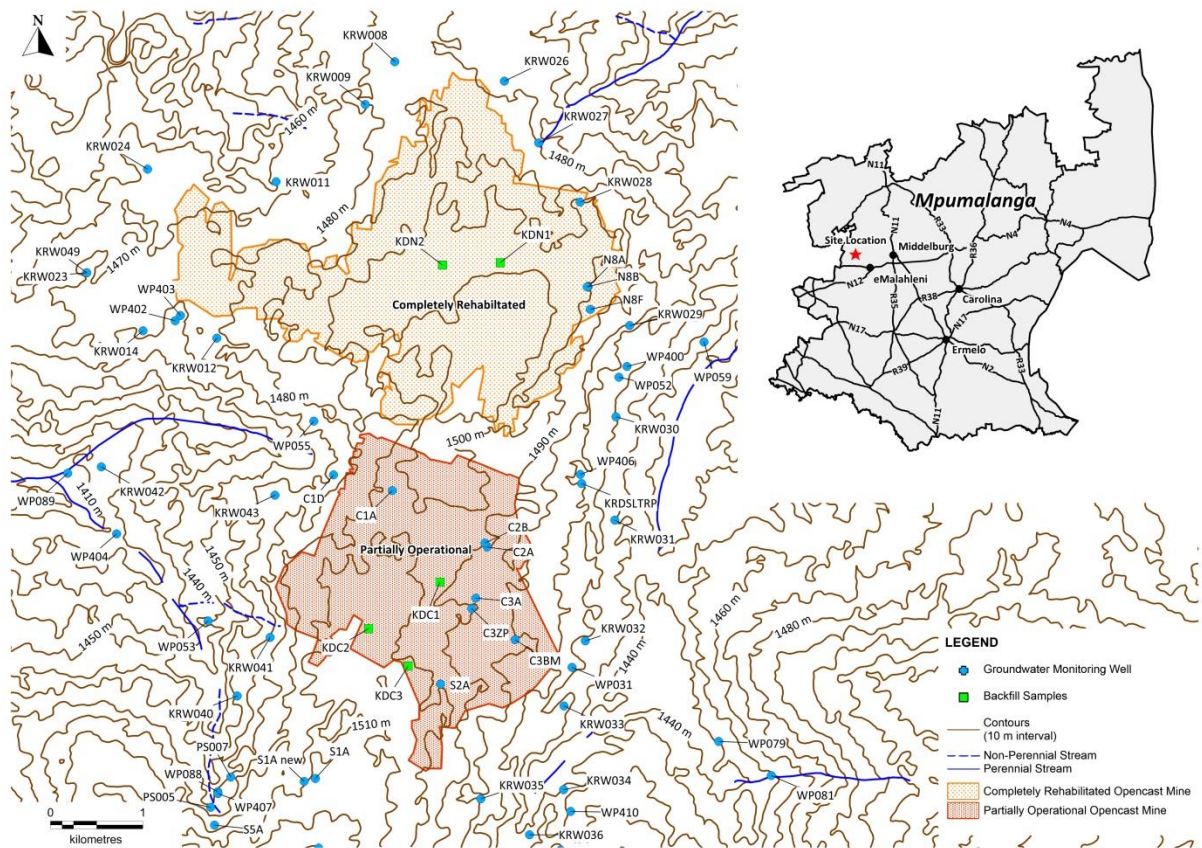

Figure 1 Geochemical Sampling Locations

This was followed by submission of the samples for whole-rock X-ray diffraction (XRD) analysis to determine the mineralogical composition of the material. Acid-base accounting was performed on the samples as an indicator test for the presence of potential sulfides to determine the potential for acid generation and to determine the potential sulfate contamination. The samples were analysed for paste pH, total sulfur, acid generation potential, acid neutralisation potential and neutralising potential ratio. Further to this, distilled water leach testing was performed on the samples to demonstrate the possible contaminants that may be leached from the material in the short term under laboratory conditions.

The geochemical modelling interface used for constructing the geochemical model was The Geochemist's Workbench (GWB) 9 (Bethke 2008). This model defines the dynamic geochemical system by using mineral abundances, water qualities, mineral reaction rates and mineral reactive surface areas. The mineral abundances used were calculated based on the XRD results. The average weight percentage of a mineral was calculated along with the standard error associated with it. Standard errors were subsequently added and subtracted from the average to determine the upper and lower limits for the weight percentage of the specific mineral, respectively.

The mineral reaction rates were obtained from literature sources. Additionally, the grain size of the material, as measured on site, was used to calculate a reactive surface area for each mineral. This calculation is based on mineral densities recorded in literature as well as the volume of grains in the sample, assuming most of the mineral grain will be available for reaction with fluids and that grains are spherical (Gautier et al. 2001).

In the event that specific elements were detected during leach testing with no mineral corresponding in the XRD analysis, saturation indices were calculated for specific secondary minerals which may not have been detected by the XRD analysis due to their amorphous nature. Acid-base accounting was also used in this regard to motivate the presence of certain minerals which were undetected by XRD.

Once the mineral assemblage, reaction rates and reactive surface areas were defined, the laboratory leach testing scenario was simulated to calibrate the mineral assemblage. The final simulated concentrations were then correlated with the final leaching test concentrations and if a statistically significant correlation existed ($R^2 > 0.8$, $\alpha = 0.95$) the assemblage was considered to be calibrated. To obtain this correlation, a trial and error approach was used for the geochemical model by adjusting parameters within statistical boundaries to obtain a representative mineral assemblage.

Upon successful calibration of the identified mineral assemblage to the leaching test data, the natural geochemical reaction on site was simulated. Inflow volumes into the opencast mine were obtained from a pre-constructed MODFLOW model. These volumes were then compared to the volume and porosity of each pit to determine the natural fluid to rock ratios over time. The natural conditions on site were then simulated in the geochemical model to provide input to a numerical transport model for a period covering the available groundwater monitoring data for the site.

Inputs generated from the geochemical model were integrated into the numerical transport model using a stress period approach to simulate the conditions within the backfilled opencast mine. The resulting transport solution was then compared to the monitoring data using an error summary graph. This was performed using a trial and error approach, with a successful transient chemical calibration indicating reliability of the geochemical model. In the event that calibration was not achieved, parameters such as oxygen fugacity and fluid to rock ratios within the geochemical model were revised to obtain a more representative input to the transport model. Once transient chemical calibration was achieved within the transport model, long term sulfate concentrations were simulated beyond the period covered by monitoring data to determine potential future environmental effects.

Results

The backfill material consists of quartz, muscovite, K-feldspar, kaolinite, plagioclase, hematite and smectite. Additional minerals assumed to be present, based on visual inspection, acid-base accounting and saturation index calculations, were gypsum and pyrite. The mean mineral abundances, standard errors, reaction rate constants and reactive surface areas (Table 1) were defined using the kinetic reactant function of GWB. The model was calibrated against leaching test constituent concentrations (Table 2).

To calibrate the geochemical model, the distilled water leach tests performed on the material samples, were simulated. Therefore, the mineral assemblage identified in the XRD analysis as well as the subsequent reactive surface areas and rate constants were specified in the model. Leaching of this assemblage by distilled water for 20 h in a 1:4 rock to water ratio was simulated. Simulated concentrations leaching from the mineral assemblage in the geochemical model were then compared

to the analysed concentrations from the leaching test (Figure 2). The regression line fitted to the data indicated a coefficient of determination of 0.9943.

Table 1 Mineral Weight Percentage Statistics

Mineral Phase Based on Analysis Data	Mean Weight Percentage	Standard Deviation of the Mean Mineral Weight Percentage	Standard Error of the Mean Mineral Weight Percentage	Initial Reaction Rate Constant $(mol \cdot cm^{-2} \cdot s^{-1})$	Initial Reactive Surface Area $(cm^2 \cdot g^{-1})$[#]
Hematite	0.77	0.46	0.19	5×10^{-11} [a]	57
Kaolinite	16.56	8.32	3.39	1×10^{-17} [b]	58
K-Feldspar	10.87	2.57	1.05	1.7×10^{-17} [c]	58
Muscovite	6.01	1.59	0.65	2.9×10^{-15} [d]	53
Plagioclase	2.03	4.53	1.85	1.0×10^{-16} [e]	55
Quartz	45.25	11.15	4.55	5.0×10^{-14} [f]	22
Smectite	36.22	2.26	0.92	3.0×10^{-15} [g]	60
Mineral Phase Assumed Present				Reaction Rate Constant $(mol \cdot cm^{-2} \cdot s^{-1})$	
Pyrite	0.03*			2.8×10^{-12} [h]	104
Gypsum	0.05*			1.3×10^{-04} [i]	26

[a]Hersman et al. (1995); [b]Huertas et al. (1999); [c]Oelkers and Schott (1998); [d]Oelkers et al. (2008); [e]Gudbrandsson et al. (2014); [f]Gautier et al. (2001); [g]Marty et al. (2015); [h]Malmström et al. (2006); [i]Jeschke et al. (2001); *Estimated based on field observations, acid-base accounting, saturation indices and literature reaction rate constants; [#]Calculated from sample average grain size and mineral density, assuming entire surface is available for reaction. See Brantley (1998); Gautier et al. (2001); and White and Brantley (2003).

Table 2 Chemical Constituent Concentration Statistics, all concentrations in mg/L, TDS: Total Dissolved Solids

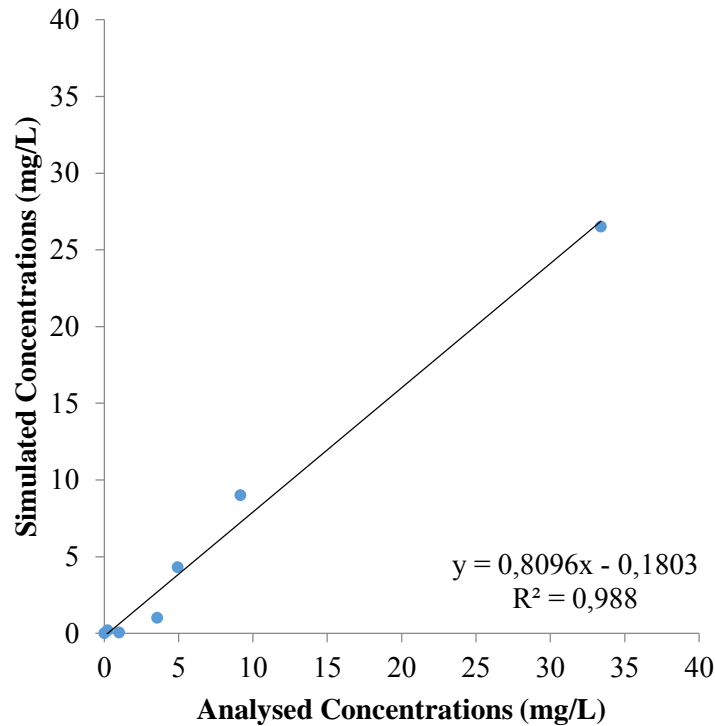| Chemical Constituent	Mean Concentration	Standard Deviation of Element Concentrations	Standard Error of Element Concentrations
Al	0.23	0.42	0.17
Ca	9.17	14.30	5.84
Fe	0.14	0.30	0.12
K	3.55	2.22	0.91
Mg	4.67	4.89	1.99
Mn	1.38	3.08	1.26
Na	2.67	1.37	0.56
Si	4.93	2.29	0.94
TDS Calculated	90.83	115.49	47.15
Alkalinity (CaCO3 eq.)	0.00	0.00	0.00
Cl	1.00	2.45	1.00
SO_4	33.40	70.34	28.72
NO_3	0.25	0.22	0.09
pH	4.92	0.75	0.30

Figure 2 Correlation Graph of Average Constituent Concentrations Measured During Leaching Test Analyses vs. Constituent Concentrations Simulated in a Geochemical Model Simulating the Leaching Test Procedure

After simulation of the leaching test, the natural conditions on site were simulated in the geochemical model for the period of groundwater monitoring. The resulting solution was integrated with the transport model as specified. The transport simulation was performed for the period which monitoring data was available. Once the simulation was completed, a transient calibration graph was constructed to determine how well the simulated sulfate concentrations compared to monitoring data. An error range of 50 mg/L was used as concentrations of sulfate observed in the monitoring wells reach levels of over 500 mg/L in some areas. Therefore, a 10% error of the monitoring concentrations for sulfate was deemed applicable (Figure 3). Results show that most of the simulated concentrations were within the specified error margin, for the simulated time period. The initial flush breakthrough curve can also be observed in certain monitoring points. Based on the chemical calibration of the numerical transport model, representative input of sulfate into the model was assumed. Therefore, long term sulfate transport could be simulated in an attempt to determine the sulfate concentrations that could potentially be released from the rehabilitated opencast mines in the long term.
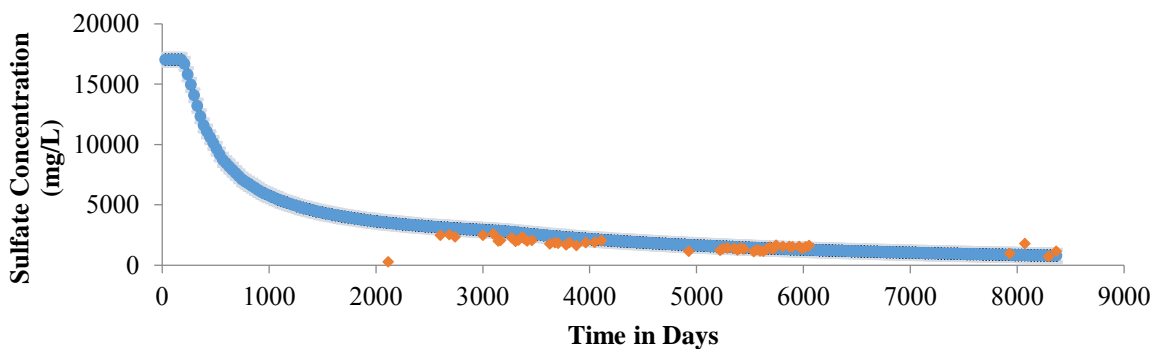

Figure 3 Example of Simulated Sulfate Concentrations at an Observation Well in the Numerical Flow Model vs. Measured Sulfate Concentrations Obtained from Monitoring Data for the Same Well in Reality (Blue dots indicate simulated concentrations. Red diamonds indicate measured concentrations).

Discussion

Modelled constituent concentrations in the geochemical and numerical models corresponded well with measured concentrations within the identified error ranges, especially in areas with higher sulfate concentrations. This shows that the focus of this modelling method depends on the controlling parameters of the site geochemistry. Pyrite oxidation and weathering, as well as carbonate mineral weathering were identified as the main controls on solution pH and chemistry, with major mineralogy playing a secondary role. Therefore, the calibration of pH and sulfate is essential for modelling representative values and was the main focus of geochemical model calibration. As pyrite and carbonate mineral weathering are the primary controls on mine water chemistry in the Mpumalanga coalfields, the correspondence of the modelled and measured constituent concentrations is explicable. Further to the identification of the primary controls on the mine water chemistry is the enhancement of calibration accuracy with abundant measured data. As a large monitoring data set was available, it was deduced that monitoring data plays an essential role in the prediction of long term mine water chemistry. This observation is based on clearer concentration trends observed over longer periods, which gives a better indication of how calculated concentration trends should behave if they are based on defensible model inputs.

Conclusions

Findings in this study illustrate that a simplified conceptual model as well as an improved understanding of mineralogy and geochemistry in decommissioned opencast mines can provide improved prediction of transient mine water chemistry. Constant source modelling and acid-base accounting can be regarded as a worst-case estimate but may prove less useful in a closure and mine water management scenario. Therefore, this methodology can be employed to provide an improved estimate of the initial flush from opencast mines as well as its subsequent duration and concentrations. This data can in turn be used to plan mitigation measures to be implemented for realistic time frames, as mining wastes are decaying contaminant sources and should therefore be treated as finite. Although defensible results have been obtained in this study, further refinement is achievable. It is suggested that the influence of microbiology as well as transient meteorological conditions be integrated into future modelling processes to improve calculations. Based on refined models, improved rehabilitation techniques and mine water management measures can be developed possibly turning opencast mines from sources of contamination to functional groundwater reservoirs.

References

Appelo CAJ, Postma D (2005) Geochemistry, groundwater & pollution, 2nd edn. Balkema, Leiden

Banks D (1994) The Abandonment of the Killingdal Sulphide Mine, Norway: a Saga of Acid Mine Drainage and Radioactive Waste Disposal. Mine Water Environ 13:35-48

Bethke CM (2008) Geochemical and Biogeochemical Reaction Modeling. Cambridge University Press, New York

Brantley SL (1998) Surface area and porosity of primary silicate minerals. Paper presented at the Goldschmidt Conference Toulouse, 62A:229-230.

Gautier JM, Oelkers EH, Schott J (2001) Are quartz dissolution rates proportional to B.E.T. surface areas? Geochim Cosmochim Acta 65(7):1059-1070

Gudbrandsson S, Wolff-Boenisch D, Gislason SR, Oelkers EH (2014) Experimental determination of plagioclase dissolution rates as a function of its composition and pH at 22°C. Geochim Cosmochim Acta 139(0):154-172. doi:http://dx.doi.org/10.1016/j.gca.2014.04.028

Gzyl G, Banks D (2007) Verification of the "first flush" phenomenon in mine water from coal mines in the Upper Silesian Coal Basin, Poland. J Contam Hydrol 92(1-2):66-86. doi:10.1016/j.jconhyd.2006.12.001

Hersman L, Lloyd T, Sposito G (1995) Siderophore-promoted dissolution of hematite. Geochim Cosmochim Acta 59(16):3327-3330. doi:http://dx.doi.org/10.1016/0016-7037(95)00221-K

Huertas FJ, Chou L, Wollast R (1999) Mechanism of kaolinite dissolution at room temperature and pressure Part II: kinetic study. Geochim Cosmochim Acta 63(19–20):3261-3275. doi:http://dx.doi.org/10.1016/S0016-7037(99)00249-5

Jeschke AA, Vosbeck K, Dreybrodt W (2001) Surface controlled dissolution rates of gypsum in aqueous solutions exhibit nonlinear dissolution kinetics. Geochim Cosmochim Acta 65(1):27-34. doi:http://dx.doi.org/10.1016/S0016-7037(00)00510-X

Malmström ME, Gleisner M, Herbert RB (2006) Element discharge from pyritic mine tailings at limited oxygen availability in column experiments. Appl Geochem 21(1):184-202. doi:http://dx.doi.org/10.1016/j.apgeochem.2005.09.006

Marty NCM, Claret F, Lassin A, Tremosa J, Blanc P, Madé B, Giffaut E, Cochepin B, Tournassat C (2015) A database of dissolution and precipitation rates for clay-rocks minerals. Appl Geochem 55(0):108-118. doi:http://dx.doi.org/10.1016/j.apgeochem.2014.10.012

Oelkers EH, Schott J (1998) Does organic acid adsorption affect alkali-feldspar dissolution rates? Chem Geol 151(1–4):235-245. doi:http://dx.doi.org/10.1016/S0009-2541(98)00082-5

Oelkers EH, Schott J, Gauthier J-M, Herrero-Roncal T (2008) An experimental study of the dissolution mechanism and rates of muscovite. Geochim Cosmochim Acta 72(20):4948-4961. doi:http://dx.doi.org/10.1016/j.gca.2008.01.040

Pinetown KL, Ward CR, van der Westhuizen WA (2007) Quantitative evaluation of minerals in coal deposits in the Witbank and Highveld Coalfields, and the potential impact on acid mine drainage. Int J Coal Geol 70(1-3):166-183. doi:10.1016/j.coal.2006.02.013

Vermeulen PD, Usher BH (2005) Sulphate generation in South African underground and opencast collieries. Env Geol 49(4):552-569. doi:10.1007/s00254-005-0091-2

White AF, Brantley SL (2003) The effect of time on the weathering of silicate minerals: why do weathering rates differ in the laboratory and field? Chem Geol 202(3-4):479-506. doi:10.1016/j.chemgeo.2003.03.001

Whitehead P, Jeffrey H (1995) Heavy metals from acid mine drainage – impacts and modelling strategies. In: Petts GE (ed) Man's Influence on Freshwater Ecosystems and Water Use. vol 230. International Association of Hydrological Sciences, Wallingford, p 55-56

Younger PL (2000) Predicting temporal changes in total iron concentrations in groundwaters flowing from abandoned deep mines: a first approximation. J Contam Hydrol 44:47-69

Younger PL (2001) Mine water pollution in Scotland: nature, extent and preventative strategies. Sci Total Environ 265:309-326

Younger PL, Robins NS (2002) Challenges in the characterization and prediction of the hydrogeology and geochemistry of mined ground. Spec Publ – Geol Soc London 198(1):1-16. doi:10.1144/gsl.sp.2002.198.01.01

Younger PL, Sapsford DJ (2004) Evaluating the potential impact of opencast coal mining on water quality (Groundwater Regulations 1998) An assessment framework for Scotland. Scottish Environmental Protection Agency, Scotland, p 1-75