

# Research Status of Valuable Metal Acid Leaching Recovery from Lead-zinc Tailings

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## Abstract

**With the depletion of primary resources, the recovery and utilization of secondary resources has gradually attracted attention. Due to the low level of early beneficiation and metallurgy in China, the lead and zinc heavy metal tailings have a large stock, and contain a large number of valuable heavy metals, including Zn, Pb, As and other heavy metals, which will cause harm to the environment. If the valuable metals can be recycled through recycling, it can not only play a resource recovery effect, but also reduce the adverse impact on the environment. This paper mainly summarizes the current situation of valuable metal-organic acid and inorganic acid leaching recovery from lead-zinc tailings. Through previous research findings, citric acid and malic acid in organic acids can be used to recover zinc, sulfuric acid and hydrochloric acid in inorganic acid can be used to recover valuable metals such as zinc and copper. It is hoped that this paper can provide some help for the research on the recovery of valuable metals from lead-zinc tailings by acid leaching.**

## Keywords

**Lead-zinc Tailing; Acid Leaching; Recovery; Valuable Metal.**

## 1. Introduction

Lead and zinc are widely used nonferrous metals, second only to aluminum and copper, and are widely used in metallurgy, electricity, defense and military industry and other fields. Since China became the world's largest producer of lead and zinc, the lead and zinc industry maintained a good momentum of development. However, China's lead-zinc and other nonferrous metal minerals are mostly symbiotic and associated minerals, with many poor minerals and few rich minerals. Moreover, the early beneficiation technology is not advanced enough, there is the phenomenon of mining the rich and discarding the poor, and the tailings are discharged randomly and stacked irregularly. These factors lead to the problems of large lead-zinc tailings stockpile, loss of valuable metal resources in tailings, and environmental pollution of heavy metals around tailings. According to statistics, 90% of tailings are discharged for each ton of lead-zinc concentrate produced. In recent years, the state has attached great importance to environmental protection, and the heavy metals contained in lead-zinc tailings will cause harm to the environment. At the same time, with the continuous mining and processing of lead-zinc mines in China, the supply of lead-zinc primary resources has become increasingly tense, and China has to face the situation of importing lead-zinc concentrates at high prices from abroad. As a secondary resource, lead-zinc tailings are urgently to be developed and utilized, If effective measures can be taken to recover valuable metals from lead-zinc tailings, it can not only meet the recovery of valuable metal resources but also solve the problem of heavy metal pollution to the environment, so the recovery of valuable metals from lead-zinc tailings has economic and environmental benefits. The method of resource recovery of valuable metals in lead-zinc tailings has been studied by predecessors, including tailings re-flotation and leaching recovery. Tailings will still be produced by tailings re-flotation, and most

of the tailings have very fine particle size, which is not conducive to flotation. Compared with other methods, the leaching recovery process is simple and cheap. The leaching recovery includes strong acid and alkali leaching, biological leaching, organic acid leaching, etc. The leaching efficiency of strong acid and strong alkali is high, but it is harmful to the environment. After leaching, acid-base neutralization treatment is required. The advantages of biological leaching are environmental protection and economy, but there are problems such as long leaching cycle and complex bacterial culture. Compared with the above leaching methods, organic acid leaching is to use various organic acids produced by biological metabolism to react with lead-zinc tailings to achieve the purpose of extracting valuable metals. Organic acids have advantages over inorganic acids in environmental protection, and most of them are biodegradable. However, the acid leaching of lead-zinc tailings is still less studied. Based on this. This paper summarizes the current research status of organic acid and inorganic acid leaching recovery of lead-zinc tailings. The purpose is to provide reference for the research on the recovery of valuable metals from lead-zinc tailings by acid leaching in China

## 2. Lead-zinc Tailings Organic Acid Leaching.

### 2.1. Citric acid leaching

Low-molecular-weight citric acid is a naturally occurring fruit acid, which is produced by microbial fermentation and is a biodegradable organic product. It is one of the largest tonnage fermentation products in the world. In the process of hydrometallurgy, the ability to recover metal or metal oxide is determined by its chemical reactivity<sup>[1]</sup>. Kaya et al<sup>[2]</sup> used citric acid to leach carbonate type lead-zinc tailings in Kayseri, Turkey, and found that under the optimal leaching conditions of 1M citric acid, 1/10 (g/mL) solid-liquid ratio, 80 °C leaching temperature, 180 min leaching time, the leaching rates of valuable metals were Zn 91%, Pb 12%, Fe 19%, As 17%. Kursunoglu et al<sup>[3]</sup> found in the same study that the optimal leaching rates of valuable metals Zn, Pb, Fe and As can reach 89.3%, 6.6%, 15.3% and 13.3% respectively when the leaching experimental parameters are citric acid concentration of 0.5M, solid-liquid ratio of 1/10, leaching temperature of 80 °C and leaching time of 120 min. This can realize the selective leaching of valuable metal zinc. In previous studies, Hussaini et al<sup>[4]</sup> had a good effect on selective extraction of zinc. Under the conditions of citric acid concentration of 1M, solid-liquid ratio of 2/10, leaching temperature of 80 °C, and leaching time was 180 min, zinc leaching rate was 90.6%, while Pb, Fe, As were 9.3%, 19.2%, and 14.5%, respectively. Iranajad et al<sup>[5]</sup> explored the optimal leaching conditions for extracting zinc from low-grade lead-zinc oxide tailings in Iran Angola with citric acid. The study showed that the leaching time and particle size had little effect on the leaching rate of zinc in ZnCO<sub>3</sub>. The optimal leaching conditions were leaching temperature 80 °C, leaching time 60 min, organic acid concentration 0.5 M, solid-liquid ratio 1/10, stirring speed 350 rpm, and the extraction rate of zinc under this condition was 82%. Seyed et al<sup>[6]</sup> proved through research that the citric acid leaching method can recover valuable metals Zn and Pb from low-grade lead-zinc oxide ores. Through software calculation, the leaching rate of Zn and Pb was optimized and finally combined with experimental verification, it was concluded that the best leaching conditions for Zn were acid concentration 1M, solid-liquid ratio 1/20, leaching temperature 80 °C, leaching time 80 min, stirring speed 400 rpm, under which the zinc extraction rate was 94%; Pb can obtain the optimal result of 78% leaching rate under the conditions of acid concentration of 1M, solid-liquid ratio of 1/25, leaching temperature of 80 °C, leaching time of 90 min and stirring speed of 500 rpm. Burckhard et al<sup>[7]</sup> showed through experiments that organic acids in the rhizosphere of plants would affect the mobility of Zn in heavy metal tailings. The study found that citric acid leached more Zn than oxalic acid, formic acid and succinic acid, which is very beneficial for citric acid leaching of valuable metal Zn from lead-zinc tailings. Park et al<sup>[8]</sup> studied the leaching behavior of citric

acid on heavy non-ferrous metals such as Pb, Zn and Cu in contaminated soil, and found that the leaching rates of three valuable metals were positively correlated with the concentration of citric acid. Under the conditions of acid concentration of 2M, reaction time of 2h, leaching temperature of 50 °C, stirring speed of 80rpm, and pulp concentration of 10%, the leaching rates of Cu, Zn and Pb reached 86.5%, 88.9%, and 83.3% respectively. Nicolas et al<sup>[9]</sup> found in the study that among the three commercial organic acids, under the same leaching conditions, compared with oxalic acid and gluconic acid, tricarboxylic citric acid have the highest solubilization rate for valuable metal Cu, and the extraction efficiency of citric acid leaching valuable metal is Cu>Zn>Pb>Ni~Cd>Fe. This study shows that commercial organic acids have great advantages in extracting valuable metals from heavy metal tailings. Munyai et al<sup>[10]</sup> obtained through batch leaching experiments that the leaching rate of valuable metals is high at low pH, short contact time, high temperature and high organic acid concentration. This study mainly aims at Al and Fe, and selects the most effective leachant citric acid and oxalic acid from a variety of organic acids. At the same time, it is also found that mixed organic acid leaching is more effective than single organic acid leaching. Crane et al<sup>[12]</sup> verified through experimental results that citric acid and methanesulfonic acid in organic acid can reach the leaching efficiency of sulfuric acid in inorganic acid and hydrochloric acid for As and Cu, and also considered that organic acid is more environmentally friendly than inorganic acid, so it also confirmed to some extent that citric acid really has the potential as a leaching agent for lead-zinc tailings.

Based on the above research, it can be basically confirmed that citric acid has advantages in recovering valuable metals from lead-zinc tailings.

## 2.2. Malic acid leaching

Similar to citric acid, malic acid is also produced by microbial fermentation. It is mostly used as food additive, non-toxic and harmless. It is also a kind of low molecular weight organic acid. Kaya et al<sup>[2]</sup> explored the optimal process parameters of malic acid as the leaching agent of lead-zinc tailings through experiments. The study found that under the conditions of malic acid concentration of 1M, solid-liquid ratio of 1/10, leaching temperature of 80 °C, and leaching time of 180 min, the highest leaching rate of valuable metal Zn in lead-zinc tailings can reach 91.6%, while the leaching rate of Pb is 8.1%, and the leaching rate of Fe is 6.5%, which can also achieve the selective leaching of Zn. In the same study, Hussaini et al<sup>[4]</sup> found that when the concentration of malic acid is 1M, the leaching temperature is 80 °C, the leaching time is 60 min, and the solid-liquid ratio is 1/10, the extraction rate of valuable metal Zn can reach 90%, and the leaching rates of Pb and Fe are 9.3% and 4.3% respectively. Again, malic acid leaching of Zn is selective. Munyai et al<sup>[10]</sup> used malic acid in the process of exploring the mobility of valuable metals in mine tailings with different organic acids, but the results showed that compared with citric acid and oxalic acid, the extraction rates of Fe and Al were not as high as those of citric acid and oxalic acid under the same conditions.

Ilyas et al<sup>[11]</sup> studied the ability of *Penicillium flavum* to produce different organic acids, and studied the chemical leaching of metal ions by malic acid in the comparative experiment. The study showed that the leaching rate of malic acid for Zn, Ni, Cu was lower than that of citric acid under the same acid concentration and other conditions.

Based on this, whether malic acid can be used as leaching agent for lead-zinc tailings remains to be further studied.

## 2.3. Oxalic acid leaching

Oxalic acid is a binary weak acid, which is also produced by organism metabolism. It has been used as valuable metal leaching agent for heavy metal tailings in previous studies. The current research is as follows. Kaya et al<sup>[2]</sup> found in the experimental study that oxalic acid has a weak affinity for Zn and Pb in lead-zinc tailings, while it has a strong affinity for Fe and As. The study

showed that under the conditions of oxalic acid concentration of 1M, solid-liquid ratio of 1/10, leaching temperature of 60 °C, and leaching time of 180 min, the leaching rates of Zn and Pb are 2.9% and 3.2% respectively, while the leaching rates of Fe can reach 96% and As can reach 69%. Kursunoglu et al<sup>[3]</sup> obtained similar results under the same experimental conditions. The leaching rates of Zn and Pb are less than 10%, and the leaching rates of Fe and As are 74.3% and 60% respectively. However, the leaching rates of As and Fe are not as high as Kaya et al<sup>[2]</sup> research. Munyai et al<sup>[10]</sup> showed that oxalic acid and citric acid are the most effective leaching agents, both of which can rapidly dissolve metals in tailings samples. Nicolas et al<sup>[9]</sup> found that under the condition of mixing citric acid and oxalic acid, the valuable metals Cu and Zn can obtain better metal leaching rate than under the conditions of citric acid+gluconic acid and gluconic acid+oxalic acid. For Pb, under the condition of 10<sup>-2</sup> g/L mixed concentration of citric acid+oxalic acid, the highest leaching rate can be achieved. The chemical leaching experiment of Ilyas et al<sup>[11]</sup> showed that no matter what concentration, compared with citric acid, malic acid and tartaric acid. Oxalic acid has the highest leaching rate of Mg, and the lowest leaching rate of valuable metal Ni.

Combined with previous studies. It can be seen that oxalic acid mixed with other organic acids has great potential as combined acid leaching agent.

## 2.4. Tartaric acid leaching

Tartaric acid is also an organic carboxylic acid. It is one of the main organic acids in wine. It is most widely used as a beverage and food additive. This use is consistent with that of citric acid and malic acid. In addition, it can also be used in the pharmaceutical industry. In the previous experimental study, Kaya et al<sup>[2,4]</sup> used 1M tartaric acid under the conditions of solid-liquid ratio of 1/10, leaching temperature of 80 °C, magnetic stirring speed of 400 rpm and leaching time of 30 min, the leaching rate of Zn was 34.4%, Pb 10% and Fe 4.2%. It may be that the leaching rate of valuable metal Zn is not high due to the short leaching time, so the leaching time can be extended later and whether the extraction rate of Zn is improved can be concerned. Ilyas et al<sup>[11]</sup> studied the potential of a fungus to produce multiple organic acids, and explored the chemical leaching of valuable metals from tailings with different organic acids. The study found that compared with glucose, honey and acidified green tea, the medium containing acidified wine grapes showed a high content of tartaric acid. In addition, the extraction rate of zinc from tartaric acid is significantly higher than that from citric acid, malic acid and oxalic acid within the range of 0-1.5% acid content, and the highest extraction rate of zinc can reach 80% when tartaric acid content is 1.5%.

To sum up, at present, the research on tailings leaching with tartaric acid is still relatively small, and further research and exploration may be needed in the future.

## 2.5. Formic acid leaching

Formic acid is the simplest organic carboxylic acid, commonly known as formic acid. Commonly used as organic chemical raw materials, it often occurs in the secretion of ants, bees and insects. Kaya et al<sup>[2,4]</sup> showed that under the conditions of formic acid concentration of 1M, solid-liquid ratio of 1/10, leaching temperature of 60 °C, and leaching time of 180 min, the leaching rate of valuable metal Zn can reach 82.6%, Pb 2.8%, and Fe 0.6%, and the selective leaching of Zn can also be realized.

In addition to the research on the leaching of valuable metals from tailings with formic acid in the above documents, the research on the use of formic acid as leaching agent for heavy metal tailings at home and abroad is very limited at present, and it still needs to be further studied in the future.

## 2.6. Ascorbic acid leaching

Ascorbic acid usually refers to vitamin C, which can participate in human metabolism and be used as a nutritional supplement to promote development and improve immunity. Kaya et al<sup>[2]</sup> explored the effect of ascorbic acid on the leaching of lead-zinc tailings in the previous study of organic acid leaching of lead-zinc tailings. The study showed that under the conditions of acid concentration of 1M, solid-liquid ratio of 1/10, leaching temperature of 60 °C, and reaction time of 60 min, the extraction rate of Zn was 34%, and the extraction rates of Pb, Fe, As were 3%, 15%, and 11% respectively. Hussaini et al<sup>[4]</sup> also obtained similar results in the same experiment.

From the above research, it can be seen that ascorbic acid is not dominant as a valuable metal leaching agent for lead-zinc tailings, and it may not be worth further research on tailings leaching in the future.

## 2.7. Methanesulfonic acid leaching

Methanesulfonic acid(MSA) is a strong organic acid. Its chemical properties are relatively active, and it has a very strong corrosive effect on metal Cu, Pb and Fe. This may be its advantage as a leaching agent for heavy metal tailings. It is often used to produce raw materials for pharmaceuticals and pesticides. In previous studies, Crane et al<sup>[12]</sup> discussed the leaching of valuable metals Cu and As in mine tailings by organic acids. The study showed that under the same leaching conditions, the acid concentration was 1M, the solid-liquid ratio was 1/10, and the reaction time was 48h. The extraction rates of As by sulfuric acid, hydrochloric acid and MSA were 58%, 56% and 55% respectively. For Cu, under the same conditions, the dissolution rates of copper by sulfuric acid, hydrochloric acid and MSA were 38%, 32% and 29% respectively. This study shows that MSA is comparable to inorganic strong acid in leaching valuable metals, and has great potential as a valuable metal leaching agent in tailings. Bevandić et al<sup>[13]</sup> conducted a leaching study on the Plombières sulfide tailings pond in eastern Belgium. In this study, MSA was used as a lead-zinc tailings leaching agent. The study showed that MSA leaching not only had the highest leaching rate of Pb and Zn, but also had a high leaching rate of Fe. It was found that MSA leaching effect of Pb was the best, superior to sodium hydroxide, and the highest leaching rate of Pb could reach 58%. Palden et al<sup>[14]</sup> recovered valuable metals Pb and Zn from jarosite slag by using MSA. The research showed that MSA has strong acidity and is easy to react with Pb, Zn and Fe in the residue. The leaching rate of Pb in pure MSA system is significantly higher than that of Zn and Fe. Under the operation of optimal experimental parameters, the leaching rate of Pb is 100%, Zn is 50%, and Fe is 9%, From this study, it can be concluded that MSA may also have advantages in the recovery of valuable metals from lead-zinc tailings.

Based on the above research, it can be seen that MSA has great potential as a valuable metal leaching agent for solid waste, especially for leaching Pb, which may be very useful in leaching valuable metal Pb from lead-zinc tailings, and may play a certain role in recovering Pb and reducing the impact on the environment in terms of tailings resource utilization.

## 3. Lead-zinc Tailings Inorganic acid Leaching

### 3.1. Sulfuric acid leaching

Sulfuric acid is a very common binary strong acid and the most important inorganic oxygen-containing acid. It is often used in metallurgy and petrochemical industry, especially in nonferrous metal metallurgy. Sulfuric acid is a very common raw material, and is often used as a leaching agent in hydrometallurgy or an electrolyte for electrolytic refining of nonferrous metals. The use of sulfuric acid as valuable metal leaching agent for lead-zinc tailings has been studied. Kaya et al<sup>[2]</sup> used sulfuric acid to leach carbonate type lead-zinc tailings in Turkey to



recover valuable metal Zn. Under the conditions of sulfuric acid concentration of 1M, solid-liquid ratio of 1/10, leaching temperature of 40 °C, and leaching time of 60min, the leaching rate of Zn can reach 92%, while the leaching rates of Fe and As are 12% and 20%. Kursunoglu et al<sup>[3]</sup> changed the experimental parameters in the same study to explore the change of Zn, Fe and As leaching rates. The study found that when the sulfuric acid concentration was 1M, the solid-liquid ratio was 2/10, the leaching temperature was 40 °C, and the leaching time was 60 min, the Zn extraction rate could reach 89.3%, Fe and As were 12.3% and 18.8% respectively. Hussaini et al<sup>[4]</sup> also discussed the effect of sulfuric acid leaching of lead-zinc tailings on the leaching rate of valuable metals under different process parameters in previous studies, and further explored its impact on the leaching rate of metals by adding four different oxidants. Without oxidant, under the conditions of sulfuric acid concentration of 1M, solid-liquid ratio of 2/10, leaching temperature of 40 °C and leaching time of 30min, the leaching rates of Zn, Fe and As are 91%, 11.2% and 18.4% respectively. When the concentration of sulfuric acid is 1M+1g/L  $\text{KMnO}_4$ , the solid-liquid ratio is 1/10, the leaching temperature is 40 °C, and the leaching time is 180 min, the leaching rates of Zn, Pb, and Fe are 87.1%, 1.9%, and 11% respectively. When the concentration of sulfuric acid is 1M+1g/L  $\text{MnO}_2$ , the solid-liquid ratio is 1/10, the leaching temperature is 40 °C, and the leaching time is 120min, the leaching rates of Zn, Pb, Fe and As are 95.1%, 0.0%, 18.8% and 27.5% respectively. The sulfuric acid concentration is 1M+1g/L  $\text{Na}_2\text{O}_5\text{S}_2$ , the solid-liquid ratio is 1/10, the leaching temperature is 40 °C, the leaching time is 60min, and the leaching rates of Zn, Pb and Fe are 81.8%, 1.1% and 8.8% respectively. The sulfuric acid concentration is 1M+20mL/L  $\text{H}_2\text{O}_2$ , the solid-liquid ratio is 1/10, the leaching temperature is 40 °C, the leaching time is 60min, and the leaching rates of Zn, Pb, Fe and As are 90.6%, 0.5%, 11.2% and 21.5% respectively. In the previous study, Asadi et al<sup>[15]</sup> explored the valuable leaching of zinc from lead-zinc tailings by mixing ferric sulfate and sulfuric acid, in which ferric sulfate is used as oxidant. Through response surface analysis and experimental verification, this study confirmed that the maximum extraction rate of zinc is 94.3% under the process parameters of stirring speed of 320rpm, sulfuric acid concentration of 1.14M, sulfuric acid/ferric sulfate of 2.49, solid-liquid ratio of 1/10.1, and leaching temperature of 80 °C. Bevandić et al<sup>[13]</sup> in the study of mine tailings leaching found that sulfuric acid has the best leaching effect on Zn, with the leaching rate ranging from 20 to 50%, but the disadvantage is that the Fe extraction rate is also high, and selective leaching of Zn cannot be achieved. Schueler et al<sup>[16]</sup> studied the extraction of valuable metals Cu, Zn and Pb from polymetallic sulphide tailings using sulfuric acid and NaCl solution through experimental design. The experimental results showed that Pb was greatly affected by the concentration of salt solution, and valuable metals Cu and Zn were more sensitive to the rise of temperature. The leaching rates of the three metals were positively correlated with the leaching time. The experiment adopts two stages of leaching, the first stage is conducive to Pb leaching, and the second stage is to completely leach Cu, Zn again, and finally Cu, Zn, Pb extraction rates can reach 66.8%, 84.1%, and 93.9% respectively. The best leaching conditions for the first stage are sodium chloride concentration of 60g/L, sulfuric acid concentration of 0.01M, leaching temperature of 45 °C, leaching time of 1h, and solid-liquid ratio of 1/10. For the second stage, the sulfuric acid concentration is increased to 0.5M, the leaching temperature is increased to 70 °C, and the extraction time is 24h based on the same conditions of brine concentration and solid-liquid ratio. Crane et al<sup>[12]</sup> research shows that under the same leaching conditions, the leaching rate of Cu and As in different kinds of acids with sulfuric acid is still slightly higher than that with hydrochloric acid, methanesulfonic acid and citric acid. The difference between the leaching rate of copper with sulfuric acid and citric acid is 16%, while the difference between the leaching rate of As is 14%. Kursunoglu et al<sup>[17]</sup> studied the effect of sulfuric acid on the leaching of valuable metal Zn from carbonate-type lead-zinc tailings. The study was divided into two stages. The first stage used sulfuric acid to explore the effects of solid-liquid ratio, leaching temperature and pH value on

the extraction rate of Zn. The optimal leaching conditions were pH 2, leaching temperature 40 °C, solid-liquid ratio 2/10, and reaction time 2h. Under this condition, the extraction rate of Zn was 82.3%, and the leaching residue in the acid leaching stage contained 99.5% Fe and 99.7% Pb, This shows that sulfuric acid can achieve selective leaching of zinc. The study also found that the leaching temperature had little effect on the leaching rate of zinc in sulfuric acid leaching. Nguyen et al<sup>[18]</sup> used sulfuric acid and hydrogen peroxide as the leaching agent in the study. The study showed that the leaching rate of metals was positively correlated with the concentration of inorganic sulfuric acid. The addition of H<sub>2</sub>O<sub>2</sub> could improve the leaching rate of arsenic in tailings. The addition of H<sub>2</sub>O<sub>2</sub> did not improve the leaching rates of Zn and Fe, but the increase of acid concentration increased the leaching rates of both.

From the above research, it can be seen that sulfuric acid can be used as an effective leaching agent for valuable metals in lead-zinc tailings, especially for metal Zn. However, considering that sulfuric acid has great harm to the environment, it should be used on the basis of considering the environmental impact to achieve a win-win economic and environmental effect.

### 3.2. Hydrochloric acid leaching

Hydrochloric acid is one of the common inorganic acids. It is an aqueous solution of hydrogen chloride gas and widely used in industry. It is also the main component of gastric acid. Kaya et al<sup>[2]</sup> found that the leaching rate of valuable metal Zn is 92%, Pb and Zn are 10% under the conditions of hydrochloric acid concentration of 1M, solid-liquid ratio of 1/10, leaching temperature of 80 °C, and leaching time of 30min through hydrochloric acid leaching of carbonate lead-zinc tailings. It is proved that hydrochloric acid can also selectively leach metal Zn from tailings. Hussaini et al<sup>[4]</sup> found in the same leaching study that under the same conditions, the leaching rate of Zn is 93%, while Pb is 8.8% and Fe is 9.3%, which is more selective for valuable metal Zn. Crane et al<sup>[12]</sup> used hydrochloric acid to leach valuable metal Cu and toxic element As from mine tailings. After 48 hours of leaching with 1M hydrochloric acid concentration, solid-liquid ratio of 1/10, the leaching rate of valuable metal Cu is 29%, and the leaching rate of As is 56%. The low leaching rate of Cu may be related to the sulfide phase of copper. Chu et al<sup>[19]</sup> carried out hydrochloric acid leaching experiment on a lead-zinc tailings in Guizhou. The study showed that most of the oxidized form of Zn in the tailings existed, mainly hemimorphite. Under the optimal leaching conditions, the concentration of hydrochloric acid was 60%, the ratio of solid to liquid was 1/4, the leaching time was 6 hours, the particle size of tailings was 200 mesh, and the leaching rate of Zn reached 95.34%.

Based on previous studies, we can see that hydrochloric acid as a valuable metal leaching agent in lead-zinc tailings is also very advantageous, with high leaching efficiency and the ability to selectively leach zinc under certain conditions, which is worthy of further research and promotion.

### 3.3. Nitric acid leaching

Nitric acid is one of the six strong inorganic acids with strong oxidation and corrosion, and is widely used in chemical, pesticide and explosive industries. Kaya et al<sup>[2]</sup> used 1M nitric acid under the conditions of solid-liquid ratio of 1/10, leaching temperature of 40 °C, and leaching time of 30 minutes, the leaching rate of Zn is 70%, Pb is 23%, and Fe is 0%. In the same experimental study, Hussaini et al<sup>[4]</sup> changed the leaching parameters and found that under the conditions of nitric acid concentration of 1M, solid-liquid ratio of 1/10, leaching temperature of 40 °C and reaction time of 60 min, the leaching rate of Zn was 69.7% and Pb was 23.2%.

In addition to the above studies, there are few studies on the use of nitric acid as tailings leaching agent, which may be related to the fact that nitric acid has no obvious advantage in the leaching rate of valuable metals, and the production and transportation are also relatively

dangerous. In addition, if only focus on leaching, it is not as good as sulfuric acid, hydrochloric acid, and some organic weak acids.

### 3.4. Perchloric acid leaching

Perchloric acid is the first of the six major inorganic strong acids, which is extremely corrosive and irritating. It is often used in the preparation of perchlorate and can also be used as an oxidant. Hussaini et al<sup>[4]</sup> studied the effect of 17 different leaching agents on the valuable leaching of carbonate lead-zinc tailings through experiments, among which the leaching of valuable metals Zn and Pb by perchloric acid was studied. The results showed that the leaching rate of valuable metals Zn and Pb was 89.3% and 10.7% when the concentration of perchloric acid was 1M, the solid-liquid ratio was 1/10, the leaching temperature was 80 °C, and the leaching time was 60 min.

Although perchloric acid has a high leaching rate of valuable metal Zn in lead-zinc tailings and a low leaching rate of Pb, which can play a selective leaching effect, considering that perchloric acid and nitric acid are highly dangerous and extremely unfriendly to the environment, we can consider replacing inorganic strong acids with other organic weak acids to achieve both environmental and resource benefits.

## 4. Summary

With the continuous depletion of primary lead and zinc resources, the recovery of valuable metals in lead-zinc tailings as secondary resources is becoming increasingly important. This paper mainly summarizes the effects of organic and inorganic acids on the leaching of valuable metals Zn, Pb, Cu, Fe, As in lead-zinc tailings. The results show that citric acid and malic acid in organic acid can achieve the recovery of Zn, and the optimal leaching rate is about 90%. However, methanesulfonic acid can achieve 100% leaching of Pb under the optimal conditions. For inorganic acids, sulfuric acid and hydrochloric acid are the best leaching agents, which can selectively recover Zn. The extraction rate of Zn in sulfuric acid and hydrochloric acid under the optimum conditions is above 90%. The leaching time is shorter than that of organic acids, and the leaching temperature is lower than that of organic acids. However, the current research focus is also on organic acid leaching, because organic acids have an advantage in the environment, and the leaching rate of some organic acids for valuable metals can reach the same level as that of inorganic strong acids. It is believed that with the continuous development of the research on the leaching of valuable metal organic acid from lead-zinc tailings, in the near future, the organic acid leaching will occupy a place in the aspects of efficiency, environment, economy, etc. in order to realize the green recovery of valuable metal and efficient and clean production.

## References

- [1] Kaya M, Hussaini S, Kursunoglu S, et al. Critical review on secondary zinc resources and their recycling technologies[J]. Hydrometallurgy, 2020, 195: 105362.
- [2] Kaya M, Kursunoglu S, Hussaini S, et al. Leaching of Turkish oxidized Pb-Zn flotation tailings by inorganic and organic acids[C]//PbZn 2020: 9th International Symposium on Lead and Zinc Processing. Springer International Publishing, 2020: 447-468.
- [3] Kursunoglu S, Kursunoglu N, Hussaini S, et al. Selection of an appropriate acid type for the recovery of zinc from a flotation tailing by the analytic hierarchy process[J]. Journal of Cleaner Production, 2021, 283: 124659.
- [4] Hussaini S, Kursunoglu S, Top S, et al. Testing of 17-different leaching agents for the recovery of zinc from a carbonate-type Pb-Zn ore flotation tailing[J]. Minerals Engineering, 2021, 168: 106935.
- [5] Irannajad M, Meshkini M, Azadmehr A R, et al. Leaching of zinc from low grade oxide ore using organic acid[J]. Physicochemical Problems of Mineral Processing, 2013, 49(2): 547--555.



- [6] Seyed Ghasemi S M, Azizi A, et al. Leaching of Lead and Zinc from a Low-Grade Oxide Ore in Citric Acid Media[J]. Iranian Journal of Chemistry and Chemical Engineering (IJCCE), 2018, 37(5): 105-110.
- [7] Burckhard S R, Schwab A P, Banks M K, et al. The effects of organic acids on the leaching of heavy metals from mine tailings[J]. Journal of Hazardous Materials, 1995, 41(2-3): 135-145.
- [8] Park H, Jung K, Alorro R D, et al. Leaching behavior of copper, zinc and lead from contaminated soil with citric acid[J]. Materials transactions, 2013, 54(7): 1220-1223.
- [9] Nicolas K, Rosa G, Abibata O, et al. Three commercial organic acids for the leaching of metals from tailings[J]. Scholars Journal of Engineering and Technology (SJET), 2017, 5(11): 629-638.
- [10] Munyai A H, Fosso-Kankeu E, Waanders F, et al. Mobility of metals from mine tailings using different types of organic acids: Batch leaching experiment[J]. International Journal of Science and Research, 2016, 5(11): 520-527.
- [11] Ilyas S, Chi R, Lee J, et al. Fungal bioleaching of metals from mine tailing[J]. Mineral Processing and Extractive Metallurgy Review, 2013, 34(3): 185-194.
- [12] Crane R A, Sapsford D J. Towards greener lixivants in value recovery from mine wastes: Efficacy of organic acids for the dissolution of copper and arsenic from legacy mine tailings[J]. Minerals, 2018, 8(9): 383.
- [13] Bevandić S, Xanthopoulos P, Muchez P, et al. Chemical leaching of sulfidic mining waste, Plombières tailings pond, eastern Belgium: insights from a mineralogical approach[J]. Journal of Sustainable Metallurgy, 2021, 7: 1444-1455.
- [14] Palden T, Onghena B, Regadío M, et al. Methanesulfonic acid: a sustainable acidic solvent for recovering metals from the jarosite residue of the zinc industry[J]. Green Chemistry, 2019, 21(19): 5394-5404.
- [15] Asadi T, Azizi A, Lee J, et al. Leaching of zinc from a lead-zinc flotation tailing sample using ferric sulphate and sulfuric acid media[J]. Journal of Environmental Chemical Engineering, 2017, 5(5): 4769-4775.
- [16] Schueler T A, de Aguiar P F, Vera Y M, et al. Leaching of Cu, Zn, and Pb from sulfidic tailings under the use of sulfuric acid and chloride solutions[J]. Journal of Sustainable Metallurgy, 2021, 7: 1523-1536.
- [17] Kursunoglu S, Soner T O P, Muammer K, et al. Recovery of zinc and lead from Yahyali non-sulphide flotation tailing by sequential acidic and sodium hydroxide leaching in the presence of potassium sodium tartrate[J]. Transactions of Nonferrous Metals Society of China, 2020, 30(12): 3367-3378.
- [18] Nguyen V K, Lee J U. A comparison of microbial leaching and chemical leaching of arsenic and heavy metals from mine tailings[J]. Biotechnology and Bioprocess Engineering, 2015, 20: 91-99.
- [19] Chu H, Zhang T, Wang Q, et al. Chemical leaching test of zinc from a lead-zinc tailings in Guizhou[J]. Modern mining, 2012, 27(07): 88-89+97.