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Original Research

Ecological Risk Assessment of Heavy Metal Occurrences in the Coal-Fired Furnace Bottom Slags of Power Plants

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Abstract

This study explored the ecological risks related to bulk resource utilization of industrial solid waste slag from the Yuanyanghu Power Plant in the Ningdong Energy and Chemical Industry Base. Scanning electron microscopy, energy spectrum analysis, and X-ray diffraction were used to characterize and analyze the physical and chemical properties of the slag. The total amount, effective forms, and different occurrence forms of six heavy metals, including lead (Pb), chromium (Cr), nickel (Ni), copper (Cu), cadmium (Cd), and arsenic (As), were determined. The ecological and environmental risks of the heavy metals in the power plant slag were comprehensively evaluated using the potential ecological risk index method and risk assessment coding (RAC) method. The results show that: (1) The slag exhibited a porous microstructure characterized by high concentrations of calcium (36.27%). The mineral composition of the furnace bottom slag was mainly mullite and quartz, and the contents of available potassium and organic matter were abundant. (2) The total concentrations of the six heavy metals in the furnace bottom slag did not exceed the screening value for soil pollution risk in agricultural land. Pb, Cd, Cr, As, and Ni in the slag mainly existed in the form of residue (F5), with Ni and As in the exchangeable state (F1), accounting for 28.05% and 25.49%, respectively. (3) The potential ecological risk index method indicates that the total RI index of the six elements in the slag is at level II, with a moderate ecological hazard level. Among all the metals, Cd and As contribute most to ecological risk. The RAC evaluation results indicate that Ni and As have moderate risk, Cd, Cu, and Cr have low risk, and Pb is risk-free. Based on a comprehensive evaluation, Cd,

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Ni, and As elements in slag are the main potential pollutants. In large-scale resource utilization, it is necessary to monitor and strengthen ecological risk prevention and control regularly.

Keywords: industrial solid waste, furnace bottom slag, heavy metals, ecological risk assessment, resource utilization

Introduction

Coal, as the main energy source in China, supports the development of China's national economy [1, 2]. Ningdong Energy and Chemical Industry Base is one of China's 14 large coal bases, each with a capacity of over 100 million tons. The region is rich in coal resources, with proven reserves reaching 38.6 billion tons, accounting for 87% of Ningxia's total proven reserves. The Ningdong Coalfield is a mining area where the Jurassic Yan'an Formation serves as the coal-bearing stratum. The Jurassic coal is characterized by extremely low to low ash content, extremely low to low sulfur content, low phosphorus, low arsenic, low fluorine, and high calorific value, making it a high-cleanliness coal suitable for power generation. In 2024, Ningdong Energy and Chemical Industry Base generated 30.41 million tons of general industrial solid waste, of which 20.07 million tons were utilized comprehensively, resulting in a utilization rate of 66 %. Bottom ash accounts for approximately 20% of the total solid waste, while its resource utilization rate is less than 10%. The rapid development of the ecological economy and society in mining areas is restricted by the large volumes of coal-based solid waste, the low utilization rate of coal, and the destruction of the ecological environment. Therefore, with the current focus on promoting "clear water and green mountains are golden hills and silver mountains" in China, the comprehensive treatment and use of coal-based solid waste such as slag and gasification slag has become urgent to secure the coal-based electrochemical base and even national energy and ecological security [3].

Coal-fired power plants produce two main types of solid waste: fly ash and slag. During coal-fired power generation, dust removal, which is done to meet the environmental requirements of flue gas emissions, produces fly ash and discharges slag from the bottom of the boiler [4, 5]. The comprehensive use of slag is much lower than that of fly ash, most of which is disposed of by burying the slag in ash fields. Only a small volume of slag is used as cement, free brick, and concrete ingredients, road fillers, water purification materials, or fillers for mine filling projects [5-10]. Due to unclear physical and chemical properties, heavy metal properties, and ecological risks, the large-scale utilization of power plant slag remains limited. In contrast, fly ash has been extensively studied and is being efficiently utilized in China. The basic material properties of fly ash are also well understood. In contrast, slag use is relatively low, and complete research on its basic material properties and the ecological risks linked to its use is lacking.

This paper determined the physical and chemical properties of the slag of Ningxia Ningdong Energy and its Chemical Base power plant. The slag was analyzed in terms of the total amount of heavy metals, the available state of the chemicals, and the leaching toxicity of the slag. The risk assessment coding (RAC) method and the potential ecological risk index method were used to evaluate the ecological risk of the heavy metals in the slag, provide a reference base for follow-up research, and improve the use of the power plant slag.

Materials and Methods

Overview of the Study Area

The Yuanyanghu Power Plant is located in the Yuanyanghu mining area of the Lingwu coal field, Ningdong. It is 25.4 km from Renjiazhuang Coal Mine and 2.5 km from Meijing Coal Mine. The total installed capacity of Yuanyanghu Power Plant (phase 1-2×660MW+ Phase 2-2×1100MW) can reach 3520 MW. It is the largest thermal power plant in Northwest China and the Guosen Group, producing about 950,000 tons of fly ash yearly. The primary source of coal for the Yuanyang Lake Power Plant is the No. 2 coal from the Meihua Well Coal Mine. The main coal-bearing strata of this mine belong to the Jurassic Yan'an Formation, with a focus on extracting No. 2, No. 6, No. 8, and No. 9 coals [11-13].

Sample Preparation and Instrumentation

Sample Pretreatment

The collected slag samples were dried, passed through a 0.075 mm sieve, and then bagged and labeled for use. The methods of total heavy metal digestion and effective leaching of heavy metals from slag samples were based on references [11] and [14]. The morphology of heavy metals in the samples, including exchangeable state (F1), carbonate bound state (F2), iron (manganese) oxide bound state (F3), organic bound state (F4), and residue state (F5), were determined using the Tessier five-step extraction method [15] (see Table 1).

Analytical Instruments and Reagents

The Shimazu X-ray diffractometer (XRD-6000) was used to analyze the mineral composition of the slag,

Table 1. Operation steps of the Tessier extraction method.

Steps	Heavy metal form	Extraction reagent	Extraction conditions
1	Exchange state (F1)	16 mL of 1.0 mol/L $MgCl_2$, pH = 7	Oscillate at 25ºC for 1 h
2	Carbonate bound state (F2)	16 mL of 1.0 mol/L NaAC, pH = 5	Oscillate at 25ºC for 5 h
3	Iron (manganese) oxide bound state (F3)	40 mL of 25% HAC solution containing 0.04 mol/L $NH_4OH{\cdot}HCl$	Oscillate at 96ºC for 6 h
4	Organic bound state (F4)	6 mL of 0.02 mol/L HNO_3 10 mL of 30% H_2O_2 6 mL of 30% H_2O_2, pH = 2 10 milliliters of 32% NH_4OAC solution with a concentration of 3.2 mol/L of H_NO_3	Water bath at 85ºC for 2 h Water bath at 85ºC for 3 h Oscillate at 25ºC for 0.5 h
5	Residual form (F5)	30 mL of HNO_3 + 20 mL of HF + 10 mL of HC_lO_4	Digestion solution for white or light yellow

while thermal field emission scanning electron microscopy (Nova Nano SEM 450) was used to determine the microstructure and perform an energy spectrum analysis on the slag. The total amount of heavy metals was determined using the American Perkinelmer inductively coupled plasma emission spectrometer (PE Avio550 Max), and the form of heavy metals was determined using the American Perkinelmer inductively coupled plasma mass spectrometer (PE NexION300X). The chemical reagents used in pretreatment and testing the power plant's bottom slag samples are all of a high-purity grade.

Ecological Risk Assessment Methods

Potential Ecological Risk Index

In 1980, Swedish scientist Hakanson proposed a potential ecological hazard index (RI) evaluation method based on the characteristics of heavy metals and their environmental behavior [16]. The calculation formula is as follows:

$$C_r^i = \frac{C_s^i}{C_n^i} \tag{1}$$

C_r^i is the single pollution coefficient of a heavy metal, C_s^i is the measured content of a heavy metal element in mg/kg, and C_n^i calculates the required parameter ratio in mg/kg for this element.

$$E_r^i = T_r^i \times C_r^i \tag{2}$$

E_r^i is the potential ecological risk coefficient of a heavy metal, and T_r^i is the toxicity corresponding coefficient of a heavy metal.

$$RI = \sum_{i=1}^{n} T_r^i C_r^i \tag{3}$$

RI is the comprehensive potential ecological risk index of multiple heavy metals at a certain point.

The E_r^i and *RI* values were used to divide the potential ecological harm levels into different levels [17]. The standard treatment values of the toxic response coefficients of the pollutants [18] were Pb = 5, Ni = 5, Cu = 5, Cr = 2, Cd = 30, and As = 10. The hazard levels were divided into different degrees based on the E_r^i and *RI* values. Table 2 shows the relationship between E_r^i and *RI* and the degree of pollution.

Risk Assessment Coding

The RAC method systematically evaluates potential risks associated with heavy metals by analyzing their morphological characteristics. It was proposed by Perin et al. [19], and the calculation formula is shown as follows:

Table 2. Hakanson ecological risk classification table.

Degree of harm	Ecological risk level	E_r^i	*RI*
Minor ecological hazard	I	E_r^i<40	*RI*<150
Medium ecological hazard	II	40≤E_r^i<80	150≤*RI*<300
Strong ecological hazard	III	80≤E_r^i<160	300≤*RI*<600
Severe ecological hazard	IV	160≤E_r^i<320	-
Extreme ecological hazard	V	E_r^i≥320	*RI* ≥600

$$F_{RAC} = \frac{C_{F1}+C_{F2}}{C_{F1}+C_{F2}+C_{F3}+C_{F4}+C_{F5}} \times 100\% \quad (4)$$

where FRAC is the percentage (%) of the exchangeable state content and the carbonate binding state content in the sum of the five forms, and CF1 is the exchangeable state content in mg/kg; CF2 is the content of carbonate binding state in mg/kg; CF3 is the content of iron (manganese) oxide binding state in mg/kg; CF4 is the content of organic binding state in mg/kg; and CF5 is residue content in mg/kg. To quantitatively evaluate environmental risks, the RAC method divides risks into five risk levels: no risk (FRAC<1%), low risk (1%≤FRAC <10%), medium risk (10%≤FRAC<30%), high risk (30%≤FRAC < 50%), and very high-risk (FRAC≥50%).

Data Analysis and Quality Control

Excel 2016 and SPSS 24.0 analyzed and statistically processed the total amount of heavy metals, various form content, comprehensive potential ecological risk index, and RAC value, while the Origin 2021 software drew the graphics. The standard reference material (GBW (E) 0300013) for analyzing heavy metal content in cement clinker was used for quality control during the test.

Results and Discussion

Physical and Chemical Properties of Slag

Morphology Observation and Energy Spectrum Analysis

As shown in Fig. 1, the slag particles exhibit a black or gray color and mainly consist of large-sized, massive particles. They possess an irregular and multi-angular surface topography that appears rough with obvious porous features after sintering. Microscopically, the surface is smooth but contains tiny holes. The particle size of the slag is generally distributed in 0.02–2 mm and is classified as sand.

In Fig. 1, particles of different sizes were selected for point scanning, and the energy spectra of the corresponding points are shown in Fig. 2. The elemental composition and mass fraction of each detected point are shown in Table 3. The slag mainly contained five elements, O, Ca, C, Si, and Al, of which the Ca concentration accounted for 36.27% of the chemistry. The slag particles were mainly calcium-based compounds.

Mineral Composition Characteristics

The minerals in the slag are mainly mullite (M) and quartz (Q), and a small amount of kaolinite (K), pyrite (P), gypsum (G), anatase (An), potassium feldspar (O), hematite (H), and other mineral phases (Fig. 3). Jade6.5 software and PowderX software analysis simulation calculations were used to perform a phase analysis. The contents were: mullite 33.0%, quartz 11.7%, kaolinite 9.8%, pyrite 6.9%, gypsum 7.4%, anatase 6.4%, potassium feldspar 19.6%, and hematite 5.2%.

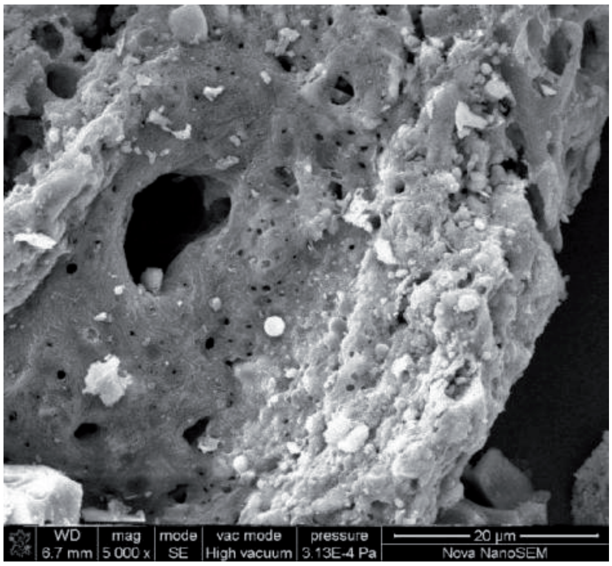

Fig. 1. Scanning electron microscopy (SEM) image of furnace bottom slag.

Nutrient Characteristics

Based on the nutrient classification standard of the second National Soil Survey [20], the pH value of the furnace slag in the power plant was 8.68, which is alkaline. The available potassium content of the slag was 268.16 mg/kg, which is in the grade I abundance level. The organic matter content was 35.11 g/kg, which is in the rich level of grade II. The available phosphorus content was 5.70 mg/kg, which was in the deficient level of IV. Lastly, the nitrogen alkali-hydrolyzed content was 26.51 mg/kg, classified in the extremely deficient class VI.

Occurrence of Heavy Metals in the Slag

Total Amount and Available State of Heavy Metals

The average total concentration of the six heavy metal elements in the slag is lower than the screening value of the soil pollution risk of agricultural land (basic items), and the average concentrations of the effective state are much lower than the lower screening value of soil pollution risk of agricultural land (Table 4).

Compared with the background concentration of the Ningxia soil, only the Pb in the slag was lower than the background concentration. The average total concentrations of the other heavy metals exceeded

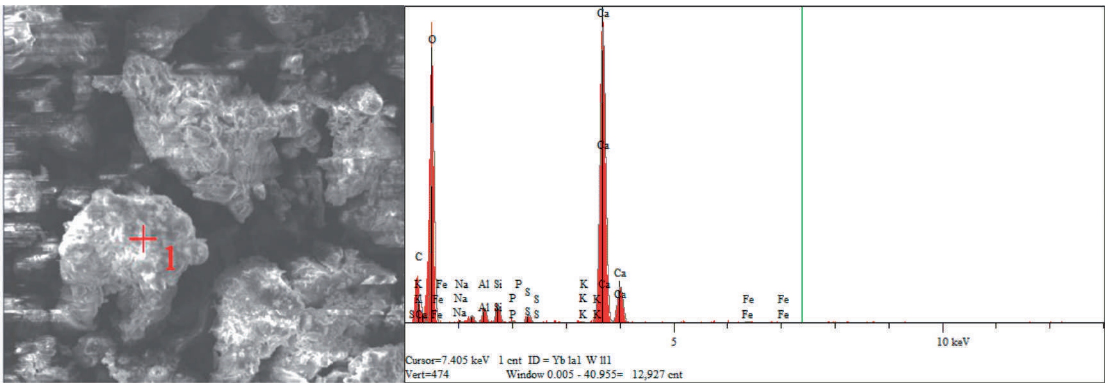

Fig. 2. Energy spectrum analysis of furnace bottom slag.

Table 3. Element composition and mass fraction of coal-based solid waste at particle detection points (%).

Element	O	Ca	C	Si	Al	S	Fe	Mg	Na	P	K
Mass Fraction	55.31	36.27	3.89	1.22	1.06	0.6	0.6	0.54	0.21	0.17	0.13

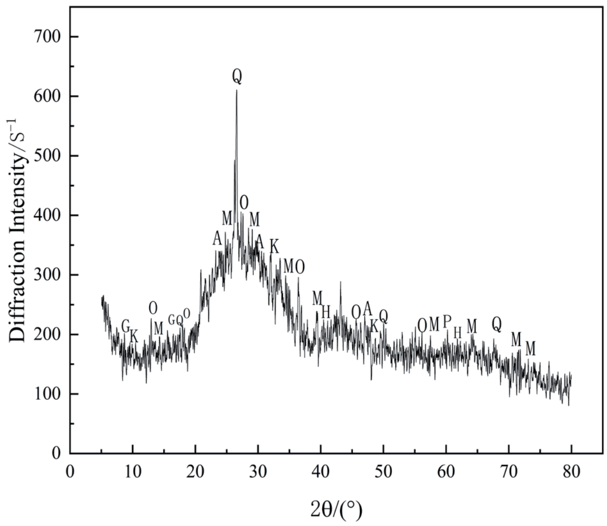

Fig. 3. X-Ray diffraction (XRD) pattern of furnace bottom slag.

the background value of the Ningxia soil. The total concentration of As exceeded the standard 5.36 times, Cd exceeded the standard 4 times, Cu exceeded the standard 2.13 times, Cr exceeded the standard 1.93 times, and Ni exceeded the standard 1.16 times. The average concentration of the six kinds of heavy metals was lower than the soil environmental background value in Ningxia.

The Occurrence Form of Heavy Metals

The Pb, Cr, Ni, Cd, and As mainly exist in the residual state (F5), and the residual state content accounts for 99.21%, 95.75%, 71.84%, 98.56%, and 74.22%, respectively (Fig. 4). Cu mainly occurs in the residual (F5) and organically combined (F4) states, and its concentration accounts for 47.61% and 32.66%, respectively. Ni and As mainly exist in residual and exchangeable states, where exchangeable state content accounts for 28.05% and 25.49%, respectively. Ni and As elements in the exchangeable states indicate

Table 4. The average concentration of heavy metals in bottom slag (mg/kg).

Heavy metal	Average	Ningxia soil environmental background value [a]	Agricultural land soil pollution risk screening value [b] (pH>7.5, others)
Pb	15.54	20.60	170.0
Cr	116.97	60.60	250.0
Ni	42.37	36.60	190.0
Cu	47.06	22.10	100.0
Cd	0.44	0.11	0.6
As	63.74	11.90	25.0

Note: a. Data from reference [21]; b. Data from reference [22].

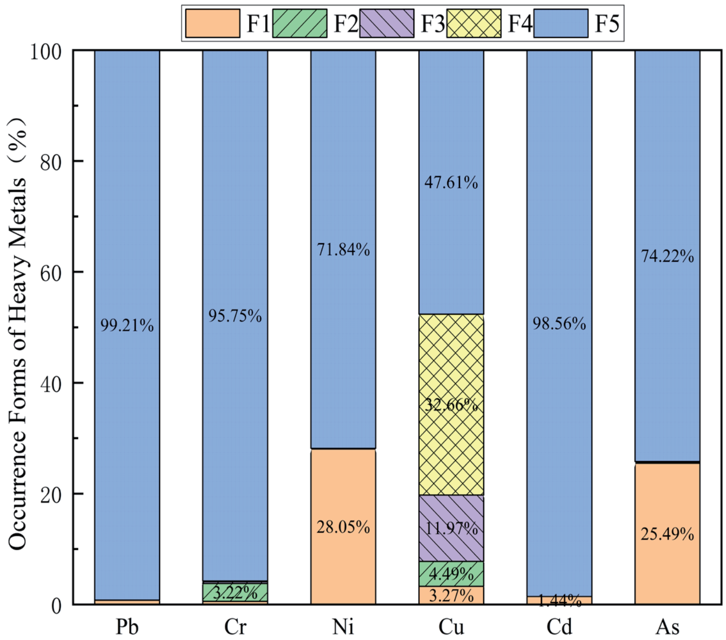

Fig. 4. Occurrence forms of six heavy metals in furnace bottom slag.

that As and Ni are enriched on the slag particles and can easily migrate into the environment.

Potential Ecological Risk Assessment of Heavy Metals in Slag

Potential Ecological Risk Index

The total amounts of E_r^i and *RI* of the six heavy metals in the slag were calculated using the Ningxia soil background value as a reference ratio. The evaluation results based on the total amount show that the E_r^i index of the potential ecological risk of six heavy metal elements in the slag is in the order of Cd>As>Cu>Ni>Cr >Pb (Table 5). The E_r^i index of Cd is 118.64, a grade III ecological hazard, and the E_r^i index of the As element is 53.56, a grade II ecological hazard (Table 5). The E_r^i of other elements was lower than 40, and the pollution degree was at the slight ecological hazard level. Cd was the most important ecological risk contributing factor, at a rate of 60.45%. The comprehensive potential ecological risk index *RI* of the six heavy metals in the slag is 196.27, and the *RI* index is less than 300, which indicates that the comprehensive potential ecological risk index *RI* value of the total six heavy metals in the slag is at a II level and a medium ecological hazard level.

Risk Assessment Coding

The F_{RAC} values of As and Ni were 25.58% and 28.15%, respectively, with moderate risk, indicating that under the influence of a certain external environment, As and Ni elements in slag will migrate and adapt to the environment (Fig. 5). The F_{RAC} values of Cd, Cr, and Cu were between 1% and 10%, with a low-risk effect. The F_{RAC} value of Pb was less than 1%, which is a risk-free grade. The ecological risk degree of the six heavy metals in the slag was Ni>As>Cu>Cr>Cd>Pb.

Table 5. Potential ecological risk index of total heavy metal content in furnace bottom slag.

Heavy metal element	Total elemental content C_si	Parameter ratio C_n^i	Single-element potential ecological risk index E_r^i	Contribution value of the total amount of single element to *RI* value %	Comprehensive potential ecological risk index *RI*
Pb	15.54	20.60	3.77	1.92	196.27
Cr	116.97	60.60	3.86	1.97	
Ni	42.37	36.60	5.79	2.95	
Cu	47.06	22.10	10.65	5.43	
Cd	0.44	0.11	118.64	60.45	
As	63.74	11.90	53.56	27.29	

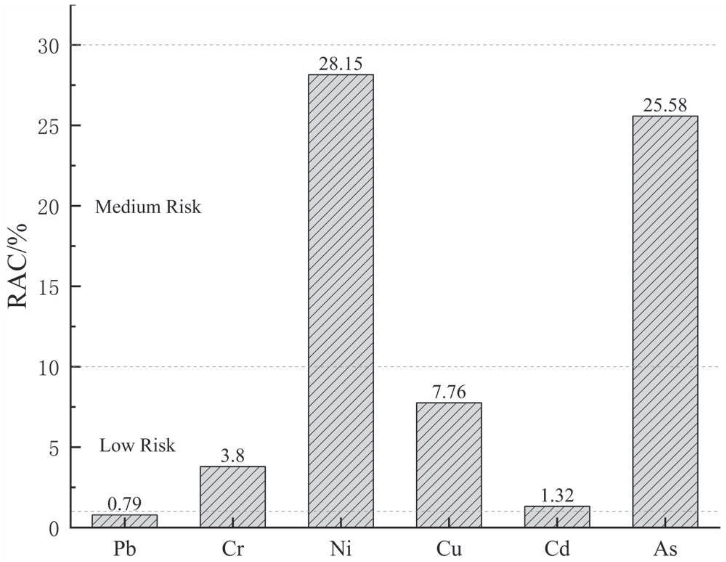

Fig. 5. Risk Assessment (RAC) evaluation index of six heavy metals in furnace bottom slag.

Combined with the results of the potential ecological risk index method and the risk evaluation coding method, the Cd, Ni, and As in the slag are the main potential polluting elements. In particular, Ni and As in the exchangeable states in the slag accounted for 28.05% and 25.49%, respectively, indicating these two elements' large potential environmental migration. If large-scale resource utilization of slag is carried out, there may be a risk of Cd, Ni, and As, which can cause environmental pollution, endangering the ecology. Although slag has a good microstructure and a high content of available potassium and organic matter, it is not recommended to be used as a soil and water conditioner. However, it can be applied to road-based paving, the production of construction materials, ceramsite firing, and cement filling. Alkaline materials can effectively solidify heavy metals, passivate heavy metal activity, improve their stability, and reduce their environmental pollution risk [23-25]. In addition, leaching agents (such as chelating agents and organic acids) can also be used to pretreat the slag, and the leaching can reduce the dissolution of Cd, Ni, and As elements in the slag to achieve harmless utilization [26].

Conclusion

(1) The slag mainly comprises sand particles with a rough and porous micro-surface morphology. The slag mainly contains five elements: O, Ca, C, Si, and Al. Of these, the highest content of Ca elements is 36.27%. The mineral composition of the slag is mainly mullite (33.0%), quartz (11.7%), and kaolinite (9.8%). The available potassium and organic matter content in the slag is high, while available phosphorus and alkali-hydrolyzed nitrogen are lacking.

(2) The average concentrations of the six heavy metals in slag were lower than the risk screening value of agricultural land soil pollution. The Pb, Cr, Ni, Cd, and As in the slag mainly exist in the residual state (F5), where the residual state accounts for 99.21%, 95.75%, 71.84%, 98.56%, and 74.22%, respectively.

(3) The comprehensive potential ecological risk index (RI) value of six heavy metals in the slag is 196.27, and the RI value is less than 300. The comprehensive potential ecological risk index RI value of heavy metal classifies in the II level, with a medium ecological hazard level. The RAC evaluation results showed that As and Ni pose a moderate risk, Cd, Cu, and Cr pose a low risk, and Pb poses no risk. The results of the potential ecological risk assessment, based on the total content, show that heavy metals Cd, Ni, and As are potential pollution factors in the main slag and that large-scale utilization of the slag may have potential threats to the surrounding environment.

(4) Although the available potassium and organic matter in power plant slag reach the Grade I abundance level and the rich level of Grade II, respectively, indicating relatively high concentrations, the comprehensive potential ecological risk index RI value of heavy metals falls within Level II, signifying a moderate ecological hazard. Therefore, power plant slag is not suitable for use as a soil conditioner. It is suggested that the slag be applied to road base construction, production of building materials, ceramsite firing, and cemented filling materials to foster bulk resource utilization and reduce the risk of heavy metal pollution to the environment during its application.

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Conflict of Interest

The authors declare no conflict of interest.

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