Study on Sludge Characteristics of Lead and Zinc Smelting Acid and Sewage

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Abstract. Taking the lead and zinc smelting acid and sewage as the research object, the indicators of sludge moisture content, leaching concentration, corrosivity, phase, chemical composition, soluble salt dissolution rate were tested. The lead and zinc smelting acid and sewage was dried to different temperature, then the leaching toxicity and corrosivity of the original samples were measured, and the arsenic and selenium of the sludge was analyzed by the effects of leaching toxicity and corrosivity at different temperatures. The conclusions show that when lead and zinc sludge were mixed, with the temperature of 160 ℃, the leaching concentrations of arsenic and selenium are lower than the leaching toxicity standard, and the pH value is between 2.5-12.5, which is lower than the corrosive standard.

1. Introduction
In recent years, the scale of lead and zinc industry had been continuously expanded in China [1]. As a result, the green development of the lead and zinc industry is arduous, and the development of the industry also facing prominent problems such as the difficulty in treating tailings and smelting slag and the serious pollution of heavy metals such as arsenic. The effective use and safe disposal of arsenic-containing solid wastes is also the primary task of non-ferrous metal industry in the field of environmental protection in China [2].

Commonly, the treatment methods in acidic arsenic wastewater include chemical precipitation and adsorption. The lime iron salt method is the main treatment method of acidic arsenic-containing wastewater in this project, so that heavy metal ions and arsenic are precipitated and dehydrated to form a semi-solid arsenic-containing sewage sludges.

This study intends to carry out the effects of sludge moisture content on pH, arsenic and selenium leaching toxicity of the lead and zinc smelting acid and sewage sludges.

2. Test materials and methods

2.1. Test materials
The selected the lead and zinc smelting acid and sewage sludges in this study includes:
(1) The sludge of the lead smelting acid and sewage sludge: brown, with a moisture content of 35%-40%, referred to as lead sludge.
(2) The sludge of the zinc smelting acid and sewage sludge: light gray, with a moisture content of 30%-35%, referred to as zinc sludge.
2.2. Status of sludge storage
The annual stacking capacity of the slag yard is about 2-3 million tons, and the stockpiling capacity is large.

2.3. Measurement indicators
The indicators are sludge moisture content, leaching concentration, corrosivity, phase, chemical composition. The raw materials for drying are electrically heated blast drying oven (BGZ-246). The moisture is measured by the soil moisture analyzer (MA150), the preparation of the leaching toxic leachate using a large flip oscillator (GGC-D), the preparation of the corrosivity leachate using a large flip oscillator (GGC-9), the toxic leachate filter device using a vacuum suction filter (imported from Australia), the corrosiveness measurement using a desktop pH / ion meter (SmartTester-CPI505); the chemical composition analysis using an ICP detector (ICAP 6000). The concentration of heavy metal ions is determined by flame atomic absorption spectrometer (Aanalyst 800), the mineral composition is analyzed by X-ray diffraction (ULTIMA-4, Japan Science Association).

The leaching toxicity test was performed in accordance with the "Solid waste-Extraction procedure for leaching toxicity-Sulphuric acid & nitric acid method (HJ / T 299-2007), and the experimental analysis was performed in accordance with the “Identification standards for hazardous wastes-Identification for extraction toxicity “(GB5085.3-2007). The experiments were performed in accordance with the "Solid waste-Glass electrode test-Method of corrosively"(GB / T 15555.12-1995), and the experimental analysis was performed in accordance with the “Identification standards for hazardous wastes-Identification for corrosivity "(GB5085.1-2007). The stirring device uses a precision booster electric mixer (JJ-1) (200w).

2.4. Test method
After the lead and zinc smelting acid and sewage sludges was naturally dried, the leaching concentration, corrosivity, phase, chemical composition, and soluble salt dissolution rate were measured.

The lead and zinc smelting acid and sewage was dried to a certain temperature (60 °C, 105 °C, 160°C, 220°C), then the leaching toxicity and corrosivity of the original samples were measured, and the arsenic and selenium of the two sludges was analyzed by the effects of leaching toxicity and corrosivity at different temperatures.

3. Experimental results and analysis

3.1. Analysis results of main chemical components of sludge from the lead and zinc smelting acid and sewage sludges.

The main chemical composition of lead and zinc sludge by ICP detector in Table1 and Table2.

| Chemical components | Al | As | Ba | Be | Bi | Ca | Cd | Co | Cr | Cu |
|---------------------|----|----|----|----|----|----|----|----|----|----|
| Measured value      | 0.35 | 2.08 | <0.05 | <0.05 | 0.07 | 19.68 | 0.08 | <0.05 | <0.05 | 0.12 |

| Chemical components | Fe | K | Na | Se | Li | Mg | Mn | Ni | Pb | Sb |
|---------------------|----|---|----|----|----|----|----|----|----|----|
| Measured value      | 3.77 | 0.025 | 0.42 | 0.016 | <0.05 | 0.16 | <0.05 | <0.05 | 0.11 | <0.05 |

| Chemical components | Sn | Sr | Ti | V | Zn | P_{2}O_{5} | S | SiO_{2} |
|---------------------|----|----|----|---|----|-------------|---|---------|
| Measured value      | <0.05 | <0.05 | 0.11 | <0.05 | 0.24 | 1.06 | 14.19 | 2.23 |
### Table 2. Analysis results of main chemical components of sludge from zinc smelting

| Chemical components% | Al | As | Ba | Be | Bi | Ca | Cd | Co | Cr | Cu |
|----------------------|----|----|----|----|----|----|----|----|----|----|
| Measured value       | 0.25 | 0.027 | <0.05 | <0.05 | <0.05 | 22.7 | 0.11 | <0.05 | <0.05 | <0.05 |
| Chemical components% | Fe | K | Na | Se | Li | Mg | Mn | Ni | Pb | Sb |
| Measured value       | 0.11 | 0.006 | 0.48 | 0.0017 | <0.05 | 0.06 | <0.05 | <0.05 | <0.05 | <0.05 |
| Chemical components% | Sn | Sr | Ti | V | Zn | P$_2$O$_5$ | S | SiO$_2$ |
| Measured value       | <0.05 | <0.05 | <0.05 | <0.05 | 0.22 | 0.044 | 17.03 | 1.35 |

From Table 1 and Table 2, it can be known that the composition of lead and zinc sludge was more complicated, including harmful components such as arsenic, selenium, and heavy metal cadmium. The higher value of S and Ca content indicates that gypsum was the main component, and other components such as Fe$_2$O$_3$, and having potential gelling activity.

#### 3.2. Phase analysis results of lead and zinc sludge

![Figure 1. X-ray diffraction pattern of lead sludge zinc sludge](image)

From Figure 1, the main phases of the lead and zinc sludge were CaSO$_4$ • 2H$_2$O and contained a small amount of CaSO$_4$ • 0.5H$_2$O. The relative content of CaSO$_4$ • 0.5H$_2$O in the lead sludge was higher than that in the zinc sludge From the experimental process, it found that the lead sludge coagulation rate was significantly faster than that in the zinc sludge.

#### 3.3. Results of leaching toxicity and corrosiveness of lead and zinc sludge

The leaching toxicity and corrosivity experiments were performed on lead and zinc sludge. The results are shown in the Table 3 and Table 4.

![Table 3. Analysis results of leaching toxicity of lead and zinc sludge (mg/ L)](image)

| No. | Hazardous ingredients | Limit of hazardous concentration in leachate | Lead sludge | Zinc sludge |
|-----|-----------------------|--------------------------------------------|-------------|-------------|
| 1   | Arsenic               | 5                                         | 6.92        | 0.13        |
| 2   | Selenium              | 1                                         | 1.34        | 0.22        |

According to the Standard for "Identification standards for hazardous wastes-Identification for extraction toxicity " (GB5085.3-2007) in the Table3, the leaching concentrations of Arsenic and...
Selenium in lead sludge were 6.917 mg/L (> 5 mg/L standard value) and 1.256 mg/L (> 1 mg/L standard), the leaching concentration of zinc sludge did not exceed the standard.

The results of the corrosivity measurement of lead and zinc sludge are shown in Table 4.

| Sample classification | pH standard limit | pH value | Corrosive |
|-----------------------|-------------------|----------|-----------|
| lead sludge           | ≤2 or ≥12.5       | 7.88     | non-corrosive |
| zinc sludge           | non-corrosive     | 12.00    | non-corrosive |

The pH value of lead sludge was 7.88 < 12.5 (standard value) in Table 3-6, non-corrosive; the pH of zinc sludge was 12.00 < 12.5 (standard value), no-corrosive. According to the Standard for “Identification standards for hazardous wastes—Identification for corrosivity” (GB5085.1-2007), the pH values of lead-zinc sludge are all greater than 2.0 and less than 12.5, which were determined that the solid waste were not corrosive.

3.4. Effect of different temperatures on leaching concentration and corrosivity of arsenic and selenium in the lead sludge

Figure 2. Effect of different temperatures on leaching concentration and pH of arsenic and selenium in lead sludge

The temperature of 80 ~ 120 °C belongs to the process of mass loss of sludge, mainly due to the evaporation of physically adsorbed water. The mass loss will increase with the temperature of 120 ~ 300 °C, mainly due to the reduction of crystal water [3]. In this study, the water was completely evaporated naturally with the temperature of 20 °C under normal temperature conditions; the loss of crystal water was with the temperature of 160 °C and 220°C under high temperature conditions.

From Figure 2, with the increase of the temperature, the leaching concentration of arsenic in lead sludge was gradually decreased, and the leaching concentration of selenium was increased first, then was decreased and then was increased again. The range of pH value was smaller, which was ranging from 7.66-7.76. Among them, the leaching concentration of arsenic was the highest, and the leaching concentration and pH of selenium were the highest at room temperature.

It shows that heating to a certain temperature had no significant effect on reducing the pH value, the leaching concentration of selenium did not decrease significantly, but an increasing trend, and the leaching concentration of selenium was changed instably. The effect of reducing the leaching concentration of arsenic was more significant, reducing 6.15%, 58.75%, and 63.36%, respectively. When the heating temperature is between 160 °C-220 °C, the leaching concentration of arsenic is less than 5mg/L.

As the leaching concentration of arsenic in untreated lead sludge is higher than the standard value of leaching toxicity, the lead sludge has the characteristics of hazardous waste and has a certain risk of contamination. After a certain heating, the temperature is 160 °C. It can effectively reduce the leaching
concentration of arsenic to less than 5mg/L, and the leaching concentration of selenium doing not exceed 1mg/L, and the pH value is between 2.5-12.5. Therefore, the lead sludge under the treatment condition has no leaching toxicity and corrosive.

3.5. Effect of different temperatures on leaching concentration and corrosion of arsenic and selenium in the zinc sludge

It can be concluded from Figure 3 that with the increase of temperature, the leaching concentration of arsenic in zinc sludge has been gradually decreased, decreasing by 70.45%, 59.09%, and 81.82% respectively. The leaching concentration is less than 5mg/L. There is no risk of pollution. The leaching concentration of selenium showed a gradual increase trend, and the growth rates were more significant, which was increasing by 0.83 times, 1.58 times, and 3.92 times respectively. The range of pH value changes is quite significant, between 9.00-9.82, with the temperature increasing, the pH value gradually was increased. Among them, the leaching concentration of control arsenic was the highest, and the leaching concentration and pH value of selenium were the highest at 220 ℃.

It shows that when the zinc sludge was heated to a certain temperature, it has a significant effect on reducing the pH value. The leaching concentration of selenium would be increased, and the leaching concentration of arsenic would be decreased. As the leaching concentrations of arsenic and selenium in zinc sludge were both lower than the leaching toxicity standard value and the pH value was also lower than the corrosive standard value. Therefore, zinc sludge does not have the characteristics of hazardous waste and has no risk of pollution.

3.6. Effect of different temperatures on leaching concentration and corrosivity of arsenic and selenium in lead-zinc mixed sludge

It shows that when the zinc sludge was heated to a certain temperature, it has a significant effect on reducing the pH value. The leaching concentration of selenium would be increased, and the leaching concentration of arsenic would be decreased. As the leaching concentrations of arsenic and selenium in zinc sludge were both lower than the leaching toxicity standard value and the pH value was also lower than the corrosive standard value. Therefore, zinc sludge does not have the characteristics of hazardous waste and has no risk of pollution.
With the rising temperature, the leaching concentration of arsenic in 1.5: 1 mixed sludge basically was decreased gradually, decreasing by 50.35%, 71.35%, and 55.63% respectively in Figure 4. The leaching concentrations were lower than 5mg/L, which had no risk of contamination. The leaching concentration of selenium was increased gradually, increasing by 6.00 times, 6.42 times, and 18.33 times, respectively, and the leaching concentrations were higher than 1 mg/L with the temperature of 20℃ and 220℃, which was exceeded the leaching toxicity standard value. With the rising temperature, the pH value gradually was increased, and the change of range of pH value was not significant, between 8.05-8.44. Among them, the leaching concentration of arsenic was the highest, the leaching concentration of selenium was the highest at 220℃, and the pH of the control was the highest.

It shows that the leaching concentrations and pH of arsenic and selenium of the mixed lead and zinc sludge was changed with temperature close to that of lead sludge, but when the temperature becoming 160 ℃, the leaching concentrations of arsenic and selenium was lower than the leaching toxicity standard, and the pH value was between 2.5-12.5, which was lower than the corrosive standard.

![Figure 5. Effects of different temperatures on the leaching concentration and pH of arsenic and selenium in lead sludge: zinc sludge = 2: 1](image)

With Figure 5, it can be concluded that with the increase of temperature, the leaching concentration of arsenic in the 2: 1 mixed sludge basically was decreased gradually, decreasing by 52.35%, 72.83%, and 53.34% respectively, and the leaching concentrations were all lower than 5mg/L. There is no risk of contamination. The leaching concentration of selenium is gradually increasing by 7.00 times, 4.00 times, and 8.86 times respectively. The leaching concentration at 20℃ and 220℃ was higher than 1 mg/L, which was exceeded the leaching toxicity standard value. As the temperature increasing, the pH value was gradually increased, and the range of pH value change was not significant between 7.82-8.28. Among them, the leaching concentration of arsenic was the highest, the leaching concentration of selenium was the highest at 220 ℃, and the pH of the control was the highest.

It shows that when lead and zinc sludge were mixed, the leaching concentrations and pH of arsenic and selenium change with temperature close to that of lead sludge. But when the temperature was 160 ℃, the leaching concentrations of arsenic and selenium were lower than the leaching toxicity standard, and the pH value was between 2.5-12.5, which was lower than the corrosive standard.

4. Conclusions and recommendations
1) The leaching concentrations of arsenic and selenium in the fresh lead sludge produced by the filter press is exceed the standard, and the corrosiveness is not exceed the standard, which has the characteristics of leaching toxicity. The leaching concentration and corrosiveness of the fresh zinc sludge generated by the filter press is not exceed the standard. It does not have leaching toxicity and corrosive characteristics.

2) The main phases of lead and zinc sludge are CaSO4 • 2H2O and contain a small amount of CaSO4 • 0.5H2O.
3) Heating to a certain temperature, it can effectively reduce the leaching concentration of arsenic in lead and zinc sludge, that is, the maximum reduction is 63.36% when heated to 160 °C.

4) The leaching concentrations of arsenic and selenium change in opposite directions with the mixed lead and zinc sludge. Heating to a certain temperature, it will reduce the leaching concentration of arsenic to a certain extent. That is, when the heating temperature is 160°C, the leaching concentrations of arsenic and selenium and the pH values are below the leaching toxicity and corrosivity standards.

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