Characterization and Two-Phase Neutralization of Acid Mine Drainage

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Abstract : Acid mine drainage (AMD) results from sulfuric acid produced by the oxidation of pyrite, and contains large amounts of toxic elements. In the neutralization of AMD, iron and aluminum hydroxides are the major precipitates and those two can be separated with two-phase neutralization. In this study, removal of toxic elements by the two phases of neutralization was investigated using an AMD collected from the abandoned antimony mine in Gachang, Taegu. Contents of As, Cd, Cu, Mn, Pb and Zn in the AMD were higher than the criteria of river water quality or permissible waste water discharge. In the first phase, the AMD was neutralized to several % (25, 50, 75, 100, and 125) of $Fe(OH)_3$ equivalence point with solid $Ca(OH)_2$. In the second phase, the supernatant of the first phase neutralization was titrated to pH 7.5. After neutralization of the AMD to 100% of the $Fe(OH)_3$ equivalence point, most of Fe and Pb were removed but levels of As, Cd, Cu, Ni, Mn, and Zn were not reduced in the supernatant solution. In the second phase neutralization, levels of those toxic elements in the supernatants dropped below the wastewater discharge or river water quality criteria. This result suggests that the precipitate formed in the first phase of the neutralization process may be disposed without any special cares. Thus the two-phase neutralization scheme can reduce the cost of disposing precipitates containing toxic metals in comparison with the monophase neutralization scheme.(Received October 13; accepted January 5, 1999)

Introduction

Biological oxidation of mine tailings and wastes has resulted in the acidic and toxic heavy metal-containing discharge known as acid mine drainage (AMD). Waters flowing from coal mines and draining from the gob piles left over from coal processing and washing are practically sterile due to high acidity. Acid mine water results from the presence of sulfuric acid produced by the oxidation of pyrite. The acidity formed by pyrite oxidation and bacterial activity can oxidize other sulfide minerals associated with the pyrite and release large amount of toxic metal ions. Therefore the AMD must be treated to meet the water quality criteria for discharge into streams.

Methods have been developed to treat mine drainage to produce water of almost any desired quality. The methods include neutralization, foam separation, ion exchange, reverse osmosis, freezing crystallization, and the use of wetlands.[1-11] Neutralization is the most common method being used today to mitigate AMD. The idea behind neutralization is that the anions of the alkaline reagents react with the available hydrogen ions in the acidic drainage waters to form weakly-ionized species.[1] When the solubility products of the anionic species are exceeded, the species will precipitate thus reducing their solution concentrations.

There are a number of factors which must be considered in this process, such as the type of alkaline material employed, how it is added and mixed with the AMD, and the pH of the final neutralization.[8] These factors are determined by the water characteristics, government regulations, equilibria, and mechanical factors such as mixing and the alkaline reagent particle size.[8] According to Vachon et al.[5] the optimum pH for neutralization and effective metal removal is dependent on the metal species present in the AMD and may range from 6.5 to 11.5, with the most common choice being pH 9.5. Another important consideration in remediating AMD by neutralization is the large volumes of precipitate that are produced and the cost associated with their disposal. Therefore, each AMD must be characterized prior to set up an optimum treatment scheme.

In this study, AMD was collected from Gachang Antimony mine in Taegu and the effect of two-phase neutralization, precipitation of Fe and Al hydroxides, on the removal of toxic metals from the aqueous phase was investigated.

Materials and Methods

Characterization of AMD
Acid mine drainage sample was collected from one of the

mineheads in Gachang antimony mine on August 23, 1998. Temperature, pH, EC, redox potential, and concentration of dissolved O_2 in the AMD were measured in the field. In laboratory, the AMD sample was filtered first through a Whatman No. 42 filter paper and then through a 0.45-μm nylon membrane filter. The AMD sample was analyzed for Al, As, Ca, Cd, Cr, Cu, Fe, Mg, Mn, Ni, Pb and Zn using a Varian Liberty Series II inductively coupled plasma atomic emission spectrometer (Varian Australia Pty Ltd., Mulgrave, Australia) and SO4 with a Dionex Dx-120 ion chromatograph (Dionex Corp., Sunnyvale, CA, USA).

Determination of iron hydroxide equivalence point

Three replicates of 150 ml AMD sample were titrated with solid $Ca(OH)_2$ to approximately pH 9.0 while vigorously stirring. The iron hydroxide equivalence point was determined by plotting the first derivative of the titration curve against the titer, fitting all the data in the plot to a single second order polynomial regression, setting the first derivative of the regression equation equal to zero and finally, calculating the amount of $Ca(OH)_2$ needed to neutralize the AMD to 100% of the iron hydroxide equivalent point.

Two-phase neutralization

For phase I, 150 ml of the AMD sample was transferred into each 250 ml polycarbonate centrifuge bottle. Three replicates were neutralized by adding 25% of the amount of $Ca(OH)_2$ necessary to reach the iron hydroxide equivalence point. In the same manner, additional sets of three replicates were neutralized by adding 50, 75, 100 and 125% of the amount of $Ca(OH)_2$ necessary to reach the iron hydroxide equivalence point, respectively. The samples were placed on an end to end shaker for at least 2 hours, and then were allowed to equilibrate in a dark cabinet at room temperature (20~23°C) for 48 hours. After equilibrating, the pH was measured in all samples. The precipitates were separated from solution by filtering first through a Whatman No. 42 filter paper and then through a 0.45-μm nylon membrane filter. Approximately 50 ml of the supernatant was saved for analyses, and Al, As, Ca, Cd, Cr, Cu, Fe, Mg, Mn, Ni, Pb, Zn and SO₄ were measured as above. Remainder of the supernatant was used in the second phase of the neutralization

scheme.

In phase II, 100 ml of the supernatant solution from each of the samples in the phase I was transferred into a 250 polycarbonate centrifuge bottle and the pH was raised to 7.5 with solid $Ca(OH)_2$ under vigorous stirring. If the pH fell below 7.5, it was readjusted with solid $Ca(OH)_2$ and then the samples were placed in a dark cabinet at room temperature (20~23°C) to equilibrate for at least 48 hours. Precipitates were then separated from the solution by filtering first through a Whatman No. 42 filter paper and then through a 0.45-μm nylon membrane filter. Approximately 50 ml of the supernatant was saved for the analyses as above.

Results and Discussion

The AMD collected from the abandoned antimony mine in Gachang was well oxidized and very clear. Some electrochemical characteristics of the sample are listed in Table 1. Since the sample was collected in the end of a long rainy season, those characteristics might be somewhat diluted. pH of the AMD was characteristic of that found in biologically oxidized AMDs which are usually buffered between pH 2 and 3.[12] The redox potential was slightly higher than the redox potential for the half reaction of ferric iron at standard state, which is 0.77 V.[13] This suggests that ferric iron is the stable species in the water. Electrical conductivity indicates that the AMD contains much more ionic species than a good quality tap water (0.05 dS/m) or river waters found in agricultural areas (0.15 dS/m).[14] The AMD was slightly undersaturated in O_2 at 80% saturation. The solubility of O_2 in pure water at 8.5°C is 11.3 mg/l.

Compositions and contents of mineral species in AMDs are various according to geological variations and weather conditions of the mine sites. Concentrations of the major dissolved mineral species and other elements of concern in the AMD from Gachang are listed in Table 2. Comparing

Table 1. Characteristics of the AMD collected from Gachang antimony mine on August 22, 1998

Temperature (°C)	pH	E_h (V)	EC (dS/m)	Dissolved O_2 (mg/l)
8.5	3.2	0.80	3.3	9.0

Table 2. Concentrations of the major dissolved mineral species and other elements of concern in the AMD collected from Gachang antimony mine on August 22, 1998

Elements	Fe	Al	SO₄	As	Ca	Cd	Cr	Cu	Mg	Mn	Ni	Pb	Zn
Concentration, mg/L	302	88.4	2733	0.50	334	0.49	0.01	64.9	165	112	0.16	0.10	28.7
RWQS[1], mg/L				0.05		0.01	0.05					0.1	
PWDS[2], mg/L	2.0			0.1		0.02	0.5	0.5		2.0		0.2	1.0

[1]River water quality standard.
[2]Permissible wastewater discharge standard for clean area.

to some published foreign data, Cu, Mn, and Zn contents were higher and Cd, Cr, Ni, and Pb contents were relatively lower.[2,15,16] Among the elements, concentrations of As, Cd, Cu, Mn and Zn were higher than the River Water Quality Standard or Permissible Wastewater Discharge Standard. Also the high contents of Fe and Al in the AMD were problematic since they could produce a large amount of visible yellowish precipitation in streams when discharged without any treatment.

The titration curve for AMD with solid $Ca(OH)_2$ is depicted in Fig. 1. The two buffering zones at pH around 4.4 and 5.4 are due to the precipitation of Fe^{3+} and Al^{3+} hydroxides, respectively, by the following reactions.

$$Fe^{3+}+3OH^- \rightarrow Fe(OH)_3 \tag{1}$$

$$Al^{3+}+3OH^- \rightarrow Al(OH)_3 \tag{2}$$

Mixed conditional equilibrium constant (pK^c) for the buffered
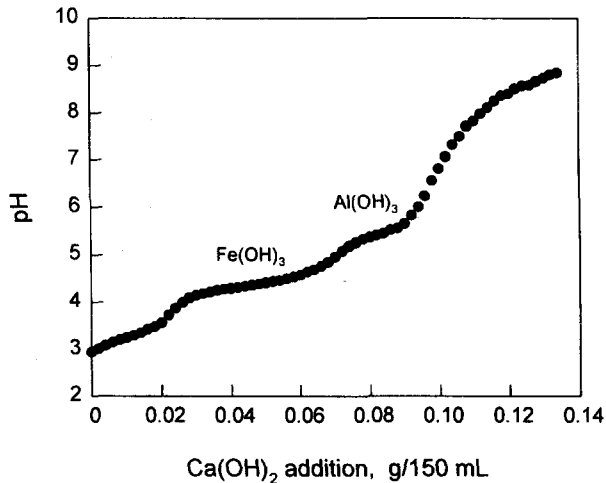
Fig. 1. Titration of 150 ml of AMD with solid $Ca(OH)_2$.
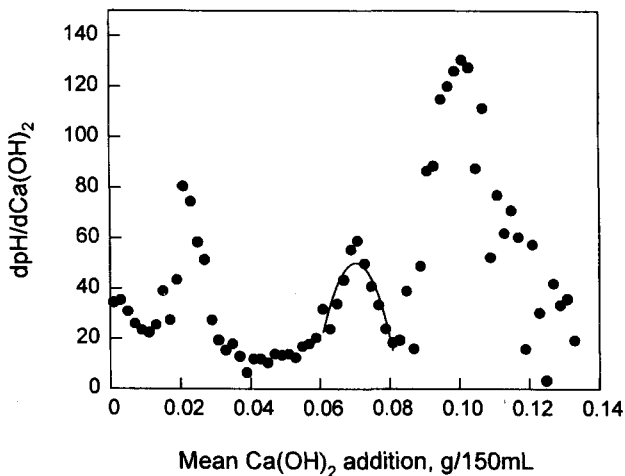

Mean Ca(OH)$_2$ addition, g/150mL

Fig. 2. First derivative of the titration curve in Fig. 1. Second order regression equation was fit to the ferric hydroxide peak. The equation was $Y=-1493.6+43848X-311334.5X^2$, where Y=dpH/dCa (OH)$_2$ and X=mean Ca(OH)$_2$ addition.

regions, calculated from the concentrations of Fe and Al, and the activity of hydroxide were 34.5 for $Fe(OH)_3$ and 32.7 for $Al(OH)_3$, and those agreed reasonably well with previously reported values; 37.4 for $Fe(OH)_3$ and 32.9 for $Al(OH)_3$.[17]

A clear separation between the precipitation of Fe^{3+} as Fe (OH)$_3$ and Al^{3+} as $Al(OH)_3$ was evident in the titration curve and should allow for the separation of the precipitate fractions at the ferric hydroxide equivalence point. This was the point at which the precipitation of iron was complete. It was also the inflection point in the steep slope of the curve between the $Fe(OH)_3$ and $Al(OH)_3$ buffering zones.

The amount of $Ca(OH)_2$ necessary to reach the $Fe(OH)_3$ equivalence point of the AMD was calculated by plotting the first derivative of the titration curve (Fig. 2). The first peak in the plot is probably due to the neutralization of sulfuric acid which is the strongest acid present in the AMD. The second strongest acid is Fe^{3+} which corresponds to the second peak and the third strongest is Al^{3+} corresponding to the third peak.

The iron peak of the first derivative curve was fit to a second order regression equation (Fig. 2). The first derivative of the regression equation was set to zero and solved to determine the amount of $Ca(OH)_2$ required to bring 150 ml of AMD to the equivalence point. The calculated amount of $Ca(OH)_2$ for the iron hydroxide equivalence point was 0.071 g $Ca(OH)_2$ for 150 ml of the AMD.

The sample was neutralized to five selected % (25, 50, 75, 100, and 125) of ferric hydroxide equivalence point (Table 3). The reason for the experiment was to optimize the separation of the precipitates and to remove as less toxic metals as possible with as much $Fe(OH)_3$ as possible. Results of neutralizing AMD to the selected % of ferric hydroxide equivalence point are shown in Fig. 3. The values at 0% of the equivalence point are those of the untreated AMD. Fig. 3 clearly shows the complete precipitation of iron from the solution in Phase I neutralization. Concentration of Fe declined from 302 mg/l in the untreated water to nearly zero at 100% of the ferric hydroxide equivalence point. Though precipitate formed, the concentration of Fe at 25% equivalence point was not 75% of the Fe concentration of untreated AMD. It may be due to some of the alkalinity neutralized the sulfuric acid

Table 3. The amount of solid $Ca(OH)_2$ required to neutralize 150 ml of AMD to selected % of the iron hydroxide equivalence point.

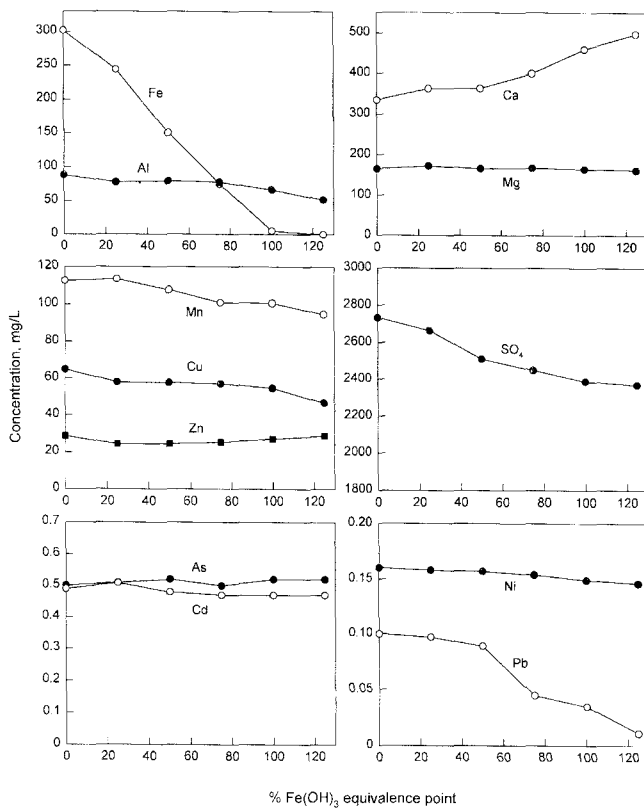| % of Fe(OH)$_3$ equivalence point	Ca(OH)$_2$, g
25	0.018
50	0.035
75	0.053
100	0.071
125	0.088

Fig. 3. Concentrations of dissolved mineral species in the supernatant solution of AMD neutralized to selected % of the ferric hydroxide equivalence points with solid Ca(OH)₂.

in solution. This plot also shows that Al can remaine in solution until the 125% equivalence point at which point the Al begins to precipitate as $Al(OH)_3$.

Sulfate was removed from solution by precipitating as gypsum, and this is corroborated by the plot of Ca (Fig. 3). Although the concentration of Ca in solution increased due to the addition of $Ca(OH)_2$, more than a half of the added Ca was removed by precipitation with SO_4. Since there is a stoichiometric excess, sulfate always exceeds calcium and the solubility exceeds that of a pure gypsum solution ($K_{sp}=$

2×10^{-4}) because of the high ionic strength of the solutions.

Magnesium, As, Cd, Ni and Zn were not removed from solution at any of the % equivalence point selected. The concentrations of Mn, Cu and Pb in the Phase I supernatant solutions slightly decreased with increasing % of ferric hydroxide equivalence point. The highest pH associated with the Phase I neutralization was 4.80, below the adsorption edges and hydroxide precipitation points of these metal cations.

In the second phase of the neutralization scheme, the supernatant solutions from Phase I were all neutralized to pH 7.5 with solid $Ca(OH)_2$. Concentrations of the elements of concern in the supernatant solutions from Phase II neutralization are found in Table 4.

The data of Fe show that this metal has essentially been removed from solution, and most of Al also has been removed. The concentration of Ca in the solutions remained fairly constant for all the treatments most likely at levels in equilibrium with precipitated gypsum. Magnesium was unaffected by the treatment and the initial concentration was maintained throughout the treatment range. Although there are evidences for the adsorption of alkaline earth elements to oxide surfaces,[18] the conditions for its sorption to the precipitates were not favorable in this study. Kinniburgh et al. found that Mg was not selectively sorbed onto Fe or Al gels until the pH was above 8.5.[18] Manganese was also unaffected in neutralizations of Phase II. The reason for this observation is unclear at this point.

The Ni, Pb, and Zn data suggested that Ni, Zn, and to some extent Pb were more sympathetically sorbed to ferric hydroxides than aluminum hydroxides since the concentration of these elements remaining in the Phase II solutions increased as the Phase I Fe concentration of the solution decreased.

After the Phase II neutralization, all of the toxic elements, except Mn and Cd, in AMD remained below the River Water Quality Standard and Permissible Wastewater Discharge Standard for clean area. Although the Cd concentrations slightly

Table 4. Concentrations of dissolved mineral species in the supernatant solutions of Phase II neutralization. In the Phase II neutralization, the supernatants from Phase I neutralization were titrated to pH 7.5 with solid Ca(OH)₂

Minerals	Concentrations in supernatant solutions from Phase II titration, mg/L				
	25%	50%	75%	100%	125%
Al	2.15	2.35	2.53	2.37	2.47
As	0.03	0.04	0.04	0.04	0.03
Ca	574.5	586.3	616.2	623.9	617.8
Cd	0.03	0.04	0.02	0.02	0.02
Cu	0.17	0.16	0.07	0.07	0.09
Fe	0.02	0.01	0.02	0.01	0.01
Mg	153.2	162.0	159.3	165.2	168.4
Mn	77.1	82.8	85.1	84.9	85.6
Ni	0.03	0.05	0.08	0.08	0.09
Pb	0.01	0.02	0.02	0.05	0.03
Zn	0.15	0.19	0.27	0.28	0.29

exceeded the standards, the levels remained low enough that the concentration of Cd should not be a problem when mixed with stream water.

Two-phase neutralization could be a promising method for removing toxic levels of dissolved mineral species from AMDs as well as for minimizing the mass of AMD sludge which must be disposed in a permitted landfill. The process may take advantage of the high concentration of Fe^{3+} in AMD. In the Phase I neutralization, if the AMD is neutralized to 100~125% of the iron hydroxide equivalence point, almost of the Fe^{3+} can be removed with iron hydroxide and with some coprecipitated Pb. This precipitates can be disposed without any special treatments. Most of the toxic elements are removed in the Phase II neutralization and the mass of AMD sludge which must be disposed at a hazardous waste site can be significantly reduced.

Acknowledgment

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두 단계 중화적정에 의한 산성 광산 유출수 중의 중금속 제거

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초 록 : Pyrite의 산화과정에서 생성되는 황산 때문에 발생하는 산성 광산 유출수는 다량의 중금속들을 함유하므로 적절한 처리 과정을 거친 후 배출되어야 한다. 산성 광산 유출수의 중화과정에서 발생하는 침전물은 주로 철과 알루미늄의 수산화물인데, 이 두 침전물은 2단계 중화과정을 거치면 분리될 수 있다. 본 연구에서는 대구시 달성군 가창면에 위치한 폐중석광산의 유출수를 이용하여 철과 알루미늄의 침전물에 의한 중금속의 제거 현상을 조사하였다. 유출수의 pH는 3.2였으며 As, Cd, Cu, Mn, Pb, Zn 등의 함량이 하천수질기준이나 폐수배출허용기준을 상회하였다. 1단계 중화에서는 Ca(OH)$_2$를 이용하여 철이 먼저 침전되도록 하였으며, 철을 100% 침전시켰을 때 납은 상당부분 침전으로 제거되었으나 대부분의 중금속은 제거되지 않았다. 2단계 중화에서는 1단계 중화 후의 상등액을 pH 7.5까지 적정하였는데, 이 때 As, Cd, Cu, Ni, Mn, Zn 등의 중금속들이 하천으로 방류가 가능한 수준으로 제거되었다. 1단계 중화에서 발생한 철 침전물은 특별한 처리 없이 폐기될 수 있을 것이며, 2단계 중화에서 생성된 침전물은 중금속을 함유하므로 특정폐기물로 취급하여 처리하여야 할 것이다. 이러한 두 단계 중화과정을 거치면 효과적인 중금속의 제거와 함께 산성 광산 유출수의 처리 후 발생하는 중금속 함유 침전물의 처리에 따른 비용의 절감이 가능할 것이다.