

Migration Behavior of Fe, Cu, Zn, and Mo in Alkaline Tailings from Lanjiagou Porphyry Molybdenum Deposits, Northeast China

Xu, Shiguo

Professor, School of Hydraulic Engineering, Dalian University of Technology | Visiting
Researcher, Department of Urban and Environmental Engineering, Kyushu University

Yu, Changwu

Doctoral Student, School of Hydraulic Engineering, Dalian University of Technology, China |
Associate Professor, College of Material and Chemistry, Liaoning University of Technology,
China

Hiroshiro, Yoshinari

Associate Professor, Department of Urban and Environmental Engineering, Kyushu University

<https://hdl.handle.net/2324/17772>

出版情報：九州大学工学紀要. 70 (2), pp.19-31, 2010-05-06. 九州大学大学院工学研究院
バージョン：
権利関係：

Migration Behavior of Fe, Cu, Zn, and Mo in Alkaline Tailings from Lanjiagou Porphyry Molybdenum Deposits, Northeast China

by

Shiguo XU^{*}, Changwu YU^{**} and Yoshinari HIROSHIRO^{***}

(Received May 6, 2010)

Abstract

The migration behavior of Fe, Cu, Zn, and Mo within an inactive tailings impoundment in Lanjiagou molybdenum mining area, northeast China, is investigated by mineralogical and geochemical methods. XRD results show that carbonate minerals consume the liberated protons during sulfide minerals oxidation and subsequent hydrolysis of secondary phase. Meanwhile, the tailings impoundment maintains an alkaline condition because of the hydrolysis of carbonate minerals (paste pH=7.3-8.24). Analyses and comparison of geochemical behavior of heavy metals show that concentrations of Fe, Cu and Zn reach maximum values between 30 and 60 cm below the surface of tailings impoundment but there is hardly any bioavailable fraction of the three metals in the tailings impoundment. Fe, Cu and Zn are retained in the tailings impoundment for precipitation, co-precipitation, adsorption, complexation and ion exchange mechanisms and a weak cemented layer is formed at the lowest part of oxidation zone accordingly. The results demonstrate that the alkaline condition becomes a natural factor for retaining Fe, Cu and Zn in Lanjiagou tailings pounds. The concentrations of Mo significantly increase with depth (1090-1146 $\mu\text{g}\cdot\text{g}^{-1}$ at 200 cm deep) and so does the proportions of bioavailable Mo fraction (34-37% at 200 cm deep) in the tailings impoundment, which further reveals that the alkaline condition is helpful to increase the solubility of molybdate and the adsorption of iron (hydr)oxides on Mo becomes weaker at $\text{pH} > 7$. Mo can leach from Lanjiagou Mo tailings pounds into outside environment and may pose a high risk to the local ecological system.

Keywords: Migration, Heavy metal, Molybdenum, Alkaline tailings, Mineralogical and geochemical method

^{*} Professor, School of Hydraulic Engineering, Dalian University of Technology, China
Visiting Researcher, Department of Urban and Environmental Engineering, Kyushu University, Japan
^{**} Doctoral Student, School of Hydraulic Engineering, Dalian University of Technology, China
Associate Professor, College of Material and Chemistry, Liaoning University of Technology, China
^{***} Associate Professor, Department of Urban and Environmental Engineering, Kyushu University, Japan

1. Introduction

Froth flotation process of sulfide-bearing ores has led to deposits of mill tailings containing a variety of residual sulfide contents. When the tailings is exposed to air, the oxidation of sulfide minerals can result in generation of acid mine drainage (AMD) and the release of sulfate, ferrous ion and some other metal ions to the tailings pore water. However, the silicate and principally the carbonate mineral assemblage are the key parameters to neutralize the liberated protons during sulfide oxidation and subsequent hydrolysis of secondary phase. Meanwhile, the hydrolysis of carbonate minerals results in the formation of neutral mine drainage (NMD). The pore solution pH values can even greater than or equal to 7. Under near-neutral or alkaline conditions, Fe^{3+} precipitates as iron hydroxides that can be retained in the tailings impoundment. Some other heavy metal cations can be also removed from the leachates by interacting processes of settling, sedimentation, sorption, co-precipitation and ion exchange¹⁾. However, the heavy metal anions may be transported outside to the environment with NMD^{2,3)}. For example, the molybdenum (Mo) concentration was approximately $20 \text{ mg}\cdot\text{L}^{-1}$ in Brenda's Cu and Mo tailings drainage ($\text{pH}=8.05\pm0.49$)⁴⁾. Lanjiagou Mo mines are the major producers of Mo in China. The sulfide minerals in tailings are molybdenite (MoS_2), pyrite (FeS_2) and minor chalcopyrite (CuFeS_2), sphalerite (ZnS) and the gangue minerals are quartz (SiO_2), calcite (CaCO_3), potassium feldspar (KAlSi_3O_8) and plagioclase ($\text{NaAlSi}_3\text{O}_8$ - $\text{CaAl}_2\text{Si}_2\text{O}_8$). With simulated laboratory studies, Yu et al. (2008) revealed that the pH values in leachates from Lanjiagou Mo tailings were greater than 7 and Mo concentrations were 7.5 - $14.2 \text{ mg}\cdot\text{L}^{-1}$ ⁵⁾. Additionally, some research works have shown that Fe (hydr)oxides can adsorb/complex Mo at a certain pH range. An adsorption maximum is at pH 3-5 and significantly less adsorption at higher pH values (up to pH 8)^{6,7)}. Thus, the alkaline condition and Fe (hydr)oxides in tailings impoundment which lead to decreased mobility of Cu, Zn and other trace metal cations may be those conditions which lead to increased mobility of Mo. But the reports on the contrast of distinct migration behavior of Fe, Cu, Zn and Mo in vertical profile of an alkaline tailings impoundment containing Mo are very few.

In this work, an alkaline tailings impoundment from Lanjiagou porphyry Mo deposits in northeast China is mineralogically and geochemically investigated. The major objectives of the present study are: (1) to study the oxidation of sulfide minerals and the acid neutralization, (2) to compare geochemical behavior of Fe, Cu and Zn with that of Mo and (3) to discuss the influence of the alkaline condition and Fe (hydr)oxides on migration of Cu, Zn and Mo. It is expected that the results generated from this present research are useful for finding out the reason for Mo leaching from Lanjiagou Mo tailings pounds.

2. Materials and Methods

2.1 Site description

The Lanjiagou Mo mines are about 25 km northwest of Huludao City with an area of about 100 km^2 , in northeast China (**Fig. 1 a**). The climate is in the semi-dry region with an annual rainfall of 450-630 mm. More than one hundred porphyry Mo deposits are distributed in the district, which have been exploited by lots of small concentration plants since 1996. The molybdenite is extracted by froth flotation technique. However, most small concentration plants were closed gradually in 2006 due to tightening safety regulations, chronic energy shortages and Mo contamination. During the past ten years, more than 300 tailings pounds with 9 million tons of tailings have been generated in this mining area. Most of the Mo tailings pounds are constructed along hills or mountains, whose primary dams are made of rubble stone and stacked dams are made of mill

tailings. The height of dam is 5-7 m.

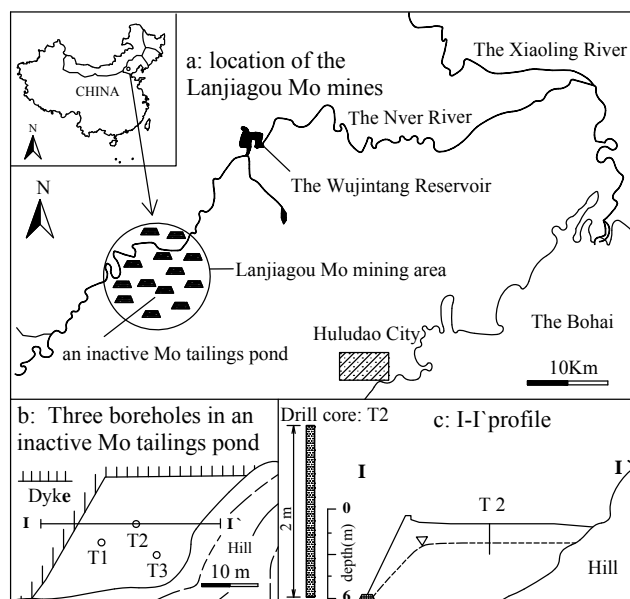


Fig. 1 a: Map showing the location of the Lanjiagou Mo mines. b: Three boreholes in an inactive Mo tailings pond. c: I-I' profile.

2.2 Sampling collection

In this investigation, one of inactive Mo tailings ponds in Lanjiagou Mo mining area, which was in operation during the period of 1996-1998, was selected for collecting samples in 2008. The dyke has a maximum height of 6 m and there are about 33 thousand tons tailings in the impoundment. Three boreholes (T1, T2 and T3) were drilled in the tailings ponds and the depths of which vary from 2.0 to 2.4 m (**Fig. 1 b, c**). The ground water level occurs at a depth between 1.62 and 1.70 m below the surface in the three boreholes. The tailings profile color from three drill cores is grey except light yellow at depths between 30 and 60 cm below the surface.

60 samples were collected from the three drill cores every 10 cm. An initial tailings sample (O1) was collected from Lianshan Mo Company in Lanjiagou mining area. The total 61 samples were stored in sealed plastic bags in an ice-packed cool box. Previously, pH measurement (Paste pH according to MEND 1990) was noted⁸⁾. Those samples were transported immediately to the laboratory for air drying (<35°C) and then were stored in sealed plastic bags again for mineralogical and geochemical determinations.

2.3 Mineralogical methods

Mineralogical study was performed by X-ray diffraction (XRD), using a D/MAX-2400 diffractometer (Japan) with CuK α radiation ($\lambda=0.154056$ nm) and a monochromator. Scan settings were 5°-90° 2 θ , 0.03° step size, 2-S count time per step.

2.4 Geochemical methods

The major elements of O1 were performed by X-ray fluorescence spectrometer (SRS3400, Germany). The 61 samples were completely digested with a mixture of HNO₃, HF, HClO₄ and HCl. Fe, Zn, Cu and Mo concentrations in the solutions were measured by ICP-AES⁹⁾. Total S¹⁰⁾ and

S_{sulfate} : the 0.2 mol·L⁻¹ NH₄-oxalate, pH 3.0, 80°C, 2 h leach was used to dissolve all sulfates such as gypsum. Sulfur in the leachate was determined by ICP-AES and was converted to S_{sulfate} ^{11, 12, 13}.

To determine the geochemical speciation of Fe, Cu, Zn and Mo, the 61 samples were sieved to the 0.5 mm fraction for sequential extraction (**Table 1**)^{14, 15}. Since hardly any organic material is presented in the tailings impoundment, the oxidisable fraction of heavy metals is probably primary sulfide mineral¹⁴.

Table 1 Sequential extraction scheme.

Extraction step	Sample weight(g)	Extractant	T (°C)	pH	Incubation time(hours)
1 Bioavailable	5	30 ml 0.01 mol·L ⁻¹ BaCl ₂	20		2 (r = 200) ^a
2 Adsorption/ ion exchangeable	5	30 ml 1 mol·L ⁻¹ NH ₄ OA	20	4.5	2 (r = 200) ^a
3 Oxidisable	5	(a) 10 ml 30% H ₂ O ₂	80		evaporated to dryness
		(b) 40 ml 1 mol·L ⁻¹ NH ₄ OAc 40 ml oxalic acid/ammonium oxalate	20	4.5	2 (r = 200) ^a
4 Reducible	2.5	(535 ml 0.2 mol·L ⁻¹ + 700 ml 0.2 mol·L ⁻¹) 2.6 ml HCl + 0.9 ml HNO ₃	20	3	2 (r = 200) ^a
5 Residual	1	Addition of 14.25 ml water before analysis	90		1.5

^a Mixing speed = 200 rounds per minute.

2.5 Acid neutralization capacity (ANC), Net Acid Producing Potential (NAPP), Net acid generation (NAG) procedures

ANC: 1 g of tailings was added to a 100 ml beaker containing 25 ml of 0.2 mol·L⁻¹ HCl acid and warmed at 90°C for 3 h. After cooling, excess acid was determined by titrating with 0.2 mol·L⁻¹ NaOH, and then the ANC of sample was calculated in terms of kg H₂SO₄·t⁻¹.

The NAPP is calculated as follows¹⁶:

$$\text{NAPP} = \text{MPA} - \text{ANC}$$

where: MPA is Maximum Potential Acidity = % S × 30.6

NAG: 2.5 g of pulverized sample was added to 250 ml of 15% H₂O₂; the mixture was placed inside a fume hood for 24 h, and then boiled for 1 h. After cooling to room temperature, the final NAG-pH was measured and then the acidity of the solution was determined by titration with 0.1 mol·L⁻¹ NaOH solution to pH 7. The NAG was calculated in terms of kg H₂SO₄·t⁻¹¹⁷.

3. Results

3.1 Mineralogical results and stratigraphy

The sulfide oxidation starts at the tailings surface, and the weathering front progressively moves downwards. As shown in **Table 2**, **Table 3** and **Fig. 2**, pyrite and molybdenite are the two most abundant residual sulfide minerals and less quantity of sphalerite and chalcopyrite (FeS₂>MoS₂>CuFeS₂~ZnS) in initial Mo tailings. Near the surface of tailings impoundment (0-30 cm deep), sulfide minerals (pyrite, molybdenite, sphalerite and chalcopyrite) are intensively oxidized, and the carbonates are depleted (**Table 2** and **Fig. 2**). The surface of tailings

impoundment can be defined as active oxidation zone. Only a few sulfide minerals are oxidized at depths of between 30 and 60 cm below the surface. However, the zone becomes accumulation zone of heavy metals (e.g. Fe, Cu and Zn), in which the concentration of these metals reaches their peak levels (see sect. 3.2 and **Fig. 3**). The zone can be defined as cemented layer and the tailings profile color from three drill cores is light yellow for Fe precipitation at the layer. The cemented layer plays an important role in acting as an O₂ diffusion barrier to restrict the extension of gas-O₂ through the tailings¹⁾. The cemented layer was also found in other tailings pounds^{1, 18)}. However, no noticeable weathering of the sulfide minerals is observed by XRD at depths of between 60 and 200 cm below the surface because of nearly no O₂. This zone below the cemented layer is defined as reducing environment, especially water-saturated zone. The intermediate horizon occurs between the cemented layer and the water-saturated zone. The concentrations of those minerals in reducing environment are similar to that of in the initial tailings sample (O1). The pH values in the vertical profile of the tailings impoundment range between 7.3 and 8.24 (**Fig. 3**). A rapid precipitates of iron hydroxides (pH > 4) are resulted¹⁾ although the iron hydroxides are not shown by XRD graphs (**Fig. 2**). The iron hydroxide must be an amorphous state in the tailings impoundment. Cu, Zn and Mo secondary minerals are also not supported by XRD graphs. Gypsum is one of the main secondary mineral in the oxidation zone and the concentration of which is about 1%, as shown in **Figure 2**. Gypsum indicates the oxidation of sulfide minerals and acid neutralization. The precipitation and dissolution of gypsum control the concentrations of Ca²⁺ and SO₄²⁻ in drainage water.

Table 2 Minerals occurring in the tailings according to XRD identification.

Minerals	Initial tailings	Active oxidation zone (0-30 cm)	Cemented layer (30-60 cm)	Intermediate zone (60-160 cm)	Water-saturated zone (160-200 cm)
Quartz	>72%	>72%	>72%	>72%	>72%
Potassium feldspar	2-5%	2-4%	2-5%	2-6%	3-6%
Plagioclase	3-8%	3-5%	3-7%	3-6%	3-9%
Calcite	3-5%	1-2%	2-4%	3-6%	3-7%
Manganese spar	<3%	—	—	—	<3%
Siderite	<2%	—	—	—	<2%
Epidote	<1%	—	—	—	<1%
Molybdenite	<1%	—	—	—	<1%
Pyrite	<3%	—	—	—	<3%
Sphalerite	<1%	—	—	—	<1%
Chalcopyrite	<1%	—	—	—	<1%
Gypsum	—	<1%	<1%	—	—
Covellite	—	—	—	—	—

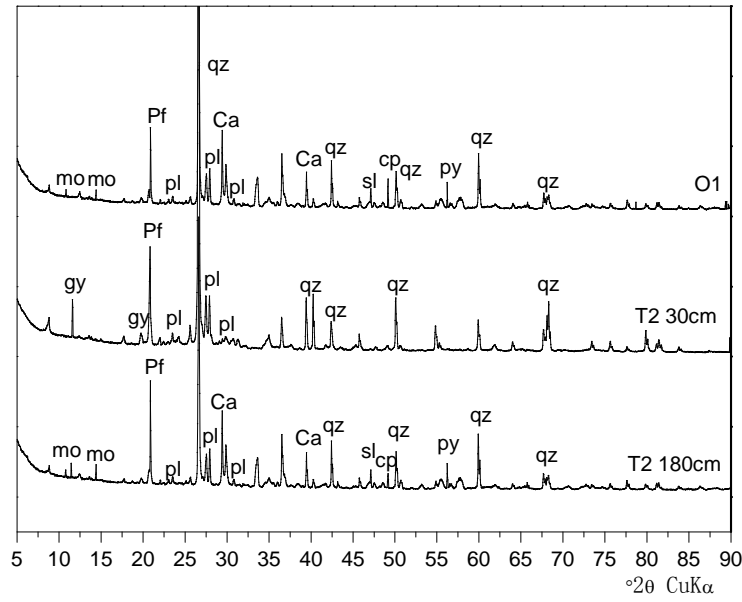
“—” not detected.

According to mineral and geochemical characteristics, light yellow at depths between 30 and 60 cm below the surface in three boreholes, the tailings impoundment stratigraphy can be divided into three major zones from the surface to a depth of 2 m by the following successions: (1) oxidation zone (between 0 and 60 cm, oxidation condition), including active oxidation zone (between 0 and 30 cm) and cemented layer (between 30 and 60 cm), (2) intermediate zone (between 60 and 160 cm) and (3) water-saturated zone (between 160 and 200 cm). Therefore, the three boreholes have

traversed the oxidation zone near the surface of the tailings impoundment, the underlying intermediate zone and the water-saturated zone.

Table 3 Chemical components of the initial tailings sample (Wt. %).

SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	K ₂ O	Sum
76.8	0.12	1.05	1.63	0.54	0.47	10.7	3.21	
P ₂ O ₅	Na ₂ O	Fe	Cu	Zn	Mo	S		
0.04	2.47	1.21	0.018	0.017	0.09	1.56		
								99.925



Abbreviations: ca=calcite, cp=chalcopyrite, gy=gypsum, mo=molybdenite, pf=potassium feldspar, pl=plagioclase, py=pyrite, sl=sphalerite, qz=quartz

Fig. 2 XRD patterns of dirll core T2.

3.2 Geochemical results

The concentrations of Fe, Cu, Zn, Mo, SO_4^{2-} and paste pH vs. depth are presented in **Figure 3**. Because of the overwhelming abundance of acid neutralization minerals and the relative scarcity acid-generating sulfide minerals such as pyrite, an alkaline condition is formed in the tailings impoundment (paste pH=7.3-8.24). Moreover, **Figure 4** shows that all samples have negative NAPP and $\text{NAP-pH} \geq 4.5$. Samples are classified as NAF (Non Acid Forming) where the NAPP value is negative and the $\text{NAG (pH)} \geq 4.5$ ¹⁹⁾. It is suggested that the AMD will not be resulted in Lanjiagou tailings pounds in future. Fe, Cu, Zn and SO_4^{2-} concentrations reach the maximum values at a depth between 30 and 60 cm (in the cemented layer) below the surface in three boreholes, and the maximum concentrations of which are 1.4, 2.4, 3.2 and 3.2 times higher than that of in the active oxidation zone (at 0-30 cm) respectively. Accordingly, a weak cemented layer is formed at the lowest part of oxidation zone (at 30-60 cm). The weak cemented layer consisted of reactive secondary minerals plays a crucial role in contaminant attenuation for Fe, Cu and Zn in the tailings impoundment. Previously, the contaminant attenuation has been reported in other inactive tailings deposits^{1, 18)}. However, this investigation reveals that the Mo concentrations increase gradually with the increase of depth and are 1090-1146 $\mu\text{g}\cdot\text{g}^{-1}$ at 200 cm deep in three drill cores.

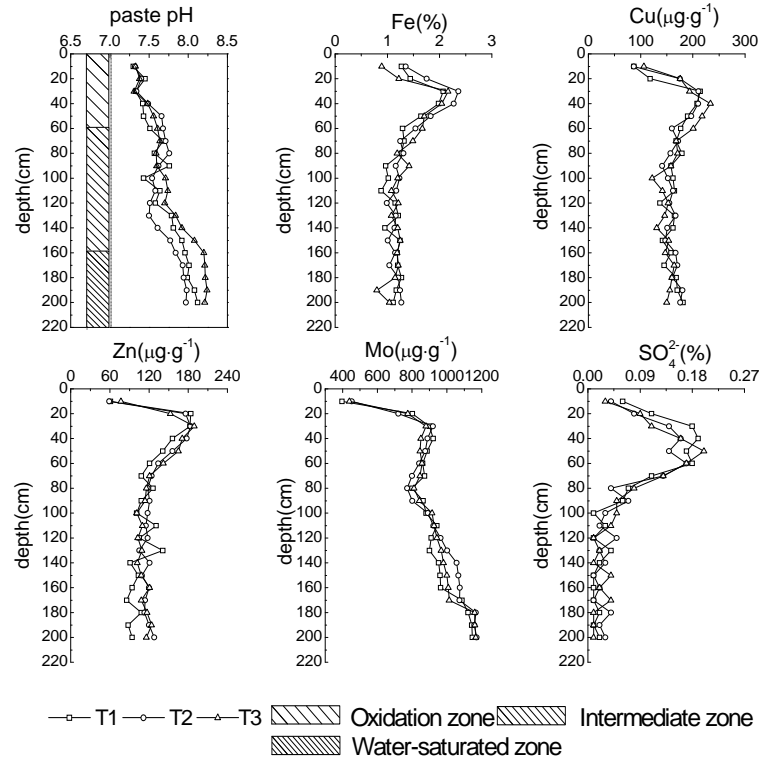


Fig. 3 Results of concentrations of Fe, Cu, Zn, Mo, SO_4^{2-} and paste pH in three boreholes (T1, T2 and T3).

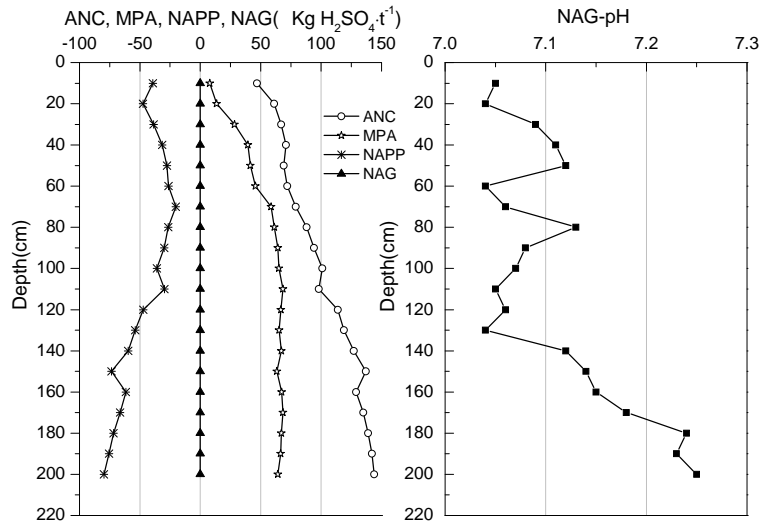


Fig. 4 The acid-forming potential of T1 core in Lanjiagou tailings. *

* NAPP<0, NAG-pH>7.0 in T2 and T3 cores.

The concentration of a heavy metal with depth in a tailings impoundment does not necessarily reflect its potential for release. The geochemical speciation in which metals exit determines how readily available they are for release to the environment. Results from sequential extractions (**Fig. 5**) show that Fe, Cu and Zn are not significantly mobilized in the alkaline condition prevailing in the tailings impoundment. The reducible Fe fraction shows maximum concentration at the lowest

part of the oxidation zone and decreases with the increase of depth because Fe^{3+} ions are removed from the solution as Fe hydroxide precipitates. The concentrations of ion exchangeable and reducible fraction of Cu and Zn in the oxidation zone are higher than that of in the intermediate zone and the water-saturated zone. The geochemical speciation of Fe, Cu and Zn in the intermediate zone and the water-saturated zone, same as the initial tailings, are not the ion exchangeable and reducible fraction but mainly the oxidisable fraction. Since hardly any organic materials are present in the tailings impoundment, the oxidisable fraction of Fe, Cu and Zn is probably primary sulfide mineral (FeS_2 , CuFeS_2 and ZnS). The precipitation, co-precipitation, adsorption and complexation mechanisms control migration of Cu and Zn.

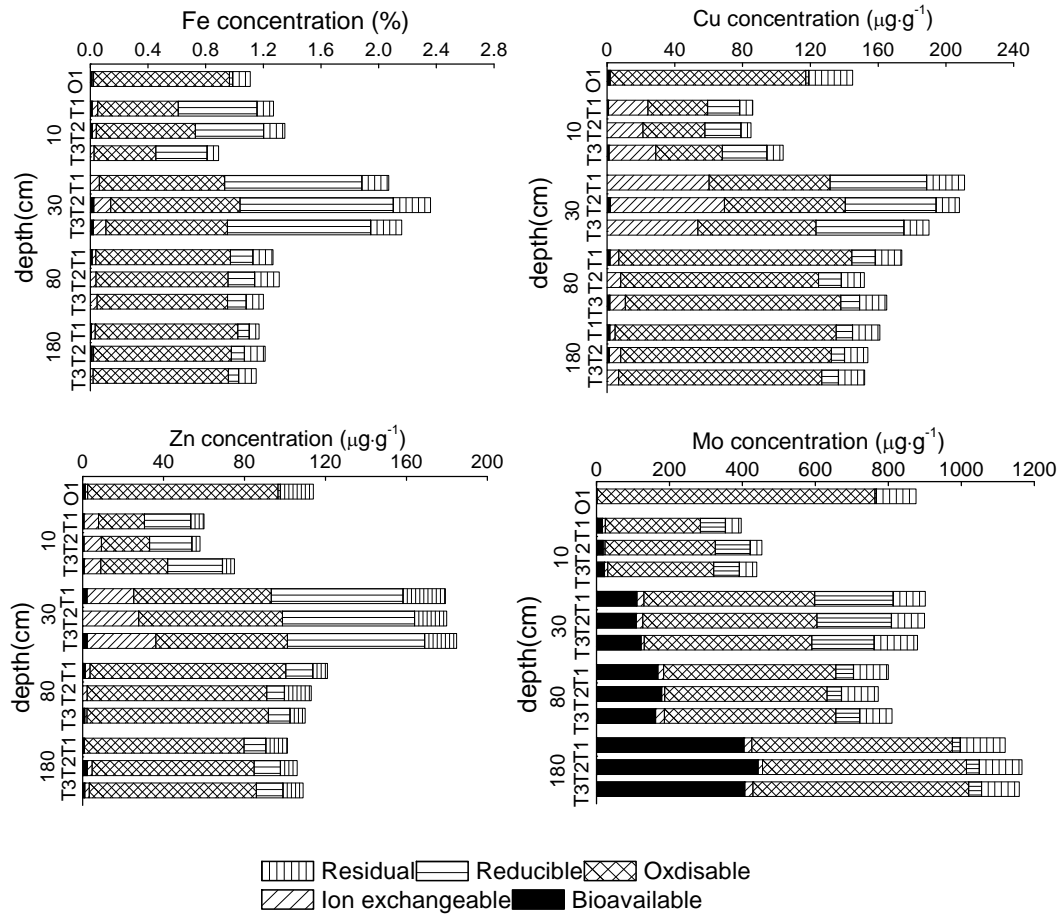


Fig. 5 Results of sequential extraction of boreholes (T1, T2 and T3).

Iron (hydro)oxides may be one of the most important sorbents for MoO_4^{2-} , as it acquires positive charge at low pH and maximum sorption (about 100%) is observed in the acidic pH range ($3 < \text{pH} < 5$). The geochemical behavior of MoO_4^{2-} in the environment is probably dependent on adsorption reactions to particle surfaces. However, the concentration of bioavailable Mo fraction increases with the increase of depth gradually and the proportions of which account for 4-5%, 12-13%, 20-23% and 34-37% of the total mass concentrations at 10 cm, 30 cm, 80 cm, 180 cm deep in three drill cores, whereas the Mo concentration in reducible fraction reach peak in cemented layer and decrease gradually with the decrease of the reducible iron fraction in the other two zone (**Fig. 5**). This indicates, in the weak alkaline condition, the iron (hydr)oxides is not an

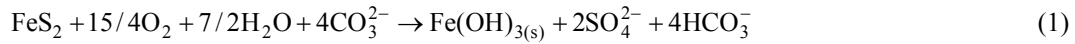
efficient scavenger in Lanjiagou Mo tailings impoundment. The proportions of reducible Mo fraction occupy 15-20%, 19-23%, 5-8% and 2-3% respectively at the same depth in three boreholes, which is because the iron (hydro)oxides can still adsorb some MoO_4^{2-} in the weak alkaline pH range ⁶⁾. Only 5-8% and 2-3% of the reducible Mo fraction at 80 cm and 180 cm deep is observed in that the concentration of Fe (hydr)oxides decreases gradually with the increase of depth (**Fig. 5**).

Based on the above analysis, there is a difference on migration behavior between Fe, Cu, Zn and Mo in an alkaline condition. The alkaline condition does not represent a significant sink for Mo but increases concentrations of bioavailable Mo fraction in tailings pond.

4. Discussion

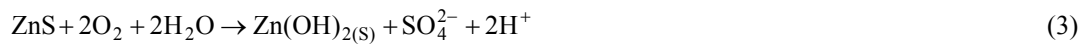
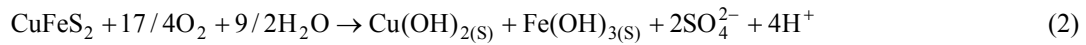
4.1 Oxidation of sulfide minerals in the alkaline tailings

The oxidation is a complex process that can involve several reactants and products under various conditions. The important oxidants in the natural tailings impoundment are O_2 and Fe^{3+} ions. Many literatures have reported the oxidation process of pyrite at low pH condition ^{1, 20, 21)}. In the Lanjiagou tailings, the concentration of calcite (carbonate mineral) is over 3% (**Table 2**) in the initial tailings (O1). Lin (1997) suggested that the oxidation of pyrite should be presented as Eq. (1) when sufficient carbonates are present to maintain near-neutral conditions ¹⁾.

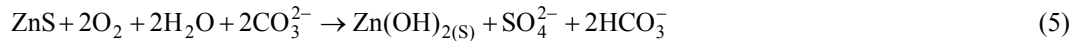


Eq. (1) indicates that the acid generated is balanced by acid consumption and the pH remains at near-neutral. The major products of the oxidation are sulfate and iron hydroxide precipitations. High carbonate content maybe decrease oxidation rate of pyrite. That is generally thought to be related to the coating of sulfide by secondary ferric phases.

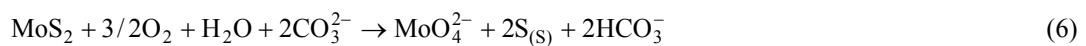
The oxidation of chalcopyrite and sphalerite is presented in Eq. (2) and (3) ²¹⁾:



When sufficient carbonates are present to maintain near-neutral conditions, the overall oxidation of chalcopyrite and sphalerite should be described by Eq. (4) and (5):



Rankama and Sahama (1950) suggested that oxidation of molybdenite to molybdate occurs readily during weathering ²²⁾. According to ε -pH of Mo-S-H₂O system ²³⁾, the oxidation of molybdenite in an alkaline condition is shown in Eq. (6):



Sulfur element shown in Eq. (6) is not found by XRD graphs from all samples, probably because it can be oxidized completely to sulfate.

Compared Eq. (6) with Eq. (1), (4) and (5), it is concluded that Mo is not

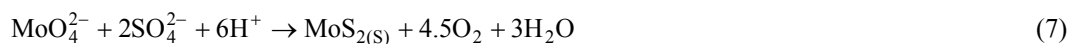
precipitated/co-precipitated in the neutral-alkaline condition. However, the oxidative kinetics of molybdenite under alkaline condition has been always remained obscure.

4.2 Migration of heavy metals in alkaline condition

The oxidation of sulfide minerals is the first step for release of the trace metal from the highly insoluble sulfide phase. Once released to solution, there are additional several types of reactions that can influence the migration behavior of heavy metals, including precipitation, co-precipitation, adsorption, complexation and ion exchange mechanisms. The pH value plays a crucial role in those reaction processes.

In the alkaline condition, the major oxidation products of pyrite are sulfate and ferric hydroxide which is the reducible Fe fraction. A red Fe precipitated layers may even be formed at a certain depth in tailings impoundment because of more residual pyrite contained in tailings, such as Lilla Bredsjön tailings situated in Sweden ¹⁾. For Lanjiagou Mo tailings, there is no more than 3% pyrite in it, so the Fe precipitated layers can not be formed. However, the reducible Fe fraction in the oxidation zone still indicates that Fe³⁺ hydroxide precipitates can be retained in the tailings impoundment (**Fig. 5**). Cu and Zn are retained in the tailings impoundment by precipitation, co-precipitation with iron precipitates and adsorption onto iron hydroxides in the alkaline condition, which is identical with some other tailings ²⁴⁾. Additionally, due to the alkaline condition, covellite can not easily be formed in water-saturated zone and which is not shown by XRD graphs. These retaining mechanisms mentioned above can explain why Fe, Cu and Zn appear maximum concentrations in the cemented layer. The alkaline condition becomes a natural factor for retaining Fe³⁺, Cu²⁺ and Zn²⁺ within Lanjiagou tailings pounds. Massive leaching of Fe³⁺, Cu²⁺ and Zn²⁺ is an impossible scenario from Lanjiagou Mo tailings pounds in future.

The adsorption of Mo on iron hydroxides is pH-controlled mechanism. An adsorption maximum is at pH 3-5 and significantly less adsorption at higher pH values (up to pH 8). Helz et al. (1996) proposed that under reducing conditions and with the reduction of sulfate, molybdate can be converted to thiomolybdate (MoS₄²⁻), which then binds to Fe, Al, and organic matter phases via sulfur bridges ²⁵⁾. This mechanism could decrease Mo solubility in water-saturated zone (reducing conditions) but the alkaline condition increases its solubility. That is because iron (hydr)oxides can adsorb a little Mo (MoO₄²⁻ and MoS₄²⁻) at pH >7 ²⁶⁾. This explains why, in the high-pH condition, only a part of the reducible Mo fraction associated with iron (hydr)oxides is formed. Moreover, ferrimolybdate ([Fe₂MoO₄]₃·7H₂O) is probably not a significant sink for molybdate because the ferrimolybdate can not be formed under this alkaline condition. Neither is powellite (CaMoO₄) likely to be a major trap for molybdate, since it is highly soluble in surface waters ^{27, 28)}. The two secondary minerals are also not found from XRD graphs in all samples. Besides that, several researchers have proposed the formation of MoS₂ in reducing condition according to Eq. (7) ^{29, 30)} but Helz et al. (1996) suggested that the formation of MoS₂ is kinetically limited ²⁵⁾. **Figure 5** proves also that the concentrations of oxidisable Mo fraction (Mo sulfide) do not increase remarkably with depth. The above mentioned analysis further reveals that the alkaline condition is helpful for increasing the solubility of molybdate.



Therefore, the alkaline condition is helpful for development of massive leaching of Mo from Lanjiagou Mo tailings pounds. Lanjiagou Mo tailings pounds become the potential Mo pollution source in the drainage basin and may pose a high risk to the local ecological system. Further studies should be undertaken how to retain Mo in the alkaline tailings pounds.

5. Conclusion

In this paper, the distinct migration behavior of Fe, Cu, Zn, and Mo within an inactive tailings pound from Lanjiagou porphyry molybdenum deposits is compared, in northeast China. The concentrations of sulfide minerals in tailings follow the sequence order: $\text{FeS}_2 > \text{MoS}_2 > \text{CuFeS}_2 \sim \text{ZnS}$. Those sulfide minerals are oxidized, but Fe, Cu and Zn are retained in the oxidation zone of tailings pound due to retention mechanisms, including mineral precipitation, co-precipitation, adsorption, complexation and ion exchange associated with iron (hydr)oxidation, under such an alkaline condition (paste pH=7.3-8.24). Accordingly, a weak cemented layer is resulted at depths between 30 and 60 cm below surface which contains secondary minerals such as gypsum and amorphous iron (hydr)oxides. In contrast, the Mo concentrations and the bioavailable Mo fraction increase gradually with the increase of depth. The proportion of bioavailable heavy metals fraction follows the order: bioavailable Mo fraction \gg bioavailable Fe fraction \sim bioavailable Cu fraction \sim bioavailable Zn fraction. These retention mechanisms are ineffective for retaining Mo in the alkaline tailings pound. The Mo tailings pounds become the potential Mo contamination source in Lanjiagou drainage basin.

Moreover, other migration mechanisms of heavy metals require arousing much attention too, which include rainfall erosion and wind erosion on the surface of tailings impoundment. The Lanjiagou Mo mine area may encounter a risk of Fe, Cu and Zn contamination besides Mo. Therefore, Lanjiagou Mo tailings require strict administration now and future.

Acknowledgements

This work has been financially supported by “the 11th Five-Year Plan” National Science and Technology supporting plan (2006BAB14B05) from China. The authors thank Mr. Yuwei Liu for his help during sampling collection. The former professor Kenji Jinno of Kyushu University has given many kind suggestions. Mr. Zhenbin Zhang, Jianjun Lian, Chenwei. Han and Ms. Huiling Du helped to do analysis and discussion. All of these helps are appreciated.

References

- 1) Lin, Z.X. Mobilization and retention of heavy metals in mill-tailings from Garpenberg sulfide mines, Sweden, *The Science of the Total Environment*, Vol. pp. 198,13-31 (1997).
- 2) Brown, R., Water management at Brenda Mines, *In Proc. of the Thirteenth Annual British Columbia Mine Reclamation Symposium*, June 7-9, Vernon, British Columbia, pp. 8-17 (1989).
- 3) Aubé, B.C., Stroiazzo, J., Molybdenum treatment at Brenda Mines, *Proceedings of the 5th Conference on Acid Rock drainage*, May 21-24, Denver, Colorado, pp.1579-1586 (2000).
- 4) Morin, K.A., Hutt, N.M., Geochemical characterization of molybdenum leaching from rock and tailings at the Brenda minsite, British Columbia, *IN: W.A. Price, B. Hart, and C. Howell, eds., Proceedings of the 1999 Workshop on Molybdenum Issues in Reclamation*, September 24, Kamloops, British Columbia, pp. 76-85 (1999).
- 5) Yu, C., Xu, S., Chen, G. Zhou, L., Leaching experiments on heavy metal Mo release from sharn molybdenum ore tailings. *Ecology and Environment (China)*, Vol. 17, No. 2, pp. 636-640 (2008).
- 6) Xu, N., Christodoulatos, C., Bratda, W., Adsorption of molybdate and tetrathiomolybdate onto

- pyrite and goethite: Effect of pH and competitive ions, *Chemosphere*, Vol. 62, No. 10, pp. 1726-1735 (2006).
- 7) Goldberg, S., Forster, H.S., Godfrey, C.L., Molybdenum adsorption on oxides, clay minerals, and soils, *Soil Science Society of America Journal*, Vol. 60, pp. 425-432 (1996).
 - 8) MEND, Acid rock drainage prediction manual-A manual of chemical evaluation procedures for the prediction of acid generation from mine wastes, MEND Project 1.16.1b. *A report prepared for CANMET-MSL Division*, Department of Energy, Mines, and Resources, Canada by Coastech Research, Inc., Vancouver, B.C.(1990).
 - 9) Dold, B., Eppinger, K.J., Kölling, M., Pyrite oxidation and the associated geochemical processes in tailings in the atacama desert, Chile: the influence of men controlled water input after disuse. In: Sanchez, M.A., Vergara, F., Castro, S.H. (Eds.), *Clean Technology for the Mining Industry*, Santiago. University of Concepción, Chile, pp. 417-427 (1996).
 - 10) GB/T 14352.9-93, Methods for chemical analysis of tungsten ores and molybdenum ores: Determination of total sulfur content-Iodometric method after combustion (in China) (1994).
 - 11) Dold, B., Mineralogical and geochemical changes of copper flotation tailings in relation to their original composition and climatic settings-implications for acid mine drainage and element mobility, *PhD thesis, Terre & Environment, University of Geneva*, Geneva, pp. 230 (1999).
 - 12) Dold, B., A 7-step sequential extraction for geochemical studies of copper sulfide mine waste, securing the future, *International Conference on Mining and the Environment*, Skellefteå, Sweden, pp. 158-170 (2001a).
 - 13) Dold, B., Dissolution kinetics of schwertmannite and ferrihydrite, securing the future, *International Conference on Mining and the Environment*, Skellefteå, Sweden, pp. 171-181 (2001b)
 - 14) Langedal, M., Dispersion of tailings in the Knabeåna-Kvina drainage basin, Norway, 2: mobility of Cu and Mo in tailings-derived fluvial sediments, *Journal of Geochemical Exploration*, Vol. 58, pp. 173-183 (1997).
 - 15) Tessier, A., Campbell, P.G.C., Bisson, M., Sequential extraction procedure for the speciation of particulated metals. *Anal. Chem.*, Vol. 51, pp. 844-851 (1979).
 - 16) Miller, S., Jeffery, J., Advances in the Prediction of Acid Generating Mine Waste Materials. p. 33-43. In: *Proceedings of the Second Australian Acid Mine Drainage Workshop* (Charters Towers, Queensland, 28-31 March 1995), eds. N.J. Grundon and L.C. Bell, Australian Centre for Minesite Rehabilitation Research, Brisbane (1995).
 - 17) Finkelman, R.B. Giffin, D.E., Hydrogen peroxide oxidation: An improved method for rapidly assessing acid-generating potential of sediments and sedimentary rocks, *Recreat Reveg Res*, Vol. 5, pp. 521-534 (1986).
 - 18) Dold, B. Fontboté, L., A mineralogical and geochemical study of element mobility in sulfide mine tailings of Fe oxide Cu-Au deposits from the Punta del Cobre belt, northern Chile, *Chemical Geology*, Vol. 189, pp.135-163 (2002).
 - 19) Stewart, W.A., Miller, S.D., Smart, R., Advances in acid rock drainage (ARD) characterisation of mine wastes. *The 7th International Conference on Acid Rock Drainage (ICARD)*, March 26-30, 2006, St. Louis MO. R.I. Barnhisel (eds.) Published by the American Society of Mining and Reclamation (ASMR), 3134 Montavesta Road, Lexington, KY 40502 (2006).
 - 20) Kleinman, R.L.P., Crerar, D.A. Pacelli, R.R., Biogeochemistry of acid mine drainage and a method to control acid formation, *Mining Engineering*, Vol. 33, No. 3, pp.300-305 (1981).
 - 21) Jennings, S.R., Dollhopf, D.J. Inskeep, W.P., Acid production from sulfide minerals using hydrogen peroxide weathering, *Applied Geochemistry*, Vol. 15, pp. 235-243 (2000).
 - 22) Rankama, K., Sahama, T.G., *Geochemistry*. The University of Chicago Press, pp. 628, (1950).

- 23) Osseo-Aasre, K., Solution chemistry of tungsten leaching systems. *Metallurgical and Materials Transactions B*, Vol. 13, No. 4, pp. 555-564 (1982).
- 24) Schwertmann, U., Taylor, R.M., *Iron Oxides*. In: J.B. Dixon and S.B. Weed (editors), *Minerals in Soil Environment, 2nd edition, Soil Science Society of America Book Series 1*, pp. 379-438 (1989).
- 25) Helz, G.R., Miller, C.V., Charnock, J.M., Mosselmans, J.F.W., Patrick, R.A.D., Garner, C.D. Vaughan, D.J., Mechanism of molybdenum removal from the sea and its concentration in black shale: EXAFS evidence. *Geochim. Cosmochim. Acta*, Vol. 60, No. 3631-3642 (1996).
- 26) Gustafsson, J.P., Modelling molybdate and tungstate adsorption to ferrihydrite, *Chemical Geology*, Vol. 200, pp.105-115 (2003).
- 27) Wedepohl, K.H., *Handbook of Geochemistry vol. II-2, Molybdenum 42*. Springer Verlag, Heidelberg, New York (1978)
- 28) Carroll, K.C., Artiola, J.F., Brusseau, M.L., Transport of molybdenum in a biosolid-amended alkaline soil. *Chemosphere*, Vol. 65, pp. 778-785 (2006).
- 29) Amrhein, C., Mosher, P.A. Brown, A.D., The effects of redox on Mo, U, B, V, and As solubility in evaporation pond soils. *Soil Sci*, Vol. 155, pp. 249-255 (1993).
- 30) Bertine, K.K., The deposition of molybdenum in anoxic waters. *Mar. Chem*, Vol. 1, No.1, pp.43-53 (1972).