Weathering behavior and metal mobility of tailings under an extremely arid climate at Jinchuan Cu-Ni sulfide deposit, Western China

Ling Wang a,b, Yan Li b,⁎, Haoran Wang b, Xinglan Cui b,c, Xiao Wang b, Anhuai Lu d,e,⁎, Xin Wang b, Changqiu Wang b, Deqing Gan a

Keywords: Jinchuan Cu-Ni sulfide deposit Cu-Ni sulfide tailings Sulfide oxidation Metal mobility Arid climate

A detailed mineralogical and geochemical study of a sulfide tailings impoundment was carried out in Jinchuan Cu-Ni sulfide deposit in western China. Since 1963, the tailings impoundment has been exposed to weathering in an extremely arid climate with dry-warm seasons. Samples from different depths of two boreholes, each located in the center and border of the impoundment, were analyzed to evaluate the oxidative weathering behaviors of the tailings. The obvious shift of Cu and Ni from the sulfide fraction to more mobile forms, increasing trend of SO4 2− in the shallow of the tailings and decreasing trend of Fe content in sulfide fraction, show direct signs of sulfides oxidation, especially in the upper part of the tailings impoundment. Besides the upward migration of Ca2+ and SO4 2− under the strong evaporation in hyper-arid climate, the heavy metals of Cu and Ni are retained by the in-situ adsorption and/or co-precipitation with secondary Fe3+ precipitates. These secondary minerals are poorly crystalline and unstable. So, for sulfide tailings with a simultaneous large production of carbonates and under extremely arid climate, acid pollutants can be avoided but heavy metal pollution from the windblown dust of secondary minerals is the key pollution source that should be taken seriously.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

The environmental pollution of the mine tailings is a worldwide problem. A huge amount of mine tailings have been generated since the industrialization (Bian et al., 2012). These tailings not only take up quantities of land and induce potential geological disasters, but also give rise to drainage, leakages and windblown dust to pollute the environment seriously (Hoffert, 1947; Trois et al., 2007; Abdalla et al., 2010; Hesketh et al., 2010; Liakopoulos et al., 2010; Bian et al., 2012). Especially for sulfide tailings that disposed in open-air impoundments, the residual sulfides are often oxidized to form acid mine drainage (AMD) and release toxic heavy metals to surroundings, thus pollute the soil, surface-water, ground-water and even hazard the ecosystem (Hoffert, 1947; Trois et al., 2007; Liakopoulos et al., 2010).

To reduce the environmental threat of sulfide tailings, the oxidation mechanism of sulfide tailings has been investigated since the early 20th century. One consensus is the action of air and water upon sulfides produces sulfuric acids with highly contaminated heavy metals, and the bacteria greatly accelerate the reactions (Hoffert, 1947; Singer and Stumm, 1970). The extent and products of tailings weathering affect the release and mobilization of the contaminants, which depends on but is not limited to the following factors: the mineralogy (i.e. mineral phase, particle size, chemical composition) of the sulfides, the associated minerals in tailings, the sites, surroundings and stockpile way of the tailings, the hydrology, atmospheric temperature and porosity etc. (Blowes and Jambor, 1990; Boulet and Larocque, 1998; Webster et al., 1998; Trivedi et al., 2001; Dang et al., 2002; Dold and Fontboté, 2002; Dold, 2003; Heikkinen and Räisänen, 2008; Kovács et al., 2009; Marescotti et al., 2009; Bogush and Lazareva, 2011). Besides, the geochemical processes of sorption, precipitation, vaporization and capillary forces also control the movement of H+, O2 and metal ions, which eventually affect the weathering status of sulfides in different vertical depth of the tailings’ impoundment (McGregor et al., 1998; Lee et al., 2002; Moncur et al., 2005; Graupner et al., 2007). Thus, a thorough investigation on the weathering behavior of the tailings is necessary, which help to properly evaluate and effectively prevent and control their environmental hazard.

Up to now, there have been few researches on the weathering behavior of sulfide tailings in the arid region (Redwan and Rammlmair, 2012), Jinchuan Cu-Ni deposit (Gansu Province, China) is such a sulfide deposit (Tang and Li, 1995; Tang et al., 2006) that enjoys a typical hyper-arid continental climate. According to the data provided by Jinchuan Group Co., almost 100 million tons of abandoned tailings...
have been generated since 1963. However, different from other common sulfide tailings, no acid mine drainage (AMD) is produced in Jinchuan. Unfortunately, little information was known about the transformation of minerals and mobility of heavy metals in Jinchuan tailings impoundments at neutral pH, extremely arid climate and dry-warm season. In fact, several studies on sulfide tailings in arid/semiarid regions indicated the intensive weathering oxidation of the residual sulfides occurred (Lei and Watkins, 2005; Lei et al., 2010; Wakelin et al., 2012; Anawar, 2013). And, the acid drainage were observed even to the non-acid forming tailings, thus brought heavy metal contaminations to the ground and surface water, etc. (Lei and Watkins, 2005). Another studies also indicated the climate was a key controlling factor on the weathering of sulfides and the freeze-thaw cycles would accelerate the oxidation of the sulfide minerals in these regions (Fennemore et al., 1998; Dold and Fontboté, 2001; Anawar, 2013; Hayes et al., 2014). Whether the Jinchuan tailings show a similar or different weathering process remains unknown. Therefore, a thorough investigation of the weathering status, metal distribution and migration characters of tailings at different depth and locations are urgently needed, which will help to make proper strategies for eliminate heavy metal pollution from the weathering minerals of windblown dust in Jinchuan region.

2. Materials and methods

2.1. Site description

Jinchuan Cu-Ni deposit is a super large-scale multi-metal inter-growth sulfide deposit (Tang and Li, 1995; Tang et al., 2006). The main metal minerals are pentlandite, chalcopyrite, pyrrhotite, pyrite and magnetite (Tang and Li, 1995; Tang et al., 2006). Gangue minerals are mainly serpentine, chlorite, tremolite, olivine, pyroxene and plagioclase (Tang and Li, 1995; Tang et al., 2006). Jinchuan Cu-Ni deposit is located at the inner draught area in northwest of China (Fig. 1). The average rainfall is 142 mm/year, and the average evaporation is 2354 mm/year. The maximal and the minimal temperature are 40 °C and −29.5 °C, respectively. Jinchuan Cu-Ni mine old tailings impoundment is about 3 × 10⁶ m² in area and 20 m in the deepest height. It stored almost 40 million tons of tailings during 1963 to 1991. The tailings were piped and discharged around the impoundment border and then flow naturally to the center, which caused a terrain with higher border and lower center. The discharge point moved periodically during operation. Unfortunately, Jinchuan Cu-Ni mine old tailings impoundment is located in the last direction of wind of Jinchuan town (Fig. 1).
To reduce the pollution of minerals dust, the tailings surface was covered with gravel in 1993 (≤10 cm thick) and Caragana microphylla was planted in the west border of impoundment.

2.2. Sampling

Two holes were drilled in the border (borehole HB) and central fields (borehole HC) of the tailings impoundment, respectively. Percussion drilling equipment was used to reach 10 m depth of the impoundment. Totally 12 tailings samples were collected from different depths of 1 m, 2 m, 3 m, 5 m, 8 m and 10 m, respectively, and each was around 0.5 kg. For comparison with the oxidized tailings, the flotation tailings on the spot of the dressing plant were also sampled and marked as fresh tailings. All samples were dried under 30 °C for 48 h before use.

2.3. Analytical methods

The moisture of the samples was determined by weight loss after drying (30 °C, for 48 h). Then, the particle-size distribution of the dried solid samples was measured by laser particle size analyzer (Mastersize 2000, Britain). For pH measurement, 10.0 g dry samples were mixed with 25.0 mL 1 M KCl solution. The mixture was fully shaken for 30 min, and after another 30 min suspension, the pH value was measured using an electronic pH-meter (METTLER, America).

The tailings were analyzed according to the method of the modified 6-step sequential extraction procedure (Table 1) involving water solution, exchangeable fraction, carbonate fraction, poorly crystalline fraction, crystalline fraction, sulfide fraction and residual fraction (Dold and Fontboté, 2001, 2002). The acid-generating (AP) and acid-neutralizing (NP) potentials of the tailings were calculated according to Eq. (1) using 1 mol/L HCl was added according to different fizz ratings representing different neutralizing potentials. The aqueous suspension of the sample was allowed to react with neutralizing minerals at room temperature for 24 h and suggested a titration end-point pH of 8.3 with 1 mol/L NaOH. Eq. (1) was used for NP calculation. The AP calculation was carried out using the content of sulfide sulfur (S_{sulfide}) (Eq. (2)).

\[ \text{Sulfide} = \text{AP} \quad \text{(Eq. (2))} \]

NP: kg CaCO3/t; x: HCl volume (mL); y: NaOH volume (mL); a: HCl normality (mol/L); b: NaOH normality (mol/L); c: sample mass (g).

\[ \text{AP} = 31.25 \% \times \text{S}_{\text{sulfide}} \quad \text{(2)} \]

\[ \text{S}_{\text{sulfide}} = 1.6 \times V \quad \text{(3)} \]

2.4. Acid-base accounting (ABA)

The acid-generating (AP) and acid-neutralizing (NP) potentials of the tailings were analyzed according to the method of the modified Sobek II proposed by Lawrence and Wang (2010). In the test, excess 1 mol/L HCl was added according to different fizzes representing different neutralizing potentials. The aqueous suspension of the sample was allowed to react with neutralizing minerals at room temperature for 24 h and suggested a titration end-point pH of 8.3 with 1 mol/L NaOH. Eq. (1) was used for NP calculation. The AP calculation was carried out using the content of sulfide sulfur (S_{sulfide}) (Eq. (2)). The S_{sulfide} was determined by peroxide experiment and calculated according to Eq. (3) (Lengke et al., 2010). In the experiment, 1 g sample was mixed with 100 mL 15% H2O2 (pH = 7). The solution was kept at room temperature for 48 h and then heated to remove peroxide traces. After cooling, the acidity of the solution was determined by titration (final point pH = 8.3, 1 mol/L NaOH solution as a titrant). The difference between the value of NP and AP is the net acid-neutralizing potential (NNP = NP – AP), which is to evaluate the net acid-generating potential of the tailings. According to previous studies, if the NNP value is between −20 and 20 kg CaCO3/t, the acid generation is uncertain; if the NNP value is below −20 kg CaCO3/t, the acid generation is likely to occur; and if the NNP value is above 20 kg CaCO3/t, it is unlikely to generate any acid (Skousen et al., 2002; Lengke et al., 2010). The content of total S of the tailings (S_{total}) was also determined by ICP-AES after the tailings were digested with a mixture of HCl, HNO3, HF and HClO4 by using the method described in Section 2.3.

NP = 50 \times \frac{[x – y(b/a)]}{c} \quad \text{(1)}

\[ \text{NP: kg CaCO3/t; x: HCl volume (mL); y: NaOH volume (mL); a: HCl normality (mol/L); b: NaOH normality (mol/L); c: sample mass (g).} \]

\[ \text{AP} = 31.25 \% \times \text{S}_{\text{sulfide}} \quad \text{(2)} \]

\[ \text{S}_{\text{sulfide}} = 1.6 \times V \quad \text{(3)} \]

2.5. Sequential extraction

The mobility and speciation of metals were studied using a modified 6-step sequential extraction procedure (Table 1) involving water soluble fraction, exchangeable fraction, carbonate fraction, poorly crystalline fraction, crystalline fraction, sulfide fraction and residual fraction (Dold and Fontboté, 2001, 2002). The residual fraction was difference of the sequential extraction results and the total chemistry.

3. Results and discussion

3.1. Description of Jinchuan mine tailings impoundment

The surface of the tailings impoundment is very dry due to the hyper-arid climate. The white efflorescent salts, mainly gypsum, are ubiquitous on the surface of the tailings impoundment. The longitudinal section of tailings shows a layered structure. As the depth increasing, the layer’s color gradually changes from buff and/or reddish brown to light gray, and then to dark gray. However, the light gray and dark gray layers are also in alternated pattern, which might be caused by different amounts of silicate minerals (serpentine and chlorite) in layers. Besides, the yellowish brown streaks and dots are observed in the deep part of the tailings, suggesting the sulfide minerals are oxidized.

Though the tailings impoundment surface looks dry, the moisture contents of the tailings in borehole HC are up to 19%–33% (Fig. 2). For borehole HB, the moisture contents sharply increase from 7% at the surface to about 20% at 3–8 m, and to nearly 30% at 10 m (Fig. 2). Generally, the moisture contents of borehole HB are lower than those of the borehole HC, which might be caused by the tailings impoundment terrain.
The shallow bowl-shaped terrain makes more water converged in the lower center area. The more moisture should also be caused by the finer particles in the borehole HC. According to McGregor et al. (1998) and Dold and Fontboté (2002), the coarse horizons usually dry out first in a hyper-arid climate. In Jinchuan, the evaporation (2354 mm/year) strongly exceeds the rainfall (142 mm/year), and the proportion of the particle size ranging from 2 to 20 μm is far greater than other particle size in borehole HC (Fig. 3). While in borehole HB, the proportions of particle size in range of 2–20 μm, 20–50 μm, 50–100 μm and 100–250 μm averagely fluctuate at around 20% (Fig. 3). That indicates the mineral particles in borehole HC are generally finer than those in HB. Thus, the water contents of the tailings depend on the higher water retention capacity/ water pertaining potential of the finer tailings. The heterogeneous particle size distribution of the tailings should be resulted from the tailings discharge way as mentioned in Section 2.1.

The pH values of the solid tailings are neutral to slightly alkaline (pH from 7.3 to 8.3) (Fig. 4), consistent with the pH of the flotation circuit.

3.2. Mineralogical characterization of the tailings

3.2.1. Features of mineral composition

XRD studies show that the primary minerals of the tailings in both boreholes are similar that mainly composed of silicate and carbonate minerals, such as serpentine, chlorite, amphibole, olivine, pyroxene and dolomite (Fig. 5). Although it is a sulfides deposit, no sulfides are identified by XRD in the tailings samples. Gypsum instead of sulfides appears, and it is probably a secondary mineral that mainly occurs in the upper part of the tailings impoundment (above 2 m). On the contrary, the characteristic peaks of dolomite (labeled as 10 in Fig. 5) significantly weaken in the tailings above 2 m. Such an opposite trend of mineral phase variation indicates the disappearance of dolomite is probably accompanied by the formation of gypsum.

However, some sulfide minerals like pyrrhotite (Fe1−xS), chalcopyrite (CuFeS2), pentlandite ((Fe,Ni)9S8) and pyrite (FeS2) are clearly observed under the optical microscope, which show evident alterations (Fig. 6). In top of the impoundment, pyrrhotite with the typical reflected color of whitish yellow is observed, and the outer contour of the grains is universally oxidized to iron oxides/oxyhydroxides. Thus, the skeletal grains are present (arrows in Fig. 6A). Besides, the ironish black magnetite is present with red iron oxides/oxyhydroxides replacement (Fig. 6B). The observations indicate the sulfides have suffered intense oxidation. With the increase of the depth to 3 m, the skeletal grains and red iron oxides/oxyhydroxides are absent and the oxidation of sulfide minerals is limited to the thin rims along rocks and/or along the rims of the sulfide crystals (Fig. 6C), indicating an initial oxidation of sulfides. However, in the upper part of the impoundment, there are also some metal sulfide particles with less oxidation or even remain intact, especially for chalcopyrite (Fig. 6D).

3.2.2. Elements contents and ABA results

According to the elements contents shown in Table 2, Si, Mg and Fe account for the top three elements existing in the tailings samples, where Si accounts for 15%–17%, Mg accounts for 15%–20%, and Fe accounts for 7%–10%. The high content of Mg is consistent with the host-rock of Jinchuan Cu-Ni deposit is Mg-rich ultramafic rock (Tang et al., 2006; Gao et al., 2009). The contents of Cu and Ni keep steady at around 0.20% in samples from both boreholes and all depths, indicating the mobility of Cu and Ni are limited.

The limited migration of the metal elements in the tailings impoundment should be attributed to the neutral to slightly alkaline of pH (Fig. 4) and the high NNP in Jinchuan. Different from other sulfide tailings reported by Dold and Fontboté (2002) and Hakkou et al. (2008), whose NNP values varied from −22.5 kg CaCO₃/t to −453 kg CaCO₃/t and −47.3 kg CaCO₃/t, respectively, the NNP values of Jinchuan tailings is much higher. As shown in Table 3, the content of S_{total} is as low as 0.64%–1.84% of Si and the NNP value are far higher than 20 kg CaCO₃/t. So, the tailings should belong to the strong neutral type without generating any AMD pollutants. This is consistent with the XRD results that the tailings mainly consist of silicates and carbonates, such as serpentine, chlorite, olivine and dolomite. During the natural weathering process, carbonate minerals such as dolomite are the most effective neutralizing minerals in the circumneutral pH range, while silicates such as olivine and wollastonite can also be important neutralizers because of their abundance in the tailings (Lawrence and Scheske, 1997).

Fig. 2. Moisture contents of the selected tailings at different depth.

<table>
<thead>
<tr>
<th>Procedure</th>
<th>Preferentially dissolved minerals</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>1)</td>
<td>Deionized H₂O, 1:50, continuous shaking for 1 h at room temperature (RT)</td>
<td>Water soluble fraction (e.g., gypsum)</td>
</tr>
<tr>
<td>2)</td>
<td>1 M NH₄Ac, 1:50, continuous shaking for 2 h at RT</td>
<td>Preferably dissolved fraction (e.g., dolomite, calcite)</td>
</tr>
<tr>
<td>3)</td>
<td>1 M NH₄Ac, pH 4.5, 1:50, pH adjusted with HAc, continuous shaking for 2 h at RT</td>
<td>Poorly crystalline fraction (e.g., schwertmannite, amorphous ferrihydrite, manganese oxides)</td>
</tr>
<tr>
<td>4)</td>
<td>0.2 M NH₄-oxalate, pH 3.3, 1:50, pH adjusted with oxalic acid, continuous shaking for 1 h in darkness</td>
<td>Crystalline fraction (e.g., goethite, hematite, magnetite, jarosite, higher ordered ferrihydrite)</td>
</tr>
<tr>
<td>5)</td>
<td>0.2 M Na₂-oxalate, pH 3.3, 1:50, pH adjusted with oxalic acid, heating in water bath 80 °C for 2 h</td>
<td>Sulfide fraction (sulfide minerals)</td>
</tr>
</tbody>
</table>

Table 1: Schemes for the sequential extraction.
generating from sulfides oxidation consumes the buffering capacity of silicate and carbonate minerals in the tailings. Besides, the increasing trend of \( S_{\text{total}} \) contents along with the decreasing depth should be caused by the upward migration of \( \text{SO}_4^{2-} \) released from sulfides oxidation.

3.3. Sequential extraction results of the tailings

The sequential extraction is usually used to investigate the speciation of the interested elements in geochemistry to indicate the transformation of minerals, especially to reveal the weathering of the metal sulfide bearing tailings (Fennemore et al., 1998; Dold and Fontboté, 2001; Dold, 2003; Heikkinen and Räisänen, 2008, 2009). The main metal elements of Jinchuan Cu-Ni sulfide tailings were also examined by the sequential extraction. The results of borehole HC and HB were shown in Fig. 7 and Fig. 8, respectively.

3.3.1. Water soluble fraction

As shown in Fig. 7, the contents of water soluble Fe, Mg, Cu, Ni and Al are very few, while the water soluble Ca is as high as 1.2% in the topmost of the impoundment, and decreases to about 0.4% as the depth increases above 3 m. This is consistent with mineralogical study that gypsum enriches in the surface of the tailings impoundment (Fig. 4). It indicates the water soluble Ca is mainly from the dissolution of gypsum. Compared with borehole HC, the water soluble Ca in borehole HB is slightly lower (Fig. 8), which corresponds to the lower content of gypsum in borehole HB. The content of water soluble Ca reflects the carbonate buffering quantity, which is closely related to the yielding amount of \( \text{H}^+ \) from sulfide oxidation. These evidences indicate the sulfide minerals in borehole HC underwent more intensive oxidation than that in borehole HB, consistent with the relative lower values of \( S_{\text{sul}}/S_{\text{total}} \) in borehole HC than HB at each depth (Table 3).

The more intensive oxidation of metal sulfides in borehole HC should be caused by mixed factors including the higher water moisture (Fig. 2), the smaller particle size (Fig. 3) and the delayed covering of the tailings. According to Lowson (1982), in the atom-transfer model, water is relegated to the role of solvent, whereas in the electrochemical model, it is a reactant. Therefore, in an undersaturated system the role of water should be more important during the weathering oxidation of tailings. In Jinchuan with extremely arid climate, the presence of water in the tailings also allows \( \text{O}_2 \) dissolution and diffusion, which is very important to ensure the oxidation of sulfides to be carried on. Consistently, both Fennemore et al. (1998) and Dold and Fontboté (2002) found the oxidation degree of sulfides increases with the humidity and the finer sulfides with richer moisture are more apt to be oxidized. In addition, the delayed covering of the tailings also provokes the oxidation of the sulfide minerals (Heikkinen and Räisänen, 2009). In Jinchuan, the tailings were piped and discharged around the impoundment border and then
flow naturally to the center of the impoundment. Borehole HC locates in the center of the tailings impoundment, far away from the discharge point. So, it takes longer time to be exposed to the air before being covered by the following tailings. Thus, the oxidation of tailings is more intense in borehole HC.

3.3.2. Exchangeable fraction

The metal ions related with exchangeable fraction mainly include ions released from tailings weathering, such as the oxidation of sulfide minerals and the dissolution of silicate minerals. These metal ions are adsorbed to or complex with secondary minerals of Fe$^{3+}$/Al$^{3+}$ as well as clay minerals (Bogush and Lazareva, 2011). Similar to the water soluble fraction, there are few Fe and Mg contents in exchangeable fraction, indicating that few Fe and Mg ions are adsorbed on tailings minerals. The exchangeable fraction of Al is also negligible in both boreholes. Compared with Fe, Mg and Al, the content of Ca is much higher in the exchangeable fraction, which slightly changes among 0.17%–0.44% in borehole HC and 0.15%–0.27% in borehole HB. Because of the strong complexing ability of acetate to the Ca, 1 M NH$_4$Ac may also attack Ca-containing carbonates (Tessier et al., 1979), which results in the dissolution of carbonates. Thus the high content of Ca may be from the dissolution of carbonate minerals during the exchangeable extraction process.

Fig. 5. XRD patterns of the tailings samples from borehole HC and HB (1 for chlorite, 2 for serpentine, 3 for tremolite, 4 for pyroxene, 5 for magnetite, 6 for olivine, 7 for biotite, 8 for talc, 9 for gypsum, 10 for dolomite).

Fig. 6. Reflected light microscopy photographs of minerals showing different alteration degree of the tailings. (A) Skeletal grain of pyrrhotite; tailings in 3 m depth; (B) magnetite with iron oxides/oxyhydroxides replacement; tailings in 1 m depth; (C) pyrrhotite with slight alteration; tailings in 3 m depth; (D) unaltered chalcopyrite; tailings in 3 m depth (Pyr-pyrrhotite, Hem-iron oxides/oxyhydroxides, Chal-chalcopyrite).
Although the exchangeable fractions of Cu and Ni show low contents, they appear to rich in the upper part of both boreholes. In borehole HC (Fig. 7), the contents of Cu are 70–90 ppm and Ni are 60–70 ppm at the depth above 5 m. At the depth deeper than 5 m, Cu and Ni contents keep constant at about 30 ppm and 40–50 ppm, respectively. In borehole HB (Fig. 8), the contents are about 60 ppm for Cu and 90–105 ppm for Ni at the depth above 2 m. At the depth deeper than 2 m, Cu and Ni contents keep constant at 30–40 ppm and 80–90 ppm, respectively.

3.3.3. Carbonate fraction
Carbonate fractions of Ca and Mg in both boreholes show a similar variation trend with the pH (Fig. 4). As the pH increase along with the depth from the surface to around 3 m, the contents of Ca and Mg in carbonate fraction also increase. And when the pH values go steady under 3 m deep, their contents go steady, too. It indicates the carbonate minerals could neutralize acid and stabilize the pH of the tailings to neutral and low alkali ranges. The relatively lower contents of Ca and Mg in carbonate fraction above 3 m are due to the neutralization of $H^+$ by dolomite to form secondary mineral gypsum. The weathering oxidation of sulfide minerals and the corresponding phase transformation, i.e. the transformation of jarosite to ferricyhrite, or schwertmannite to ferricyhrite-dite, etc. would generate significant $H^+$ (Boulet and Larocque, 1998; McGregor et al., 1998; Dold and Fontboté, 2001, 2002), thus results in the consumption of carbonates. Therefore, as shown in Fig. 5, the characteristic peak intensity of dolomite is low and that of gypsum is high when the depth is above 3 m.

In Jinchuan Cu-Ni flotation tailings impoundment, besides the insitu generation of $Ca^{2+}$ and $SO_4^{2-}$ caused by the intense oxidation in the shallow part of the tailings, the migration of Ca$^{2+}$ and SO$_4^{2-}$ from the deeper section of the tailings to the surface along with the evaporated upward water also contribute to the formation of gypsum. Especially under arid climate with strong evaporation, the water-flow direction driven by the capillary forces is critical to the surface components of the tailings (Dold and Fontboté, 2001). It is also consistent with the increasing trend of $S_{total}$ of the tailings (Table 3).

The variation trends of Cu and Ni in carbonate fraction show a distinct increase at the upper part of the tailings impoundment, which is abnormal with the decreasing trend of carbonate minerals of the tailings impoundment. This phenomenon may be resulted from the inefficient extraction by neutral ammonium acetate solution in the previous exchangeable fraction step.

3.3.4. Poorly crystalline fraction
The poorly crystalline fraction contains the metal cations related with secondary oxy-hydroxides of Fe$^{3+}$, Al$^{3+}$ and Mn$^{2+}$, including schwertmannite, 2-line ferricyhrite, secondary jarosite and manganese oxides (Sondag, 1981; Dold and Fontboté, 2001). In this fraction, the content of Ca is as low as negligible, indicating it does not exist in those secondary minerals. Comparatively, the poorly crystalline Fe is significant and varies little in the whole profile, suggesting the high contents of the secondary minerals of iron. In addition, the elements of Cu, Ni and Mg may be co-precipitated during the formation of the secondary minerals. So, there are also some amounts of these metals in the poorly crystalline fraction.

The contents of Cu and Ni decrease from the top to 5 m depth in borehole HC and to 3 m depth in borehole HB. At the deeper depth, they keep constant with depth increase. It demonstrates that the intensive weathering has occurred in the top part of Jinchuan Cu-Ni flotation tailings impoundment. Since the tailings were discharged around the impoundment border resulting in the delayed covering of the tailings by the new tailings, the tailings in the central locations endured longer period of weathering. This could be reflected by the deeper weathering depth of 5 m in borehole HC than HB (3 m).

In addition, the higher amount of Ni than that of Cu in poorly crystalline fraction suggests the more intensive oxidation of Ni-bearing sulfide minerals (mainly pyrrhotite and pentlandite) than Cu-bearing sulfide minerals (mainly chalcopyrite). This is coincident with the observation of optical microscopy and also consistent with the results of other researchers (Blowes and Jambor, 1990; Moncur et al., 2005; Heikkinen and Räisänen, 2008, 2009; Marescotti et al., 2009), who conclude that pyrrhotite is the sulfide mineral susceptible to weathering, whereas chalcopyrite is resistant to oxidation.

3.3.5. Crystalline fraction
Crystalline fractions are mainly from Fe-containing minerals such as magnetite in the original tailings. The contents of crystalline Ca and Cu are few, while Fe, Mg and Al are relatively abundant. Further, the content of Fe in borehole HC is generally higher than borehole HB. As the moisture variation of the tailings mentioned above, this should also be caused by the grain size fractionation during the deposition of the tailings. Compared with the majority of silicate minerals (serpentine, tremolite and chlorite), the iron-bearing crystal fraction (mainly magnetite) is more difficult to be grounded, which results in the coarser particles of this kind of minerals. Similarly, the specific gravity of magnetite is also

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Elements contents of the selected tailings samples (wt.%).</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition</td>
<td>Si</td>
</tr>
<tr>
<td>HB 1 m</td>
<td>1.09</td>
</tr>
<tr>
<td>2 m</td>
<td>0.98</td>
</tr>
<tr>
<td>3 m</td>
<td>0.97</td>
</tr>
<tr>
<td>5 m</td>
<td>0.79</td>
</tr>
<tr>
<td>8 m</td>
<td>0.66</td>
</tr>
<tr>
<td>10 m</td>
<td>0.64</td>
</tr>
<tr>
<td>HC 1 m</td>
<td>1.17</td>
</tr>
<tr>
<td>2 m</td>
<td>1.06</td>
</tr>
<tr>
<td>3 m</td>
<td>1.05</td>
</tr>
<tr>
<td>5 m</td>
<td>0.99</td>
</tr>
<tr>
<td>8 m</td>
<td>0.88</td>
</tr>
<tr>
<td>10 m</td>
<td>0.86</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 3</th>
<th>Sulfur contents and ABA results.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Borehole</td>
<td>Depth/m</td>
</tr>
<tr>
<td>HC</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>0.98</td>
</tr>
<tr>
<td>3</td>
<td>0.97</td>
</tr>
<tr>
<td>5</td>
<td>0.79</td>
</tr>
<tr>
<td>8</td>
<td>0.66</td>
</tr>
<tr>
<td>10</td>
<td>0.64</td>
</tr>
<tr>
<td>HB</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>1.06</td>
</tr>
<tr>
<td>3</td>
<td>1.05</td>
</tr>
<tr>
<td>5</td>
<td>0.99</td>
</tr>
<tr>
<td>8</td>
<td>0.88</td>
</tr>
<tr>
<td>10</td>
<td>0.86</td>
</tr>
</tbody>
</table>
higher. Since coarser and heavier mineral particles will be firstly deposited close to the border of the tailings impoundment, the content of Fe in borehole HB is generally higher than that in borehole HC.

Different from Cu, the contents of Ni in the crystalline fraction are much higher and show a clear enrichment at the topmost of the tailings impoundment. The results of this study are consistent with other studies that indicate Ni can be absorbed onto the surface or be incorporated into the structure of Fe(III) oxyhydroxide minerals such as goethite (Cornell, 1991; Bigham et al., 1996; Lee et al., 2002; Hakkou et al., 2008). The increased Ni in the crystalline fraction in the upper part of the impoundment suggests a stronger weathering of Ni-bearing sulfides and silicates occurred and released more mobile Ni$^{2+}$, which was then quickly sequestered and immobilized by Fe(III) oxyhydroxide minerals.

### 3.3.6. Sulfide fraction

To avoid the silicate minerals dissolution during the extraction of sulfide minerals, H$_2$O$_2$ is used instead of the strong acid as HNO$_3$ and HCl proposed by Gong (2007). In his experiment, under the boiling...
solution of 35% H₂O₂ and chloroacetic acid buffer at pH 3.1, the leaching ratios of Ni and Co from sulfide minerals were 96%–100% and 90%–100% respectively, while the silicate minerals, such as olivine, serpentine, pyroxene and amphibole, were almost not dissolved. Due to the high toxicity of chloroacetic acid, the buffer solution of succinic acid and sodium borate was used in our extraction process.

All the selected elements have relatively high contents in the sulfide fraction. The contents of Fe, Cu and Ni show an apparent decreasing trend near the surface of the tailings, indicating the decrease of Fe, Cu and Ni-bearing sulfides due to the oxidation at the top part of the tailings. Notably, Cu in the sulfide fraction accounts for the most content in all fractions (942–1523 ppm in borehole HC and 767–1633 ppm in borehole HB). Comparatively, the content of Ni related with sulfide fraction is much lower (214–517 ppm in borehole HC and 351–885 ppm in borehole HB). It indicates that Cu mainly occurs in sulfide minerals while Ni is included in but not limited to sulfide minerals. Nevertheless, the abnormal high value of Mg and Al in the sulfide fraction may be still caused by the simultaneous dissolution of silicates in the extraction step.

3.3.7. Residual fraction

The residual fractions mainly relate with silicate minerals in the tailings. The contents of Mg and Al in the residual fraction are higher than any other fractions, which coincides with the high contents of silicate minerals in the tailings. Apparently, Al is mainly related to the occurrence of micas, amphiboles and plagioclase; Ca is mainly from carbonate minerals. Mg and Fe are more complex and related with many silicate minerals. The contents of Ni in the sulfide and residual fraction are roughly equivalent, which again demonstrates Ni exists in both sulfides and silicates.

3.4. XANES of S, Cu and Ni in the tailings

Recently heavy-metal and metalloid speciation in the complex materials is more and more extensively analyzed by direct techniques of X-ray spectroscopy (Minkina et al., 2016). XANES is sensitive to chemical species and valence states (Ohta and Kubota, 2016). So, the K-edge XANES of S, Cu and Ni were conducted in our investigation.

3.4.1. Speciation of S in the tailings

The S K-edge is attributed to the transition of S 1s electrons to the unoccupied antibonding orbitals at the bottom of the conduction band. The position of the edge changes as a function of S oxidation state with up to a 12 eV difference between S²⁻ and S⁶⁺ (Li et al., 1995). Therefore, the relative peak intensity indicates the changes in mass fraction of different oxidation states (Hayes et al., 2014). The S K-edge XANES spectra of the tailings were shown in Fig. 9A and B. There are three primary valence states of sulfur element: −2 (sulfide), −1 (disulfide) and +6 (sulfate), which correspond to the peaks labeled out by dash lines at 2470.2 eV, 2472.0 eV and 2482.4 eV, respectively. It is clear that the peak intensity of both S²⁻ and S⁶⁺ becomes weaker as the depth reduces to 2 m and 1 m, and the peak of S⁰ even disappears at 1 m, suggesting the sulfides suffer stronger oxidation in the upper part of the tailings impoundment. Correspondingly, the peak intensity of S⁶⁺ (SO₄²⁻) is stronger and the subtle peak features of gypsum appear in this part. Factually, gypsum is present in all samples, but has its maximum contribution to total S mass at the surface depth. The prevalence of gypsum in all depths reflects not only the strong oxidative weathering of the sulfides, but also the great buffering capacity of the carbonate minerals.

In agree with the variation trend of S_{sulfide}/S_{total}, the XANES results of S K-edge also indicate the oxidation degree of the tailings gradually increased with the decreasing depth. The weaker intensity of S²⁻ and S⁰ in the upper part of the tailings impoundment corresponds with the decreasing of the ratio of S_{sulfide}/S_{total} in the upper part of the tailings impoundment (Table 3), which results from the more intensive oxidation of sulfides toward the ground surface.

3.4.2. Speciation of Cu and Ni in the tailings

The peak at 8986.6 eV in Cu K-edge XANES spectra (Fig. 10A) indicates the tetrahedrally coordinated Cu in chalcopyrite (Buckley and Woods, 1984; Acres et al., 2010). This peak could be observed in samples at all depths even though it became weaker in the shallow part of the tailings. Therefore, chalcopyrite exists in the whole profile of the tailings impoundment, which is coincident with the results of the sequential extraction. The variation trend of chalcopyrite in the tailings is similar to that of S²⁻ and S⁰ (Fig. 9), in which the peak of chalcopyrite became weaker as approaching the surface tailings,
i.e. the weathering oxidation of chalcopyrite became more intense in the shallow part of the tailings impoundment. In addition, the broad convex peaks of 8995–9005 eV (Fig. 10A) indicate the secondary minerals of CuO, CuCO3·Cu(OH)2·H2O or Cu-doped FeOOH (Ohta and Kubota, 2016) existed and became more intense in the upper part of the tailings.

Ni in Jinchuan Cu-Ni sulfide deposit mainly occurs in sulfide minerals such as pentlandite and pyrrhotite (Tang and Li, 1995; Tang et al., 2006). However, Ni-hydroxide and Ni-oxide existed in the whole profile of the tailings indicated by the comparison of Ni K-edge XANES spectra between the tailings samples and standard Ni-hydroxide and Ni-oxide (Fig. 10B) (Carvalho-E-Silva et al., 2003; Essilfie-Dughan et al., 2012; Ettler et al., 2016). Furthermore, the resonance indicated by arrow is mainly associated with multiple scattering by the oxygen next-nearest-neighbors (Carvalho-E-Silva et al., 2003).

Hence, the results of Cu and Ni K-edge XANES spectra agree well with the results of sequential extraction about the secondary minerals, i.e., the secondary minerals in Jinchuan Ni-Cu tailings should mainly be Fe(OH)3, FeOOH or Fe2O3·9H2O-like phases, with which Cu and Ni were co-precipitated or adsorbed. This is also proved by the hand-selected yellow-brown colors sample (Fig. 11A) examined by SEM combined with EDS (Fig. 11A and C), which show the minerals are usually in the shape of spherical fine grain and have complex compositions of metal elements, prominent oxygen, but no sulfur.

4. Conclusions

Jinchuan Cu-Ni sulfide flotation tailings are mainly composed of serpentine, chlorite, tremolite, pyroxene, biotite, talc, magnetite and dolomite, with small amount of plagioclase, pyrrhotite,
pentrlandite, chalcocite and pyrite. The tailings have strong neutralizing ability due to the existence of dolomite and abundance of silicate minerals like olivine and serpentine. Although some of metal sulfides have been oxidized to sulfates, especially in the upper part of the tailings impoundment (from surface to 2 m depth), no AMD was generated. Ni-containing sulfides as nickeliferous pyrrhotite and pentlandite are more apt to be oxidized than Cu-containing sulfides as chalcopyrite. Gypsum is the only secondary minerals identified by XRD. The strong evaporation under the hyper-arid climate of Jinchuan drives the rapid migration of mobile Ca$^{2+}$ and SO$_4^{2-}$ to the surface tailings, contributing to the special enrichment of gypsum in the upper part of the tailings impoundment. Due to the higher moisture and smaller particle size, the sulfide minerals in borehole HC underwent more intensive oxidation than that in borehole HB. The oxidation of sulfides release divalent metal ions of Cu$^{2+}$ and Ni$^{2+}$, which are in-situ retained by mineral surface absorption or secondary mineral precipitation throughout the whole profile of the tailings impoundments. No obvious metal elements mobilization occurs in the tailings impoundment, but these secondary minerals are poorly crystalline and unstable. So, heavy metal ions in the windblown dust are the biggest pollution hazard in Jinchuan region that should be avoided spreading especially under a strong wind climate.

Acknowledgements

This work was supported by the National Basic Research Program of China (973 Program, Program No. 2014CB840001) and the National Natural Science Foundation of China (Grant No. 41230103 & 41272003 & 51374087).

References


Acknowlegements

Jinchuan region that should be avoided spreading especially under a strong wind climate.


References


