Occurrence and release of cadmium, chromium, and lead from stone coal combustion

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Abstract Stone coal, which has high ash yield, low carbon content, and low calorific value, releases toxic elements during the combustion process. In this study, samples were collected from an open-pit stone coal mine in the southern Shaanxi province, China. A simulated combustion experiment and sequential chemical extraction were applied to investigate the enrichment, occurrence, and release of Cr, Cd, and Pb in raw stone coal and ash. The contents of Cr, Cd, and Pb in raw stone coal were larger than those reported for other coals in China and worldwide. The enrichment factors of Cr, Cd, and Pb in ash at different temperatures exceeded 0.7, with the exception of Cd at 1000 °C. This indicates that Cr, Cd, and Pb were first enriched at low temperature (below 600 °C) and then volatilized at high temperature due to the decomposition of clay minerals. The dominant forms of toxic elements in raw stone coal were Fe–Mn-bound Cr and Cd and carbonates of Pb. As the temperature increased, the organic forms decreased obviously, and the residual forms increased; however, the Fe–Mn-bound forms remained the dominant forms of Cr, Cd, and Pb.

Keywords Stone coal · Occurrence and release · Combustion · Cadmium · Chromium · Lead

1 Introduction

Coal, as the major energy, bears certain microelements which are beneficial or harmful. Stone coal is an inferior type of anthracite with high ash content, low carbon content, and low calorific value; stone coal is also a low-grade polymetallic symbiotic ore (Cheng 2001). Stone coal is formed by the saprofication and coalification of living organisms such as bacteria, algae, and other organisms in shallow seas, lagoons, and bays. China has abundant stone coal resources totaling 618.8×10^8 t, which are mainly distributed in the middle and lower reaches of the Yangtze River in Hunan, Hubei, Anhui, Jiangxi, Zhejiang, Shaanxi, and other provinces. Among them, the South Qinling District has the most abundant reserves and the highest coal quality. Stone coal contains trace elements such as U, As, Pb, Zn, Cu, Mn, Cd, Se, P, and Cr, some of which have value for extraction and recycling (Du et al. 2017).

The use of cheap stone coal in power plants can effectively alleviate shortages of power supply in remote areas. Furthermore, the high contents of minerals such as quartz and kaolinites in stone coal can be applied to produce cement, brick, and other building materials. As a low-calorific energy source, stone coal is developed and utilized in areas where coal resources are relatively scarce. This saves high-quality coal resources and promotes local economic development (Liu et al. 2016a, b; Chu and Zhang 2014; Li et al. 2005).

Coal is a composite mixture containing trace elements such as Hg, Se, Pb, Cr, Cd, and Mn. During the combustion of coal, the trace elements in coal are redistributed through complex physicochemical changes. Nonvolatile elements (e.g., Ba and Sn) are not volatilized during combustion and are uniformly distributed in the fly ash and bottom slag

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produced by combustion. Volatile condensing elements (e.g., As, Pb, Cr, and Cd) are enriched in the fine fly ash. Some or all of the volatilization during the combustion process along with physical and chemical changes (e.g., homogeneous nucleation and heterogeneous condensation) occur after the coal enters a lower-temperature environment. Volatile noncondensing elements (e.g., Hg and Se) in the unobvious enrichment of fly ash are emitted to the atmosphere in gaseous form (Swaine and Goodarzi 1995).

The Pb contents of the World coal were reported to range from 0.1 to 7900 μg/g, with the contents in most coal samples being 2–80 μg/g (Yao et al. 2002). Bai (2003) analyzed 1018 coal samples from China and reported lead contents ranging from 0 to 93.5 μg/g with an average of 17.68 μg/g. Numerous studies have shown that lead in coal is mainly found in the form of sulfides (e.g., galena and pyrite) (Swaine 2013; Finkelman 2005; Zhang et al. 2000), leading to chemical reactions under high-temperature and reducing conditions. During the process of separating lead and sulfur into simple substances or oxides, if the temperature does not reach the condition where the gas-phase metal or its oxide is stable, lead chloride is easily produced (Wen and Xu 2010; Xu 2004; Uberoi and Shadman 1990). To study the changes in the chemical forms of trace elements during coal combustion, the possible chemical forms of the trace elements and their distributions were predicted based on the chemical equilibrium as the temperature increased from 400 to 2000 K (Yu et al. 2004). The results indicated that the volatility of trace elements during coal combustion increased in the following order: $Cd < Pb < Cr$. The forms of heavy metals in different types of coal varied widely, and the presence of organic materials enhanced the heavy metal volatility. Therefore, the volatility of Pb, Cd, and Cr should be determined by the type of coal and its occurrence (Chen et al. 2001). Shi and Wu (2016) reported that the volatility of heavy metals is proportional to the combustion temperature.

While the occurrence of coal has been widely studied, few studies have evaluated the environmental geochemistry of toxic elements contained in stone coal and its combustion ash. In particular, the occurrence and release of toxic elements during combustion are poorly understood. Because of the composition of stone coal and the diverse forms of different elements, basic systematic research on the occurrence, speciation, and associated minerals of heavy metals in raw stone coal and its ash products under different combustion conditions is needed. The results of such studies would be useful to understand the transformation of toxic elements during stone coal combustion.

2 Materials and methods

2.1 Sampling

Coal samples were collected from an open-pit stone coal mine in Haoping river basin, Ankang City, Shaanxi Province, China. The stone coal-bearing rock structure is a Cambrian and Silurian series of Marine sedimentary black rock. The main coal-bearing stratum in the area is the late Ordovician and early Silurian Jiaguguan formation ((O$_3$–S$_1$) b) (Jia 2014). Representative test samples were obtained by mixing four raw coal samples. The stone coal samples were stored immediately in sealed plastic bags to prevent contamination and weathering. After being transported to the laboratory, the stone coal samples were air-dried, crushed, pulverized, and passed through a 200-mesh sieve for analysis.

2.2 Proximate analysis

Proximate analysis (M_{ad}, A_d, V_{daf}, and F_{Cd}) of the stone coal samples was performed according to Chinese coal standard GB/T212-2008, which is comparable to ASTM standards (ASTM-D3173-11, 2011; ASTM-D3174-11, 2011; and ASTM-D3175-11, 2011). The total sulfur content and contents of different forms of sulfur were measured using a WS-S101 automatic sulfur analyzer according to Chinese standards GB/T 214-2007 (equivalent to ASTM standard D3177-02, 2002) and GB/T 215-2003 (equivalent to ASTM standard D2492-02, 2012), respectively.

2.3 Stimulated combustion experiment

Stimulated combustion experiments were carried out in a muffle furnace. Six combustion temperature points were chosen between 500 and 1000 °C in 100 °C intervals to study the occurrence and release behavior of trace elements (Cr, Cd, and Pb) during stone coal combustion. Each crucible contained approximately 2 g of stone coal sample. The crucibles were placed into the muffle furnace for burning and ashing. After reaching the set temperature, the crucible was warmed for 4 h. The burned coal samples were then removed from the muffle furnace and cooled to room temperature in a dryer. The following notations were used to identify the raw and heated coal samples: HS (experimental raw stone coal), HS5 (coal ash burning at 500 °C), HS6 (coal ash burning at 600 °C), HS7 (coal ash burning at 700 °C), HS8 (coal ash burning at 800 °C), HS9 (coal ash burning at 900 °C), and HS10 (coal ash burning at 1000 °C).

2.4 Elemental analysis

Approximately 0.1 g of raw stone coal (burned for 3.5 h at 450 °C to remove carbon and increase digestion efficiency) and the burned stone coal samples were digested with 8 ml HNO_3, 2 ml H_2O_2, 3 ml HF, and 4 ml $HClO_4$ in Teflon digestion vessels. The samples were then gradually heated on a hot plate from 100 to 210 °C for 12 h. After cooling, the digested solutions were diluted to 25 ml with 5% HNO_3. The total concentrations of Cd, Cr, and Pb were determined by inductively coupled plasma mass spectroscopy (ICP-MS; Thermo Fisher Scientific). The accuracy of the determination was evaluated using a standard coal reference material (SARM20). The instrument was calibrated using multi-elemental standard solutions containing known concentrations of Cr, Cd, and Pb. The calibration curves for all three elements were linear ($R^2 > 0.999$, $n = 6$) over the studied concentration range. The precision for each of these elements was within ± 5%.

2.5 Sequential chemical extraction of heavy metals

According to the method of Tessier et al. (1979), the five forms which are exchangeable, carbonates, Fe–Mn oxides, organic matter, and residual forms of raw stone coal and the stone coal samples heated at 600 °C and 1000 °C were surveyed as follows. The sample (1 g) was added to a 50-ml plastic centrifugation tube. After adding 8 ml of 1 mol/l $MgCl_2 \cdot 6H_2O$, the contents of the tube were oscillated for 1 h at 200 rpm at 25 °C and then centrifuged for 10 min at 4000 rpm. The supernatant was completely removed and filtered to determine the exchangeable forms. Then, the residue was extracted by NaAc (pH = 5.0) at room temperature, oscillated for 8 h (200 rpm), and centrifuged for 10 min at 4000 rpm. The supernatant was filtered to analyze carbonate-bound forms. The above residue was sequentially extracted by adding 20 ml 25% (v/v) acetic acid (HAC) solution and 0.04 mol/l hydroxylamine hydrochloride ($NH_2OH \cdot HCl$) followed by oscillation for 4 h at 96 °C ± 3 °C. The supernatant was centrifuged for 10 min at 4000 rpm, removed, and filtered to determine the forms of Cr, Cd, and Pb bound to Fe–Mn oxides. HNO_3 (3 ml, 0.02 mol/l) and 5 ml 30% (v/v) H_2O_2 were added to the above residue. The mixture was then heated at 85 °C in a water bath for 2 h. After adding 5 ml H_2O_2, the mixture was further heated at 85 °C ± 2 °C for 3 h. The solution pH oscillated intermittently during extraction and was adjusted to 2 with HNO_3. After cooling the extracted solution, 5 ml NH_4Ac (3.2 mol/l) was added, and the solution was diluted to 20 ml with 20% (v/v) HNO_3 followed by continual oscillation for 30 min and centrifugation for 10 min at 4000 rpm. The supernatant was removed and filtered to determine the organic forms of Cr, Cd, and

Pb. After extracting the organic forms, the residue was digested using the same method as for raw coal samples, coal ash samples extracted by HNO_3–HF–$HClO_4$. All the extracted solutions were analyzed by ICP-MS using the same instrument conditions as for the analysis of raw stone coal samples.

2.6 Mineralogy and microstructure of stone coal and its ash

The mineral compositions of stone coal and heated stone coal ash were determined by X-ray diffraction (XRD; Panalytical X'Pert 3 Power). XRD patterns were recorded over a 2θ interval of 10°–70° with a step increase of 0.01°. The minerals were demarcated in terms of the International Centre For Diffraction Data (ICDD) powder diffraction files. The morphologies of raw stone coal and its ash were observed by scanning electron microscopy (SEM; Carl Zeiss SIGMA).

2.7 Data manipulation

The arithmetic means were used for all parameters. Pairwise comparison between means were made with independent-sample T tests at the confidence level of 0.05. Data analysis and equation fitting were performed using SPSS and Origin software.

3 Results and discussion

3.1 Proximate and ultimate analysis of raw stone coal

Table 1 shows the results of proximate and ultimate analyses of experimental raw coal. The raw stone coal contained 2.40% moisture, 39.16% ash, 4.87% volatile matter, and 53.57% fixed carbon. The calorific value was 5.53 MJ/kg, much lower than that of standard coal (290 MJ/kg). Pyrite was the primary form of sulfur, accounting for 96.7% of total sulfur. The raw stone coal was characterized by high ash yield, medium sulfur content, low moisture content, low volatile matter content, and low calorific value according to Chinese coal classification standards (MT/T 850-2000, GB/T 15224.1, MT/T 849, GB/T 15224.2, and GB/T 15224.3).

3.2 Occurrence of Cr, Cd, and Pb in stone coal

The stone coal mine in Haoping is situated in southern Shaanxi, and the samples collected belong to the Ziyang–Zhenping stone coal belt in southern Qinling. Over 60 elements are found in Chinese stone coal, including Se, V,

Table 1 Proximate and ultimate analysis of a raw stone coal sample

M_{ad} (wt%)	A_d (%)	V_{daf} (wt%)	FC_d (wt%)	$S_{t,d}$ (wt%)	$S_{s,d}$ (wt%)	$S_{p,d}$ (wt%)	$S_{o,d}$ (wt%)	$Q_{gr,ad}$ (MJ/kg)
2.40	39.16	4.87	53.57	1.82	0.03	1.76	0.03	5.53

Notes air dry basis; d: dry; daf: dry ash free; M: moisture; A: ash yield; V: volatile matter; FC: fixed carbon; St,d: total sulfur; Sp,d: pyritic sulfur; Ss,d: sulfate sulfur; So,d: organic sulfur; Qgr,ad: the gross calorific value of air drying base

Table 2 Average contents of Cr, Cd, and Pb in raw stone coal from different regions in China (Dai et al. 2012; Ketris and Yudovich 2009; Chen et al. 2013; Luo et al. 1995; Liu 1984)

Regions	Cr (μg/g)	Cd (μg/g)	Pb (μg/g)	References
Stone coal, China				
Enshi, Hubei	1000	27.5	–	Chen et al. (2013), Mao et al. (1999)
Danjiang, Henan	55	1.0	15	Luo et al. (1995)
Ziyang, Shaanxi	168	20.0	39	Luo et al. (1995)
Pingli, Shaanxi	224	1.0	27	Luo et al. (1995)
Langao, Shaanxi	306	200	56	Luo et al. (1995)
Zhengping, Shaanxi	164	16	97	Du et al. (2017)
Haoping, Shaanxi	121	3.55	40.6	This study
Average value in earth crust	110	0.2	12	Liu (1984)
World coal	16	0.22	7.8	Ketris and Yudovich (2009), Dai et al. (2012)
China coal	15.4	0.25	15.1	Ketris and Yudovich (2009), Dai et al. (2012)

Cr, Ni, Cd, Pb, Cu, Ga, and As (Du et al. 2017). The contents of Cr, Cd, and Pb in stone coal in some regions of China are listed in Table 2. The contents of Cr, Cd, and Pb in stone coal vary largely by area, with particularly large variations observed for Cr and Cd. The Cr, Cd, and Pb contents of stone coal in China are generally higher than the average values for world coal, Chinese coal, and the earth's crust. For the stone coal samples from the Haoping open-pit mine analyzed in this study, the mean contents of Cr, Cd, and Pb were 121, 3.55, and 40.6 μg/g, respectively. According to the Standards of the Coal Industry of the People's Republic of China (MT/T 964-2005), these values indicate that the stone coal belongs to high-Cr (H_{Cr}), high-Cd (H_{Cd}), and high-Pb (H_{Pb}) coal. Furthermore, the contents of Cr, Cd, and Pb in raw stone coal in this study were 7.9, 14.2, and 2.7 times that of Chinese coal (Dai et al. 2012) and 7.6, 16.1, and 5.2 times that of World coal (Ketris and Yudovich 2009), respectively. Compared to stone coal from other mines in Shaanxi, the Cr content in the stone coal from Haoping was lower, while the contents of Cd and Pb were higher. This indicates that the elemental contents might differ greatly between mines even when the coal-bearing strata are the same.

3.3 Enrichment of Cr, Cd, and Pb in stone coal under different combustion temperatures

The elemental contents in heated coal samples depend on two processes during combustion: enrichment and volatilization (Dai et al. 2017; Wang et al. 2013). The relative enrichment factors (EFs) are normally used to assess the degree of enrichment and volatilization. According to definition of the mass loss ratio of elements, the EF is expressed as follows (Liu et al. 2003; Mei 1994):

$$EF = Xa \times \eta / Xc,$$

where Xa is the ash-based content of element X in the heated coal, Xc is the content of element X in raw coal; and η is the corresponding ash yield per mass unit at the temperature of interest. The EF value is generally between 0 and 1, with a large EF indicating high enrichment and low volatility.

The ash yield gradually increases with increasing combustion temperature. To effectively compare the enrichment characteristics of samples heated to different temperatures, the ash-based contents of elements in the heated coal samples should be converted to total coal-based contents. The total coal-based element contents in the heated coal samples were determined as the products of Xa and η.

The EF values of the stone coal samples heated at temperatures ranging from 500 to 1000 °C are presented in

Table 3 Contents and EFs of Cr, Cd, and Pb in raw stone coal and ash samples

Coal sample	η (%)	Cr (µg/g)	EFs	Cd (µg/g)	EFs	Pb (µg/g)	EFs
HS	39.16	121	–	3.55	–	40.6	–
HS5	41.16	228	0.78	6.93	0.80	82.2	0.83
HS6	39.74	299	0.95	6.47	0.83	89.7	0.88
HS7	34.9	321	0.93	9.02	0.89	108	0.93
HS8	35.29	301	0.88	8.94	0.89	108	0.94
HS9	33.79	314	0.88	8.42	0.80	107	0.89
HS10	27.79	323	0.74	6.45	0.50	107	0.73

Notes η is the corresponding ash yield per mass unit at the temperature of interest; ash-based content of elemental contents the heated coal samples refers to the total coal-based content

Table 3. The EFs of Cr, Cd, and Pb first increased and then decreased slightly with increasing combustion temperature from 500 to 1000 °C. The rapid increase in EFs, especially for Cr, can be attributed to the decomposition of low-volatile components as the temperature increased from 500 to 600 °C. As the temperature increased further to 700 °C and 800 °C, the EF gradually decreased. When the temperature reached 1000 °C, the EFs of Cr, Cd, and Pb were 0.74, 0.50, and 0.73, respectively. These results differ from those of previous studies suggesting that the EFs of Co, Cr, Ni, and V all decreased as the combustion temperature increased from 100 to 1200 °C (Tang et al. 2018; Li et al. 2018).

The EFs of Cr, Cd, and Pb in stone coal ash heated at 500–900 °C were greater than 0.8, indicating relatively low Cr, Cd, and Pb volatilization. At the high temperature of 1000 °C, the melting of clay minerals such as kaolinite and illite may have resulted in the release of heavy metals. Compared to Cr and Pb, the EF of Cd was slightly lower at each combustion temperature, indicating the greater volatilization of Cd compared to Cr and Pb. Swaine and Goodarzi (1995) speculated that organic matter is the main factor driving the increase in the EFs of low-volatile elements at relatively low temperatures (500 °C and 700 °C). As the temperature increased from 700 to 1000 °C in this study, the EFs of Cr, Cd, and Pb in stone coal ash decreased slowly due to the decomposition of inert minerals such as silicates (Tang et al. 2018).

3.4 Volatilization of Cr, Cd, and Pb in stone coal under different combustion temperatures

The volatilization ratio (Vr) was used to further investigate the enrichment of Cr, Cd, and Pb during coal combustion. Vr was calculated as follows (Liu et al. 2016a, b):
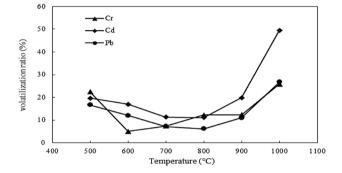
$$Vr = (1 - EF) \times 100\%.$$

Fig. 1 Volatilization ratios of Cr, Cd, and Pb in stone coal under different combustion temperatures

As shown in Fig. 1, the Vr values of Cr, Cd, and Pb first decreased and then increased with increasing combustion temperature, opposite to the trend observed in the EF values. At low combustion temperature, the decrease in Vr and increase in EF may be due to the decomposition of organic matter and loss of water from stone coal. As the temperature increased further, the EFs gradually decreased, while Vr increased. At the combustion temperature of 1000 °C, the Vr values of Cr, Cd, and Pb were 26%, 50%, and 27%, respectively, indicating that the high temperature increased the volatilization of the heavy metals and Cd in particular. However, the volatile contents of Cr and Pb were still relatively low, accounting for only approximately one quarter of the total Cr and Pb content in raw stone coal. This further demonstrates that Cr, Cd, and Pb are low-volatile elements.

3.5 Mineral compositions and microstructures of stone coal after combustion

To further explore the enrichment and volatilization of Cr, Cd, and Pb in stone coal during combustion, the mineral compositions and microstructures of the stone coal samples were characterized by XRD and SEM. Table 4 shows the

Table 4 Minerals in raw stone coal and ash samples (%)

Samples	Quartz	Potassium feldspar	Plagioclase	Hematite	TCCM
HS	62.0	13.0	11.0	–	14.0
HS6	60.0	16.0	14.0	3.0	7.0
HS10	67.0	17.0	–	15.0	1.0

TCCM total clay minerals, mainly referring to kaolinites, dickites, and illites

mineral compositions of raw stone coal samples and coal ash heated to 600 °C and 1000 °C. The minerals in raw coal were dominated by quartz, clay minerals (kaolinite, dickite, and illite), potassium feldspar, and plagioclase. As the combustion temperature increased, the fractions of clay minerals and plagioclase decreased, the fraction of hematite (Fe$_2$O$_3$) significantly increased, and the fraction of quartz (SiO$_2$) increased slightly. Upon heating, the hydroxyl (–OH) groups in the lattice were dehydrated, corresponding to the observed endothermic process. When the combustion temperature reached 600 °C, kaolinite, a dioctahedral layered aluminosilicate, was dehydrated to form meta-kaolinite, a semi-amorphous intermediate phase (Vassileva and Vassilev 2006; Vassilev et al. 1992, 2005). When the combustion temperature reached 1000 °C, the illites were initially dehydrated and then formed a glass phase at 950 °C followed by the final generation of silicon spinel, hematite, quartz, and other minerals (Tang et al. 2018). In this study, when stone coal was heated at high temperature, the Al in plagioclase might have been replaced by Fe, and hematite was formed during the process of mineral restructuring. The main mineral phase was reformed quartz, which was consistently present in both the raw and heated coal samples (Table 4 and Figs. 2 and 3) (Erarslan and Örgün 2017; Vassileva and Vassilev 2006). Similar results have also reported in other studies on coal
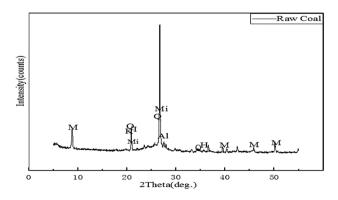

Fig. 2 XRD spectrum of raw stone coal. The minerals identified are: *H* hematite, *I* illite, *K* kaolinite, *M* muscovite, *Mi* microcline, *Q* quartz, *Al* albite

transformation (Cutruneo et al. 2014; Martinello et al. 2014; Oliveira et al. 2014; Saikia et al. 2014; Silva et al. 2009a, b). When the combustion temperature reached 1000 °C, the mineral phases tended to be simple and included primarily amorphous glass phases along with hematite and quartz.

As for aluminosilicates, the decomposition of clay minerals in stone coal resulted in the release of Cr, Cd, and Pb from the clay minerals during combustion (Fig. 2b, c). The changes in the contents of low-volatile Cr, Cd, and Pb in stone coal ash depended on two aspects: releasing from the organic matter at low temperature and the clay minerals at high temperature. These results verify that volatile elements such as As, Pb, Cr, and Cd are easily enriched in fine fly ash after combustion (Swaine and Goodarzi 1995).

3.6 Release of Cr, Cd, and Pb from stone coal during combustion

To explore the migration of elements during coal combustion, the chemical species in raw coal and coal ash heated to 600 °C and 1000 °C were determined. The forms of Cr, Cd, and Pb in stone coal and its combustion products produced at 600 °C and 1000 °C are shown in Fig. 4. Five forms of heavy metals were determined by sequential chemical extraction: exchangeable, carbonates, Fe–Mn oxides, organic matter, and residual forms.

The dominant form of Cr in raw stone coal was Fe–Mn-bound Cr, accounting for 59% of total Cr, followed by organic-bound Cr, accounting for 24% of total Cr, similar to the findings of a previous study (Gentzis and Goodarzi 2000). However, the fractions of different forms of Cr differed significantly by sample (Xiong et al. 2017). Most Cr in coal exists bound to organic matter (Robert et al. 2018) or as residual Cr (Li et al. 2018). In coal ash, the major forms of Cr were carbonates and Fe–Mn-bound Cr (accounting for slightly more than 25% of total Cr) at 600 °C, and organic-bound Cr (accounting for 32% of total Cr) at 1000 °C. As the combustion temperature increased, the residual fraction of Cr gradually increased. Unlike the organic fraction of Cr, the exchangeable and carbonate-bound forms of Cr first increased and then decreased with increasing combustion temperature. This indicates that the burning of stone coal affected the forms of elements in the coal. During coal combustion, the internal energy of the molecules in coal increases, and the elemental activity increases due to the increase in temperature. The trace elements may be separated from the original molecules and recombined and redistributed in different combustion products. Trace elements in coal, which are found in the form of minerals, elements, and chelates, will differentiate at the beginning of combustion and continue to be
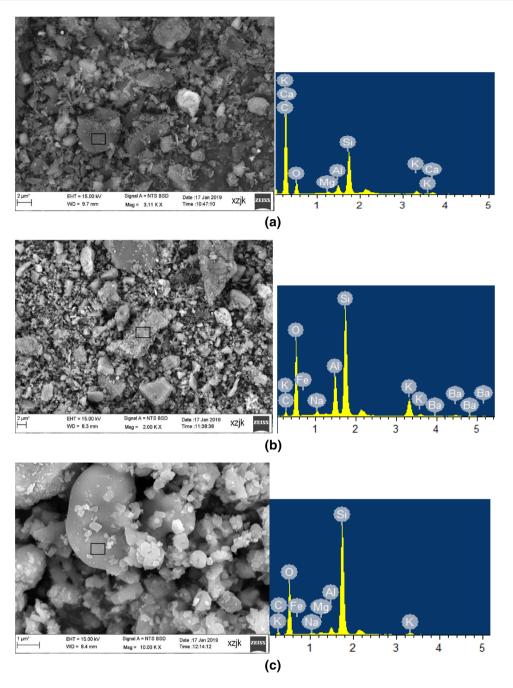
Fig. 3 SEM images and mineral components of **a** raw stone coal, **b** coal ash heated at 600 °C, and **c** coal ash heated at 1000 °C

decomposed and transferred at high temperature (Liu et al. 2003).

The exchangeable fractions of elements are associated with clay minerals, humic acids, and hydrated oxides of iron and manganese (Tessier et al. 1979). Heating promoted the transformation of Cr in stone coal from organic matter-bound Cr to exchangeable and carbonate-bound Cr at 600 °C. The fraction of Cr associated with organic matter increased again in coal ash at 1000 °C.

As for Cr, the major forms of Cd were Fe–Mn-bound Cd in raw stone coal and carbonate- and Fe–Mn-bound Cd in coal ash heated at 600 °C. However, at 1000 °C, residual Cd was the primary form of Cd in coal ash. During combustion, the fraction of Cd associated with organic matter decreased, accounting for 1%–7% of total Cd, while the fraction of residual Cd increased significantly from 8% to 55%. Similarly, in past studies, carbonates and monosulfides were the dominant fractions of Cd in stone coal, while only a small amount of Cd was associated with organic and
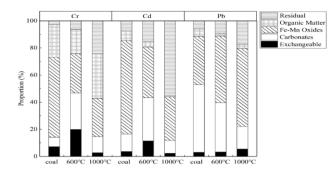
Fig. 4 Proportions of different forms of Cr, Cd, and Pb in the raw stone coal and its combustion ash generated at 600 °C and 1000 °C

insoluble matter (Robert et al. 2018; Xiong et al. 2017). Finkelman (1981a, b) and Swaine (1990) concluded that the majority of cadmium in coal is associated with sphalerite as shielded sulfides. The burning process increased the residual fraction of Cd in this study; however, the EF of Cd at 1000 °C was only 0.50, indicating that Pb was more volatile than chromium and cadmium during the combustion of stone coal; thus, lead would be released to the atmosphere, resulting in risks to human life.

In this study, substantial amounts of lead were present as carbonate forms (50% of total lead) and Fe–Mn-bound forms (36% of total lead), while the fractions of exchangeable, organic matter-bound, and residual lead were small. The results are similar with previous findings. Finkelman (1981a, b) reported that the dominant form of lead in most coals was galena with some lead occurring in sulfates, carbonates, phosphates, and silicates, especially in sulfide-poor coals. Swaine (1990) suggested that lead may occur as pyrite or as organic-associated forms in low-rank coals. Robert et al. (2018) found that in bituminous coal, only a small amount (5%–10%) of lead was associated with silicates (Robert et al. 2018).

Burning the stone coal changed the forms of Pb present in the coal ash, as for Cr and Cd. For example, the Fe–Mn-bound and residual lead fractions in coal ash increased notably with increasing combustion temperature. The Fe–Mn-bound forms accounted for 49% of total lead at 600 °C and 58% at 1000 °C. In contrast, the fraction of Pb associated with carbonates decreased, while the small fractions of organic matter-bound and exchangeable Pb in stone coal did not change noticeably. This further verified that coal combustion transformed the forms of Pb found in stone coal by changing the mineral structure and composition.

4 Conclusions

This study investigated the enrichment, occurrence, and migration of chromium, cadmium, and lead in stone coal and coal ash from the southern area of Shaanxi province,

China. Compared with other Chinese coals, the stone coal from the study area was enriched in Cr, Cd, and Pb. As the combustion temperature increased, the contents of Cr, Cd, and Pb first increased (at temperatures below 600 °C) due to the burning of organic matter followed by volatilization at higher temperatures (above 700 °C) due to the decomposition of clay minerals (e.g., kaolinites and illites). The dominant forms of occurrence of the heavy metals in stone coal were Fe–Mn-bound forms for Cr and Cd and carbonates for Pb. The forms of occurrence of Cr, Cd, and Pb changed with combustion temperature. Upon combustion, the residual fractions of Cr, Cd, and Pb all increased, and the dominant forms in coal ash were Fe–Mn oxides, organic matter, and residual forms for Cr, residual forms for Cd, and Fe–Mn oxides for Pb. The combustion of the studied stone coal could release hazardous elements to the atmosphere via fly ash from the power plant. This is particularly true for Cd, for which almost half of the total amount was released. This release of hazardous elements would pollute the soil and crops and pose a risk to public health.

Compliance with ethical standards

Conflict of interest The authors declare no conflict of interest.

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