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Heavy metals contamination characteristics in soil of different mining activity zones

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Abstract: Depending upon the polluted features of various mining activities in a typical nonferrous metal mine, the contaminated soil area was divided into four zones which were polluted by tailings, mine drainage, dust deposition in wind and spreading minerals during vehicle transportation, respectively. In each zone, soil samples were collected. Total 28 soil samples were dug and analyzed by ICP-AES and other relevant methods. The results indicate that the average contents of Zn, Pb, Cd, Cu and As in soils are 508.6, 384.8, 7.53, 356 and 44.6 mg/kg, respectively. But the contents of heavy metals in different zone have distinct differences. The proportion of oxidizing association with organic substance is small. Difference of the association of heavy metals is small in different polluted zones.

Key words: mining activity; heavy metals; contamination; soil pollution; metal form

1 Introduction

The evaluation, mechanism and characteristic of heavy metals pollution near the mine were hotly discussed in recent years all over the world[1−9]. But the topic of recent studies is mostly tailing dam. These studies have achieved efforts on oxygenation of pyrites and sulf-pyrites and the origination of the acid mine drainage[3−6]. Due to the complexity of geochemistry process of bullocks, tailing oxygenation and metals transference in mine environment, there are still a lot of problems existed especially about the different characteristic of heavy metals pollution in different areas near the mine in China. The studies of solid waste in mine environment mostly were focused on phase, but the level of prevention and elimination is low comparatively, which is far behind studies overseas. The pollution occurs during the whole exploitation, and each process exposes different characteristics. So it is not rational to do the research generally to get information of heavy metal pollution. In this work, a Zn-Pb mine in Hunan Province, China, was chosen as an example, and full information of heavy metals pollution in different areas near the mine was got from investigation. It is useful for heavy metals pollution exclusion and reduction, as well as restoring and improving the polluted earth. The most important theory worthiness and practical meaning is to accelerate green resources mining and achieve harmonization between mine industry and environment.

2 Field situations of investigation

2.1 General information

The mine is located in Guiyang area of Chenzhou, Hunan Province, China, and was set up in 1967. The mine is exploited by the method of underground with 1 500 t day-production, and 3.9×10^5 t year-production. The main ore is Zn and Pb, accompanied by Cu, Ag, W, Sn, Mo and Fe, even U and Ra. The percent of dissociation SiO_2 in the ore is 5%−10%. The average height of the mine is 310 m and coverage is 50 km^2. The weather near the mine is following: year-average temperature is 19.3 ℃, north wind usually with average speed of 2.8 m/s. The tailing mine dam occupies an area of 1 km^2 and stores 5×10^6 m^3 tailing. The tailing mine is

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seated in the billabong between two mountains. The lower reach of the mine is field. The drainage from mine runs to the 4 000 t cistern by 24 pumps, then to the river. Wind-excluding-well is situated in the Baoling mountainside, which is covered by shrubs. The underground of the mountain is the deposit area of mine. On the foot of the mountain is field. The railway of rude mine, with shrubs at both sides, across mountainside, is 21 m higher than living section.

2.2 Zones division

Nonferrous metal mining activity includes mining, transportation and selective smelting, and each process will produce castoff in the form of solid, liquid and gas. Firstly, when ore is crushed, some heavy metals go to the earth surface along with polluted wind which comes from chiselling under well and explosion, then settle into the soil and water by air diffusion. Some enter into groundwater or surface water by sap drainage, some go into water or soil because of drop or dust during transportation on and under the ground. The selection process produces tailings which are stored in mine drainage recycles or used for irrigation or excluded by tailings dam holes after treatment. At the same time, the medicines for selection, mostly are heavy metals which are resembled with deleterious heavy metals such as Cu, Zn, Hg, Mn, Pb and Cd, and cause complex pollution. The fine ore goes into the soil of road sides because of drop and dust during transportation. So we can see that there are mainly 5 sources of heavy metals pollution as follows: 1) River accepted mine drainage; 2) Well settling dust in wind; 3) Tailings; 4) Railway transporting ore; and 5) Vehicle transporting minerals. The pollution affects neighbouring people little and don't include in this research, because the railway of rude mine is across mountainside and with shrubs at both sides.

According to the analysis above, each process can cause pollution. Thus, the contaminated soil area was divided into four zones which were polluted by tailings, mine drainage, settling dust in wind and spreading minerals during vehicle transportation, respectively. The four zones were called briefly W1 (tailings pollution soil), W2 (mine drainage pollution soil), W3 (dust in wind pollution soil) and W4 (minerals transportation pollution soil) in this work respectively. As the pollution areas of these zones are different, sample numbers are different. The area of W1 is the biggest, so we got 10 samples. The area of W2 is 4 500 m^2 which is centralized as a triangle in the south of mine. We got 8 samples there. W3 is more centralized and its pollution area is less, so 4 samples was enough. W4 is far away from field, and is separated by shrubs. Its pollution for field from dust wind changes from season to season. Then we selected 6 representative samples.

3 Investigation procedures

3.1 Samples collection and treatment

The 28 samples were taken by multi-mix manner opposite to the source of pollution. 2 referenced samples were got in the neighbouring area (depth is 100 cm)[8]. All the samples were ground after air-drying, passing through 10 mesh and 20 mesh screen, and reserved. Some samples by quartation were taken for the analysis of heavy metals quality and chemical configuration, ground again by carnelian mortar, and past through 100 mesh screen.

3.2 Assay

The sample passing 100 mesh screen was treated as the following steps: put 0.100 0 g sample in the tetrafluoroethylene plastics crucible, add 10 mL HF, 12 mL $HClO_4^-$, then heat to smoking disappearing. After cooling, add 1:1 HCl 10 mL, dissolve, then put into measuring flask. Apparatus type: PS-6 vacuum inductance coupling plasma atom emission spectrum (ICP-AES). Condition: frequency 40.68 MHz, power 1 100 W, cooling gas 10 L/min, carrying gas 0.3 L/min, plasma gas 0.4 L/min, integral time 5 s, integral degree 3. Standard: State No.1 GSS-1 and GSS-5.

Heavy metals chemical configuration assay method was as follows. After nitration by HNO_3^- - $HClO_4^-$ - HF, mine elements and heavy metal elements were measured by ICP-AES. European three-step-continuous-extract process was adopted for heavy metals elements classification. The classification has four groups: acid-extract form, oxide form, organic form and remains form.

The approach of extraction was as follows[10−14]. Firstly, add 0.1mo1/L HoAc 40 mL to 1.000 0 g sample, surge for 16 h at 20 ℃ to get acid-extract form elements. Secondly, the remains continued to surge for 16 h at 20 ℃ after adding 0.5 mol/L hydrochloric hydroxylamine and 0.05 mo1/L HNO_3^- 40 mL to get oxide form elements. Thirdly, the remains of step 2 were added with H_2O_2 (pH 2−3) 10 mL, deposited for 1 h at 20 ℃, then heated to 85 ℃ (1 h). Add 10 mL H_2O_2 again, keep at 85 ℃ for 1 h. Then use 1 mol/L acetic ammonium 50 mL (pH 2) to get organic form elements. The remains form elements could be calculated. The concentration of elements was measured by ICP-AES.

The statistic analyses such as environment quality index, the average of heavy mental elements, standard deviation and analysis of elements relation were carried out by MATLAB.

4 Results and discussion

4.1 Distribution of heavy metals in different zones

The results are listed in Table 1. It is obvious that heavy metals of four zones are different, especially Pb and Zn. In minerals transportation pollution area, the maximum contents of Pb and Zn are up to 926 mg/kg and 976 mg/kg, respectively. But the difference of Cd, As, Cu in four zones is little. We estimate the degree of heavy metals pollution by Nemero pollution comprehensive index[15]:

$$P_{ij}=\sqrt{\frac{(\max c_i/S_{ij})^2+(1/n\sum c_i/S_{ij})^2}{2}} \quad (1)$$

where j represents the number of polluted zone, i represents the kind of heavy metals element, c_i represents the determined concentration of heavy metals element, S_{ij} represents the referenced value, and n represents the total kinds of heavy metals (n=5).

The referenced value that is not unified at home and abroad, affects Nemero pollution comprehensive index greatly. HE et al[15] took heavy metal contents of polluted zones background samples as reference. LIAO and WU[16] and CHEN and ZHOU[17] used the highest background value before modern industrialization as reference. In this work, control samples are taken as reference.

Nemero index is listed in Table 1. We can see that all zones are seriously polluted by heavy metals. Ranking of pollution intension of different zones from heavy to light is in the sequence of tailing zone, mineral transportation zone, mine drainage zone, and dust deposition zone.

Fig.1 shows the results of comparison in all samples. It is easy to see that each zone is characterized by Pb-Zn pollution as its main product is Pb-Zn. The average contents of Pb and Zn in the original mine are both 10.63%, while those in the fine mine are 70.91% and 44.6%, respectively. So Pb-Zn pollution is serious especially in the mineral transportation zone, and a drop can bring considerable pollution. There is direct relativity between heavy metal elements, which is notable between Pb and Zn and also exists among Cu, Cd and As. The relativity represents the similarity of pollution degree or the same pollution origin to a certain extent.

Generally, tailing zone is weak acid (pH 5.6−7.8). Maybe it is caused by the oxidation of sulfide. The other three zones are neutral, so the oxidation of heavy metals doesn’t influence pH of soil. But the oxidation is related with the content and form of heavy metals. The survey reveals that the reason for serious Pb-Zn pollution in the mineral transportation zone is undefended measures during the transport process. According to this work, it is suggested that all the tracks should be refitted and coated with awning, then the pollution can be under control.

4.2 Different form of heavy metals in each zone

Compare the contents of Zn, Pb, As, Cu and Cd in all samples, then get Fig.2. Remainder is the main form while organic form takes the least rate in each zone. Pb is predominant in the organic form as its average content is over 61.5%. The highest value is 70.8% in W1 zone while the least value is 49.9% in W4 zone. The rates of acid-extract form and organic form are low, 13.03% and 17.25% respectively. Zn is nearly equal in other 4 forms except low rate in organic form (only 2.95%). In despite of low Pb rate of acid-extract form and organic form, its absolute content is high, so its latent harm can’t be omitted. The Pb absorption of plant is directly related with the rate in the soil. It is reported that when Pb content is over 20 mg/kg in the soil, and it can reach 1 mg/kg in most wheat seed in the perennial pollution irrigation zone. So some plants sensitive to Pb such as soybean and rice in these areas are hard to satisfy the standard of SFDA. The average content of Pb in the pollution zones researched is up to 384.8 mg/kg. Although Zn is the necessary element for life-form, it is harmful when its supply exceeds a certain value.

Table 1 Comparison of heavy metal contents in soil samples of different polluted zones

Polluted zone	Number of sample	pH	Content of heavy metal elements/(mg·kg^{-1})					P_{ij}
			Zn	Pb	Cd	Cu	As	
W_1	10	5.60−7.80	447.0−821.0	162.0−568.4	5.3−11.5	164.3−417.9	80.5−207.0	17.3
W_2	8	7.09−8.20	59.7−768.1	46.1−167.5	4.9−11.5	318.9−561.0	18.9−82.6	16.9
W_3	4	6.65−7.10	52.1−234.1	16.8−78.9	1.6−8.9	318.1−351.2	38.4−114.1	13.1
W_4	6	7.56−8.40	864.0−976.0	741.0−926.0	4.1−11.0	316.9−377.9	37.2−167.1	17.0
M		7.50	508.6	348.3	7.53	356	44.6	16.1
S			96	81.6	0.5	27.3	66.54	
M/*S*			5.30	4.27	15.06	13.04	0.67	

M represents average value; *S* represents referenced value

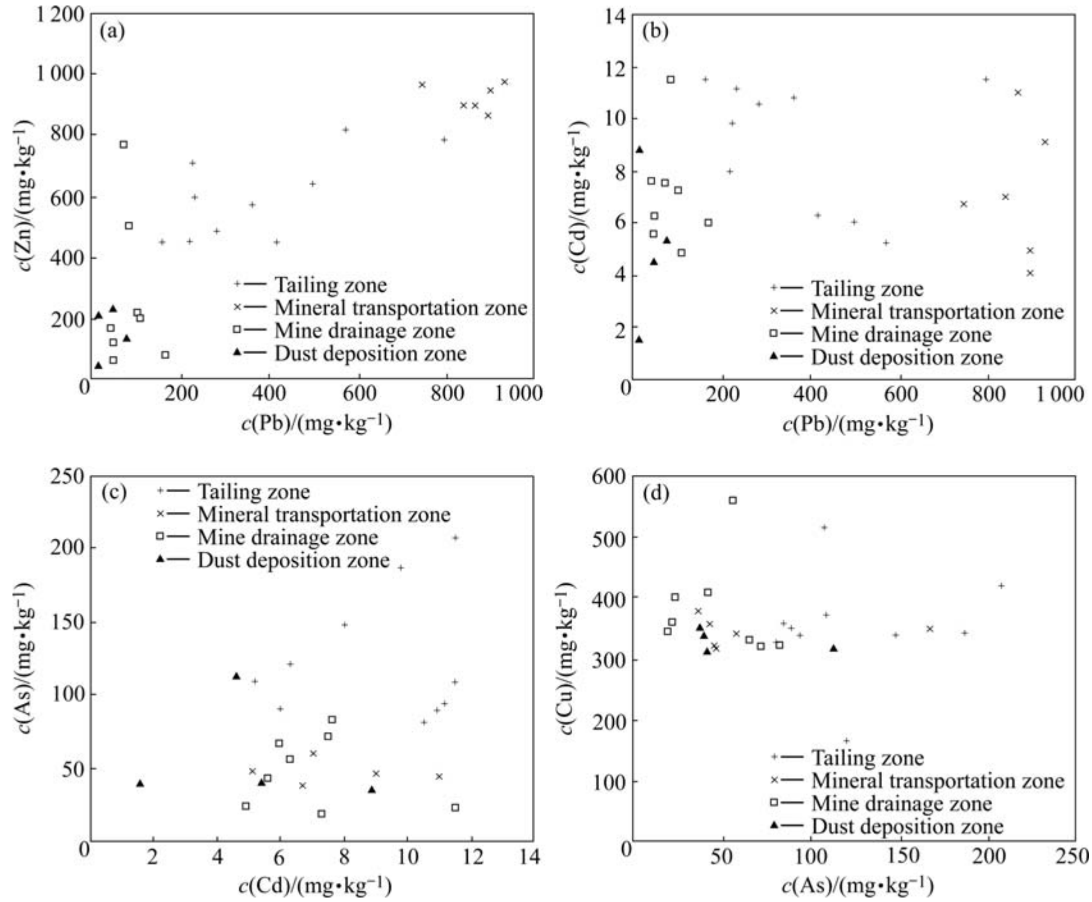

Fig.1 Correlation of heavy metal contents in soil samples of different polluted zones

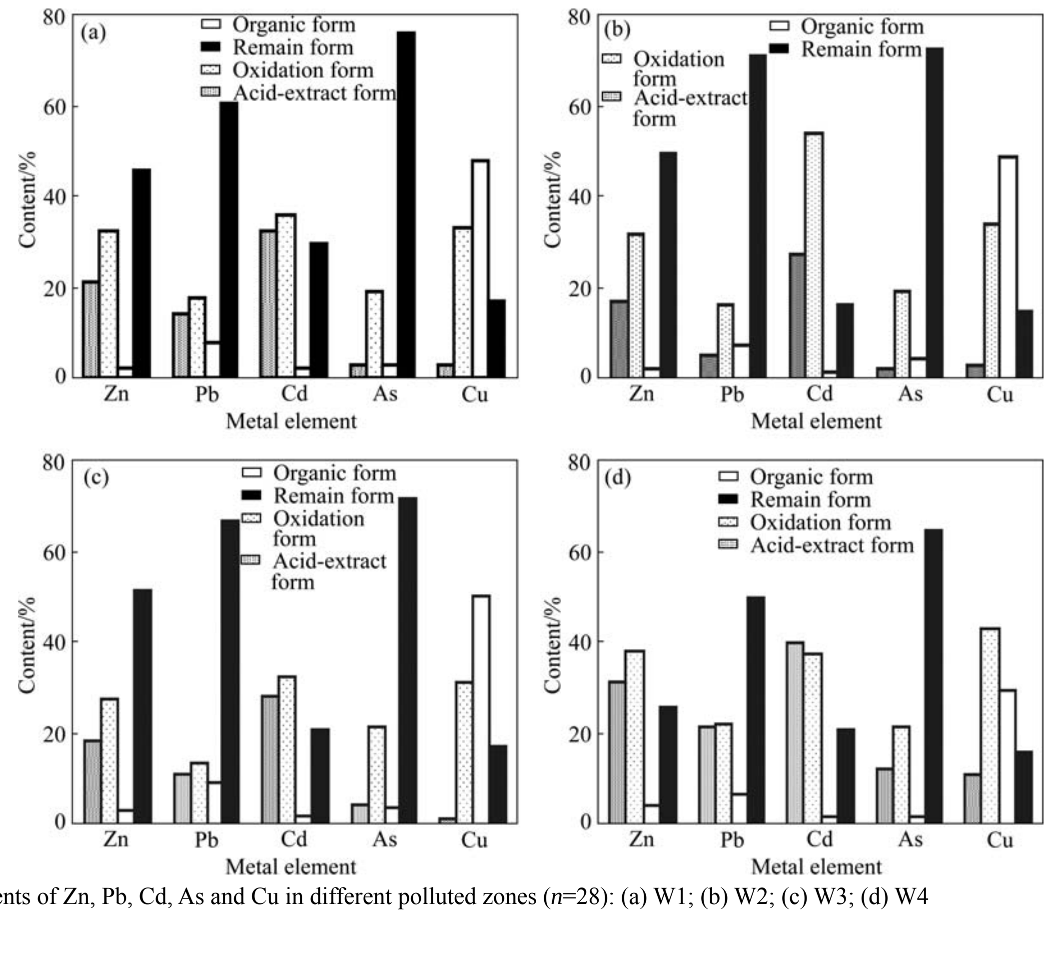

Fig.2 Contents of Zn, Pb, Cd, As and Cu in different polluted zones (n=28): (a) W1; (b) W2; (c) W3; (d) W4

5 Conclusions

1) Mining activity brings about serious heavy metal pollution. The soil is seriously polluted by heavy metals. The contents of Zn, Pb, Cd, Cu and As in soil are separately 508.6, 384.8, 7.53, 356 and 44.6 mg/kg in average, which are 5.3, 4.27, 15.06, 13.04 and 0.67 times those of the reference.

2) According to Nemero integration index, the most seriously contaminated soil area is tailings pollution soil. This reveals that tailing mine is the main way of introducing heavy metal into environment. So in order to effectively control and exclude pollution, we should pay most attention to it.

3) Remaining form is the main state in each zone, while organic form is the least. There is no notable difference in different kinds of element or pollution zones. Pb and Zn that are the main polluted heavy metals are predominant in remaining form, while the rates of acid-extract form and oxidation form are low.

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