Mine Water Environ (2009) 28:74–78
DOI 10.1007/s10230-008-0062-4

TECHNICAL COMMUNICATION

Prediction of Minerals Producing Acid Mine Drainage Using a Computer-Assisted Thermodynamic Chemical Equilibrium Model

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Received: 3 November 2008 / Accepted: 17 December 2008 / Published online: 22 January 2009

Abstract Methods such as optical microscopy, electron microscopy, and X-ray diffraction are sometimes used to identify minerals involved in the production of acid mine drainage (AMD). A simpler method to identify the minerals without losing accuracy would decrease costs. This paper presents an overview of the important oxidation reactions of sulphide minerals and related chemical components produced by these oxidation reactions. A methodology for predicting the minerals producing AMD using MINTEQ is also discussed. This method can be used in conjunction with analytical techniques to characterize AMD for a specific site. While it does not replace analytical tests, it can decrease the number and frequency of these expensive tests. The model has been validated with data from the Wolverine coal mine in northeastern BC, Canada.

Keywords Acid generation · Chemical components · Coal mine · Minerals · Oxidation reactions

Introduction

Acid mine drainage (AMD) is characterized by elevated acidity, high concentration of sulphate, and metals such as Fe, Cu, Zn, Co, Cr, Mn, Pb, Cd, etc. (Nieto et al. 2007). AMD is produced from mine waste rock, tailings, mine pits, and underground workings, and its composition is affected by the local rock materials and the availability of water and oxygen. Mineralogy and other factors affecting AMD production are highly variable from site to site; therefore, prediction of AMD potential can be challenging and costly (USEPA 1994). This paper provides readers who are relatively new to the field a brief review of the reactions that take place in AMD and typical minerals that participate in AMD production. The paper also provides a methodology to identify and characterize AMD based on transport modeling. This information could be used in conjunction with analytical AMD characterization methods to better predict the composition of AMD. Finally, the Wolverine coal mine in BC, Canada is used as a case study to validate the methodology.

Typical AMD Reactions

Iron sulphides are the underlying cause of most AMD production (Akcil and Koldas 2006). Pyrite oxidation is initiated according to reaction 1a in Table 1 (Ravengai et al. 2004; Sherriff et al. 2007). In this reaction, both the Fe and S are oxidized. When sufficient oxygen is dissolved in the water, the oxidation of ferrous (Fe^{+2}) to ferric (Fe^{+3}) iron occurs (reaction 11). The Fe^{3+} produced in this reaction can precipitate as ochre (an iron oxide compound of reddish-brown to yellow colour) by reaction 12. In this process, more hydrogen ions are released into the environment; this may lead to pH reduction (Romano et al. 2003; Lonesiy 2006). It should be noted that $Fe(OH)_3$ is not stable at a pH below 3.5, where Fe^{3+} remains in solution (Dold 2005).

The Fe^{3+} may react with pyrite (as an oxidant) to produce more Fe^{+2} and acidity (reaction 1b). Fe^{+3} is a strong oxidant of FeS_2 at low pH where oxidation of Fe^{+2} to Fe^{3+} is catalyzed by bacteria. However, at moderate pH,

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Table 1 Selected oxidation reactions for mine tailing with oxygen and iron (Fe^{3+})

Mineral		Oxidation reactions
(1a)	Pyrite (by oxygen)	$FeS_{2(S)} + 3.5O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4{}^{2-} + 2H^+$
(1b)	Pyrite (by iron)	$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 2SO_4^{-2} + 15Fe^{+2} + 16H^+$
(2a)	Marcasite (by oxygen)	Same as pyrite
(2b)	Marcasite (by iron)	Same as pyrite
(3a)	Chalcopyrite (by oxygen)	$CuFeS_{2(S)} + 4O_{2(aq)} \rightarrow Cu^{2+} + Fe^{2+} + SO_4{}^{2-}$
(3b)	Chalcopyrite (by iron)	$CuFeS_{2(S)} + 16Fe^{3+} + 8H_2O \rightarrow Cu^{2+} + 17Fe^{2+} + 2SO_4{}^{2-} + 16H^+$
(4a)	Pyrrhotite (by oxygen)	$Fe_{(1-x)}S + (2 - 0.5x)\ O_2 + x\ H_2O \rightarrow (1 - x)\ Fe^{2+} + SO_4{}^{2-} + 2xH^+$
(4b)	Pyrrhotite (with iron)	$Fe_{(1-x)}\ S + (8 - 2x)\ Fe^{3+} + 2H_2O \rightarrow (9 - 3x)Fe^{2+} + SO_4{}^{2-} + 8H^+$
(5a)	Arsenopyrite (with oxygen)	$FeAsS + 13/4\ O_2 + 3/2\ H_2O \rightarrow Fe^{2+} + SO_4{}^{2-} + H_2AsO_4{}^- + H^+$
(5b)	Arsenopyrite (with iron)	$FeAsS_{(S)} + 14Fe^{3+} + 7H_2O \rightarrow 15Fe^{2+} + SO_4{}^{2-} + H_3AsO_{3(aq)} + 14H^+$
(6a)	Sphalerite (with oxygen)	$ZnS_{(s)} + 2O_{2(aq)} \rightarrow Zn^{2+} + SO_4{}^{2-}$
(6b)	Sphalerite (with iron)	$ZnS_{(S)} + 8Fe^{3+} + 4H_2O \rightarrow Zn^{2+} + SO_4{}^{2-} + 8Fe^{2+} + 8H^+$
(7a)	Covellite (with oxygen)	$CuS_{(S)} + 2O_{2(aq)} \rightarrow Cu^{2+} + SO_4{}^{2-}$
(7b)	Covelite (with iron)	$CuS(s) + 8Fe^{3+} + 4H_2O \rightarrow Cu^{2+} + SO_4{}^{2-} + 8Fe^{2+} + 8H^+$
(8a)	Millerite (with oxygen)	$NiS_{(S)} + 2O_{2(aq)} \rightarrow Ni^{2+} + SO_4{}^{2+}$
(8b)	Millerite (with iron)	$NiS(s) + 8Fe^{3+} + 4H_2O \rightarrow Ni^{2+} + SO_4{}^{2-} + 8Fe^{2+} + 8H^+$
(9a)	Greenockite (with oxygen)	$CdS_{(S)} + 2O_{2(aq)} \rightarrow Cd^{2+} + SO_4{}^{2-}$
(9b)	Greenockite (with iron)	$CdS(s) + 8Fe^{3+} + 4H_2O \rightarrow Cd^{2+} + SO_4{}^{2-} + 8Fe^{2+} + 8H^+$
(10a)	Galena (with oxygen)	$PbS_{(S)} + 2O_{2(aq)} \rightarrow Pb^{2+} + SO_4{}^{2-}$
(10b)	Galena (with iron)	$PbS_{(S)} + 8Fe^{3+} + 4H_2O \rightarrow Pb^{2+} + SO_4{}^{2-} + 8Fe^{2+} + 8H^+$
Oxidation of ferrous iron (Fe^{2+}) and precipitation of ferric hydroxide ($Fe(OH)_3$)		
(11)	Ferrous iron oxidation	$Fe^{+2} + 1/2O_2 + 2H^+ \rightarrow 2Fe^{+3} + H_2O$
(12)	Ferric iron precipitation	$3Fe^{3+} + H_2O \rightarrow Fe(OH)_{3\ (s)} + 3H^+$

oxidation of pyrite by Fe^{3+} is less significant and pyrite oxidation is via O_2.

Other sulphide minerals also react with O_2 and produce acidity. The reaction of pyrrhotite, chalcopyrite, arsenopyrite, and marcasite with O_2 are shown in Table 1 as reactions 2a, 4a, and 5a, respectively. Other sulphides can oxidize and release metal iron into solution, but may not produce acidity. Examples of such reactions can be seen as reactions 3a, 6a, 7a, 8a, 9a, and 10a in Table 1 (Costello 2003; Da Silva et al. 2003); sphalerite and galena are the most important of these minerals. However, different oxidants produce different products. For example, the oxidation of sphalerite by Fe^{3+} can be seen in reaction 6b in Table 1. Although sphalerite oxidation by the oxygen path does not produce acidity, oxidation via Fe^{3+} does produce acidity.

Identifying the Minerals Producing AMD

Due to the complex nature of AMD, no specific methodology is standard for qualitative and quantitative characterization of AMD formation. Optical and scanning electron microscopes (SEM) are often used for mineral matter characterization. Although these techniques are widely used for identifying and characterizing different minerals, the low resolution of optical microscopes for a particle size less than 5–10 µm is a major problem. Many minerals, particularly clay and accessory minerals, with a grain size less than 5–10 µm cannot be identified and characterized. SEM decreases the problematic grain size by an order of magnitude, but this is still a problem for many accessory minerals in coal (Kortenski 1992; Vassilev and Tascon 2003).

One of the most common and useful methods for identifying minerals is X-Ray diffraction (XRD) (Yaman et al. 2001). This technique is useful for the detection of different minerals (Pollack 1979), although factors such as different absorption characteristics and crystallite size may reduce the degree of accuracy. The method is costly, needs a degree of interpretation, and therefore highly trained personnel. However, identification of many minerals by only XRD is not possible, and so this technique is used in conjunction with other techniques such as separation procedures, optical, and scanning electron microscopy. Though these tests are important and necessary, the number of analyses and cost could be decreased by coupling the analyses with a methodology that employs equilibrium and transport models. In addition, these tests tell us little on how the minerals will react and transform in the pond. In

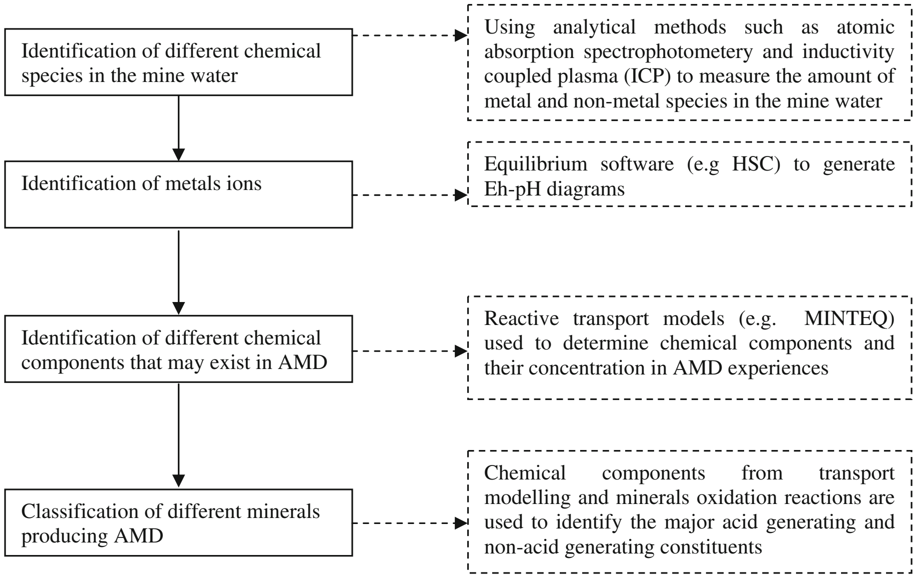

Fig. 1 Different steps for characterization of AMD and identifying the minerals that produce AMD

this paper, a methodology is presented to identify and characterize the minerals, their oxidation reactions producing AMD, and chemical components in AMD. The overall method is presented in Fig. 1 and detailed below.

Sulphides oxidize and generate an acidic leachate that can act as an agent carrying heavy metals and dissolved salts. Analytical methods such as atomic absorption spectrophotometery and inductivity coupled plasma (ICP) are used to measure the amount of metal and non-metal species in the mine water. It should be noted that the pH, temperature, and alkalinity of the specific AMD should be measured to assess how the chemical species will exist in the specific mine water.

The major metals and non-metals in AMD exist in different forms, e.g. iron as Fe^{2+} or Fe^{3+}, according to the conditions that exist at the mine site. Eh–pH diagrams (also called Pourbaix diagrams) have been in use for more than 30 years (Garrels and Christ 1965) to illustrate thermodynamic stability of chemical species in terms of the activity of hydrogen ions (pH) and the activity of electrons (Eh).

HSC chemistry software (Roine 2002) is one of several packages that generate Eh–pH diagrams and was used in this study to determine conditions where chemical constituents may be thermodynamically favoured over others. For instance, according to the Eh–pH diagram for different iron species, at a pH of approximately 7 and equilibrium conditions, Fe can be assumed to be present as Fe^{2+} (Ball et al. 1999).

After identifying chemical constituents in the AMD from equilibrium, the chemistry as a result of chemical reaction equilibria and transport in AMD are evaluated. To this end, computer-assisted thermodynamic chemical equilibrium models are useful tools to predict the behaviour of chemical system. MINTEQ is one of these chemical equilibrium models. MINTEQ is geochemical equilibrium speciation software for dilute solution and calculates mass distribution between dissolved, adsorbed, and gas phases. Using the information on chemical composition generated in the previous steps, along with pH, specific ionic strength, and alkalinity, MINTEQ can provide all of the possible chemical components that may exist in the AMD.

Then, the information from MINTEQ can be used to classify chemical constituents as acid producing or non-acid producing and acid consuming or non-acid consuming. This classification assists in identifying the important oxidizing processes. Finally, according to different reactions described in the introduction and evaluating the chemical components received by MINTEQ, the key minerals and reactions are identified. This information is key to efficient water management.

Application of AMD Characterization at the Wolverine Coal Mine: A Case Study

The Wolverine (Perry Creek) coal mine, located 23 km west of Tumbler Ridge in northeastern BC, Canada, was used to verify this methodology (Yukon Zinc Corporation and AXYS Environmental Consulting Ltd 2005). The water quality at this mine site during operation is shown in Table 2.

In this step, the HSC software is used to generate the Eh–pH diagrams for the mine AMD (the pH of the mine water is 7.4). As an example, the Eh–pH diagram for iron can be seen in Fig. 2. After identifying all possible metals and ions, MINTEQ (Version 2.52) is used to predict the possible minerals in the AMD based on the major reactions.

Table 2 Wolverine AMD parameters and dissolved metals in mg/L

Parameter	Concentration	Parameter	Concentration	Parameter	Concentration	Parameter	Concentration
Cond. (uS/cm)	1,860	Thio.	452	Cr	0.00125	P	0.08
Ph	7.4	Ag	0.0113	Cu	0.0267	Pb	0.0166
TDS	1,510	Al	0.07	Fe	0.03	Sb	0.0216
TSS	31	As	0.012	Hg	0.000075	Se	1.825
Acidity*	365	Ba	0.3485	K	10	Si	0.35
Alkalinity*	37	Be	0.0038	Li	0.0038	Sn	0.007
Hardness*	452	B	0.019	Mg	4.97	Sr	0.293
F	0.25	Bi	0.00023	Mn	0.0165	Ti	0.0023
Cl	19	Ca	175	Mo	0.03015	Tl	0.0056
NO_3	0.22	Cd	0.002	Na	201	U	0.0003
SO_4	605	Co	0.0008	Ni	0.014	V	0.0005
CN(T)	0.02	CNO	1.85	CNS	3.7	Zn	0.024

* In mg/L as $CaCO_3$

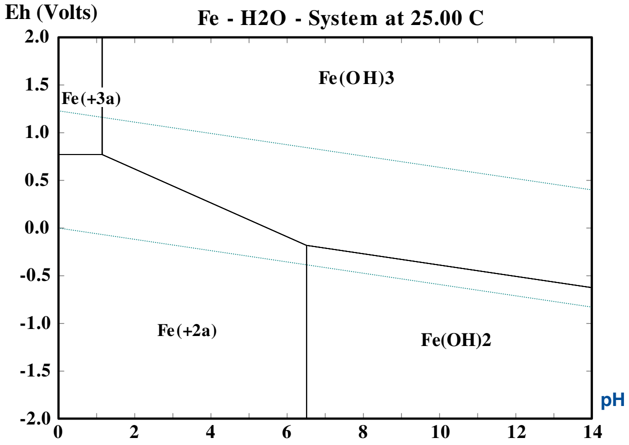

Fig. 2 Eh–pH diagram for Fe (iron) at 25°C

Table 3 Typical minerals in Wolverine coal mine

Chemical components	Chemical formula	Acid producing condition
Pyrite	FeS_2	Acid forming sulphide
Pyrrhotite	$Fe_{0.95}S$	Acid forming sulphide
Arsenopyrite	FeAsS	Acid forming sulphide
Sphalerite	ZnS	Acid forming sulphide
Chalcopyrite	$CuFeS_2$	Acid forming sulphide
Chalcocite	Cu_2S	Non-acid forming sulphide
Galena	PbS	Non-acid forming sulphide

The results of MINTEQ outline the following acid forming minerals as present in the Wolverine AMD: pyrite, pyrrhotite, chalcopyrite, marcasite, and sphalerite (Table 3). How the MINTEQ output was used to determine the presence of these minerals is outlined below.

The acidity stems principally from the oxidation of pyrite and the hydrolysis of the oxidation products (iron sulphates). The oxidation process (reactions 1–5, Table 1) produces acidity where O_2 and water are the oxidizing agents. The ferrihydrite ($Fe(OH)_3$) produced in these oxidation processes would not be stable at very low pH, but it is more stable at a pH of approximately 8. The oxidation of pyrite and pyrrhotite produces $Fe(OH)_3$ and acidity; therefore, it is likely that one or both of these minerals are present. Arsenopyrite is also expected to yield acid according to reaction 5b in Table 1. The existence of AsO_4^{3-} in the output of MINTEQ for this mine site indicates the likely existence of arsenopyrite. Acid generation is also demonstrated by chalcopyrite (reaction 3b, Table 1). Finally, sphalerite is an acid-generating sulphide mineral with an indefinite composition ((Zn, Fe)S). The oxidation of sphalerite may produce acidity (reaction 6a, Table 1). The existence of $Zn(OH)_2$ indicates the likely presence of sphalerite in the Wolverine coal AMD, which is confirmed by other studies as well (Schroeter et al. 2001).

Minerals such as chalcocite and galena, which sometimes occur in coal mines, oxidize, but do not produce acidity. The concentrations of Cu and Pb, though relatively low, indicate the likely presence of chalcocite and galena. The minerals identified by this process were all found at the Wolverine coal mine (Schroeter et al. 2001; Matthews et al. 2008).

Conclusion

AMD impacts the surrounding ecosystem and therefore must be properly managed. Determining the likely chemical nature of AMD is critical in water management and treatment system design. Analytical methods to determine mineral content are time consuming and costly. A methodology is proposed to decrease the requisite number of analyses using predictive models to determine the possible presence of problematic minerals. This methodology can assist in directing analysis of the wastewater, focusing attention on important or key components for analysis rather than a carte blanche approach. In addition, it could assist with the interpretation of the analytical output and thereby reduce analytical costs. After finding possible metal and non-metal species in the mine water, HSC chemistry software is used to generate Eh–pH diagrams. These diagrams help identify the key metals and oxidative state. This information is used to elucidate the chemical analyses of the AMD to determine the oxidative state of the metals measured. Finally, chemical reaction equilibrium models are used to determine possible mineral sources of in the AMD, based on input from the previous steps. This is critical as it will identify major acid producing/consuming minerals present and thereby help determine the optimal water management and treatment system. This method must be used in conjunction with analytical methods.

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