

Immobilization of Multiple Heavy Metals in Copper Smelter's Sludge and Wastewater

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ABSTRACT: Ion-exchange is useful in hazardous wastewater or sludge treatments, where through the ion-exchange process toxic metals become stable. One of the well-documented ion-exchange materials is inorganic sodium aluminosilicates called zeolites. These are naturally occurred mineral group having a microporous structure with interconnecting cavities available for ion movement. The lattice carries a negative electric charge balanced by cations, which can be replaced by other cations such as toxic heavy metal ions. Lime amendment is the chemical precipitation method for immobilizes inorganic metals. The metal hydroxides are usually less soluble and non-toxic. Therefore, the combination of these methods, ion exchange and chemical precipitation, is expected to be useful for hazardous wastewater and waste treatments. The author reports a experimental result of the combination treatment with ore-processing sludge.

Keywords: Ore-processing sludge, Ion-exchange, Zeolite, Lime

1. INTRODUCTION

Mining has played a key role in the economic development of many countries for thousands of years. Concurrently, it has brought potential toxic risks. Mining or ore-processing wastes contaminated by heavy metals and other toxic substances provoke environmental pollution to groundwater and soils, which causes both short- and long-term effects on human health and the ecological system if they introduced in any area due to a spill or other mismanagement. However, only in the last decades the environmental impacts of mining activities became a social concern. In order to prevent the environmental pollutions or to mitigate the contamination, various treatment methods for mine/ore-processing effluents have been developed (Azcue, 1999, etc).

In this paper, the author describes a laboratory experiment result of combination treatment, ion-exchange treatment by natural zeolite and chemical precipitation treatment by lime, with the intention of examining their applicability to mitigation and remediation of ore-processing sludge that is contaminated by various toxic heavy metals.

2. PRINCIPLES

Heavy metal ions and other toxic cations in water can be removed by a cation-exchange process of natural zeolites (Breck, 1974 etc). The chemical formula of natural zeolites is generally expressed as: $(Na,K)_x(Mg,Ca,Sr,Ba)_y[Al_x+2ySi_{n-(x+2y)}O_{2n}] + mH_2O$, where the part in square brackets represents the framework atoms (aluminosilicate) and the other parts the extraframework atoms. Zeolites have a microporous structure, and the lattice carries a negative electric charge balanced by cations described above, which can be replaced by other cations. Thus, the ion-exchange process results in the replacement of toxic metal cations with the non-toxic ions. This process is applicable for toxic cations contaminated wastewater (Ma and Lee, 1978; Mercer and Ames, 1978).

The usual method for removal of inorganic heavy metals is chemical precipitation. Metals precipitate at varying pH levels, depending on the metal ion, resulting in the formation of an insoluble salt. The hydroxides of heavy metals are usually less soluble and non-toxic, so lime (CaO) is commonly used to precipitate them. By raising the pH of most soils to 7, most cationic heavy metals, including Cd, Cu, Cr, Ni, Pb, and Zn can be rendered more strongly adsorbed, immobilized, and less available for uptake by plants (Alloway, 1999). The combination treatment of zeolites, lime, and clays is recently applying to remedial action and environmental protection in contaminated wastes (Minato et al. 1996; Minato & Shibue, 1999).

3. CHARACTERIZATION OF WASTE

The sample studied is collected from a dumping pool of ore-processing waste and wastewater (sludge) in a copper smelter plant. The waste is black-colored sludge that is wet and pulpy. Mineral composition of the sludge was analyzed by X-ray diffraction method (XRD). The diffraction pattern is shown in Figure 1 and the minerals

detected by XRD are summarized in Table 1. The sludge sample contains various sulfide and sulfate minerals and, characteristically, it contains two arsenic minerals, arsenolite and scorodite.

Table 1. Mineral composition of the sludge determined by XRD.

Mineral type	Mineral (abbreviation)	Chemistry
Sulfides	pyrrhotite (P)	$\text{Fe}_7\text{S}_8 - \text{FeS}$
	pyrite (Py)	FeS_2
	chalcopyrite (C)	CuFeS_2
Sulfates	gypsum (G)	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
	anglesite (An)	PbSO_4
Arsenic minerals	arsenolite (As)	As_2O_3
	scorodite (S)	$\text{Fe}(\text{AsO}_4) \cdot 2\text{H}_2\text{O}$
Silicates	quartz (Q)	SiO_2

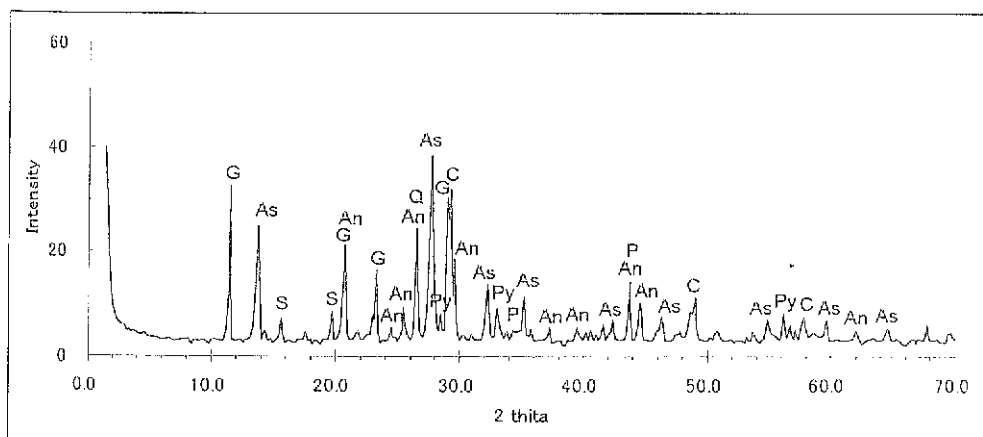


Figure 1. X-ray diffraction pattern ($\text{CuK}\alpha$) of powdered sample of the sludge. Abbreviations are summarized in Table 1.

The sludge consists of black-colored which emits a foul of sulfur, of which pH is very low (pH 1.0). The low pH sludge is corrosive which can react dangerously with other wastes or cause toxic contaminants to migrate. Chemical composition of the sludge indicates that the sludge contaminated by multiple toxic heavy metals, such as arsenic, lead, and cadmium. The chemical composition is consistent with the mineral composition described in previous section. In particular, the high concentration of arsenic (ca. 10%) shows the waste sludge is hazardous without appropriate environmental protection.

4. LEACHING AND MOBILITY CHANGE BY THE TREATMENTS

Six elements, Cd, Pb, Cr(VI), As, Hg, and Se, are well-known as toxic metals (or substances) in the regulation. Their mobility is represented by the concentration of leaching in leaching test with water ($5.8 \leq \text{pH} \leq 6.3$), where the sample quantity is 10 % in weight of total solution and the time length of leaching takes six hours. The result of leaching test for the sludge (untreated sample) is shown in Table 2. The concentration of leaching of four toxic elements, cadmium, lead, arsenic, and mercury, exceeds the EQS values. No leaching was detected in hexavalent chromium and selenium from untreated sample.

Table 2. Result of leaching test of the sludge.

Toxic substance	Regulation (mg/l)	Leaching (ng/l)	Detection limit (mg/l)
Cadmium (Cd)	<0.01	4.3	0.001
Lead (Pb)	<0.01	4.2	0.005
Hexavalent chromium (Cr(VI))	<0.05	<0.04	0.04
Arsenic (As)	<0.01	890	0.005
Total mercury (Hg^{I})	<0.0005	0.012	0.0005
Selenium (Se)	<0.01	<0.001	0.002

Powdered natural zeolite was admixed with the sludge and the effect of prevention (adsorption and/or ion-exchange) to leaching of toxic ions was examined. Mordenite ($(\text{Na}_2, \text{K}_2, \text{Ca})\text{Al}_3\text{Si}_{10}\text{O}_{24} \cdot 7\text{H}_2\text{O}$) was used as the natural zeolite. Its mixing ratio differs from 1 wt% to 32 wt% (Sample 2-7). The samples admixed with powdered mordenite were stored one week under a room temperature and then leaching test with water was per-

formed. The results of leaching test are shown in Figure 2. It is inerrant that the concentration of leaching of cadmium, arsenic, and mercury become low with the increase of zeolite component. However, that of lead does not shows distinct trend of decreasing.

Lime (CaO) was admixed with the ore-processing waste sludge for precipitation of heavy metals. Its mixing ratio was 20 wt% (Sample 8) where the sludge becomes high pH (pH10). In addition to the 20 wt% of lime, natural zeolite (mordenite) also admixed in the Samples 9-14 (Tab.4). The samples were stored one week under a room temperature and then the leachability was analyzed. The results of leaching test for each admixture are summarized in Figure 2. The effect of precipitation by lime treatment is distinct especially for cadmium, arsenic, and mercury. These metals become less-soluble and immobile after the treatment. The concentration of leaching of these three toxic elements become below the EQS level after the treatment.

Particularly the concentration of leaching (mobility) of arsenic drastically decreases, i.e. the concentration after the treatment is only 0.03% of that before the treatment. However, the concentration of leaching of lead rather increases after the lime treatment. Selenium also becomes mobile after the treatment of lime, of which concentration of leaching was below the detection limit before the lime treatment.

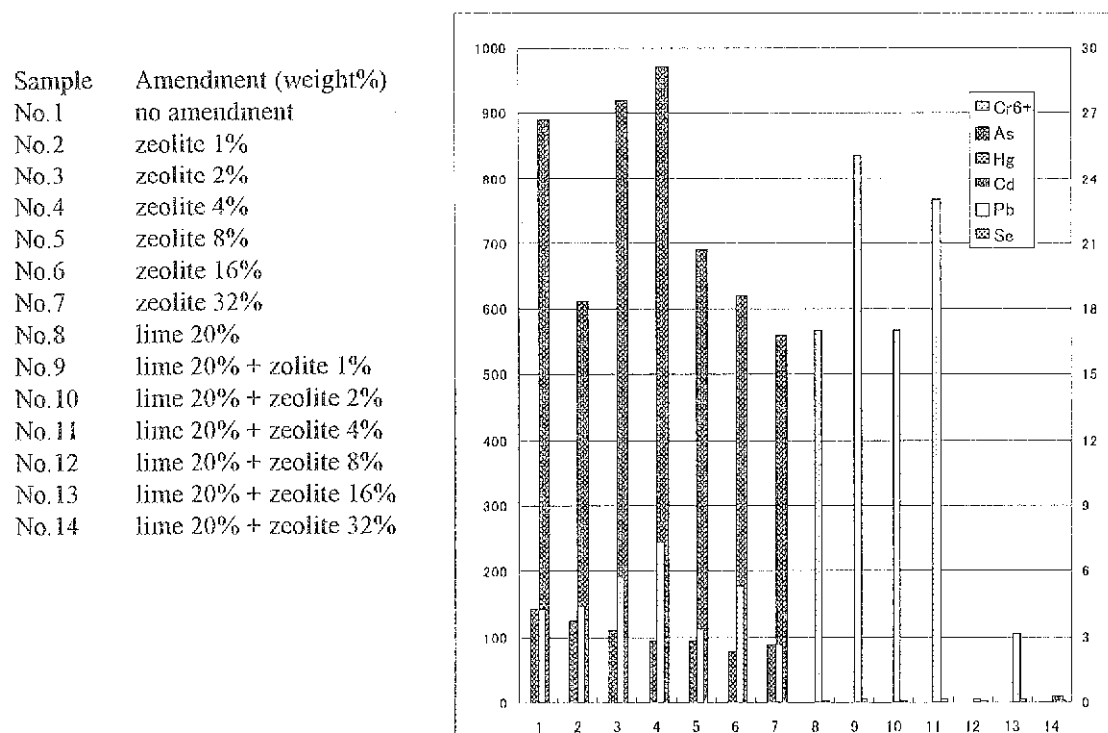


Figure 2. Variation of the concentration of leaching (mobilization) for different amendment conditions in the treatment. Horizontal axis depicts the sample ID (see Tabs. 4 and 5). Left vertical axis shows the concentration of leaching of arsenic, while right vertical axis does that of other elements.

5. DISCUSSION

The treatment solely admixing mordenite is useful for reducing the concentration of leaching of Cd, Pb, As, and Hg, which can reduce the concentration around 60 % of initial (untreated) level. It is an effect of cation exchange reaction in mordenite. Despite the fact of cation exchange, the concentration of leaching is still above the EQS values.

The lime treatment is very effective for decreasing the concentration of leaching less than the EQS values; i.e. three toxic heavy metals, Cd, As, and Hg, become insoluble after the lime treatment (Samples 8-14). According to the mineral and chemical compositions, the heavy metals in the sludge are presented as the forms of metal sulfides. In general, solubility of metal sulfides in aqueous system greatly decreases with increasing pH. (Wentz, 1995). The lime treatment induces the formation of insoluble metal hydroxide, which also contributes the reduction of leaching of heavy metals (Davis et al., 1999). Significant drop of As leaching after the lime treatment is possibly due to the As/Ca interaction pointed by Mahuli et al. (1997).

However, the concentration of Pb leaching increases after the lime treatment. Lead hydroxide is exceptionally soluble under high pH (Wentz, 1995), which causes the increase of Pb leaching after the lime treatment. It is notable that high content of mordenite (> 8 wt%) with lime successfully reduce the Pb leaching even under high pH.

Augmented concentration of leaching of selenium (Samples 8-14) is only one disadvantage in the lime or lime + zeolite treatment. The selenium in the sludge sample is insoluble form in untreated condition, but it becomes soluble after the lime treatment. Selenium (Se) is a metalloid that exists in a variety of oxidation states including selenide (Se(-II)), elemental selenium (Se(0)), selenite (Se(IV)), selenate (Se(VI)), and several organic compounds. The different chemical forms of Se control Se solubility and toxicity (Zhang et al. 1999). Se(VI) is highly soluble and potentially toxic. Se(IV) is also soluble but not mobile because it can strongly adsorb onto surfaces of common soil minerals and clay particles (Tokunaga et al., 1997; Farmer & Graham, 1999). The reduced forms, selenide and elemental selenium are insoluble and much less bioavailable (Hansen et al. 1998). Under alkaline conditions, oxidation of selenide forms selenate, $\text{Se}^{\text{VI}}\text{O}_4^{2-}$, in preference to selenite, $\text{Se}^{\text{IV}}\text{O}_3^{2-}$, or biselenite, $\text{HSe}^{\text{IV}}\text{O}_3^-$ (Farmer & Graham, 1999). The augmented leaching is probably due to the formation of soluble and mobile Se(VI). Thus, another treatment is additionally required for this pollutant.

References

- Alloway, B.J. 1999. Land contamination and reclamation. In R.M. Harrison (ed.), *Understanding our environment - An introduction to environmental chemistry and pollution 3rd edition*: 199-236. London: Royal Society of Chemistry.
- Azcue, J.M. 1999. *Environmental impacts of mining activities*. Berlin: Springer-Verlag.
- Barrer, R.M. 1978. Cation-exchange equilibria in zeolites and feldspaths. In Sand, L.B. & Mumpton, F.A. (eds.), *Natural zeolites, occurrence, properties, use*: 385-395. Oxford: Pergamon Press.
- Barrer, R.M. 1982. *Hydrothermal chemistry of zeolites*. London: Academic Press.
- Breck, D.W. 1974. *Zeolite molecular sieve: structure, chemistry, and use*. New York: John Wiley.
- Davis, A., Eary, L.E. & Helgen, S. 1999. Assessing the efficacy of lime amendment to geochemically stabilize mine tailings. *Environmental Science & Technology*, 33 : 2626-2632.
- Farmer, J.G. & Graham, M.C. 1999. Freshwaters. In R.M. Harrison (ed.), *Understanding our environment - An introduction to environmental chemistry and pollution 3rd edition*: 71-138. London: Royal Society of Chemistry.
- Hansen, D., Duda, P.J., Zayed, A. & Terry, N. 1998. Selenium removal by constructed wetlands: Role of biological volatilization. *Environmental Science & Technology*, 32: 591-597.
- Ma, Y.H. & Ting Yueh Lee. 1978. Sorption and diffusion properties of natural zeolites. In Sand, L.B. & Mumpton, F.A. (eds.), *Natural zeolites, occurrence, properties, use*: 373-383. Oxford: Pergamon Press.
- Mahuli, S., Agnihotri, R., Chauk, S., Ghosh-Dastidar, A. & Fan, L.-S. 1997. Mechanism of arsenic sorption by hydrated lime. *Environmental Science & Technology*, 31: 3226-3231.
- Mercer, B.W. & Ames, L.L. 1978. Zeolite ion exchange in radioactive and municipal wastewater treatment. In Sand, L.B. & Mumpton, F.A. (eds.), *Natural zeolites, occurrence, properties, use*: 451-462. Oxford: Pergamon Press.
- Minato, H., Okano, H. & Wada, N. 1996. Basic research concerning shielding wall of waste final disposal site (I) - About the raw material -. *Proc. 6th Symp. Geo-environ. and Geo-tech.*: 389-392.
- Minato, H. & Shibue, Y. 1999. A case for utilization of clays to raw materials of outside wall at final disposal site of town waste matters and new treatment techniques for pollution soils. *Clay Science (Nendo Kagaku)*, 38: 167-180.
- Tokunaga, T.K., Brown, G.E.Jr, Pickering, I.J., Sutton, S.R. & Bajt, S. 1997. Selenium redox reactions and transport between ponded waters and sediments. *Environmental Science & Technology*, 31: 1419-1425.
- Wentz, C.A. 1995. *Hazardous Waste Management*. McGraw-Hill, New York. 580p.
- Zhang, Y., Moore, J.N. & Frankenberger, W.T.Jr. 1999. Speciation of soluble selenium in agricultural drainage waters and aqueous soil-sediment extracts using hydride generation atomic absorption spectrometry. *Environmental Science & Technology*, 33: 1652-1656.