

Analysis of the Influence of Heavy Metal Pollution in the Pb-Zn Mining Area on Environment Ecology

Bo Tang^{1,2}

¹*College of Geology and Environment, Xian University of Science and Technology, Xian 710054
Shaanxi, China*

²*College of Chemical and Environment Science, Shaanxi University of Technology, Hanzhong
723001, Shaanxi, China*

Xiaoguang Zhao*

*College of Geology and Environment, Xian University of Science and Technology, Xian 710054
Shaanxi, China*

**Corresponding Email: 898678322@qq.com*

Abstract

With the rapid development of mining and purchase of mineral resources, the pollution caused by heavy metals in the Pb-Zn ore area has posed a serious threat to environment. The Pb-Zn Mining Areas and the smelting plants have a great influence on their surrounding environment. Shaanxi Province of China is abundant in Pb-Zn ore. The environmental pollution incurred by heavy metals is mainly reflected as the pollution of heavy metal chromium, lead, zinc and arsenic. The pollution can do a great harm to soil, plants, microorganism, waters, air and the growth and health of humans and animals. The serious of ecological environment problems has a negative impact on the current social and economic life. Worse still, tailings contain a large number of heavy metals. Through the biogeochemical effect, these heavy metals can be released and migrated to soil and rivers. Due to polyphyly, elusiveness, sustainability and severity of pollution consequences, the problem has drawn the attention of more and more researchers. This paper mainly analyzes the status quo and trend of pollution caused by heavy metals in the Pb-Zn Mining Area in south Shaanxi Province. Based on the soil investigation, the ecological hazard index method is employed, and the average content of heavy metal elements in the deep soil is adopted as the reference value to evaluate the potential ecological risks of heavy metal pollution and explore its ecological environment effect. At last, countermeasures aiming at improving heavy metal pollution in the Pb-Zn Mining Area of south Shaanxi Province are put forward.

Key words: HEAVY METAL, POLLUTION, ECOLOGICAL ENVIRONMENT, SHAANXI PROVINCE, PB-ZN ORE

1. Introduction

Xunyang County is located in the northeast of Shaanxi Province and the eastern section of Qinling-Daba Mountains, with the Han River going through it. Its attitude is within the range of 185 to 2,358m. Characterized as the northern sub-tropical warm and humid climate, Xunyang County has an average precipitation of 851mm and an average temperature of 15.4°C. The whole county covers an area of 3,554km, with a total population of 450,000 living in 28 townships and 319 villages. Thanks to the special geological history and favorable mineralizing conditions, Xunyang County has bred rich mineral resources. The local geological department has found more than 39 mineral resources, including mercury, stibium, lead, zinc, gold, copper, manganese,

sium, ferrum, limestone, barite and dolomite. Among them, mercury and antimony ore have formed the national large-scale deposits, topping in the national list by maintaining a reserve of nearly 150,000t. Besides, it is reputed as “Chin’s Mercury Capital.” Its Pb-Zn deposit rolls for more than one hundred kilometers, registering a possible ore of more than two million tons.

Located in 12km away from the east of Xunyang County, Xunyang County Mengjiagou Pb-Zn Ore Area is 26km long from the east to the west and 2km wide from the south to the north, covering an area of 54.1km². Its geographical location is E109°20'00"-109°37'00"N32°49'00 "-32°53'00." The area is characterized by convenient transportation and ample electrical supply.

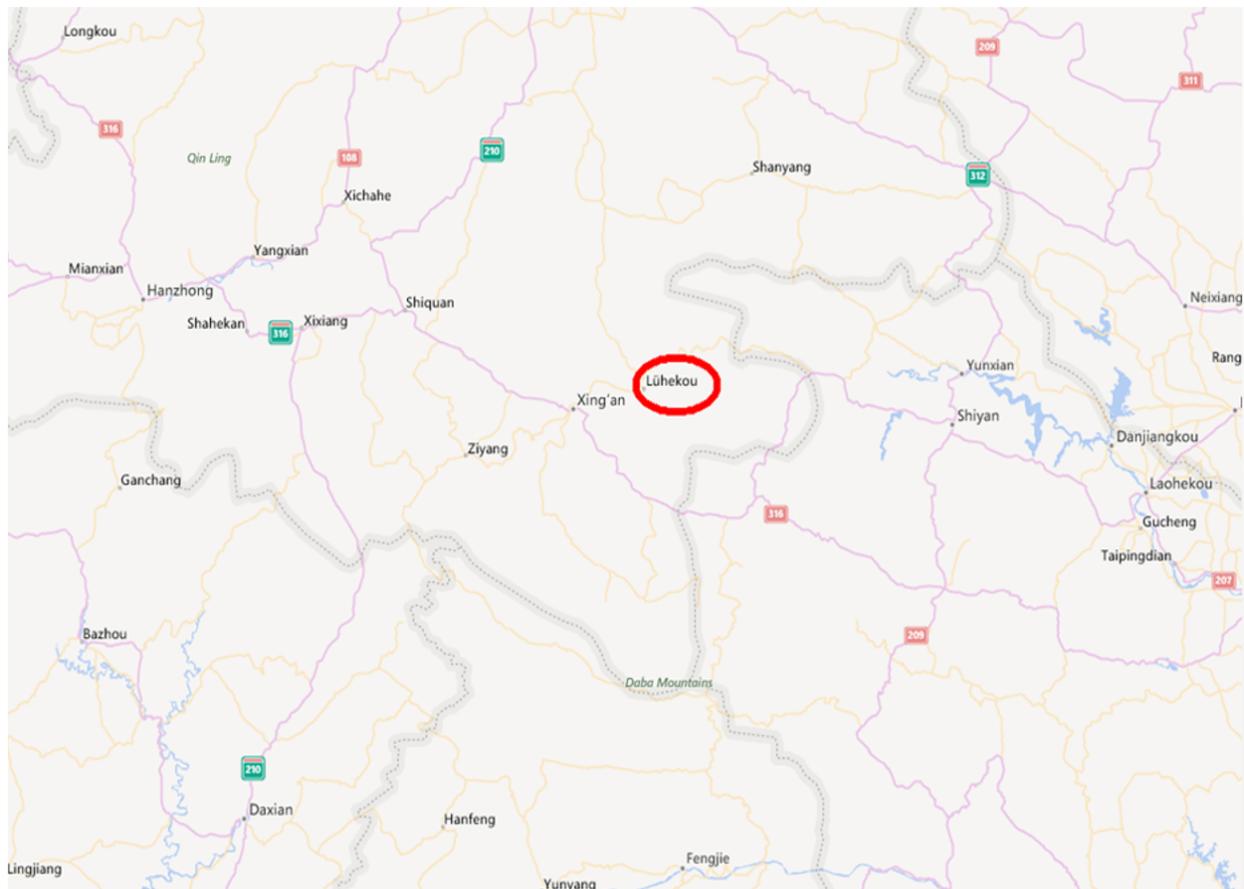


Figure 1. Geological position of the research area in Mengjiagou, Xunyang County, Ankang City, Shaanxi Province

2. Geological environment and pollution status quo of the research area

The development of the Pb-Zn ore resources in south Shaanxi Province has created huge economic benefits, but has also caused serious environment problems. The Pb-Zn ore features intergrowth and concomitant ore. Apart from lead and zinc, the ore also contains metal elements, including copper, cad-

mium, mercury, chromium, etc. Besides, in the current period, the Pb-Zn mining models in south Shaanxi Province are simple, the recovery-rat of mineral-processing and smelting and the comprehensive utilization rate are low, having caused not only serious waste of resources, but also serious environmental pollution, damage of ecological environment and threat of geological disasters.

1) Water pollution: In recent years, a large number of wastewater and waste residues containing a large number of heavy metals have been generated during the mining process of Pb-Zn ore. The multi-channel wastewater discharge of the mining and purchase enterprises has brought fatal damage to the ecological system of rivers. As water pollution events keep popping up and influencing the farmland featuring the irrigation of surface water, polluting crops and threatening human health. The large amount of wastewater discharged during the whole development process of the ore area includes pit wastewater, mineral separation wastewater, percolating water of the tailings pond, filtrates water of mining residue stones, smelting wastewater, life wastewater, etc. Currently, most of the above wastewater is directly discharged without being handled. Moreover, Xunyang County is located in the mountainous area, where the annual precipitation is huge, the surface runoff and convergence speed is fast and the waters are densely distributed. Thus, large-area and long-term pollution has been caused in the surface water, and the water quality keeps on degrading on an annual basis, seriously threatening the survival and safety of residents on two sides of the river. Due to changes of mountainous territory and the surface water and the underground water, pollution of the surface water must result in the pollution of the underground water. With the continuous accumulation of tailing sands in the tailings pond, and the penetration of the filtrated water containing heavy metal ions and the other chemical pollutants, the underground water in the lower rock stratum in the tailing pond is polluted. As a result, the quality of the underground water declines and shows partial pollution phenomena. Once the underground water suffers a large-scale pollution, the influence of the pollution can be hardly removed.

2) Air pollution: Air pollution in the Pb-Zn area of south Shaanxi Province is mainly caused by the dust pollution during the mining, separation and smelting process. The hillocks arbitrarily abandoned in valleys and the tailings ponds which have never undergone earth backing and field making are the major sources of atmosphere dust pollution. Every spring and winter when the climate is arid and windy, dust rising along with wind causes serious pollution to partial air. The blowing sand in tailings, and dust, SO₂ and flue gas containing Pb of the smelting and cement manufacturing plants can directly pollute the air in the ore area, imposing a negative influence on animals, plants and humans' ecological environment, especially the local ecological environment. Besides, the flue gas containing Pb and SO₂ generated by mining and

separation enterprises can constitute another type of air pollutants, which can seriously influence the life and health of residents in the ore area.

3) Soil pollution: Due to long-term pollution of mining and separation enterprises on surface water and the increase of heavy metals and other chemical pollutants caused by surface water irrigation, the soil pH value is low, the physical property of the soil worsens and the growth of some crops is inhibited. Some crops seem to grow well, but are still faced with dangers of high heavy metal content. The stability of tailings ponds without earth backing and field making is poor. The tailing sands fly along with the wind, which can directly pollute the surrounding agricultural fields and crops. There have been research findings suggesting that the lead zinc ore area in the south of Shaanxi Province has suffered serious soil pollution. Besides, there have been few systematic researches exploring the space distribution status of agricultural soil and agricultural heavy metal pollution in Xunyang County [1].

4) Ecological damage: The development of mineral resources in Xunyang County has caused serious damage to the ecological environment in many aspects. The mining enterprises cover an area of 832ha; the tailings pond covers an area of 43ha; the hillocks cover an area of 51ha. The land occupation has damaged the original vegetation. Mountain cracking, surface collapse, landside and debris flow caused by mining are the direct factors of ecological environment damage. The multi-channel wastewater pollution discharge of mining enterprises has caused fatal destruction to the river's ecological system. It can also negatively influence animals, plants and humans' ecological environment. To the end, this paper evaluates the pollution status quo of agricultural soil and crops in the Pb-Zn ore area of Xunyang County in south Shaanxi Province, and studies the space distribution of heavy metal pollution in soil and crops, attempting at providing scientific bases for the treatment of regional environment.



2. Materials and methods

2.1. Layout of sampling points

The sampling points in this paper are mainly chosen from the Pb-Zn ore area in Mengjiagou, Xunyang County, whose geological position is within the range of $E109^{\circ}20'00''-109^{\circ}37'00''N32^{\circ}49'00''-32^{\circ}53'00''$. The sampling points are laid out in the whole research scope, with the major ones in the area with concentrated tailings and serious pollution. GPS is used to record the longitudes and latitudes, and elevations of the sampling points.

2.2. Collection of samples

From the theoretic perspective, the higher the number of sampling points of every mix sample is, the higher representativeness of samples is. In this paper, the mixed samples are made up of multi-point mix. In fact, it equals to an average number, which can reduce the uneven difference of soil. Therefore, the sampling of soil samples must be in line with certain sampling routes, the principle of random multi-point mix, *Procedural Regulations Regarding the Environment Quality Monitoring of Soil* (NY/T395-2000), and uneven soil and territory in the research area. In order to ensure representativeness of soil samples, the "plum point sampling method" is adopted to collect the surface soil within 50m of the research area. The surface soil whose depth ranges within 0~20cm is collected to scrape the surface capping mass (<1cm). Things

like weeds and bricks should be removed. Generally speaking, two to three sub-samples are combined to scrape the surface capping mass (<1cm). Things like weeds and bricks should be removed. Generally speaking, two to three sub-samples are combined into one sample. The quartering method is adopted to preserve 1kg of samples. These samples mainly come from cropland, vegetable plots and so on, so they can basically reflect the agricultural soil pollution in Xunyang County. The overall number of samples collected is far higher than the number of samples to be analyzed. In this experiment, As, Pb, Cu, Cr, Zn and other heavy metal elements with relatively complete, and GIS[2] (ARCGIS8.01 and ARCVIEW3.2 manufactured by the American company, ESRI. The attribute data are edited and processed with FOXPRO6.0) is used to evaluate the heavy metal pollution in the ecological environment of the Pb-Zn ore area, and formulate the element space distribution chart of the Pb-Zn ore area. The metal pollution evaluation model is established and undergoes the single factor evaluation and the evaluation of comprehensive pollution. This paper mainly adopts the index method to evaluate heavy metal pollution in reference to National Environmental Quality Standards for Soils (GB15618-1995) and the evaluation standards actually adopted by the research area. (See Table 1)

Table 1. Evaluation standards for heavy metal pollution in the Pb-Zn ore area of Xunyang County

Items	Elements/mg kg ⁻¹				
	As	Pb	Cu	Zn	Cr
Initial value of pollution accumulation	15	35	35	100	90
Initial value of medium pollution	40	250	50	200	150
Initial value of serious pollution	40	500	400	300	300

2.3. Sample analysis

Soil PH value: Adopt the potentiometry, soil: water=1:5 (w/w); use PHs-3C precision pH meter for the measurement;

Soil electric conductivity: Adopt the conductivity method, soil: water =1: 5 (w/w); and use DDS-IIC conductivity meter for the measurement;

Soil organic matter: Adopt the heat of dilution to measure potassium dichromate content, and calculate according to formulae;

Soil organic carbon

$$(g \cdot kg^{-1}) \frac{c(v_0 - v) \times 10^{-3} \times 3.0 \times 1.33}{\text{Oven} - \text{dried weight soil}} \times 1000 \quad (1)$$

$$\text{Soil organic matter } (g \cdot kg^{-1}) = \text{Soil organic carbon } (g \cdot kg^{-1}) \times 1.724 \quad (2)$$

Where,

1.33—oxidation correction coefficient;

C—volume of 0.5mol·L⁻¹FeSo(ml);

V₀—consumed volume of FeSo 4 by the blank titration(ml);

3.0—molar mass of one fourth of the carbon atom(g·mol⁻¹);

10⁻³—convert ml into L.

Total nitrogen (N) in soil

$$(g \cdot kg^{-1}) \times = \frac{(V - v_0) \times c \left(\frac{1}{2}H_2SO_4\right) \times 14.0 \times 10^{-3}}{m} \times 1000 \quad (3)$$

Where,

V—volume (ml) of standard acid solution during titration of test solution;

V0—volume (ml) of standard acid solution during the blank titration;

C—concentration of $0.01 \text{ mol} \cdot \text{L}^{-1} (1/2\text{H}_2\text{SO}_4)$ or HCl standard solution;

14.0—molar mass of the nitrogen atom ($g \cdot \text{mol}^{-1}$);

m—mass (g) of dried soil samples.

Total phosphorus in soil: NaOH-Mo-Sb colorimetric measurement method. Calculate according to the following formula:

Total phosphorus (P) in soil: NaOH-Mo-Sb colorimetric measurement method. Calculate according to the following formula:

$$g \cdot \text{kg}^{-1} = P \times \frac{V_1}{m} \times \frac{V_2}{V_3} \times \frac{100}{100-H} \times 10^{-3} \quad (4)$$

Where,

P—volume (ml) of solution to be tested on the calibration curve;

m—mass (g) of chosen samples;

V1—constant volume (ml) of samples after dissolution;

V2—constant volume (ml) of solution during coloration;

V3—separated volume (ml) after the volume of samples becomes constant;

10-3—factors influencing the conversion from the concentration unit of $\text{mg} \cdot \text{L}^{-1}$ to the mass unit of kg ;

H—percentage of moisture content in the dried soil.

The measurement of the total content of Cu, Cd, Pb, Zn, Hg and As: The soil heavy metal adopts the wet process, microwave – digestion (MWD). Add 0.25g dried soil samples and 9ml HN0_3 , 4ml H into the polytetrafluoroethylene (PTFE) digestion tank. After the boiling of the microwave digestion system and the cooling of the digestive liquid, turn to the PTFE crucible. Add 3ml HClO_4 and heat it to achieve evaporation and white smoke. Evaporation can help remove the redundant acids. After that, the digestive liquid can be transferred to the volumetric flask. Add 5ml lanthanum nitrate. After cooling down, add deionized water to achieve constant volume of the water. Use the atomic absorption spectrometry (ASS) to measure the content of Cu, Cd, Pb, Zn, Hg and As.

The effective state content of the soil heavy metal:

Fetch 10.00g of dried soil going through the 20-mesh sieve into 100ml plastic wide-mouth bottle. Adopt 0.1M HCl as the extracting agent and set the room temperature at 25°C . Then, the effective state content of the soil heavy metal is shown below:

$$(\text{mg} \cdot \text{kg}^{-1}) = \rho \cdot V/m \quad (5)$$

Where,

ρ —mass concentration ($\mu\text{g} \cdot \text{ml}^{-1}$) of heavy metals in the solution to be tested on the standard curve;

V—volume (ml) of the extracting agent, $0.1 \text{ mol} \cdot \text{L}^{-1} \text{HCl}$;

m—mass (g) of the fetched soil samples.

Besides, the index method evaluation model adopted includes the evaluation of the single-factor pollution indexes and the comprehensive pollution indexes. Among them, the formula for the evaluation, of the single-factor pollution is shown below:

$$P_i = \frac{C_i}{S_i} \quad (6)$$

When $C_i \leq X_a$, $C_i/S_i = C_i/X_a$ and $X_a < C_i \leq X_c$; or $C_i/S_i = 1 + (C_i - X_a)/(X_c - X_a)$; $X_c < C_i \leq X_p$; or

$C_i/S_i = 2 + (C_i - X_c)/(X_p - X_c)$ and $X_p < C_i$, $C_i/S_i = 3 + (C_i - X_p)/(X_p - X_c)$. In the above formula, P_i stands

for the pollution index of the soil pollution element of i ; C_i stands for the actually-measured value of the pollution element of i in the soil; S_i stands for the evaluation standards for the pollution element of i in the soil; X_a , X_c and X_p stand for the initial value of the soil pollution accumulation, the initial value of medium pollution and the initial value of the serious pollution, respectively. When $P_i \leq 1$, it means there is no pollution and the corresponding area can be defined as the pollution-free area; when $1 < P_i \leq 2$, it means light pollution and the corresponding area can be defined as the lightly-polluted area; when $2 < P_i \leq 3$, it means medium pollution and the corresponding area should be defined as the medium-polluted area; when, $P_i > 3$, it means serious pollution and the corresponding area should be defined as seriously-polluted area.

Comprehensive Nemerow Pollution Index:

$$P_{\max} = \sqrt{\frac{P_{\max}^2 + P_{\text{am}}^2}{2}} \quad (7)$$

Where,

P_{\max} stands for the maximum value of the soil pollution index; P_{am} stands for the average value of the pollution index

The multi-factor comprehensive pollution index formula is shown below:

$$P = \sqrt{\frac{\left[\frac{1}{n} \sum_i \left(\frac{C_i}{S_i}\right)^2\right] + \left(\frac{C_i}{S_i}\right)_{\max}^2}{2}} \quad (8)$$

Where, P stands for the comprehensive pollution index of soil pollution elements; C_i stands for the actually measured value of the pollution element, i ; S_i stands for the evaluation standards for the pollution element, i . When $P \leq 1$, the area is defined as pollution-free area; when $1 \leq P \leq 2$, the area is defined as

light pollution; when $2 \leq P \leq 3$, the area is defined as the medium-polluted area.

2.4. Results and analysis

According to the single-factor pollution evaluation results of the ecological environment in the Pb-Zn area of Xunyang County, it can be seen that the area soil features the alkalescence soil. The average content of organic matters is 1.21%. The content of As, Cu and Zn does not exceed the secondary standard of soil environment quality. Comparatively speaking, the pollution caused by Pb, Cd and Hg is serious. Specifically speaking, research suggested that the content of Pb, Cd and Hg in soil samples is

12.1%, 57.1% and 89.8%, respectively, which exceeds the secondary standard value of soil quality. [3] The distribution of the Pb-Zn area is not even and the waste discharge differs from each other, thus leading to spatial changes of heavy metal content in soil. [4] Research showed that, the closer it is to the mining area of the Pb-Zn area, the higher the content of Pb, Cd and Hg is. Thus, it can be seen that mining activities have a significant influence on Pb, Cd and Hg.

The evaluation results of the single-pollution index method and the Nemerow Pollution Index are shown in Table 2 and Table 3.

Table 2. Soil single-factor pollution indexes and evaluation grade

Single-factor pollution index	Pollution grade	Frequency distribution (%)		
		Hg	Cd	Pb
$P \leq 0.7$	Safe	2.0	20.3	69.8
$0.7 < P \leq 1$	Warning line	8.4	21.2	18.7
$1 < P \leq 2$	Light pollution	23.8	31.8	8.2
$2 < P \leq 3$	Medium pollution	29.7	8.1	2.2
$P > 3$	Serious pollution	35.6	15.9	2.4

Table 3. Nemerow Comprehensive Pollution Index and evaluation grades

Single-factor pollution index	Pollution grade	Frequency distribution(%)
$P \leq 0.7$	Safe	8.2
$0.7 < P \leq 1$	Warning line	8.2
$1 < P \leq 2$	Light pollution	35.8
$2 < P \leq 3$	Medium pollution	15.9
$P > 3$	Serious pollution	29.7

From Table 2, it can be seen that the soil seriously polluted by Hg, Pb and Cd is 35.6%, 2.4% and 15.9%, respectively. Generally speaking, 35.8% belongs to light pollution, 15.9% belongs to medium pollution and 29.7% belongs to serious pollution. Only 8.2% of the soil samples are safe.

Generally speaking, heavy metals in soil can be conveyed through the food chain, and finally does

harm to human health. Therefore, the evaluation of the potential ecological hazards of soil with heavy metal pollution is of vital importance. [5] In order to reflect the differences of specific regions, the soil background value of the central Shaanxi Plain is chosen as the benchmark to evaluate the potential ecological hazards of Hg, Cd and Pb.

Table 4. Potential ecological hazards coefficient and grade evaluation

Potential ecological hazards coefficient, E	Pollution grade	Frequency distribution (%)		
		Hg	Cd	Pb
$P \leq 0.7$	Light	10.3	58.4	100
$0.7 < P \leq 1$	Medium	23.6	27.2	0
$1 < P \leq 2$	Strong	43.5	13.5	0
$2 < P \leq 3$	Very strong	13.8	4.3	0
$P > 3$	Extremely strong	8.2	0	0

58.4% of soil samples shows light ecological hazards; Cd in 41.6% of soil samples shows moderate ecological hazards; only Pb shows light ecological hazards. The space distribution of Hg and Cd content in soil, potential ecological hazards coefficient of Hg and Cd and potential ecological hazards indexes shows good consistence. Thus, it can be seen that Hg and Cd contributes greatly to the soil pollution in the research area. The research findings coincide with the status investigation of soil heavy metal pollution.

3. Treatment strategies for heavy metal polluted area in the Pb-Zn ore area of south Shaanxi Province

As is known to all, waste water, residues, discards and radioactive poisons and noises are major factors influencing the surrounding ecological environment. In view of the ecological environment status and existing problems facing the heavy metal polluted Pb-Zn ore area of south Shaanxi Province, the following strategies are put forward.

3.1. Enhance the treatment of the wastewater pollution in the ore area

During the mining process, new techniques should be employed to achieve clean production and reduce the generation and discharge of pollutants during the mining and separation process. Through the improvement of the wastewater reuse rate, the adjustment of the agent regime, the natural purification treatment, the neutralization method and the oxidation treatment, the wastewater can reach the discharge standards or can be reused. For example, Mengjiawan Pb-Zn Mining Plant can recycle the mineral processing wastewater. The mixture fresh water and the reused water can be mixed according to the ratio of 1:1 for mineral separation. Under the condition, the bubbles are thick, the operation conditions are stable and the ore dressing recovery percentage of Pb, Zn and S can be considerably improved. The mining plant can adopt the oxidation method to significantly reduce the concentration of sulfides from 15mg/L to 1mg/L to reach the wastewater discharge standards. Through the employment of new techniques and processes and the adjustment of agent regime, the cyanogen-free or low-cyanogen flotation can be employed to reduce the pollution of cyanides.

At present, the wastewater treatment in Xunyang County Pb-Zn Mining Plant can adopt natural purification treatment, which will be extremely efficient. The buildings adopting the natural purification method are mainly tailings ponds. The treatment method can not only avoid the occurrence of collapses of tailings ponds and the discharge of acid wastewater, but also dilute, sediment and hydrolyze wastewater. On

the one hand, the organics in wastewater can undergo oxidative degradation; on the other hand, the poisonous elements in the rural wastewater can be absorbed. According to statistics, it can be seen that, after natural clarification of tailings ponds, most mining plants in Xunyang County shows a significant decline in terms of the content of the poisonous content. Generally speaking, the tailings water can stay in ponds for one to three days and nights and the concentration of suspended substances in the clear water is lower than the national standard [6].

3.2. Intensify the treatment of the residue pollution in the ore area

In terms of the treatment of overburden materials and barren rocks during the residue and mining process, and the tailings abandoned during the mineral separation process, the hillocks and tailings dams can be built up to turn waste into wealth and harm into benefits through comprehensive utilization. For example, Mengjiawan Pb-Zn Mining Plant can recycle the useful minerals and elements in barren stocks and tailings. To adopt tailings as the filling raw materials can not only help tailings get proper treatment, but also achieve good application effects.

Besides, in order to prevent tailings ponds from the rain wash and erosion, the tailings ponds can be reinforced and heightened. Most Pb-Zn mining plants in Xunyang County has undergone reclamation and field making through leveling, earthwork and vegetating, which have succeeded in controlling water and soil loss, preventing dust hazards and better purifying the ecological environment. The dust content has also been reduced by several or dozens of times. Besides, some agricultural crops, plants and flowers are built to achieve environmental greening and better social and economic benefits.

3.3. Strengthen the treatment of the waste gas pollution in the mining area

The treatment of waste gas in the Pb-Zn mines is mainly realized through enhancement of exhaust ventilation and inhibition of the harm of Rn and its product done to the mining workers. Major measures adopted include: To improve the anti-dust and water supply system, implement the all-around wet-type operation, ensure the airtightness of the gob and the roadway operation, improve the reliability of the ventilation system, do a good work of partial purification and promote and apply the successfully-developed JBF high-voltage static electrostatic air cleaner and the RDC-1 composite purifier. The adoption of these comprehensive treatment measures can effectively inhibit the harm that dust, Rn and its product do to human health.

4. Conclusions

To sum up, the importance of the Pb-Zn ore resources and the shortage of soil resources cannot be ignored. How to cope with the soil pollution towards ecological environment during the Pb-Zn mining process is an important issue for future research. Currently, the heavy metal pollution of the Pb-Zn heavy metal area in south Shaanxi Province has been extremely serious. Thus, it is imperative to give priority to precautions and combine precautions and treatment to achieve a harmonious relationship between humans and the nature and boost economic development.

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