Characteristics of migration and speciation of trace elements during co-processing of antibiotic residues in a circulating fluidized bed

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Abstract

In order to study the emission characteristics of the products during the blending of antibiotic residues in coal-fired power plants, blending tests were performed on a 140 t/h circulating fluidized bed boiler. It was found that during combustion, 64 to 87.6% of Cr, As, and Pb are concentrated in the fly ash, and 11.4 to 35% are concentrated in the bottom ash. Only a small amount of these elements are captured by the desulfurization system or enter the environment. During the material distribution of the desulfurization system, trace elements are mostly concentrated in gypsum. In the desulfurization system, the proportion of Cr, As, Pb, Be, Mn, Co, Ni, Se, and Mo in the gypsum range from 82.8 to 99.9%, and the content has reached the level of ppm. When the blending ratio is controlled within 7%, the blending of antibiotic residues has little effect on the elemental composition of coal. The contents of Cr, Ni, Cu, Zn, and Ba in the products increased by 9.5 to 22.3%. This may mean when the blending ratio is increased, it will be harmful to the environment.

Keywords Circulating fluidized bed · Desulfurization · Distribution · Environmental risk · Trace element

Introduction

With the acceleration of industrialization, the discharge of hazardous wastes increases rapidly. The preliminary estimate of hazardous waste production in China in 2019 is 94.08 million tons. Compared with the huge amount of hazardous waste generated, China's hazardous waste treatment capacity is seriously insufficient. In 2020, affected by the outbreak of the coronavirus during the Chinese New Year, it is estimated that the output of medical waste in China will increase by more than 20%. It is estimated that the output of hazardous waste in China will be driven by the growth of the output of medical waste in 2020, or more than 100 million tons (National bureau

of statistics 2018). Sources of hazardous waste are relatively common, mainly from the waste liquid, waste residue, sludge produced by the paper industry, chemical plant sludge, petrochemical sludge, laboratory organic waste liquid, industrial organic waste liquid, and medical waste. The hazardous waste treatment technologies mainly include physical treatment (Tong et al. 2019), chemical treatment, and biological treatment, and the final waste disposal technologies include landfill, incineration technology, surface treatment, and marine disposal (Wang 2017; Liu 2014). Because of the shortage of land resources, incineration technology is currently the most effective method for large-scale hazardous waste treatment. It can completely eliminate the toxicity and hazards of waste while reducing the volume of hazardous waste to the greatest extent (Zhao et al. 2002; Sandelin and Backman 2001). At present, research and practical operation of industrial boilers for incineration of hazardous wastes are mainly circulating fluidized bed boilers and pulverized coal furnaces.

Due to the uneven diameter of the antibiotic residue, the discharge may exceed the standard during the operation of the circulating fluidized bed. At the same time, the material in the fluidized bed boiler has the characteristics of high concentration and high wind speed (Jiang et al. 2020), which leads to serious wear of the boiler components. In comparison, the

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circulating fluidized bed has more advantages for solid waste disposal. During the combustion of the circulating fluidized bed, in order to prevent the environmental pollution caused by the leakage of hazardous waste, the furnace is maintained to operate at a negative pressure of 30–50Pa (Liu et al. 2020). Due to the strong adaptability of the circulating fluidized bed to the materials entering the furnace, it has perfect combustion performance for hazardous wastes with high moisture content and low heating value (Zhu et al. 2019). During the combustion process, the bed material has a large contact area and a long residence time, which can effectively pyrolyze hazardous waste. At the same time, the low-temperature, staged combustion used in the circulating fluidized bed can effectively limit the harmful gases generated during the combustion of hazardous waste. Therefore, the circulating fluidized bed is more suitable for the co-processing of hazardous waste.

The content of trace elements in hazardous wastes is quite different from that in coals. During the co-processing process, it may lead to changes in the distribution and enrichment of trace elements or an increase in pollutants in the flue gas. The discharge of trace elements in coal and its harm to the environment become an issue of increasing concern. Studying the characteristics of migration and speciation of trace elements in the combustion process can lay the foundation for the clean utilization of coal in the study area. Liu et al. (2009) studied the combustion characteristics, flue gas emissions, and ash and slag emissions in a CFB simulation test bench under co-processing of sludge and coal water slurry. The results show that the content of trace elements As, Cd, Cr, Cu, Co, Ni, Pb, and Zn in the bottom ash and fly ash after blending with oil sludge is lower than the standard line, and it can be used as cultivated soil recycling. Zhu et al. (2009) studied the emission characteristics of trace elements Hg, Pb, Ni, Cr, Cu, and Zn in the co-combustion process of petrochemical sludge and coal on a 0.2MW pilot-scale circulating fluidized bed experimental bench, and found that when the mass ratio of petrochemical sludge to coal increased from 10 to 40%, Hg and Zn emissions increased, while Pb and Ni emissions decreased. Duan et al. (2017) studied the distribution rule of arsenic during the co-processing of petroleum coke by three 440 t/h circulating fluidized bed boilers, and found that As mainly exists in electrostatic dust removal and bag dust removal, accounting for 17.4 to 37.5% and 55.6 to 77.5%, respectively. Morphological analysis shows that As^{5+} is the main water-soluble substance in the incoming fuel, bottom ash, and fly ash, while As^{3+} is the main water-soluble substance in wet flue gas desulfurization (WFGD) wastewater. Dong et al. (2015) carried out experiments on co-combustion of coal and tannery sludge on a 35-kW fluidized bed burner, studied the combustion process and emission characteristics of the fuel, and found that due to the long residence time of the fuel in the high temperature area of the furnace, the oxidation degree of Cr in ash is high, and CrO_3 and $\text{CrO}_2(\text{OH})_2$ are mainly produced.

In this paper, the antibiotic residues are divided into wet antibiotic residues before drying and dry residues after drying. Residues are added under different working conditions. The sampling and analysis of the material in and out of circulating fluidized bed mixed with antibiotic residue are carried out to explore the migration and occurrence of various heavy metals in the combustion process. This paper can provide some data and theoretical basis for the effective control of trace element emission.

Test object and analysis method

Basic conditions of the test

This test was carried out in a 140 t/h circulating fluidized bed boiler in Shandong province. The boiler flue gas desulfurization project (FGD) uses a limestone-gypsum wet desulfurization process. Figure 1 shows a circulating fluidized bed system diagram:

There are three fuel sampling points in the furnace. The first is the belt under the coal bunker, which is the sampling point of dry coal slime or a mixture of dry coal slime and dry antibiotic residues; the second is mixing chambers, which are sampling points for coal water slurry or coal water slurry and wet antibiotic residues; the third sampling point is the outlet of the lime tank. Dry antibiotic residues and wet antibiotic residues are sampled separately before blending. There are three solid samples taken out of the furnace. Fly ash is sampled at the outlet of the ash storehouse, bottom ash is sampled at the boiler slag outlet, and gypsum is sampled at the belt of the vacuum filter, as shown in Fig. 2.

Analysis of raw coal

The antibiotic residue during the co-processing process comes from a local pharmaceutical factory. The residue is the mixed bacteria residue in the purification process of the raw material medicine. It contains four antibiotics: kanamycin, abamectin, salinomycin, and monensin. The antibiotic residues are classified as pharmaceutical wastes in China's "National Hazardous Waste List," and their hazardous characteristics are T-level (toxicity). The field test is divided into three working conditions: blank working condition, wet drug residue working condition, and dry drug residue working condition. During the test, the mass ratio of dry coal slime and coal water slurry was stable at 6:4, the boiler load was stable at 100 t/h, and the test time under different conditions was 8 h. Under the condition of wet medicine slag, the blending ratio of wet medicine slag and wet slime is stable at 1:15, and under the condition of dry medicine slag, the blending ratio of dry medicine slag and dry slime is stable at 1:20.

Fig. 1 CFB system diagram

The industrial analysis and calorific value of the incoming coal and antibiotic residue are shown in Table 1. The reference standard for industrial analysis is GBT212-2008 and for calorific value is GB213-87.

According to the data in Table 1, the volatile content of antibiotic residues is relatively high. Especially in dry residues, volatiles account for 53.01% of the total solids, and the fixed carbon content is lower than 8.6%. The dried slag has a large calorific value, reaching 12.69 MJ/kg, and its high volatility ensures the combustion performance in the furnace, which can be used as an excellent alternative fuel.

Table 2 shows the content of each trace element in the furnace material during the test. The contents of trace elements Cr, As, Pb, Mn, Ni, and Mo all reached the ppm level. The contents of Cr, Mn, Co, and Ni in the residue are similar to the corresponding heavy metal content in raw coal.

Samples of coal (dry coal slime and coal slurry), antibiotic residues (dry antibiotic residues and wet antibiotic residues), quicklime, fly ash, gypsum, desulfurized wastewater, and flue gas were sampled at 2 h and 6 h after the test started. The smoke sampling method refers to USEPA Method 2. The smoke sampling for each working condition lasts for 1 h, and the sampling point is the section of the chimney discharge port, during which the operating conditions parameters are kept stable.

Digestion experiment

The samples collected during the test were brought back to the laboratory for analysis. The reagents used in the test were loaded with national standard premium grade pure (GR) chemical reagents, and the experimental water was freshly prepared deionized water. The retrieved samples were analyzed using an inductively coupled plasma mass spectrometer (ICP-MS), model Agilent 7500a. During the experiment, 0.1–0.2 g of the sample was weighed back, and 1 ml of hydrochloric acid (superior pure 1.19 g/ml), 1 ml of hydrogen peroxide (30%), and 4 ml of nitric acid (superior pure 1.42 g/ml) were added. The electric heating plate is heated at a low temperature of 120 °C. When the solution in the digestion tank is brought to 3 ml, it is removed and cooled. After adding 5 ml of nitric acid to cover, it is heated on a hotplate at 180 °C. The digestion tank is placed on an acid drive instrument at 150 °C. Heat the acid until the content of the soy is the size of soybeans. Transfer the solution to a 50-ml volumetric flask and filter with qualitative filter paper in the middle. During the experiment, a blank group and a blank spiking group are added, which are detected after the same test steps as the sample to be tested, to prevent the trace elements in the reagent from affecting the experimental results.

Fig. 2 Location of sampling points

Table 1 Industrial analysis and low calorific value of incoming coal and biotin residue

Working condition	materials	Mt (%)	Mad (%)	Aad (%)	Vad (%)	Fcad (%)	Low calorific value (MJ/kg)
Blank condition	Dry slime	7.90	0.86	39.07	8.84	44.19	15.94
	Coal water slurry	31.46	12.14	26.84	21.57	20.13	13.83
Working conditions of wet antibiotic residues	Dry slime	7.64	1.44	36.87	8.58	46.91	17.58
	Coal water slurry	32.86	15.79	24.39	19.46	23.29	13.70
	Wet antibiotic residues	60.07	43.23	18.26	16.29	5.38	5.71
Working condition of dry antibiotic residues	Dry slime	6.62	0.70	38.55	8.62	46.21	16.58
	Coal water slurry	32.13	11.09	24.37	21.67	21.83	13.56
	Dry antibiotic residues	10.75	5.17	27.68	53.01	8.56	12.69

Leaching experiment

According to HJ/T 299-2007 “Solid waste-Extraction procedure for leaching toxicity-sulphuric acid & nitric acid method,” after measuring the moisture content of the sample, add a mixed solution of concentrated sulfuric acid and concentrated nitric acid with a mass ratio of 2:1 to the reagent water and adjust the pH to 3.20 ± 0.05 , used as the extractant to determine the leaching toxicity of trace elements in samples. Weigh 150–200 g sample and place it in a 2-l extraction bottle. According to the water content of the sample, calculate the volume of the required extractant according to the liquid-solid ratio of 10:1 (l/kg), and add the configured extractant. After the bottle cap is tightly closed, it is fixed on a flip-type oscillating device, the rotation speed is adjusted to 30 ± 2 r/min, and the oscillation is performed at $23 \pm 2^\circ$ for 18 ± 2 h. When gas is generated during the shaking process, open the extraction bottle in a fume hood to release excessive pressure. As in the digestion experiment, a blank group was set during the leaching experiment to eliminate the effect of trace elements in the extractant on the experimental results.

Analytical method

To explore the migration and conversion of heavy metals in the process of collaborative disposal, we used the mass balance ratio and mass distribution law of trace elements.

According to the experimental test results and the output rate of the product during the test, the output rate of trace

elements in the product per unit time can be calculated. The total distribution of trace elements in the coal-fired product follows mass conservation:

$$M_{ic} = M_{if} + M_{ib} + M_{ia} + M_{ig}$$

where M_{ic} is the total amount of heavy metal i input, M_{if} is the content of heavy metal i in fly ash, M_{ib} is the content of heavy metal i in the bottom slag, M_{ia} is the total amount of heavy metal i in the flue gas, and M_{ig} is the total amount of heavy metal i in gypsum, the amount definition:

$$R_i = (M_{if} + M_{ib} + M_{ia} + M_{ig}) / M_{ic} \times 100\%$$

R_i is the mass balance ratio of trace elements. It is used to verify the accuracy and reliability of field test data of coal-fired power plants. Mass balance analysis of nine different heavy metals (Cr, As, Pb, Be, Mn, Co, Ni, Se, Mo) was carried out. Because the mass fraction of trace elements is usually very low, and there are fluctuations in unit load during sampling and unavoidable human errors, the mass balance rate of trace elements is 70~130% which is generally acceptable (Wang et al. 2009; Quick and Irons 2002).

The mass distribution of a trace element refers to the ratio of the mass of the heavy metal element migrated to a certain combustion by-product to the total amount of heavy metal during the migration process. According to the content of trace elements in the product and the output rate of the product, the occurrence of different trace elements during the experiment can be calculated to obtain the mass distribution rate (Honghong et al. 2008). The calculation formula is as follows:

Table 2 Content of trace elements in furnace fuel (ppm)

Trace element	Cr	As	Pb	Mn	Co	Ni	Se	Mo
Wet antibiotic residues	23.59	3.99	8.61	75.60	4.99	18.34	2.97	<0.80
Dry antibiotic residues	14.67	0.86	2.59	121.00	2.80	6.89	<0.68	4.01
Coal water slurry	17.68	4.54	15.09	112.70	4.91	14.74	2.49	<0.80
Dry coal slime	52.89	7.61	21.71	168.00	5.68	31.32	4.17	2.15

$$K_i = \frac{N_i \times V_i}{N_1 \times V_1 + N_2 \times V_2 + \cdots N_4 \times V_4}$$

where K_i is the mass distribution rate, N_i is the content of heavy metal in the product, and V_i is the discharge rate of the corresponding product.

Results and analysis

Mass balance ratio of trace elements

The calculated mass balance of trace elements is shown in Fig. 3. The area between the dotted lines indicates that the mass balance rate is acceptable. In the course of the test, there are fluctuation of the rate of fuel in the furnace, non-uniformity in the sampling process, human error, and instrument error in the laboratory measurement process. Mo under wet residue condition is 132%. The content of Mo in fuel and solid waste is at a low level, so a slight error will cause the mass balance rate to exceed the required range. The mass balance rates of all trace elements under other conditions are between 70 and 130%. In Fig. 3, the mass balance rate basically falls between the dotted lines, which indicates that the data of this sampling experiment is accurate and reliable, and provides a basis for the analysis and discussion below.

Distribution of trace elements in the combustion process

During the combustion stage in the circulating fluidized bed furnace, the mixture of raw coal and slag is fed into the boiler at a uniform speed, and the primary air enters the combustion chamber from the air distribution plate at the bottom of the

furnace. At the beginning, a reducing atmosphere is formed in the combustion area. This area is called dense phase zone. In the dense phase zone, the large particles of the bed material flow downward due to gravity. The small particles flow upward with the flue gas and enter the rare phase zone. They are mixed with the secondary air in an oxidizing atmosphere to maintain the boiler load and burning condition of the furnace during the test (Table 3).

The furnace temperature distribution of the circulating fluidized bed under different working conditions is shown in Table 4.

During the combustion of the circulating fluidized bed, the particle concentration in the dense phase zone is higher. There is a transition zone between the dense phase zone and the lean phase zone. At the same time the high particle concentration is gradually reduced to the lower particle concentration. Most trace elements are easier to volatilize and vaporize in the reducing atmosphere in the dense phase zone, and are easier to activate in the oxidizing atmosphere in the dilute phase zone. Trace elements react with oxygen to generate a higher melting point and more stable chemical oxidation and thus migrate into the ash. At the same time, there are a large number of particle maps formed by the aggregation or agglomeration of fine particles in the dilute phase zone, and these particles continue to form and adsorb other fine particles. The distribution ratios of different trace elements during the test were analyzed, as shown in Fig. 4, Fig. 5, and Fig. 6.

During the combustion in a circulating fluidized bed furnace, the main combustion zones are the lean phase zone and the dense phase zone. The slag in the antibiotic residues is high, and the mixed fuel burns quickly after entering the furnace, and the combustion share in the dense phase zone is low. During the test, the temperature in the dense phase zone was about 850°C. The mixture of slag and coal was first burned in a reducing atmosphere between 800 and 900° (Frandsen et al. 1994).

Fig. 3 Mass balance ratio of trace element

Table 3 Material input and output rate Vi

Working condition	Dry slime (t/h)	Coal water slurry (t/h)	Dry antibiotic residues (t/h)	Wet antibiotic residues (t/h)	Lime powder (t/h)	Fly ash (t/h)	Slag (t/h)	Gypsum (t/h)	Waste water (t/h)	Gas (m ³ /h)
Blank	11.5	9.4	0	0	1.29	9.00	4.50	3.78	0.33	257588
Wet antibiotic residues	12.4	9.3	0	0.55	1.25	9.80	4.70	3.38	0.37	242286
Dry antibiotic residues	12.3	9.5	0.59	0	1.22	9.10	4.50	3.38	0.37	257588

Due to the high melting point of Cr and its main compounds, it was mainly in the dense phase zone. CrCl_3 decomposes into elemental substance and becomes gaseous phase; entering the transition zone, the temperature is reduced to 750 °C. Cr reacts with sulfur compounds generated by combustion, and mainly exists stably as solid $\text{Cr}_2(\text{SO}_4)_3$. Feng (2004) used the thermodynamic calculation software F*A*C*T to make predictions. Results show that all Cr compounds have stable chemical and physical properties. The compounds decompose only at temperatures above 2000 °C. The predicted results show that Cr mainly exists in the form of $\text{Cr}_2(\text{SO}_4)_3$ and CrO_2Cl_2 at 600 ~ 800 °C; when the temperature is higher than 800 °C, all turned into solid Cr_2O_3 (Kashireninov and Fontijn 1998). After entering the dilute phase zone, the temperature is 825 °C. During this process, Cr is transformed from solid $\text{Cr}_2(\text{SO}_4)_3$ into Cr oxides such as Cr_2O_3 , FeCr_2O_4 , CrO_2OH , and $\text{Cr}(\text{OH})_2$. Cr oxides have stable chemical properties and the melting and boiling point is low, so Cr migrates mainly to fly ash and bottom slag (Goodarzi and Huggins 2005).

As can be seen from Fig. 4, Cr is mainly present in fly ash under three operating conditions, accounting for 64 to 72.4%, and part of it is present in the slag, accounting for 26.6 to 35%. After bag dust removal and static electricity dust removal, a small amount is distributed in desulfurized gypsum, desulfurized wastewater, and flue gas. Cheng et al. (2002) studied the distribution of Cr in the products after combustion at different temperatures, and showed that there was no significant difference in the occurrence of Cr in fly ash and bottom slag with the rise of temperature. More than 78.2% of Cr

was deposited in fly ash, and 19.7% was deposited in bottom slag. This is slightly different from the experimental results in this paper. Because the circulating fluidized bed first experiences a reducing atmosphere to an oxidizing atmosphere, it is different from a pulverized coal furnace. This led to a certain difference in the occurrence of Cr.

As is mainly present in the form of sulfide in coal powder and antibiotic residue. When it is burned in the dense phase zone, the sulfur state is converted to the gaseous state, As_2S_3 is decomposed into As_2 and As_4 , and the elemental As is more easily vaporized and released; Shah et al. (2008) studied the chemical forms of As during combustion. During the transition from the dilute phase zone to the transition zone, the temperature decreases, and the elemental As is converted into As_2O_3 and As_4O_6 in the oxidation state. Huang et al. (2020) studied the form of arsenic in the pulverized coal-fired boiler, and found that arsenic was completely released at 1000 °C and mainly present in the gaseous form of As_2O_3 below 1050 °C. The combustion temperature of fluidized bed boiler in this test is between 750 and 850 °C (Zhou et al. 2016).

There is a mutual conversion relationship between the two oxides:

When the particle size of the coarse particles decreases and the flue gas enters the 825 °C dilute phase zone, the coal particles themselves contain some mineral components, such

Table 4 Temperature distribution in different areas of the furnace (°C)

Project	Blank condition	Working conditions of wet antibiotic residue	Working condition of dry antibiotic residues
Dense phase zone temperature	844.05	846.39	853.58
Transition zone temperature	780.40	776.07	782.55
Lean phase zone temperature	828.74	823.59	829.42
Furnace outlet temperature	845.92	850.10	840.50
Cyclone return temperature	871.05	863.29	876.76
Main steam temperature	544.28	539.98	542.60
Feedwater temperature	216.36	212.89	218.49

Fig. 4 Distribution of Cr in different products

as silicon oxide, iron oxide, and calcium oxide. In the oxidizing atmosphere in the dilute phase zone under As, it is easy for Fe_2O_3 and CaO to react under oxygen-rich conditions:

Because $\text{Ca}_3(\text{AsO}_4)_2$ and FeAsO_4 are relatively stable in chemical properties, and the particle porosity increases at the temperature of the dilute phase zone, the diffusion resistance of As is reduced, which leads to an increase in the volatilization rate of As compounds. Therefore, As in solid waste and pulverized coal after combustion is more likely to occur in fly ash. Compared with pulverized coal furnace, more As is enriched in the bottom slag during CFB combustion. The content of As in bottom slag of pulverized coal furnace is between 1.4 and 5% (Cheng et al. 2009; Zhao et al. 2017; Fu et al. 2019). In the circulating fluidized bed boiler in this experiment, the content of As in the bottom slag was 11.7 to 14.5% of the total amount.

In a reducing atmosphere at 750 °C, Pb mainly comes from the decomposition of PbCl_2 and exists in the form of gaseous

Fig. 5 As distribution in different products

Fig. 6 Distribution of Pb in different products

Pb. When the temperature of the dense phase zone in the furnace is as high as 850 °C, the decomposition of PbCl_2 is accelerated and the content of Pb decomposed is increased. In an oxidizing atmosphere, the stability of PbCl_2 is improved, and the higher oxygen concentration inhibits its volatilization, which reduces the migration ability of Pb. With the flow of the flue gas, a part of the gaseous Pb volatilized into the gas phase will be in the process of flue gas cooling. Sub-micron particles are formed through homogeneous nucleation, or are re-adsorbed by fly ash particles through heterogeneous coagulation. At the same time, Pb will also chemically adsorb with fly ash, and some metal oxides on the surface of fly ash will chemically react with Pb. The Pb in the flue gas is adsorbed, so that Pb is concentrated in the fly ash, and very few compounds of Pb such as PbO_2 or PbCl_2 enter the desulfurization system with the flue gas. It can be seen from Fig. 5 that As basically occurs in fly ash and bottom slag. The percentage of As in fly ash and bottom slag is 81.5% and 11.8%, respectively. This is related to the form of compounds formed after As is burned in the furnace. The products of As after combustion are mainly oxides, with a small amount of Fe and Ca compounds. These compounds have the physical properties of high melting and boiling point, so they are easy to enter the bottom slag directly or combine with fly ash particles through homogeneous condensation and heterogeneous nucleation. The distribution of Pb, which has similar properties with As, also has similar laws during the combustion process. As compounds have a higher melting and boiling point than Pb compounds and have more stable chemical properties. The content of Pb in fly ash reached 87.5%, only 11.4% in bottom slag. The Cl element in the hazardous waste will cause Pb to be more easily enriched in the fly ash, thereby making the content of Pb in the fly ash and bottom slag higher.

Compared with pulverized coal furnace, CFB furnace temperature is lower. Lower furnace temperature inhibits the release of the less thermally stable compounds of arsenic. At the same time, the circulation fluidized bed combustion disturbance is severe, the material residence time is long, and the

return system makes the compounds of heavy metal with poor thermal stability released again. In the process of CFB combustion, the yield of bottom slag is much higher than that of pulverized coal furnace, and the ratio of fly ash to bottom slag can reach 1:1. These factors lead to the distribution of As and Pb in the bottom slag of CFB is significantly higher than that of pulverized coal furnace.

Distribution of trace elements in desulfurization system

The WFGD system will change the emission distribution of the original trace elements in coal-fired power plants; WFGD can be used as a repurification device to capture trace elements that escape from fly ash and gas. The WFGD system can dissolve and absorb water-soluble gas phase components in the flue gas on the one hand, and on the other hand, it can also wash away some of the fine particles that are not captured by the ESP. If these trace elements enter the flue gas directly, the content of them in the flue gas will be higher than the emission standard. These particles are small in size and can be enriched in a certain amount of harmful trace elements.

During the test, the desulfurization wastewater and wet electricity wastewater were directly returned to the lime slurry pond through the pipeline to prepare lime slurry. Therefore, the materials entering the desulfurization system were limestone, flue gas before desulfurization, and process water, and the materials leaving the desulfurization system were gypsum and clean flue gas. To establish a mass balance for this process, see Fig. 7.

Figure 8 shows the distribution of trace elements in the desulfurization system among the products of the desulfurization system.

In the desulfurization system, trace elements mainly exist in lime powder and desulfurized gypsum. In the desulfurized gypsum, the trace elements occupied by Cr, As, Pb, Be, Mn, Co, Ni, Se, and Mo are 99.6% of trace elements entering the desulfurization system 96.9%, 97.9%, 99.1%, 97.6%, 99.2%, 99.9%, 99.1%, and 82.8%. The content of trace elements in the desulfurized gypsum has reached the ppm level, while the trace elements are less distributed in the flue gas and desulfurized waste water. The various trace elements in the net flue gas only account for 0.01 to 1.95% of the trace elements in the flue gas entering the desulfurization system. Trace elements in waste water account for 1.4 to 13.5% of the amount entering the desulfurization system. Therefore, the desulfurization system has a good removal effect for trace elements, and the desulfurized gypsum has a good enrichment effect on the trace elements trapped in the gypsum slurry. After the trace elements in the flue gas have been washed by the limestone slurry in the desulfurization system, some soluble trace elements were enriched in the gypsum slurry and finally existed in the desulfurized gypsum. Table 5 shows

the contents of trace elements in desulfurized gypsum under three operating conditions.

Under different working conditions, the content of trace elements in desulfurized gypsum does not vary widely. The contents of Cr, Mn, Ni, and Se are in the ppm level, which are 3.89 to 5.55 mg/kg, 4.67 to 5.32 mg/kg, and 1.85 to 2.04 mg/kg. However, other trace elements such as As, Pb, Be, Co, and Mo are distributed in the desulfurized gypsum very little, and the detection results are all below the detection limit. It is worth noting that the contents of Mn and Se in gypsum increased after adding the residue. Under the two residue conditions, the Mn content increased by 9.4% and 9.2%, and the Se content increased by 8.9% and 9.3%, respectively. The distribution content of different trace elements in gypsum is arranged from large to small as: Cr > Mn > Ni > Se. The test results of this test are consistent with the results (Cordoba et al. 2012; Koralegedara et al. 2017; Li et al. 2015a; Li et al. 2015b). In order to better explore the enrichment of trace elements in the desulfurization system, the pH value was measured by taking out the pump slurry from the absorption tower and the pump slurry from the gypsum slurry tank during the test.

As can be seen in Table 6, after the reaction with SO_2 in the desulfurization tower, the slurry in the tower and the bottom of the tower were discharged from the pump. The pH value of the gypsum slurry is slightly higher than 7, which is slightly alkaline. Studies have shown that when the pH value of the desulfurization system slurry is greater than 7, the molar fraction of HSO_3^- decreases sharply, while the molar fraction of SO_3^{2-} increases sharply. Because SO_3^{2-} cannot provide H^+ , it cannot enhance the dissolution process of limestone. The dissolution rate of limestone slows down significantly after pH value exceeds 7.0, Ca^{2+} in the slurry, and Ca^{2+} are prone to react with trace elements of acid oxides. Therefore, the introduction of the WFGD system changed the emission distribution of the original trace elements in coal-fired power plants.

Fig. 7 Material balance of desulfurization system

Fig. 8 Distribution of trace elements in desulfurization system

Some trace elements originally emitted directly from the flue gas into the atmosphere are captured by the WFGD system.

Because of As, its volatile content is relatively high. From the circulating fluidized bed to the desulfurization system, it mainly exists in the gas phase in the flue gas. At this time, As exists as an oxide. That is, As_2O_3 , under the desulfurization system, the lower temperature As_2O_3 will gradually transform into As_2O_5 and $Ca_3(AsO_4)_2$ with acidic characteristics. When the flue gas enters the desulfurization system, the temperature is 160–170 °C. Similarly, Se also exists in the form of oxides after it exits the boiler, mainly SeO_2 , which is liable to react with alkaline substances, thereby generating $CaSeO_4$ in the desulfurization tower. Since Se and S are the same group of elements in the periodic table, they have relatively similar chemical properties, leading to the enrichment of Se in desulfurized gypsum. The two kinds of acid compounds are easy to react with the basic $Ca(OH)_2$ in the limestone slurry to generate chemical properties. Goodarzi and Huggins (2005) proved that $Ca_3(AsO_4)_2$ and $Ca(OH)_2$, which are relatively stable and have low solubility, are slightly soluble in water, and their solubility will decrease with the increase of the pH value of the solution, resulting in a greater concentration of As in the desulfurized gypsum. Not only does As and Se have a chemical reaction in the desulfurization tower, but also the homogeneous and heterogeneous condensation of the particles occurs due to the sudden drop in temperature, so that the heavy metal particles tend to be enriched in the desulfurized gypsum. After Pb comes out of the combustion

link, it mainly exists as highly oxidizing compounds, namely PbO_2 and $PbCl_2$, and reacts with SO_2 in the desulfurization tower to generate $PbSO_4$ through an oxidation process. Cr is likely to exist in the form of Cr_2O_3 in the original flue gas. In the desulfurization system, Cr_2O_3 is easy to react with the desulfurization slurry under alkaline conditions to generate $CaCr_2O_4$ which makes Cr more concentrated in the desulfurization slurry and gypsum.

For semi-volatile and hardly volatile elements such as Be, Co, and Ni, the flue gas mainly exists in the form of particulate phase after circulating fluidized bed. After entering the desulfurization system, these particles were partially captured by the spray washing action of the limestone slurry, and the captured small particles were adsorbed and fixed by the gypsum, which led to the enrichment of these elements on the gypsum.

Leaching toxicity of by-products

Table 6 shows the results of leaching toxicity test of fly ash, slag, and gypsum in the process of collaborative disposal and the comparison of China's current hazardous waste identification standard leaching toxicity identification (GB5085.3-2007). The leaching concentration of all trace elements was far below the standard limit of the leaching concentration. The high content of trace elements in the residue of mixed firing led to the increase of leaching concentration of trace elements in the by-products, especially fly ash and slag. The leaching concentrations of Cu in fly ash and slag were 12.95 and 14.59

Table 5 Heavy metal content in desulfurized gypsum under different working conditions

Working condition	Heavy metal (ppm)								
	Cr	As	Pb	Be	Mn	Co	Ni	Mo	Se
Blank condition	5.55	<0.95	<0.61	<2.5	4.67	<0.95	2.66	<0.80	1.85
Wet antibiotic residues	4.66	<0.95	<0.61	<2.5	5.11	<0.95	3.60	<0.80	2.03
Dry antibiotic residues	3.89	<0.95	<0.61	<2.5	5.10	<0.95	1.65	<0.80	2.04

Table 6 PH value of desulfurization system materials under different working conditions

Working condition	Position	PH value
Blank condition	Absorption tower	7.73
	Gypsum slurry	7.48
Wet antibiotic residues	Absorption tower	7.81
	Gypsum slurry	7.13
Dry antibiotic residues	Absorption tower	7.05
	Gypsum slurry	7.13

g/L in blank condition, 14.79 and 15.97 g/L in wet residue condition, and 16.58 and 16.47 g/L in dry residue condition, which increased by 14.2%, 9.5%, 28%, and 12.9% in blank condition. The leaching concentrations of Ba in fly ash and slag were 12.85 and 62.83 g/L in blank condition, 16.19 and 72.78 g/L in wet residue condition, and 19.58 and 83.65 g/L in dry residue condition, which increased by 26%, 15.7%, 52.4% and 33.1%, respectively, compared with blank condition (Table 7). Similar to Cu and Ba, the concentration of other trace elements also showed an increasing trend after the addition of burnt residue. However, the overall leaching concentration of trace elements with different by-products was relatively low, and the concentration of major trace elements in the by-product leaching solution was far lower than the relevant national standards. Therefore, in terms of leaching characteristics, under the condition of 5–6.7% ratio of mixing and burning of drug residue, the by-products of coal burning are

not hazardous wastes and can be reused. However, after mixing and burning, the inlet and outlet concentrations of different trace elements show an increasing trend.

Conclusion

(1) During the combustion process, Cr, As, and Pb are mainly present in fly ash, accounting for 64 to 87.6%, and some are present in slag, accounting for 11.4 to 35%. Only three trace elements are captured by the desulfurization system or follow Smoke enters the environment. The incoming fuel passes through the reducing zone and then through the oxidizing zone. The three trace elements in the reducing zone are decomposed from the common forms of chloride and sulfide into simple substances and exist in gaseous form. After entering the oxidizing zone, they form oxides with higher melting points, and oxides with different trace elements have high melting point and high boiling point. The melting point characteristics make it enriched in fly ash and slag.

(2) During the desulfurization process, trace elements are mainly concentrated in gypsum. Among them, 82.8 to 99.9% of Cr, As, Pb, Be, Mn, Co, Ni, Se, and Mo are present in gypsum, and the concentration of trace elements in gypsum has reached ppm level. The heavy metal content in the flue gas accounts for 0.01 to 1.95%, indicating that the desulfurization system has a good removal effect on the trace elements studied. Volatile heavy metal compounds in the flue gas, such as As_2O_3 , As_2O_5 , SeO_2 , Cr_2O_3 , and PbO_2 , react under acidic conditions of the desulfurization slurry to form the corresponding sulfate form, which is enriched in the desulfurization slurry

Table 7 Heavy metal leaching concentration in each product under different working conditions

Heavy metal	Blank condition			Wet antibiotic residues			Dry antibiotic residues			Standard limit
	Fly ash	Slag	Gypsum	Fly ash	Slag	Gypsum	Fly ash	Slag	Gypsum	
Be	0.07	0.27	0.00	0.04	0.19	0.00	0.06	0.30	0.00	20
Cr	5.18	4.74	0.04	3.78	4.35	0.27	4.26	5.79	0.23	15000
Ni	3.84	3.25	0.01	3.22	3.38	0.03	3.33	3.79	0.00	5000
Cu	6.45	7.55	0.08	4.86	8.08	0.06	4.64	9.64	0.06	100000
Zn	12.95	14.59	0.12	14.79	15.97	0.16	16.58	16.47	0.10	100000
As	1.02	2.73	0.01	0.43	1.87	0.01	0.60	2.87	0.01	5000
Se	2.79	4.25	0.00	0.02	1.29	0.00	2.54	4.45	0.00	1000
Ag	0.02	0.01	0.00	0.00	0.01	0.00	0.00	0.01	0.00	5000
Cd	0.02	0.20	0.00	0.02	0.06	0.00	0.02	0.05	0.00	1000
Ba	12.85	62.83	0.06	16.19	72.78	0.07	19.58	83.65	0.07	100000
Hg	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	100
Pb	0.44	2.30	0.01	0.42	3.16	0.02	0.39	2.64	0.01	100000

and finally enters the gypsum. Hardly volatile trace elements such as Be, Co, and Ni exist in the form of particles in the flue gas, and are partially captured by the spray washing action of the limestone slurry, thereby being enriched in gypsum.

(3) The leaching toxicity of the by-products of the circulating fluidized bed is lower than the current standards in China when the blending ratios of the wet antibiotic residues and the dry antibiotic residues are 1:15 and 1:20, respectively. When the blending rate is less than 6.7%, coal by-products are not hazardous waste and can be reused; the contents of Cr, Ni, Cu, Zn, and Ba in the products increased by 9.5 to 22.3%. In addition, in the case of increasing the blending ratio, may cause harm to the environment.

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Declarations

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