Variations in the Concentration of Dissolved Metal Ions and their Buffering Effect in an Acidified River Environment

Masatoshi ENDO*, Eishi YOSHIKAWA*, Yusaku TAMAKI*, Akira HARA*, Kazuhiro HIKICHI*, Atsushi SASAKI**

*Graduate School of Science and Engineering, Yamagata University, 4-3-16 Jonan, Yonezawa, Yamagata 992-8510, Japan
**Technical Division of Instrumental Analysis, Faculty of Engineering, Yamagata University, 4-3-16 Jonan, Yonezawa, Yamagata 992-8510, Japan

ABSTRACT
The concentration variations of dissolved metal ions and their buffering effect in an acidified river were investigated by analyzing the data collected through a long-term field investigation and an intensive field investigation. The field investigations targeted Matsukawa River in Japan, which is acidified by the inflow of acid mine drainage. In periods of rainfall and snowmelt, Al, Mn, Fe, Cu, and Zn ions exhibited different decreasing trends than did alkali and alkaline earth metal ions and sulfate. These findings suggested that the decreases in Al, Mn, Fe, Cu, and Zn ion concentration were attributable not only to dilution by the inflow of rainwater and snowmelt but also to the hydrolysis of Al. Additionally, the mineral phases of Al in this acidified river were analyzed by using the geochemical modeling software (PHREEQC). From the results, dissolved Al ions acted as a buffer from pH 4 to 6, and the basaluminite (Al₄(SO₄)(OH)₁₀) as the dominant chemical species, mainly controlled the solubility of Al from pH 4 to 6.

Keywords: acid mine drainage, aluminum, river acidification

INTRODUCTION
The inflow of acid mine drainage (AMD) leads to high metal concentrations in rivers and acidification as a result of the oxidation of sulfide minerals (Akcil and Koldas, 2006). The AMD has been generated by the oxidation of sulfide minerals, mainly pyrite (FeS₂). When pyrite contacts with air and water, it is oxidized to hydrogen ions and sulfate, which are the dissociation products of sulfuric acid. On the other hand, oxidation of the ferrous ion to ferric ion occurs.

\[ 4Fe^{2+} + O_2 + 4H^+ \rightarrow 4Fe^{3+} + 2H_2O \] (1)

Further dissolution of the pyrite can occur by the reaction of pyrite with the generated ferric ion.

\[ FeS_2(s) + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \] (2)

This reaction generates more H⁺ ions and increases the acidity of water. The oxidation of sulfide releases dissolved iron and H⁺ ion into water which subsequently releases other metal ions such as aluminum, manganese, zinc and smaller amount of cadmium, lead, copper, and nickel among others. Although AMD is naturally occurring, pit mining may extremely accelerate its production because the areas of ore deposits exposed to oxygen and water increase. The acidification of rivers disrupts the natural environment.
in surrounding areas (Gerhardt, 1993; DeNicola and Stapleton, 2002; Nieto et al., 2007). Especially, the decrease in pH has a fatal adverse effect on inhabitations of the attached algae which have an important role as primary producers in the food web of aquatic ecosystem (Sasaki, A. et al., 2005). Additionally, it was reported that the adsorption and/or dissolution of metals have been closely involved in the buffering processes of acidified groundwater (Franken, G. et al., 2009). Therefore, it is likely that the changes in concentrations and forms of metal ions have also some influence on the behavior of pH in acidified surface waters such as an acidified river environment. However, few studies have focused specifically on the buffering effect by such metal ions in acidified surface waters. The aim of this study was to determine the main factors affecting the behavior of pH from the seasonal and temporal field investigations and to clarify the buffering mechanism in an acidified river environment.

METHODS

Study area

Matsukawa River is a typical acidified river of Japan. The source of the river is located near Mount Azuma, overlooking the city of Yonezawa in southeast Yamagata Prefecture. The abandoned Nishiazuma mine is located on Mount Azuma and continues to discharge AMD. Infiltration treatment has been attempted by diverting AMD into the ground through 80 permeable wells of about 80 m in depth. The AMD discharged into the permeable wells is diluted by groundwater and neutralized by cation exchange upon contact with soil and bedrock; the treated AMD leaches out and flows into nearby rivers. Seven stations (Fig. 1) were selected to comprehensively investigate the Matsukawa River area. Station 1 was located at the device used to divert AMD into the permeable wells. Station 2 was in a stream that received leachate from the permeable wells. Stations 3 and 4 were located in the transition zone between the mountainous area and the agricultural and urban areas. Stations 5 to 7 received flow from several tributaries of Matsukawa River and were situated in an agricultural or urban area.

![Fig. 1 - Location of AMD treatment facility and monitoring stations in the Matsukawa River area.](image-url)
Field investigations
In our long-term investigation, water sampling was conducted at the seven stations (Fig. 1) during the summer and fall seasons within 10 years from 2002 to 2011 (June 25 and October 17, 2002; June 30 and October 28, 2003; July 8 and October 29, 2004; July 19 and October 27, 2005; August 9 and November 9, 2006; July 9 and October 25, 2007; July 3 and October 21, 2008; July 7 and October 28, 2009; June 24 and November 5, and July 19 and October 12, 2011). The pH and electrical conductivity (EC) values were measured on site. Anions (NO$_3^-$, Cl$^-$, and SO$_4^{2-}$) in the water samples were measured by ion chromatography (DX-500, Nippon Dionex K. K.) after filtration through a membrane filter (pore size: 0.45 μm). After the filtered water samples were treated with HNO$_3$, dissolved Na, K, Al, As, Ca, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, and Zn were analyzed by atomic absorption spectroscopy (Z-5010, Hitachi) and inductively coupled plasma mass spectrometry (Elan DRCII, PerkinElmer) in accordance with the standard methods of the American Public Health Association (APHA, 1998). The ion activities of the water samples were calculated by aqueous speciation modeling in PHREEQC (Parkhurst and Appelo, 1999) using the default thermodynamic database.

In the intensive field investigation, daily water sampling was conducted at Station 5. The pH and EC values, anions (NO$_3^-$, Cl$^-$, and SO$_4^{2-}$) and dissolved metals (Na, K, Ca, Cu, Fe, Mn, and Zn) were measured by the same methods as in the long-term field investigation. The intensive investigation period covered 72 days from April 20 to June 30, 2011. In addition, water level data collected at a monitoring site (shown in Fig. 1) managed by the Department of Land Development, Yamagata Prefecture, Japan were used in data analysis. Using conversion factors, the equivalent concentrations measured for NO$_3^-$, Cl$^-$, SO$_4^{2-}$, Na, Mg, K, Al, As, Ca, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, and Zn were 0.016, 0.028, 0.021, 0.043, 0.082, 0.026, 0.111, 0.026, 0.111, 0.040, 0.050, 0.018, 0.058, 0.031, 0.054, 0.010, 0.036, 0.034, 0.010, and 0.031 mEq/mg, respectively.

RESULTS AND DISCUSSION
Long-term field investigation
Figure 2 shows the mean pH and equivalent concentrations of the major ions at each station. The concentration of SO$_4^{2-}$ was more than 8.33 mEq/L (400 mg/L) in Station 1. It was due to the inflow of AMD with high concentrations of acid and SO$_4^{2-}$ from many discharge spots in the abandoned mine. The concentration of SO$_4^{2-}$ in Station 2 which the infiltration treatment has been conducted showed a sharp decrease down to less than 2.71 mEq/L (130 mg/L). Thereafter, SO$_4^{2-}$ decreased gradually downstream by the inflow of the tributaries. On the other hand, Cl$^-$ and NO$_3^-$ increased downstream from Station 6. These behaviors of Cl$^-$ and NO$_3^-$ were due to an increase in the inflow of domestic and agricultural drainages with a change in the land use from the mountainous areas to the agricultural and urban areas. The pH value was less than 3 at Station 1, but was dramatically higher at Station 2, which was situated beyond the infiltration treatment site. The concentrations of dissolved metals (especially Fe and Al) were high at Station 1, and the concentrations of all metals except Ca decreased downstream of Station 2. These decreases in dissolved metal concentrations and increase in pH were attributable to the infiltration treatment. The increase in Ca concentration was probably due to leaching from soil and bedrock at the infiltration treatment site. Although the concentrations of dissolved metal ions and sulfate decreased downstream of Station 2, pH did not exceed 5.5 between Stations 2 and 5 where the dissolved Al content
remained above 0.034 mEq/L (0.31 mg/L). The pH rapidly increased to above 6.5 between Stations 5 and 6, where the dissolved Al content was less than 0.016 mEq/L (0.15 mg/L). Station 5 appeared to be located in transition zone of water quality, where pH and dissolved Al concentration in Matsukawa River changed sharply. In an acidified river, riverbed sediments have been reported to have much higher Al content where pH is greater than 5 (Sasaki et al., 2005), so the observed change in the concentration of dissolved Al was likely due to the lower solubility of aluminum hydroxide when pH was raised by dilution. The higher alkalinity can be attributed to the inflow from tributaries and domestic and agricultural drainages.

**Intensive field investigation**

The intensive field investigation was conducted to evaluate the buffering effect of dissolved metal ions such as Al at Station 5 in the transition zone of water quality. Figure 3 shows the time courses of pH and EC together with water levels during spring and summer (April 20 to June 30, 2011). From April 20 to 30, pH remained relatively high. At the same time, the water level showed an increasing trend, although there was no rainfall greater than 10 mm/day. Considering the time of year, the increase in pH likely resulted from dilution due to snowmelt. From May 4 to 29, the water levels decreased as the inflow of snowmelt tapered off. At the same time, pH decreased to less than 5.5. On May 30 and June 23, when rainfall was 19.0 and 62.5 mm/day, respectively, the pH value increased rapidly as the EC value decreased together with a sharp increase in the water level. In addition, from June 19 to 30, which marks the start of the rainy season, pH increased again as the water level gradually increased.

Table 1 shows the correlation coefficient between each ion concentration and $H^+$ ion concentration as calculated from the data collected during the intensive field investigation. The correlation coefficient between Al concentration and $H^+$ ion concentration was the highest one calculated for the investigation period. Table 2 shows the mean equivalent concentrations of metal ions and of anions, the percent decrease in equivalent concentrations in Matsukawa River before (June 8 to 20) and after (June 23 to 30) the start of the rainy season, and the correlation coefficient between the ion concentration and water level during the sampling period from June 8 to 30, a period
during which water levels increased. The metal ions and the anions could be divided into two groups according to the percent decrease in concentration; the percent decrease in concentration was significantly higher (> 76%) for H⁺, Al, Mn, Fe, Cu, and Zn ions than for the other ions. The ions in the group with a low percent decrease (Na, Mg, K, Ca, Cl⁻, NO₃⁻, and SO₄²⁻) had high negative correlations with water level around the start of the rainy season (June 8 to 30).

**Table 1 - Correlation coefficient between each ion concentration and H⁺ ion concentration (April 20 to June 30, 2011).**

<table>
<thead>
<tr>
<th>Name</th>
<th>Correlation constant with the hydrogen ion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn</td>
<td>0.47</td>
</tr>
<tr>
<td>Cu</td>
<td>0.30</td>
</tr>
<tr>
<td>Al</td>
<td>0.88</td>
</tr>
<tr>
<td>Zn</td>
<td>0.20</td>
</tr>
<tr>
<td>Fe</td>
<td>0.22</td>
</tr>
</tbody>
</table>

**Table 2 - Measured mean equivalent concentrations, percent decrease and correlation coefficients for metal ions and anions.**

<table>
<thead>
<tr>
<th>Name</th>
<th>H⁺</th>
<th>Mn</th>
<th>Cu</th>
<th>Al</th>
<th>Zn</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean values from 8 to 20 Jun.</td>
<td>4.00E-06</td>
<td>3.42E-03</td>
<td>3.31E-04</td>
<td>2.49E-02</td>
<td>1.16E-03</td>
<td>8.88E-03</td>
</tr>
<tr>
<td>Mean values from 23 to 30 Jun.</td>
<td>2.97E-07</td>
<td>5.64E-04</td>
<td>5.71E-05</td>
<td>4.43E-03</td>
<td>2.57E-04</td>
<td>2.07E-03</td>
</tr>
<tr>
<td>Percent decrease</td>
<td>%</td>
<td>93</td>
<td>84</td>
<td>83</td>
<td>82</td>
<td>78</td>
</tr>
<tr>
<td>Correlation constant with the water level</td>
<td>-0.75</td>
<td>-0.67</td>
<td>-0.60</td>
<td>-0.62</td>
<td>-0.46</td>
<td>-0.61</td>
</tr>
</tbody>
</table>

**Table 3 - Correlation coefficient between each ion concentration and H⁺ ion concentration (April 20 to June 30, 2011).**

<table>
<thead>
<tr>
<th>Name</th>
<th>K</th>
<th>SO₄²⁻</th>
<th>NO₃⁻</th>
<th>Ca</th>
<th>Cl⁻</th>
<th>Mg</th>
<th>Na</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean values from 8 to 20 Jun.</td>
<td>0.058</td>
<td>0.962</td>
<td>0.033</td>
<td>0.720</td>
<td>0.176</td>
<td>0.156</td>
<td>0.291</td>
</tr>
<tr>
<td>Mean values from 23 to 30 Jun.</td>
<td>0.027</td>
<td>0.530</td>
<td>0.019</td>
<td>0.431</td>
<td>0.118</td>
<td>0.108</td>
<td>0.227</td>
</tr>
<tr>
<td>Percent decrease</td>
<td>%</td>
<td>53</td>
<td>45</td>
<td>41</td>
<td>40</td>
<td>33</td>
<td>31</td>
</tr>
<tr>
<td>Correlation constant with the water level</td>
<td>-0.92</td>
<td>-0.96</td>
<td>-0.80</td>
<td>-0.95</td>
<td>-0.92</td>
<td>-0.90</td>
<td>-0.89</td>
</tr>
</tbody>
</table>

**Fig. 3 - Time courses of pH and EC together with water levels during spring and summer (April 20 to June 30, 2011).**
The decreases in the concentrations of the ions were probably the result of dilution due to increased water inflow. The concentration decreases of H⁺, Al, Mn, Fe, Cu, and Zn ions, however, appeared to involve another factor in addition to dilution, since they exhibited high decreases with relatively low correlation to water level. These results might be indicative of buffering against a pH rise by dissolved Al, which remained in high concentration. Additionally, the concentrations of H⁺, Al, Mn, Fe, Cu, and Zn ions might have decreased as a result of coprecipitation with hydrolyzed Al. The results in the long-term field investigation also showed that the increase in pH was associated with a decrease in dissolved Al concentration, as well as with dilution by rainwater and snowmelt. Thus, the data in both the long-term and intensive field investigations suggest that dissolved Al acted as a buffer in the acidified river.

**Theoretical modeling of Al minerals in an acidified river**

The log Al³⁺ activity of water samples collected in the long-term field investigation was calculated by aqueous speciation modeling in PHREEQC (Parkhurst and Appelo, 1999) using the default thermodynamic database (phreeqc.dat) and the field data on water quality. Then, solubility diagrams were generated by plotting the log Al³⁺ activity against the measured pH. Additionally, the field data with pH less than 3 were excluded from the analysis in order to focus on the pH zone where solid-phase Al forms. The most common Al minerals predicted to form in AMD and acid sulfate soil environments are amorphous Al(OH)₃, alunite (KAl₃(SO₄)₂(OH)₆), basaluminite (Al₄(SO₄)(OH)₁₀·5H₂O), and jurbanite (Al(OH)SO₄·5H₂O) (Espana et al., 2005; Simon et al., 2005; Sherriff et al., 2007; Jones et al., 2011). The following solubility products were used to model the log Al³⁺ activity of these Al minerals:

\[
\text{Amorphous: } \text{Al(OH)}₃: \text{Al}^{3+} + 3\text{H}_2\text{O} \rightleftharpoons \text{Al(OH)}₃ + 3\text{H}^+ \\
\log K_{sp} = -33.71 \quad (3)
\]

\[
\text{Basaluminite: } 4\text{Al}^{3+} + \text{SO}_4^{2-} + 10\text{H}_2\text{O} \rightleftharpoons \text{Al}_4(\text{SO}_4)(\text{OH})_{10}(s) + 10\text{H}^+ \\
\log K_{sp} = -116.0 \quad (4)
\]

\[
\text{Jurbanite: } \text{Al}^{3+} + \text{SO}_4^{2-} + 6\text{H}_2\text{O} \rightleftharpoons \text{Al(OH)}(\text{SO}_4)\cdot5\text{H}_2\text{O} + \text{H}^+ \\
\log K_{sp} = -17.23 \quad (5)
\]

To determine the log Al³⁺ activity when solubility is controlled by one of the Al minerals from equations (3) to (5), pH, K concentration, and SO₄²⁻ concentration obtained from the long-term field investigation were used to find pOH, pK, and pSO₄ values, respectively, to be inputted into the model. Furthermore, the total solubility of Al for its common dissolved forms, when solubility is controlled by one of the minerals (amorphous Al(OH)₃, basaluminite, or jurbanite), was predicted to determine the most abundant Al minerals. Common dissolved forms of Al in river water are Al³⁺, Al-OH₂⁺, Al(OH)₂⁺, Al(OH)₄⁻, AlSO₄⁺, and Al(SO₄)₂⁻ (Zhang et al., 2009). Therefore, the total solubility of the aluminum (ΣAl) in the solution can be expressed as

\[
\Sigma \text{Al} = [\text{Al}^{3+}] + [\text{Al(OH)}^{2+}] + [\text{Al(OH)}_2^{+}] + [\text{Al(OH)}_4^-] + [\text{AlSO}_4^+] + [\text{Al(SO}_4)_2^-] \quad (6)
\]
Moreover, the complexation reactions of each dissolved form of aluminum can be described as follows:

\[
\begin{align*}
\text{Al}^{3+} + \text{H}_2\text{O} & \rightleftharpoons \text{AlOH}^{2+} + \text{H}^+ & \log K = -4.99 \\
\text{Al}^{3+} + 2\text{H}_2\text{O} & \rightleftharpoons \text{Al(OH)}_2^+ + 2\text{H}^+ & \log K = -10.13 \\
\text{Al}^{3+} + 4\text{H}_2\text{O} & \rightleftharpoons \text{Al(OH)}_4^- + 4\text{H}^+ & \log K = -22.16 \\
\text{Al}^{3+} + \text{SO}_4^{2-} & \rightleftharpoons \text{AlSO}_4^+ & \log K = 3.20 \\
\text{Al}^{3+} + 2\text{SO}_4^{2-} & \rightleftharpoons \text{Al}_2\text{(SO}_4)_2^- & \log K = 1.90
\end{align*}
\]

The total solubility of aluminum when solubility is controlled by amorphous Al(OH)$_3$, basaluminite, or jurbanite was determined by using equations (3), (4), or (5), respectively, and by using equations (7) through (11) for the dissolved forms of aluminum, together with the pOH and pSO$_4$ determined from the long-term field investigation. The equilibrium solubility of the different forms of Al and the corresponding total aluminum activity when solubility is controlled by jurbanite and basaluminite, and the aluminum activity of the field data in the long-term field investigation are shown in Fig. 4(a) and 4(b), respectively. In addition, the residual standard deviations of the field data for the curves of the predicted total aluminum activity (log $\Sigma$Al) are shown in Table 3. The residual standard deviation was lowest in the case of basaluminite, suggesting that the field data most closely correspond to the total aluminum activity controlled by basaluminite. Therefore, it is suggested that primarily basaluminite controlled the solubility of Al in the sulfuric acidified environment of Matsukawa River. In Fig. 4(b), from pH 6 to 8, plots of field data increased along the line for Al(OH)$_4^-$ at pH 6 to 8 in the sulfate-rich river water. The crystallization of gibbsite from amorphous aluminum has been reported to be greatly inhibited by the presence of SO$_4^{2-}$ (Zhang et al., 2009), and the analysis of precipitates formed upon the neutralisation of acid sulfate soil leachates by X-ray absorption near-edge structure spectroscopy has verified the presence of basaluminite and aluminum hydroxide (Jones et al., 2011). Therefore, the excess Al ions over the solubility limit likely precipitate as basaluminite and/or a more highly crystalline form in a sulfuric acidified environment such as Matsukawa River.
CONCLUSIONS
Matsukawa River as a typical acidified river has a transition zone of water quality with a sharp change in pH and dissolved Al concentration. Data from field investigations suggested that dissolved Al acted as a buffer from pH 4 to 6 in the acidified river environment and that pH was affected by a factor other than dilution due to rainfall and snowmelt. From theoretical modeling of aluminum minerals, it was found that mainly basaluminite($\text{Al}_4(\text{SO}_4)(\text{OH})_{10}$) controlled the solubility of Al in the sulfuric acidified environment of Matsukawa River from pH 4 to 6. Additionally, $\text{Al(OH)}_4^{-}$ was identified as the dominant chemical species of Al from pH 6 to 8 in the sulfate-rich river water.

REFERENCES


