Clay Science 14, 203–210 (2010)

–2010 TMC Special Paper–

A NOVEL REMEDIATION METHOD LEARNT FROM NATURAL ATTENUATION PROCESS FOR Cu- AND Zn-BEARING WASTEWATER

HIROKI OKAMOTO[a], KAZUYA MORIMOTO[b], SOHTARO ANRAKU[a], TSUTOMU SATO[c, *] and TETSURO YONEDA[c]

[a]*Graduate school of Engineering, Hokkaido University, Kita 13 Nishi 8, Sapporo, Hokkaido, 060-8628, Japan*
[b]*Photocatalytic Materials Center, National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki, 305-0044, Japan*
[c]*Faculty of Engineering, Hokkaido University, Kita 13 Nishi 8, Sapporo, Hokkaido, 060-8628, Japan*

(Received August 13, 2010. Accepted August 27, 2010)

ABSTRACT

To develop a novel remediation for Cu- and Zn-bearing wastewater, the natural attenuation process in Dougamaru abandoned mine at Shimane Prefecture, Japan was investigated. In the Dougamaru abandoned mine, Cu- and Zn-bearing mine drainage was naturally attenuated by formation of green precipitate composed of Cu-bearing layered double hydroxide (LDH), hydrowoodwardite (HW) with chemical formula such as $Cu_{0.66}Zn_{0.09}Fe_{0.01}Al_{0.23}(OH)_2(SO_4)_{0.15} \cdot mH_2O$. This attenuation was achieved at pH 6.0 with aeration and bacterial respiration and without any neutralization process attributed to the mixing with spring or surface water. The formation of the HW at pH 6 is also confirmed by thermodynamic consideration in this study. The formation process of the HW at the Dougamaru abandoned mine teaches us a novel technology for remediation system with addition of Al ion to wastewater and without employing any extensive chemical treatment processes.

From the experiment to check applicability of Cu- and Zn-bearing LDHs to wastewater treatment, HW (Cu-bearing LDH) and zincowoodwardite (ZW; Zn-bearing LDH) were obtained by addition of Al ion to the Cu- and Zn-bearing wastewater from lower pH condition. The improvement of removal efficiency by adding Al ion in Cu-bearing wastewater system was not so clear in the experiment because Cu ion is removed from the synthetic wastewater due to Cu-hydroxyl sulfate precipitation at the experimental condition. On the other hand, the removal efficiencies of Zn ion showed the range from 0 to 30% even at pH 6.0 and improved with increasing initial Al ion content. The experimental results in Zn-bearing wastewater system indicate that the safety remediation of Zn ion can be achieved even at lower pH than 6.0–7.0 by selection of the ZW as a candidate of the solubility-limiting solid phase. Moreover, because of high anion exchange capacity of LDH, the method with addition of Al ion source for the wastewater treatment may also be useful for the treatment of wastewater containing Cu and Zn ions and simultaneously with As, Se, and Sb anions, which shows good performance in terms of anion remediation.

Key words: Remediation, Hydrowoodwardite, Natural attenuation, Layered double hydroxide

INTRODUCTION

Cu and Zn are valuable heavy metals for electronics and metalizing plating industries. Due to the advancement in technology, these metals are being mined all over the world and the demands for these metals are expected to increase extensively in the future. Although utilization of these metals is materially and economically advantageous for the society, there are associated risks during the mining of these metals. Nowadays, the inevitable generation of contaminated mine drainage as a result of mining operation is a source of environmental and health concerns. Hence, the treatment and remediation of contaminated mine drainage must be carried out not only during the mining operation but also after closure of the mining site in order to avoid health and environmental disasters.

Generally, the remediation of Cu and Zn ions from wastewater has been carried out by neutralization to pH 7.7–9.8. (Pearson and Mcdonnell, 1975; Vermaak et al., 2006; Rios et al., 2008). The remediation has been attained by formation of Cu- and Zn-hydroxides. For the neutralization, various antalkaline regents are currently being used which includes limestone (Maree and Plessis, 1994), lime (Geldenhuys et al., 2001), blast furnace slag (Feng et al., 2004) and fly ash (Xenidis et al., 2000; Petrik et al., 2003). However, the reme-

---

[*] Corresponding author: Tsutomu Sato, e-mail: tomsato@eng.hokudai.ac.jp

diation method using antalkaline has some problems such as high cost, production of large amount of sludge that needs to be disposed and the release of hazardous elements from the sludge in the disposal sites. Therefore, a novel remediation method that is low cost with small amount of sludge production and minimum risks to human health and the environment must be developed in order to achieve sustainability in the remediation of contaminated mine drainage.

On the other hand, natural attenuation of toxic elements which is characterized by the reduction of concentrations of toxic elements without the interventions of human activities are occasionally observed at some abandoned mine sites. This natural attenuation process is definitely free, safe and environmentally friendly. Therefore, a sustainable remediation method can be developed by understanding and applying the mechanisms involved in natural attenuation process.

In Eve verda spring in Italy (Tumiati et al., 2008), the mixing of acid mine drainage containing high Cu ion content with the hot spring generates hydrowoodwardite (HW), which is composed of Cu-hydroxyl sulfate and classified as layered double hydroxide (LDH) with structural chemical formula of $Cu_{1-x}Al_x(OH)_2(SO4)_{x/2} \cdot mH_2O$. During the mixing process, the Cu-bearing drainage was naturally attenuated due to the formation of HW as a result of the neutralization of acid drainage (pH 3.0) with hot spring water (pH 8.1). However, this kind of natural attenuation process is economically disadvantageous because the increase in pH during neutralization is comparable to that of ordinary neutralization process used in traditional wastewater treatment. In addition, Witzke (1999) reported the natural occurrence of HW for the first time.

In Dougamaru abandoned mine at Shimane Prefecture, Japan, the formation of HW in the mine drainage was also reported. In this mine drainage, the pH in which the HW precipitate was formed is around 6 without any neutralization process by the mixing with spring or surface water (Watanabe et al., 2003). Therefore, understanding of the HW formation process at the Dougamaru abandoned mine may lead us to a novel technology for wastewater treatment without employing any extensive chemical treatment processes. However, the Watanabe et al. (2003) did not discuss on various chemical conditions such as pH, concentration of dissolved species, etc. in order to form HW. Although the mineralogical characterization of the precipitates was carefully conducted in their study, the information needed as a basis to select HW as a good solid phase candidate for Cu-bearing wastewater treatment is insufficient.

Generally, natural Cu-rich minerals are commonly associated to carbonates, sulfides, and silicates but very rare to oxides and hydroxides phases. However, occurrence of HW discussed above, LDHs can be also one of a desirable candidate as a solubility-limiting solid phase for wastewater treatment contaminated with Cu and Zn ions. Although the LDHs have been extensively studied by many workers in various research fields, the information regarding the chemical conditions of HW formation and utilization of LDHs for wastewater treatment is still insufficient.

In this context, the precipitates and mine drainage water at the Dogamaru abandoned mine were investigated in order to understand the chemical conditions of the ongoing natural attenuation process due to HW formation. The thermodynamic consideration on the formation of HW was also examined. Moreover, experimental investigations were conducted in order to evaluate applicability of Cu- and Zn-bearing LDHs to wastewater treatment.

EXPERIMENTAL

Water analysis

In the Dogamaru abandoned mine, pH, Eh, electric conductivity (EC) and temperature were measured on site (pH meter, WM-22, TOADKK). In laboratory experiment to check the removal efficiency of Cu and Zn ions from synthetic wastewater, the same parameters were measured by the same pH meter. Water samples from the Dogamaru abandoned mine were collected by using mixed cellulose membrane filter (< 0.45 μm) and then 1 volume % nitric acid added to the collected water sample to avoid precipitation during the transformation to our laboratory. Water samples from laboratory experiments were collected by the same filtration. Concentrations of major elements containing Cu, Zn and Al in the filtrates from the Dogamaru abandoned mine and the laboratory experiments were determined by an inductively coupled plasma atomic emission spectrometry (ICP-AES, ICPE-9000, Shimadzu). On the other hand, the anion concentrations such as SO_4^{2-} were measured by ion chromatography (IC, Metrohm 861 Compact IC) with 0.1% Na_2CO_3 solution as eluent.

Precipitate analysis

Powdered samples of the precipitates with random orientation were analyzed using X-ray diffractometer (XRD, Rint2000, Rigaku) operating at 30 kV and 20 mA with 1° divergence, 1° scattering, and 0.3 mm receiving slits, respectively to determine the mineral phases in the precipitates. For the natural sample, XRD equipped graphite-monochromated CuKα radiation (Multi Flex, Rigaku) was used due to low signal/noise ratio in the XRD pattern of the sample.

For observation by scanning electron microscope (SEM, SSX-550, Shimadzu), natural sample was mounted on carbon stubs with carbon tape and coated with carbon using carbon coater machine. The element mapping was also conducted by SEM equipped with an energy dispersive X-ray spectrometry (EDS) at 15.0 kV in accelerating voltage. Chemical compositions of the natural samples were analyzed by ICP-AES for the solution dissolving the precipitates.

NATURAL ATTENUATION AT DOUGAMARU MINE

Site and samples

Dougamaru abandoned mine is located near Gouno River in the Cu-Zn-sulfide mining district of Shimane prefecture in Japan. Ores from the Dogamaru abandoned mine are mainly consisted of chalcopyrite, marcasite and sphalerite. Although the Dogamaru mine is abandoned mine, mine drainage containing high concentrations of Cu and Zn ions is still flowing from the mine pit and dump. The drainage is cascading as water fall, and green precipitate is observed on the wall rock. However, the precipitate was not observed in the drainage before the cascading and after mixing with river water at bottom of the waterfall. Water samples were collected and labeled such as RW1 (upstream in river water; before mixing with mine drainage), RW2 (downstream in river water; after mixing with mine drainage) and mine drainage (MD). Photograph of the green precipitate and schematic diagram showing positional relation of sampling locations of water (MD, RW1 and RW2) and precipitate are shown in Fig. 1.

Water quality

The mine drainage was characterized by pH around 6.0 and Eh around 260 mV, while the river water displayed a little difference in pH and Eh (6.2 and 240 mV, respectively). The above two water samples also showed the difference in concentration of dissolved species. For example, the sulfate concentrations in MD and RW1 were 123 mg/L and 6.44 mg/L, respectively. The concentrations of dissolved Cu and Zn ions in MD and RW1 were ranging 3.35–19.20 mg/L and 0.04–0.12 mg/L, respectively. Dissolved Al ion was detected only in MD (0.13 mg/L). Apparently, Cu and Zn ion concentrations go beyond regulatory limits of the effluent (3 mg/L for Cu and 2 mg/L for Zn).

On the contrary, concentrations of the dissolved sulfate, Cu and Zn ions in RW2 were 8.08, 0.08 and 0.46 mg/L, respectively. As the result of dilution by RW1, concentrations of Cu and Zn ions are lowered and below the regulatory limits. Because the precipitate does not contain K ion, mixing ratio of MD and RW1 can calculate based on K ion concentrations in both water samples. If the natural attenuation was only caused by the dilution, the concentrations of Cu and Zn ions in RW2 are expected to be 0.41 and 2.21 mg/L, respectively. However, the measured actual values were 0.08 and 0.46 mg/L. This may indicate that the natural attenuation was not only due to the dilution but also the precipitation. Equally, the concentrations of sulfate and fluorine ions were also attenuated by the formation of the precipitate.

Characterization of the precipitate

The XRD pattern of the dried precipitate is shown in Fig. 2. The precipitate displayed broad peaks which were completely consistent with those of HW shown in Watanabe et al. (2003). Therefore, it is determined that the precipitate consists of single phase of HW. In order to investigate the homogeneity of chemical composition in the precipitate, element mappings were carried out by using SEM-EDS. The obtained X-ray image of element distribution maps showed that the particles were always consisted of the same components of Cu, Al, Zn, S and F (Fig. 3). The XRD and chemical analyses suggested that the precipitate was composed of HW consisting with Cu, Al, Zn, S and F. Average formula of the HW from the Dougamaru abandoned mine was calculated as $Cu_{0.66}Zn_{0.09}Fe_{0.01}Al_{0.23}(OH)_2(SO_4)_{0.15} \cdot mH_2O$.

Geochemical modeling for the formation of HW

Geochemical modeling was performed to consider the chemical condition for the formation of HW at the Dougamaru abandoned mine. Considering the situation of the sampling

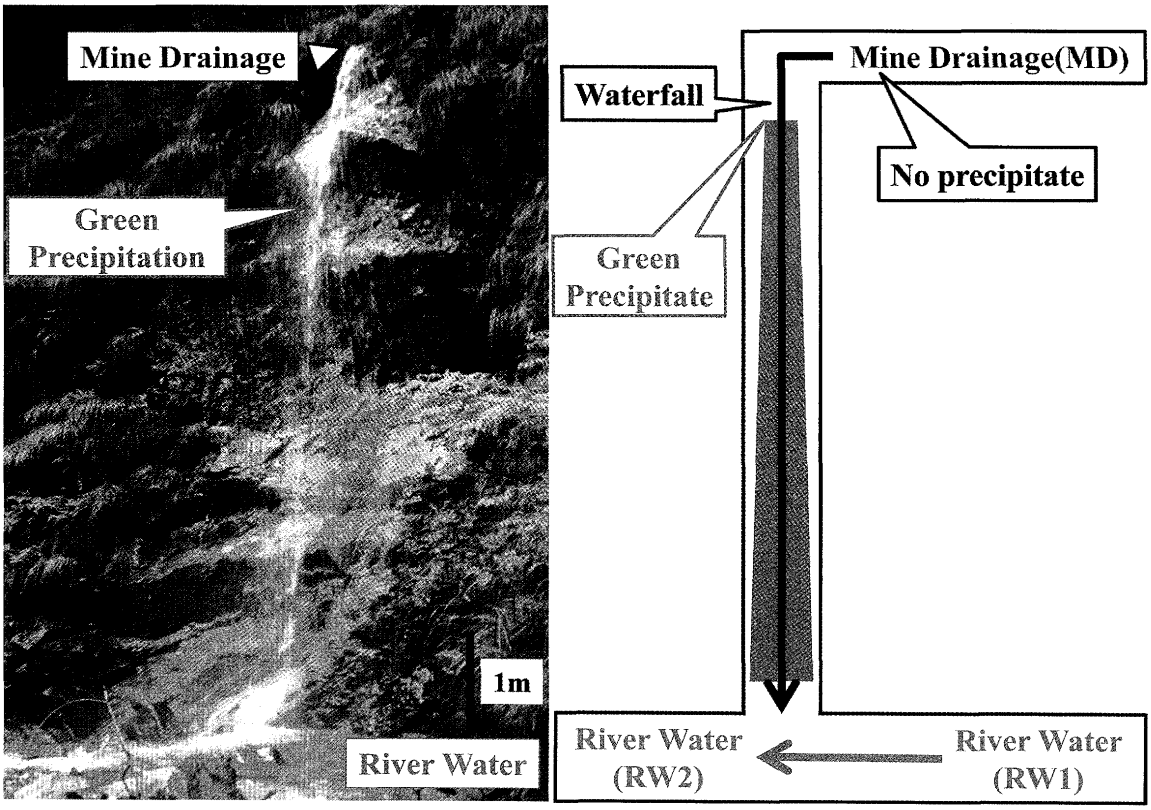

Fig. 1. Photo of the green precipitate occur on the wall rock at the Dougamaru abandoned mine and schematic diagram showing positional relation of sampling locations of water (MD, RW1 and RW2) and precipitate.

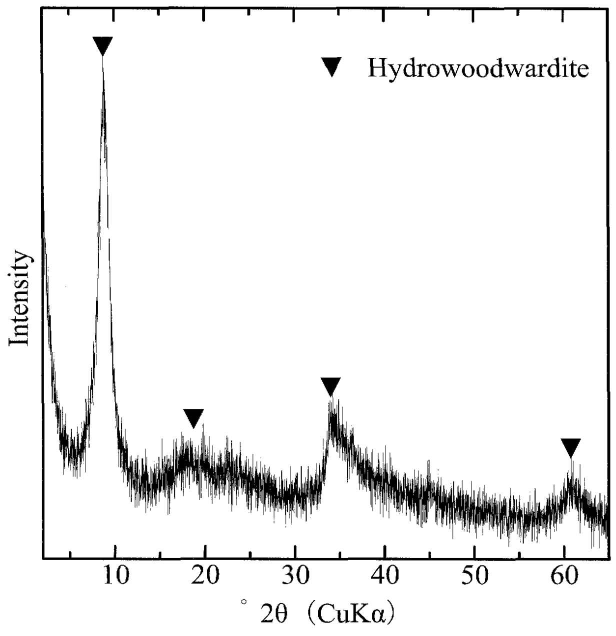

FIG. 2. XRD pattern of the green precipitate from the Dougamaru abandoned mine.

field, the formation of HW would be attributed to the changes in chemical condition of the drainage during the cascading at the waterfall. Aeration should occur during the cascading. However, the change in redox condition due to the aeration is out of relation to the formation of HW because the HW contained mainly redox insensitive elements such as Cu, Zn and Al. By the aeration due to the cascading and respiration by cyanobacteria (identified by 16S rDNA analysis of isolated strain) living on the wall rock, partial pressure of CO_2 should be increased. When the partial pressure of CO_2 is increased, HW containing CO_3^{2-} as interlayer anions (CO_3^{2-}-HW) may generate. However, the formation of HW cannot be modeled due to lack of the thermodynamic data.

According to Allada et al. (2002), the solubility products of LDHs with different anions in their interlayers can be calculated from solubility products of minerals with fixed composition, particularly, simple hydroxides, carbonates, sulfates and others, for which thermodynamic data are available. These data were calculated on the enthalpy of generation determined by calorimetry (Allada et al., 2002; Peltier et al., 2006; Allada et al., 2006) and on the solubility product constant determined by solubility measurements (Johnson and Glasser, 2003).

Firstly, because of luck for the thermodynamic data of HW, ΔG^0_f of HW was calculated using the model of Bravo-Suárez et al. (2004). From this calculation, ΔG^0_f of HW can be estimated by the formula; $G^0_f = -974.19 \cdot x - 357.70$, where the value of x is Al/(Al + Cu). As the result of calculation, ΔG^0_f of the HW from the Dogamaru abandoned mine is estimated as −649.96 kJ/mol.

Secondary, ΔG^0_f of CO_3^{2-}-HW was calculated. In the calculation, ΔG^0_f of the CO_3^{2-}-HW was not reported, but those of Co-bearing LDHs (cf. Allada et al., 2002; Peltier et al., 2006; Allada et al., 2006) were available. Therefore, we tried to estimate the ΔG^0_f by subtracting the contributions of $Co(OH)_2$ and $CoCO_3$ (data from Bravo-Suárez et al., 2004; Johnson and Glasser, 2003) and adding those of $Cu(OH)_2$ and $CuCO_3$. The ΔG^0_f of the CO_3^{2-}-HW [$Cu_{0.70}Al_{0.30}(OH)_2(CO_3)_{0.15} \cdot mH_2O$] was calculated from the following formula;

$$\begin{aligned}&\Delta G^0_{fCu0.70Al0.30(OH)2(CO3)0.15 \cdot mH2O}\\&\quad = \Delta G^0_{fCo0.70Al0.30(OH)2(CO3)0.15 \cdot mH2O} - 0.15\Delta G^0_{fCoCO3}\\&\qquad + 0.15\Delta G^0_{fCuCO3} - 0.55\Delta G^0_{fCo(OH)2} + 0.55\Delta G^0_{fCu(OH)2}\end{aligned}$$

The ΔG^0_f of the resulting CO_3^{2-}-HW in the Dougamaru abandoned mine was −614.60 kJ/mol.

Stability diagrams obtained using Act2 software in Geochemist's Workbench package with the ΔG^0_f value mentioned

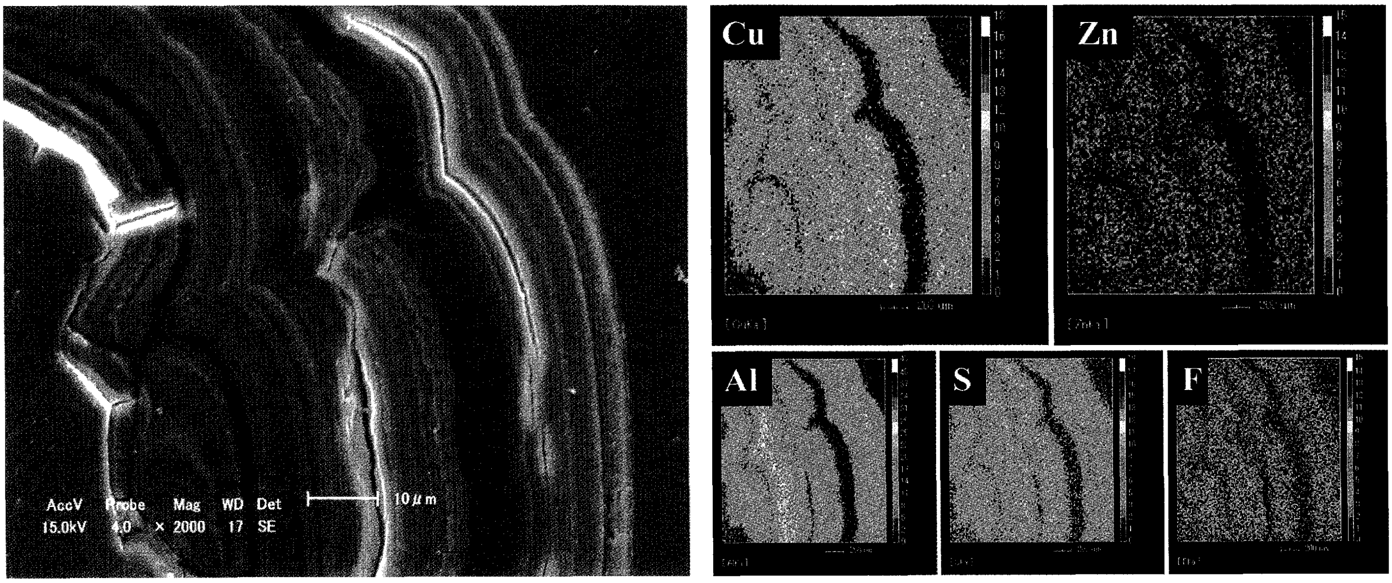

FIG. 3. SEM image and element distribution maps of cross-section of the precipitate.

above are shown in Fig. 4. If Cu- and Zn-hydroxides were selected as solubility-limiting solid phases, Cu- and Zn-hydroxides can precipitate at pH 6.6 and 8.0 in the drainage at the Dogamaru abandoned mine, respectively. Therefore, the precipitation does not occur for the both elements at pH of the drainage at the Dogamaru abandoned mine (pH = 6.0). As shown in Fig. 4, however, HW can be precipitated at pH 6.0 if the system contains Al ion. Consequently, if HW is selected as a candidate solid phase for the treatment of wastewater, reductions of Cu and Zn ion concentrations would be available by neutralization up to pH 6.0. If it is available, we can get the remediation method with low cost, less sludge volume and low risk of the sludge disposal for long term.

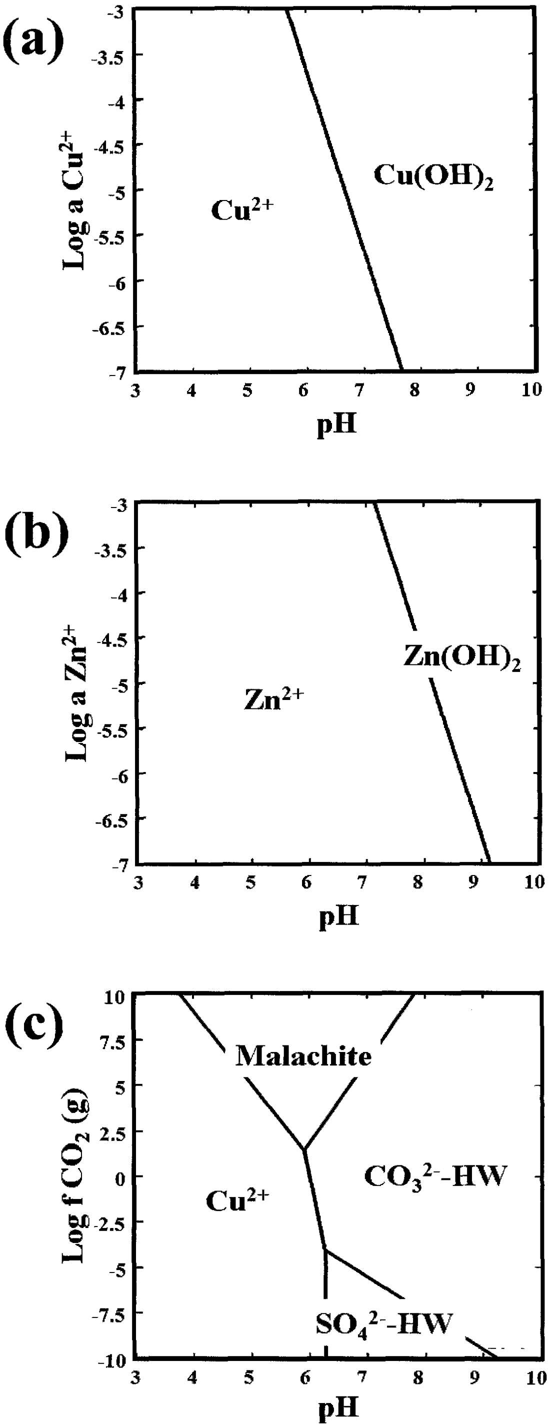

FIG. 4. Stability diagrams of the Cu- and Zn-hydroxides, hydrowoodwardite in $Cu\text{-}CO_2\text{-}H_2O$ (a), $Zn\text{-}CO_2\text{-}H_2O$ (b), and $Al\text{-}Cu\text{-}CO_2\text{-}SO_4^{2-}\text{-}H_2O$ (c) systems.

APPLICATION OF Cu- AND Zn-BEARING LDHS FOR WASTEWATER TREATMENT

Chemical conditions such as pH and dissolved Al ion concentration for the formation of Cu- and Zn-bearing LDHs were experimentally investigated and the applicability of these LDHs for wastewater treatment was evaluated. The synthetic wastewater containing 1000 ppm of Cu ion was prepared using $CuSO_4$. $Al_2(SO_4)_3$ was added to set Al/Cu ratio as 0, 0.1, 0.2 and 0.3, respectively. After mixing of the synthetic wastewater with the Al-bearing solution, pHs of the mixed solutions were adjusted to 5.0, 7.0 and 9.0 ± 0.02 using 0.1M NaOH solution. The dried precipitates formed after the mixing were analyzed by XRD to determined the mineralogical composition of the precipitates and the filtrated solution samples were analyzed by ICP-AES to obtain the removal efficiency of Cu ion from the synthetic wastewater. Moreover, a similar experiment was conducted for Zn-bearing wastewater system. In the Zn-bearing wastewater system, no precipitate was observed in all samples synthesized at pH 5.0. Therefore, the pHs of the solutions were adjusted to be 6.0, 7.0 and 9.0 in the Zn-bearing wastewater system.

Cu-hydroxyl sulfate minerals such as brochantite ($Cu_4(OH)_6(SO_4)$) and/or posnjakite ($Cu_4(OH)_6(SO_4) \cdot H_2O$) were formed at the Al/Cu ratios of 0 and 0.1 at pH 5.0, 7.0 and 9.0. Figures 5, 6 and 7 showed the XRD patterns of the precipitates formed

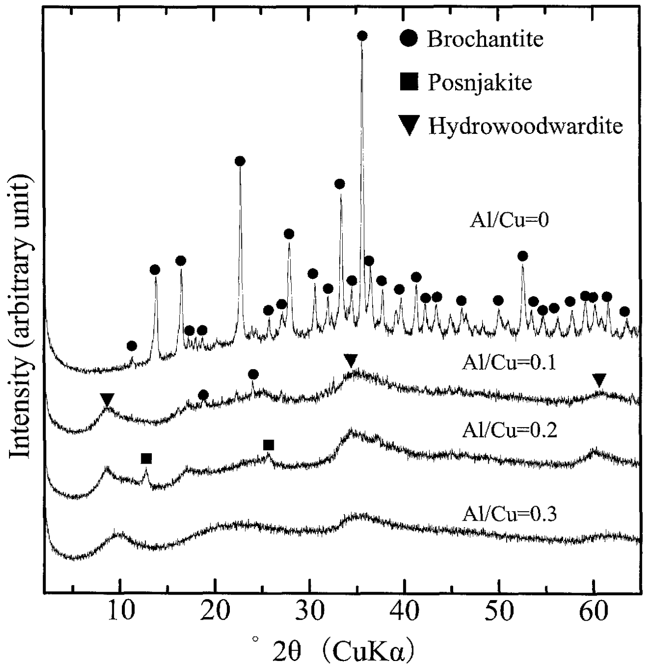

FIG. 5. XRD patterns of the precipitates in Cu system at pH 5.0.

at pH 5.0, 7.0 and 9.0, respectively. The broad peaks of HW were observed in the samples initially adding Al ion. Moreover, the XRD patterns of the precipitates at Al/Cu ratio = 0.3 at pH 5.0, 7.0 and 9.0 showed only the broad peaks of HW.

On the other hand, the peaks of zincowoodwardite (ZW) were observed in the samples with Al/Zn ratio = 0.2 and 0.3, but no precipitates were observed in those with Al/Zn ratio = 0 and 0.1 at pH 6.0. The natural occurrence of ZW was firstly reported by Witzke and Raade (2000). Zn-hydroxyl sulfate mineral such as guarinoite [$(Zn, Co, Ni)_6(OH, Cl)_{10}(SO_4) \cdot 5H_2O$] was observed with lower Al/Zn ratio. Figures 8, 9 and 10 showed the XRD patterns of the samples formed at pH 6.0, 7.0 and 9.0, respectively. The peaks of ZW were observed in the samples with Al/Zn ratio = 0.2 and 0.3 at pH 7.0 and 9.0.

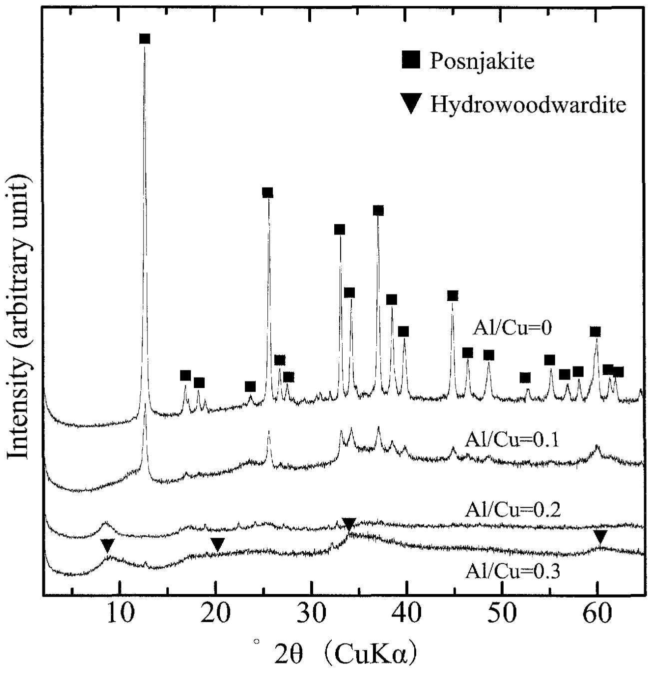

FIG. 6. XRD patterns of the precipitates in Cu system at pH 7.0.

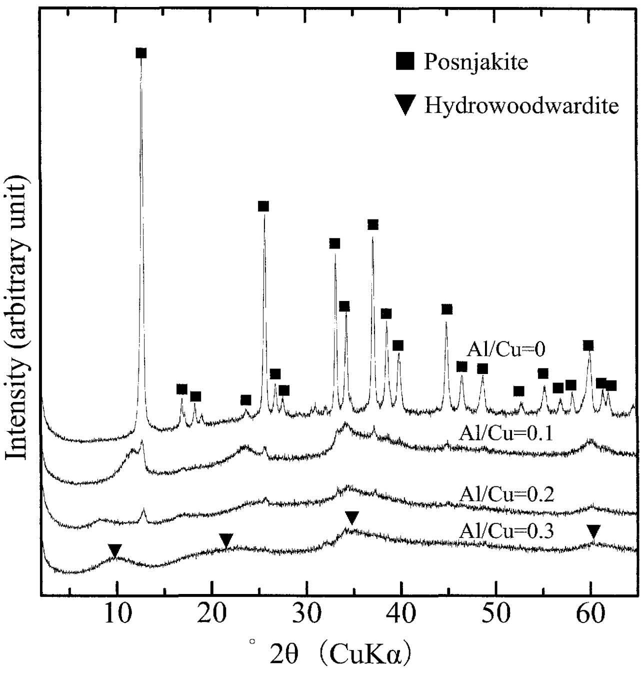

FIG. 7. XRD patterns of the precipitates in Cu system at pH 9.0.

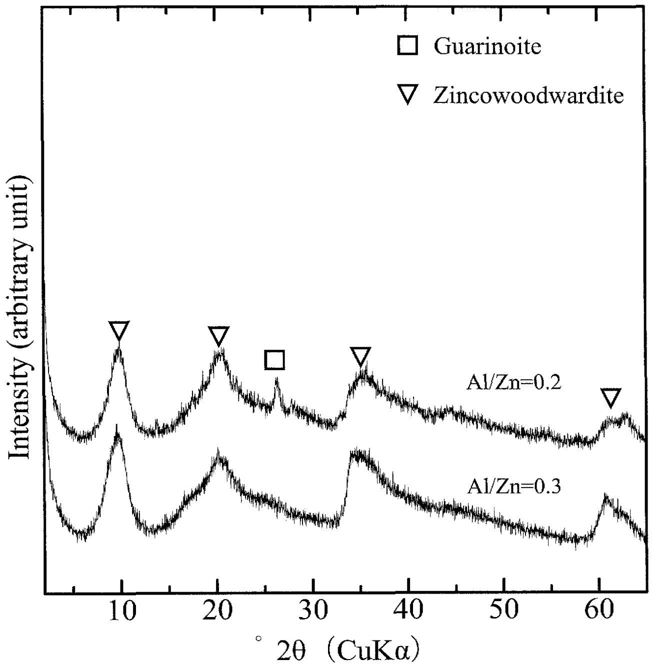

FIG. 8. XRD patterns of the precipitates in Zn system at pH 6.0.

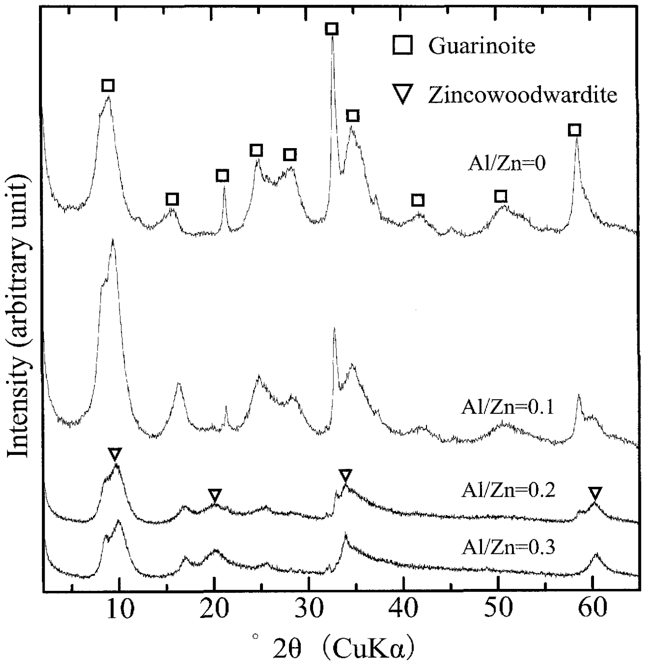

FIG. 9. XRD patterns of the precipitates in Zn system at pH 7.0.

Therefore, the generation of Cu- and Zn-bearing LDHs as the main minerals in the precipitates will occur in the presence of high Al ion content. Figure 11(a) and (b) showed the removal efficiencies of Cu and Zn ions from the synthetic wastewater by the precipitation. In the Cu-bearing wastewater system at pH 5.0, the removal efficiencies were from 30 to 40% and independent with Al/Cu ratios. On the other hand, even at pH 6.0, the removal efficiencies of Zn ion were from 0 to 30% and improved with increasing initial Al ion content. This is due to higher solubility of Zn ion than that of Cu ion at pH 6.0. However, precipitated phase (ZW) was observed when Al ion was added in the solution even at pH 6.0. In the traditional remediation method of Zn-bearing wastewater, antalkaline reagent is added to the wastewater to increase pH until formation of the precipitate. However, as mentioned above, Zn ion can precipitate at lower pH in the presence of Al ion, indicating cost saving for antalkaline regent. Basically, the safety remediation of Zn ion can be achieved even at low pH such as 6.0 and 7.0 by selecting ZW as a candidate of the solubility-limiting solid phase. The interlayer anions of Cu-LDH can be exchanged for other anions (Yamaoka et al., 2000), and Cu- and Zn-bearing LDHs presumably play a role of adsorbents for toxic anions. From this aspect, the method with addition of Al ion source

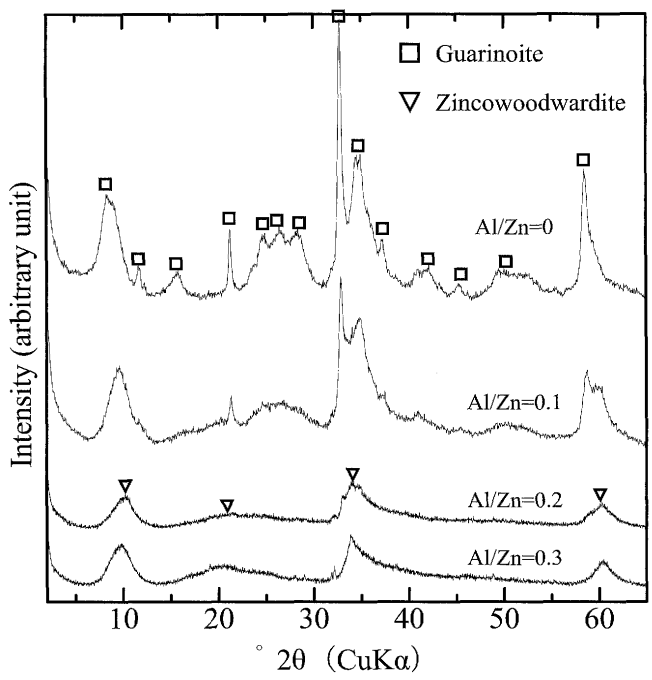

FIG. 10. XRD patterns of the precipitates in Zn system at pH 9.0.

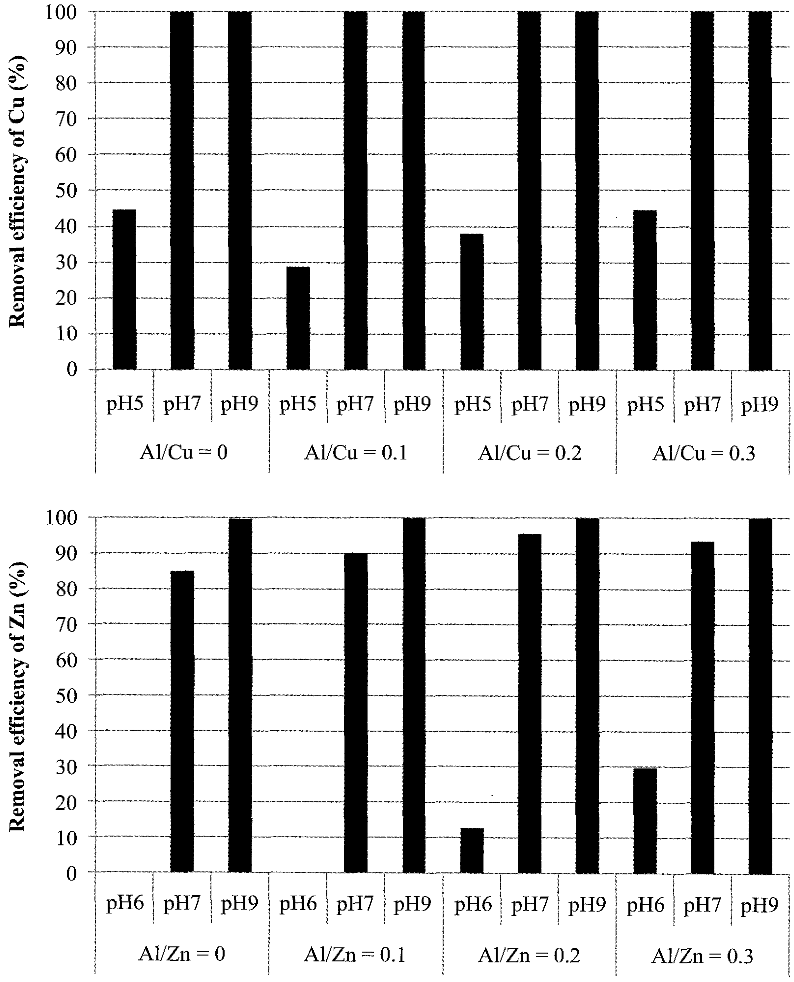

FIG. 11. Removal efficiencies from the synthetic wastewater in Cu (a) and Zn (b) systems.

for the wastewater treatment may also be useful for the wastewater containing Cu and Zn ions and simultaneously with anions such as As, Se, and Sb.

CONCLUSION

In the Dougamaru abandoned mine, Cu- and Zn-bearing mine drainage was naturally attenuated by formation of green precipitate composed of Cu-bearing LDH, HW ($Cu_{0.66}Zn_{0.09}Fe_{0.01}Al_{0.23}(OH)_2(SO_4)_{0.15} \cdot mH_2O$). This attenuation was achieved at pH 6.0 with aeration and bacterial respiration without any neutralization process by mixing with spring and/or surface water. Generally, using antalkaline reagents such as limestone, blast furnace slag and fly ash, the remediation of Cu and Zn ions from wastewater has been carried out by neutralization to pH 7.7–9.8. Therefore, the formation process of HW at the Dougamaru abandoned mine taught us a novel technology for wastewater treatment without employing any extensive chemical treatment processes. From our learning at the Dogamaru abandoned mine, reductions of Cu and Zn ion concentrations would be available by neutralization up to pH 6 when HW is selected as a candidate solid phase for the wastewater treatment with addition of Al ion to the remediation system. The formation of HW at pH 6 is also confirmed by thermodynamic consideration in this study.

From the experiment to check applicability of Cu- and Zn-bearing LDHs to wastewater treatment, HW and ZW were obtained by addition of Al ion to the Cu- and Zn-bearing wastewater from lower pH conditions. The improvement of removal efficiency of Cu ion by adding Al ion was not so clear in the experiment because Cu ion was removed from the synthetic wastewater by Cu-hydroxyl sulfate precipitation at the experimental conditions. On the other hand, even at pH 6.0, the removal efficiencies of Zn ion showed the range from 0 to 30% and improved with increasing initial Al ion content. The experimental results in Zn-bearing wastewater system indicate that the safety remediation of Zn ion can be achieved even at low pH 6.0–7.0 by selection of the ZW as a candidate of the solubility-limiting solid phase. Moreover, because of the high anion exchange capacity of LDHs, addition of Al ion source in the wastewater may also be useful for the treatment of Cu- and Zn-bearing wastewater and simultaneously with anions such as As, Se, and Sb, which shows good performance in terms of anion remediation.

ACKNOWLEDGMENTS

The authors express sincere thanks to Professor Satoshi Okabe of Hokkaido University for the support in 16S rDNA analysis.

REFERENCES

Allada, R.K., Navrotsky, A., Berbeco, H.T. and Casey, W.H. (2002) Thermochemistry and aqueous solubilities of hydrotalcite-like solids. *Science*, **296**, 721–723.

Allada, R.K., Peltier, E., Navrotsky, A., Casey, W.H., Johnson, C.A., Berbeco, H.T. and Sparks, D.L. (2006) Calorimetric determination of the enthalpies of formation of hydrotalcite-like solids and their use in the geochemical modeling of metals in natural waters. *Clays Clay Minerals*, **54**, 409–417.

Bravo-Suárez, J.J., Páez-Mozo, E.A. and Oyama, S.T. (2004) Models for the estimation of thermodynamic properties of layered double hydroxides: application to the study of their anion exchange characteristics. *Quimica Nova*, **27**, 574–581.

Feng, D., Van Deventer, J.S.J. and Aldrich, C. (2004) Removal of pollutants from acid mine wastewater using metallurgical by-product slags. *Separation and Purification Technology*, **40**, 61–67.

Geldenhuys, A.J., Maree, J.P., De Beer, M. and Hlabela, P. (2001) An integrated limestone/lime process for partial sulphate removal. *South African Institute of Mining and Metallurgy*, **103(6)**, 345–371.

Johnson, C.A. and Glasser, F.P. (2003) Hydrotalcite-like minerals ($M_2Al(OH)_6(CO_3)_{0.5} \cdot xH_2O$, where M = Mg, Zn, Co, Ni) in the environment: synthesis, characterization and thermodynamic stability. *Clays Clay Minerals*, **51**, 1–8.

Maree, J.P. and Plessis, P. (1994) Neutralization of acidic effluents with limestone. *Water Science Technology*, **29(9)**, 285–296.

Pearson, F.H. and McDonnell, A.J. (1975) Use of crushed limestone to neutralize acid wastes. *Journal of the Environmental Enineering Division*, **101**, 139–158.

Peltier, E., Allada, R., Navrotsky, A. and Sparks, D.L. (2006): Nickel solubility and precipitation in soils: a thermodynamic study. *Clays Clay Minerals*, **54**, 153–164.

Petrik, L.F., White, R.A., Klink, M.J., Somerset, V.S., Burgers, C.L. and Frey, M.V. (2003) Utilisation of South African fly ash to treat acid mine drainage, and production of high quality zeolites from the residual solids. In: Proceedings of the 2003 International Ash Utilisation Symposium, University of Kentucky, USA, Paper no. 61.

Rios, C.A., Williamsand, C.D. and Roberts, C.L. (2008) Removal of heavy metals from acid mine drainage (AMD) using coal fly ash, natural clinker and synthetic zeolites. *Journal of Hazardous Materials*, **156**, 23–35.

Tumiati, S., Godard, G., Masciocchi, N., Martin, S. and Monticelli, D. (2008) Environmental factors controlling the precipitation of Cu-bearing hydrotalcite-like compounds from mine waters. The case of the "Eve verda" spring (Aosta Valley, Italy). *European Journal of Mineralogy*, **20**,73–94.

Vermaak, S.S.P., Potgieter, J.H., Monama, P. and Grieken, R.V. (2006) Comparison of limestone, dolomite and fly ash as pre-treatment agents for acid mine drainage. *Minerals Engineering*, **19**, 454–462.

Watanabe, H., Tazaki, K., Islam, A.B.M.R. and Chaerun, S.K. (2003) Copper biomineralization with banded structure at Dogamaru mine, Shimane Prefecture, Japan. in "Water and Soil Environments: Microorganisms play an important role", ed., K. Tazaki, Kanazawa University Press, Kanazawa, 91–140.

Witzke, T. (1999): Hydrowoodwardite, a new mineral of the hydrotalcite group from Königswalde near Annaberg, Saxony/Germany and other localities. *Neues Jahrbuch fur Mineralogie-Monatshefte*, **2**, 75–86

Witzke, T. and Raade, G. (2000) Zincowoodwardite,$[Zn_{1-X}Al_X(OH)_2][(SO_4)_{X/2}(H_2O)n]$, a new mineral of the hydrotalcite group. *Neues Jahrbuch fur Mineralogie-Monatshefte*, **10**, 455–465.

Xenidis, A., Mylona, E. and Paspaliaris, I. (2000) Potential use of lignite fly ash for control of acid generation from sulphuric wastes. *Waste Management*, **22**, 631–641.

Yamaoka, T., Abe, M. and Tsuji, M. (1989): Synthesis of Cu–Al hydrotalcite like compound and its ion exchange property. *Materials Research Bulletin*, **24**, 1183–1199.