Effect of red mud on the mobility of heavy metals in mining-contaminated soils

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Abstract   The mobility of Cu^{2+}, Zn^{2+}, Ni^{2+}, and Cd^{2+} in soils treated with red mud was experimentally studied to explore the feasibility of remediation of smelter-contaminated soils. Red mud samples were collected with the Bayer process (BRM) and confederate process (CRM) in the Aluminous Plant of Guizhou Province. Two farmed soil samples were collected from the Niujiaotang mining area, Guizhou Province, Southwest China. One sample was weakly polluted by fly ash; and the other was polluted severely by waste water from the smelter. For evaluating the potential of remediation, the concentrations of free metal ions and the distributions of metals in the soil were determined. The concentrations of free metal ions were measured by using the Donnan Membrane Technique, and the contributions of soil sorbents to the heavy metals adsorptions were calculated with Equilibrium Calculation of Speciation and Transport (ECOSAT). BRM reduced the concentrations of free metal ions in two kinds of soils, while CRM only favored the decrease of the concentrations of free metal ions in seriously contaminated soils. The experimental data also showed a tendency that the concentrations of free metal ions decreased proportionally with the amount of added red mud, which resulted from the increasing adsorption of heavy metal ions in the form of metal ion hydroxides.

Key words   soil; red mud; mobility; free metal ion; concentration

1 Introduction

Heavy metal contamination of soil is a worldwide environmental problem. Metals can be accumulated either directly from a range of anthropogenic activities or indirectly from the mobilization of naturally occurring metals due to mining activities, aquifer oxidation, or acidic rain (Nriagu, 1984; Ross, 1994; Alloway, 1995; Cancès et al., 2003; Kuang Shaoping and Song Feng, 2008; Wu Yongfeng et al., 2008). Corresponding adverse effects may be connected with food quality, soil health, and the environment. A variety of technologies have been developed to decontaminate and remediate soils polluted by heavy metals. There are generally two kinds of technologies (Hong Kyungjin et al., 2002). One technique can promote heavy metal mobility and migrate them to the liquid by desorption and solubilization, which is a permanent solution, but it is very expensive and often depends on the environment. Therefore, that technique can be only applied in heavily polluted soils and slightly contaminated areas. The other technique is named the *in-situ* approach, and can immobilize heavy metals and minimize migration by addition of various amendments with low cost. The *in-situ* approach has attracted much attention for its ability to meet the needs for soil remediation and community demand because the area of metal contaminated soils is much large in the world.

In-situ immobilization of metals relies on the addition of amendments to increase the proportion of metal burden within the soil solid phase, either through precipitation or through increasing metal sorption, thereby reducing its mobility and availability (Oste et al., 2002; Basta and McGowen, 2004; Gray et al., 2006). A large number of amendments have been proposed and tested for *in-situ* immobilization of heavy metals in degraded soils. The amendments include traditional agricultural materials, organic matter, and industrial by-products (Boisson et al., 1998; Lombi et al., 2002a, b; Friesl et al., 2003; Melamed et al., 2003; Walker et al., 2003; Brown et al., 2004; Farfel et al., 2005). Among those, it is promising to use various industrial residues to remedy soils, which could also reduce waste disposal and give new value to industrial wastes through revaluating them into in-

dustrial by-products.

Red mud has great potential to immobilize heavy metals and reduce plant uptake. More and more attention is being paid to the red mud which is a fine-textured residue, derived from the digestion of bauxite for aluminium manufacturing, with alkaline property and enrichment in iron oxide. Müller and Pluquet (1998) applied red mud to treat harbor dredging contaminated with Cd and Zn and found that it could reduce metal mobility and availability. Philips (1998) and Lombi et al. (2002a) showed that red mud could also significantly increase metal sorption and decrease soluble metal concentrations in heavy metal contaminated soils. Furthermore, the laboratory column leaching results demonstrated that adding red mud in severely mining-contaminated soils and disused mine tailings could drastically reduce heavy metal contents in effluents (Ciccu et al., 2003; Bertocchi et al., 2006). Red mud could also reduce the intake of heavy metals by plants (Lombi et al., 2002b; Friesl et al., 2003). Lombi et al. (2002b) found that adding 2% of red mud (*w/w*) in two contaminated soils could reduce intake of Cd, Zn, Cu, and Ni by oilseed rape, pea, wheat, and lettuce. In another experiment, Friesl et al. (2003) showed that compared with un-amended soil, red mud (10%, *w/w*) could significantly reduce intake of Cd, Zn, and Ni by fescue and amaranthus.

Efficacy of the amendments is controlled by many factors, such as the particular combination of elements at a site, the range of biological endpoints of concern (Brown et al., 2005), and the exact composition of red mud which is responsible for the reduction of metal mobility and depends on the particular chemical and mineralogical compositions of the baux-

ite (Komnitsas et al., 2004). It is important to conduct laboratory experiments on the exacted red mud and soil before extending to field scale. The goal of this paper is to highlight immobilization techniques and investigate the possibility of application of red mud from the Aluminous Plant of Guizhou Province in rehabilitating mining-contaminated soils in the Niujiaotang mining area, Guizhou Province, Southwest China. To characterize the metal mobility in soil, the concentrations of free metal ions and distributions of metals were determined.

2 Materials and methods

2.1 Sampling

The experimental investigation was conducted on two kinds of mining-contaminated soils, taken from the Niujiaotang mining area, Guizhou Province, Southwest China. They were collected from paddy fields. One (QBT) was polluted weakly by fly ash; the other (BXT) was polluted severely by waste water from a smelter (Ye Lin and Liu Tiegeng, 2001; Liu Tiegeng et al., 2004). Their chemical properties and total adsorbed metal contents extracted with 2 mol·L^{-1} HNO$_3$ are listed in Table 1.

Red mud samples added as metal immobilizing agents were collected from the product lines in the Aluminous Plant of Guizhou Province. One sample (BRM) was collected with the Bayer process and the other (CRM) was collected with the confederate process. They were dried at ambient condition and sieved with a sieve of mesh <2 mm. Their characteristics concerning adsorptive action are listed in Table 2.

Table 1. Soil characteristics and contents of total adsorbed metals extracted with 2 mol·L^{-1} HNO$_3$

Sample	pH	CEC-BaCl$_2$ (mmol· kg^{-1})	OM (%)	Clay (%)(<2μm)	Fe-ox (g· kg^{-1})	Fe-DCB (g· kg^{-1})	Total metal content extracted with 2 mol·L^{-1} HNO$_3$ (mmol· kg^{-1})			
							Cu	Zn	Ni	Cd
QBT	7.59±0.02	11.89±0.51	4.82±0.07	2.3±0.2	5.05±0.08	19.57±0.41	1.154±0.028	13.138±0.074	0.169±0.001	0.046±0.0002
BXT	7.51±0.01	13.14±0.39	4.90±0.09	2.5±0.3	5.00±0.06	47.23±0.82	3.209±0.034	38.648±0.068	0.411±0.003	0.538±0.002

Table 2. Red mud characteristics and contents of total adsorbed metals extracted with 2 mol·L^{-1} HNO$_3$

Sample	Clay (%)(<2μm)	Fe-ox (g· kg^{-1})	Fe-DCB (g· kg^{-1})	Total adsorbed metal content extracted with 2 mol·L^{-1} HNO$_3$ (mmol· kg^{-1})			
				Cu	Zn	Ni	Cd
BRM	30.11±2.76	21.11±0.74	63.77±2.99	0.922±0.028	1.356±0.053	0.661±0.015	0.006±0.0002
CRM	4.66±0.37	6.74±0.25	31.09±1.36	1.797±0.055	1.422±0.062	0.914±0.023	0.005±0.0001

Experiment samples include soil and red mud samples. Red mud was applied at the ratios of 0.5% and 2% (*w/w*) according to previous work (Lombi et al., 2002a, b). Samples have been samming for a month before the experiment.

2.2 Sample analysis

The concentrations of free metal ions in soil solution were analyzed with the Donnan Membrane

Technique (Fig. 1). The cation exchange membrane was 0.11–0.13 mm thick and the ion-exchange capacity was about 1.6 mol·kg^{-1}. There were background electrolyte solutions and studied samples in the Donor cell. They had reached equilibrium before experiment. The acceptor solution only includes the background electrolyte solution. It was 2 mmol/L KNO$_3$. As equilibrium reached, the concentration ratios of the metal ions in the donor and acceptor solutions were equal (Temminghoff et al., 1997). At the end of the experi-

ment, donor solutions were sampled for [K$^+$], and acceptor solutions for both [K$^+$] and [M^{2+}]. [K$^+$] was measured by AAS, and [M^{2+}] by ICP-MS.
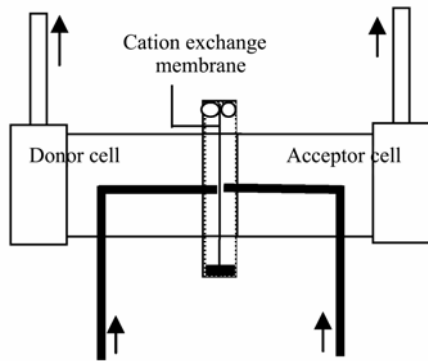

Fig. 1. Diagram of the Donnan membrane technique.

2.3 Modeling

The ECOSAT program was used to study metal speciation in soils. The sorbents in soils considered in this program were independent and included soil organic matter, iron hydroxides, and clay, each one has its own model in this program (Weng Liping et al., 2001; Keizer and van Riemsdijk, 2002). Soil organic matter (SOM) was modeled by using the Non Ideal Competitive Adsorption Donnan (NICA-Donna) model (Kinniburgh et al., 1999; Koopal et al., 2005). Amorphous (HFO) and crystalline ferric oxides (goethite) were modeled by using a two-site surface complexation diffuse double layer (DDL) model and the charge distribution multi-site complexation (CD-MUSIC) model, respectively (Dzombak and Morel, 1990; Hiemstra and van Riemsdijk, 1996, 1999). X-ray diffraction showed that most clay silicates were illite in the two soils studied (Yi Li, 2005), so illite was taken as a representative for clay in the model. Its binding metals were modeled through a Donnan approach (Weng Liping et al., 2001).

3 Results and discussion

3.1 Effects of red mud on the concentrations of free metal ions

Figure 2 showed the concentration ratios of free heavy metal ions with the ratios of soils to soil solutions (SSR) in QBT. After the soil was treated with red mud, the concentrations of free Cu^{2+} increased by about 5%, but the concentrations of free Zn^{2+} decreased at the same degree. The concentrations of Ni^{2+} increased largely, except for 2% Bayer red mud, in which it decreased to about 56% of that in the untreated soil. The CRM averagely enhanced the concentrations of free Cd^{2+} to 150%, but 2% and 0.5% BRM reduced it to 45% and 77%, respectively. In

BXT (Fig. 3), the concentrations of Cu^{2+} were hardly affected by red mud, except for SSR at 1:25. CRM and BRM decreased the Zn^{2+} concentrations to about 95% and 87%, respectively. Free Ni^{2+} concentrations increased by 10% by CRM, but decreased by 20% by BRM. BRM reduced the free Cd^{2+} concentrations at different degrees, depending on SSR, while CRM decreased the concentrations at larger SSR, but increase the concentrations at smaller SSR.

The different characteristics of red mud responded for the result. The total concentrations of adsorbed metals of Cu and Ni in CRM were appreciably higher than those in QBT, but those of adsorbed metals of Zn and Cd were much lower than those in the soil. The total concentrations of adsorbed metals in BXT were far higher than those in CRM except Ni. The concentrations of iron hydroxides in CRM, especially the amorphous iron hydroxides (HFO) with strong absorbability for metals were slightly higher than those in soils (Tables 1 and 2). The addition of red mud led to a decrease in the ratio of soil organic matter, the strongest sorbent in the soils studied. Therefore, CRM increased the concentrations of free metal ions in the soils, except for Zn ions. The total concentrations of adsorbed Zn in CRM were far lower than those in soils, so CRM addition led to a decrease in the concentrations of free Zn ions. BRM had more amorphous iron hydroxides (HFO) and clay, and the total adsorbed metal contents were lower than those in soils except for Ni. So the concentrations of free metal ions were reduced by BRM. It was proved by the distribution of heavy metals that more heavy metals existed in the form of iron hydroxides in soils when treated with BRM. This indicates that the specific chemisorption of metals by iron hydroxides may be the dominant mechanism for the immobilization of heavy metals.

The concentrations of free Cu^{2+} and Zn^{2+} decreased proportionately with increasing dilution. In contrast, concentrations of free Ni^{2+} and Cd^{2+} increased with increasing dilution except for those in BXT with the SSR at 1:100. They decreased sharply, and were lower than those with the SSR at 1:25. The increase of free Ni^{2+} and Cd^{2+} concentrations was probably the result of the release of Ni^{2+} and Cd^{2+} from organic matter. Also, pH decrease may have contributed to the increase of free Ni^{2+} and Cd^{2+} concentrations (Yi Li et al., 2007). It is indicated that abundant dilution would significantly reduce the concentrations of free metal ions, thereby decrease their mobility and availability.

3.2 Effects of red mud on the distribution of heavy metals

Contributions of soil sorbents to the adsorptions

of heavy metals were modeled through ECOSAT at different ratios of soils to soil solutions. The sorbents considered in the program include soil organic matter, iron hydroxides, clay and the Donnan gel of soil organic matter.
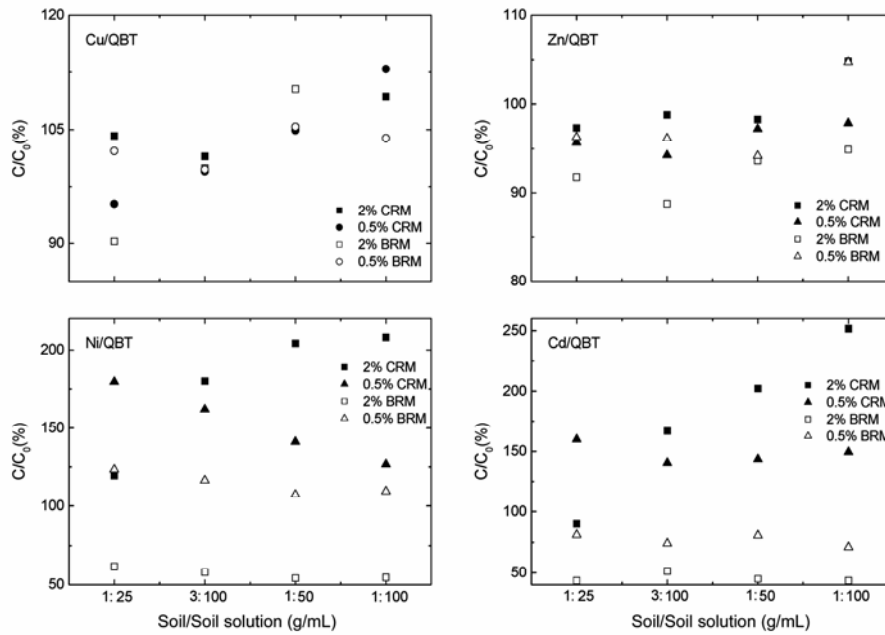

Fig. 2. Concentration ratios of free heavy metal ions affected by red mud in QBT. 2% CRM and 0.5% CRM represent soils added with red mud from the confederate process at the ratios of 2% and 0.5%, respectively; 2% BRM and 0.5% BRM represent soils added with red mud from the Bayer process at the ratios of 2% and 0.5%, respectively.
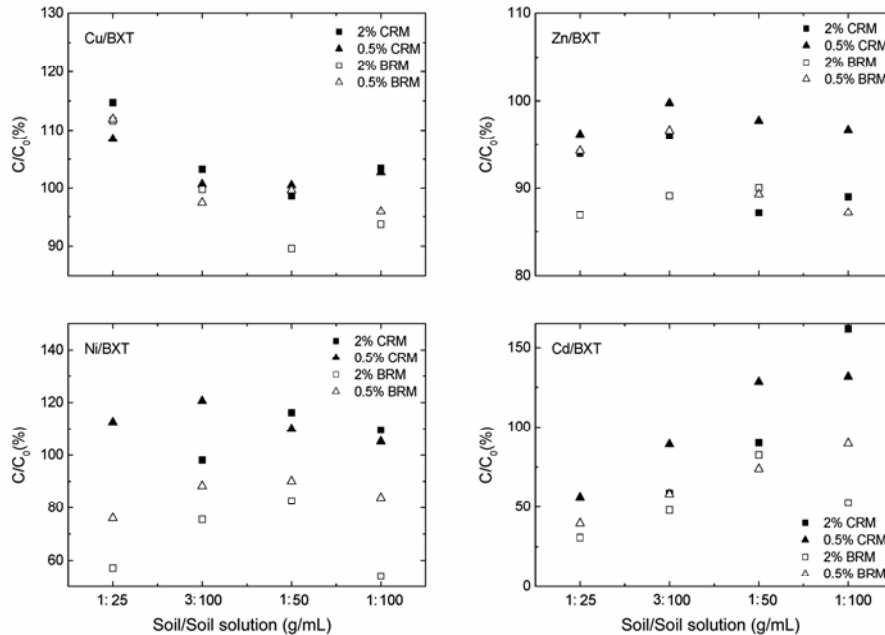

Fig. 3. Concentration ratios of free heavy metal ions affected by red mud in BXT. 2% CRM and 0.5% CRM represent soils added with red mud from the confederate process at the ratios of 2% and 0.5%, respectively; 2% BRM and 0.5% BRM represent soils added with red mud from the Bayer process at the ratios of 2% and 0.5%, respectively.

Figure 4 showed the predicted metal distributions in soils with the SSR at 1:25. The contribution bound to clay was very weak. The improper model selected for clay may cause incorrect results. The Donnan ap-proach model should be used to calculate the clay ad-sorption at low pH, but in this study soil pH was slightly high. The organically bound copper and nickel account for about 80%. The model predicted that Cd

bound to soil organic matter accounts for more than 95% of the total adsorbed Cd, and only less than 5% of Cd adsorbed by iron hydroxides. Zinc was mainly distributed in soil organic matter and iron hydroxides, accounting for about 40% each. It is indicated that soil organic matter is an important surface adsorbing Cu, Cd, and Ni in soils. As for Zn, it was controlled by both soil organic matter and iron hydroxides.
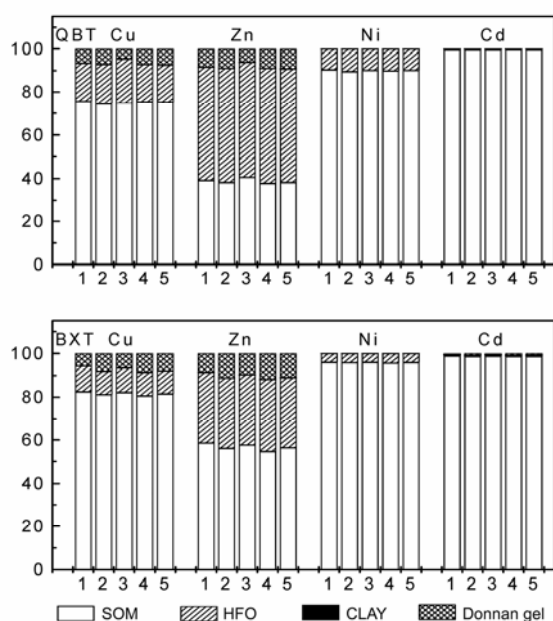

Fig. 4. Calculated metal distributions in soils with the SSR at 1:25. 1. No RM; 2. 2% CRM; 3. 0.5% CRM; 4. 2% BRM; 5. 0.5% BRM. SOM. The contribution of soil organic matter to metal adsorption; HFO. the contribution of iron hydroxides to metal adsorption; CLAY. the contribution of clay to metal adsorption; Donnan gel. the contribution of the Donnan gel of soil organic matter to metal adsorption.

Although soil organic matter is a dominant sorbent, it is still possible that a considerable proportion of metals is adsorbed by iron hydroxides, especially for Zn. By applying red mud to soils, Cu, Cd, and Ni contributions in the QBT hardly changed, and in BXT the contribution of soil organic matter decreased slightly, while the proportions of iron hydroxides and Donnan gel of soil organic matter correspondingly increased. Zn distribution changed largely. The contribution of iron hydroxides increased by about 3% when BRM was added at the ratio of 2%. In different SSR the variation trends were the same, but the ranges were different. In the study, BRM was more effective than CRM, and the more the red mud was added, the more the contributions would change.

4 Conclusions

The effects of two kinds of red mud on the mobility of heavy metals are different. In general, CRM increased free metal concentrations, but BRM decreased them. Although addition of red mud only slightly changed the contributions of soil sorbents to heavy metals, it increased soil pH and metal proportions in the solid phase of soils according to the calculated results.

The concentrations of free Cu^{2+} and Zn^{2+} were hardly affected by red mud. Those of free Ni^{2+} and Cd^{2+} decreased to about 62% and 44% in QBT, and decreased to about 57% and 31% in BXT when 2% of BRM was added in soils with the SSR at 1:25, respectively. As the SSR at 1:100, they were 54% and 53%, respectively, and the concentrations of free Ni^{2+} and Cd^{2+} were lower than those with the SSR at 1:25. 2% of CRM reduced the concentrations of free Ni^{2+} and Cd^{2+} in BXT to 59% and 31% as in untreated soils, respectively. It is shown that BRM was effective to reduce the concentrations of free Ni and Cd ions in the soils studied, which is the key factor reducing plant uptake and metal transport. So BRM is a good amendment for the remediation of Ni and Cd contaminated soils, and CRM only works on the serious polluted soils.

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