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TECHNICAL ARTICLE

A Model for Prediction of Neutralizer Usage and Sludge Generation in the Treatment of Acid Mine Drainage from Abandoned Mines: Case Studies in Japan

Ryu Koide · Chiharu Tokoro · Shinsuke Murakami · Tsuyoshi Adachi · Akihiro Takahashi

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Abstract Acid mine drainage (AMD) from about 80 abandoned or closed mines in Japan are actively treated by neutralization; the government spends billions of yen every year to protect the environment from these discharges, and treatment will have to continue for many years. However, it is difficult to predict the future AMD chemistry, neutralizer requirements, and volume of sludge to establish future costs, chemical inputs, and wastes. The water monitoring data or source rock samples for conventional predictive methods are not available. In this study, a predictive model for AMD composition and the neutralization process was constructed based on geochemical modeling, assuming first order kinetics for the dissolution of several minerals. The solution composition, neutralizer requirements, and sludge generation were estimated for case studies at two abandoned mines in Japan: a sulfur mine, and a copper and iron mine. The model effectively predicted AMD composition after termination of mining and was also useful for estimating future neutralizer requirements and sludge volumes. This research will increase understanding of the lifecycle environmental costs in the mining industry.

Keywords First order kinetic model · Geochemical modeling · Mine pollution · Predictive model

Introduction

Acid mine drainage (AMD) is a major source of mining pollution worldwide (Johnson and Hallberg 2005; Sheoran et al. 2010; Wolkersdorfer and Bowell 2004; 2005a, b). There are about 7,000 abandoned or closed mines in Japan and AMD has been observed at about 450 of these mines (JOGMEC 2003); neutralization facilities are currently being operated at about 80 of them (METI 2006a). At some mines, the companies responsible for the mine no longer exist and treating the AMD is now the responsibility of the local and national governments. From 1973 to 2003, 181 of these mines had received anti-pollution assistance funds from Japan's Oil, Gas and Metals National Corporation (JOGMEC), which is the national agency responsible for mine pollution control (JOGMEC (Japan Oil, Gas and Metals National Corporation) 2003). The government subsidies for these anti-pollution measures cost more than two billion yen (18 million US dollars) in 2005 (METI (Ministry of Economy, Trade and Industry 2006a).

At-source control (prevention) and wastewater treatment are used to avoid severe pollution downstream of abandoned or closed mines. Mine water treatment requires a large amount of alkaline neutralizers, such as slaked lime,

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R. Koide · A. Takahashi
Department of Resources and Environmental Engineering,
Waseda University, 3-4-1 Okubo, Shinjuku-ku,
Tokyo 169–8555, Japan

C. Tokoro (✉)
Faculty of Science and Engineering, Waseda University,
3-4-1 Okubo, Shinjuku-ku, Tokyo 169–8555, Japan
e-mail: tokoro@waseda.jp

S. Murakami
Graduate School of Engineering, University of Tokyo,
7-3-1 Hongo, Bunkyo-ku, Tokyo 113–8656, Japan

T. Adachi
International Center for Research and Education
on Mineral and Energy Resources, Akita University,
1–1 Tegata Gakuen-machi, Akita-shi, Akita 010–8502, Japan

as well as a flocculating agent, and a substantial amount of energy, and must be sustained for many years. The neutralization process also generates large volumes of metal hydroxide sludge. Passive treatment methods can reduce chemical inputs and waste generation (Gazea et al. 1996; Johnson and Hallberg 2005; Warrender et al. 2011; Wolkersdorfer 2011; Ziemkiewicz et al. 2003), but is difficult to implement at many abandoned or closed mines in Japan because of limited land availability.

Geographical, paleo-environmental, and geochemical tests and mathematical models have generally been used to predict AMD (Ferguson and Erickson 1998; Jennings et al. 2008). Most research has focused on qualitative predictions using geochemical tests, such as static tests based on acid–base accounting, NAG/pH, or kinetic leaching methods (Akabzaa et al. 2007; Perry 2000; White and Jeffers 1994). Although these are very useful for assessing potential AMD generation at a new or active mine, it is extremely difficult to acquire samples of source rocks after a mine has been closed and flooded. In addition, these methods cannot be used to estimate the volume and composition of future AMD or possible treatment costs. Although several mathematical modeling studies have been conducted, their application and validation are limited, especially for future prediction of AMD (Ferguson and Erickson 1998; Jennings et al. 2008).

In Japan, most of the mines where AMD is treated are abandoned or closed mines, which typically ceased operating more than 40 years ago. For these mines, information such as mineral deposit characterization, hydrological characterization, and mine design is often unavailable or no longer relevant. Even when the mine designs are available, changes that may have taken place limit their usefulness. As these mine pits can be devastated or submerged, rock samples for geochemical tests are difficult to acquire, and in the absence of the companies responsible, it is not feasible to conduct large-scale investigations to acquire additional data to characterize the mines. The only commonly available current data is water quality records.

Generally, neither the government nor the companies responsible have a clear idea of when neutralization treatment can be terminated, how much neutralizer will be needed, and how much sludge will be generated. This inability to make reliable predictions for future treatment costs makes it difficult for policy makers or corporate administrators to understand the total costs associated with AMD treatment and to develop a clear strategy for future treatment.

The objective of this study was to construct a model based on a first-order kinetics curve for abandoned or closed mines that could be used to predict the amount of neutralizer inputs and sludge generation required for active neutralizing treatment using only water monitoring data. The model outputs would predict when treatment could be terminated, allowing the user to evaluate the future costs associated with AMD treatment and to develop a better AMD management strategy. The model was applied to two case studies: an abandoned sulfur mine and an abandoned copper mine. From these case studies, the parameters of the predictive model were estimated, and the future AMD composition, including inorganic contaminant concentrations and pH, was predicted. From these results, the future and historical total neutralizer use and sludge generation for neutralization treatment using limestone or lime were estimated. The model was validated using comparisons between measured and estimated historical data for neutralizer requirements and sludge generation.

Materials and Methods

Predictive Model

The model that was developed involves: preparation of input data; regression analysis based on first-order kinetics; solution composition simulation; and neutralization simulation. The input data included historical water quality data from monitoring of inorganic contaminant concentrations and pH. First, the contaminant concentrations and pH data were converted into absolute amounts of source rocks leached per unit time; infrequent data were supplemented using the Phreeqc software (Parkhurst and Appelo 1999) and the Minteq.v4 database (US Geological Survey 2005). Second, a multiple regression analysis was conducted, assuming first-order kinetics, using the statistical analysis software, R (Venables et al. 2011), to estimate the amount of source rocks likely to be leached at any point in the future. Next, the solution composition was simulated using Phreeqc and the Minteq.v4 database. Finally, the neutralizer use and sludge generation during the AMD treatment process were predicted from geochemical simulations using Phreeqc and the Minteq.v4 database, based on the AMD volume and composition data obtained in the earlier steps, assuming chemical equilibrium and the oxidation state of each element present. The methods for each step are discussed in more detail later in this paper.

Preparation of Input Data

Regression analysis, assuming first-order kinetic curves, was conducted for each type of source rock that was being leached. We made assumptions about the types of source rocks to predict the concentrations of various elements in the AMD. Abbassi et al. (2009) presented a list of sulfide minerals that produce AMD. The source rocks considered in this study, and their reaction pathways, are shown in

Table 1 Selected AMD mineral leaching reactions in this study

Mineral	Reactions
Pyrite	$FeS_2(s) + 7/2\ O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+$
Chalcopyrite	$CuFeS_2(s) + 4O_2 \rightarrow Cu^{2+} + Fe^{2+} + 2SO_4^{2-}$
Arsenopyrite	$FeAsS(s) + 13/4\ O_2 + 3/2\ H_2O \rightarrow Fe^{2+} + SO_4^{2-} + H_2AsO_4^- + H^+$
Sphalerite	$ZnS(s) + 2O_2 \rightarrow Zn^{2+} + SO_4^{2-}$
Sulfur	$S(s) + 3/2\ O_2 + H_2O \rightarrow SO_4^{2-} + 2H^+$

Table 1. Aluminum is leached from aluminum-containing minerals, such as aluminosilicate or gibbsite. However, in this study, a regression analysis was not conducted for these minerals because the concentration of dissolved aluminum was too low to affect the predicted neutralizer requirements and sludge generation results. Other reaction paths, such as oxidation reactions mediated by bacteria or Fe(III), are also not shown in Table 1 because these reaction paths would not affect the results of the chemical equilibrium simulation.

Data that were not available were supplemented by geochemical simulations using Phreeqc and the Minteq.v4 database. In particular, the sulfate concentration was often unavailable, e.g., not weekly or monthly as for other contaminants but only annually or less frequently. Therefore, in this study, additional sulfate ion data were estimated assuming that sulfate was the principal anion, based on the pH and cation concentrations, which were measured more frequently than the sulfate ion concentrations. The ion balance of the AMD solution was also simulated using Phreeqc as the concentration of other ions that are not available in water monitoring data can affect simulation results. If the dissolved ions were not balanced with the given pH, further water analysis or a reconsideration of the source rocks assumptions would have been necessary, but at the mines studied in this paper, all ions were balanced by the assumed source rocks.

For each element detected in the AMD, the absolute amount of the element leached was calculated by multiplying the ion concentration by the water volume per unit time. Finally, the amount of each element in the AMD was converted into an amount in the source rocks, based on the chemical formulae shown in Table 1.

Regression Analysis

To predict the amount of leaching from source rocks at a given time in the future, a regression analysis was conducted assuming a first-order kinetic curve. First-order kinetics is the assumption for calculating the rate of reaction of chemical reactions. In this study, we assumed that the rate of leaching from the source rocks was proportional to the amount of source rocks remaining, as shown in Eq. 1.

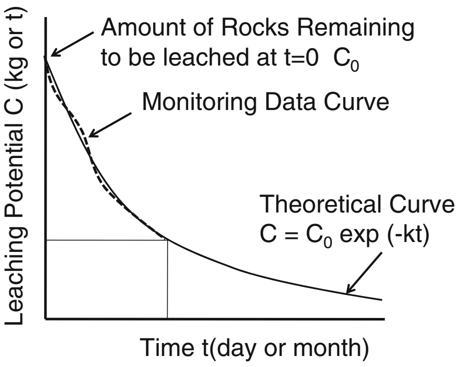

Fig. 1 Outline of multiple regression analysis

$$-\frac{dC}{dt} = kC \qquad (1)$$

where C refers to the amount of source rocks remaining to be leached in the future, and k and t are coefficients of the first-order reaction, and time, respectively. By solving Eqs. 1, 2 was obtained. The source rocks are thought to leach into AMD over a long time, as shown by the following first order equation:

$$C = C_0 \exp(-kt) \qquad (2)$$

where C, C_0, k, and t are the amount of source rocks remaining to be leached at time t, the amount of source rocks remaining at the beginning of the monitoring period ($t = 0$), the coefficient of the first-order reaction, and time, respectively. The relationship between C and t was estimated from the chronological monitoring data for AMD composition and volume. C_0 and k in Eq. 1 were determined by multiple non-linear regression analyses of the historical monitoring data with respect to each source rock. Figrue 1 shows the graphical interpretation of Eq. 2.

The amount of source rocks remaining to be leached at the beginning of the monitoring period, C_0 in Eq. 1, and the coefficient of the first-order reaction, k, were determined by a multiple non-linear regression analysis using the statistical software R. The amount of source rocks remaining, C, was then estimated for future leaching. Finally, the concentration of each element in the AMD was calculated based on estimated parameters, using the chemical formulae shown in Table 1 and the predicted AMD volume. The future AMD volume was estimated by averaging the historical volumes of AMD because no statistically significant long-term trend was observed at either studied mine.

Solution Composition Simulation

After the regression analysis, another chemical equilibrium simulation, for the prediction of future AMD composition was conducted by geochemical simulation with Phreeqc and Minteq.v4. This simulation was required because the output of the regression analysis does not include the oxidation of ferrous to ferric, pH estimation, the precipitation of hydroxides, or surface complexation of arsenate or sulfate ions on ferrihydrite (Dzombak and Morel 1990) or gibbsite (Athanasios and Dzombak 2010) with increased pH. The steps of the solution composition simulation are explained below.

First, the future pH of the AMD was calculated by geochemical simulation in chemical equilibrium using the concentrations of all elements obtained from the regression analysis. Then, the metal concentrations and the pH were recalculated to consider the effects of mineral precipitation, such as ferrihydrate or other hydroxides, and surface complexation of arsenate or sulfate ions on ferrihydrite and gibbsite. The required length of the neutralization treatment, or the period to termination, was estimated from Japanese effluent standards: 0.1 mg/L for cadmium, lead, and arsenic; 3 mg/L for copper; 5 mg/L for zinc; 10 mg/L for iron, and; 5.8–8.6 for pH (METI 2006b). As discussed above, future AMD volume was estimated by averaging the historical volumes of AMD from the monitoring data.

The redox status of iron as ferric or ferrous ions was carefully considered. In general, ferrous ions, which are leached from sulfide minerals (Table 1), are gradually oxidized to ferric ions after being discharged into a wastewater pit. This process accelerates the oxidation of other ions, such as sulfur and arsenic (Abbassi et al. 2009). Therefore, in this study, the assumption was that sulfur, copper, and arsenic were present as sulfate, cupric and arsenate ions, respectively. The partial oxidation of ferrous ions to ferric ions was assumed. The ratio of ferrous to ferric ions was estimated from historical data. All of the chemical and surface complexation species considered in this geochemical simulation are shown in Table 2. The values for several of the parameters used in the surface complexation model were obtained from earlier studies (Athanasios and Dzombak 2010; Dzombak and Morel 1990). We have previously confirmed that the surface complexation model is effective for the estimation of arsenic sorption to ferrihydrite or gibbsite (Tokoro et al. 2005, 2008a, b). However, the amount of arsenic sorbed to ferrihydrite would be greater than the value estimated from the surface complexation model using Dzombak and Morel's parameter because co-precipitation of arsenate and ferrihydrite would occur more than surface complexation (Tokoro et al. 2010, 2011). Furthermore, when the pH in the AMD was increased, the aluminum actually precipitated as aluminum hydroxide rather than gibbsite, and aluminum hydroxide has a larger sorption capacity for arsenate or sulfate ions than gibbsite (Tokoro et al. 2005). Therefore, it should be noted that the estimated concentration of arsenate in the AMD with increasing pH could be higher in the model than the actual value. The amount of CO_2 in the AMD solution was set as its partial pressure in the atmosphere and an open system was assumed.

Neutralization Process Simulation

The neutralization process was simulated by geochemical equilibrium modeling using Phreeqc and Minteq.v4. Calcium carbonate or calcium oxide (limestone or lime, respectively) was used as the neutralizer and added to the predicted AMD composition. In this simulation, all iron was assumed to exist as ferric ions, because ferrous ions are completely oxidized to ferric ions in neutralization plants and ferrous ions are not observed after the neutralization process. Stumm and Lee (1961) showed that the oxidation of ferrous ions to ferric ions was complete when the solution was neutralized. The chemical and surface complexation species considered in this simulation are shown in Table 2 and the source rocks are shown in Table 3. The final pH was set to the same value as in an actual neutralization plant. The level of CO_2 generation from adding neutralizer was checked with measured data when available. The predicted historical neutralization requirements and sludge generation results were validated based on comparisons with the available historical data.

In this simulation, the neutralizer usage and sludge generation were primarily calculated based on pure dry weight, using the molar mass of the neutralizer or precipitate and the water volume. This pure neutralizer weight can be converted into the weight of impure neutralizer based on the purity of the neutralizer used in the actual operation. The dry sludge weight could also be converted into sludge volume based on the water volume fraction of the sludge measured at the actual treatment plant.

Mine Sites and Input Data of Case Studies

Two case studies of abandoned mines in northeastern Japan, i.e. a sulfur mine, and a copper and iron mine, were analyzed using the predictive model. Water monitoring data were available for both mines, although other characterization data, such as hydraulic information and source rock samples, were not. Therefore, the model proposed in this paper was useful for both case studies.

Case Study A

The case study A mine is located in northeast Japan, as shown in Fig. 2. The mine produced at least 29 million tonnes (t) of native sulfur and some iron sulfide, equivalent to 2.5 million t of sulfur, until it closed in the early 1970 s. Throughout the 1970 s, it discharged highly acidic mine water into a river. Source prevention was implemented,

Table 2 Chemical and surface complexation species considered in this study

Element	Species
Chemical species	
Fe(II)	Fe^{2+}, $FeOH^{+}$, $Fe(OH)_2^0$, $Fe(OH)_3^-$, $FeSO_4^0$
Fe(III)	Fe^{3+}, $FeOH^{2+}$, $Fe(OH)_2^+$, $Fe(OH)_3^0$, $Fe(OH)_4^-$, $Fe_2(OH)_2^{4+}$, $Fe_3(OH)_4^{5+}$, $FeSO_4^0$, $Fe(SO_4)_2^-$
As(V)	${AsO_4}^{3-}$, ${HAsO_4}^{2-}$, ${H_2AsO_4}^-$, $H_3AsO_4^0$
Cu(II)	Cu^{2+}, $CuOH^{+}$, $Cu(OH)_2^0$, $Cu(OH)^{3-}$, $Cu(OH)_4^{2-}$, $Cu_2(OH)_2^{2+}$
Zn(II)	Zn^{2+}, $ZnOH^{+}$, $Zn(OH)_2^0$, $Zn(OH)_3^-$, $Zn(OH)_4^{2-}$, $ZnSO_4^0$, $Zn(SO_4)_2^{2-}$
Al(III)	Al^{3+}, $AlOH^{2+}$, $Al(OH)_2^+$, $Al(OH)_3^0$, $Al(OH)_4^-$, ${AlSO_4}^+$, $Al(SO_4)^{2-}$
SO_4(-II)	${SO_4}^{2-}$, ${HSO_4}^-$
Surface complexation species	
HFO/gibbsite (M = Fe or Al)	$\equiv MOH^0$, $\equiv {MOH_2}^+$, $\equiv MO^-$, $\equiv MH_2AsO_4$, $\equiv {MHAsO_4}^-$, $\equiv {MOHAsO_4}^{3-}$, $\equiv {MSO_4}^-$, $\equiv {MOHSO_4}^{2-}$, $\equiv MOCu^+$, $\equiv MOZn^+$

HFO hydrous ferric oxide

Table 3 Source minerals considered in the neutralization process simulation

Mineral	Reactions
Ferrihydrite	$Fe(OH)_3(s) + 3H^+ \leftrightarrow Fe^{3+} + 3H_2O$
Gibbsite	$Al(OH)_3(s) + 3H^+ \leftrightarrow Al^{3+} + 3H_2O$
Gypsum	$CaSO_4{\cdot}2H_2O(s) \leftrightarrow Ca^{2+} + {SO_4}^{2-} + 2H_2O$
Calcite	$CaCO_3(s) \leftrightarrow Ca^{2+} + {CO_3}^{2-}$
Lime	$CaO(s) + 2H^+ \leftrightarrow Ca^{2+} + H_2O$
Copper hydroxide	$Cu(OH)_2(s) + 2H^+ \leftrightarrow Cu^{2+} + 2H_2O$
Zinc hydroxide	$Zn(OH)_2(s) + 2H^+ \leftrightarrow Zn^{2+} + 2H_2O$

including submerging part of the mined cavities by plugging and covering open pits with soil and grass. At this mine, the AMD originated from an old open pit, the underground mined area, and an old tailings dam, which all now flow into the drainage tunnel and is being treated by a neutralization plant (a detailed map is published in the electronic version of this journal, as supplementary figure S-1; all journal subscribers can electronically access all of the papers published in this journal for the past 15 years for free using Springer's Online First database). After dewatering, the sludge generated during neutralization is transferred to the sludge dam located next to the neutralization plant. Monthly monitoring data for total iron, ferrous, arsenic, and aluminum ions, and pH are available for several decades. The quality of the AMD has been gradually improving, but continued AMD treatment is necessary (Table 4).

A neutralization facility, with a treatment capacity of more than 10 t/minute, began operating at this mine in the early 1980 s. The treatment process includes ferrous oxidation with iron-oxidizing bacteria (Hosoda 1999) and neutralization with limestone, which comprises more than 99 % $CaCO_3$, to a target pH of 4.2, which is higher than the natural pH of the river near the mine, to ensure that the final effluent does not harm the environment.

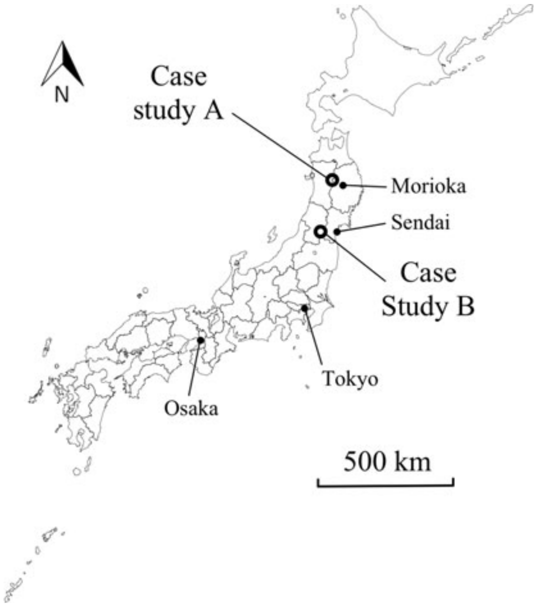

Fig. 2 Location of case study mines

Historical water monitoring data, which included total iron, arsenic, aluminum, ferrous ions, and pH every month from April 1982 to August 2008, was used as the input data. Sulfate ion data were supplemented by geochemical simulation, as this was only measured annually rather than monthly. Ferric ion data were calculated by subtracting the ferrous ion concentration from the total iron concentration.

Case Study B

Case study B mine is also located in northeastern Japan (Fig. 2). The mine produced copper, equivalent to at least 160,000 t, and iron until the early 1970 s. The AMD contains iron, copper, zinc, and arsenic. Source prevention work, including submerging part of the mined cavities by plugging and the development of a watercourse, has been

Table 4 AMD characterization for case study A and B

	Case study A		Case study B		Japanese effluent standard
	April 1982	August 2008	April 1989	December 2008	
pH	2.0	2.3	2.0	2.5	5.8–8.6[a]
Fe	547 mg/L	212 mg/L	2100 mg/L	480 mg/L	10 mg/L
Cu	N.A.	N.A.	630 mg/L	120 mg/L	3 mg/L
Zn	N.A.	N.A.	45 mg/L	7.9 mg/L	5 mg/L[b]
As	3.3 mg/L	1.0 mg/L	2.8 mg/L	0.50 mg/L	0.1 mg/L
Al	135 mg/L	70 mg/L	N.A	N.A.	N.A.
Q.[c]	17.6 m^3/min	16.2 m^3/min	0.17 m^3/min	0.15 m^3/min	N.A.

N.A. not available; there is no effluent standard for Al in Japan and the other data are not available

[a] Effluent standard of pH for case study A is set as 4.0, as natural pH level in rivers around the mine

[b] the Japanese effluent standard for Zn has been altered to 2 mg/L but the provisional standard of 5 mg/L is still applied to the mining sector

[c] Q. refers to quantity of mine water drainage

carried out. At this mine, the AMD that originates underground and from the old tailings dam flows in a drainage tunnel to a neutralization plant, which began operating in the mid-1970 s; lime is used to bring the pH to 8.5 (a detailed map is provided as supplementary Fig. S-2). After dewatering, the neutralized sludge is transferred to a sludge dam. AMD monitoring data (total iron, copper, zinc and arsenic ions, pH, and water volume) for the wastewater from each pit and leaching water from the tailing dams were available for a few decades. The quality of the AMD has been gradually improving, but in December 2008, the arsenic, iron, copper, and zinc concentrations, and the pH of the AMD were 0.5, 480, 120, 7.9 mg/L and 2.5, respectively (Table 4). These values are all above the Japanese effluent standards (METI 2006b).

Historical water monitoring data, including monthly concentrations of total iron, copper, zinc, and arsenic ions, and pH from April 1989 to December 2008 was used as the input data. As in case study A, the sulfate ion data was infrequent, and was only available for a few years, rather than for decades like the other species data. Consequently, the sulfate concentration was again estimated using a geochemical equilibrium simulation. The available monitoring data for the sulfate concentrations agreed well with the estimated results.

Results

Case Study A

Simulation of Future Composition of the AMD

Figure 3 is graphical interpretation of the results of the multiple regression analysis with prediction intervals. Estimated parameters are provided in supplementary Table S-1, along with their 95 % confidence limits. In this analysis, pyrite, arsenopyrite, native sulfur (Table 3), and aluminum minerals were assumed to be the source rocks. This assumption was based on analysis of water monitoring data, as well as a literature study of the rocks produced when the mine was operational. The parameters of the model were statistically significant if the *t* values were as shown in Table S-1.

To simulate future AMD composition, precipitation of ferrihydrite and gibbsite with surface complexation of arsenate and sulfate were assumed to occur. The results showed that the concentrations of total iron and arsenate would decrease to below the Japanese effluent standard (10 and 0.1 mg/L; METI 2006b) in 2109 and 2113, respectively (Fig. 4). This result was not sensitive to the estimation error of regression analysis. Sensitivity analyses for the estimated parameters were carried out by replacing the parameters with their 95 % confidence limit values. Total iron and arsenate would decrease to below the standard in 2107–2111, and 2110–2116 (earliest to latest), respectively. The pH would exceed the pH of the river, 4.0, in 2088.

Simulation of the Neutralization Process

The precipitation of ferrihydrite, gibbsite, calcite, and gypsum, and the surface complexation of arsenate and sulfate on ferrihydrite and gibbsite were assumed for the neutralization process simulation. In the actual AMD treatment process, iron-oxidizing bacteria completely oxidize the ferrous ions to ferric ions. Therefore, in this simulation, all iron was assumed to be in the ferric state. The neutralizer was assumed to be pure $CaCO_3$ and the target pH was 4.2. The target pH was the same as that set in the actual operation, which aims to discharge an effluent with a pH higher than the river water near the mine. This pH value also ensures sufficient precipitation or

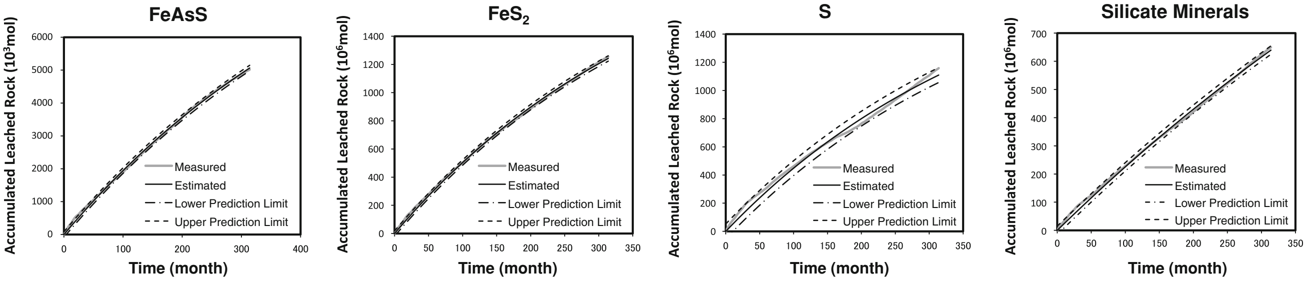

Fig. 3 Regression analysis fitting results for case study A

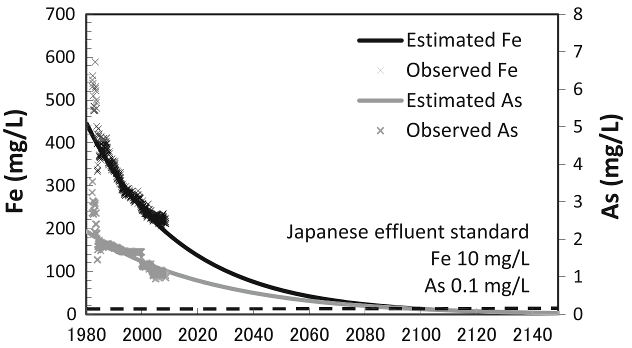

Fig. 4 Estimated AMD composition from case study A (Fe and As)

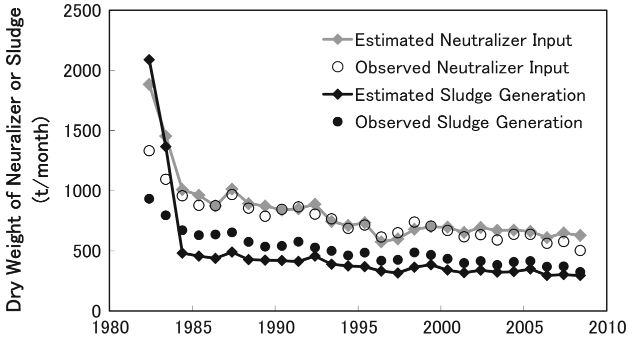

Fig. 5 Comparison between the neutralization simulation results and measured amount in case study A

co-precipitation of the inorganic contaminants to meet the Japanese effluent standards (METI 2006b). The annual variation in the temperature of the mine water was expected to be negligible because most of the drainage water flows from underground mined cavities, with nearly constant water temperature.

To validate the model, the historical neutralizer usage and sludge generation estimated in this study were compared with measured historical data from the mine (Fig. 5). Except for the first 2 years, the error was within the acceptable tolerance level, with annual average errors of 6.8 % and −12.6 % for the neutralizer and sludge, respectively. Possible reasons for the error are incorrect estimation of the sulfate ion concentration, pH measurement errors, insufficient data for other ions, and neutralizer impurities.

The model indicated that the CO_2 concentration in the gas phase in equilibrium with the solution would be about 150,000 ppm but the measured CO_2 concentration in the plant was about 7,000 ppm. However, the CO_2 meter had been installed at a distance from the reaction tank, so that the generated CO_2 was diluted before arriving at the meter. This explains the apparent contradiction between the simulated and measured values.

Figure 6 presents the estimated neutralizer requirements and sludge generation until 2113, when all contaminants would satisfy the final effluent standard. Although both neutralizer requirements and sludge volumes gradually decreased over time, it is important to note that neutralization and sludge generation would continue for 132 years. The total neutralizer requirements from 1,982–2,113 were estimated at 455,000 t, and the amount of sludge generated over the same period was 267,000 t (Table 5). The expected neutralizer requirements and amount of sludge generated between 2,009 and 2,113 (the remaining treatment period) would be 182,000 and 127,000 t, respectively. These results were insensitive to the estimation error of the regression analysis. In the sensitivity analyses, the estimated errors were −2.9 to 3.2 % (total neutralizer input) and −4.7 to 5.2 % (total sludge generation).

Case Study B

Simulation of Future AMD Composition

Figure 7 is graphical interpretation of the results of the multiple regression analysis with prediction intervals. Estimated parameters are provided in supplementary Table S-1 with their 95 % confidence limits. In this analysis, pyrite, chalcopyrite, sphalerite, and arsenopyrite were the assumed source rocks (Table 3), and the parameters of the model were statistically significant if the *t* values were as shown in Table S-1. The sulfate concentrations estimated from the equilibrium simulation agreed with those calculated by the regression analysis. These results show that the selection of the source rocks was reasonable.

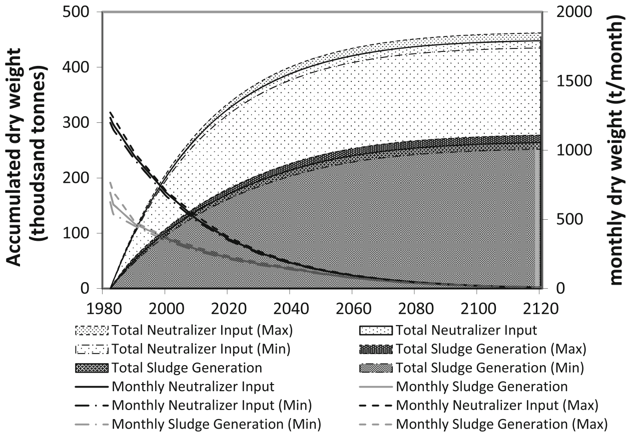

Fig. 6 Estimated neutralizer requirements and sludge generation for the lifecycle of treatment for case study A

To simulate future AMD composition, the precipitation of ferrihydrite, copper hydroxide, and zinc hydroxide, and the surface complexation of arsenate and sulfate on ferrihydrite were assumed. The ratio of ferrous to ferric ions in the solution was set to 3:22, based on historical data. With this analysis, the Japanese effluent standards (METI 2006b) for total iron (10 mg/L), copper (3 mg/L), arsenic (0.1 mg/L), and zinc (5 mg/L) ions would be met in 2117, 2104, 2086, and 2022, respectively. This result was not sensitive to the estimation error; in the sensitivity analyses for the parameters with their 95 % confidence limit values, total iron, copper, arsenic, and zinc would decrease to below the standard in 2111–2125, 2101–2108, 2081–2092, and 2022–2023 (earliest to latest), respectively. Graphical interpretation of AMD prediction is shown in supplementary Figures S-4 and S-5. Based on this simulation, the pH would reach 5.8 (the Japanese effluent standard) in 2422 without CO_2 pressure. The pH would converge to 5.7 with the partial pressure of the atmosphere, but it is not likely to happen because the AMD in the underground mined area contains less CO_2.

Neutralization Process Simulation

For the neutralization process simulation, precipitation of ferrihydrite, copper hydroxide, zinc hydroxide, and gypsum, and surface complexation of arsenate, sulfate, copper, and zinc on ferrihydrite, were assumed. All ferrous ions were assumed to be oxidized to ferric ions at the final target pH (8.5) in the slaked lime neutralization operation (Stumm and Lee 1961). At this pH, most of the inorganic contaminants would precipitate. The annual temperature variation of the mine water was estimated to be less than 6 °C for this mine, based on limited temperature data for the mine water and treated water. Again, the major source of the mine water is the underground mine, so the effects of temperature are negligible.

To validate the simulation, estimated and measured historical neutralizer uses were compared (supplementary Fig. S-6). The average error (5.7 %) was within an acceptable range, with the same possible causes as for case study A. Unfortunately, no monitoring data were available for sludge generation validation.

As shown in Fig. 8 and Table 5, the predicted neutralizer requirements and sludge generation volumes were 17,600 and 19,900 t, respectively, for a period of 129 years (from 1989 to 2117, when all of the contaminant concentrations are expected to be below Japan's effluent standards). The expected remaining neutralizer requirements and sludge generated from 2009 to 2117 (the remaining treatment period) would total 9,690 and 6,800 t, respectively. In the sensitivity analyses for the estimated parameters in the regression analysis, the amounts were changed to −6.0 to 7.2 % (neutralizer input) and −9.8 to 11.7 % (sludge generation). The simulation result shows that the pH will reach 5.8 in 2422, as discussed above. However, it is anticipated that it will increase earlier because ferric hydroxide and aluminum hydroxide should start to precipitate on the surfaces of the source rocks, which should reduce future metal leaching. In addition, the result of neutralizer requirements and sludge generation would not be sensitive to this difference. If the treatment were to be terminated in 2422, neutralizer use and sludge generation would only be increased by 3 and 0.3 %, respectively.

Discussion of the Simulation Results

An important application of the simulation results from this study is in construction of sludge dams. Sludge dams are

Table 5 Neutralization simulation results for case study A and B

	Case study A			Case study B		
	1982–2008	2009–2113	1982–2113	1989–2008	2009–2117	1989–2117
Neutralizer Input						
Dry *t*	272,000	182,000	455,000	7,860	9,690	17,600
%	60	40	100	45	55	100
Sludge Generation						
Dry *t*	140,000	127,000	267,000	13,100	6,800	19,900
%	52	48	100	66	34	100

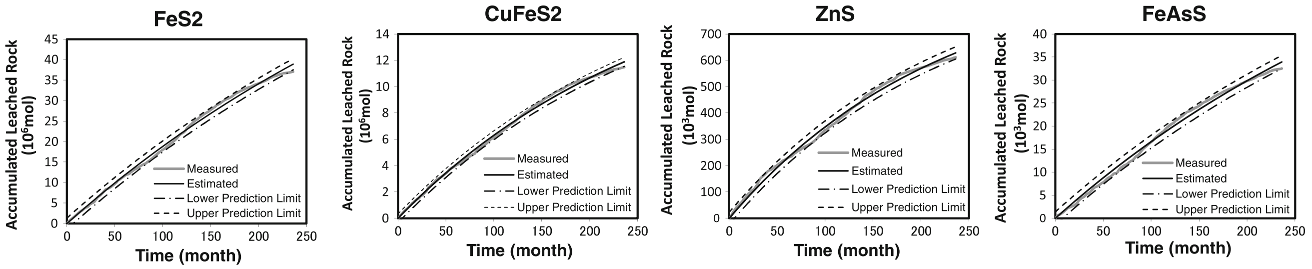

Fig. 7 Regression analysis fitting results for case study B

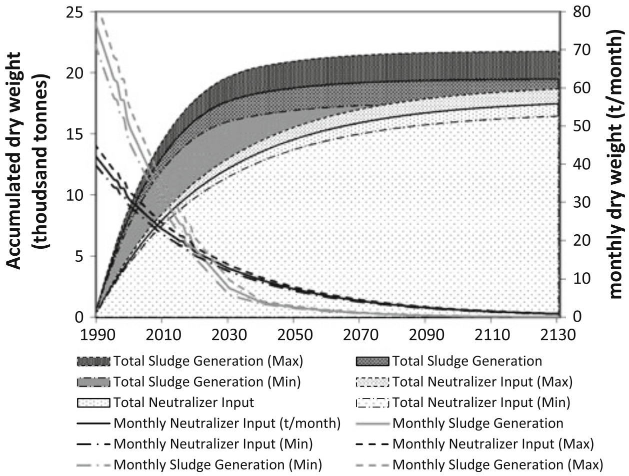

Fig. 8 Estimated neutralizer requirements and sludge generation for the lifecycle of treatment for case study B

expensive to construct and maintain but are very important for avoiding environmental disasters. In case study A, the amount of sludge generated from 2009 to 2113 (the remaining treatment period, 127,000 t) would be about 91 % of the amount generated from 1982 to 2008 (140,000 t). On the other hand, in case study B, the amount of sludge generated from 2009 to 2117 (the remaining treatment period, 6,800 t) would be about 52 % of the amount generated from 1989 to 2008 (13,100 t). Based on interviews with the treatment operators, the current sludge dam at case study A mine is large enough to store the expected sludge generated until 2113, so construction of a dam with a larger capacity will not be necessary. However, the existing dam at case study B would not have the capacity to store the estimated amount of sludge generated by 2,117, as the existing sludge dam is nearly full. This suggests that the development of additional sludge storage capacity or removal and proper disposal of much of the sludge currently present is necessary. The simulation results can also be used to determine the size of any additional dam requirements.

Conclusions

This study established a predictive model using only water monitoring data to estimate the future neutralization requirements and amount of sludge generation for AMD treatment at abandoned or closed mines. Water monitoring data for AMD was input in a two-step predictive model. First, the future volume and composition of the AMD were predicted; then, the neutralizer requirements and sludge generation for future AMD treatment were predicted. The simulation method incorporated multiple regression analysis and geochemical simulation with a surface complexation model. The future AMD composition, neutralizer requirements, and sludge generation were estimated for two abandoned mines in Japan. The estimated values for the neutralizer and sludge amounts agreed with historical monitoring data, suggesting that the model constructed for this study was valid. These case studies demonstrate the effectiveness of this model for predicting AMD composition and treatment inputs and outputs at abandoned mines. It should be especially applicable and useful for abandoned or closed mines where data other than water monitoring is not available, such as at these abandoned Japanese mines. We recommend that an analysis using this model be conducted for other AMD-generating mines where historical water monitoring data is available. The results of this analysis will be useful for knowing when the treatment can be terminated, the amount of neutralizer required, and the amount of sludge that will be generated. The results also show that it is important to continuously monitor AMD to allow future predictions. This model can also be used to quantitatively determine the need for additional sludge storage space and total operational treatment costs. Other studies, including Ueda and Masuda (2005) and AMD treat (McKenzie 2005) are also useful for cost estimation. The results from the model increase understanding and predictions of the lifecycle environmental costs of the mining industry.

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