

Multivariate analysis of Co, Fe and Ni leaching from tailings following simulated temperature change

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Abstract. A series of column leaching experiments were performed to understand the leaching behavior of Co, Fe and Ni in Ballangen mine tailings. Multivariate statistical approaches to evaluate potential risk variations in leachate quality and identifies temperature effects on their leaching behavior. Results from column leaching test indicated that the mobility of showed higher temperature may encourage oxidation and sulfuration in tailings that promoted heavy metal release from tailings through runoff and erosion. Ni and Co have the similar resource from tailings and positive correlation in the leaching activity. The leaching of Fe was closely related to temperature change and affected the leaching of other metals. Temperature, however, increased risk of heavy metal leaching from tailings by temperature change should be caught more attention.

1. Introduction

Every year, almost 100 billion tons of tailings were discharged all around the world [1,2]. Tailings deposit not only destroys surround ecological environment, but also poses a threat to water, soil, plants, animal and human beings by differentiation, transformation and migration of heavy metals from tailings [3-9]. Under the effects of temperature and precipitant, tailings released different hazards by the variation of forms and migration [10-12].

The annual tailings discharge all around the world is about 8 billion tons, the discharge of Norway is about 80 million tons [2]. When tailings are discharged, the activity of heavy metals was low. After contacted with water and air, the activity of heavy metals increased, and many heavy metals released and migrated to surround soils and water [13]. Many factors affect heavy metals release from tailings [4], such as Chemical properties of tailings, temperature, precipitant, microorganism and O₂ content [6-9,14-16]. Temperature has been found to result in rapid heavy metals releasing from tailings. Higher temperature is not only increase the solubility of the leachate, but also accelerated the biochemical reaction in the tailings [15]. And temperature had different effect on heavy metals leaching in various areas. Tailings characteristic and microorganism different between places, and the biochemical reaction was not the same. This is why temperature has different effect on heavy metals leaching from tailings in different area. There is lack of research focusing on temperature effect on heavy metals leaching from tailings in arctic area. So get the rules of heavy metals leaching from tailings under different is good for tailings management in the arctic area.



It is aim of this study to determine if temperature rapid Ni, Co and Fe releasing from tailing in the arctic area. The objectives are to firstly quantify if temperature is an effective barrier to heavy metals leaching from tailings. Secondly to indicate how temperature affect the release of Ni, Co and Fe. Finally to understand the release rule of Ni, Co and Fe under temperature change in arctic area. To explore the mechanism and effect of changing temperature on heavy metals releasing from tailings will provide scientific guidance for tailings management.

2. Experimental

2.1. Sampling and storage

The tailings samples described elsewhere [17,18], have been selected to sample to study. Sampled tailings from Banllagen tailings deposit in 2016. The former sample was collected by a plastic shovel excluding the most superficial soil to avoid any possible surface contamination. Tailings collected directly by using plastic tray during the soils move away. About 10kg of samples were placed in polyethylene bags and carried to the laboratory. Some tailings were sent to ALS (Physical & chemical analysis) to measure its composition and mineral. And rest were dried at 30°C and stored in polyethylene for leaching test.

2.2. Leaching experiment

The rate and amount of heavy metals released in leaching test depend on several factors including chemical and mineral composition of tailings, leaching solution type, pH, potential electric, and temperature. Among these factors, there is a group intrinsically linked to the properties and composition of tailings, whereas some others depend on leaching solution and surround environment. For the key factor of controlling heavy metals leaching from tailings may be fixed considered in the leaching test. Change temperature and steady precipitation were design in the experiment. A series of column leach test was conducted in the greenhouse to investigate the impacts of temperature change on heavy metals leaching from mine tailings. Four temperature degrees was set in the experiment: 5°C, 10°C, 14°C and 18°C. All the experiment carried at the steady precipitation of 20mm/week. Each treatment was established with a repetition.

Leachate collected each two weeks, pH, electric potential (Pe) and conductivity of the leachates were measured at once by HI98193. In order to determine total concentrations of heavy metals (Fe, Ni, Co), tailings samples were subjected to microwave-assisted digestion with concentrated HNO₃ according to ASTM 3682. Leachate was treated follow EPA 200.8. Heavy metals of leachate and tailings were determined by an inductively coupled plasma atomic emission spectrometry (ICP-AES).

2.3. Statistical analysis

Basic statistics of the raw data were carried out using SPSS24.0 and Origin9.0 software. Two multivariate analysis techniques, principal component analysis (PCA) and correlation analysis (CA) were applied to the data set for identifying associations (common origin) between metals. PCA was performed with Varimax rotation, and CA was developed according to the Pearson method. A probability level of less than 0.05 was considered to be significantly.

3. Results and discussion

3.1. Heavy metals leaching from tailings at different temperature

Results of heavy metals column leaching at 5°C, 10°C, 14°C and 18°C as shown in figure 1. Generally, the cumulative leaching concentration of Fe, Co and Ni linear grew with leaching times increased except Ni at 18°C. It indicated that they had a steady leaching concentration in the leaching activity, and Ni had a various leaching concentration. The maximum and minimum concentrations of Co in leachate at first cycle were 10170 µg/L at 10°C and 102 µg/L at 5°C, respectively. Highest rate of accumulative concentration rise of Co was got at 10°C, and followed with 18°C, 14°C and 5°C. A

similar trend was observed for leachate Co concentration as leachate amount increased, while the highest leaching rate of Ni was at 10°C, followed by 18°C, 14°C and 5°C. But the highest leaching concentration of Ni at the first cycle was found at 18°C (609 mg/L). For Fe, both the leaching concentration of first cycle and rise rate were highest at 18°C.

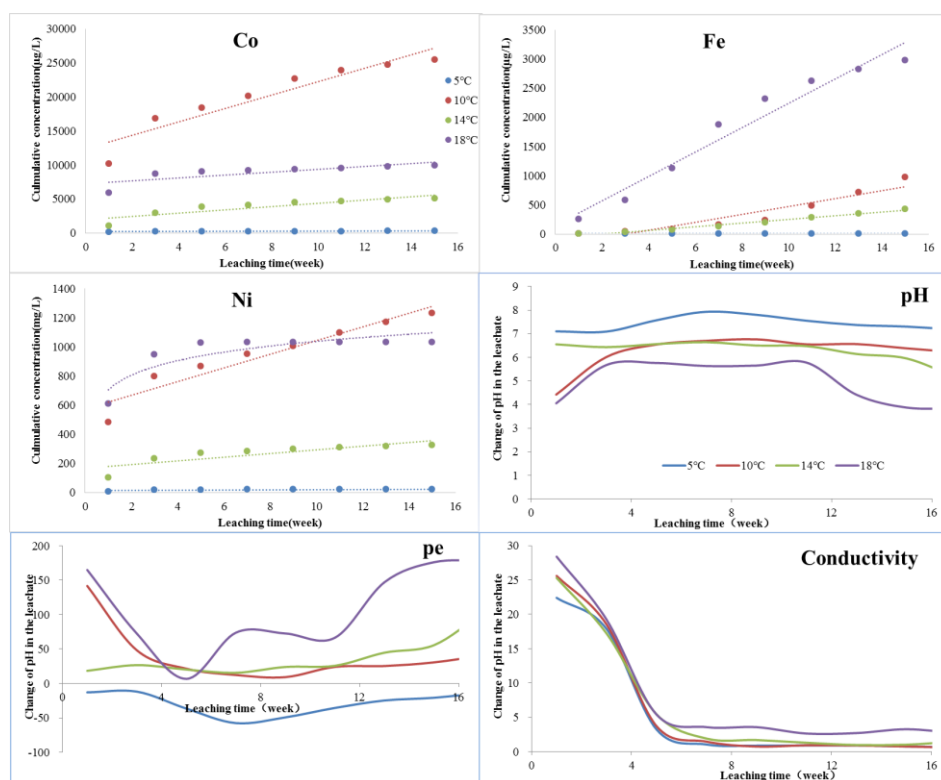


Figure 1. Co, Fe, Ni concentration and physicochemical property of leachates.

Leaching ability of heavy metals from tailings was different with changing temperature. At 5°C, 10°C and 14°C, the order of heavy metal ions leaching from tailings is $\text{Ni} > \text{Fe} > \text{Co}$, and the order became $\text{Fe} > \text{Ni} > \text{Co}$ at 18°C. For the same heavy metal element, leaching concentration at higher temperature was much larger than that at lower temperature from 5°C to 10°C, Co, Ni and Fe had higher leaching concentration at 10°C than at 14°C. And from 14°C to 18°C, Co, Ni and Fe showed higher leaching concentration at higher temperature.

There are two reasons cause difference between heavy metals leaching out at changing temperature, first heavy metals changed their form in the leaching, and the second is acid mine drainage generation in the leaching active. As shown in figure 1, the value of pH of leachate at 5°C was the highest in the experiment, and lowest at 18°C with large change. Pe is another index to indicate heavy metals leaching from tailings, it is a good index of redox ability of matter. Highest and lowest were got at 18°C and 5°C, respectively. Conductivity of leachate is another index to indicate heavy metals icon leaching from tailings, higher conductivity was shown at first three cycles, so most heavy metals were leached out at the first three cycles.

3.2. Relationship between heavy metals leaching at different temperature

Heavy metals leaching from tailings showed different correlation among various air temperature. As the results shown in table 1, when the leaching temperature is 5°C, pH had significant negative correlation with Co, Fe and Ni leaching, Pe and conductivity showed significant positive correlation

with Co, Fe and Ni, and there was significant positive correlation between Co, Fe and Ni leaching. As the temperature increased to 10°C, pH and Pe showed similar correlation with Co, Fe and Ni leaching at 5°C, Ni was significant positive correlated with Co, there was negative correlation between Fe and Co leaching from the tailings. At 14°C, Fe was significant positive correlated with pH, negative correlated with Pe, conductivity, Co and Ni, contrary to the correlation of 5°C.

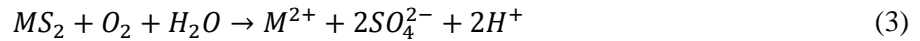
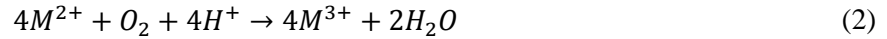
Table 1. Correlation of heavy metals leaching from tailings at 5°C, 10°C, 14°C and 18°C.

		pH	Pe	Conductivity	Co	Fe	Ni
5	pH	1					
	Pe	-,999**	1				
	Conductivity	-,837**	,825*	1			
	Co	-,888**	,877**	,970**	1		
	Fe	-,794*	,783*	,809*	,924**	1	
	Ni	-,838**	,824*	,926**	,984**	,966**	1
10	pH	1					
	Pe	-,996**	1				
	Conductivity	-0,269	0,241	1			
	Co	-0,257	0,229	,985**	1		
	Fe	-0,252	0,27	-0,625	-0,69	1	
	Ni	-0,239	0,213	,987**	,979**	-0,576	1
14	pH	1					
	Pe	-,998**	1				
	Conductivity	-,872**	,860**	1			
	Co	-0,385	0,363	,777*	1		
	Fe	,767*	-,761*	-,898**	-,738*	1	
	Ni	-0,653	0,634	,936**	,947**	-,846**	1
18	pH	1					
	Pe	-1,000**	1				
	Conductivity	0,337	-0,359	1			
	Co	0,319	-0,338	,978**	1		
	Fe	0,684	-0,67	-0,231	-0,248	1	
	Ni	0,341	-0,361	,991**	,996**	-0,229	1

Correlation is significant at the 0.01 level (2-tailed). Correlation is significant at the 0.05 level (2-tailed).

3.3. Temperature effect on Co, Fe and Ni leaching

PH has significant impact on heavy metals leaching from tailing in the arctic area. The pH value of 10°C and 18°C were lower than that at 5°C and 14°C, and the leaching concentrations of Fe, Co and Ni at lower pH were higher in each cycle (figure 1). This agrees with present research that low pH promote heavy metals leach from tailings, and high pH restrain their leaching [19,20]. When pH is higher than 7, leaching concentration is very small. Tailings or leachate with lower pH is good for H^+ generating and releasing, which is benefit for replacement of metal ions from tailings and then dissolved in solution [21]. As shown in equations (1) and (2) (M: heavy metal), lower pH promoted metal oxidized dissolving and chemical oxidation occur, led to high leaching concentration in the leachate [21]. So in the arctic area, keep tailings at high pH will decrease heavy metals leach from tailings. SO_4^{2-} is produced in the sulphidation and oxidation of tailings (equation (3)) [22,23], it changed with the same with H^+ content. So higher SO_4^{2-} is a good indicated of heavy metals dissolving and acid generation. Because there was little change of pH in the experiment (figure 1), so there was there was significant correlation between pH and heavy metals (table 1).



Conductivity is measured by the combined content of all inorganic and organic substances contained in a liquid different form and salinity is the similar index to reflect the water quality by some ions constituting the definition of conductivity. So they have the same change trend in the leaching cycle. Highest TDS and salinity showed at 18°C and lowest at 5°C. Conductivity sharply decreased to 1/10 at the 6th week, means that most of the Na⁺, Ca²⁺, Mg²⁺ and K⁺ leached out at the front cycles. Which means most of these sulfur oxides leached out in the front 6 weeks. Buffer solution formation coupled with such ions releasing, it is good at keep solution pH value and benefit for Ni and Co releasing. So pH values decreased after the 7th leaching week for less buffer solution (figure 1). Although high conductivity is at balancing pH, they are good indication of heavy metals leaching. As it shown in the table, conductivity had significant positive correlation with Ni and Co (table 2), so they are a good indication of heavy metals of leaching, and they may have the same origin source. pH was negative correlated with heavy metals leaching in the experiment, it means lower pH is benefit for heavy metals leaching. Lower pH lead Fe oxidizing (equation (4)) and higher buffer will keep Fe out of precipitant (equation (5)) [24-26]. Therefore both low pH and high conductivity promoted Fe leaching.

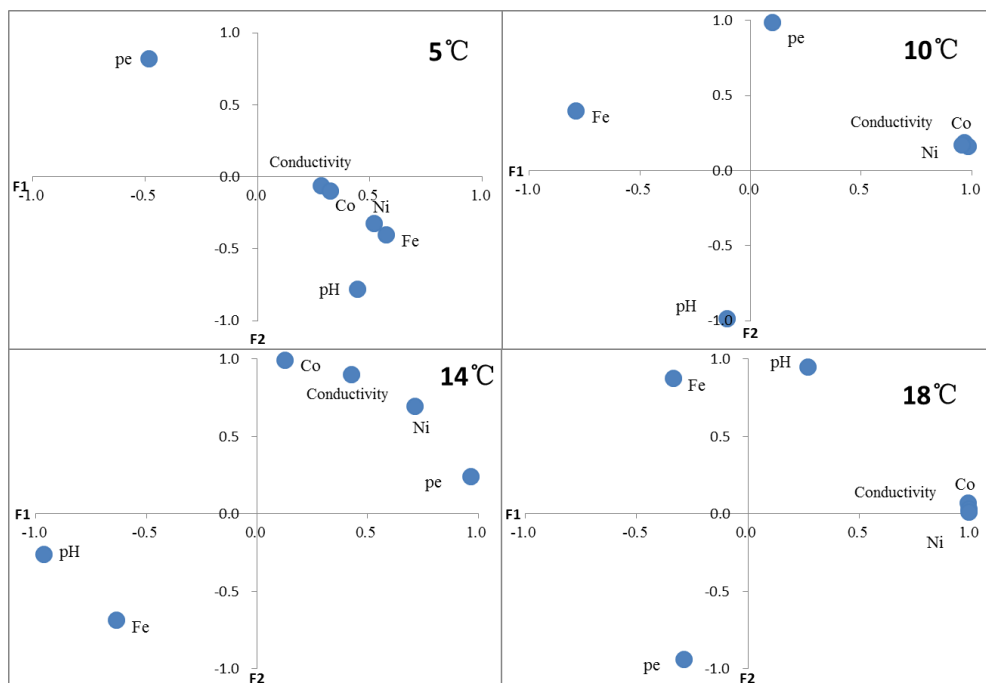
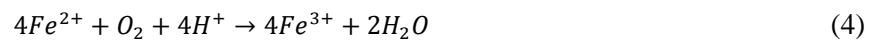


Figure 2. Factor score map of heavy metals leaching at 5, 10, 14 and 18°C.

Correlation analysis was used to detect the relationship between heavy metals leaching under temperature change, and principal component analysis was used to detect the similarity groups between leaching characteristics. All the experiment temperature, PCA analysis showed that 80% of

the total variance could be explained when two principal components with eigenvalues greater than 1 were considered (figure 2). At 5°C, Fe, Ni, Co, Conductivity and pH being associated with the first component, Pe with the second component (figure 2). With temperature increasing, Co, Ni and Conductivity keep in the first component, and Fe became in the second component. Proper temperature will accelerate tailings vulcanize, and change Fe activity and decrease solution pH [27]. It is another way to effect heavy metals leaching. Therefore, both of the colloids, acid generation and sulphur oxidation reaction will change heavy metals form and promote leaching. Change the leaching temperature properly will improve tailings sulphur oxidation reaction [28], and decrease tailings pH, so as to promote heavy metals leaching [29]. Temperature is a main factor to affect biochemical reaction in heavy metals leaching from tailings. In order to prevent leaching of heavy metals from tailings into the surrounding environment, it is very important that the tailings always have a neutral or near neutral pH value. Maintaining a high pH in the tailings has two effects: on the one hand, the solubility of heavy metals at high pH is greatly reduced, and the leaching of heavy metals can be effectively prevented; on the other hand, the formation of hydroxides at high pH causes sulfide. The rate of oxidation decreases over time. So keep tailings stay in the proper temperature is a good way to maintain pH value.

4. Conclusion

This experiment of different temperature of heavy metals leaching from tailings revealed an obvious effect of temperature on Fe, Co and Ni leaching, with temperature climbing that were higher leaching concentration than that of lower temperature. From 5°C to 14°C, heavy metal leaching from tailings followed Ni>Fe>Co, and changed to Fe>Ni>Co at 18°C, and most heavy metals were leached out at the first three cycles. Co and Ni had significant positive correlation and showed in the component at the simulated temperatures. Increase temperature will accelerate tailings vulcanize, and change Fe activity and decrease solution pH. Keep tailings in the proper temperature is a good way to maintain pH value and control heavy metals leach out.

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