한국지하수토양환경학회 추계학술발표회
2003년 9월 26~27일 제 주 대 학 교

Geochemical speciation of dissolved heavy metals in acid mine drainage: effects of pH and total concentration

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Abstract

In this study, we examined the influences of pH and total concentration on the speciation of heavy metals (Cd, Cu, Zn) in acid mine drainage. Their labile concentrations were analyzed by Anodic Stripping Voltammetry (ASV) at both natural pH and adjusted pHs (from 2 to 8). We obtained regression equations for predicting labile concentrations as a function of the water pH and contamination level (total dissolved metal concentration). Our data show that labile Cu depends on both the total concentration and pH, while labile Cd and Zn concentrations are controlled mainly by their total concentration rather than pH. Therefore, the pH variation of AMD may significantly change the toxicity and bioavailability especially of Cu, owing to its speciation change.

Key words: Heavy metals, Speciation, Toxicity and bioavailability, Anodic Stripping Voltammetry

Introduction

Mining activity leads to contamination of aquatic systems by toxic heavy metals such as cadmium, copper and zinc. The level of heavy-metal contamination in aquatic systems has been usually evaluated by total concentration. However, it is now well established that speciation measurements are required to investigate the toxicity of metals for aquatic organisms and to understand trace metal transport in rivers and estuaries. Recent ecotoxicological studies also revealed that metal speciation in solution is one of the key factors that regulate the metal uptake by plants as well as the toxicity for soil and aquatic organisms. The free metal activity is widely recognized as the factor best correlated to toxicity in aquatic studies and therefore it is important to measure and predict it in aquatic systems. In spite of the importance of metal speciation, most studies on acid mine drainage have dealt only with total concentration. Among physicochemical factors such as pH, Eh, temperature and ionic strength, pH is the master variable to control the interaction between protons and natural organic matter and therefore causes a sensible influence on chemical speciation, bioavailability and toxicity of metals. Recently, Anodic Stripping Voltammetry (ASV) has been used as a powerful technique for studying metal speciation. The purposes of this paper are (1) to evaluate the effect of pH on complexation of Cd, Cu and Zn, (2) to determine the relationship between water properties such as pH and total dissolved metal content and the metal speciation, and (3) to understand the influence of metal speciation on the transport and toxicity in acid mine drainage (AMD). Metal contaminated, acidic mine drainage of the Chonam-ri creek in the Kwangyang Au-Ag mine area was collected and examined for this study.

Sampling and Analyses

Mine drainage samples of Chonam-ri creek were collected during July 1997 to August 1999. Samples for determining total dissolved metals were acidified with concentrated nitric acid after filtering through a 0.45 μm membrane filter. Samples for the speciation measurement were also filtered but not acidified. Those samples were transported immediately to the laboratory within one day for various laboratory analyses.

Chemical analysis for total dissolved metals (Cd, Cu and Zn) was performed by inductively coupled plasma atomic emission spectroscopy (ICP-AES; Perkin Elmer Model OPTIMA 3000XL) and ICP-mass spectrometry (Perkin Elmer model ELAN 6000). Labile metal concentrations were measured using Anodic Stripping Voltammetry (ASV) (TEA-3000) at a natural pH without acidification. The difference between ICP data and ASV data was assumed to represent the concentration of metals bound in inert organic complexes. For the measurement of pH effect on metal speciation, pH of the samples was adjusted (from 2 to 8) by adding HNO_3 or NaOH. After stabilization of pH condition, the labile concentrations were also measured by ASV and were compared with those obtained under natural pH.

Results and Discussion

1. Cadmium: As the sample pH increased gradually from 2 to 8, the decrease of concentration of labile Cd was minimal. This indicates that the formation of inert Cd complexes with natural organics was not significant in Chonam-ri creek (Fig. 1). Hence, the bioavailability and/or toxicity of cadmium in the creek seem to be unchanged with pH variation. The relationship between labile Cd and natural pH showed a regression equation as follow (Fig. 2):

$$\text{Log labile Cd} = -0.39\ \text{pH} + 3.06\ (R^2 = 0.738,\ n = 37) \quad (1)$$

The labile Cd concentration at natural pH also varied with total dissolved Cd concentration (Fig. 3) and could be expressed by the relationship as follow:

$$\text{Log labile Cd} = 0.96\ \log\ (\text{total dissolved Cd}) + 0.06\ (R^2 = 0.978,\ n = 37) \quad (2)$$

Likewise, the relationship between labile Cd and total Cd during the pH modification between 2 and 8 was expressed as:

$$\text{Log labile Cd} = 0.97 \log (\text{total dissolved Cd}) + 0.06 \qquad (3)$$

The R^2 for the regression was very high (0.974; n = 161).

From the equations (1) and (2), the following multiple regression equation was obtained for the relationship between total Cd and labile Cd:

$$\text{Log labile Cd} = -0.19 \text{ pH} + 0.48 \log (\text{total dissolved Cd}) + 1.50 \qquad (4)$$

Above equations suggest that labile Cd content is controlled mainly by the level of contamination (namely, total dissolved Cd) rather than pH.

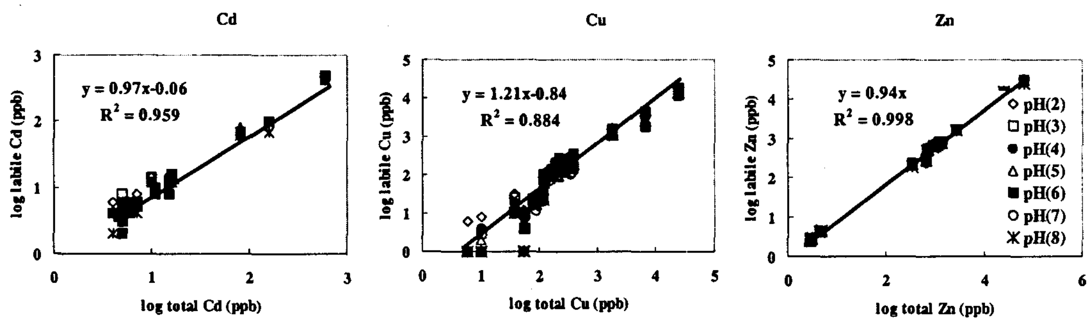

Fig. 1. Relationships between labile metal concentration (determined by ASV) and total metal concentration (determined by ICP), showing the change of labile metal concentration by the adjustment of pH (from 2 to 8)

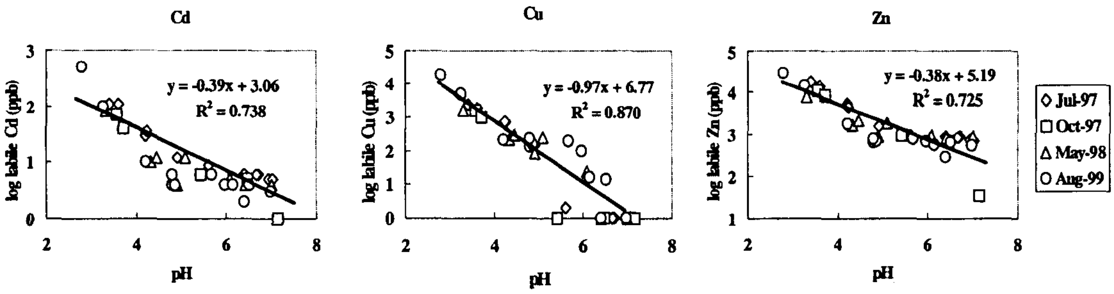

Fig. 2. Natural pH versus labile metal concentration (determined by ASV) relationship.

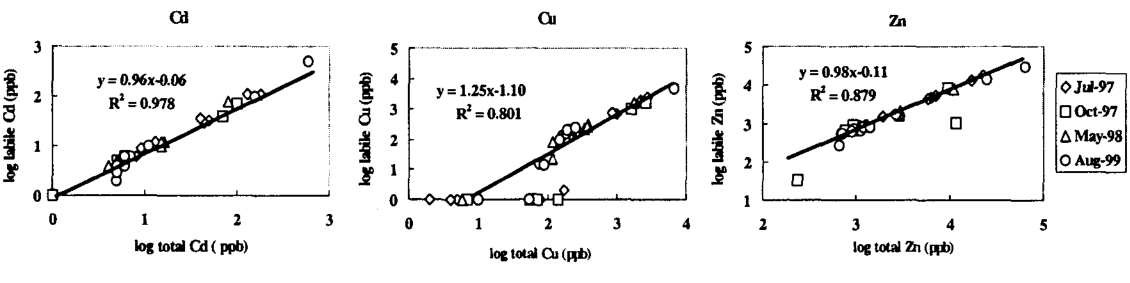

Fig. 3. Log labile concentration versus log total concentration for dissolved Cd, Cu, and Zn in natural pH condition

2. Copper: The importance of dissolved organic matter in complexation of Cu in freshwater has been demonstrated in many papers. For Chonam-ri creek water, the variation of Cu concentration under both natural and adjusted pH conditions showed that pH causes a strong influence in Cu speciation, possibly due to the competition between the H^+ and Cu^{2+} ions onto the binding sites of organic matter. During the pH change from 2 to 8 for a sample in laboratory, the ASV concentration of Cu changed significantly up to 1 log unit (Fig. 1). Fig. 2 shows a log labile Cu concentration versus pH relationship in natural conditions, indicating the labile Cu decreases with increasing pH. The following regression equation was obtained for the relationship:

$$\text{Log labile Cu} = -0.97\ \text{pH} + 6.77\ (R^2 = 0.870;\ n = 37) \quad (5)$$

The labile Cu concentration was also influenced by total dissolved Cu concentration, as can be expressed by the following equation (Fig. 3):

$$\text{Log labile Cu} = 1.25\ \log\ (\text{total dissolved Cu}) + 1.10\ (R^2 = 0.801;\ n = 37) \quad (6)$$

Likewise, we obtained the following regression equation for the relationship between labile Cu and total Cu concentrations during the pH modification between 2 and 8:

$$\text{Log labile Cu} = 1.21\ \log\ (\text{total dissolved Cu}) + 0.84\ (R^2 = 0.884;\ n = 154) \quad (7)$$

The equations 5, 6 and 7 suggest that labile Cu concentration is controlled by both the level of contamination (total dissolved Cu) and the acidity (pH). By combining the equations 5 and 6, the following multiple regression equation was obtained:

$$\text{Log labile Cu} = -0.49\ \text{pH} + 0.62\ \log\ (\text{total dissolved Cu}) + 2.84 \quad (8)$$

This relationship may be used to estimate the labile Cu in freshwater (especially, acid mine drainage) from water pH and total dissolved Cu concentration.

3. Zinc: For the Chonam-ri creek water, the pH modification from 2 to 8 for each sample had little effect on ASV concentration (Fig. 1). This indicates that organic complexes of Zn are negligible in the Chonam-ri creek. The relationship among the natural pH, total concentration (degree of contamination), and labile Zn concentration was obtained as a following equation, which showed a negligible contribution of pH for the change of labile Cu concentration.

$$\text{Log labile Zn} = -0.19\ \text{pH} + 0.49\ \log\ (\text{total dissolved Zn}) + 2.54 \quad (9)$$

Therefore, the increase of pH cannot reduce the bioavailability or toxicity of zinc in Chonam-ri creek. On the other hand, a strong dependence of labile Zn concentration on total dissolved Zn was observed. Likewise, the relationship between labile Zn and total dissolved Zn at natural pH condition was obtained as follow:

$$\text{Log labile Zn} = 0.98 \log (\text{total dissolved Zn}) + 0.11 \quad (R^2 = 0.879;\ n = 37) \tag{10}$$

This result agrees well with the following equation obtained by the pH modification experiments.

$$\text{Log labile Zn} = 0.94 \log (\text{total dissolved Zn}) \quad (R^2 = 0.998;\ n = 161) \tag{11}$$

We should note that the slope of this equation is close to 1. This clearly indicates that dissolved Zn exists dominantly as labile Zn, irrespective of pH. The equations 12, 13 and 14 suggest that labile Zn concentration is controlled mainly by the level of contamination (total dissolved Zn) rather than acidity (pH).

Conclusion

During the pH adjustment (from 2 to 8) of the Chonam-ri mine drainage water, the change of labile concentration (determined by ASV) was remarkable for Cu but was minimal for Cd and Zn. This indicates that Cu forms strong complexes with dissolved organic matter upon the increase of pH, which may reduce the bioavalability and toxicity to aquatic organisms. In this study, we obtained the relationships among pH, total metal concentration, and labile metal concentration for dissolved Cd, Cu and Zn in mine drainage sample. These relationships can be used to estimate the speciation of heavy metals from pH and total concentration data and hence to evaluate the bioavailability and toxicity. Our results demonstrate that labile Cu concentration is controlled by both the level of contamination (total dissolved Cu) and the acidity (pH) of water, while labile Cd and Zn are controlled mainly by the level of contamination.

Acknowledgements: This work was supported by the Environmental Geosphere Research Lab (EGRL) of Korea University and partly by the Natural Hazard Prevention Research Group of KIGAM.