Study on Leaching Mechanism and Safety Evaluation of Lead and Zinc Contaminated Soil

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Abstract. Taking the tailing pond of the Qiaokou lead-zinc mine in Hunan province as the research object, the lead-zinc-contaminated soil was leached by citric acid, and the phase characteristics of the contaminated soil before and after leaching were analyzed by SEM-EDS, combined with BCR. The continuous extraction method was used to study the occurrence of four kinds of heavy metals in contaminated soil, and then analyze the potential migration and transformation ability and migration law to evaluate the potential hazards of heavy metals to the surrounding environment, and to repair the lead and zinc tailings pond. Provide theoretical basis and technical support with governance.

1. Introduction
The environmental pollution caused by metallurgical mining and smelting could not be ignored, especially the pollution of heavy metals such as copper, arsenic, mercury, and cadmium in the surrounding soil. Due to the long-term, concealed and irreversible characteristics of heavy metal pollution, it would directly or indirectly pollute surface water, groundwater, air, plants and crops, and even endanger human health and life[1-2]. Therefore, repairing heavy metal contaminated soil and restoring the original functions of the soil has always been a difficult point and hotspot at home and abroad[3], and it is also important to conduct a safety assessment of the repaired soil[4].

2. Test materials and methods
2.1. Test materials
1) Test soil: The selected lead-zinc contaminated soil was taken from the tailing pond of the Qiaokou lead-zinc mine in Hunan.
   2) Eluent: citric acid, analytically pure, prepared at a concentration of 0.4 mol•L⁻¹.
   3) Test water: once deionized water.
   4) Leaching equipment: using portable heavy metal contaminated soil leaching device (Patent No.: 2014201925927)[5]

2.2. Test methods
2.2.1. Determination of indicators
X-ray scanning and X-ray scanning micro-analysis of lead-zinc contaminated soil was performed using JSM-5600 LV scanning electron microscope and IE 300 X EDS spectrum. The existence of heavy metals was analyzed by BCR continuous extraction method.
2.2.2. Citric acid leaching test
The experiment was carried out with leaching agent citric acid. The leaching concentration was 0.4 mol/L and the time was 8 min. The migration of lead before and after leaching was determined.

3. Test results analysis

3.1. SEM-EDS analysis of contaminated soil
The results of scanning electron microscopy showed that before leaching, the content of silicon-zinc was relatively high, the content of lead was low, and elements such as lead, zinc, silicon and aluminum were partially wrapped. After leaching, the lead content was significantly reduced, and the removal rate was 12.3%.

On the side of the bridge-lead zinc-zinc tailings reservoir, the grid method is used to lay points at four different depth levels (1 layer, 0~0.2, 0.4~0.6, 0.8~1.0, 1.2~1.4 m). 2, 3, and 4 layers were sampled and tested. The typical 2# sampling point was used to analyze the existence and trends of a class of heavy metals.

The results show the existence of lead in different depth levels and its relationship with the depth level. Before leaching, the lead content in the surface layer was the lowest, and the content increased as the depth increased, as shown in Figure 1. The decrease in the depth of lead in the reducible state is reduced, because the eluted lead is adsorbed by the iron-manganese hydroxide and remains in the surface layer, while the lower layer is caused by the low oxygen content and the small amount of adsorbed lead. After leaching, the heavy metal lead is basically in the form of acid extractable state, indicating that citric acid can effectively remove the heavy metal ions with strong mobility, high bioavailability and high environmental risk, and achieve the repair effect; Part of the residual and oxidized heavy metal ions reduce potential environmental risks. This shows that citric acid can change the existence of heavy metals and achieve the desired repair effect.

![Figure 1. Shows the relationship between the existence of lead and depth](image)

3.2. Safety evaluation of soil after leaching
According to the national soil environmental quality standard (GB 15618-1995) and the soil background value of the study area, the index method was used to evaluate the soil environmental quality and pollution status.

The pollution index of soil pollutants is marked by the ratio of the measured value of soil pollution to the evaluation value. The method is simple and convenient, and the meaning of the index is relatively clear. The calculation formula is Pi= Ci/Si, where: Pi represents the pollution index of pollutant i in soil; Ci represents the measured value of pollutant i in soil; Si represents the evaluation standard of pollutant i. Pi≤1 indicates soil is not Contaminated; Pi>1 indicates that the soil is contaminated, and the larger the
value of Pi, the more serious the soil is contaminated. The results of the monitoring and pollution index calculation are shown in Tables 1 to 4.

Table 1. Determination results of lead and zinc contaminated soil before leaching Unit: mg/kg

| Number | Monitoring project | Cr  | Ni  | Cu  | Zn  | Pb  | Cr  |
|--------|--------------------|-----|-----|-----|-----|-----|-----|
| 1      | 133.0              | 82.7| 60.6| 566 | 937.0| 4.48|
| 2      | 129.2              | 70.5| 52.5| 48.9| 924.1| 5.37|
| 3      | 137.1              | 67.4| 74.1| 553 | 940.3| 6.45|
| 4      | 88.4               | 55.5| 75.9| 504 | 898.6| 5.60|
| 5      | 116.9              | 97.7| 40.5| 442 | 937.7| 5.39|
| 6      | 116.6              | 90.4| 32.2| 288 | 935.4| 5.69|
| 7      | 121.0              | 74.8| 53.9| 301 | 877.5| 6.92|
| 8      | 121.3              | 77.5| 44.9| 355 | 899.9| 5.44|
| 9      | 99.1               | 54.2| 63.7| 283 | 847.5| 5.1 |
| 10     | 127.0              | 71.1| 72.7| 594 | 927.7| 5.26|
| Soil background value | 60.2 | 19.5 | 30.2 | 124.9 | 83.7 | 5.60 |

Table 2. Calculation results of soil surface standard index before leaching

| Number | Monitoring project | Cr  | Ni  | Cu  | Zn  | Pb  |
|--------|--------------------|-----|-----|-----|-----|-----|
| 1      | 0.33               | 0.41| 0.15| 1.13| 1.87|
| 2      | 0.32               | 0.35| 0.13| 0.10| 1.85|
| 3      | 0.34               | 0.34| 0.19| 1.11| 1.88|
| 4      | 0.22               | 0.28| 0.19| 1.01| 1.80|
| 5      | 0.29               | 0.49| 0.10| 0.88| 1.88|
| 6      | 0.29               | 0.45| 0.08| 0.58| 1.87|
| 7      | 0.30               | 0.37| 0.13| 0.60| 1.76|
| 8      | 0.30               | 0.39| 0.11| 0.71| 1.80|
| 9      | 0.25               | 0.27| 0.16| 0.57| 1.70|
| 10     | 0.32               | 0.36| 0.18| 1.19| 1.86|

From Tables 3 and 4, the lead and zinc heavy metal pollution indicators have exceeded the national secondary standards, posing a great threat to the growth of surrounding vegetation, and also posing great health risks to surrounding organisms and residents, indicating heavy metals. The pollution is already extremely serious and there is an urgent need for governance. Therefore, it is particularly important to use the leaching method to treat the contaminated soil around the lead-zinc tailings pond and waste rock yard.

Table 3. Determination results of lead and zinc contaminated soil after leaching Unit: mg/kg

| Number | Monitoring project | Cr  | Ni  | Cu  | Zn  | Pb  |
|--------|--------------------|-----|-----|-----|-----|-----|
| 1      | 94.7               | 37.4| 32.5| 177.7| 492.9|
| 2      | 92.0               | 31.9| 28.1| 15.4 | 486.1|
| 3      | 97.6               | 30.5| 39.7| 173.6| 494.6|
| 4      | 62.9               | 25.1| 40.7| 158.3| 472.7|
| 5      | 83.2               | 44.2| 21.7| 138.8| 493.2|
| 6      | 83.0               | 40.9| 17.3| 90.4 | 492.0|
| 7      | 86.2               | 33.8| 28.9| 94.5 | 461.6|
| Numble | Cr  | Ni  | Cu  | Zn  | Pb  |
|-------|-----|-----|-----|-----|-----|
| 1     | 0.24| 0.19| 0.08| 0.36| 0.99|
| 2     | 0.23| 0.16| 0.07| 0.03| 0.97|
| 3     | 0.24| 0.15| 0.10| 0.35| 0.99|
| 4     | 0.16| 0.13| 0.10| 0.32| 0.95|
| 5     | 0.21| 0.22| 0.05| 0.28| 0.99|
| 6     | 0.21| 0.20| 0.04| 0.18| 0.98|
| 7     | 0.22| 0.17| 0.07| 0.19| 0.92|
| 8     | 0.22| 0.18| 0.06| 0.22| 0.95|
| 9     | 0.18| 0.12| 0.09| 0.18| 0.89|
| 10    | 0.23| 0.16| 0.10| 0.37| 0.98|

Table 4. Calculation results of soil surface standard index after leaching

It is concluded from Table 3 and Table 4 that after the soil is repaired, the growth of the plant is reduced, and the leaching concentration of each metal element in the mixed soil after repair is within the standard value, reaching the soil quality level three. The standard guarantees the growth of agroforestry and the normal growth of plants. The quality of the soil is basically no harm or pollution to plants and the environment.

4. Conclusions

1) The citric acid test shows that the lead content in the surface layer was the lowest before leaching. It exists in the form of acid extractable state of the heavy metal lead after leaching, and also removes some residual metal ions in the residual state and oxidation state, which reduces the potential environmental risk.

2) Citric acid can change the existence of heavy metals and achieve the desired repair effect. After being repaired, the contaminated soil reduces the risk of plant growth, and the leaching concentration of each metal element in the mixed soil after repair is within the standard value range, reaching the soil quality level 3 standard.

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