# Chemical state analysis of lead and zinc in soil of xitieshan mining area in the northern margin of qaidam basin

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**Abstract.** The chemical state of Pb, Zn can explain the migration law, and evaluate the threat of heavy metal pollution. The three-step continuous extraction method of BCR was adopted to divide the chemical forms of Pb and Zn in the soil into the acid-exchanged, oxidizable, reducible, and residual states. It was found that the coefficient of variation and the degree of dispersion of exchangeable, oxidizable, and reducible states were large, the results showed that all the chemical forms of Pb, Zn in soil were greatly affected by external sources except the residual state. Most of the Pb chemical forms in the mining area exist in the reducible and residual state, Zn is mainly in the oxidizable state and the reducible state; Pb is mainly in the oxidizable state, and most of the Zn is in the residual state in reference area. The oxidizable state and the reducible state are easily released when the redox potential changes, and the residual Zn may be released under severe environmental conditions, it is shown that the migration of silicate, primary and secondary minerals is difficult after natural geological weathering, etc. The contents of Pb, Zn in all forms were positively correlated with Ph of soil, positively correlated with sand content, and negatively correlated with clay content. The reasons were related to the enrichment of Pb, Zn mineralization elements in the mining area. These chemical states can indicate the chemical effects and accumulation patterns of Pb, Zn in soil.

## 1. Introduction

The northern margin of the Qaidam Basin is a very important lead-zinc metallogenic belt in Qinghai. The Xitieshan lead-zinc deposit is one of the most typical large-scale lead-zinc deposits in the region, the lead-zinc ore body is layered, Vein and lenticular. The deposit was discovered in the 1950s and was developed on a large scale in 1982, the ore body is NW-distributed, the strips are irregular, the area is about 9km$^2$, the geological structure is very complex, and the tectonic fissures develop strongly. The amount of resources in Xitieshan Pb-Zn concentrate area in the northern margin of Qaidam is about 70% of the total resources in the whole province. Since the mine was put into operation, the accumulated mining volume has reached 1,796.45 x 10$^4$ tons. According to statistics, 0. 42 t of waste rock and 0. 52 t of tailings will be produced per ton of ore on average, and 0. 04 t of waste slag will be produced. When galena sphalerite is exposed to the surface environment, the chemical composition and flow state of the galena will change, It is easy to be oxidized and hydrolyzed, which causes the release and migration of Pb, Zn elements to the ecological environment, and continue to accumulate in the carrier[1-4]. Pb$^{+2}$ can replace clay minerals that adsorbed by Ca$^{+2}$, Zn participates in the substitution reaction in the soil and occurs fixed accumulation, and can form sulfates, phosphates, carbonates, hydroxides, and sulphide precipitates, which has strong Regional, long-term, irreversibility and other characteristics. The lower the pH value of leaching fluid, the higher the oxidation rate of galena and

sphalerite, which increases the contamination risk of Pb, Zn element and biological effects[5-7]. A series of chemical properties of Pb, Zn determine its complexity in the ecological environment. During the migration process of Pb and Zn, a series of complex physical-chemical interactions such as precipitation-hydrolysis, ion exchange, and adsorption occur, the state of occurrence of elements changes obviously with the chemical properties of solid minerals and solution. Through research and analysis of chemical reaction mechanism and transformation about galenite, sphalerite, and find out its reductive state, silicate state, general reductive state, exchangeable state, oxidizable state and carbonate state[8-9], it is of scientific significance to understand the geochemical behavior process of Pb, Zn elements and to explore the migration mechanism of heavy metals in this area.

## 2. Experimental design and methods

### 2.1. Sample collection and processing
Xitieshan mining area is located in the eastern part of Dachaidan, Haixi, Qinghai Province, about 72km. The mining area as the study area, and the surrounding area of Dachaidan is taken as the reference area. Two sections of soil samples are selected in the mining area and the reference area respectively, and the section length is about 300m. The distance between samples on each section is controlled at 10m, sampling depth is 0-10cm, continuous collection, soil analysis is made by multi-point collection and mixing, according to azimuth in the range of 100m$^2$, collect 5 samples, take 1.000kg as mixture sample after mixing. The samples are stored in plastic bags, marked with the number and corresponding records. After being brought back to the laboratory, 100 g of soil is weighed and dried at a constant temperature. The agate ball mill is finely crushed, passed by a 100 mesh steel screen, and stored in a dry place.

### 2.2. Experimental Design
The plasma and mass spectrometry techniques (ICP-MS) were used to optimize the measurement conditions and experimental conditions of the instrument and equipment, including the preparation of the standard solution, the pre-treatment of the samples, the instrument parameters. Discussing the distribution characteristics, potential hazards, screening of effective indicators, calculating of morphological content distribution of Pb, Zn elements, in order to reveal geochemical processes of sedimentation, release and migration of the Pb, Zn elements in the mining area in a particular environment. Being familiar with the distribution characteristics, overall morphology, mineral composition, crystal grain size, color, lightness and composition changes in galena and sphalerite minerals, mastering the distribution of chemical forms of Pb and Zn, significance levels, content gradients, background values change period and other datas.

## 3. Experimental analysis

### 3.1. Ore light identification
Through field observation and laboratory light slice identification, there are more than 10 types of minerals being found in the mining area. Among them, galena has the characteristics of grayish white, semi-automorphic crystal to other granular, opaque, white under reflected light, markedly triangular, holes and scratches on the surface are identification features with a content of about 6%. It is semi-angular in shape, often produced together with pyrite and sphalerite, with a particle size between 60 and 200 μm, typically 80 to 100 μm. Some parts of the sphalerite cracks are distributed in a certain direction. Characteristics of sphalerite: dark gray, high iron content makes the internal reflection color more black or blue-black, semi-automorphic crystal to other crystal, brown to black, there is galena in the sphalerite sharp angle syndrome, symbiotic with galena, reflection color is pure gray, homogeneous, content 5%. Under the mirror, it is pure gray, granular, often produced with pyrite, chalcopyrite and galena, common emulsion or grid solid solution decomposition, particle size between 10-250μm, generally 100-150μm (Figure 1).
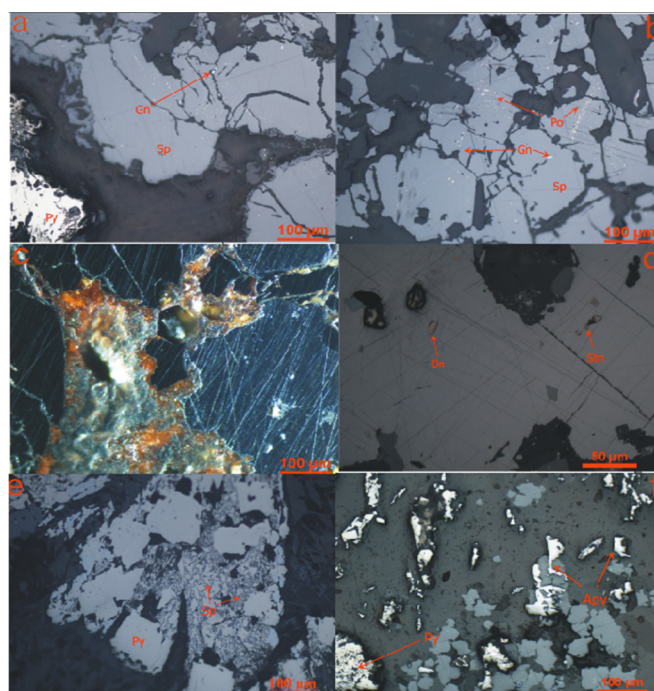
Figure 1. Identification of the composition of lead-zinc ore

### 3.2. Tailings sample main element content

The content of major elements in the tailings was measured using a PANalytical Axios type X-ray fluorescence spectrometer (XRF) (Table 1), the results showed that the elements with higher contents were Al, Si, Fe, K, and Ca, and the sum of the five elements exceeded 80%.

Table 1. A Sample constant element analysis results feature value.

| Serial number Wt% | Xts-1 | Xts-2 | Xts-3 | Xts-4 | Xts-5 | Xts-6 | Xts-7 |
|---|---|---|---|---|---|---|---|
| $Na_2O$ | 0.04 | 0.05 | 0.03 | 0.53 | 2.63 | 2.97 | 2.72 |
| $MgO$ | 0.31 | 0.47 | 0.50 | 0.51 | 3.20 | 3.20 | 3.32 |
| $Al_2O_3$ | 14.70 | 15.28 | 12.54 | 14.73 | 16.24 | 16.20 | 16.22 |
| $SiO_2$ | 67.64 | 67.30 | 71.23 | 66.07 | 55.43 | 55.75 | 56.03 |
| $P_2O_5$ | 0.12 | 0.12 | 0.08 | 0.13 | 0.35 | 0.35 | 0.35 |
| $K_2O$ | 5.12 | 3.67 | 3.70 | 7.31 | 2.15 | 2.18 | 2.05 |
| $CaO$ | 2.86 | 2.67 | 3.20 | 2.33 | 6.42 | 6.20 | 6.72 |
| $TiO_2$ | 0.37 | 0.43 | 0.33 | 0.44 | 1.32 | 1.33 | 1.30 |
| $MnO$ | 0.18 | 0.14 | 0.17 | 0.11 | 0.12 | 0.21 | 0.13 |
| $Fe_2O_3$ | 2.81 | 2.46 | 1.76 | 2.77 | 3.82 | 4.12 | 4.49 |
| $FeO$ | 0.46 | 1.30 | 1.20 | 0.90 | 5.52 | 5.23 | 4.92 |
| $H_2O+$ | 2.64 | 3.42 | 2.26 | 1.56 | 1.78 | 1.87 | 1.49 |
| $CO_2$ | 2.52 | 2.56 | 2.86 | 2.43 | 0.82 | 0.16 | 0.03 |
| Sum | 99.77 | 99.87 | 99.86 | 99.89 | 99.80 | 99.77 | 99.78 |

### 3.3. Morphological analysis

According to the three-step continuous extraction method proposed by the European Community Standards Agency, the chemical forms of Pb, Zn are divided into the acid exchange state, the oxidizable state, the reducible state, and the residual state. Accurately weigh 1.000g samples in a

50mL centrifuge tube, adding 20mL to 0.11mol/L HAc solution, oscillate (25±0.5) °C, centrifuge for 20min, transferring the supernatant to polyethylene tube, saving for acid exchange. In the above residue, 20 mL of a freshly prepared 0.5 mol/L $NH_2HC$ solution (hydroxylamine hydrochloride) solution was added, oscillated at (25±0.5)° C, centrifuged for 20 minutes, and the supernatant was transferred to a polyethylene tube for storage, reducible state in storage solution.

Add 5mL of 30% $H_2O_2$ solution to the residue slowly, place it at room temperature for 1h, then eva porate to a solution in (85±2) °C water bath, and repeat adding 30% $H_2O_2$ solution (the amount is redu ced), and the solution is nearly dry, after cooling 20 mL of 1.0 mol/L $NH_4Ac$ solution was added and s haken at (25±0.5)°C. After centrifugation for 20 min, the supernatant was transferred to a polyethylene tube for storage. The preservation solution was oxidizable, the residue after extraction in organic form was $HNO_3$-HCL-HF (volume ratio is 3:1:1) mixed acid was subjected to microwave digestion and the digestion solution was in a residual state.

*3.4. Dissolution test*
The dissolution experiment was adopted in June 2017 (study area and reference area), the sampling depth was 0-10cm, the sampling was based on the actual design of the mining area, each sample was weighed in 5 pieces, and soaked in 150 mL of HCL, the leachate was filtered through a 0.45μm filter with a certain period of time, the concentration of the extract, Pb and Zn was measured by using an ICP-OES (US PE 5300 model), the ICP-MS was used for each form of Pb, Zn (US Thermo X series II) (Table 2).

Table2. Pb and Zn contents in various forms of soil in the study and reference area(mg/kg)

| Chemical form | Xitieshan mining area Pb, Zn | | Dachaidan reference area Pb, Zn | |
|---|---|---|---|---|
| | Pb | Zn | Pb | Zn |
| Acid exchange state | 12.16 | 15.86 | 2.21 | 0.96 |
| Reducible state | 289.68 | 789.61 | 3.16 | 8.17 |
| Oxidizable state | 116.21 | 998.67 | 9.24 | 13.69 |
| Residual state | 256.39 | 416.24 | 1.56 | 41.18 |
| Total amount | 674.44 | 2220.38 | 16.17 | 64.00 |

## 4. Pb, Zn geochemical effects
The oxidation of sulphides in Xitieshan lead-zinc mines promotes the violent dissolution of metals, and the soil surface environment is the important media for the migration of Pb and Zn. In this study, microwave digestion and BCR method were used to analyze the total and morphological values of Pb, Zn in the soil environment. The distribution of total Pb, Zn in soil also showed obvious spatial distribution characteristics. The total amount of Pb, Zn in the mining area is significantly higher than that in the reference area, which indicates that mining activities are the direct cause of heavy metal pollution. Pb, Zn migrate to the surrounding areas in the mining area, and the sedimentation area is enriched obviously. The content of Pb, Zn in the soil varies in different seasons. The dry season was relatively higher than the rainy season, indicating that the rainwater increased the leaching effect of the soil, and the soil profile analysis better reflected the characteristics of long-term and irreversible soil pollution. The soil sampling depth was negatively correlated with the Pb, Zn content. The four forms of Pb, Zn in the soil, such as acid exchangeable, reducible, oxidizable and residual, can reflect the mechanism of lead and zinc distribution in the mining area.

The analysis results can be seen (Fig.2-Fig.3), the Pb chemical state in the soil environment of the mining area has the distribution law: reducible state > residual state > oxidizable state > acid exchange state, Zn chemical state: oxidizable state > reducible state > Residual state > acid exchange state; Pb chemical state in the reference area has distribution pattern; oxidizable state > reducible state > acid exchange state > residual state, Zn chemical state has residual state > oxidizable state > Reduced state >

Distribution pattern of acid exchange state. It was found that the coefficient of variation and the degree of dispersion of the exchangeable, oxidizable, and reducible states were large, indicating that the existence of Pb and Zn in the soil was greatly affected by exogenous sources. Most of the Pb exist in the reducible and residual state in the mining area, Zn is mainly in the oxidizable state and the reducible state; Pb is mainly in the oxidizable state in the reference area, and most of the Zn is the residual state. The oxidizable state and the reducible state are easily released when the redox potential changes, and the residual Zn may be released under severe environmental conditions, indicating that natural geological weathering exists in silicates, primary and secondary minerals, etc., migration is more difficult. These chemical states better track the chemical effects and accumulation patterns of Pb, Zn in soil.
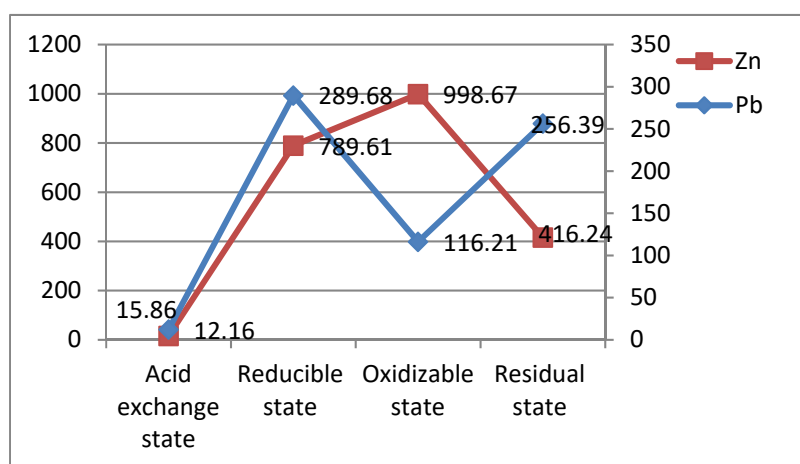


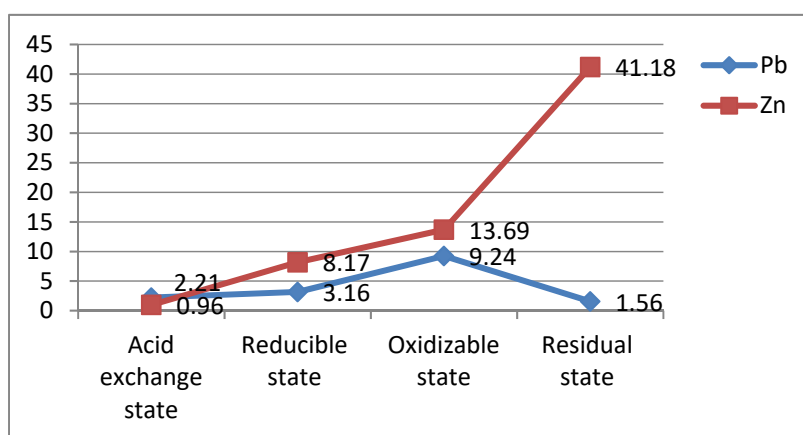Figure 2. Occurrence patterns of Pb and Zn in the mining area



Figure 3. Reference pattern Pb and Zn

## 5. Conclusion

(1) The determination of the composition of the ore and the analysis of the main quantity are carried out, datas of galena and sphalerite mineralogy and chemical composition were obtained. The chemical forms of Pb, Zn in soil were distinguished by the three-step continuous extraction method of BCR, it is an acid exchange state, an oxidizable state, a reducible state, and a residual state. The morphological analysis and dissolution experiments of Pb, Zn in soil were carried out. The total and morphological values of Pb, Zn in soils in the study areas and reference areas were determined. The coefficient of variation of exchangeable, oxidizable, and reducible states was obvious. The strong degree of dispersion indicates that the existence of Pb and Zn in the soil is greatly influenced by exogenous sources.

(2) The results of geochemical analysis indicate that the chemical state of Pb in the soil environment of the mining area has the distribution law: reducible state > residual state > oxidizable state > acid exchange state, distribution pattern of Zn chemical state is oxidizable state > reducible state > residual state > the acid exchange state; Pb chemical state in the reference area has distribution rule: oxidizable state > reducible state > acid exchange state > residual state, The distribution pattern of Zn chemical state is residual state > oxidizable state > reducible state > the acid exchange state. These chemical states can better track the chemical effects and accumulation patterns of Pb and Zn in soil.

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