Study on the Law of Release of Heavy Metal from Waste Rock of Dexing Copper Mine

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Abstract. Release law of heavy metals from waste rock are significant to the heavy metal pollution control in nonferrous metal mining-area. We took the waste rock of Dexing Copper mine as the object and carried out the leaching experiment with with simulated acid rain(pH3.0, pH 4.0, pH6.0 and pH8.0) which were conducted to investigate the release law of heavy metals(Cu, Pb, Zn, Cd and As) from waste rock. The results of the experiments were as follows: Waste rocks have relatively acid producing capacity in natural rainfall; with the increase of pH value of added liquid, the electric conductivity reduces gradually, and the amount of heavy metal release reduces. The release process of 5 heavy metal elements (Cu, Pb, Zn, Cd and As) from the waste rocks can be classified into two stages, i.e. rapid release stage and slow release stage. They are the mostly easily to be released and migrated under the action of strong acid with the lowest pH, and the leaching quantity is relatively low if leached by leachate with pH nearly neutral.

Introduction

Natural rainwater penetrating into waste rock dumps can accelerate or inhibit the occurrence of a variety of chemical reactions as the substances and the acidity and alkaline contained in the rainwater change the internal environment of the waste rock dump and damage the original reaction equilibrium. Some scientific research reveals acid rain improves the dissolution and release of heavy metal ions and other hazardous elements, acidic leachate can eminently increase the release speed and concentration of heavy metal ions in the waste rock dump, and the pH value of acid rain has certain correlation with the leaching concentration of heavy metals in waste rock dumps[1-3]. A large number of scientific experiments revealed that common acidic leaching may accelerate the leaching of heavy metal ions[4-6].

According to the rainfall monitoring data in recent 5 years, Dexing City is a high incidence areaof acid rain, and the pH of rainfall falls between 3.93-6.81. To achieve full knowledge of the law and characteristics of leaching of heavy metals in the tailings under natural rainfall of Dexing City, this experiment adopts the method of simulated acid rain leaching to explore the law of variation of heavy metal contents in the leachate over time.

Materials and methods

Objects of study. Fresh ores of Dexing Copper Mine is selected as the study objects (≤1a), and the samples are not less than 25kg.

Experiment design. Variable parameters considered in the experiment include pH, temperature, time and leachate flux, etc. The initial condition for experiment chosen is similar to the conditions of natural environment and acid rain: temperature selected: 20-30℃, leachate of four acidities (pH values of 3, 5, 6 and 8) are prepared.

Preparation of leachate: water samples with pH values of 3, 5, 6 and 8 are prepared with distilled water, and respectively tagged as pH_3, pH_5, pH_6 and pH_8.

Leaching device: As shown in Fig 1, the leaching column is 80cm in length, diameter 6cm, and 5cm quartz is put onto the bottom of the column, and then waste rock samples are added.

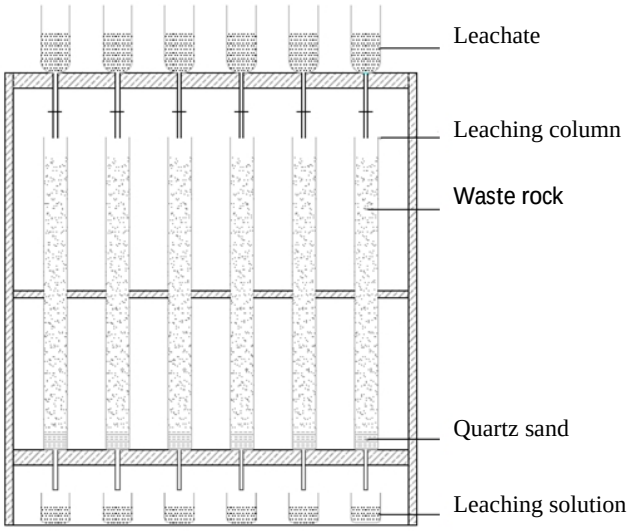

Fig 1 Leaching experiment device

In order to reduce experimental errors, each leachate is repeated three times. Four types of leachate and 12 leaching columns in total are taken. The pH and electric conductivity of each group of water samples are measured every 24 hours, and the contents of heavy metals in the leachate are measured on the 1st, 7th, 14th, 30th, 45th, 60th and 75th days respectively.

Results and analysis

Law of pH variation of leachate over time. As can be seen in Fig 2, the pH value of leachate is very low under leaching of different pH values, the maximum value is only 1.87; if it maintains within 2-3, it's the same even after 75d leaching. This illustrates that waste rock itself produces large quantity of acid, as a result, the value of leachate is lower than the pH value of acid rain. Moreover, the value of leachate is lower than the value of waste rock due to the import of H^+ in acid rain, which reduces pH value, on the other hand, Na^+, Ca^{2+}, Mg^{2+} and other positive ions displace the exchangeable H^+ adsorbed onto the waste rock surface and enter the leachate, and the pH is lowered as a result.

Seen from the leaching time, the values of leachate are close regardless the pH value of initial leachate. This indicates waste rock has relatively strong acid producing capacity in natural rainfall.

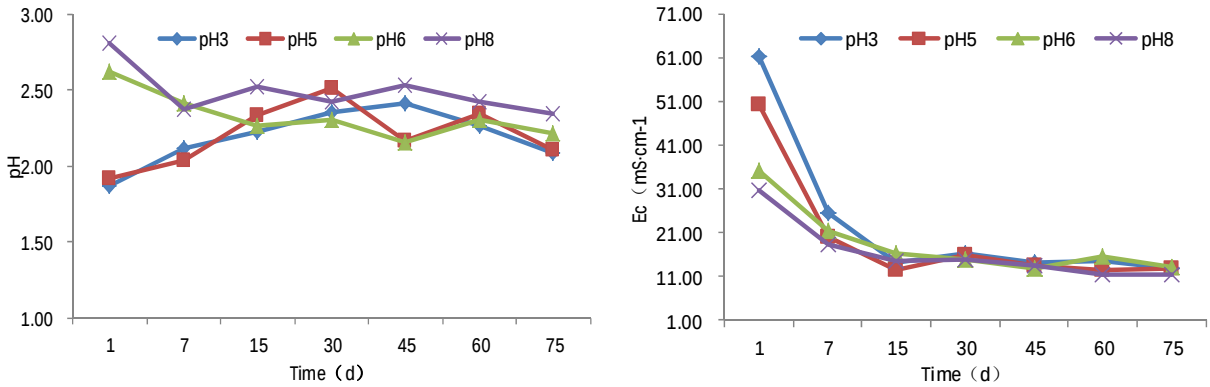

Fig2 Curve of variation of leachate pH of waste rock under different pH and Ec values over time

Law of variation of leachate (Ec) over time. The law of variation of Ec can be seen from Fig 2, When pH remains unchanged, Ec value is relatively high as more salt is leached at the early stage. The electric conductivity is relatively low at the initial stage of leaching, the value of leachate reduces slowly in 15d, and the decreasing trend and degree are relatively stable. During the leaching process, the electric conductivity of leachate reduces gradually, and the difference is relatively big before and after. The electric conductivity of the leachate reduces rapidly at the initial stage, and then the reducing speed turns stable. Meanwhile, Ec value of pH_3 leachate is the highest, but Ec value reduces gradually with the increase of pH value of the added liquid. The value of added liquid is equivalent to

the values of pH_6 leachate and pH_8 leachate. It indicates the ion concentration in the leachate is relatively stable.

Characteristics of Cu release. As shown in Fig 3, the leaching speed is relatively high at the early stage of leaching, subsequently Cu content in leachate decreases sharply and gradually transfers to slow decrease. Under different conditions, or under the condition of the same value, there is eminent difference in the leaching quantity in different leaching periods. Seen from the total amount, after 75d leaching, the leaching amount is the highest under pH_3 condition, the leachate with pH value of 5 comes the second, the total quantity of leaching is minimum where pH_8 leachate is used, indicating it's more favorable for the leaching of waste rock under strong acid condition.

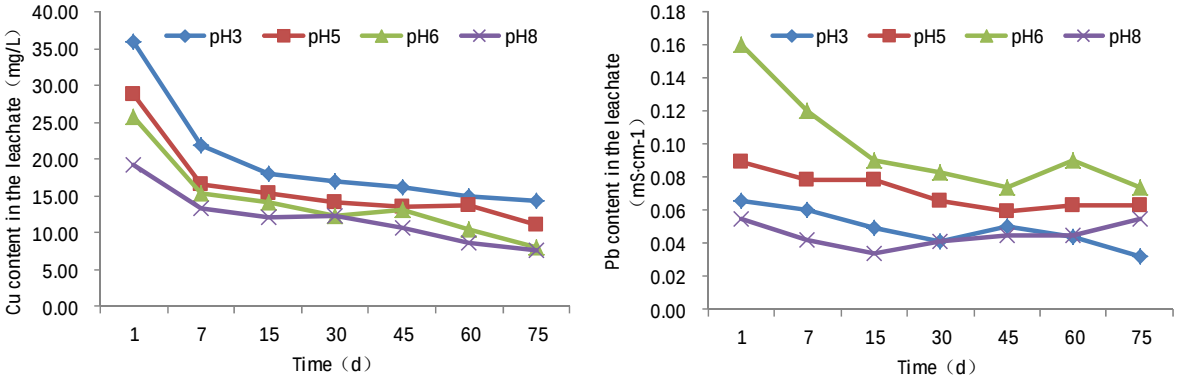

Fig3 Curve of Cu and Pb content in leachate with the variation of pH and leaching time

Characteristics of Pb release. Compared with Cu, the leaching quantity of Pb is much lower. It's relevant to its chemical properties. In general condition, Pbis almost unreactive with dilute hydrochloric acid and dilute sulfuric acid, and the solubilities of the products $PbCl_2$ and $PbSO_4$ are small; however, dilute nitric acid is soluble, and can produce soluble $Pb(NO_3)_2$. Both the oxide and hydroxide of Pb are amphoteric, high-peroxide PbO_2 and $Pb(OH)_4$ are mainly acidic, low-peroxide PbO and $Pb(OH)_2$ are mainly alkalic, namely, they are soluble in both acid and alkali, however, PbS isn't soluble in dilute hydrochloric acid but soluble in dilute nitric acid and concentrated hydrochloric acid.

As shown in Fig 3, within the same period of time, Pb content in pH3 leachate is remarkably higher than that in pH_5, pH_6 and pH_8 leachate. Pb content in leachate of different pH values shows a descending trend over time.

Characteristics of Zn release. Zn exists in waste rock mainly in the form of ZnS, Zn may react with chloride to achieve strong complex compounds which accelerate dissolution. During the 75d leaching period, the total leaching quantity of Zn is the highest (11.32mg/L) under the condition of pH_3, and it comes the second (9.43mg/L) under the condition of pH_5, and it's the lowest (7.12mg/L) under the condition of pH_8.

As shown in Fig 4, the law of variation of Zn concentration of leachate over time is: Zn release is very fast at the initial stage, and then turns mild.

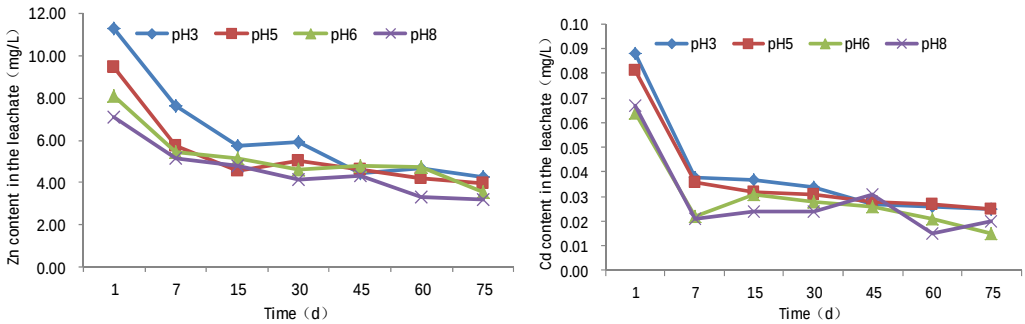

Fig 4 Curve of Zn and Cd content in leachate with the variation of pH and leaching time

Characteristics of Cd release. As shown in Fig 4, Cd tends to be released the most easily under the condition of pH_3 in the 75d leaching period, it comes the second under the condition of pH_5, and

it's the weakest under the condition of pH_8. As shown in Fig 6, the law of variation of Zn concentration of leachate over time is: Zn release is very fast at the initial stage, and then turns mild. This is relevant to rapid oxygenolysis of blende which contains Cd.

Characteristics of As release. As shown in Fig 5, pH value of leachate has great influence on the leaching quantity in the same leaching period. Seen from the total amount, As content of pH_3 leachate is the highest, it comes the second in case of pH_5, and the least in case of pH_8.

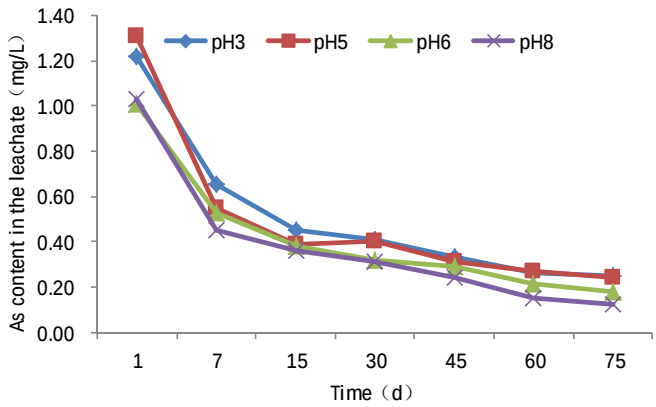

Fig 5 Curve of As content in leachate with the variation of pH and leaching time

Conclusions

Acid rain leaching method is adopted in this paper to conduct dynamic leaching experiments on the waste rock in Dexing Copper Mine, for the purpose of finding out the law of variation of heavy metal contents in leachate over time. The result of study is shown below:

1) As for the waste rock of Dexing Copper Mine, the value of leachate falls between 1.9-3.9, indicating that waste rock of Dexing Copper Mine have relatively strong acid producing capacity under natural rainfall.

2) With the increase of pH value of added liquid, Ec value decreases gradually, and it's relatively different before and after adding. The electric conductivity of the leachate reduces rapidly at the beginning, and then the reducing speed turns stable.

3) 5 heavy metal elements (Cu, Pb, Zn, Cd and As) in the waste rock are the most easily to be released and migrated under the action of strong acid with the lowest pH, and the leaching quantity is relatively low if leached when the leachate pH is nearly neutral. The release quantities of the 5 heavy metals are constant over time, and the release process can be divided into two stages: the first stage is a rapid release process.The release quantity of the 5 heavy metals increases rapidly over time within 7d, but the speed of increase slows down continuously. The second stage is a slow release process, during which the release quantities of the 5 heavy metals increase slowly over time within 7d, indicating the release speed of heavy metals tends to become stable.

Acknowledgements

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