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Chapter 6

Trace Elements in Coal Gangue: A Review

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Abstract

Coal gangue is one of the largest industrial residues. It has high ash content, low carbonaceous content, and heating value. Meanwhile, it has some trace elements. Large quantities of coal gangue cause serious environmental problems by polluting the air, water, and soil as well as occupying a tremendous amount of land. Now, coal gangue utilization is a matter of great concern and has attracted wide interest. However, some toxic trace elements in coal gangue should be paid more attention during the utilization of coal gangue. In this article, the modes of occurrence and the leaching characters of trace elements in coal gangue were introduced according to the result of the sequential extraction method and the leaching method. The release character of trace elements during combustion of coal gangue and the environmental implication of trace elements in coal gangue were also discussed. The sulfide-bound trace elements are dominant form in coal gangue. Leaching behavior of trace elements from coal gangue is affected by many factors. Different trace elements presented different transformation behaviors. Trace elements in coal gangue could release out and produce environmental implication in various degrees, depending on the type of trace elements.

Keywords: trace elements, coal gangue, modes of occurrence, release, environmental implication

1. Introduction

Coal gangue is a significant residue during the processing of coal mining and coal washing, which accounts for approximately 10–15% of raw coal production and becomes one of the largest industrial residues in China [1]. The rapid growth of the mining industry in China over the last decades has resulted in large amounts of coal gangue piled in wastelands. According to Zhao et al., there are 1500 coal waste gobs in China and 108 are located in Shanxi province [4]. It is estimated that about 40% of coal gangue gobs undergo spontaneous combustion in Shanxi province [3].

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Coal gangue contains inorganic minerals and organic matter with high ash content, high pyrite content, and low heating value [1]. Besides the conventional pollutants of sulfur and nitrogen, it is enriched in some toxic elements which are present in less than 0.1% in coal gangue matrix [2–5]. Because of the existence of harmful trace elements in coal gangue, large quantities of coal gangue piled on the land can cause serious environmental problems by polluting the air, water, and soil as well as resulting in ecological risk [6–11]. Therefore, some reasonable methods should be taken to reduce the amount of coal gangue.

Recently, coal gangue utilization is a matter of great concern and has attracted wide interest in China [12]. Due to the lack of energy resources in China, coal gangue has been extensively utilized as a raw material for power plants to effectively utilize its calorific value [13, 14]. It is considered as a reasonable way to reduce the amount of coal gangue and environmental problems as well as bring some economic benefits [15]. According to the China resources utilization annual report 2014, the utilization of coal gangue as feed fuel for power plant was up to 150 million tons in 2013 in China [15]. However, during the utilization of coal gangue for power generation, the emissions of trace elements may have some severe environmental impacts besides the emission of sulfur dioxide, NOx or particulate matter [16]. It is well known that the trace element emissions during power generation may cause serious effects on human beings and the environment [15]. It is also reported that high emissions of trace element can cause some adverse effects for human health including acute and chronic lung injuries, inflammation and changed immunological mechanisms as well as increased cancer risk [17].

Over the past decades, extensive studies have been conducted on trace element in coal, especially trace element emissions from coal-firing power plants [18–21]. It is reported that the emission of trace elements is influenced by the thermodynamic properties of elements, the forms of elements in the feed fuel as well as the combustion environment [22–27]. Besides the experimental investigation, thermodynamic equilibrium calculation is also widely used to study the trace element behavior during coal combustion [28–32]. In addition, some studies have investigated the interactions between trace elements with the ash components and reported that the interactions play an important role in the emission behavior of trace element [33, 34]. Meanwhile, some studies such as the modes of occurrence and leaching behavior of trace element in coal have been conducted. Overall, the studies about the trace element in coal have provided meaningful information for the development of trace element control technologies.

In comparison to coal, coal gangue has a higher content of trace element and mineral [15]. Therefore, it can be inferred that the emission behavior of trace elements in coal gangue may be significantly different from that of coal, and thus the emission control of trace element from coal gangue is extremely important, especially from the combustion of coal gangue [15]. Although the combustion of coal gangue for power generation is rapidly developing, the studies on the trace element emissions are limited thus far. Some studies about the trace elements in coal gangue have been conducted, such as trace elements abundance properties, partitioning character or the release behavior during coal gangue spontaneous combustion [3, 4, 14, 35]. For the sustainable development of coal gangue utilization, the present work intends to provide information regarding the modes of occurrence of trace elements in coal

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gangue and the leaching character of trace elements from coal gangue. Also, the release character of trace element during combustion of coal gangue as well as the environmental implication of trace element in coal gangue is discussed in this chapter.

2. Modes of occurrence of trace elements in coal gangue

2.1. The mineral and chemical composition of coal gangue

Generally, the main mineral phases of coal gangue are kaolinite, quartz, pyrite, illite, calcite, ankerite, and montmorillonite [36, 37]. The coal gangue samples are usually dominated by silicon dioxide and aluminum oxide, followed by ferric oxide and potassium oxide accompanied with some trace elements [37]. For example, it is reported that the mineral phases in the Huainan coal gangue samples are kaolinite, quartz, illite, calcite, pyrite, siderite, and muscovite. The major chemical compositions in the samples are silicon dioxide, aluminum oxide, ferric oxide, and calcium oxide. Traces components such as potassium oxide, sodium oxide, magnesium oxide, and titanium dioxide are also identified [38]. The properties of the coal gangue samples from the Huainan Coalfield are presented in **Table 1** [38]. According to the mineralogical analysis, silicon, aluminum, potassium, and magnesium are mainly associated with the clay and quartz minerals. Calcium is mainly associated with carbonate minerals while iron is mainly associated with sulfide minerals, carbonate minerals, and the clay minerals [38].

Trace elements in coal gangue could be associated with the organic matter and inorganic matter in coal gangue matrix, but prefer to be associated with inorganic matrix, such as clay, sulfides, and carbonate minerals in coal gangue [39, 40]. In comparison with the background values, the content of the total trace element in coal gangue could provide important information about environment pollution [38]. Therefore, some researches regarding of the content of the total trace element in coal gangue have been conducted. For example, 12 trace elements,

Proximate analysis, dry basis (wt.%)							
Moisture	**Ash**	**Fixed carbon**	**Volatile matter**				
2.63	70.79	18.24	23.37				
Ultimate analysis (wt.%)							
C	**H**	**N**	**O**	**S**			
20.14	2.07	0.27	9.87	1.21			
Ash analysis (wt.%)							
SiO_2	**Al_2O_3**	**Fe_2O_3**	**CaO**	**MgO**	**K_2O**	**Na_2O**	**TiO_2**
54.18	20.40	9.28	13.60	0.18	0.44	0.64	1.33

Table 1. The chemical compositions of the coal gangue.

including As, V, Cr, Co, Ni, Cu, Zn, Se, Cd, Sn, Pb, and Hg, were selected by Yang et al. for the study of trace element in coal gangue at an open-cast coal mine area, Inner Mongolia, China [37]. Also, 20 trace elements, including Ba, Co, Cr, Cu, Ga, Mn, Ni, Li, Se, Zn, V, As, etc., were selected by Zhou et al. for the study of trace element in coal gangue at the Huainan Coalfield in China [38]. The comparison of trace element content in the coal gangue with black shales and Clarke values were used to evaluate the trace element enrichment by Zhou et al. [38]. It is reported that compared with the background values of black shales, the trace elements in coal gangue are enriched in Ga and depleted in Ba, Co, Cr, Cu, Li, Mn, Ni, Zn, V, Ce, Dy, Er, Gd, La, Lu, Nd, Yb, and Y, and the other trace elements are nearly equal to the background values of black shales [38, 41]. Meanwhile, the content of Ga, Se, As, and Sn are much higher in the Huainan Coalfield coal gangue compared with the Clarke values, while the content of other trace elements are lower [38]. The coal gangue in the Wulantuga open-cast coal mine area is enriched in Co and depleted in Se, Cd, and Hg, and the other trace elements are close to the concentrations of the world Clarke values [37].

2.2. The sequential extraction method

The sequential extraction method was organically employed to determine the mode of occurrence of toxic trace elements in soil samples and was later modified to evaluate the trace elements in coal [42]. This method identifies trace elements species on the basis of the chemical leaching of the complex substrate, which have been proved to be an effective method in determining the modes of occurrence of trace element in the solids [43, 44]. Based on sequential extraction procedures, the mode of occurrence of trace element in coal can be classified into five fractions (exchangeable, carbon bound, Fe-Mn oxides bound, organic matter bound, and residual) or six fractions (water-leachable, ion-exchangeable, organic-bound, carbonate-bound, silicate-bound, and sulfide-bound) [38, 43]. Because coal gangue is similar to coal, the sequential extraction method was also preformed to determine the modes of occurrence of trace elements in coal gangue [12, 38, 43]. For example, the six-step sequential extraction procedure was adopted by Zhou to study the modes of occurrence of trace element in coal gangue [15]. Also, the six-step sequential extraction procedure was modified to study the modes of occurrence of Hg in four coal gangues in our previous work [12]. Generally, the sequential extraction method is an effective way to identify the modes of occurrence of trace element in coal gangue.

2.3. Mode of occurrence of mercury

Mercury is a toxic element that is hazardous to the environment and all living organisms, including human beings [45]. Six sequential extraction procedures were performed to identify the modes of occurrence of mercury in the four coal gangues (ED, GD, PL, and TX) in our previous work and the result is shown in **Table 2** [12].

It can be seen from **Table 2** that the sulfide-bound mercury is the dominant form of mercury in the four coal gangues; the levels of sulfide-bound mercury are 74.22, 51.49, 78.88, and 74.70% for ED, GD, PL, and TX, respectively; this result is similar to the results of other reports on coal [43, 46]. The result also shows that the second most abundant mercury form is the silicate-bound mercury, accounting for 10.32, 20.81, 18.55, and 21.96% of the total

Sample	Ion-exchangeable	Carbonate bound	Iron-manganese oxide	Organic bound	Sulfide bound	Silicate bound	Residue
ED	0.91	0.38	Undetected	2.41	74.22	10.32	13.85
GD	0.67	1.76	11.48	0.09	51.49	20.81	14.33
PL	0.98	0.08	6.28	0.27	78.88	18.55	9.49
TX	0.27	0.77	Undetected	3.40	74.70	21.96	8.39

Table 2. Distribution of Hg in the sequential extractions of the coal gangue samples (%).

mercury in the coal gangues of ED, GD, PL, and TX, respectively. This result is close to the amount of silicate-bound mercury in the coal considered in other literature reports [47]. Iron-manganese oxide-bound mercury accounts for 11.48 and 6.28% in GD and PL coal gangue, whereas it is undetected in ED and TX coal gangue. Moreover, the content of ion-exchangeable mercury for ED, GD, PL, and TX are calculated to be 0.91, 0.67, 0.98, and 0.27%, respectively, being almost negligible at less than 1%. Similar to ion-exchangeable mercury, carbonate-bound mercury is also nearly negligible and accounts for 0.38–1.76% of the total mercury in coal gangue; this result is consistent with the other reports on coals [43, 46]. Organic-bound mercury accounts for approximately 2–4% in ED and TX and less than 0.3% in GD and PL, whereas the content of organic-bound mercury almost exceeded 40% in coal [43]. This result indicates that a small portion of organic-bound mercury exists in coal gangue because of the high content of minerals and low content of organic matter in coal gangue. However, a portion of mercury remains in the residue, which is possibly insoluble mercury, such as $HgSO_4$ or HgS [48]. As a result, the modes of occurrence of mercury in the four coal gangues is generally in the order of sulfide-bound mercury > silicate-bound mercury > iron-manganese oxide-bound mercury > organic-bound mercury > carbonate-bound mercury ≈ ion-exchangeable mercury [12].

2.4. Mode of occurrence of arsenic

Arsenic is considered as an environmentally sensitive element [49]. Extensive studies have demonstrated that arsenic is mainly associated with pyrite [5, 9, 50, 51]. The sequential extraction procedures of arsenic in Huainan coal gangue show that a major portion is bound to the sulfide fraction, followed by the silicate, carbonate, and organic fractions, which is consistent with the previous hypothesis that arsenic is predominately associated with pyrite [38]. In addition, the sequential extraction procedures were also performed to identify the modes of occurrence of arsenic in three coal gangues in Shanxi province by Cao et al. [52]. The modes of occurrence of arsenic could be characterized as ion-exchangeable, carbonate-bound, iron-manganese oxide-bound, sulfide-bound, organic-bound, and residual forms. The experimental results show that the sulfide-bound arsenic is dominant form, accounting for 56.71–79.36% of the arsenic in the coal gangues. The residual arsenic is the second most abundant form, accounting for 11.47–18.02% of the total arsenic. The organic-bound arsenic is the third most abundant form in the coal gangues. However, the ion-exchangeable arsenic, the carbonate-bound arsenic, and iron-manganese oxide-bound arsenic in the coal gangues are all less than 2% [52].

2.5. Mode of occurrence of other trace elements

The modes of occurrence of other trace elements in coal gangue were also identified by the six-step sequential extraction procedures [38, 53]. The result shows that the trace elements of Co, Cr, Cu, Mn, Ni, Se, Sn, V, and Zn in Huainan coal gangue are predominantly existed in silicate-bound, sulfide-bound, and carbonate-bound forms while a small portion of them was found to be associated with the organic-bound, ion-exchangeable, and water-leachable form [38]. The positive correlation between the trace element concentration in Huainan coal gangue with ash yield, aluminum, calcium, and iron-sulfur has been found, indicating that the trace elements in Huainan coal gangue are mainly associated with sulfide minerals, which could release out from coal gangue easily and can disperse into the environment [38]. Meanwhile, the results show that the trace elements of Be, V, Cr, Co, Ni, Cu, Sr, Mo, Cd, Sb, Ba, Pb, Th, U, and Se in coal gangue from Pingdingshan Mine Area mainly exist in the residual form, then in carbonate-bound form, iron and manganese oxides form, organic matter and sulfide form, and the percentage of the exchangeable form is relatively low [53]. For one mode of occurrence of trace element, the potential hazardous to environment are different with other modes of occurrence of trace element [53].

Overall, the sulfide-bound trace elements are dominant form in coal gangue, which should be ascribed to the large amount of pyrite in coal gangue. Silicate-bound trace elements also are one of the main forms, which is due to the silicate mineral in coal gangue.

3. Leaching character of trace elements from coal gangue

3.1. Leaching method

Extensive studies on the leaching behavior of trace elements from coal, coal fly ash, and bottom ash have been conducted and it proves that leaching is one of the primary pathways for trace elements entering into the ecosystem [9, 54, 55]. Therefore, some studies about the leaching behavior of trace elements from coal gangue, especially from coal gangue piles, have been done by some authors [37, 56]. The leaching behavior of the trace elements from coal gangue indicated that leaching is a very complex process, which might be affected by many factors. Generally, the pH of the leaching solutions plays an important role on the leaching behavior of trace elements from coal gangue [56]. Also, leaching time is another important impact factor on the leaching behavior of trace elements from coal gangue [57–59]. Meanwhile, the concentration of the trace elements in coal gangue can influence the leaching behavior [37].

3.2. Leaching behavior of trace elements from coal gangue under column leaching experiments

The study by Yang et al. was conducted to focus on investigations on the leaching behavior of trace elements from coal gangue in an open-cast coal mine, Inner Mongolia, China [37]. Four comparative column leaching experiments were carried out to investigate the influences of leaching time, the pH values of solution, and the sample amount on the leaching behavior of trace elements from coal gangue. Based on the results of comparative column leaching experiments of coal gangue, the environmental and ecological risks caused by the trace elements of the resulting leachates from coal gangue piles were evaluated in detail by some semi-quantitative methods. In the study, the leached concentrations, leached amount, leachability, maximum leached amount, and maximum leachability of trace elements were used to illustrate the leaching behavior of the trace elements from coal gangue piles. The leaching behavior of the 12 trace elements in coal gangue piles including As, V, Cr, Co, Ni, Cu, Zn, Se, Cd, Sn, Pb, and Hg was studied [37].

The result showed that leaching time and sample amount presented significantly influence on leaching behavior of trace elements such as leached concentrations, leached amounts, and leachability. This result is consistent with the results of other literatures [52, 57, 58, 60]. For example, column leaching experiments were performed on the samples of feed coal, fly ash, and bottom ashes from the Shizuishan coal-fired power plant to investigate the leaching behavior of the 11 potentially hazardous elements and the results show that the leaching behavior of the elements from the solid samples is mainly influenced by leaching time and pH value of solution [57]. Also, different acid solutions were used to investigate the leaching behavior of bromine in coal and the results show that leaching time and pH value played an important role in controlling the leaching behavior of bromine in coal [58]. Overall, the leaching behavior of the trace elements was mainly affected by the pH values of the leaching solutions [57–60]. However, the pH values of the leaching solution showed a weak effect on the leaching behavior of the trace elements in this study. The leaching result at different sample amount indicated that the sample amount showed little effect on the change trends of the concentration of the trace element with time while it showed a remarkable effect on the concentrations of the elements in the resulting leachates, indicating that the sample amount possibly had an effect on the leaching behavior of some hazardous trace elements [37].

3.3. Leaching behavior of trace elements from coal gangue under simulation leaching conditions

A leaching test of trace elements (Cr, Mn, Cu, Zn, Pb, and Cd) in the coal gangues from the Jiulong Coal Mine was carried out in the laboratory under simulation leaching conditions by Zhang and Ouyang [56]. The influences of pH values on the leaching behavior from the coal gangue samples were studied through static leaching experiments. At the same time, the trace elements of raining water around the coal gangue dumps were also investigated, which can give valuable information about the migration mechanism and influence factors of trace element during leaching process of coal gangues. The results showed that the concentration of trace elements dissolved out during the leaching, and the release rate of trace elements from coal gangue was not only related to the pH value of solution but also related to the trace element concentrations in coal gangues. The concentrations of trace elements in the filter water and rainwater collected around the coal gangue dumps were both higher than the standards limit of the third-class surface water according to the environmental quality standards.

The leaching rates of trace elements are different with different pH value of solutions. The leaching rates of Zn and Cd can reach the maximum value in solutions of pH = 7 under the static leaching experiment. The leaching rates of Cr, Mn, Ni, Cu, and Pb reach a minimum value in solutions of pH = 5 under the static leaching experiment. Among all the trace elements, Mn presents the minimum release rate. The concentration of trace elements in rainwater sample is in the order of Zn > Ni > Cr > Cu > Mn > Pb > Cd. The concentration of trace elements in leachate is in the order of Zn > Ni > Cu > Cr > Mn > Pb > Cd, which shows a similar tendency with that in rainwater sample except Cu and Cr. It should be noted that the concentrations of Mn, Cu, Zn, Cr, Cd, and Pb are all higher than the standards limit of the third-class surface water of the environmental quality standards, indicating that the leaching of trace elements from coal gangue can cause potential environment problems [56].

3.4. Leaching characteristics of trace elements in fresh, weathering, and filling coal gangue

The fresh, weathering, and filling coal gangue samples, as well as coal slime were collected from Xinzhuangzi Coal Mine in Huainan area [61]. The batch leaching experiments of trace elements (Cd, Cr, Pb, and Mn) from all the samples were carried out under different leaching solution and different leaching time with different particle size of the sample. The concentration of trace elements (Cd, Cr, Pb, and Mn) in different leaching solutions was measured by graphite furnace atomic absorption spectrometry. The leaching concentration and total leaching rate of trace elements were combined to analyze the leaching characteristics of the trace element in the samples. Meanwhile, the environmental effects of trace elements were assessed according to the environmental quality standard of underground water. The results show that the leaching efficiency is enhanced with the decline of particle size of sample and pH of leaching solutions and leaching amount of trace elements is increased as time prolongs. The total leaching rate of trace elements in coal slime is higher than that of other coal gangues. The total leaching rate of trace elements in weathering coal gangue is less than other samples. Cd in all the samples presents the maximum leaching performance among all the trace element studied, indicating that Cd is the most hazardous trace element under the same leaching conditions of sample type, particle size of sample, and leaching solution. Mn shows the minimum leaching performance among all the trace elements and almost has no risk to the environment. The leaching performance of the four trace elements are in the order of Cd > Pb > Cr > Mn [61].

In summary, leaching behavior of trace elements from coal gangue is affected by many factors. Leaching is the main pathway for trace elements in coal gangue into the water environment. More attention should be paid on the toxic trace elements in water environment near coal gangue piles.

4. Release character of trace element during combustion of coal gangue

4.1. Trace element partitioning behavior of coal gangue-fired CFB plant

Combustion of coal gangue in power generation is a promising method of energy recovery of coal gangue. However, the prevention of toxic trace metal emission is a significant concern during coal gangue combustion.

The trace element partitioning behavior of the Pingshuo coal gangue-fired power plant in Shanxi province of China has been investigated [15]. The feed fuel, bottom ash, and fly ash samples were collected from the coal gangue-fired power plant. The experimental analysis and the thermodynamic equilibrium calculation were conducted to study the trace element partitioning behavior during coal gangue combustion. The result of analysis shows that the trace elements can be divided into three groups, including highly volatile elements, semi-volatile elements, and non-volatile elements. The highly volatile elements including Hg, As, Be, and Cd, may be emitted into the atmosphere through the gas phase or as fine particles in the flue gas. The semi-volatile elements contain Pb, Co, Zn, Cu, and Ni, which may be enriched in the fly ash relative to the bottom ash. The non-volatile elements contain Cr and Mn, which are relatively enriched in the bottom ash. The result of thermodynamic equilibrium calculation shows that the existence of chlorine may increase the volatility of several trace elements and the presence of mineral phases such as aluminosilicates can decrease the volatility of elements by chemical immobilization effect. The air/fuel ratio and the mode of occurrence of trace elements may also largely influence the release behavior of trace elements [15].

A study on some toxic trace elements behaviors of a 330 MW coal gangue CFB power plant in Huainan of China was performed by Zhou et al. [1]. The feed fuel, bottom ash, fly ash, and flue gas samples were all collected. The partitioning behavior of toxic elements in the power plants was analyzed systemically. The result shows that the toxic elements can be classified into three groups. The first group includes the elements of As, Cd, Cu, Pb, Se, and Sn, which have high volatile tendencies with the volatilization ratio more than 20% and are mainly enriched in fly ash. The second group includes the elements of Co, Cr, Mn, and V, which have low volatilization rate and are equally distributed between bottom ash and fly ash. The third group includes the element of Bi, Ni, and Zn, which have moderate volatile tendencies. The modes of occurrence of trace elements have significant effect on the transformation behaviors of toxic elements during coal gangue combustion [1].

4.2. Trace element behavior during spontaneous combustion of coal gangue

When the rate of heat generated by the oxidation of organic matter or pyrite in coal gangue exceeds the rate of heat dissipation, the spontaneous combustion of coal gangue can be occurred [62]. Because the amount of coal gangue is very high and coal gangue spontaneous combustion is widespread in Yangquan of Shanxi Province, the coal gangue dumps in this area were investigated to study the trace element behavior during coal gangue spontaneous combustion [3].

All kinds of coal gangue samples including bulk gangue, specific lithologies, fired coal gangue and condensate products from gas vents were fully characterized regarding the mineralogy, chemistry, and leaching potential [3]. The result showed that the temperature during the spontaneous combustion of coal gangue could reach to 1200°C, which was also verified by laboratory calcination tests [3]. During spontaneous combustion of coal gangue, some elements (C, Cl, F, As, Cd, Hg, Pb, Sn, Ge, and Se) may be released into the atmosphere, which well agreed with Zhao [4]. However, the gaseous emissions of As, S, N, Hg, and Se can be partially trapped by the important condensation processes. Therefore, the condensate mineralizations enriched in Se, As, and other trace elements in the gas vent [3]. It should be pointed out that a quick cover of soil on coal gangue can help to avoid oxidation of the organic material or the pyrite and thus reduce the risk of self-ignition of coal gangue [3].

4.3. Transformation behavior of trace elements during coal gangue combustion

It is of great interest to study the trace element behaviors concerning coal gangue combustion in order to understand their fate during coal gangue combustion. Several factors, such as volatilization tendency of trace elements, modes of occurrence of trace elements, and concentrations of trace elements in coal gangue may influence the trace elements behavior during coal gangue combustion [63–66]. Also, the combustion condition, especially temperature is a key factor to influence the transformation behavior of trace elements.

The transformation behavior of trace elements during combustion of coal gangue under different temperatures had been studied by Zhou et al. [14]. The coal gangue samples were collected from the Xinzhuangzi Mine, China. Eight combustion temperatures (500, 600, 700, 800, 900, 1000, 1100, and 1200°C) were selected to study the trace elements behavior during coal gangue combustion. The coal gangue sample was placed in a muffle roaster at determined temperature and sustained a time of 30 min. Then, the coal gangue samples were taken out from muffle roaster and cooled down to the room temperature in a dryer. The content of trace elements (Ni, Cu, Zn, Cd, Sn, Pb, As, Co, Cr, and V) in coal gangue and combustion ash was determined by inductively coupled plasma mass spectrometry (ICP-MS). The results show that the trace element behavior during coal gangue combustion mainly relies on the combustion temperature. The volatilize ratios of trace elements increase with increasing combustion temperature. It indicates that higher temperature could lead to a relatively thorough coal gangue thermal decomposing, and the trace elements originally existed in coal gangue could easily release out. Moreover, 10 trace elements studied in the current study could be divided into two groups according to their volatilize ratios. The first group contains Ni, Cu, Zn, Cd, Sn, Pb, and As, which show a high volatilize tendencies. The second group is represented by Co, Cr, and V, which were relative non-volatile. It is reported that the volatility of trace elements during coal combustion mainly relies on the modes of occurrence and the concentrations in coals as well as the combustion parameters [64–67]. During coal gangue combustion, the combustion temperature and the modes of occurrence of trace elements in coal gangue are the main factors. However, the content of trace elements in coal gangue was not the key factor to influence its transformation behavior. For example, the Cd content in the coal gangue was quite low, but its volatilize ratio was quite high.

In a word, different trace elements presented different transformation behaviors because of the different thermal stability and the different modes of occurrence of trace elements in coal gangue.

5. Environmental implication of trace element in coal gangue

5.1. Potential environmental effects of trace elements in coal gangue of an open-cast coal mine area

The environmental effects of trace elements from coal gangue piles of an open-cast coal mine area, Inner Mongolia, China have been investigated by Yang et al. Twelve trace elements, including As, V, Cr, Co, Ni, Cu, Zn, Se, Cd, Sn, Pb, and Hg, were selected for investigation to assess their environmental and ecological hazards levels in coal gangue piles [37].

The enrichment factor was an important parameter to evaluate the pollution level of an element [38, 68]. Therefore, the enrichment factor values of elements in coal gangue were applied to assess the potential environmental effect of the 12 trace elements [37]. The results show that the enrichment factor values for elements of As and Se were 4.86 and 7.41, respectively, indicating that they can cause a high pollution level due to their high concentration in the coal gangue.

It is reported that "Maximum leached amount" (Lam) can act as an important indicator for trace element environmental risk assessment because it can provide valuable information of the maximum transformation ability of element in environment [57]. Thus, the value of Lam is used to evaluate the environmental risk caused by trace element in coal gangue. Meanwhile, the concentration limits of the trace elements in groundwater and soil were also investigated in this research. The results show that the Lam values of the 12 trace elements are all less than the corresponding concentrations limits of the elements in the environmental quality standard for soils as well as the limits of contaminants in foods. It indicated that the 12 trace elements in the coal gangue almost had no potential risk to soils and vegetation. However, since the Lam values of some trace elements are higher than the corresponding concentration in the quality standard for groundwater, the trace elements could possibly have some potential impacts on the groundwater. Meanwhile, the evaluation result of biological toxicity showed that the 12 trace elements from coal gangue could produce moderate to high level of ecological risk to the environment [37].

5.2. Environmental implications of trace elements associated with coal gangue

In order to evaluate the potential environmental implications of the trace elements associated with coal gangue, the mobility behavior of 10 trace elements (As, Co, Cr, Cu, Mn, Ni, Se, Sn, V, and Zn) in coal gangue from the Huainan Coalfield was studied by Zhou et al. [38]. The sequential extraction was also used to analyze the chemical properties of trace elements in coal gangue because the toxicity of trace elements mainly depends on its chemical properties. The result showed that the chemical properties of trace elements in the coal gangue are mainly as silicate-bound, sulfide-bound and carbonate-bound form. The positive correlation of the trace element concentration with ash yield or iron-sulfur material indicated that the trace elements of As, Co, Cu, Ni, Se, and Zn in coal gangue are basically bounded with sulfide minerals in coal gangue. Therefore, they could release out and disperse into the environment easily during the natural weathering of coal gangue, leading to potential hazardous to environment.

To evaluate the biological toxicity of trace elements of Cr, Cu, Zn, Ni, and As in coal gangue, international sediment quality guidelines calculations such as effects range low (ERL) and effects range median (ERM) were adopted [69, 70]. The result showed that the trace elements of Zn, Cr, and Cu are below ERLs, indicating unobvious adverse biological effects. The trace elements of Ni and As are in the middle range, indicating occasional adverse biological effects. None of the trace elements in the samples are higher than ERMs value, suggesting limited adverse biological effects [38]. The result of the risk assessment code reveals that the trace elements of Mn, Cr, Se, Ni, Zn, As, and Cu can pose serious environmental risks to the ecosystem while Co, Sn, and V pose no risk or low risk [38].

5.3. Environmental characterization of burnt coal gangue banks

The coal gangue dumps in Yangquan of Shanxi Province, China were selected to investigate the environmental characteristics of burnt coal gangue banks [3]. The fresh coal gangue, weathered coal gangue, and the gas vents condensates were sampled and studied by leaching technique to evaluate their environment impacts. The result showed that the trace elements in the fresh coal gangue presented relatively low leaching potential. However, the weathered coal gangue and the gas vents condensates could produce acidic leachates, leading to relatively high leachable levels of trace elements and thus giving rise to environmental problems [3].

In summary, trace elements in coal gangue could release out and produce environmental implication in various degrees, depending on the type of trace elements. The potential environmental effects should not be neglected and some measures to eliminate them should be taken.

6. Conclusion

Trace elements in coal gangue could be associated with the organic matter or inorganic matter in coal gangue. The sequential extraction method is an effective way to identify the modes of occurrence of trace element in coal gangue. The modes of occurrence of trace elements are different with coal gangue type. The sample amount, pH values of solution or trace element concentrations affect the leaching behavior of trace elements. The leaching characteristics of trace elements in fresh, weathering, and filling coal gangue are different. During coal gangue combustion, the trace elements can be divided into three groups, including highly volatile elements, semi-volatile elements, and non-volatile elements. The modes of occurrence of trace elements have significant effect on the behaviors of trace elements. The trace elements could possibly have some potential impacts on the groundwater and could produce moderate to high level of ecological risk to the environment. Compared with fresh coal gangue, the weathered coal gangue and the gas vents condensates presented relatively high leaching potential and could give rise to environmental problems.

Generally, the study of trace elements in coal gangue is still limited. Most of experimental method adopted were traditional methods in geology area and some modern technique should be taken, such as online determining method. Also, the study about the removal of toxic trace elements is scare and should be done at present; and the controlling technology of toxic trace elements during coal gangue utilization should be developed to alleviate the adverse impact made to the environment.

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