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A quantitative estimation of the factors affecting pH changes using simple geochemical data from acid mine drainage

Ji-Eun Lee · Yeongkyoo Kim

Abstract The behavior of heavy metals in acid mine drainage (AMD) is mainly controlled by pH values. Therefore, a quantitative estimation of factors affecting pH values in AMD is very important in predicting the behavior of those metals. Many different factors cause pH changes in streams affected by AMD and we quantitatively estimated those factors by making simple equations from geochemical data collected from the Dalsung mine. In a stream from that mine, the pH values decrease as the stream flows downstream from the AMD source, which is different from normal streams affected by AMD. The stream shows low pH ranges (4.04–5.96), high electrical conductivity (1,407–1,664 µS/cm), and sulfate concentration (680–854 ppm). Most ion concentrations decrease or do not show noticeable changes mainly due to dilution. The change of the iron content is most significant, even though the concentration of iron is relatively low compared with other ions. The iron concentration (13.4 ppm) becomes almost 0 ppm due to precipitation. Schwertmannite is the dominant precipitated phase downstream and whitish basaluminite is observed in the upstream. From our pH estimation, precipitation is the most important process lowering pH values from 5.96 to 4.04. The dilution factor was calculated by the concentration changes in sulfate ions. Dilution increases pH values, but compared with the precipitation factor, the contribution of the dilution factor to pH is relatively small. Alkalinity is the main factor that buffers hydrogen, which is released by precipitation. The redox changes, which were calculated from the pH and Eh values, also affect pH at each sampling site. The trend of estimated pH changes is almost identical to the observed ones, but the values are slightly different. Some errors are expected mainly due to the uncertainty in the observed Eh values and the chemistry of the added water for dilution.

Keywords AMD · Schwertmannite · Precipitation · pH change · Dilution · Alkalinity · Redox change

Introduction

Acid mine drainage (AMD) has been known to affect the ecological system and water resources mainly by effluent and tailings with its toxicity and low pH after closures (Cherry et al. 2001; Marsden et al. 2003; Zis et al. 2004). In addition, suspended precipitates from AMD are also hazardous to organisms in the aqueous systems (Achterberg et al. 2003). Therefore, the aqueous systems and soils located near AMD are most vulnerable to contamination.

AMD generally has a low pH in the range between 2 and 4 (Bigham and Nordstrom 2000, and references therein), and such a low pH can cause many environmental problems including increasing the mobility of toxic metals. At low pH, Fe and Al are the main dissolved species in AMD, and high concentrations of these cations, especially Al, are toxic to both plants and animals (Soucek et al. 2001). At low pH, Al shows high solubility, but at about pH 5, it rapidly forms amorphous basaluminite and gibbsite by hydrolyzing, which decreases the Al contents in aqueous systems (Bigham and Nordstrom 2000). With an increase in pH, in the solution of high Fe concentration, iron oxide, hydroxide, or sulfate also precipitate with the release of H^+ ions into streams and acidify the aqueous systems. Several minerals such as ferrihydrite, goethite, jarosite and schwertmannite are reported to precipitate from AMD (Cornell and

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Schwertman 1996; Kim et al. 2002; Regenspurg et al. 2004; Jönsson et al. 2005). Ferrihydrite is a poorly crystalline ferric hydroxide and precipitates above pH 6.4. Goethite, crystalline oxyhydroxide, is formed in a wide range of pH. It is a relatively stable mineral compared with other precipitated minerals, and is the last product to be found in AMD. Jarosite is normally precipitated below pH 3 and has a high content of SO_4. Schwertmannite has been reported as a new mineral by Bigham et al. (1994) and it has been recognized as a common precipitate in AMD (Bigham et al. 1996a). This mineral is usually precipitated between a pH of 2.8 and 4.5, and contains moderate to high SO_4 content. Bigham et al. (1996b) suggested that this mineral has a variable chemical formula $Fe_8O_8(OH)_{8-2x}(SO_4)_x$ ($1 \leq x$ 1.75). Schwertmannite is, however, metastable and can be easily transformed to goethite, which is considered to be more stable (Bigham et al. 1996b).

Even though the Al and Fe concentrations decrease in a solution with an increasing pH, suspended colloidal Al and Fe precipitates still have influence on the aqueous systems by increasing turbidity. Toxic heavy metals released into aqueous systems from AMD by the oxidation of ore minerals can co-precipitate with Al and Fe or can be adsorbed on precipitates (Yu and Heo 2001; Lee et al. 2002; Fukushi et al. 2003a, b, 2004; Casiot et al. 2005; Sánchez Espana et al. 2005; Munk et al. 2006). Therefore, these co-precipitation and adsorption processes play important roles in immobilizing and removing toxic heavy metals from AMD. With changes in pH, these precipitates can be dissolved and the adsorbed cations can be desorbed from precipitates, thus resulting in the activation of toxic metals in the aqueous systems. Therefore, pH plays an important role in controlling precipitation and the potential toxicity of AMD.

There have been numerous studies on factors controlling pH values in AMD, including the hydrogeochemical characteristics of AMD (Prieto 1998; Yu and Heo 2001), precipitates including schwertmannite (Yu et al. 1999; Bigham and Nordstrom 2000; Rose and Elliott 2000; Sánchez Espana et al. 2006), the effect of bacteria in acidic mine water (Bigham et al. 1996a; Fortin et al. 1996; Konhauser 1998; Little et al. 1998; Nakamura et al. 1997;

Kawano and Tomita 2001) and other factors such as redox change, dilution, and adsorption (Yu and Heo 2001; Lee et al. 2002; Casiot et al. 2005). The pH values in AMD can be also controlled by many combined factors, and there have been several studies estimating pH and heavy metal changes in AMD using reactive solute transport model (Broshears et al. 1996; Runkel et al. 1996). This calculation requires hydrologic transport information obtained by injections of tracers and different set of geochemical data. Sometimes, however, it is necessary to estimate the factors affecting pH changes from simple hydrogeochemical data.

In most cases of acid mine drainage-impacted streams, pH usually increases downstream by dilution and the bottom of the drainage becomes whitish or reddish due to the Al and Fe precipitates (Bigham and Nordstrom 2000; Kim et al. 2002; Casiot et al. 2005; Sánchez-Rodas et al. 2005; Sánchez Espana et al. 2005). Contrary to common AMD, the small stream, which is mainly composed of leachate from the landfill in the Dalsung mine, a closed tungsten mine located in the southeastern part of Korea (Fig. 1), shows a decrease in pH. The mine was in operation for tungsten since 1938, stopped in 1975 and was completely closed in 1994. The waste rock and tailings from the mine were landfilled. The stream from the Dalsung mine runs a relatively short distance (400 m) until it meets another stream and it is a good candidate for the quantitative estimation of pH changes. A simple equation was derived using field and laboratory geochemical data. The pH changes were also calculated and the effect of each controlling factor on pH values was estimated to quantitatively understand the hydrogeochemical processes in AMD. This study could lead to better reliability in pH development prediction from simple data and resulting changes in the behavior of heavy metals in streams affected by AMD.

Methods

Geologic setting

The study area is composed of Cretaceous andesitic rock intruded by granite porphyry and quartz monzonite, and

Fig. 1 Hydrological system and sampling sites in the study area
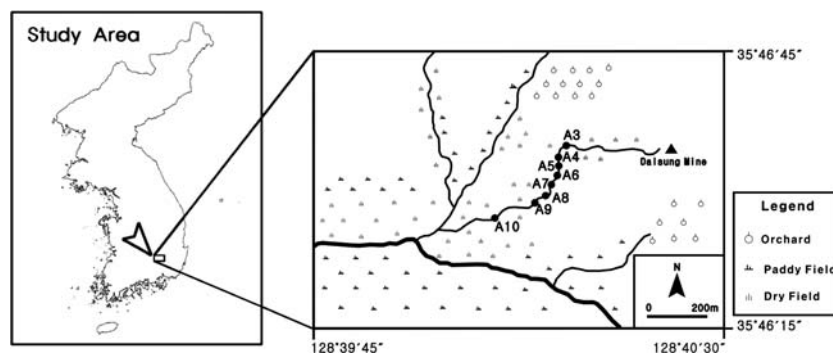
hydrothermal ore deposit was developed in andesitic rock (Lee et al. 1996, Fig. 2). The main ore minerals were chalcopyrite, wolframite, arsenopyrite, bismuthinite, and pyrite.

Sampling

Water samples were collected at intervals of 50–100 m along the stream about 400 m from the landfill site. Temperature, pH, Eh, EC, and alkalinity were immediately measured by an Orion 250A pH-Eh meter and a Trans Instruments EC Meter at each sampling site. Water sample and precipitate on the bottom of the stream were collected from the stream for analysis. Alkalinity was determined by titration with 0.05 N HCl against methyl orange at the first sampling site. Water samples for the analysis of cation and anion were separately collected, filtered through 0.45 μm cellulose nitrate membrane filters, and stored in pre-cleaned 100 mL HDPE bottles with screw caps. Samples for cation analysis were acidified below pH 2 using 1 N HNO_3 to avoid precipitating and adsorbing on the walls of the bottle. Those samples were placed in an icebox and moved to a laboratory. Precipitate samples, which were mainly composed of thin reddish and whitish layers on the bottom of the stream, were collected using a pipette.

Laboratory analyses

Cations and anions of water samples were analyzed using Inductively Coupled Plasma–Atomic Emission Spectrometer (ICP-AES, Perkin Elmer optima 4300DV) and Ion Chromatography (IC, Shimadzu LC-10AVP Series), respectively, at the Korea Basic Science Institute in Daegu.

Saturation indices (SI) of the possible precipitates in AMD such as ferrihydrite, basaluminite, goethite, jarosite, and schwertmannite, were calculated by MINTEQA2 (Allison et al. 1991) using the analyzed geochemical data. Several studies have estimated thermodynamic values such as solubility product and enthalpy for schwertmannite (Bigham et al. 1996b; Yu et al. 1999, 2002; Majzlan et al. 2004). These estimations are based on many assumed factors, and as a result, those values encompass a wide range. Therefore, it is hard to obtain reliable thermodynamic data of schwertmannite and their SI values were calculated using previously reported solubility product data (log $K = 18.5 \pm 2.5$ from Bigham et al. 1996b and log $K = 10.5 \pm 2.5$ from Yu et al. 1999).

Precipitates were dried in air overnight. X-ray diffraction (XRD, Rigaku Geigerflex RAD3-C, Co. Kα, $\lambda = 1.789$Å) was used for identifying the mineral phases of the precipitates by counting 3 s interval steps of $0.05°2\theta$, from 3 to $80°2\theta$ at the Daegu Branch of Korea Basic Science Institute. These identified mineral phases were compared with the calculated SI values of the possible precipitates. Scanning electron microscope (SEM, HITA-CHIS-4200) and transmission electron microscope (TEM, HITACHI H-7100) were used for the characterization of these phases at the Daegu Branch of Korea Basic Science Institute

Results and discussion

Hydrogeochemistry

The results of the field data and chemical analyses are summarized in Table 1. The stream water samples are acidic and show high EC values. Major cations are Ca, Na, and Mg, and the anions are mostly composed of SO_4. Several trends are observed in the stream flowing from the landfill site in the Dalsung mine. Field data such as pH and EC values (5.96–4.00 and 1,664–1,407 μS/cm) decrease with an increase in distance away from the landfill site (Fig. 3). For dissolved ions including Na, Mg, Fe, and SO_4, they clearly decrease compared with other ions (Figs. 4 and 5). The decreasing rate of the Fe concentration is dramatic and at pH 4 the Fe content becomes almost 0 ppm. Apart from other ions, the concentrations of Al and NO_3, however, increase (Figs. 4 and 5).

The saturation indices (SI) of possible precipitates in AMD, calculated by MINTEQA2 from collected geochemical data, are plotted in Fig. 6. All SI values decrease downward mainly due to the decreasing concentrations of Fe and SO_4. According to this calculation, basaluminite
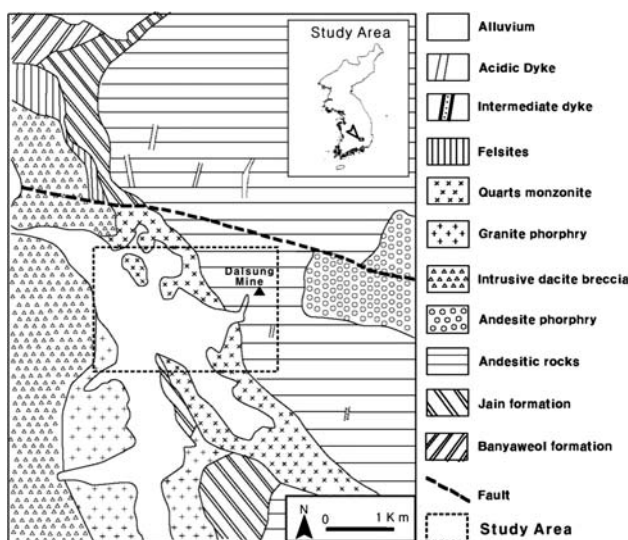

Fig. 2 Geologic setting of the study area

Table 1 Field data and geochemistry of water samples from the study area

Sample No.	Field measures					Chemical compositions (mg/l)																					
	Distance (m)	Temp. (°C)	pH	Eh (mV)	EC (µS/cm)	Ca	Na	Mg	Si	Mn	Fe	K	Zn	Cu	Al	Sr	As	Co	Ni	Li	Pb	Cr	Cd	Bi	Cl	NO₃	SO₄
A3	0	18	5.96	470	1,664	220	142	72.9	34.3	31.8	13.4	5.4	3.0	2.5	0.1	1.1	0.3	0.2	0.1	0.0	n.d.	n.d.	n.d.	n.d.	3.7	0.7	854
A4	45	20	5.03	507	1,660	220	135	70.3	34.0	30.8	10.7	6.4	2.9	2.6	0.8	1.1	0.3	0.3	0.0	0.0	n.d.	n.d.	n.d.	n.d.	3.6	0.8	794
A5	70	22	4.90	525	1,588	204	131	67.7	36.0	28.9	9.4	6.4	2.9	2.7	1.1	1.0	0.3	0.3	0.0	0.0	n.d.	n.d.	n.d.	n.d.	3.7	0.8	815
A6	85	23	4.24	561	1,575	211	133	68.3	34.8	28.9	3.8	6.4	3.0	2.8	2.0	1.1	0.3	0.2	0.1	0.0	n.d.	n.d.	n.d.	n.d.	3.6	0.9	787
A7	145	23	4.11	631	1,571	206	139	68.9	33.2	29.2	2.5	6.7	2.9	2.9	2.3	1.1	0.3	0.2	0.1	0.0	n.d.	n.d.	n.d.	n.d.	3.5	1.0	789
A8	175	23	4.00	628	1,495	213	125	64.3	32.9	27.0	0.3	6.3	3.0	3.1	2.6	1.0	0.4	0.2	0.0	0.0	n.d.	n.d.	n.d.	n.d.	3.5	1.2	728
A9	230	23	4.04	658	1,429	192	115	58.2	35.0	24.0	0.1	5.6	2.5	2.9	2.7	1.0	0.4	0.2	0.0	n.d.	n.d.	n.d.	n.d.	n.d.	3.5	1.5	692
A10	375	23	4.04	631	1,407	194	112	58.0	31.6	23.7	0.1	5.9	2.5	3.1	2.0	1.0	0.3	0.2	0.0	0.0	n.d.	n.d.	n.d.	n.d.	3.7	1.7	680

n.d. not detected

and ferrihydrite are supersaturated upstream, but become undersaturated at 85 and 175 m respectively, from the landfill site. Other mineral phases, including schwertmannite except for these two minerals are supersaturated throughout the stream range.

Typically, the pH values of streams affected by the acid mine drainage increase with an increase in distance from the AMD source (Yu and Heo 2001; Kim et al. 2002; Sánchez-Rodas et al. 2005), which could be explained by the dilution caused by the addition of groundwater and other stream water from the tributary. In our study area, however, the pH of the stream decreases over distance unlike other abandoned mines (Fig. 3). Nevertheless, this stream is still affected by dilution, as suggested by the significant decrease in SO₄ content, which is considered as a conservative ion (Bencala et al. 1987; Yu and Heo 2001). The decrease in contents of other ions except Fe is also affected by dilution. The decreasing rate of the Fe content is, however, too high to be affected only by dilution. This indicates that the precipitation of Fe oxide or hydroxide is the main factor controlling the Fe content in this stream. The increase of NO₃ may be caused by an influx of fertilizers or organic matter in soil from a nearby cultivated field (Fig. 5). Aluminum is the only cation that shows an increase in content downstream. Several factors may contribute to this increase over distance including the dissolution of Al silicate minerals and dissolution of suspended Al precipitate by a low pH (Figs. 3, 4). Sulfates of Al, such as basaluminite, are usually precipitated at pH 4.4∼5.9 (Kim et al. 2002), and are dissolved below pH 4.5. In other common abandoned mines, these precipitates are usually observed downstream showing a relatively high pH, as compared with AMD sources. These white precipitates, however, are observed only at the upper stream, just out of the landfill area in the Dalsung mine and the suspended precipitates can be dissolved with a decrease in pH as they move downstream.

The colors of the upstream precipitates change from whitish to reddish or brownish and the precipitates were not found after 350 m downstream. The precipitates with reddish or brownish colors were identified as schwertmannite by XRD analysis (Fig. 7). The XRD pattern of A3 for the sample was collected from the whitish precipitates and that of A6 from the reddish ones. A whitish sample does not show resolved peaks, indicating that it may be amorphous, probably with the chemical composition of basaluminite, which is commonly found in Al sulfate phases in AMD (Kim et al. 2002). The XRD pattern of the A6 sample is that of typical schwertmannite with a minor amount of quartz (Fig. 7). The TEM and SEM images of this sample show typical schwertmannite shape, i.e. spherical and globular aggregates (Bigham et al. 1994; Fig. 8).

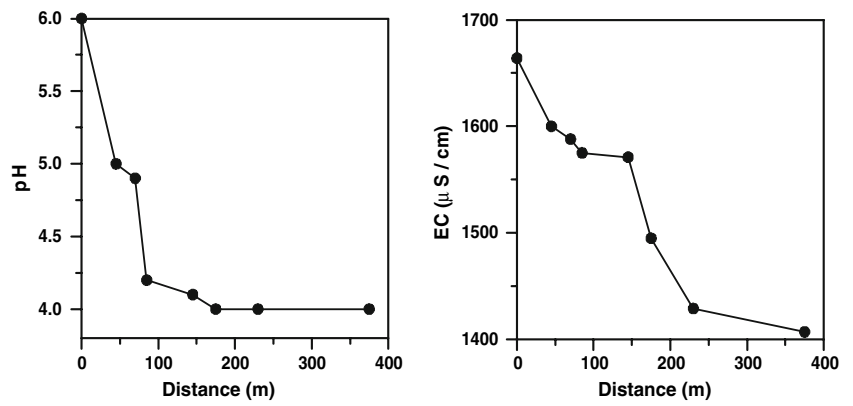**Fig. 3** Plots of pH and EC as a function of distance

Fig. 4 Plots of cation concentrations as a function of distance

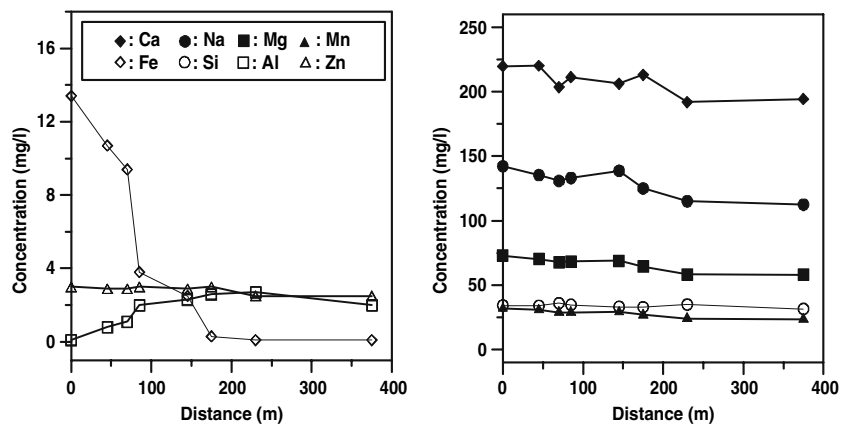**Fig. 5** Plots of anion concentrations as a function of distance
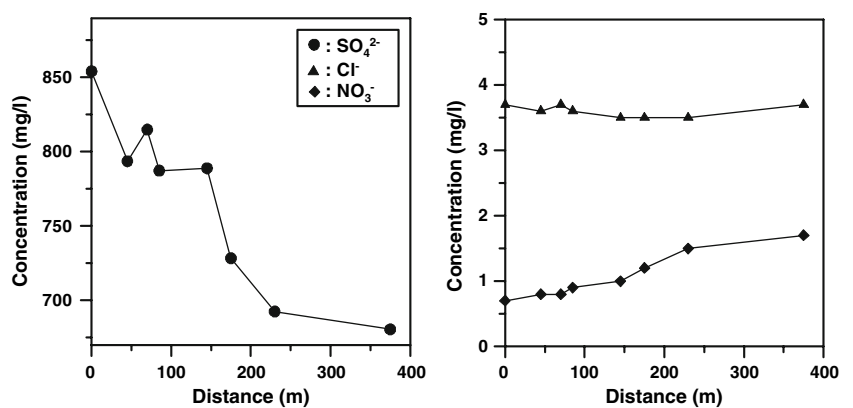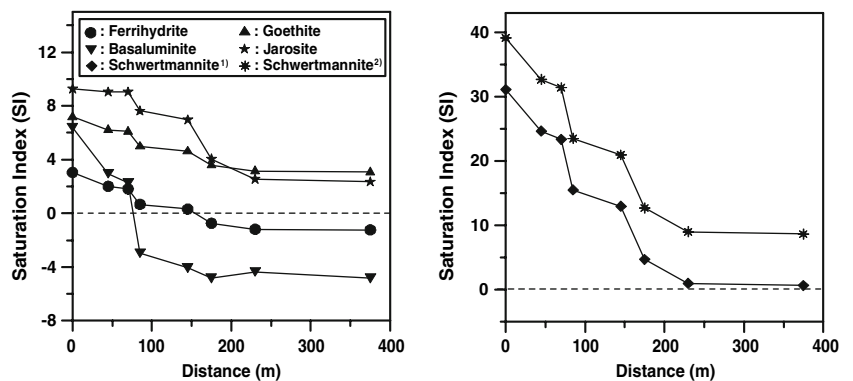

Fig. 6 Changes of saturation indices calculated by MINTEQA2 at different distances
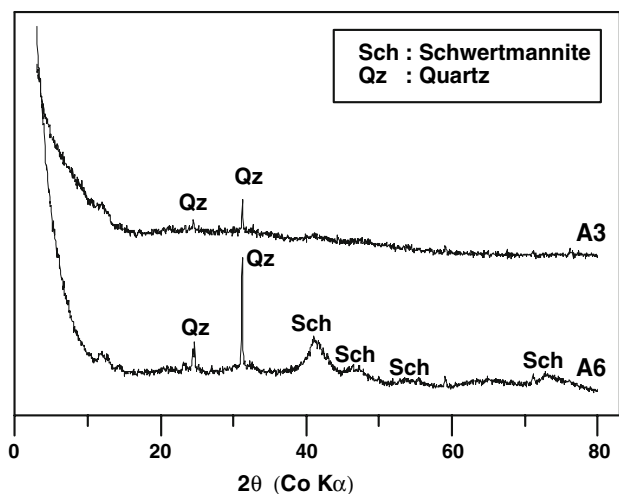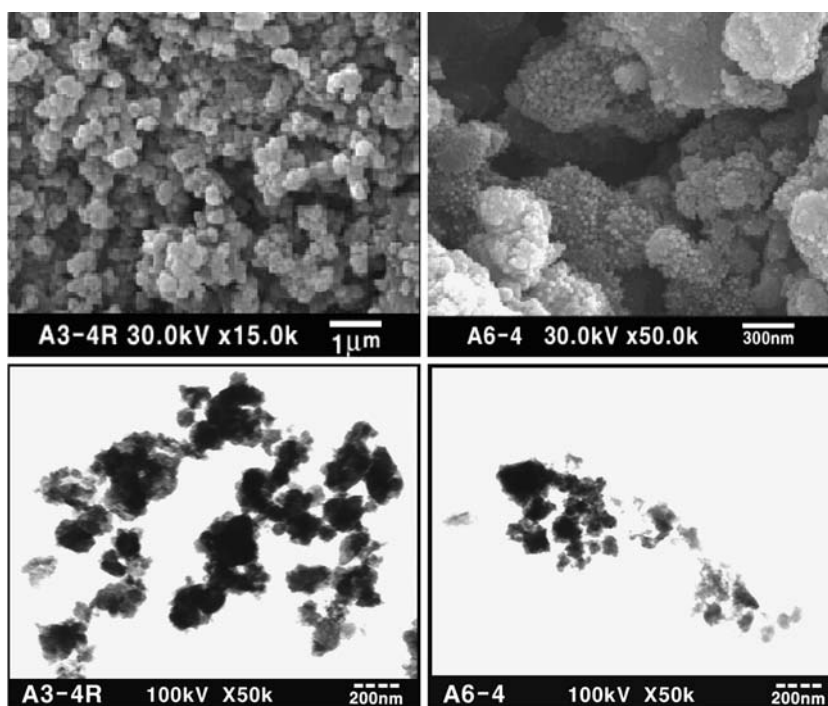
Fig. 7 X-ray diffraction patterns of precipitates collected from the bottom of stream

The Fe and SO_4 content decreases downstream, thus affecting pH (Figs. 4, 5). The decreased content of Fe is much smaller than that of SO_4 in this stream and the amount of SO_4 removed by the precipitation of schwertmannite should be very small considering the composition of schwertmannite, $Fe_8O_8(OH)_{8-2x}(SO_4)_x$. Therefore, the decrease of the SO_4 content is influenced mainly by dilution, and only slightly by precipitation. The formation of schwertmannite is, however, the main factor which causes a decrease in Fe content in this stream.

Factors controlling pH

The streams affected by the AMD experience the changes in pH. Dilution is the most commonly observed factor that increases pH values in streams. The precipitation of iron minerals, however, releases hydrogen and decreases the pH value (Langmuir 1997; Casiot et al. 2005; Verplanck et al. 2004; Sánchez-Rodas et al. 2005). The oxidation and reduction of Fe in the AMD can increase or decrease pH values depending on the oxidation state. Alkalinity neutralizes acidity caused by the release of hydrogen from the precipitation of schwertmannite and oxidation of sulfide minerals (Sánchez Espana et al. 2005; Munk et al. 2006). The effect of each factor on pH change was calculated quantitatively from the collected data.

Dilution factor

The increase in pH values in the stream, affected by the AMD, is commonly observed and is mainly attributed to the dilution from the tributary or groundwater. The concentration of some dissolved ions decreases by dilution, adsorption, and/or precipitation. Dilution is the most significant factor controlling the concentrations of ions in stream water affected by AMD (Yu and Heo 2001; Casiot et al. 2005). Therefore, if we consider an ion, which is not reactive with sediments or other dissolved ions, and the solution concentration is only controlled by dilution, the amount of water added for dilution can be calculated in

Fig. 8 Scanning electron micrographs and transmission electron micrographs of precipitates composed schwertmannite

the streams. Sulfate is normally considered as a non-reactive ion and can be used to calculate the amount of dilution. Even though other ions such as Na, Mg, and Ca can also be considered as non-reactive tracers (Bencala et al. 1987), they were not considered in our study because they can be added to the stream water by the dissolution of silicate and carbonate minerals. If there is no loss of this ion and dilution is the only factor that controls pH values, the degree of dilution (dilution factor) in the ith sampling sites can be defined as $D_i = \frac{[SO_4]_o}{[SO_4]_i}$, in which $[SO_4]_{o,i}$ are molal concentrations of sulfate at the initial sampling site (o) and ith sites, respectively. This simple calculation is based on the assumption that groundwater is very dilute and the sulfate concentration of the added water is close to 0 ppm. If water is added and the volume increases two fold, the value of D_i is 2 and this notation is the inverse value of D_i used by Yu (1998) and Yu and Heo (2001). If the concentrations of SO_4 in groundwater or the tributary ($[SO_4]_{g,t}$) are not 0 ppm, and the added water volume is y times larger than that of the stream at o site, $D_i = 1 + y$. To get the y value, the relationship between $[SO_4]_o$ and $[SO_4]_i$ can be used,

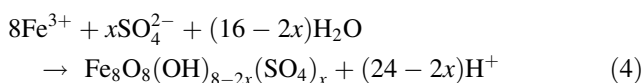$$\frac{[SO_4]_o + [SO_4]_{g,t} \times y}{1 + y} = [SO_4]_i \tag{1}$$

From that y can be derived as

$$y = \frac{[SO_4]_o - [SO_4]_i}{[SO_4]_i - [SO_4]_{g,t}} \tag{2}$$

Therefore, if groundwater or the tributary water contain SO_4 ion, the dilution factor will be

$$D_i = 1 + y = 1 + \frac{[SO_4]_o - [SO_4]_i}{[SO_4]_i - [SO_4]_{g,t}} \tag{3}$$

Here, the precipitation of schwertmannite, the only identified precipitated iron mineral phase, was not considered because the sulfate concentration consumed by the precipitation of schwertmannite is very small compared with that reduced by dilution. If the reduced sulfate concentration, caused by precipitation, is large enough to affect the calculated dilution factor, the sulfate concentration reduced by the precipitation can be calculated stoichiometrically, based on the precipitation reaction of schwertmannite with $1 \leq x \leq 1.75$ (Bigham et al. 1996b) and $1.74 \leq x \leq 1.86$ (Yu et al. 1999).

$$8Fe^{3+} + xSO_4^{2-} + (16 - 2x)H_2O$$
$$\rightarrow Fe_8O_8(OH)_{8-2x}(SO_4)_x + (24 - 2x)H^+ \tag{4}$$

If the decreased molal concentration of sulfate, by precipitation, is significant enough to affect the calculated

dilution factor, the decreased amount of sulfate, by precipitation, should be considered in the calculation of the dilution factor. Therefore, from (4), the decreased molal concentration of sulfate by the precipitation of schwertmannite, corresponds to $\frac{x}{8}\left(\frac{[Fe^t]_o}{D_i} - [Fe^t]_i\right)$ at the ith site, where $[Fe^t]_{o,i}$ is the total molal concentration of iron at the initial (o) and ith sites. This term should be added to calculate the dilution factor. If $[SO_4]_{g,t}$ is near 0 ppm, with the addition of this term, the relationship appears as

$$D_i = \frac{[SO_4]_o}{[SO_4]_i + \frac{x}{8}\left(\frac{[Fe^t]_o}{D_i} - [Fe^t]_i\right)} \tag{5}$$

From this relationship, the dilution factor considering the precipitation of schwertmannite becomes

$$D_i = \frac{[SO_4]_o - \frac{x}{8}[Fe^t]_o}{[SO_4]_i - \frac{x}{8}[Fe^t]_i} \tag{6}$$

Equation 6 is also exactly the inverse value of dilution factor with precipitation described by Yu (1998). If the precipitated phases do not contain sulfate, such as ferrihydrite, the changes in the iron concentration at the initial and ith sites is not included in the calculation of the dilution factor. Due to the reported variable chemical composition of schwertmannite and the impurities in our precipitated samples, an accurate estimate of the chemical composition of our schwertmannite sample was impossible. Here, $x = 1.8$, which is the average value suggested by Yu (1998), and was used in order to calculate pH changes by dilution and other factors in Table 2.

The dilution factor, however, will be more complex if the groundwater or the tributary water contain significant amounts of SO_4 ions ($[SO_4]_{g,t}$) and the more accurate dilution factor can be calculated from (3) with the addition of new terms,

$$D_i = 1 + \frac{[SO_4]_o - \left\{[SO_4]_i + \frac{x}{8}\left(\frac{[Fe^t]_o}{D_i} - [Fe^t]_i\right)\right\}}{\left\{[SO_4]_i + \frac{x}{8}\left(\frac{[Fe^t]_o}{D_i} - [Fe^t]_i\right)\right\} - [SO_4]_{g,t}} \tag{7}$$
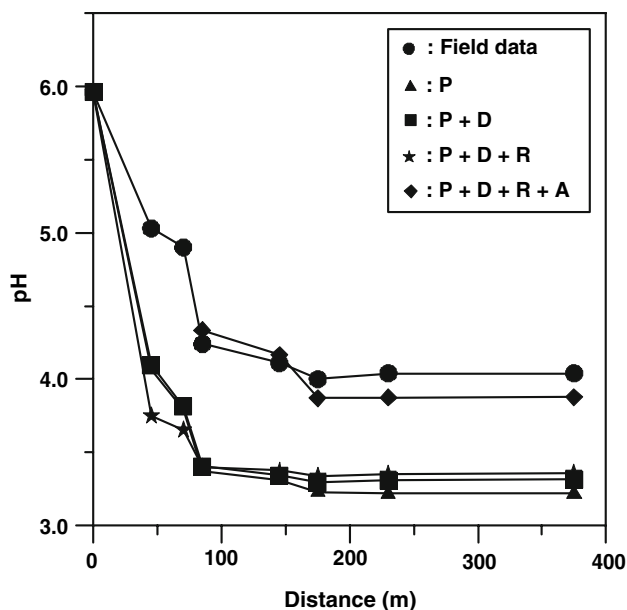
The final dilution factor becomes

$$D_i = \frac{[SO_4]_o - \frac{x}{8}[Fe^t]_o - [SO_4]_{g,t}}{[SO_4]_i - \frac{x}{8}[Fe^t]_i - [SO_4]_{g,t}} \tag{8}$$

In other abandoned mines, dilution is one of the main factors that increase pH values. In the case of the stream in Dalsung mine, however, pH decreases downstream, indicating that this dilution effect is not as significant as precipitation (Figs. 9, 10).
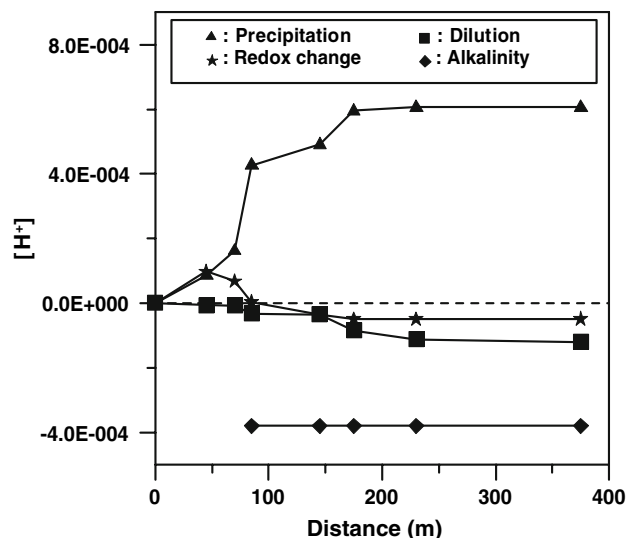
Table 2 Calculated pH considering each factor

Sampling site	Observed pH	Calculated pH				
		P	P + R	P + D + O	P + D + O + A	P + D$_{gt}$ + O + A
A3	5.96					
A4	5.03	4.07	4.10	3.75		
A5	4.90	3.79	3.81	3.65		
A6	4.24	3.37	3.40	3.40	4.33	4.36
A7	4.11	3.31	3.34	3.38	4.17	4.18
A8	4.00	3.23	3.29	3.34	3.87	3.89
A9	4.04	3.22	3.31	3.35	3.87	3.89
A10	4.04	3.22	3.31	3.36	3.88	3.90

P precipitation, *D* dilution, *D*$_{gt}$ dilution considering sulfate concentration of groundwater, *R* redox change, *A* alkalinity

Fig. 10 Concentration of H$^+$ calculated by each factor at different distances

Fig. 9 Changes of pH values calculated by each factor at different distances. *P* precipitation, *D* dilution, *R* redox change, *A* alkalinity)

Precipitation factor

Schwertmannite precipitation decreases pH, thus releasing hydrogen into the solution (Langmuir 1997; Casiot et al. 2005; Verplanck et al. 2004; Sánchez-Rodas et al. 2005). The amount of released hydrogen can be calculated from the molal ratio of the precipitated Fe and released hydrogen from the precipitation reaction (4). When calculating, the dilution should be also considered. One mole of precipitated Fe produces $\left([Fe^t]_o - [Fe^t]_i\right) \times \frac{24-2x}{8}$ moles of hydrogen if there is no dilution. If only precipitation factor is considered, the total Fe content at the *i*th site must be

corrected excluding dilution and the hydrogen produced by only precipitation of one mole Fe and the calculated pH values becomes

$$[H^+]_{i,p} = \left([Fe^t]_o - [Fe^t]_i \times D_i\right) \times \frac{24-2x}{8}, \qquad (9)$$

$$pH_{i,p} = -\log\left\{[H^+]_o + \left([Fe^t]_o - [Fe^t]_i \times D_i\right) \times \frac{24-2x}{8}\right\} \qquad (10)$$

The calculated pH values, when considering only precipitation, are plotted in Fig. 9. The dilution factor is based on the assumption that the sulfate concentration of added groundwater is near 0 ppm. The precipitation of schwertmannite can decrease pH values at the last sampling site to as low as 3.22 (Table 2), which is lower than the values measured in the field. The patterns of decreasing pH values are, however, similar for both calculated and measured pH values, indicating that precipitation is the most important factor that controls pH here, even with the precipitation of a very small concentration of iron (13.4 ppm).

In order to calculate the effect of dilution and precipitation together, the increased hydrogen molal concentration must be divided by D_i, and the final pH values after the precipitation of schwertmannite and dilution will be

$$pH_{i,p,d} = -\log\left\{\frac{[H^+]_o}{D_i} + \left(\frac{[Fe^t]_o}{D_i} - [Fe^t]_i\right) \times \frac{24-2x}{8}\right\} \qquad (11)$$

The pH values, including the effects of both precipitation and dilution, are also plotted in Fig. 9.

Calculated pH value only increases to 3.31 at the last sampling site. This shows that the effect of dilution on pH is less than that of precipitation. This calculated pH value is still lower than the measured one and other factors must be considered when estimating the final pH values.

Redox factor

By the oxidation of Fe^{2+}, as shown in reaction (12), hydrogen is consumed and the pH increases.

$$2Fe^{2+} + 1/2\ O_2 + 2H^+ \rightarrow 2Fe^{3+} + H_2O \qquad (12)$$

The contents of the stream Fe^{2+} ions were obtained from the ratio of Fe^{2+} versus Fe^{3+} for the dissolved iron, which is calculated by PHREEQC from the Eh measured in the field (Parkhurst and Appelo 1999). This calculated ratio of Fe^{2+}/Fe^{3+} is used to determine the redox effect on pH values. This is because recent studies have reported that there is a good correlation between the Eh measured in the field and the calculated one using Fe^{2+}/Fe^{3+} ratio, indicating that the oxidation of Fe^{2+} governs redox potential (Sánchez Espana et al. 2005; Sidenko and Sherriff 2005). Sometimes photo-reduction of iron is an important role affecting dissolved Fe concentrations and pH values (McKnight et al. 1998, 2001). The final concentration of iron was, however, close to 0 ppm and this indicates that photo-reduction probably was not important in this study area. One mole of Fe^{2+} ion consumes one mole of hydrogen by oxidation at the ith site and the decreased hydrogen content ($[H^+]_{i,ox}$) will be $[Fe^{2+}]_o - [Fe^{2+}]_i \times D_i$ if there is no dilution. After dilution and oxidation, the decreased content of hydrogen ($[H^+]_{i,ox,d}$) becomes $\frac{[Fe^{2+}]_o}{D_i} - [Fe^{2+}]_i$. The concentration of Fe^{2+} can also increase by reduction at the ith site with a decrease of the pH, which is the case at site A4 in the stream (Fig. 10). The pH can be calculated from the hydrogen concentrations affected by dilution, precipitation, and redox factors and it will be

$$pH_{i,p,d,ox} = -\log\left\{ \frac{[H^+]_o}{D_i} + \left(\frac{[Fe^t]_o}{D_i} - [Fe^t]_i \right) \times \frac{24 - 2x}{8} \right.$$
$$\left. - \left(\frac{[Fe^{2+}]_o}{D_i} - [Fe^{2+}]_i \right) \right\} \qquad (13)$$

As shown in Fig. 9, redox change, however, has only a slight effect on pH, at least in the stream from the landfill in the Dalsung mine. By combining those three factors, the final values of the calculated pH and its decreasing pattern are still similar to those calculated using a precipitation reaction (11), slightly increased at the final measured site. A discrepancy, however, still remains between the measured and calculated pH values.

Alkalinity and other factors

The final calculated pH values are less than the measured ones. One factor that was missed in the calculation is alkalinity. In AMD, alkalinity sometimes plays an important role in neutralizing acidity caused by the oxidation of pyrite (Sánchez Espana et al. 2005; Munk et al. 2006). At the pH range of this stream (4–6), most carbonate phases will be H_2CO_3, but some are in the form of HCO_3^-. HCO_3^- consumes hydrogen and is converted to H_2CO_3.

If alkalinity factor is also considered in the quantitative calculation of pH, the equation will be

$$pH_{i,p,d,ox,al} = -\log\left\{ \frac{[H^+]_o}{D_i} + \left(\frac{[Fe^t]_o}{D_i} - [Fe^t]_i \right) \times \frac{24 - 2x}{8} \right.$$
$$\left. - \left(\frac{[Fe^{2+}]_o}{D_i} - [Fe^{2+}]_i \right) - \left(\frac{[Alk]_0}{D_i} - [Alk]_i \right) \right\} \qquad (14)$$

Here, $[Alk]_{o,i}$ is alkalinity as equi/L at initial and ith sites. Unfortunately, alkalinity was only measured at the first site in this study. Therefore, we only calculated the pH values at the sampling sites showing pH values lower than 4.3, at which all HCO_3^- is assumed to be converted to H_2CO_3. At these sites, $[Alk]_i$ was considered as 0. The final calculated pH value of 3.88 is quite close to the measured one, even though it does not exactly match with the measured one at the final site. The slight difference between the observed and calculated pH values can be caused by several factors. For this calculation, the SO_4 content of the added groundwater was not considered due to the lack of data. If we used the sulfate concentration (126 ppm) of the groundwater sampled in the well near site 6, the dilution factor can be recalculated using Eq. 8 and with an increase in the dilution factor, the final pH value slightly increased to 3.90. The sulfate concentration used here, however, represents that of the groundwater in limited areas, which may be different between sites. The inaccuracy in the measured Eh can cause errors in the final pH. For example, from these calculations, a 10 mV difference in Eh appears to result in a 0.1 difference in the final pH values. The dissolution of andesitic rock may increase the alkalinity, which was not considered in this study, and this also causes errors.

In considering all possible errors that could affect the estimated pH values, the similar decreasing trend of the calculated pH values and the encouraging match between the measured and calculated values indicate that the pH values in the AMD can be estimated accurately and can be used for the quantitative estimation of each factor that affects pH changes and for pH development prediction, and eventually, such calculations may be able to determine the behavior of heavy metals.

In this study area, the contribution of each factor can be calculated based on the hydrogen release (+) and consumption (−). Figure 10 shows the changes of those contributions at each site compared with the initial sampling sites. Alkalinity factor was considered only at the final five sites. The factors that affect the pH change of the stream, which are influenced by AMD include precipitation, dilution, redox change, and alkalinity. The most significant factor affecting pH is precipitation and its influence is mainly in the upstream. This is due to the fast precipitation of schwertmannite and the hydrogen content which released from the precipitation. The hydrogen content decreases and eventually disappears. This is because most of the iron was already precipitated. The reduction releases hydrogen in the upstream, but eventually all iron is oxidized and this oxidation of iron increases pH in the stream. Other factors, such as dilution and alkalinity, decrease the hydrogen concentration. Alkalinity is the main factor buffering acidity caused by the precipitation of schwertmannite.

Conclusions

Field and laboratory geochemical data were collected from the stream affected by AMD in the Dalsung mine. Many different factors affect the pH changes in the streams affected by AMD. From those data, a simple equation was derived to calculate pH changes and the effect of each controlling factor on pH values was estimated to quantitatively understand the hydrogeochemical processes in AMD. The stream shows low pH ranges (4.04–5.96), high electrical conductivity (1,407–1,664 µS/cm), and sulfate concentration (680–854 ppm). The pH decrease in the flowing downstream is abnormal in the stream affected by AMD. Other geochemical factors, such as EC and ion concentrations, generally decrease. This is mainly due to dilution. Iron content decreases to almost 0 ppm from 13.4 ppm due to schwertmannite precipitation. According to the calculations, among those factors, the contribution from the precipitation of schwertmannite is the most influential factor that lowers pH values among the factors affecting pH. Alkalinity is the main factor which consumes hydrogen and buffers acidity caused by precipitation. The effects of alkalinity are, however, not significant enough to buffer the hydrogen released from the precipitation of schwertmannite and, as a result, the pH decreases. Other factors, such as dilution and redox change, also contribute to changes in pH, to a certain degree. The pH decreases significantly upstream due to the fast precipitation of schwertmannite and the release of hydrogen into the stream. Downstream, most iron is consumed and the pH values become constant. Even though the calculated pH values differ slightly from the calculated ones, due to the uncertainty in the observed Eh values and the calculation of the dilution factors, our results show that fairly accurate pH values in the stream, which are affected by AMD, can be estimated by simple calculation and the hydrogeochemical processes that affect the toxicity of heavy metals can be predicted.

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