

# Leaching Behavior of Trace Elements in Coal Spoils from Yangquan Coal Mine, Northern China

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**ABSTRACT:** The long-term dumping of coal waste piles has caused serious environmental problems. Release of trace elements (including rare earth elements, REEs) from coal spoils gobs was investigated at Yangquan coal mine, Shanxi Province, China. X-ray diffraction (XRD) was used to analyze the mineral composition of the coal spoils. The minerals of the coal-spoil samples are mainly kaolinite and quartz, with a minor proportion of pyrite. The batch and column tests were employed to simulate the leaching behavior of trace elements from coal spoils. Elements V, Cr, Zn, As, Pb, and Cd are highly enriched in all coal spoils. The coal spoils also have elevated levels of Ga, Ge, Se, Sn, Hf, and Th. The leachate of coal spoils, fried coal spoils and CSFGM (coal spoils fire gas mineral) samples are acidic, with the pH values ranging between 3.0 and 6.6. The released elements with high concentrations (over 100 µg/L) include Fe, Mn, Co, Ni and Zn, while moderately-released elements are Cu, Se, Mo and As. A high content of heavy metals in batch-test leachate with CSFGM indicates an increased mobility of heavy metals in coal spoil combustion byproduct. Within the first hour washing with the electrolyte solution, a rapid rise of common cations, trace elements, and REEs content, as well as a drop of pH value, in effluent was observed. An increased leaching velocity favors the release of trace elements from coal spoils. In addition, the pulse input of precipitation led to more elements to be released than continuous leaching.

**KEY WORDS:** trace elements, coal spoil, contamination, leaching, column test.

## 0 INTRODUCTION

Significant environmental pollution and health impact issues caused by mining activity and coal usage have been reported worldwide (Ao et al., 2008; Zhao et al., 2008; Villalba et al., 2007; Shigeo et al., 2006; Finkelman, 2004; Huang, 2004; Luo et al., 2004; Cernuschi and Giugliano, 1987). In the areas where air deposited coal spoil dump banks exist, negative environmental and health impacts are found. Toxic substances, including heavy metal elements, PAHs, HF, CO, SO<sub>2</sub>, H<sub>2</sub>S, and particulate matter, are released into the atmosphere due to spontaneous combustion or leaching process (Querol et al., 2008; Pone et al., 2007; Finkelman, 2004; Stracher and Taylor, 2004; Wu et al., 2004; Ando et al., 2001; Swaine, 1990; Cosca et al., 1989; Germani and Zoller, 1988). Environmental scientists have many concerns about the heavy metals as they are potent toxins and genotoxins. The impact of long-term

deposition of coal waste on aquatic environment also receives much attention. Oxidation of pyrite leads to a sequence of geochemical reactions in interaction with dumped coal spoils. The leachate solution, with enriched concentrations for metals especially Fe, Cu, Mn and Ni, is found from coal waste dump piles. The formation of leachate with high contaminant content may cause surface- and ground-water contamination. A field experiment was employed by Donovan and Ziemkiewicz (2013) to determine the feasibility of sequestering dissolved selenium (Se) leached from coal-mine waste rocks. Se concentrations in outlet vary from several µg/L to three to four hundreds of µg/L, under the dynamic leaching processes. Long time deposit of coal spoils may result in salinity and trace elements pollution (Park et al., 2013). The salinity in coal mine environments is from the geogenic salt accumulations and weathering of spoils upon surface exposure. The salts are mainly sulfates and chlorides of calcium, magnesium and sodium with trace heavy metals. The leaching behavior of elements from coal spoils into groundwater was studied by Denimal et al. (2001) using isotope tracer methods. Heavy metal leached from coal tailings and spoil is a challenge for mining operations in southern West Virginia (Ziemkiewicz et al., 2011). The study reported that after 96 weeks, about 35% of the original, potentially mobile selenium had leached. However, a systemic investigation on the

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leaching release of major cations, trace elements and REEs are important for the full understand of the potential environmental pollution of air deposited coal spoils banks in Yangquan City, northern China.

More than 300 coal spoil banks deposit in Shanxi Province, the province with the highest coal production in China (The Ministry of Land and Resources P.R.C., 2008). The total amount of coal waste is more than 3.1 Gigatons (Gt) in 2008, occupying a land area of 300 hectares. Yangquan No. 15 coal spoil bank was chosen for this study, where a largest coal spoils banks have deposited over decades (Fig. 1). Coal spoil and soil samples were collected in the field. Laboratory batch and column tests were employed to evaluate the leaching behavior of heavy metal under precipitation processes.

Bulk studies have focused on the leaching behavior of heavy metals in coal spoils. In our study, a systematic investigation on the leaching release of major cations, trace elements and REEs were performed. The aims of this study are: (1) to assess the release of heavy metal and REE from the coal spoil banks as a result of precipitation leaching; (2) to evaluate the potential impact of leaching speed and pulse leaching on elements release.

## 1 GEOLOGICAL BACKGROUND

The Yangquan coal mining district is located to the south-west of the town of Yangquan City (Shanxi Province, 113°36'E, 37°53'N). Yangquan has a coal reserves estimated to be 104 Gt, covering an area of 1 015 km<sup>2</sup>. The major periods of coal formation are Carboniferous (Taiyuan Formation) and Early Permian (Shanxi Formation). The coal-bearing strata overlay Ordovician and Cambrian marine limestone and are overlain by the Xiashihezi Formation (Early Permian), the Shangshihezi Formation (Later Permian) and Triassic clastic units. The lithology of the formations consists of mainly quartz sandstone, siltite, silty mudstone, mudstone, limestone and coal.

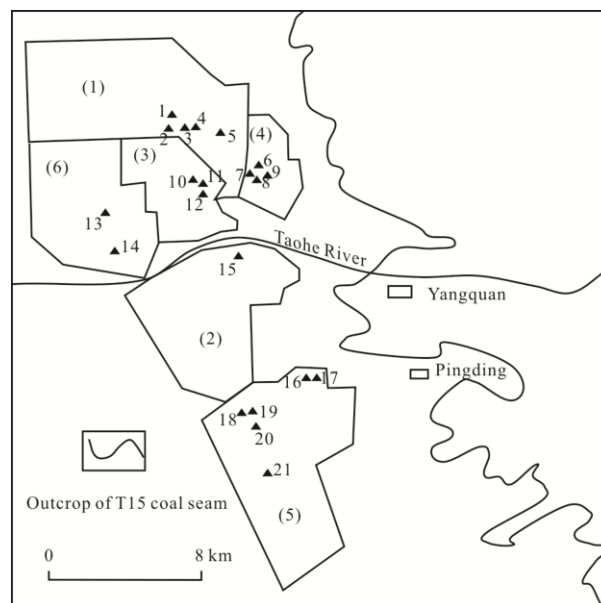
The coal spoil piles in Yangquan have a total amount of 1.0 Gt, producing from 194 sub-coal mines. The coal spoil deposits located in the upstream of the Yangquan City and Pingding County, have been suffering from spontaneous combustion and precipitation leaching (elemental leaching from precipitation). Precipitation leaching of coal spoils piles has resulted in negative impact on surface water and groundwater quality.

## 2 SAMPLING AND LABORATORY EXPERIMENTS

Samples of coal spoils and coal spoils fire gas mineral (CSFGM) were collected from the largest coal spoils banks in Yangquan coal mines. The coal-spoils sample was collected around the piedmont of the bank.

The mineral composition of the coal spoil and fired coal spoil was analyzed using X-ray diffraction (XRD, D8-Focus, Bruker, Germany; Chung, 1974). Before laboratory tests, coal spoils sample were dried, and crushed to be less than 200 mesh (74 µm) in particle size.

Batch leaching test was applied to the coal spoil and fired spoil to identify the leaching potential of target elements from the coal spoils. Four coal-spoils samples, including one



**Figure 1.** Location of major coal spoils piles in the study area (coal spoil samples used in the study was collected from the No. 15 coal waste bank). (1)–(6) stand for Nos. 1–5 coal mines and Xinjing coal mines; ▲ Coal spoils piles.

limestone (CS1), one mudstone (CS2), one shale (CS3) and one sandstone (CS4), were used in this work. All samples were ground and screened through 200 mesh sieve. The homogenized sample was dried in an oven at 100 °C for 2 h and then stored in a desiccator. Fired coal spoils was prepared by a smelting burning process as below: about 100 g of each coal-spoils sample was heated at 1 100±30 °C in a muffle furnace for four hours, and their ruminants were labeled as fired coal spoils samples (i.e., CSF1, CSF2, CSF3 and CSF4). Coal spoils and fired coal spoils were leached with 8 mL of 1 mM Ca(NO<sub>3</sub>)<sub>2</sub> (an electrolyte to simulate the leaching background) to approximately 2 g of solid in capped 15 mL centrifuge tubes at pH 6.7 (the pH value of rainwater detected in the study area). The mixture was shaken for 24 h on a round shaker, and then filtrated through 0.2 µm filter. Heavy metals in the filtrate solution were analyzed using an Inductively Coupled Plasma-Mass Spectrometer (ICP-MS, Elan(R) DRC II, PerkinElmer SCIEX, USA). The accuracy of the analyses was confirmed using the certified reference material TMDA-54.4. The analyze limitation is 0.02 µg/L with the standard solution.

The coal spoils mainly consists of sandstone, according to field investigation. The predominant sandstone coal spoils sample (CS4) was therefore chosen for the column leaching test. A total of ca. 12.5 g coal spoils was packed into a 10 cm height omega column. The column test was employed up-flow of 1 mM Ca(NO<sub>3</sub>)<sub>2</sub> (electrolyte, pH 6.7), operated at a flow rate of about four column pore volumes per hour (PV/h) with a total volume of 500 mL. The column was connected to a peristaltic pump and the effluent solution was collected with an automatic fraction collector. An increasing pumping speed method (from four to five PV/h) was applied to simulate the possible velocity change of leaching solution. To represent the pulsed input of precipitation, a stop-flow method (stopped for 2 h) was applied, followed by another consecutive leaching. The effluent solution

was filtrated through 0.2  $\mu\text{m}$  filter and analyzed with an ICP-MS for major cations and target trace elements.

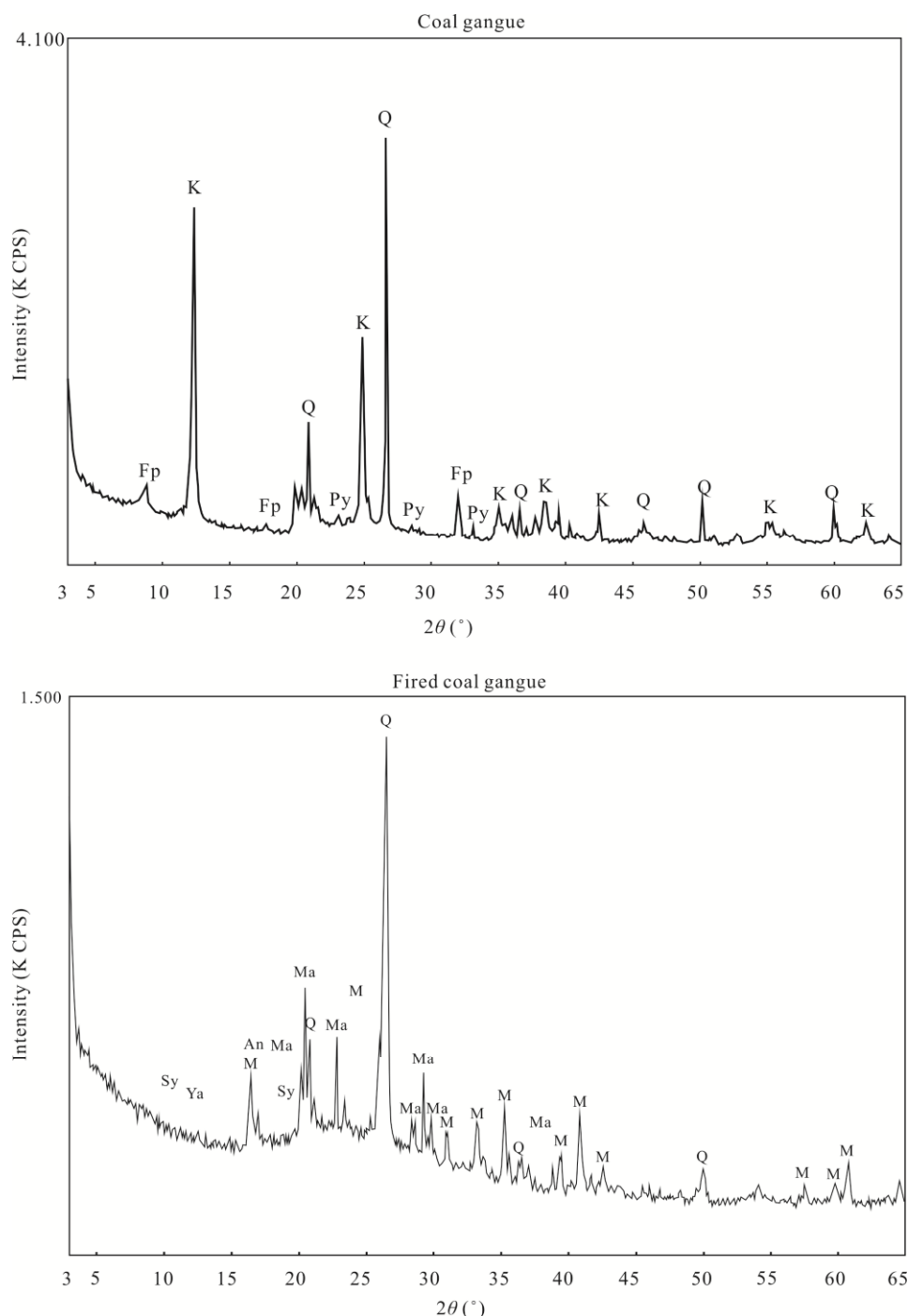
### 3 RESULTS AND DISCUSSION

#### 3.1 Mineralogy and Trace Element Composition

The minerals of the coal-spoil samples are mainly kaolinite and quartz, with minor proportions of pyrite (Fig. 2). The mineral assemblage of the fired spoil contains quartz, mullite, mascagnine, syngenite, lazurite and anhydrite. The coal-spoils samples from the Yangquan coal mine are characterized by a

low volatile matter (7.4%–13.3%, dry ash free), medium- to high-ash yields (13.3%–29.3%, dry basis), and medium- to high-sulfur contents (1.2%–6.7%, dry basis).

The elemental contents for coal spoils are shown in Table 1. Elements V, Cr, Zn, As, Pb, and Cd are highly enriched in all coal spoils, and elements Ga, Ge, Se, Sn, Hf, and they are moderately rich. The contents of all other elements are similar to their abundances in continental crust (Li, 1984), as shown in Table 1. For elements such as Ti, V, Cr, Ge, and As in coal spoils, the confidence intervals of the means are wide,



**Figure 2.** XRD patterns for coal spoil, and fired coal spoil. Q. quartz ( $\text{SiO}_2$ ); K. kaolinite ( $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ ); M. mullite ( $\text{AlSi}_2\text{O}_7$ ); Ma. mascagnine ( $(\text{NH}_4)_2\text{SO}_4$ ); Py. pyrite ( $\text{FeS}_2$ ); Fp. fluorphlogopite ( $\text{KMg}_3(\text{AlSi}_3\text{O}_{10})\text{F}_2$ ); Sy. syngenite ( $\text{K}_2\text{Ca}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ ); Ya. Yavapaiite ( $\text{KFe}(\text{SO}_4)_2$ ); Fa. ferroactinolite ( $\text{Ca}_2\text{Fe}_3\text{Si}_8\text{O}_{22}(\text{OH})_2$ ); La. lazurite ( $\text{Na}_4\text{Al}_3\text{Si}_3\text{O}_{12}\text{S}$ ); An. anhydrite ( $\text{CaSO}_4$ ).

**Table 1** Trace elements in coal spoils from Yangquan coal mine (ppm)

Elements (ppb)	Mudstone CS1	Shale CS2	Limestone CS3	Sandstone CS4	Abundance in continental crust (Li, 1984)
Be	4.24	4.22	4.21	4.08	1.5
B	21.6	20.4	13.6	9.24	-
Sc	7.35	8.29	6.90	7.60	17
Ti	3 434	4 901	1 297	8 265	5 300
V	110	182	71.7	354	120
Cr	105	215	101.0	565	90
Fe (%)	2.22	3.29	3.39	4.52	5.1
Mn	400	944	450	1 118	1 100
Co	5.17	24.9	12.8	31.7	20
Ni	8.57	18.8	17.5	41.7	71
Cu	14.4	34.9	72.4	86.4	54
Zn	131	286	99.4	488	85
Ga	40.8	49.5	28.3	25.7	18
Ge	1.64	14.0	3.28	20.0	1.4
As	13.4	9.83	8.83	45.8	2.2
Se	11.5	6.81	1.66	2.42	0.08
Rb	40.4	62.0	64.2	44.2	87
Sr	149	243	171	378	480
Y	34.7	38.1	35.7	41.3	25
Zr	87.1	60.7	34.6	122	140
Nb	25.8	24.9	24.4	24.9	19
Mo	1.56	1.73	2.15	0.10	1.2
Pd	0.02	0.02	0.019	0.02	0.01
Ag	0.13	0.14	0.14	0.14	0.07
Cd	1.33	1.46	1.62	12.54	0.14
Sn	5.01	4.50	3.72	7.63	1.7
Sb	0.12	0.15	0.12	0.19	0.5
Cs	2.27	2.32	2.30	2.28	1.5
Ba	362	719.2	388	596	400
La	52.4	56.6	52.0	56.2	-
Pr	12.8	12.9	12.8	13.3	-
Nd	42.0	44.1	41.4	49.2	-
Ce	140	157	137	184	-
Sm	8.70	9.63	8.57	10.1	-
Eu	1.25	1.26	1.25	1.26	-
Gd	8.67	9.73	8.68	10.5	-
Tb	0.14	0.14	0.14	0.14	-
Dy	5.25	5.31	5.27	5.37	-
Ho	0.01	0.01	0.01	0.03	-
Er	2.61	2.63	2.62	2.65	-
Tm	0.02	0.02	0.02	0.02	-
Yb	2.98	2.99	2.98	3.00	-
Lu	0.01	0.01	0.01	0.01	-
Hf	7.07	6.78	6.68	6.76	1.7
Ta	1.40	1.40	1.40	1.40	1.9
W	2.77	2.69	2.65	2.69	1.1
Pb	32.85	34.46	32.20	52.30	13
Th	27.99	26.46	25.62	26.66	6.5
U	4.57	4.54	4.54	4.60	2.0

indicating an uneven distribution of these elements. The content of most elements in coal spoils increases more or less from the limestone, mudstone, shale and sandstone samples (Table 1).

### 3.2 Batch Leaching Test

The coal mine spoils undergo a massive elemental release caused by weathering, once they are removed from a high pressure environment and exposed to the air (Godbeer et al., 1994; Gluskoter et al., 1977; Taylor, 1974). The results of the batch leaching test with coal spoils, fired coal spoils and CSFGM samples are shown in Table 2. Sulphides (mainly pyrite), as one of the common components of coal spoils, oxidize during coal mine spoil weathering, which further increase the weathering rate, reduce the pH value and favor the release of trace elements (Wiggering, 1993). The leachate of coal spoils, fired coal spoils and CSFGM samples are found to be acidic, with the pH values ranging between 3.0 and 6.6. Therefore, the heavy metals in the leaching solution may include water-soluble, exchangeable, and some acid-soluble matrix fractions (Gao et al., 2013). The highest content of heavy metals in leachate solutions was normally found in the samples with the lowest pH value (e.g., CS4, CSF4 and CSFGM).

Elements linked to sulfide mineral weathering, showed the different release potential. The elements with high release con-

centrations (over 100  $\mu\text{g/L}$  concentrations in the leachate) include Fe, Mn, Co, Ni and Zn. While Cu, Se, Mo and As show a medium-level release concentration (10–100  $\mu\text{g/L}$ ), and Sb a low-level release concentration (less than 10  $\mu\text{g/L}$ ). The high concentrations of Fe, Mn, Mo, Co, Ni and Zn in leachate of fresh coal spoils indicate the high mobility of these elements under leaching process.

The Se concentration in leachate of coal spoils and fired coal spoils is low, while the in leachate with CSFGM is as high as 1 727  $\mu\text{g/L}$ . It means that firing is one of the major release methods of Se from coal spoils into environment. And element Se is more leachable in CSFGM than that in coal spoils.

A concentration of toxic element Cr in leachate with fresh coal spoils range between 0.09 and 115  $\mu\text{g/L}$ . The Cr content in leachate of the fresh coal spoils was less than the fired coal spoils, except for CS2 and CSF2. The highest Cr content in leachate in batch test solutions was found with CSFGM (584  $\mu\text{g/L}$ ). Other potentially harmful elements such as Cd and Pb are immobile, as their leachable concentrations are relatively low (Table 2). Overall, the highest content of heavy metals is found in sandstone (CS4, CSF4) and CSFGM leaching samples, with a lower pH value. A significant elevation of heavy metals' content in leachate with CSFGM was found. As the production of coal spoils consumption, the compounds of CSFGM all come from coal spoils. High contents of heavy metals in

**Table 2** Concentration of trace elements and rare earth element in batch leaching solution of coal spoils, fired coal spoils and CSFGM ( $\mu\text{g/L}$ )

Parameters	CS1	CS2	CS3	CS4	CSF1	CSF2	CSF3	CSF4	CSFGM
pH	6.13	6.35	5.13	3.01	6.56	6.61	6.23	4.02	3.07
Be	0.57	N.D.	0.67	15.2	N.D.	N.D.	0.06	1.03	0.34
B	6.87	1 409	57	14.3	57.6	12.4	74.3	183	58.0
V	0.23	10.2	0.72	22.4	5.95	N.D.	183	2.15	227
Cr	0.11	0.51	0.09	115	0.2	N.D.	20.3	4.78	584
Fe	10.4	0.97	8.95	27 728	3.36	11.7	62.9	16 537	6 991
Mn	114	N.D.	1.84	4 478	1.29	4.66	8.5	20 681	396
Co	6.68	0.07	0.19	228	0.1	0.13	1.07	156	12.2
Ni	26.1	0.7	0.87	1 114	1.12	0.43	4.41	724	201
Cu	1.32	0.36	N.D.	9.22	N.D.	N.D.	N.D.	37.0	97.4
Zn	31.7	1.94	0.65	753	1.99	0.42	5.01	2 380	61.0
Ga	0.01	0.35	0.03	0.48	0.07	0.23	0.04	2.64	2.22
Ge	N.D.	N.D.	0.03	8.63	0.97	0.13	0.69	6.5	4.10
As	0.31	9.09	0.5	4.28	0.48	0.03	18.35	0.9	63.4
Se	12.8	9.89	1.87	5.46	0.19	0.21	N.D.	1.58	1 727
Rb	2.11	0.23	0.35	3.5	0.72	2.22	3.8	23.3	5.09
Sr	213	0.18	3.84	1 368	11.3	49.2	14.63	5 726	62.7
Mo	0.02	24.21	6.13	0.26	38.9	3.42	29.4	0.56	3.18
Cd	4.55	0.29	0.24	5.21	0.71	0.12	0.35	2.18	1.58
Sb	0.04	2.95	0.2	0.12	2.83	0.03	0.18	0.15	1.39
Cs	0.19	0.01	0.02	0.15	0.01	0.03	0.03	0.48	0.56
Ba	11.2	0.25	1.24	8.05	1.83	4.05	13.7	26.4	42.7
Ce	0.11	0.01	0.02	19.7	0.02	0.01	0.06	256	7.43
Pb	0.71	0.02	0.01	2.92	0.01	0.01	0.01	1.85	8.37
U	0.11	0.1	0.03	4.97	0.01	0.04	0.01	0.27	0.17

Note: N.D., not detected.

leachate with CSFGM indicate an increased mobility of heavy metals after coal spoils consumption.

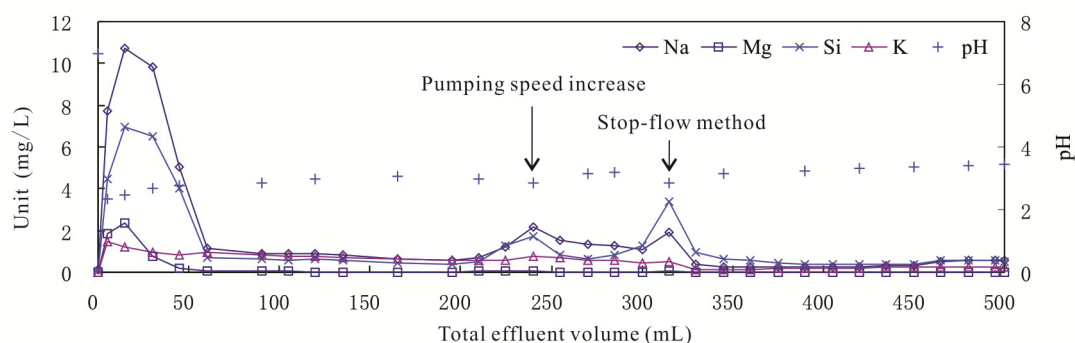
### 3.3 Column Leaching Test

A small-scale column leaching test was employed to study the leaching mobilization of heavy metals under dynamic flow conditions. The results of column test are shown in Table 3. Common major elements (K, Na, Mg, Si) and pH value of the effluent solution were monitored to understand the possible geochemical processes involved (Table 3, Fig. 3; since Ca is included in the input solution, so it is not considered here). After the addition of electrolyte solution, a rapid rise of K, Na,

Mg and Si concentration in effluent was observed. The pH value of the effluent drops to 2.35 from about 6.7 (the pH value of the input electrolyte solution). According to experiment results, the elevated concentration of major cations and a drop of pH value all happened in the first hour. Based on this short time, the dissolution of free soluble minerals is supposed to be the major contribution of cations in the effluent. A gradual decrease of cation concentration was observed in the effluent, while the total effluent volume is larger than 15 mL. It can be interpreted by the theory of mass transport in saturated media at column scale.

**Table 3** Content of major elements (mg/L) and pH in column effluent solution

Effluent ID	pH	Na	Mg	Si	K	Effluent ID	pH	Na	Mg	Si	K
0	6.70	0.104	0.005	0.089	0.017	17	3.21	1.248	0.028	0.811	0.596
1	2.35	7.734	1.861	4.483	1.485	18	-	1.096	0.023	1.273	0.453
2	2.48	10.722	2.360	6.946	1.190	19	2.84	1.913	0.077	3.398	0.487
3	2.68	9.813	0.758	6.498	0.938	20	-	0.366	0.021	0.987	0.127
4	2.75	5.072	0.197	4.034	0.852	21	3.14	0.266	0.015	0.663	0.140
5	-	1.120	0.077	0.682	0.946	22	-	0.252	0.014	0.577	0.159
6	2.87	0.923	0.049	0.621	0.847	23	-	0.225	0.012	0.467	0.170
7	-	0.878	0.045	0.577	0.780	24	3.23	0.243	0.014	0.401	0.192
8	2.98	0.894	0.031	0.625	0.754	25	-	0.242	0.010	0.377	0.204
9	-	0.842	0.027	0.552	0.704	26	3.33	0.282	0.010	0.389	0.216
10	3.08	0.643	0.031	0.422	0.609	27	-	0.318	0.011	0.407	0.234
11	-	0.602	0.026	0.387	0.585	28	3.37	0.343	0.014	0.402	0.239
12	2.97	0.704	0.034	0.537	0.586	29	-	0.535	0.010	0.571	0.249
13	-	1.217	0.033	1.257	0.590	30	3.39	0.600	0.012	0.601	0.266
14	2.84	2.177	0.037	1.701	0.797	31	-	0.594	0.014	0.574	0.262
15	-	1.547	0.027	0.847	0.701	32	3.45	0.563	0.013	0.517	0.254
16	3.17	1.322	0.023	0.665	0.596						



**Figure 3.** Contents of major elements in the effluent solution of column test. Total effluent volume is calculated from collected effluent during the experiment.

A significant concentration peak of major cations and Si was observed when the pumping speed was raised from four to five pore volumes per hour. It means that a slightly increased leaching velocity may favor the release of Na and Si from coal spoils. A decrease of pH value (about 2.84) was also found at this point. For coal spoils, the pH value of leachate solution is closely linked to the dissolution of sulfur-bearing minerals,

such as sulfide or sulfate. For the elevated ions concentration in effluent, it is difficult to give a clear evidence to prove which process is dominating: increased  $H^+$  due to pH decrease, enhanced ion exchange, or desorption of ions from mineral surface. But it is confirmed that an increased leaching velocity does result in more release of some ions in column experiment (Fig. 3).

The third ion content peak was found in a total effluent volume about 315 mL, where a stop-flow method was employed. The pH value decreased immediately in this stop-flow event. These results collectively indicated that element release from the coal spoils was a kinetic process that either resulted from the mineral dissolution/precipitation reactions and/or ion exchange process. The result of stop-flow events reveal that pulse input of precipitation may cause additional release of trace elements than continuous leaching condition. The natural precipitation and thus water remain at the coal spoil bank is an important aspect of trace elements leaching. Increased contact time of coal spoil and precipitation water may bring more pol-

lutants into the aqueous solution. These pollutants will mostly be discharged during the following leaching event.

The temporal change of ten possible harmful trace elements in the effluent solution was also investigated (Table 4, Fig. 4). The concentration peak linked to the dissolution of soluble minerals appearing in the first one hour (Fig. 4). The highest released content of individual elements was Ni (534 µg/L), followed by Pb (222 µg/L), Cr (157 µg/L), Co (97.6 µg/L), As (28.5 µg/L), Se (12.7 µg/L), Cd (7.40 µg/L), Mo (2.90 µg/L), Hg (1.48 µg/L), and Pd (1.13 µg/L). According to the appearance time, the concentration peak of Pb, As, Cd, Hg, and Pd is earlier than others. The dissolution of their hosting

**Table 4** Content of possible harmful trace elements (µg/L) in effluent solution of coal spoils sample CS4

Effluent ID	V <sub>T</sub> (mL)	Cr	Co	Ni	As	Se	Mo	Pd	Cd	Hg	Pb
C <sub>0</sub>	0	0.034	0.078	0.070	0.035	0.001	0.021	0.045	0.012	0.108	0.014
1	5	29.10	1.74	13.27	28.48	0.582	0.651	1.13	7.40	1.48	221.6
2	15	157.1	97.65	533.8	25.24	7.29	2.90	0.758	3.74	0.314	17.51
3	30	70.67	35.86	216.23	24.73	12.69	0.595	0.608	2.48	0.280	7.28
4	45	20.47	13.09	86.69	14.07	5.67	0.416	0.585	1.45	0.250	3.34
5	60	4.71	5.87	41.39	4.49	1.79	0.061	0.544	0.499	0.266	0.333
6	90	3.52	4.07	33.09	3.21	2.68	0.047	0.538	0.330	0.236	0.348
7	105	3.16	3.40	29.59	2.75	2.97	0.034	0.517	0.415	0.229	0.385
8	120	2.94	3.10	27.97	2.72	2.84	0.037	0.515	0.261	0.214	0.302
9	135	2.60	2.81	26.04	2.45	3.15	0.031	0.509	0.247	0.232	0.279
10	165	2.00	2.24	21.51	1.80	2.36	0.022	0.507	0.204	0.181	0.304
11	195	1.85	2.11	20.54	1.68	2.46	0.035	0.611	0.176	0.256	0.345
12	210	1.92	2.04	19.79	1.63	2.27	0.050	0.514	0.204	0.378	0.354
13	225	2.64	2.83	25.52	2.71	3.67	0.061	0.504	0.224	0.402	0.433
14	240	3.59	5.01	42.43	4.57	5.07	0.187	0.557	0.407	0.924	1.12
15	255	2.28	3.85	33.75	2.86	3.17	0.069	0.481	0.313	0.553	0.278
16	270	1.61	2.93	26.82	1.92	2.51	0.041	0.494	0.232	0.396	0.180
17	285	2.37	3.52	32.33	1.96	3.13	0.058	0.472	0.369	0.343	0.175
18	300	1.70	3.88	36.00	2.00	4.61	0.048	0.486	0.262	0.294	0.107
19	315	4.89	11.59	91.55	4.61	15.58	0.121	0.579	1.448	0.280	3.53
20	330	3.24	8.90	72.39	1.81	5.36	0.031	0.462	0.572	0.207	0.050
21	345	1.88	5.84	50.23	1.51	3.58	0.020	0.464	0.373	0.202	0.057
22	360	1.62	5.04	44.03	1.37	2.85	0.019	0.456	0.336	0.191	0.079
23	375	1.25	4.08	36.41	1.22	2.25	0.012	0.456	0.266	0.180	0.087
24	390	1.16	3.66	33.35	1.22	2.20	0.024	0.528	0.249	0.230	0.076
25	405	0.962	3.02	27.82	0.97	1.77	0.022	0.481	0.212	0.245	0.078
26	420	0.932	2.85	26.16	0.93	1.77	0.028	0.477	0.197	0.353	0.076
27	435	0.916	2.81	25.69	0.92	1.82	0.016	0.467	0.208	0.315	0.073
28	450	0.961	2.60	23.84	0.88	1.43	0.019	0.463	0.158	0.276	0.075
29	465	0.882	2.54	24.36	0.94	2.07	0.016	0.465	0.166	0.235	0.089
30	480	0.892	2.71	26.34	1.07	2.05	0.012	0.455	0.183	0.250	0.098
31	495	0.970	2.56	24.33	0.968	2.10	0.013	0.460	0.218	0.200	0.087
32	500	0.861	2.32	21.97	0.855	1.85	0.011	0.458	0.150	0.208	0.099
Av.		10.17	7.78	54.40	4.50	3.50	0.174	0.517	0.726	0.324	7.86

Note. C<sub>0</sub> is the initial input electrolyte solution; V<sub>T</sub> is the calculation of total effluent solution volume; Av. is the average value of elements content in effluent solution.

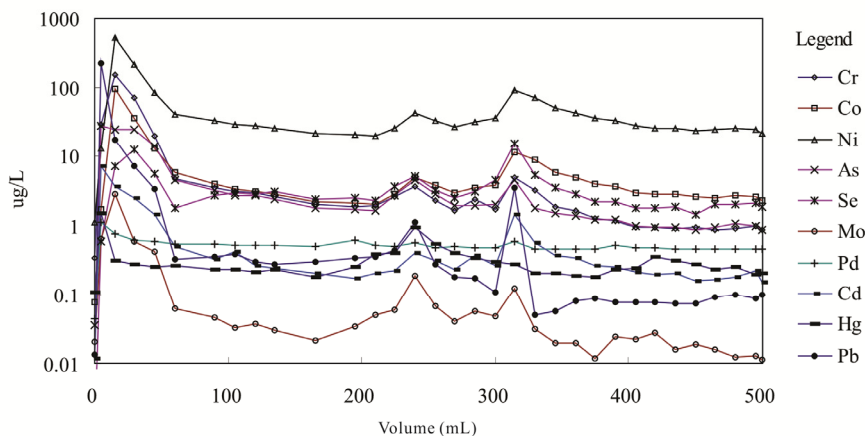


Figure 4. Content of possible harmful trace elements in the effluent solution of column test.

mineral is faster than others. It is very interesting that all these elements belong to sulfide-related minerals. On the other hand, the lowest pH value was also found in their effluent solutions. Therefore, it is moderately deduced that Pb, As, Cd, Hg, and Pd are mostly released from the dissolution of sulfide minerals. Two other concentration peaks responding to the flow their mean contents of 54.40, 10.17, 7.86, 7.78, 4.50, and 3.50  $\mu\text{g/L}$ , respectively.

Heavy metals also deserve more attention, because of their increasing potential risk on ecosystem in modern times. The results of heavy metals (Fe, Mn, Cu, Zn, Sr, Ag, Ba, and Au) in effluent solution of column test are shown in Table 5 and Fig. 5. A rapid dissolution of soluble minerals in coal spoils led to a correspondingly sharp concentration peak of heavy metal Fe, Mn, Cu, Zn, Sr, Ag, Ba, and Au in effluent solution (Table 5; Fig. 5). Among them, Fe has a higher mobility with the maximum content of 181 mg/L and an average content of 23.3 mg/L in effluent solution. The kinetic dissolution of pyrite may be one of the major sources of iron in effluent solution, as pyrite is the major mineral of iron in coals spoils. Since pyrite is not a kind of free soluble mineral, it is not expected to be the only supply of the sharp elevation of iron in effluent solution in the first 50 mL (at about one hour). There should be other easy soluble iron-bearing minerals, such as amorphous iron oxides.

The other heavy metals showed a relatively high mobility including Sr, Mn and Zn. Their mean contents in effluent solution are 693, 197, and 193  $\mu\text{g/L}$ , respectively. Responding to the flow rate-increase event and stop-flow event, two concentration peaks for individual elements were found in the point with a volume of 210 and 315 mL, except for Sr (Fig. 5). This indicates that the release of heavy metals was a kinetically controlled process, which may be affected by varying of leaching velocity and pulse input of precipitation.

The effluent solutions collected are all found to be weakly acidic, it could be expected to extract most of the heavy metals bound to carbonate. Therefore, the moderately high contents of Sr in effluent solution may mostly come from the dissolution of carbonate rock, and the low response of Sr content on flow rate-increase and stop-flow events is reasonable, because the acidic condition was the primary factor for carbonate dissolution. Therefore, a gradual decrease of Sr content and a continuous elevation of pH value in effluent solution are expected.

Table 5 Contents of heavy metals ( $\mu\text{g/L}$ ; except for Fe at mg/L) in effluent solution of coal spoils sample CS4

Effluent ID	Fe	Mn	Cu	Zn	Sr	Ag	Au
0	0.012	0.105	0.102	0.200	0.310	0.118	0.040
1	6.93	145.3	38.24	282.1	23.06	1.66	2.70
2	137.5	2464.3	20.01	1501.4	2775.9	0.428	1.87
3	181.0	904.3	9.80	1121.9	4553.5	0.174	1.57
4	93.99	321.6	2.32	579.8	2501.7	0.230	0.988
5	40.05	145.8	0.746	246.5	1946.7	0.355	0.498
6	23.48	107.3	0.620	152.8	1673.6	0.368	0.497
7	17.72	90.00	0.730	134.0	1388.4	0.323	0.342
8	14.31	80.80	0.824	100.7	1159.0	0.360	0.200
9	12.24	72.81	0.734	85.29	931.5	0.318	0.198
10	7.13	73.69	0.642	73.72	655.1	0.274	0.233
11	10.36	78.64	1.95	68.37	578.2	0.280	1.16
12	26.62	131.6	12.58	162.1	517.5	1.50	2.13
13	19.69	99.58	1.70	127.4	482.8	0.318	0.538
14	12.10	99.58	0.533	90.60	397.5	0.253	0.478
15	11.03	75.73	0.487	85.45	381.7	0.266	0.410
16	12.10	75.73	0.577	90.60	339.3	0.236	0.407
17	12.86	88.96	0.581	100.3	331.7	0.192	0.269
18	11.05	102.8	1.67	97.45	279.7	0.172	0.374
19	25.82	310.0	3.49	302.9	385.8	0.222	1.30
20	13.51	150.8	2.06	155.5	177.0	0.083	0.142
21	9.17	99.02	0.954	107.1	161.8	0.097	0.099
22	8.33	82.45	0.703	95.48	162.9	0.099	0.140
23	7.13	78.22	0.634	74.77	151.3	0.104	0.145
24	6.62	76.74	0.567	67.79	154.1	0.125	0.138
25	5.85	70.88	0.593	66.15	135.5	0.134	0.148
26	5.82	69.92	0.658	66.26	120.1	0.142	0.174
27	5.91	74.44	0.579	52.55	112.7	0.111	0.109
28	5.71	68.34	0.532	60.56	102.8	0.112	0.115
29	6.01	62.38	0.572	54.75	76.49	0.096	0.076
30	6.74	74.44	0.535	54.47	70.96	0.062	0.120
31	6.30	68.34	0.493	54.75	65.95	0.068	0.104
32	5.74	62.38	0.501	54.47	61.86	0.066	0.094
Av.	23.30	197.2	3.26	193.0	692.6	0.283	0.540

Note: Av. is the average value of elements content in effluent solution.



Though the contents of most REEs are low in the batch-test leachate solution, a continuous release of the elements from the column test was observed (Fig. 6). According to Gao et al. (2011), the first concentration peak mostly contribute from the freely soluble mineral dissolution. High part of the REEs (Ce, Y, Nd, Gd, Sm, Dy, Pr, Er, Tb, Yb, Ho, Tm, Lu) in the first 60 mL effluent solution demonstrates that free soluble REEs is the major source in leachate solution (data not show). This indicates that the REEs from the soluble minerals are one of the major sources in the effluent solution. On the other hand,

flow rate-increase and stop-flow events account for another 12 % to 20 % of the total REEs in the effluent solution (Fig. 6; data not show). Since flow rate-increase event and stop-flow event were utilized to simulate a varying leaching velocity and pulse input of precipitation, it can be deduced that these events do result in an increase of REEs release. According to the column test results, the REEs with a mobility from high to low is in a sequence of La, Ce, Y, Nd, Gd, Sm, Dy, Eu, Pr, Er, Tb, Yb, Ho, Tm, and Lu.

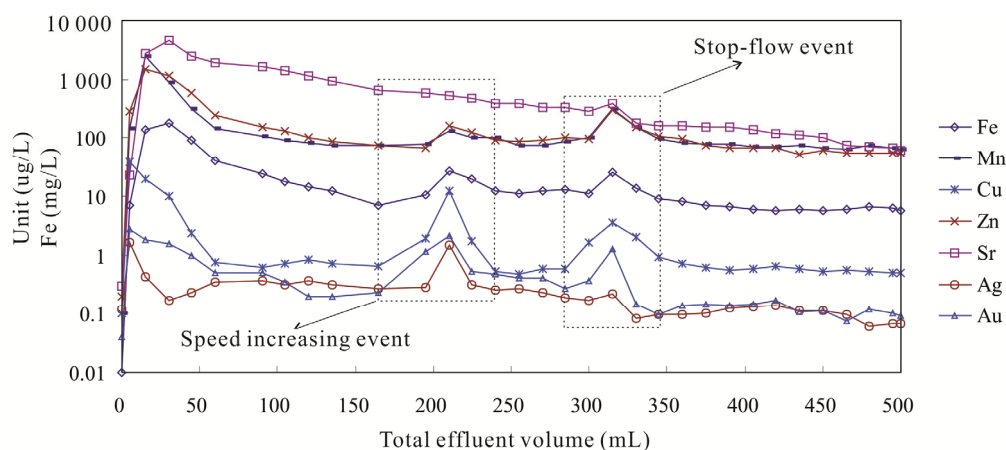


Figure 5. Contents of some heavy metals in the effluent solution of column test.

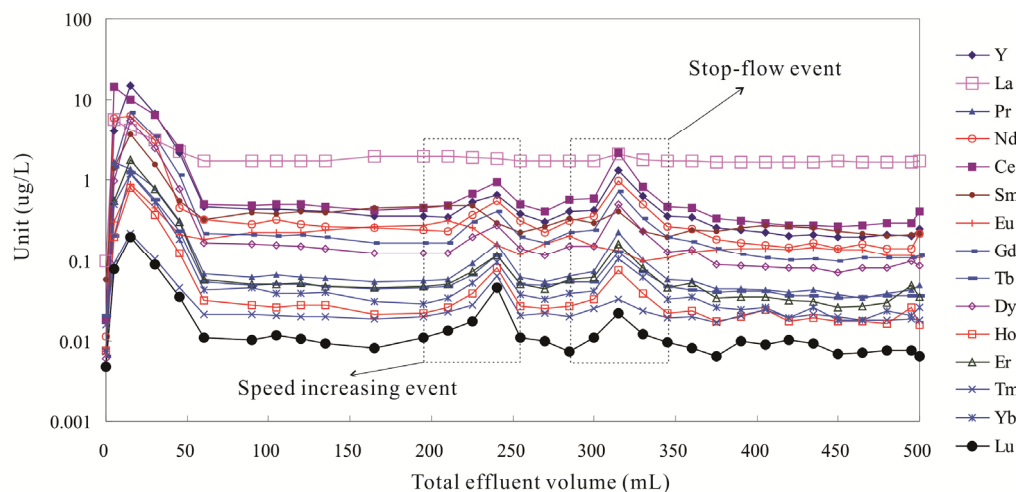


Figure 6. Contents of some REE in the effluent solution of column test.

#### 4 CONCLUSIONS

(1) The minerals of the coal spoil samples are mainly kaolinite and quartz, with minor proportions of pyrite. Elements V, Cr, Zn, As, Pb, and Cd are highly enriched in all coal spoils, while elements Ga, Ge, Se, Sn, Hf, and Th are also enhanced in the coal spoils. Most elements in coal spoils confidence intervals of the means are wide, indicating an uneven distribution of the elements. The content of most elements in coal spoils increases more or less from the limestone, mudstone, shale and sandstone.

(2) The leachate of coal spoils, fried coal spoils and CSFGM samples are acidulous with the pH value ranges be-

tween 3.0 and 6.6. The highest-release elements include Fe, Mn, Co, Ni and Zn; medium-release elements are Cu, Se, Mo and As, and Sb is a low-release element. A high content of heavy metals in batch test leachate with CSFGM indicates an increased mobility of heavy metals after coal spoils consumption.

(3) The dissolution of free soluble minerals is supposed to be the major contribution of the first peak of ions in the effluent. The increased leaching velocity may favor the release of most elements from coal spoils. A significant concentration peak of major cations, trace elements and REEs were observed when the pumping speed was raised. The results of a stop-flow method prove that pulse input of precipitation may led to in-

creased element release than under continuous leaching condition.

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