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Leaching characteristic and environmental implication of rejection rocks from Huainan Coalfield, Anhui Province, China

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ABSTRACT

Rejection rocks including intra-seam parting, boundary roof and floor intimately associated with coal seams, are commonly produced along with bulk coal. In general, these non-combustible rocks are rejected during coal processing activities, accumulated on the surface, and subjected to natural weathering and leaching. The degree that the rejection rocks threaten the surrounding ecosystems is determined by total concentrations, modes of occurrence of hazardous elements and minerals therein. Three hundred and ninety-four samples of coal seam parting (30), roof (182) and floor (182) in the Huainan coalfield were collected to investigate the geochemical characteristics and environmental risks of rejection rocks. The morphological analysis revealed that rejection rocks are composed of lithic fragments with organic and inorganic layering, clay minerals, quartz, pyrite and chlorite. Correlation analysis between elements and ash yield suggested that most of the environmentally sensitive elements (As, Cd, Co, Cr, Cu, Mn, Ni, Pb, Se, Sn V and Zn) are associated with inorganic matter, but boron is mainly associated with organic matter. In-house sequential leaching experiments conducted on selected rejection rocks showed that the rejection rocks from Huainan Coalfield could be suitable for landfill under high regularization and management. However, in the currently unconfined deposits, trace elements (such as Cu, Ni, Pb, Sb, Sn and Zn possibly) may pose a medium risk to the ecosystem.

Introduction

Coal mining and utilization have caused wide environmental concern (Fang et al., 2003; Finkelman et al., 2002; Liu et al., 2004a, 2005, 2006; Querol et al., 2001). Rejection rocks are non-combustible materials physically separated from bulk coal during coal-mining activities (Bell et al., 2001). According to incomplete statistics collected, China accumulated more than 4.5 billion tons of rejection rocks up to 2010, which covered more than 15,000 km^2 of land (Yu and Zhao, 2008). Therefore, a range of environmental consequences including spontaneous combustion, landslides, acid and toxic element drainage caused by leaching and weathering, and dust hazards can occur where rejection rocks are deposited. Human health risks relevant to trace element content in coal, for example, endemic arsenosis, selenosis and lung cancer, are serious in some areas of China (Larsen and Mann, 2005; Liu et al., 2004b).

Some environmental-sensitive trace elements could enrich in these rejection rocks by a tenfold factor when compared with coal (Dai et al., 2004; Goodarzi and Swaine, 1994). Many studies reported that the environmental behaviors of trace elements in rejection rocks are determined by concentrations and modes of occurrence of elements (Boruvka et al., 2012; Dai et al., 2008; Paul, 2005; Swaine and Goodarzi, 1995). In addition, the modes of occurrence of elements are dependent largely on the minerals therein (Zheng et al., 2007). Consequently, information on mineral composition, major and trace element concentrations and modes of occurrence of elements are suggestive of potential environmental impacts of rejection rocks (Finkelman, 1995; Swaine and Goodarzi, 1995).

As one of the largest industrial coal bases in China, the mining activities in the Huainan Coalfield have contributed significantly to the economic development of East China. However, the environmental impacts associated with mining activities have attracted little attention. Therefore, 30 parting, 182 floor and 182 roof samples were collected to investigate: 1) the geochemical characterization of the rejection rocks; and 2) potential environmental risks of rejection rocks.

Sampling and analytical methods

Samples collection

A large sampling strategy was used to accurately reflect the geochemistry of rejection rocks at the Huainan Coalfield (Fig. 1). Three types of rejection rocks, i.e. roof (182), parting (30) and floor (182), were taken by cutting channels downwards at each of the coal mines

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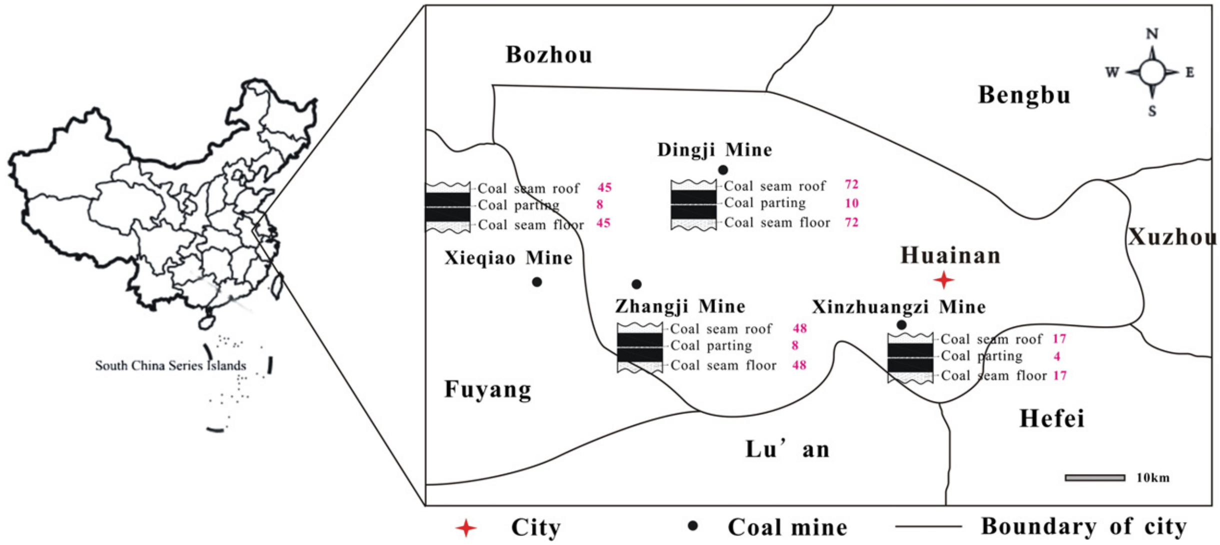

Fig. 1. Location of the selected coal mine in Huainan coalfield.

(98 from Xieqiao Mine (XQ), 104 from Zhangji Mine (ZJ), 38 from Xinzhuangzi Mine (XZZ) and 154 from Dingji Mine (DJ)). The samples were collected from Nos. 4, 6, 7 and 8 coal seams, which are the primary mineable coal beds. All the collected samples were stored in a sealed plastic bag immediately to prevent contamination. The bulk rejection rock samples were air-dried and crushed to pass through a 150-mesh sieve (0.1 mm) for subsequent analysis.

Petrographic analysis

Mineralogical analyses of rejection rock samples were performed by X-ray powder diffraction (XRD, PHILIPS X' Pert PRO) equipped with Cu K-alpha radiation. The pattern is recorded over a 2θ interval of 3–65°, with a step increment of 0.02°/s. The minerals in each sample are identified from the diffractograms by reference to the ICDD Powder Diffraction File. A Scan Electron Microscope (SEM) was used to investigate the morphology of varying minerals.

Elemental analysis

The ultimate analysis (C, H, O, N and S) was determined by Vario EL cube Elementar, and the moisture, ash yield and volatile matter were analyzed by muffle furnace. X-ray fluorescence (XRF) was performed to analyze the chemical compositions of rejection rocks. The powdered rejection rocks and standard reference materials were digested using an acid mixture (HCl:HNO_3:HF) ratio of 3:3:2 in a microwave oven in Teflon beaker at 120 °C maintained for 20 min followed by 180 °C for 25 min. After digestion, the solution was heated at 210 °C to evaporate the redundant acid. Finally, the digestion solution was quantified to 25 ml for the subsequent analysis. The concentrations of trace elements in rejection rocks were determined by inductively coupled plasma mass spectrometry (ICP-MS). The accuracy of the trace elements are corrected by standard reference materials NIST 1632b (coal) and GBW07406 (GSS-6) (soli). If the difference between the calibrated values and the standards is more than 5%, the apparatus needed to recalibrate.

In order to evaluate the potential mobility of trace elements, the compliance leaching test EN 12457 Part 2 procedure was applied (EN, 12457-2, 2002) in the present study. Briefly, tested samples are leached by deionized water at a liquid to solid ratio of 10 L/kg and with an agitation time of 24 h. Each sample is leached in duplicate. The trace element concentrations in leachates were determined by inductively coupled plasma mass spectrometry (ICP-MS), and the anion concentrations (F^-, SO_4^{2-}, Cl^-) in leachates are analyzed by high-performance ion chromatography (HPIC).

In addition, based on Risk assessment code (RAC) (Perin et al., 1985), the sequential extraction experiment (Tessier et al., 1979) was also employed to provide information about the environmental risk of trace element in rejection rocks. Samples are subjected to specific solvents in the five-step sequential extraction procedure (Table 1). Accordingly, modes of occurrences of trace elements are classified into five fractions: exchangeable, carbonate-bound, Fe–Mn oxides bound, organic matter bound, and residual. The fractions acquired after each extraction step were analyzed for As, Ba, Cd, Cr, Cu, Mn, Ni, Pb, Sn, Sb, V and Zn by inductively coupled plasma mass spectrometry (ICP-MS).

Table 1
Sequential extraction procedure.

Step	Extraction procedure	Mode of occurrence
1	1.0 g sample was extracted with 10 ml 1.0 M $MgCl_2$ (pH = 7.0) under room temperature for 1 h, suspension was achieved by centrifugation at 3500 rpm for 20 min.	Exchangeable
2	The residual solid from step 1 was extracted with 10 ml 1 M sodium acetate (pH = 5.0) under room temperature and agitated continuously for 5 h, suspension was achieved by centrifugation at 3500 rpm for 20 min.	Carbonate-bound
3	The residual solid from step 2 was treated with 20 ml 0.04 M $NH_2OH \cdot HCl$ in 25% (v/v) under room temperature and agitated continuously for 6 h, suspension was achieved by centrifugation at 3500 rpm for 20 min.	Fe–Mn oxides bound
4	The residual solid from step 3 was treated with 3 ml 0.02 M HNO_3 and 5 ml 30% H_2O_2 (pH = 2.0) under 85 °C for 2 h. A second 3 ml aliquot of 30% H_2O_2 (pH = 2.0 with HNO_3) was then added under 85 °C and agitated for 3 h. After cooling, 5 ml of 3.2 M NH_4OAc in 20% (v/v) HNO_3 was added and the sample was diluted to 100 ml and agitated continuously for 30 min.	Organic matter bound
5	The residual solid from step 4 was digested with a HCl–HNO_3–HF mixture according to the procedure used for bulk samples	Residual

Table 2
The properties and chemical composition of rejection rocks from Huainan Coalfield.

Proximate analysis, dry basis (wt.%)	Moisture	Ash yield	Volatile matter
XQ (n = 98)	2.35 ± 1.12	68.9 ± 5.2	24.7 ± 2.7
DJ (n = 104)	2.07 ± 0.54	65.4 ± 3.1	28.4 ± 1.6
XZZ (n = 38)	2.56 ± 0.82	70.2 ± 2.6	21.2 ± 2.2
ZJ (n = 154)	2.95 ± 1.36	63.1 ± 3.7	26.9 ± 1.3

Ultimate analysis, daf (wt.%)	C	H	N	O	S
XQ (n = 98)	21.2 ± 2.4	2.05 ± 0.63	0.32 ± 0.16	10.6 ± 3.2	1.31 ± 0.82
DJ (n = 104)	23.5 ± 1.3	2.36 ± 1.25	0.27 ± 0.13	11.2 ± 2.8	2.04 ± 1.16
XZZ (n = 38)	18.3 ± 0.9	1.97 ± 0.67	0.15 ± 0.06	9.36 ± 1.54	1.56 ± 0.63
ZJ (n = 154)	22.1 ± 2.1	2.21 ± 1.72	0.38 ± 0.14	11.7 ± 2.9	1.95 ± 0.45

Ash analysis (wt.%)	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	TiO_2
XQ (n = 98)	51.9 ± 6.2	24.8 ± 3.7	7.74 ± 1.73	14.4 ± 4.3	0.15 ± 0.05	0.44 ± 0.22	0.35 ± 0.31	1.12 ± 0.43
DJ (n = 104)	55.3 ± 5.7	21.2 ± 4.5	8.45 ± 2.47	12.8 ± 3.6	0.13 ± 0.08	0.17 ± 0.15	0.32 ± 0.19	1.45 ± 0.64
XZZ (n = 38)	58.7 ± 7.5	27.0 ± 2.7	6.58 ± 1.64	5.06 ± 2.24	0.16 ± 0.03	0.38 ± 0.18	0.60 ± 0.25	1.51 ± 0.28
ZJ (n = 154)	57.3 ± 8.3	27.7 ± 3.3	6.33 ± 2.68	6.05 ± 1.85	0.13 ± 0.54	0.28 ± 0.12	0.45 ± 0.17	1.46 ± 0.45

Notes: XQ — Xieqiao Mine, DJ — Dingji Mine, XZZ — Xinzhuangzi Mine, ZJ — Zhangji Mine.

Results and discussion

The properties of rejection rocks

The proximate and ultimate analysis results are presented in Table 2. The ash yields of rejection rocks ranged between 63 wt.% and 70 wt.% (dry basis), which is 3–4 fold higher than corresponding coal seams. As indicated previously, most coals in the Huainan Coalfield are characterized by low sulfur content, generally below 0.5% (Sun et al., 2010). However, sulfur in rejection rocks is highly enriched.

The results of XRD analysis showed that minerals in rejection rocks consistently occurred as kaolinite, quartz, illite, calcite, pyrite, siderite, dolomite, ankerite and chlorite (Fig. 2). The ash of rejection rocks are dominated by SiO_2 (51%–59%) and Al_2O_3 (21%–28%), suggesting that the abundant occurrence of clay minerals (Fig. 2), are consistent with those in coal ash (Liu et al., 2005; Sun et al., 2010). Inorganic sulfur in rejection rocks likely occurred as sulfide such as pyrite. The high content of Fe_2O_3 (6%–9%) in ash is possibly derived from the oxidation of pyrite in rejection rocks. The relatively high contents of CaO in ash of rejection rocks from Xieqiao Mine (14.40 wt.%) and Dingji Mine (12.83 wt.%) is suggestive of high carbonate minerals in rejection rocks. The SEM images also indicated the occurrence of abundant clay minerals, quartz, pyrite and chlorite (Fig. 3).

The concentrations of trace elements in the studied samples are listed in Table 3. For comparison, the background values of black shales and the Clarke values of crust are presented in Table 3. A total of 25 trace elements and rare earth elements (REE) are determined in the studies. According to Table 3, the selected trace elements (Ba, Cu, Ga, Mn and Sb) from Dingji Mine are much higher than the other three coal mines, respectively. A significant difference between these trace elements (Ba, Cu, Ga, Mn and Sb) from Dingji Mine and the other three coal mines are also determined by the analysis of variance. For the same depositional environment, the variations of the elements can be explained by the inhomogeneity in these samples. The variations of trace elements in rejection rocks from different types (coal seam roof, parting and floor) are shown in Fig. 4. It shows that the trace elements

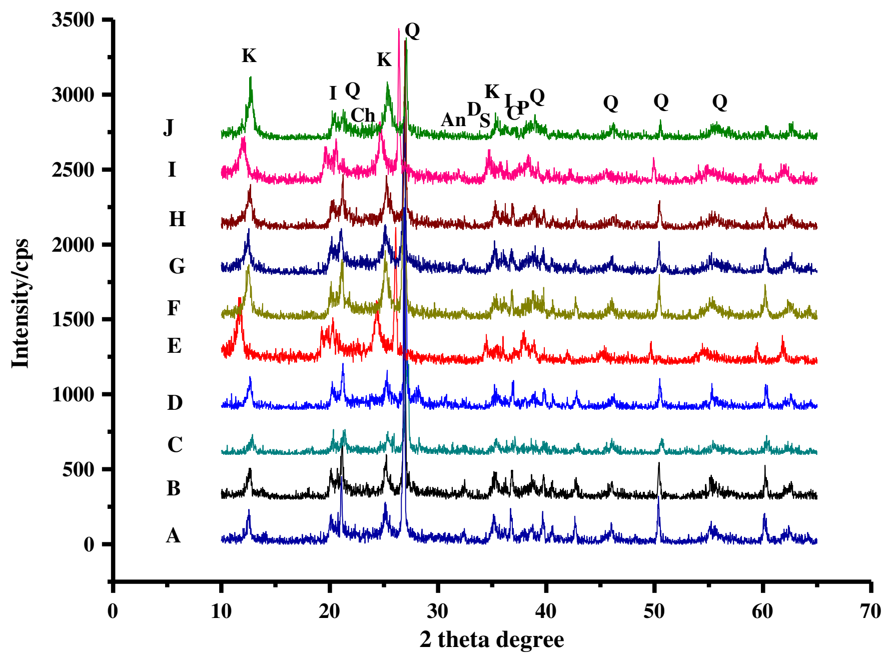

Fig. 2. The X-ray powder diffraction patterns of rejection rocks. Mineral abbreviations: An — ankerite, C — calcite, Ch — chorite, D — dolomite, I — illite, K — kaolinite, P — pyrite, Q — quartz, S — siderite.

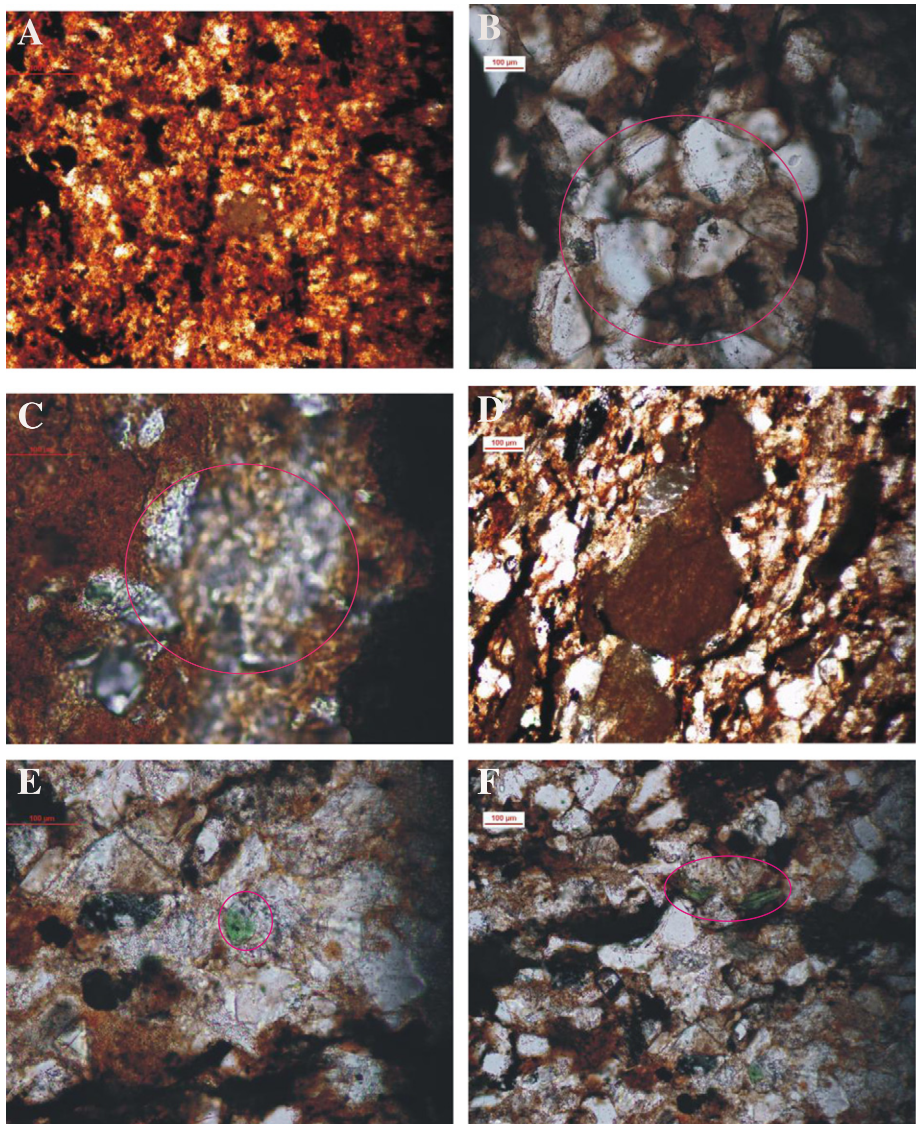

Fig. 3. The SEM micro-images of minerals in rejection rocks. A — lithic fragments with organic and inorganic layering; B — clay minerals; C — quartz; D — pyrite; E — chlorite; F — chlorite.

(except boron) from the coal seam roof/floor have much higher concentrations when compared with the corresponding elements from the coal seam parting, respectively.

In comparison with the background values of black shales, the trace elements (B, Bi, Ga, Sc and W) are much higher in the Huainan Coalfield, and the remaining trace elements are lower (Ketris and Yudovich, 2009). In addition, when competed with the Clarke value of crust (Tayor, 1964), the following trace elements are much higher in Huainan Coalfield rejection rocks: B, Bi, Cd, Ga, Se, Mo, As, Sn, W and Sb.

Modes of occurrence of trace elements

Under natural weathering conditions, the mobility behavior of trace elements in rejection rocks are determined by the stability of its host minerals. Goldich (1938) reported that the stability of minerals is related to the lattice energy; trace elements in host minerals having lower lattice energies could be easily released. Trace elements in rejection rocks are associated either with inorganic compounds such as silicates, sulfides, carbonates, or with organic constituents in a variety of modes. Modes of occurrence of trace elements in rejection rocks determine their behaviors (mobility) during combustion and weathering, and are informative in evaluating their potential environmental impacts (Finkelman and Gross, 1999; Swaine and Goodarzi, 1995). Several studies have been published on the modes of occurrence of trace elements in coal, and it has been suggested that trace elements in coal are perhaps associated with both organic and mineral matter, and probably most of them can exist simultaneously in both forms (Finkelman and Gross, 1999; Swaine and Goodarzi, 1995). The selected minerals contain the following lattice energy values: $CaCO_3$ (2711.2 kJ/mol), ZnS (3234.7 kJ/mol), $CuFeS_2$ (3498 kJ/mol), FeS_2 (3506 kJ/mol), and SiO_2 (6280 kJ/mol); the lattice energy values of sulfides are close to the lattice energy of calcite, indicating that the sulfide minerals would decompose in the chemical weathering processes.

Correlation coefficient and cluster analysis are the most common methods to indirectly determine the modes of occurrence of trace elements. The correlation of the element concentration with ash yield, aluminum, calcium and iron–sulfur could provide preliminary information for their association with inorganic minerals, aluminosilicate minerals, carbonate minerals and sulfide minerals, respectively. Therefore, correlation analysis and cluster analysis were used in this study to identify the possible modes of occurrence.

With respect to environmental quality and health, the US National Resources Committee (NRC, 1980) clustered trace elements into six groups, among which, As, B, Cd, Hg, Mo, Ni, Pb and Se are the elements

Table 3
The concentration of trace elements in rejection rocks from Huainan Coalfield (mg/kg).

Coal waste	XQ (n = 98)	ZJ (n = 104)	XZZ (n = 38)	DJ (n = 154)	AM (n = 394)	BBS	Clarke value	EF
As	15.7 ± 2.7	10.8 ± 1.8	11.9 ± 2.4	12.4 ± 1.3	12.6 ± 2.8	10–80	1.80	7.02
B	75.3 ± 8.3	229 ± 12	228 ± 16	35.6 ± 8.4	166 ± 22	30–120	2.80	59.5
Ba	43.1 ± 6.8	55.1 ± 7.5	55.7 ± 3.4	89.8 ± 8.3	55.2 ± 9.5	270–800	425	0.13
Bi	16.9 ± 3.5	12.4 ± 2.8	15.4 ± 3.7	11.0 ± 1.8	14.4 ± 4.8	0–4	0.17	85.1
Cd	0.42 ± 0.13	0.45 ± 0.22	0.53 ± 0.16	0.76 ± 0.24	0.47 ± 0.24	2–12	0.20	2.38
Co	3.73 ± 0.67	4.26 ± 1.21	4.58 ± 2.11	3.77 ± 1.37	4.25 ± 2.61	10–30	25.0	0.17
Cr	47.4 ± 5.7	48.0 ± 6.8	48.7 ± 6.4	46.3 ± 5.2	48.2 ± 7.3	50–160	100	0.48
Cu	27.4 ± 3.2	21.9 ± 2.7	23.0 ± 2.3	86.4 ± 8.3	31.9 ± 7.4	35–150	55.0	0.58
Ga	16.4 ± 3.7	25.6 ± 5.3	25.9 ± 4.8	35.3 ± 4.9	24.6 ± 6.7	9–25	15.0	1.64
Li	7.73 ± 1.45	5.26 ± 2.15	5.27 ± 1.56	8.82 ± 1.37	6.25 ± 2.21	15–50	20.0	0.31
Mn	47.5 ± 6.7	53.1 ± 8.3	52.3 ± 5.9	74.6 ± 6.3	54.4 ± 8.7	200–800	100	0.54
Mo	8.43 ± 2.24	4.48 ± 1.38	6.57 ± 1.73	3.55 ± 1.89	6.07 ± 2.29	6–60	1.50	4.05
Ni	28.6 ± 5.6	31.4 ± 4.8	31.0 ± 3.7	28.5 ± 2.8	30.0 ± 4.6	40–140	75.0	0.40
Pb	1.26 ± 0.24	1.44 ± 0.46	2.43 ± 0.34	0.29 ± 0.15	1.78 ± 0.35	10–40	/	/
REE	34.1 ± 6.2	36.7 ± 5.6	35.7 ± 4.2	41.8 ± 5.8	37.8 ± 4.6	94–225.4	/	/
Sb	7.43 ± 1.72	2.34 ± 1.03	4.32 ± 1.34	10.7 ± 2.15	5.37 ± 3.58	2–11	4.80	1.12
Sc	19.0 ± 2.5	24.6 ± 2.6	21.9 ± 1.7	17.4 ± 2.9	21.3 ± 2.8	7–20	22.0	0.97
Se	2.62 ± 1.23	3.47 ± 0.84	3.49 ± 0.46	2.35 ± 1.34	3.06 ± 0.74	3–30	0.10	30.6
Sn	2.68 ± 0.68	2.63 ± 0.71	2.76 ± 0.83	2.47 ± 0.25	2.62 ± 0.64	2–10	2.00	1.31
Sr	125 ± 12	115 ± 8	116 ± 8	79.2 ± 8.3	112 ± 12	100–300	375	0.30
Th	0.32 ± 0.08	0.35 ± 0.12	0.41 ± 0.06	0.46 ± 0.13	0.38 ± 0.16	4–11	9.60	0.04
V	50.5 ± 8.2	47.2 ± 3.7	49.1 ± 4.5	48.4 ± 3.5	48.6 ± 6.7	100–400	135	0.36
W	31.6 ± 4.9	30.9 ± 5.7	28.4 ± 3.5	39.2 ± 4.9	31.1 ± 4.9	0–15	1.00	31.1
Y	8.76 ± 1.32	9.15 ± 0.87	8.63 ± 1.25	10.2 ± 1.36	8.91 ± 1.43	15–40	33.0	0.27
Zn	39.4 ± 6.3	27.9 ± 5.3	30.5 ± 4.9	46.1 ± 5.2	34.3 ± 5.8	60–300	70.0	0.49

Notes: XQ — Xieqiao Mine, ZJ — Zhangji Mine, XZZ — Xinzhuangzi Mine, DJ — Dingji Mine, AM — the arithmetic mean value of Huainan Coalfield rejection rocks, BBS — background values of black shales, EF — the enrichment factor (the ratio of the concentration of trace element in rejection rock to the Clarke value).

of greatest concern. Finkelman and Gross (1999) suggested that 25 trace elements in coal are of environmental interest, including As, Cd, Cr, Cu, Ni, Pb, Se and Zn. Considering the aforementioned results, the environmentally sensitive elements (including As, B, Cd, Co, Cr, Cu, Mn, Ni, Pb, Se, Sn V and Zn) in rejection rocks are discussed in detail with emphasis on the mode of occurrence.

Pearson's correlation coefficients of trace elements with ash yield, Al, Ca and Fe in the Huainan Coalfield rejection rocks are presented in Table 4. The highly positive correlation of Fe with S (r = 0.886) indicated that both elements mainly occurred in sulfide minerals.

Arsenic is considered to be a dominating environmentally sensitive element (Gurdal, 2008; Swaine, 2000; Swaine and Goodarzi, 1995). The concentrations in the studied samples are varied from 2.5 to 30.4 mg/kg and have an arithmetic mean of 12.6 mg/kg, which is higher by a factor of 7 than the Clarke value (1.8 mg/kg, Tayor, 1964). Many studies have demonstrated that As is mainly associated with pyrite (Huggins and Huffman, 1996; Ward, 2002). Swaine (1990) reported that As could also be associated with clay minerals and organic matter. The positive correlation with ash yield (r = 0.434) indicated an inorganic affinity. In addition, the correlation coefficient with Fe (r = 0.502) and Cu (r = 0.923) suggests that As is associated with sulfide minerals.

Boron occurrence was generally associated with organic matter (Finkelman, 1995; Querol et al., 1998). Goodarzi (2002) reported that high contents in coals are deposited under a brackish environment. The concentration of B in the selected samples ranged between 7.6 and 357.5 mg/kg, and the strong negative correlation with ash yield (r = −0.527) pointed towards an organic affinity.

The concentration of Cd in Huainan Coalfield rejection rocks varied from 0 to 0.8 mg/kg and had a mean of 0.47 mg/kg, which is higher

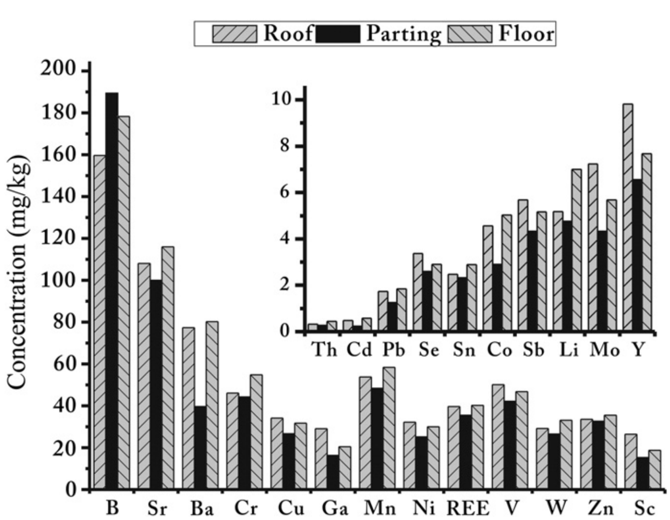

Fig. 4. Variations of trace elements in rejection rocks from different types.

Table 4
Pearson's correlation coefficients of trace elements with ash yield, Al, Ca, Fe or selected elements in rejection rocks.

Correlation coefficients with ash yield		
Group 1: r > 0.7	No elements	
Group 2: r = 0.5–0.69	Co (0.532), Cr (0.624), Mn (0.645), Sn (0.674), Zn (0.572)	
Group 3:r = 0.35–0.49	As (0.434), Ni (0.403), Se (0.434), V (0.416)	
Correlation coefficients with Al (aluminosilicate affinity)		
r > 0.7	No elements	
r = 0.5–0.69	Sn (0.521), V (0.573)	
Correlation coefficients with Ca (carbonate affinity)		
r > 0.7	Mn (0.826)	
r = 0.5–0.69	No elements	
Correlation coefficients with Fe (Sulfide affinity)		
r > 0.7	No elements	
r = 0.5–0.69	As (0.502), Cd (0.547), Cu (0.623), Ni (0.569), Pb (0.527), Zn (0.556)	
r = 0.35–0.49	Co (0.436), Cr (0.387), Se (0.468)	
Correlation coefficients between selected elements		
Fe–S = 0.886;	As–Cu = 0.923	Cd–Zn = 0.962
Pb–Se = 0.697;	Co–Ni = 0.721	B–Ash yield = −0.527

Notes: Significant at 0.05 level (2-tailed).

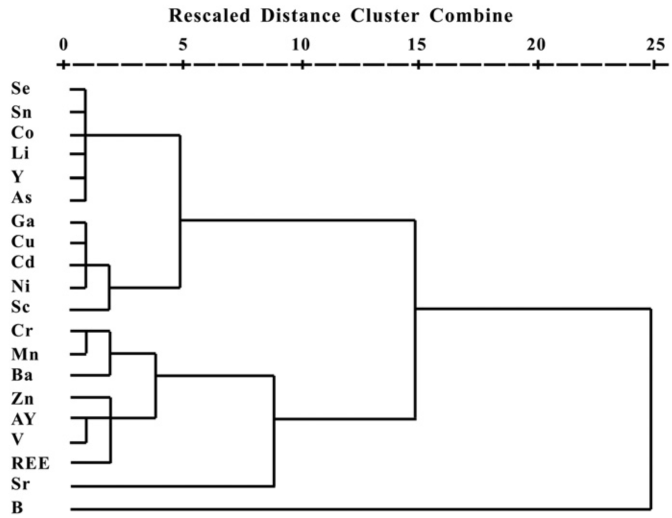

Fig. 5. Dendogram showing hierarchical cluster analysis. AY — ash yield.

than that of the Clark values (0.2 mg/kg). Cadmium is generally associated with pyrite and sphalerite (Finkelman and Gross, 1999; Gurdal, 2008), and the positive correlation with Fe (0.5470) and Zn ($r = 0.962$) suggested an association with sulfides.

The Huainan Coalfield rejection rocks had a lower Co content (3.77 mg/kg) when compared with the background value of black shales (10–30 mg/kg) and Clark value (25 mg/kg). Cobalt is generally related to sulfides (Finkelman, 1995; Querol et al., 1998). The positive correlation of Co with ash yield ($r = 0.532$), Fe ($r = 0.436$) and Ni ($r = 0.638$) indicated that Co is associated with inorganic materials and existed in sulfide minerals.

The concentration of Cr in Huainan Coalfield rejection rocks varied from 10.2 to 58.1 mg/kg and had an arithmetic mean of 48.2 mg/kg. Various studies demonstrated that Cr could be associated with various matter, in particular, Cr mainly exists in association with clays and organic matter (Finkelman, 1995; Swaine and Goodarzi, 1995). However, the strong correlation coefficient between Cr and ash yield ($r = 0.624$) indicated that Cr had an inorganic affinity.

The copper content of Huainan Coalfield rejection rocks ranged from 3.4 to 160.4 mg/kg. Copper occurrence was generally associated with sulfide minerals (pyrite) (Finkelman, 1995; Swaine, 1990). Xu et al. (1990) reported that Cu has a positive correlation with clays. The positive correlation of Cu with Fe ($r = 0.623$) and As ($r = 0.923$) suggested that Cu is associated with sulfide minerals.

The Huainan Coalfield rejection rocks have a lower Mn content (mean 54.4 mg/kg) in comparison with the background value of black shales (200–800 mg/kg) and Clark value (100 mg/kg). Manganese is mainly associated with carbonate minerals ($r = 0.826$), an occurrence with carbonates is also reported by Finkelman and Gross (1999). In addition, the positive correlation with ash yield ($r = 0.645$) indicated an inorganic affinity.

Many studies have reported that Ni is associated with both inorganic and organic matter in coal, and also exists in sulfide minerals (Finkelman, 1995; Goodarzi, 2002; Querol et al., 1998). However, the strong correlation coefficient between Ni and ash yield indicated that Ni has mainly an inorganic affinity. The modes of occurrence of Ni in rejection rocks are associated with sulfide minerals (with Fe $r = 0.569$, with Co $r = 0.638$). The concentration of Ni in the studied samples ranged between 5.3 and 45.7 mg/kg.

Finkelman and Gross demonstrated that Pb existed mainly in sulfides (1999); an organic affinity is also suggested (Swaine, 1990). The weak correlation between Pb and ash yield ($r = 0.168$) suggested that Pb in studied samples could also have an organic affinity. The positive correlation with Fe ($r = 0.527$) and Se ($r = 0.697$) represents an association with sulfide minerals.

The concentration of Se in Huainan Coalfield rejection rocks varied from 0.6 to 5.9 mg/kg and had an arithmetic mean of 3.06 mg/kg, which is higher by a factor of 30 than that of the Clark value (0.1 mg/kg). Selenium in rejection rocks had a strong association with sulfide minerals ($r = 0.421$); the occurrence with sulfides is also published by Swaine (1990). Finkelman and Gross (1999) hypothesized that Se had an association with organic matter, but the positive correlation between Se and ash yield ($r = 0.435$) suggested an inorganic affinity in Huainan Coalfield rejection rocks.

Ren et al. (1999) hypothesized that Sn has a positive correlation with clay minerals in coal. Finkelman (1995) reported that Sn is associated with sulfides. As shown in Table 4, Sn mainly existed in aluminosilicate minerals ($r = 0.521$); Sn is also associated with sulfide minerals ($r = 0.302$). The strong correlation between Sn and ash yield ($r = 0.674$) suggested an inorganic affinity.

Vanadium occurred mostly in clays and organic matter (Dai et al., 2008; Finkelman, 1995; Goodarzi, 2002). According to the Pearson's correlation coefficient, V in rejection rocks is predominantly in association with aluminosilicates ($r = 0.573$). The positive correlation between V and ash yield indicated an inorganic affinity in the studied samples.

Zin is reported to be associated with inorganic matter, in particular with pyrite and sphalerite (Finkelman, 1995; Goodarzi, 2002; Swaine and Goodarzi, 1995). In the studied samples, the strong correlation with ash yield ($r = 0.572$), indicated an inorganic affinity of Zn in rejection rocks. In addition, the positive correlation with Fe ($r = 0.556$) and Cd ($r = 0.962$) represented an association with sulfide minerals.

Cluster analysis is devoted to the classification of the selected factors: ash yield, As, B, Ba, Cd, Co, Cr, Cu, Ga, Li, Mn, Ni, Sc, Se, Sn, Sr, V, Y, Zn and

Table 5
The concentration of trace elements of rejection rocks leachates and waste acceptance criteria for landfilling according to the Annex 2 of the 2003/33/EC Council decision.

	Coal waste leachates (mg/L)				Waste acceptance criteria (mg/L)			Leaching rate (%)
	XQ($n = 16$)	DJ ($n = 16$)	XZZ ($n = 16$)	ZJ ($n = 16$)	Inert	Nonhazardous	Hazardous	
As	NA	NA	NA	NA	0.50	2.00	25.0	<1
Ba	1.08 ± 0.32	0.30 ± 0.06	0.90 ± 0.41	0.08 ± 0.03	20.0	100	300	<1
Cd	NA	0.03	NA	NA	0.04	1.00	5.00	<1
Cr	0.21 ± 0.05	0.18 ± 0.06	0.12 ± 0.08	0.06 ± 0.04	0.50	10.0	70.0	<1
Cu	1.01 ± 0.26	0.86 ± 0.35	2.13 ± 0.57	1.45 ± 0.21	2.00	50.0	100	<1
Mn	0.11 ± 0.06	0.01	NA	NA				<1
Ni	0.55 ± 0.17	0.64 ± 0.25	0.70 ± 0.18	0.49 ± 0.21	0.40	10.0	40.0	<1
Pb	0.17 ± 0.02	0.03 ± 0.03	0.19 ± 0.06	0.14 ± 0.05	0.50	10.0	50.0	14.1
Sn	0.09 ± 0.02	0.19 ± 0.05	0.14 ± 0.03	0.09 ± 0.01				8.00
Sb	0.11 ± 0.03	0.10 ± 0.01	0.08 ± 0.04	0.07 ± 0.03	0.06	0.70	5.00	2.40
V	0.56 ± 0.06	0.40 ± 0.12	0.37 ± 0.08	0.25 ± 0.06				<1
Zn	0.19 ± 0.04	0.33 ± 0.09	0.20 ± 0.03	0.18 ± 0.05	4.00	50.0	200	<1
F^-	7.11 ± 1.23	3.92 ± 1.07	3.04 ± 0.87	6.39 ± 1.36	10	150	500	
Cl^-	4.03 ± 0.89	4.01 ± 1.16	5.93 ± 0.76	5.14 ± 2.43	800	15000	25000	
SO_4^{2-}	5.23 ± 1.35	16.1 ± 3.15	5.56 ± 0.57	3.58 ± 0.66	1000	20000	50000	

REE. The optimal dendogram is obtained by the Euclidean distances and the Ward method (Lu et al., 1995). The dendrogram showing Hierarchical Cluster Analysis is illustrated in Fig. 5. According to the dendrogram (Fig. 5), the selected elements could be classified into three distinct clusters. The elements Cd, Se, Sn, Co, Li, As, Cu, Ga, Ni and Sc are clustered into Cluster 1. In this cluster, a sulfide fraction is represented by the association of Cd, Se, As, Cu, Co and Ni (Finkelman and Gross, 1999), simultaneously, the association of Sn, Y and Ga suggested that these elements may be associated with silicate minerals (clay minerals). Cluster 2 is represented by Cr, Mn, Ba, Zn, REE, V, ash yield and Sr. The associated between Ba, REE, V, ash yield and Sr probably indicated the existence of silicate minerals. Boron had low correlation coefficients with other elements and is external to the two associations.

According to the aforementioned results, most of the selected environmentally sensitive elements (As, Cd, Co, Cu, Ni, Pb, Se and Zn) have a strong correlation with Fe and are associated with sulfide minerals. Under the natural weathering and leaching of rejection rocks, sulfides can be oxidized easily and the environmentally sensitive elements can migrate into the environment.

Leaching of potentially hazardous elements

The trace element and ion concentrations in rejection rock leachates were analyzed to evaluate the elemental mobility under natural conditions. The chemical composition of leachates and waste acceptance criteria for landfilling according to Annex 2 of the 2003/33/CE Council Decision are shown in Table 5.

The environmental sensitive elements (As, Cd, Co, Cr, Cu, Mn, Ni, Pb, Se, Sn, V, and Zn) are associated with water-leachable and ion-changeable phases, which are consistent with the conclusions obtained from the sequential chemical extraction (Fig. 6). In the current study, the leaching rate of trace elements is used to evaluate the degree of the trace element mobility in the rejection rocks during leaching, which is defined as:

$$\mathrm{Lr} = \frac{Trace\ element\ concentration\ in\ the\ leachates}{Trace\ element\ concentration\ in\ the\ samples} \times 100\%.$$

According to Table 5, the leaching rates of most trace elements are less than 1%. When comparing the trace element concentration in the leachates with the waste acceptance criteria for landfilling stated in the Annex 2 of the Council Decision (2003/33/EC), the content of Ni and Sb are higher than the limit values for insert wastes demonstrating that the rejection rocks in Huainan Coalfield is considered as nonhazardous wastes. Therefore the rejection rocks at Huainan Coalfield could be classified as non-hazardous waste materials if disposed of under well regulated and managed conditions. In their current state (unconfined deposits), these materials pose a medium risk to the environment.

According to the results of the sequential extraction studies (Fig. 6), the trace elements in rejection rocks are associated with varying proportions of fractions. The strength values can be used as an indication to evaluate the potential environmental risk (Rath et al., 2009). The risk assessment code (RAC) determined that trace elements can be considered safe for the ecosystem environment when exchangeable and carbonate bound fractions are less than 1%. When both fractions exceed 50%, the related trace elements can lead to high environmental impacts (Perin et al., 1985).

When applied in the present study, the code indicated that about 11–30% of Cu, Ni, Pb, Sb, Sn and Zn existed in exchangeable and carbonate bound and therefore could lead to medium risk to the ecosystem. The speciation patterns of As, Ba, Cd, Cr, Mn and V suggested low risk to the environment. If no countermeasure will be adopted, the rejection rocks piled up on the surface may lead to potential environmental impacts.

Conclusion

The following conclusions about the geochemical and environmental characterization of Huainan Coalfield rejection rocks are reached:

(1) The mineral phases found in the samples are kaolinite, quartz, illite, calcite, pyrite, siderite, ankerite, dolomite and chlorite.
(2) The selected environmentally sensitive elements (As, B, Cd, Co, Cr, Cu, Mn, Ni, Pb, Se, Sn V and Zn) are generally associated with inorganic matter, on the other hand, the strong negative correlation of boron with ash yield ($r = -0.527$) points towards an organic affinity. Most of the selected environmentally sensitive elements (As, Cd, Co, Cu, Ni, Pb, Se and Zn) have a strong correlation with Fe and are associated with sulfide minerals. Under the natural weathering and leaching of rejection rocks, sulfides

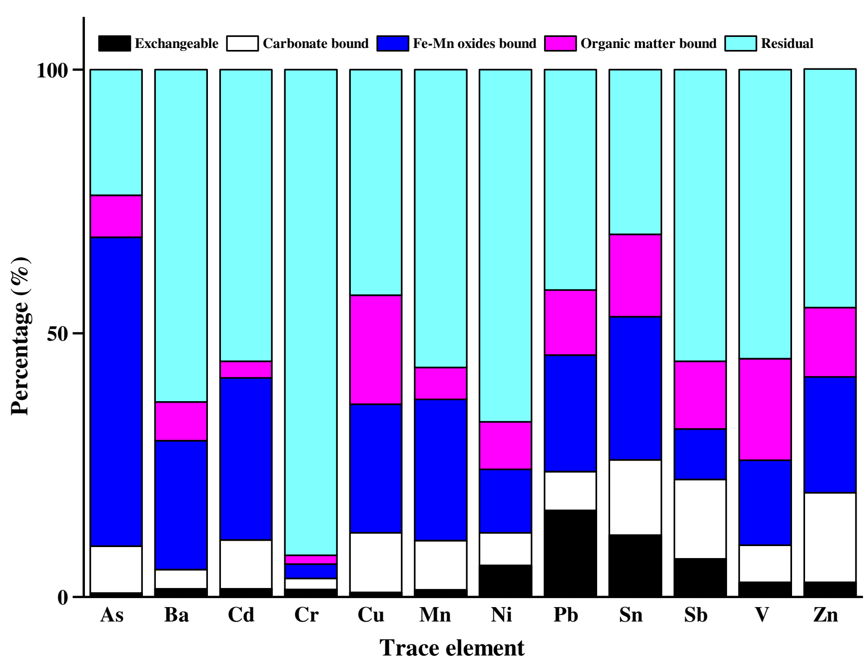

Fig. 6. Average percentage of trace element in different fractions in rejection rocks.

can be oxidized easily and the environmentally sensitive elements can migrate into the environment.

(3) According to waste acceptance criteria the rejection rocks are considered non-hazardous wastes, indicating that they are suitable for disposal in a conventionally managed landfill.

(4) The Risk Assessment Code revealed that the trace elements (Cu, Ni, Pb, Sb, Sn and Zn) in rejection rocks may pose medium risk to the ecosystem. Fractionation profiles of other elements (As, Ba, Cd, Cr, Mn and V) suggested low risk to the environment. If no countermeasure will be adopted, the rejection rocks may cause potential environmental issues.

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