# Toxicity Identification of Ancient Smelting Slag

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**Abstract**: By taking the ancient smelted residue in Fengdu County Chongqing as research object，the waste residue's corrosion and leaching toxicity is analyzed and leaching ability of heavy metal in waste residue is analyzed through leaching toxicity test under different pH value conditions. The test results show that the waste residue is alkaline; the residual quantity of heavy metal is high; and the average content of heavy metal (zinc and plumbum) is up to 6.97%. However, heavy metal of waste residue is based mainly on residual state. Its leaching toxicity is low and potential harmful ability for environment is weakened obviously. It can indicate that forecasting the waste residue's potential harmful ability for environment by heavy metal's total quantity of waste residue is not exact. Leaching ability of heavy metal is significantly enhanced in extremely acidic and alkaline conditions. The leaching content of zinc，plumbum，chromium and cadmium is all up to maximum when pH is lower than three. The leaching ability of zinc，plumbum，chromium and cadmium is all increase when pH is higher than twelve，but its leaching content is lower than that in acidic condition. leaching ability of zinc，plumbum，chromium and cadmium is weakest in neutral condition.Under normal condition (pH of rainfall)，harmful ability for environment of ancient smelted residue has decreased to a lower level.It can be treated according to the requirement of general industrial solid wastes.

**Key words**: ancient smelted residue；heavy metal；leaching toxicity；leaching ability

A slag dump from smelting zinc ore during late Ming and early Qing Dynasty had been piled up along the Yangtze River which runs through Fengdu county of Chongqing municipality, southwest China. It potentially pollutes soil beneath and underground water since it contains a lot of heavy metals and poisonous elements[1,2]. The approach to measuring total quantity of heavy metal elements is most frequently used to evaluate the impact of tailings and mine slag on environment around, usually, the higher the heavy metal content, the more serious the influence on the surroundings[3]. J.M.Azcue et al[4] estimated the pollution that a tailings area has caused to its downstream lake areas based on the comparison of As and Pb contents contained in lake deposits which has tailings dump around and no tailings piled up, respectively. Baron S et al[5] has evaluated the contaminative characteristics of a pile of smelting slag of middle ages situated in a South France mountainous area by measuring the metal content and the isotope in the slag. Schreck P et al[6] indicate that the spread of heavy metal pollutants is due mainly to weathering and rainwater erosion after they investigated the mechanisms of heavy metal pollution in a copper mine area of Central German. Wu Chao et al[7] show that the mine refuse from a lead zinc mine has the soil beneath tailings greatly polluted. Zeng Min et al[8] have evaluated the potential risk for heavy metals from mine and smelting to pollute the rice-planted soil in Hunan Province, Central China. It is, however, supposed that the single total quantity of heavy metals contained in surrounding soil is not appropriate to predict their potential pollution to environment. The present paper is aimed to investigate the environmental toxicity of the old smelting slag so that appropriate methods can be used to deal with such pollution.

## 1 Test materials and procedures

### 1.1 sampling and preparation

The test samples were randomly sampled from Shanfutou smelting slag area in Fengdu county in November 2007[10]. The sampling depth is within the average slag depth of 2m and classified into the surface layer(0-30cm), the middle layer( 80-110cm) and the bottom layer(150-180cm). Samples were then sifted through a 20-mech sieve to separate out stones after naturally air-dried. Finally, the sifted samples were 200-mesh sieved again and oven-dried at 105℃.

### 1.2 test procedures

The pH of and heavy metals contained in slag at different layers were measured according to GB/T15555.12-1995[11] and HJ/T299-2007[12], respectively, see table 1.

Table 1 pH value and contents of Zn, Pb, Cr and Cd(mg/kg) of slag at different layer

| sample | depth | pH | Zn | Pb | Cr | Cd |
|---|---|---|---|---|---|---|
| 1 | Surface | 8.42 | 67000 | 1380 | 25 | 120 |

| | | | | | | |
|---|---|---|---|---|---|---|
| | Middle | 7.84 | 85000 | 2200 | 28 | 300 |
| | bottom | 7.33 | 84000 | 2300 | 40 | 320 |
| 2 | Surface | 8.56 | 54000 | 580 | 13 | 90 |
| | Middle | 7.94 | 63800 | 630 | 15 | 140 |
| | bottom | 7.42 | 67500 | 780 | 20 | 130 |
| 3 | Surface | 8.32 | 57800 | 580 | 0.1 | 80 |
| | Middle | 7.32 | 67300 | 730 | 5 | 120 |
| | bottom | 6.88 | 71000 | 680 | 10 | 150 |
| Average content | | | 68600 | 1095.6 | 17.3 | 161.1 |
| Maxmum | | 8.56 | 85000 | 2300 | 40 | 320 |
| minimum | | 6.88 | 54000 | 580 | 0.1 | 80 |

# 2 test results and analysis

## 2.1 Quantity of heavy metals in slag

Table 1 shows that the slag, dating back to late Ming and early Qing Dynasty, contains still a large quantity of heavy metals although several hundred years passed. Among them the content of Zinc ranges from 85000mg/kg to 54000mg/kg(averaging 68600mg/kg), that of Pb is within 580mg/kg -2300mg/kg(averaging 1095.6mg/kg), the content of Zn plus Pb averages 69695.6mg/kg, from which the grade of lead zinc ore is 14%. Assuming that the recovery coefficient is 38%(maybe smaller practically), the content of Zn plus Pb remaining in slag should be 14%×（1-38%）, i.e. 8.68%, which indicates that over 1.71% Pb+Zn has been released into the surrounding soils after several hundred years of lixiviation. The release of heavy metals into surroundings is a sophisticated and slow process. Form Figure 1, it can be seen that the quantity of remaining heavy metals in slag at surface layer is small, while that of middle and bottom layer is relatively high because the surface slag released more heavy metals under greater environmental impact than both the middle and bottom layers.

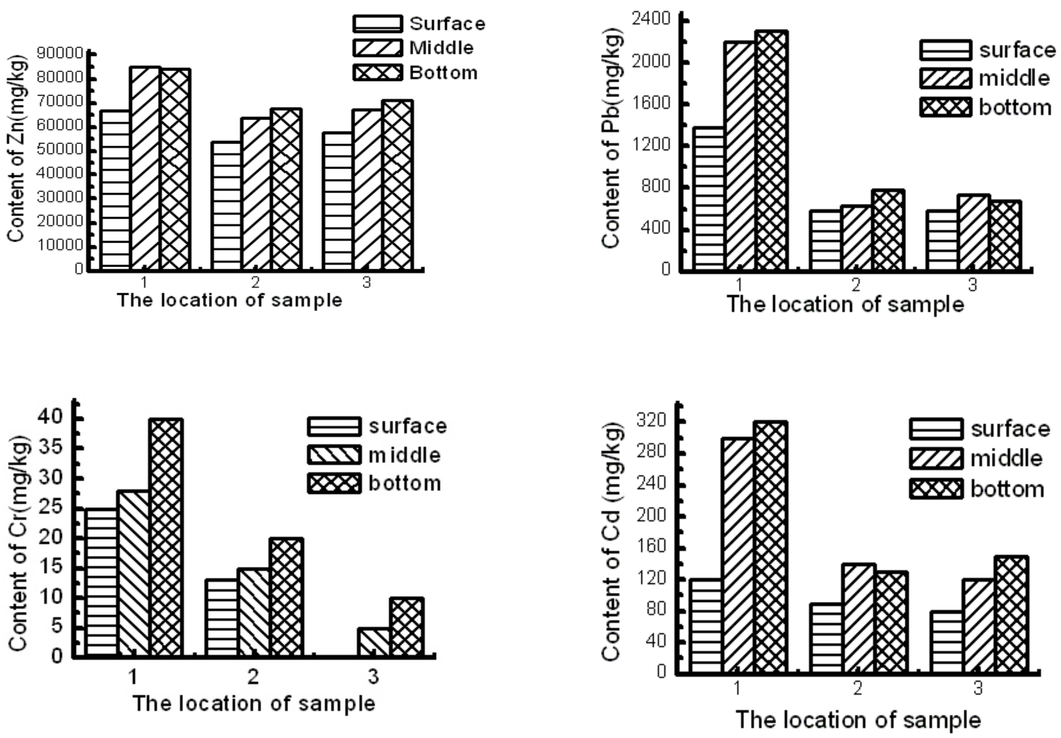


Fig.1 content of heavy metals for a section of the old slag area

### 2.2 Analysis of corrosivity

From table 1, it is seen that the pH values ranging from 6.88 to 8.56 indicate a slightly alkaline slag area. The higher pH values at surface layer signify the rainwater leaching is greater than both at middle and bottom layers, i.e. a slightly alkaline surrounding of pH value between 8-9 is not helpful for slag to release heavy metals. According to [14], it is, therefore, determined that the old smelting slag is a hazardous waste without corrosivity.

### 2.3 Toxicity identification test

The toxicity identification of various kinds of industry slag is paid great attention from home and abroad[15-16]. The lixivium from Fengdu slag area has been prepared according to HJ/T299-2007, the analysis results of which are listed in Table 2.

Table 2 Toxicity analysis (mg/L)

| Sample | depth | Total Zn | Total Pb | Total Cr | Total Cd |
|---|---|---|---|---|---|
| 1 | Surface | 0.005L | 0.013L | 0.015 | 0.070 |
| | middle | 0.008 | 0.013L | 0.017 | 0.202 |
| | bottom | 0.015 | 0.013L | 0.022 | 0.173 |
| 2 | Surface | 0.005L | 0.013L | 0.049 | 0.016 |
| | middle | 0.005L | 0.013L | 0.036 | 0.138 |
| | bottom | 0.01 | 0.013L | 0.026 | 0.598 |
| 3 | Surface | 0.005L | 0.013L | 0.024 | 0.134 |
| | middle | 0.005L | 0.013L | 0.017 | 0.150 |
| | bottom | 0.023 | 0.013L | 0.032 | 0.162 |

The slag from smelting lead zinc ore contains a large portion of heavy metals in residual form, implying the content of non-exchangeable heavy metals is low[17,18]. The several hundred years of leaching has migrated a portion of heavy metals in Fengdu slag into its surrounding soils, and the decrease of exchangeable heavy metals greatly reduces the leaching capability of slag. The investigation shows that few sampling spots leached Zn, which is similar to Cr and Cd, in addition, the leaching of Pb is below test limits. The leaching test on Fengdu smelting slag indicates that the time to leach Cr and Cd to a maximum content is longer than that for leahcing Zn and Pb, and the leaching behavior of Zn is similar to that of Pb, that of Cr similar to Cd, which agrees to the conclusions drawn by Yan Jianhua from leaching experiments of heavy metals in fly ash[19]. Tests results illustrate that the dominant residual form of heavy metals in slag leads to a weak lixiviation capability. Test results reveal that the slightly alkaline surrounding accounts for the low leaching toxicity of smelting slag. High contents of heavy metals and low leaching toxicity show that the single index of total heavy metal content in slag is not appropriate to predict the slag's environmental toxicity.

From above comparison and analysis, it is clear that the content of each item in lixivium does not exceed that of GB 5085.3-2007[20], i.e. the Fengdu slag is some hazardous waste without leaching toxicity.

2.4 Effect of pH value on leaching heavy metals

The pH value is commonly considered the most significant factor influencing the metal leaching[21-23]. All leaching experiments show a greatly strong relativity of heavy metals to pH value. From fig.2, it is seen that the leached quantities of Zn, Pb, Cr and Cd vary with pH value in some regular way, though the leached quantity are not great. Under extremely alkaline or acidic conditions, the four kinds of metals including Zn, Pb, Cr and Cd could be leached to some extent, and the leached quantities of Zn and Pb are larger that that of Cr and Cd. The leaching capability of Zn, Pb, Cr and Cd increases with decrease of pH value, and the leached quantity reaches the maximum under conditions of pH<3. when pH is within 5-11, the four metal leaching is all small, Cr leaching is smallest at pH being 11, while the leached quantities of four metals rise with pH>12, but smaller than that under acidic conditions. The above analysis indicates that the old smelting slag is characteristic of low leaching toxicity under ordinary rainfall[24]. The leaching properties of Cr is different from other metals due to its various state of existence. For example, Cr exists mainly in $CrO_4^{2-}$ in alkaline solutions, 100% at pH 11. Chromates but $K^+$,$Na^+$ and $NH_4^+$ seldom dissolve in water, while most dichromate dissolves in water, which accounts for the greater leached quantity of Cr under acidic conditions[25].

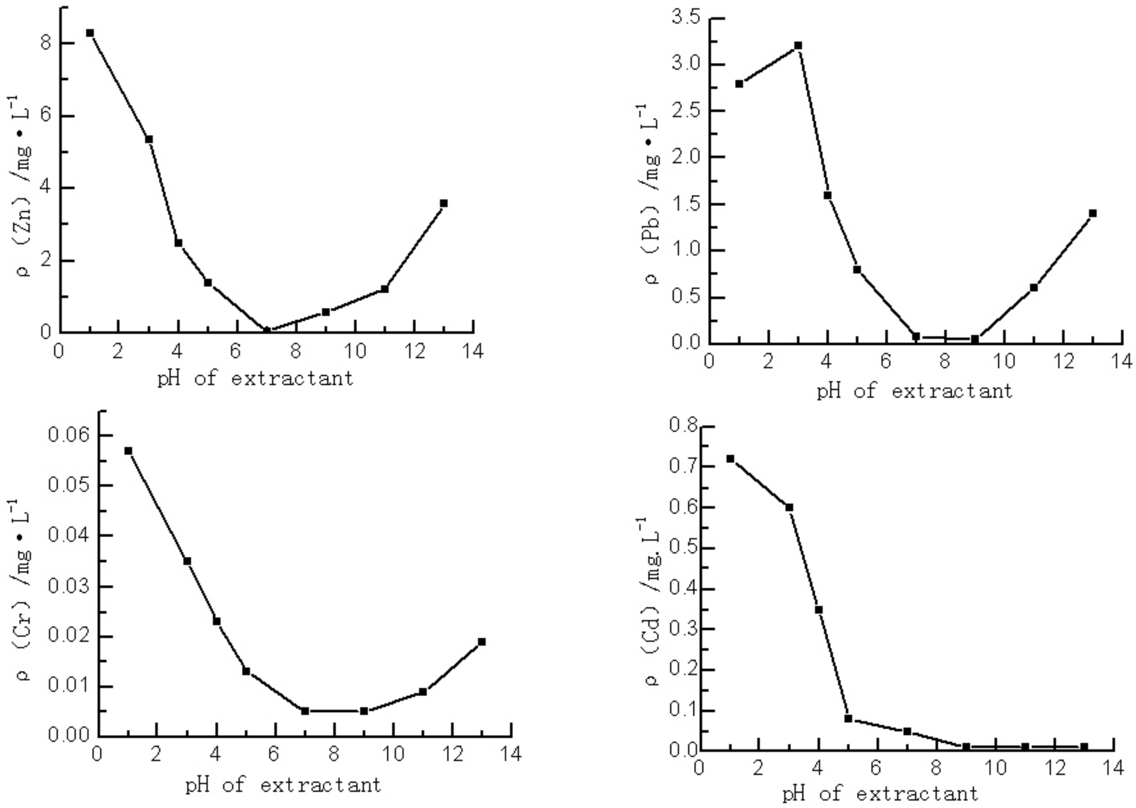


Fig.2. Variation of lixiviation quantity of heavy metals with pH value

# 3 Conclusions

(1) The slag is characteristic of slight alkalinity, which decreases leaching of metals under acidic conditions. The content of remaining Zn plus Pb in slag averages 6.97%. The remaining heavy metals, however, mainly exist in residual form, the four metals of Zn, Pb, Cr and Cd seldom leach and have greatly reduced adverse effect on the environment. Therefore, the evaluation of smelting slag's impact on the surrounding can't be dependant uniquely on the total quantity of heavy metals in slag.

(2) All leaching tests of heavy metals are greatly related to pH value. The leaching capability of Zn, Pb, Cr and Cd increases with decrease of pH value, and the leached quantity reaches the maximum under conditions of pH<3. when pH is within 5-11, the four metal leaching is all small, Cr leaching is smallest at pH being 11, while the leached quantities of four metals rise with pH>12, but smaller than that under acidic conditions. The old smelting slag is characterized by low leaching toxicity under ordinary rainfall, which indicates that the Fengdu slag could be dealt with according to standards for common industry solid wastes.

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