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Research Article

Speciation, Fate and Transport, and Ecological Risks of Cu, Pb, and Zn in Tailings from Huogeqi Copper Mine, Inner Mongolia, China

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Tailings collected from the tailing reservoir at Huogeqi Copper Mine, located in Inner Mongolia, China, were used in a leachate study to evaluate the acid potential, neutralization potential, and possibility for producing acid mine drainage (AMD) from the site. The speciation of Cu, Pb, and Zn contained in the tailings was also determined during the leachate study to further access the potential migration abilities of these metals. The results showed that the tailings did not produce significant AMD as the pH of the leachate ranged from 7 to 9 and decreased with time. The Cu, Pb, and Zn concentrations were high, ranging from 439.1 to 4527 mg/kg in the tailings and from 0.162 to 7.964 mg/L in the leachate, respectively. Concentrations of metals in the leachate and tailings were positively correlated. Over 60% of the Cu in the tailing samples existed in an oxidizable form. Most of the Pb also existed in its oxidized form, as did the silicate and Zn. Metals usually have higher mobility in their exchangeable and oxidizable forms and as such represent a higher potential risk to the environment. Results of risk assessment code also revealed that metals in tailings exerted medium to high risks to the environment.

1. Introduction

Mining activities are known to significantly alter the geochemical background of the environment. Environmental pollution caused by mining activities includes large amounts of particulate and dust, solid wastes, soil pollution, metal-rich effluents, and acid mine drainage (AMD). AMD is drainage with a pH of 2.0 to 4.5 from mines and mine wastes [1]. Metal-rich effluents and AMD, just like metals in dust and solid wastes, have become a serious environmental problem all over the world [2, 3]. With introduction of AMD, metals are more easily dissolved to migrate into the surrounding water and soil [4, 5]. Due to their toxicity and persistence, metals can exert serious risks to ecosystems and human health [6].

Tailings are the primary solid waste associated with mining activities. Oxidation of tailings can produce large amounts of acids leading to the mobilization and potential release of metals [7] and posing potential health risks [8]. Ore-mining activities over the last century have resulted in an enormous amount of tailings around the world. Almost all of these tailings are piled up in the open pit or in the tailing ponds. Exposure of sulfide minerals in the tailings to atmospheric oxygen and moisture can result in the formation of AMD and the release of high concentrations of metals [9–12].

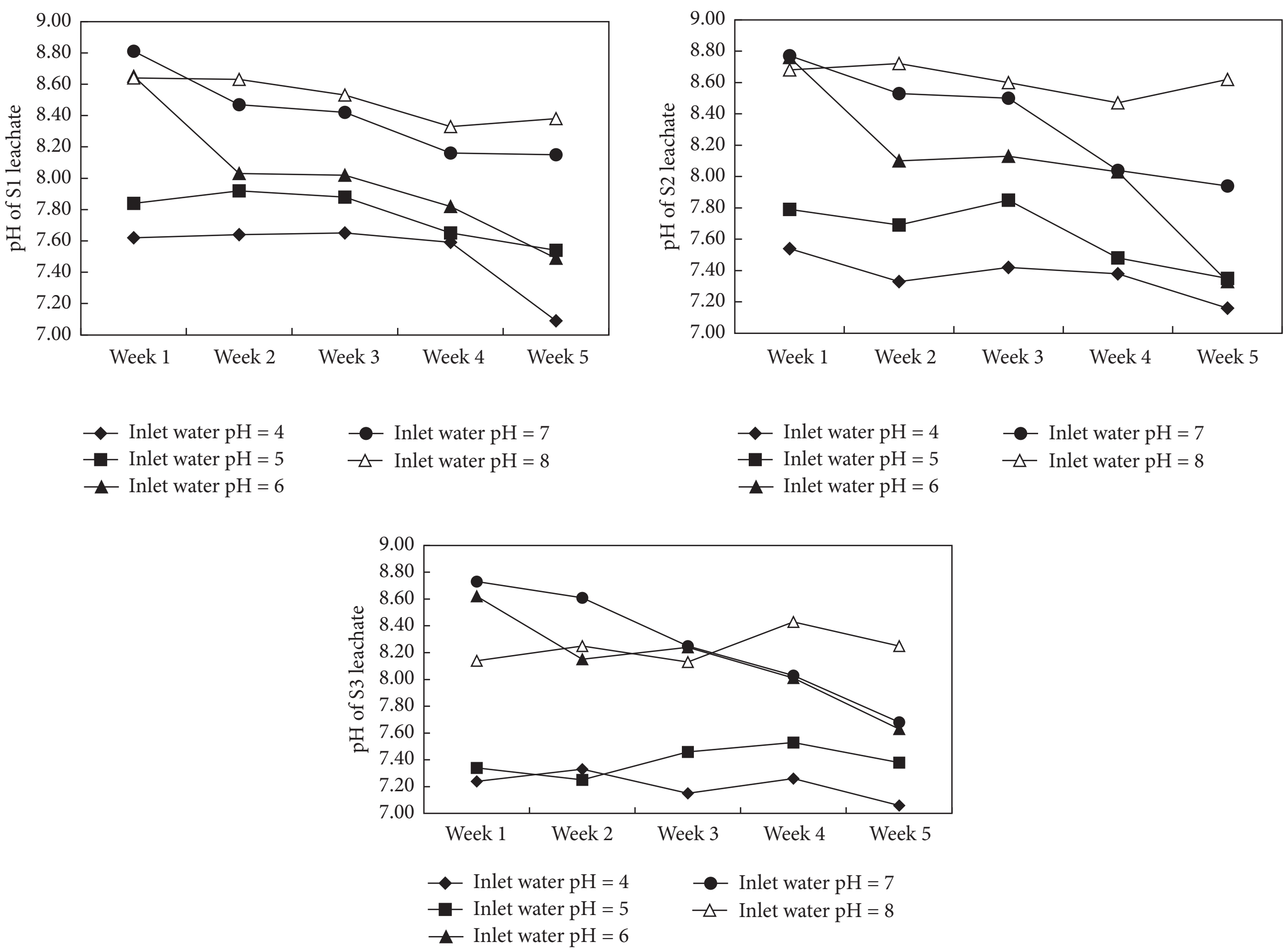

Figure 1: pH variations of tailing leachate.

The release of metals and their environmental fate and transport are a topic of great concern [13–16]. The relationship between metals in tailings and the surrounding environment and properties of tailings/soil/water have also been widely explored [17, 18]. The chemical speciation of metals is also a good indicator for assessing their potential mobility, availability, and toxicity [19, 20].

Mining activities at the Huogeqi Copper Mine, located in Inner Mongolia, China, have been conducted since 1986, resulting in a large quantity of mining wastes including tailings and waste rock. Although most of the CuO, FeS, ZnS, and PbS in the tailings and waste rock are not recycled, the environmental effects have not been well studied. Therefore, the focus of this study is the speciation and potential for migration of Cu, Pb, and Zn in the tailings with the aim of quantitatively describing the distribution and potential for metal migration.

2. Materials and Methods

2.1. Sampling and Sample Preparation. Fresh tailing samples were collected from 3 different sites of the tailing reservoir on March 25, 2015. Sampling sites 1 and 3 were located on the back of the east side and the front edge of the west side of the tailing reservoir while sampling site 2 was located in the middle of the reservoir. Approximately 5 kg of surface tailings was collected at each sampling site using a spade. The tailings were collected in polyethylene containers and transported to the laboratory. The samples were then air dried, crushed, and passed through a 100 micron nylon sieve. The sieved samples were then transferred to polyethylene bottles and stored at room temperature for further use.

2.2. Chemical Analysis. Chemical analysis was carried out at the Analytical Centre of Qinghai University. The concentrations of main elements, including S, were measured by X-ray fluorescence (XRF) spectroscopy (ZSXPrimus II, Rigaku, Japan). The concentrations of Cu, Pb, and Zn were measured by Atomic Absorption Spectrometer (TAS-990, Persee, China) after digestion by H_2SO_4-HNO_3-HF-$HClO_4$. Only guarantee reagents (GR) were used in the study and all test methods followed the National Standardization of China (GB/T14506-1993). The acid potential (AP) values of the tailing samples were obtained according to the counting method (AP = S% × 31.25) [21] and the neutralization potential (NP) was determined by the improved neutralization potential

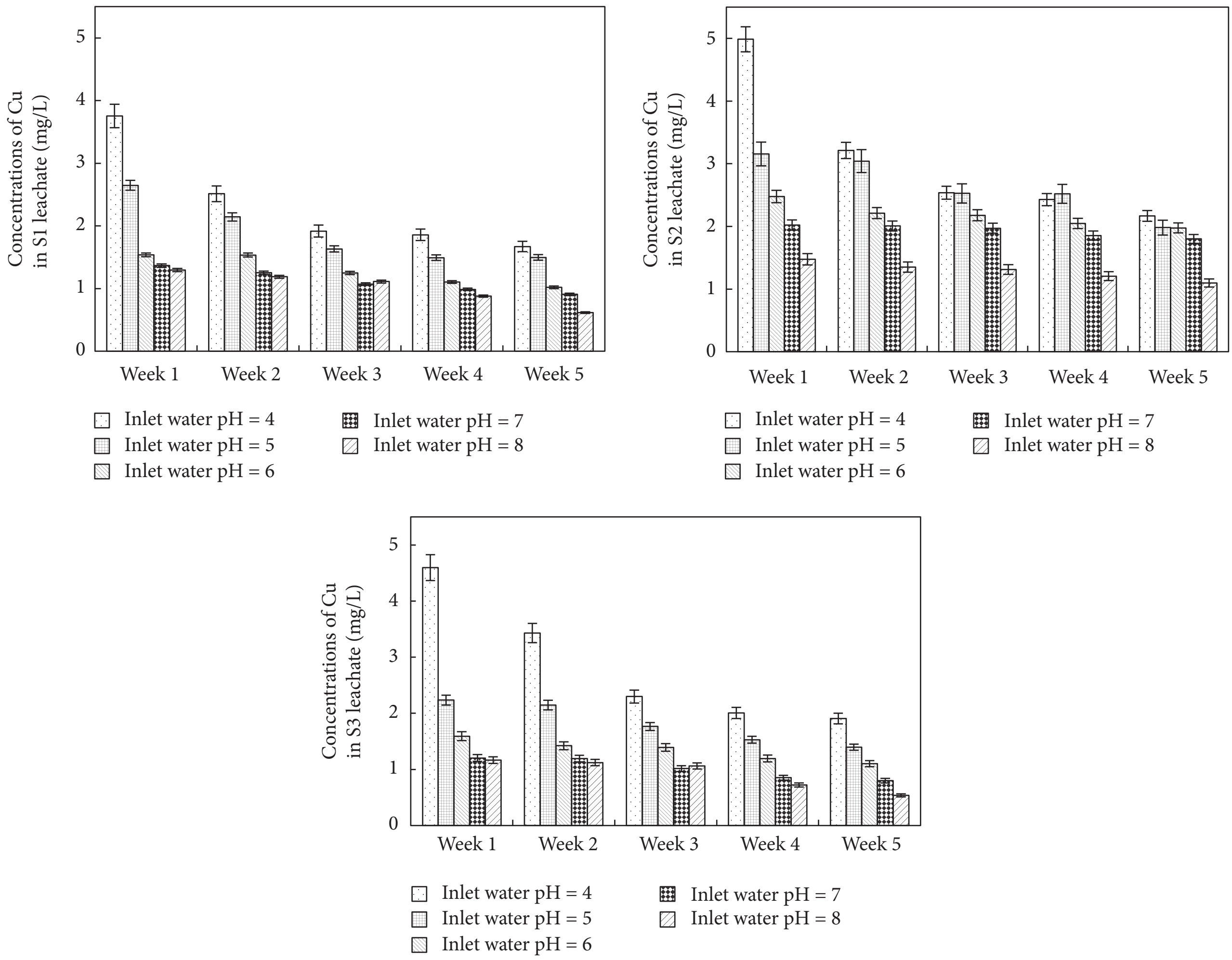

Figure 2: Variation of Cu concentrations in leachate of different tailings.

acid-alkali counting method [22]. In summary, the weight of every tailing sample was 1 g. The concentrations of HCl and NaOH were 12.3 and 0.70 mol/L, respectively. The ratio of volume of HCl and NaOH of blank experiment was 0.057. Thus, NP = {[volume of HCl (mL) × the concentration of HCl (mol/L) − volume of NaOH (mL) × the concentration of NaOH (mol/L)] × 49 × 0.057}/2. NAPP was used to represent AP-NP; and APR was used to represent NP/AP.

2.3. Leaching Study. The leaching study was performed in laboratory to investigate the migration of heavy metals from the tailings. Each column was loaded with 50 g tailings and saturated with deionized water. Then 4 ml of deionized water with different pH values (4, 5, 6, 7, and 8) was added to the top of the columns each week for 5 weeks. Thus, the total quantity of water added in a column during the experiment was 16 mL, corresponding to a local average annual precipitation.

After each addition of water, the percolation rate was monitored and the leachate was collected. Each leachate sample was analyzed in terms of pH (PHSJ-3F, Leici, China) and trace metal element concentrations (Atomic Absorption Spectrometer).

2.4. Sequential Extraction Procedure. The classical sequential extraction technique [23] was employed to study the speciation of heavy metals in the tailings. This method was widely proved to be effective in the studies on speciation of metals in soils, sediments, and tailings [24–26]. The speciation (exchangeable, carbonate, deoxidize, oxidizable, and silicate) of Cu, Pb, and Zn was obtained by Tessier et al. The experiments were performed in duplicate.

2.5. Risk Assessment of Heavy Metals. Based on the method of sequential extraction procedure, risk assessment code (RAC) was proposed as (exchangeable fraction + carbonate fraction) percent concentration [27]. The metals in the samples can be classified by RAC as no risk (less than 1%), low risk (1–10%), medium risk (11–30%), high risk (31–50%), and very high risk (more than 50%) [28].

3. Results and Discussion

3.1. Possibility of Producing AMD of Tailings. All samples based on the classification of NAPP and APR had negative NAPP values (Table 1). They were all larger than −20. APR

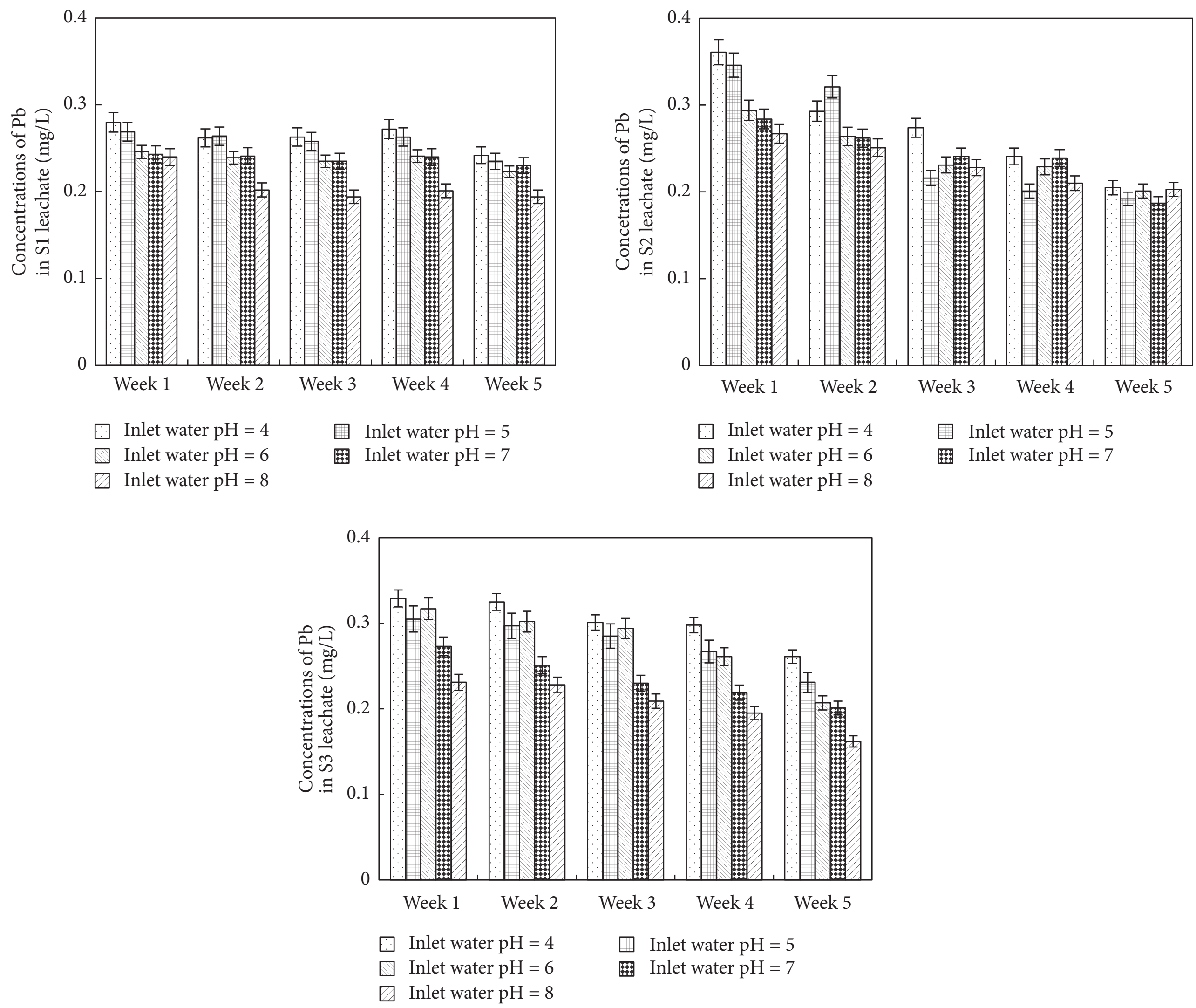

Figure 3: Variation of Pb concentrations in leachate of different tailings.

Table 1: Physicochemical properties and producing-AMD features of tailings.

Sample	Cu (mg/kg)	Pb (mg/kg)	Zn (mg/kg)	S (%)	AP	NP	APR	NAPP
S1	2141	439.1	3939	3.89%	1.22	12.57	10.30	−11.35
S2	3561	528.5	4527	6.21%	1.94	8.07	4.16	−6.13
S3	2945	487.2	4103	5.54%	1.73	9.24	5.34	−7.51

Note. AMD refers to acid mine drainage; AP and NP mean acid potential and neutralization potential, respectively; NAPP represents AP-NP; APR refers to NP/AP.

values were all larger than 3. According to NAPP and APR criteria [29], all tailings did not generate significant AMD.

3.2. pH of Leachate. The pH of the various leachates is shown in Figure 1. All leachate samples collected were alkaline with pH ranging from 7 to 9, which might be caused by the higher NP of the tailings. The H^+ in the acidic inlet water were neutralized by tailings so that the pH of the leachate increased. Although all collected tailing samples did not produce significant AMD, the pH of mine drainage was shown to gradually decrease over time. Therefore, the potential for the production of AMD may still exist.

3.3. Migration Regularity of Cu, Pb, and Zn. The concentrations of Cu, Pb, and Zn in leachate were measured under different leaching conditions (Figures 2–4). As shown, the concentrations of each metal decreased with time. The metals also showed a direct correlation with the concentration of the hydronium ion. In other words, a lower pH resulted in higher metal concentrations. Table 1 summarizes the concentrations

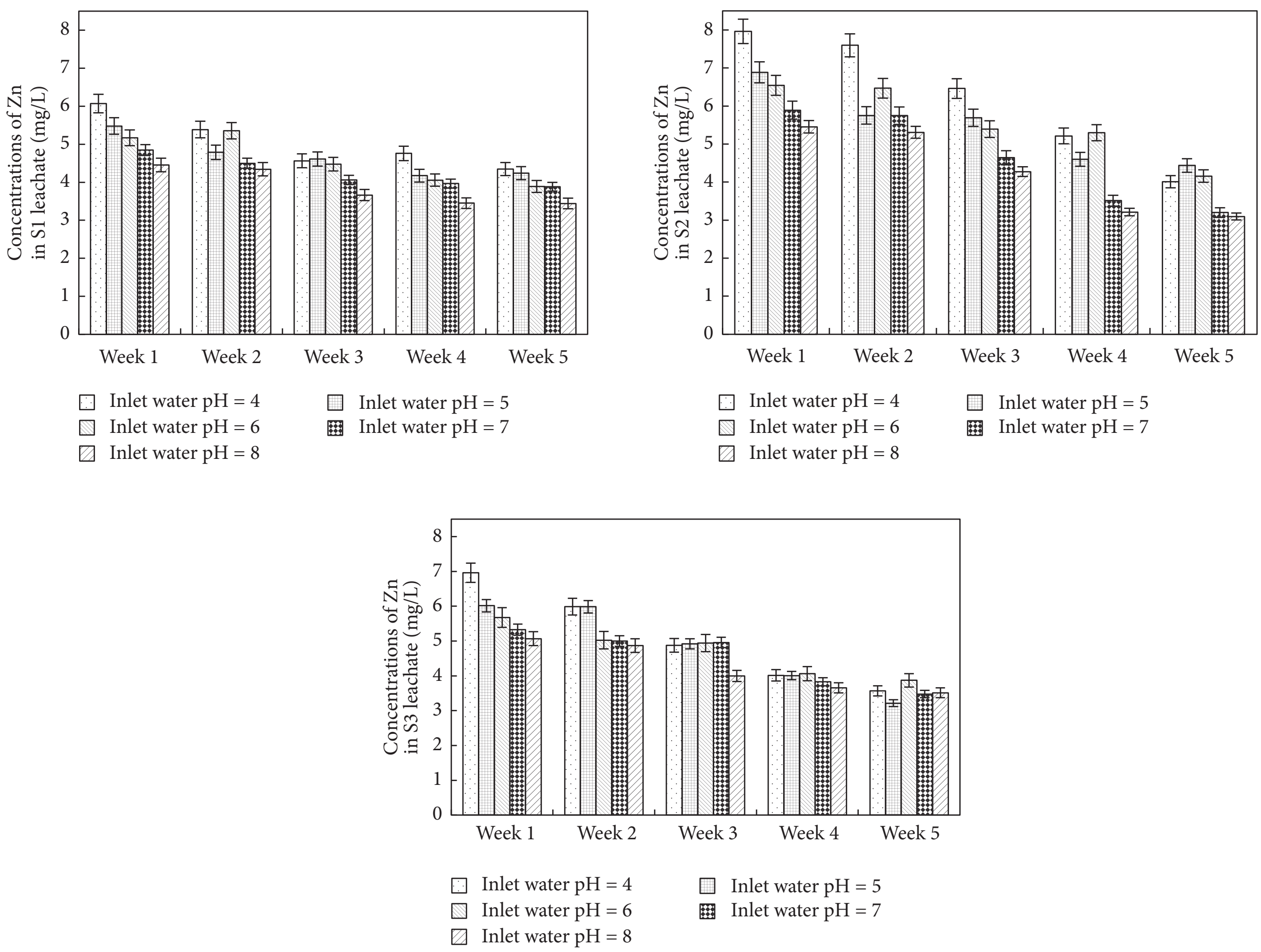

Figure 4: Variation of Zn concentrations in leachate of different tailings.

of heavy metals in the tailings which followed the order of Zn > Cu > Pb. There was also a strong correlation between the concentration of metals in the leachate and tailings, which is similar to the findings of other researchers [30, 31].

The variation of the Pb concentration in the leachate was relatively small while concentrations of Cu varied sharply, especially under acidic leaching conditions. Different tailings exhibited different leaching features, indicating that that tailing properties had a significant effect impact on the metal distribution of the leachate. The concentrations of the three metals in the leachate were higher than the limits of Surface Water Quality Standards (GB 3838-2002, level IV). It showed that the metals in tailings could migrate and pollute the environment.

3.4. Speciation of Cu, Pb, and Zn. The speciation of metals in tailings is shown in Figure 5. Copper existed mainly in oxidizable form (over 60%). Silicate was the second form for Cu in the tailings while deoxidized and exchangeable forms existed little. Contents of carbonate-form Cu and oxidizable form Cu in S2 and S3 were higher than those in S1. Cu in silicate form was very stable so as not to do harm to the environment under normal conditions. The oxidizable form Cu could slightly decline under specific environmental conditions such as acid rains to potentially cause a drastic increase in the dissolved contaminants to subsequently pose pollution threats to the environment [32]. Deoxidized form and oxidizable form heavy metals would easily transform to the exchangeable form. Therefore, heavy metals in these forms would be released from the tailings and migrate into the water and soil to pollute the environment [33]. Therefore Cu in tailings potentially posed risks to the surroundings.

Pb was mainly in the silicate, oxidizable and exchangeable forms, while small portion was observed in the deoxidize-form and carbonate-form. Deoxidized form Pb was produced on the surface of Fe-oxyhydroxides and Mn-oxyhydroxides or lied in the structures of Fe-oxyhydroxides and Mn-oxyhydroxides by isomorphous replacement of Fe and Mn elements [34]. The oxidizable and exchangeable forms of Pb covered more than 56% in three samples, indicating that the migration ability of Pb was stronger to potentially do harm to the environment.

Zn was mainly in the exchangeable and oxidizable forms while forms of deoxidize, silicate, and carbonate were in small

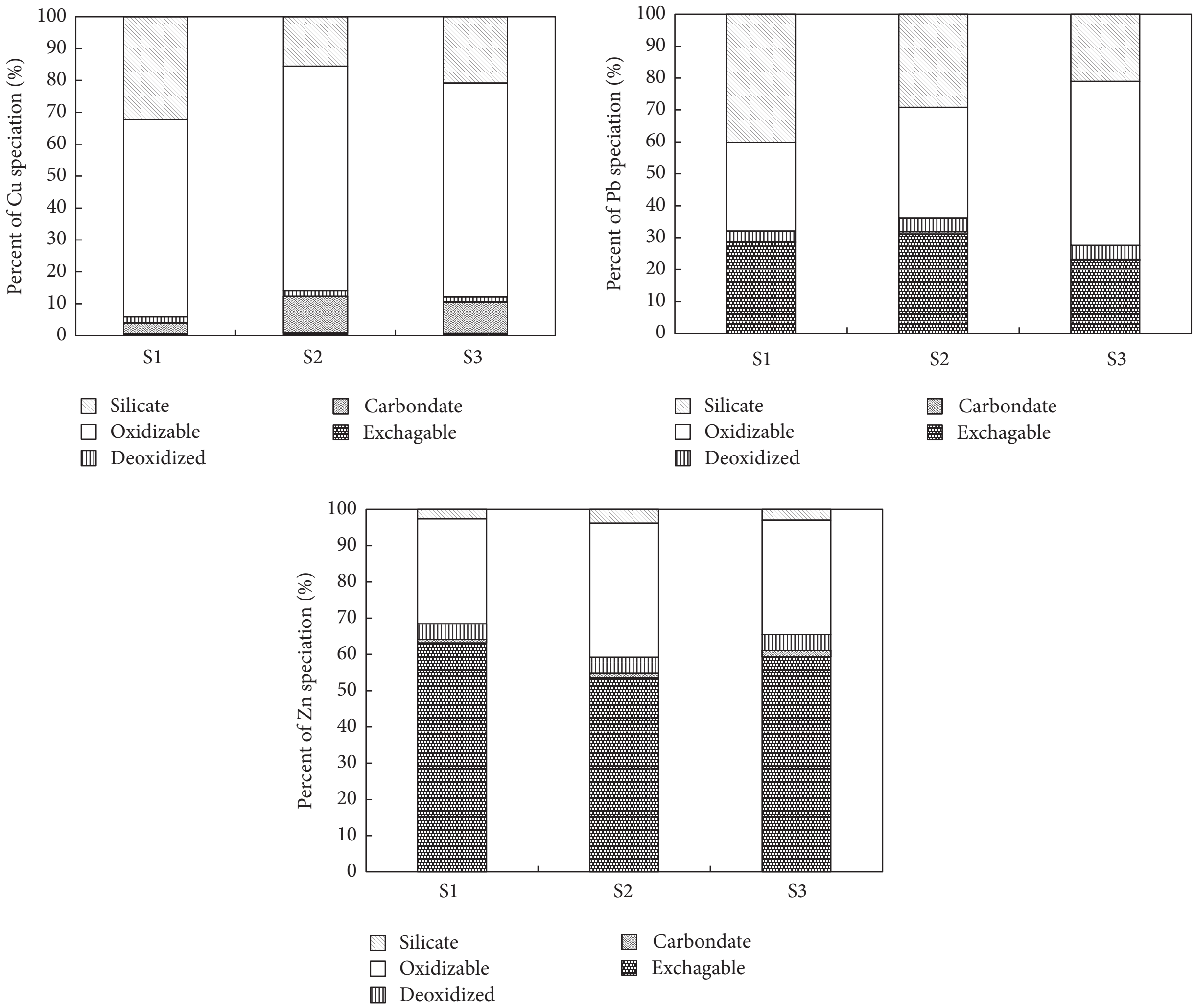

Figure 5: Speciation of heavy metals in different tailings.

portion. The oxidizable and exchangeable forms covered more than 90% in three samples, suggesting that the migration ability of Pb was the strongest in three heavy metals.

3.5. Potential Risk Assessment. Results of RAC were displayed in Figure 6. The RAC values of Cu in S1 showed low risk while Cu in S2 and S3 showed medium risk to the environment. Pd in S1 and S3 exerted medium risk whereas Pd in S2 exerted high risk. RAC values of Zn in all samples were higher than 50%, indicating high risk. The risk levels of heavy metals in tailings by RAC assessment followed the order of Zn > Pb > Cu.

4. Conclusions

Though the neutralization capability of target tailings was high, there was still a potential possibility of producing AMD so as to pose potential risks to the environment. Metal concentrations in the leachate and tailings were positively correlated. The concentrations of metals in leachate followed the order of Zn > Cu > Pb. Moreover, the concentrations of metals in leachate decreased with longer leaching time and increased pH. Therefore, the metals in tailings could potentially migrate and pollute the environment, especially under the condition of rainfall. Cu in tailings was mainly in oxidizable and silicate forms. Pb was mainly in the silicate, oxidizable and exchangeable forms while Zn was mainly in the exchangeable and oxidizable forms. They were potentially hazardous to the environment. The evaluation results of risk assessment code approach exhibited that these metals exerted medium to high risks to the environment, following the order of Zn > Pb > Cu. The influence of specific hydrological geological and climate conditions is important in evaluating the damage degree to the environment caused by metals in tailings. It will be the focus of future research.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

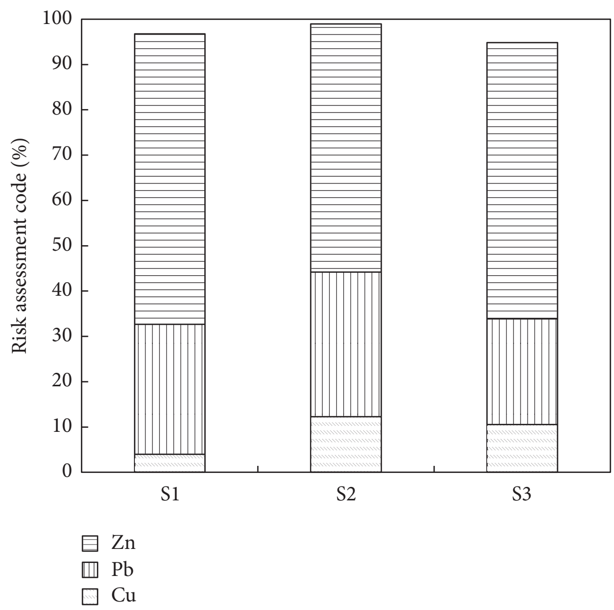

Figure 6: Risk assessment code of heavy metals in different tailings.

Acknowledgments

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