

Article

Geochemistry of Toxic Elements and Their Removal via the Preparation of High-Uranium Coal in Southwestern China

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Abstract: High-uranium (U) coal is the dominant form of coal in Southwestern China. However, directly utilizing this resource can also harm the environment because this element is radioactive; it is, therefore, necessary to clean this kind of coal before burning. This research studied the geochemistry of toxic elements and their partitioning during the preparation of high-U coal in China. The results show that high-U coals are mainly distributed in Southwestern China and are characterized by a high organic sulfur (S) content and vanadium (V)-chromium (Cr)-molybdenum (Mo)-U element assemblage. These elements are well-correlated with one another, but are all negatively related to ash yield, indicating that all four are syngenetic in origin and associated with organic materials. A mineralogical analysis shows that U in Ganhe and Rongyang coal occurs within fine-grained anatase, clay minerals, guadarramite, and pyrite, while V occurs in clay minerals, pyrite, and dolomite, and Cr occurs in dolomite. Other elements, such as fluorine (F), lead (Pb), selenium (Se), and mercury (Hg), mainly occur in pyrite. By applying a gravity separation method to separate minerals from coal, the content of the enrichment element assemblage of V-Cr-Mo-U in Rongyang coal is still shown to be higher than, or close to, that of the original feed because this element assemblage is derived from hydrothermal fluids during syngenetic or early diagenetic phases, but other elements (beryllium [Be], F, manganese [Mn], zinc [Zn], Pb, arsenic [As], Se, Hg) can be efficiently removed. Once cleaned, the coal obtained by gravity separation was subject to a flotation test to separate minerals; these results indicate that while a portion of V and Cr can be removed, Mo and U remain difficult to extract. It is evident that the two most commonly utilized industrialized coal preparation methods, gravity separation and flotation, cannot effectively remove U from coal where this element occurs in large proportions. Finally, dilute hydrochloric acid (HCl) leaching experiments show that the majority of Mo and a portion of V, Cr, and U are adsorbed in clay minerals and organic matter and, therefore, exist in an adsorbed state. In this state, these elements can be removed using the acid method. Thus, as U cannot be fully removed from coal, the use of high-U coals is not recommended.

Keywords: coal of Southwestern China; high-uranium coal; mode of occurrence; acid leaching method; coal preparation

1. Introduction

Coal resources in China are unevenly distributed; the reserves in the southwest of the country comprise ~10% of the total [1]. Thus, to ensure the development of the economy in Southwestern China, demand for coal from this area is increasing. Previous reports showed that some coals in Southern and Southwestern China are rich in U, including those from Yanshan in Yunnan Province [2], as well as Heshan [3], Fusui [4], and Yishan [5] from Guangxi Province, Chenxi from Hunan Province [6], and Guiding from Guizhou Province [7]; these coals are referred to as “high-U coals” [7]. The element U is naturally radioactive, however, and so the direct use of high-U coals has potentially adverse effects on human health and the environment [1,8–14]. In previous work, Lauer et al. [15] showed that coal ash residues derived from coals with U occurring at concentrations greater than 10 ppm exceed the standards for radiation in building materials, while Melo and Burkart [16] showed that U-rich ultra-fine particles released from coal during combustion from coal-fired power plants are harmful to human health. The preparation of coal is one effective approach to reduce the pollution of toxic elements [17–26]. The current, most commonly applied approach to do this is gravity separation, which uses differences in density to separate minerals from coal [27]; in contrast, limited research has been carried out on the removal of toxic elements from coal by flotation using differences in surface properties to separate minerals from coal [28,29].

Rongyang and Ganhe coals from Guizhou and Yunnan provinces were selected for investigation in this study as both are high in U. Indeed, Rongyang coal is characterized by the presence of high pyritic S, while Ganhe coal is characterized by a high organic S content. High-U coal can also be enriched with other toxic elements, such as V, Cr, Se, and Mo [30]. Our previous work in this area has shown that the elements U, V, Cr, and Mo in high-U coal occur in organic matter and in fine-grained minerals; these elements, therefore, cannot be removed from coal by gravity separation [31]. Flotation tests were, therefore, conducted on Rongyang cleaned coals by gravity separation, as well as on whole coals from Rongyan and Ganhe. Toxic elements from the Ganhe cleaned coal obtained by flotation were extracted using dilute HCl, while the geochemistry of U and other toxic elements from Rongyang and Ganhe were also analyzed in this study to provide a sound theoretical basis for the removal of toxic elements from high-U coal.

2. Geological Setting

Most Chinese high-U coals are found in the southwestern part of the country (Figure 1). One such location, the Rongyang Mine, is located in the southwestern part of Guizhou Province. The coal-bearing formation in this mine is the Upper Permian Longtan Formation, which was formed in a tidal flat environment of an open carbonate platform [32] and is mainly composed of siltstones, chert limestones, mudstones, shales, and coal seams. This formation disconformably overlies the Middle Permian Maokou Formation, while the thickness of the Longtan Formation is ~260 m [31].

The Ganhe Mine within the Yanshan Coalfield is located in the southeast of Yunnan Province, China (Figure 1). Coal-bearing strata within this coalfield is composed of the Upper Permian Wujiaping Formation (P_2w) and the Changxing Formation (P_2ch), the latter of which is overlain by the Lower Triassic Ximatang Formation. The P_2w unit disconformably overlies the Middle Permian Maokou Formation (P_1m) [2]; this sequence is mainly constituted of limestones, mudstones, carbonaceous mudstones, calcareous mudstones, a small proportion of siliceous limestones, a thin layer of siliceous rocks, and clay siltstone. Both the P_2ch and P_2w units formed in marine carbonate successions [2–4]. Mineable coal seams within the Ganhe Mine include the No. 3 and No. 4 coal seams, both of which have been developed within the P_2w sequence. The thickness of the No. 3 coal seam is 99 cm, overlain by the 204 cm thick No. 4 coal seam [33].

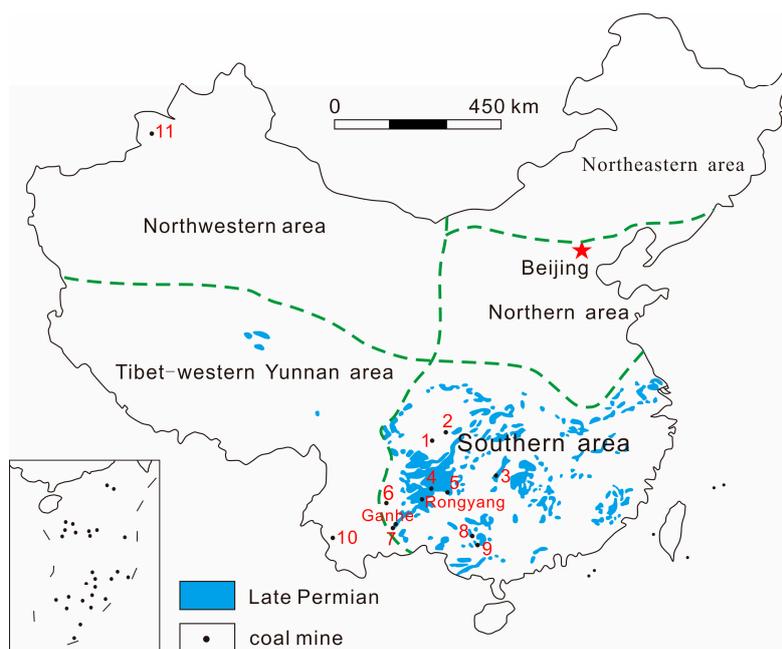


Figure 1. The distribution of high-U coal mines within China: 1, Moxinpo; 2, Guxu; 3, Chenxi; 4, Zhijin; 5, Guiding; 6, Longquan; 7, Yanshan; 8, Yishan; 9, Heshan; 10, Lincang; 11, Yili (after Dai et al. [30]).

3. Samples and Methods

3.1. Samples

One channel coal sample (identified as RY1) was collected from the Rongyang Mine within the Longtan Formation, while two bench samples (GH1 and GH2) were collected from Ganhe Mine. Samples GH1 and GH2 were collected from the upper portion near the roof and the lower portion of the No. 4 coal seam, respectively.

3.2. Methods

Proximate analysis of moisture, ash, and volatile matter, total S, as well as forms of S, were performed following the standards reported in detail by Duan et al. [31]. Trace elements in samples were determined using inductively-coupled plasma-mass spectrometry (ICP-MS) (Thermal Fisher, X Series II, Waltham, MA, USA). Prior to ICP-MS analysis, samples were digested using a Microwave Digestion (UltraCLAVE, Milestone, Sorisole, Italy); the digestion solution used for coal samples consists of 5 mL of 65% HNO₃ and 2 mL of 40% HF, while reagents for non-coal samples included 5 mL of 40% HF and 2 mL of 65% HNO₃. All ICP-MS analyses and our sample microwave digestion program for samples followed the methods described by Dai et al. [34–36].

An electron probe (EMPA, 8050G, Kyoto, Japan) was used for quantitative analyses and for determining the elemental distributions of coal samples. Images were captured using backscattered electron imaging (BSE) and secondary electrons (SE), and the contents of major and trace elements were semi-quantified by energy dispersive spectrometry (EDS). The working conditions of the EDS were a 20-kV accelerating voltage, a 0.3-nA beam current, and a 1- μ m beam diameter.

Transmission electron microscopy (TEM, FEI, Tecnai G2 F20, Hillsboro, OR, USA) equipped with EDS was used to determine the elemental compositions of nanominerals. Coal samples were ground to <1 μ m using a planetary ball mill. The powder was put into absolute ethyl alcohol and dispersed through ultrasonic-sound suspension, and the suspended liquid was pipetted onto Lacy Carbon films supported by Cu grids.

Coal flotation tests were performed according to the Chinese national standard GB/T 4757 [37]. Samples were initially crushed to <0.5 mm; in order to pre-wet samples, water and 50 g coal samples were added into a 1.5-L single flotation cell (XFD-63) and stirred for 3 min to make the coal slurry uniformly mixed. Subsequently, collector (diesel), and frother (octanol) were added in sequence. After 30 s aeration, flotation process began. The froth was scraped for 3 min. Both cleaned coal and tailings were collected, filtered, and dried. Gravity separation methods and conditions were presented in earlier work by Duan et al. [31].

The extraction method for adsorption state ions used in this study is based on that presented by Fisher et al. [38] and Qin et al. [39] with some modifications. The four extraction methods for toxic elements described in Appendix A were applied here; coal samples were ground to less than 200 mesh (75 μm) and, once extracted, were centrifuged for 20 mins at 5000 r/min to separate solids from the solution. The supernatant was removed and then diluted to determine trace element contents, and the proportion of supernatant in the total extraction solution, as well as the rate of extraction of toxic elements by dilute HCl was then calculated.

4. Results and Discussion

4.1. Geochemistry of Toxic Elements in High-U Coal from China

The distribution of high-U coals in China is not uniform. In addition to the Yili deposit [39], high-U coals are mainly distributed in Southern China (Figure 1). High-U coals are rich in the element assemblage of V-Cr-Mo-U, the concentrations of which are much higher than the averages for world hard coals (Table 1). Some high-U coals from Guiding [7], Yanshan [2], Heshan [3], Chenxi [6], Yishan [5] coalfields are characterized by high organic S content (Table 1); however, compared with the high-U coals from Southwestern China, the organic S content of the Yili high-U coal [40] is lower.

Table 1. Ash yield (%), $S_{o,d}$ (%), and concentrations of V, Cr, Mo, and U ($\mu\text{g/g}$) in high-U coals from China (on a whole coal basis).

Coalfield	A_d	$S_{o,d}$	V	Cr	Mo	U	Sources
Guiding	23.10	5.19	892	391	364	211	Dai et al. [7]
Yanshan	27.51	9.51	567	329	204	153	Dai et al. [2]
Heshan *	36.69	7.2	136.13	69	44.7	51.13	Dai et al. [3]
Chenxi	17.97	7.12	296.3	407.75	23.19	75.2	Li et al. [6]
Yishan *	34.26	7.16	278.33	102.47	101.97	72.2	Dai et al. [5]
Guxu	20.95	nd	60.7	22.8	2.48	15.4	Dai et al. [41]
Yili *	26.88	nd	114	82.84	80.77	312	Dai et al. [40]
Lincang *	25.59	0.72	18.48	5.56	3.94	54.6	Dai et al. [42]
Longquan	35.37	0.89	98.4	79	58.8	34.1	Dai et al. [43]
Zhijin	26.41	0.33	432.1	113.1	63.1	49.6	Dai et al. [44]
Moxinpo *	26.83	nd	1507	1180	4.72	190.5	Dai et al. [45]
Rongyang	19	1.06	283	62.3	87.5	70.5	This study
Ganhe *	23.79	10.09	568	273	145	201	This study
World	nd	nd	25	16	2.2	2.4	Ketris and Yudovich [46]

* Data are the arithmetical averages; nd, no data; A, ash yield; S_o , organic S; d, dry basis.

The correlation analysis results of V, Cr, Mo, and U in high-U coal (Table 1) from Southwestern China are shown in Figure 2. These data show that both V and Cr exhibit strong positive correlations with Mo. Mo^{6+} , Mo^{4+} , V^{3+} , and Cr^{3+} can be substituted for each other because they have a similar ionic radius [47], and U is positively correlated with V, Cr, and Mo. Under reduction conditions, the ion phase of V, Cr, Mo, and U are all in their lowest valence states, so they can be released from hydrothermal fluids because of their strong migration ability; then, these elements are adsorbed by organic matter and clay minerals [6]. These geochemical properties show that the V, Cr, Mo, and U in high-U coals have the same enrichment origin and, possibly, similar modes of occurrence.

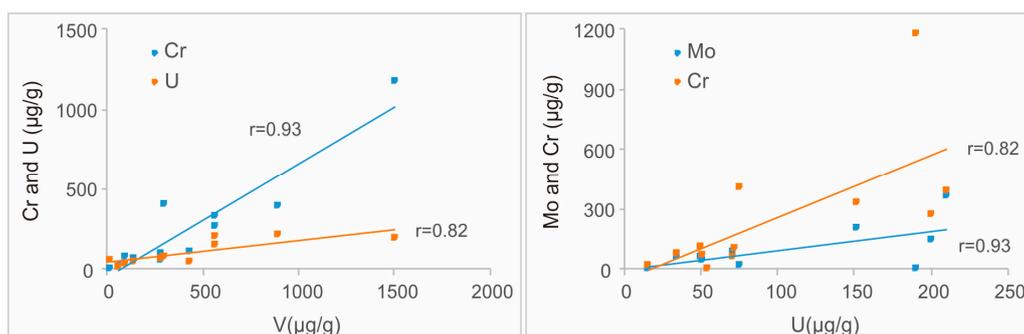


Figure 2. Correlations of V, Cr, Mo, and U.

Correlations between trace elements and ash yield indicate the mode of occurrence of trace elements in coal [48,49]. The data in Figure 3 are the results of a correlation analysis of elements (V, Cr, Mo, and U) and A_d as well as $S_{o,d}$ in high-U coal from Southwestern China (Table 1). The elements V, Cr, Mo, and U are all negatively correlated with ash yield, but positively correlated with organic S, indicating that the former four elements are mainly associated with organic matter. Organic S is formed in a stage of syngeneses or early diagenesis [50], also indicating that V, Cr, Mo, and U in these high-U coals have a similar formation stage with organic S.

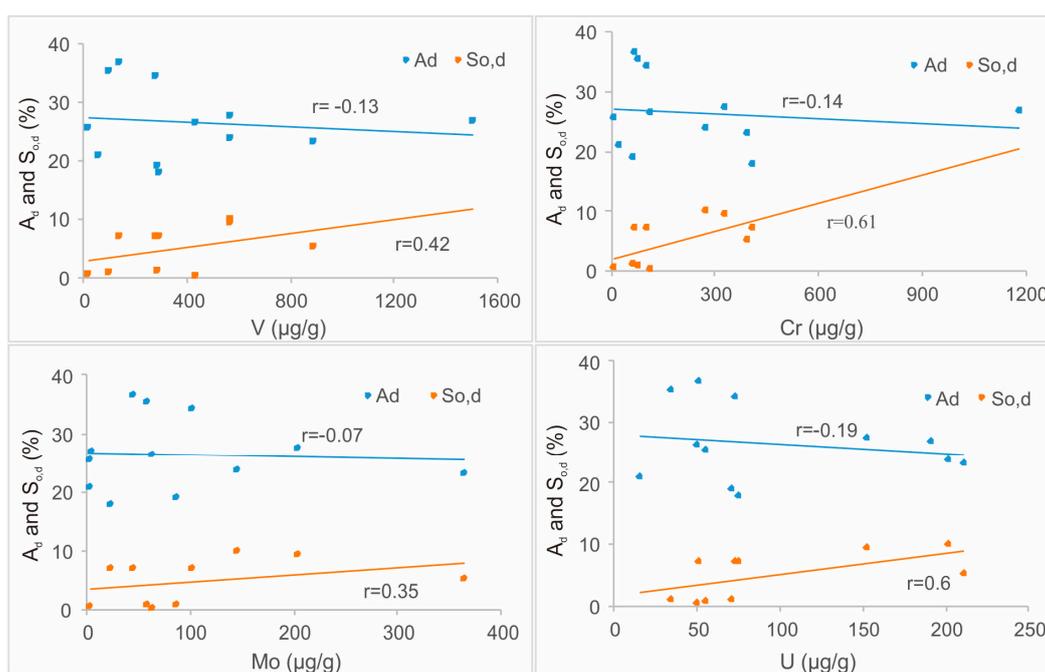


Figure 3. Correlations of elements (V, Cr, Mo, U) and A_d as well as $S_{o,d}$.

4.2. Geochemistry of High-U Coal from Southwestern China

4.2.1. Coal Chemistry

The results of proximate analysis, as well as values for total and forms of S, for the Rongyang and Ganhe coals are listed in Table 2. Data show that the volatile matter content in the Rongyang coal is 8.9%, a low-volatile anthracite based on the ASTM classification standard [51]. According to GB/T 15224.1-2004 [52], coals with ash yields between 16.01% and 29.00% are medium-ash while, according to Chou [53] and GB/T 15224.2-2004 [54], those with a total S content greater than 3% are

high-S examples. These data show that the Rongyang coal is a medium ash, high S coal, while the Ganhe variety is a low-volatile anthracite. Thus, as the total S content of the Ganhe coal is higher than 12% and its organic S content is greater than 10%, this can be classified as a super high-organic S coal. In contrast, data show that pyritic S is dominant in the Rongyang coals (Table 2); thus, for comparative purposes, two different types of high-S coals are selected to reveal the removal effect of toxic elements during preparation.

Table 2. Proximate analysis (%), total S and forms of S (%) in coals from the Rongyang and Ganhe mines.

Sample	M _{ad}	A _d	V _{daf}	S _{t,d}	S _{p,d}	S _{s,d}	S _{o,d}
Ronyang	2.6	19	8.9	5.44	4.19	0.19	1.06
Ganhe	0.66	23.79	12.11	12.085	1.98	0.015	10.09

Abbreviations: M, moisture; V, volatile matter; S_t, total sulfur; S_p, pyritic sulfur; S_s, sulfate sulfur; ad, air-dry basis.

4.2.2. Trace Elements

The data presented in this paper show that the Ganhe (GH1 and GH2) and Rongyang (RY1) coals, as well as Rongyang cleaned coal with a particle size between 3 mm and 6 mm (RY2), is characterized by high removability compared to other particle sizes via gravity separation, and all exhibit elevated U concentrations [31]. These are all used as feed coals for flotation, and their concentrations are listed in Table 5. The concentrations of the four samples (GH1, GH2, RY1, and RY2), in comparison with the average values for hard coals worldwide [46], are shown in Figure 4.

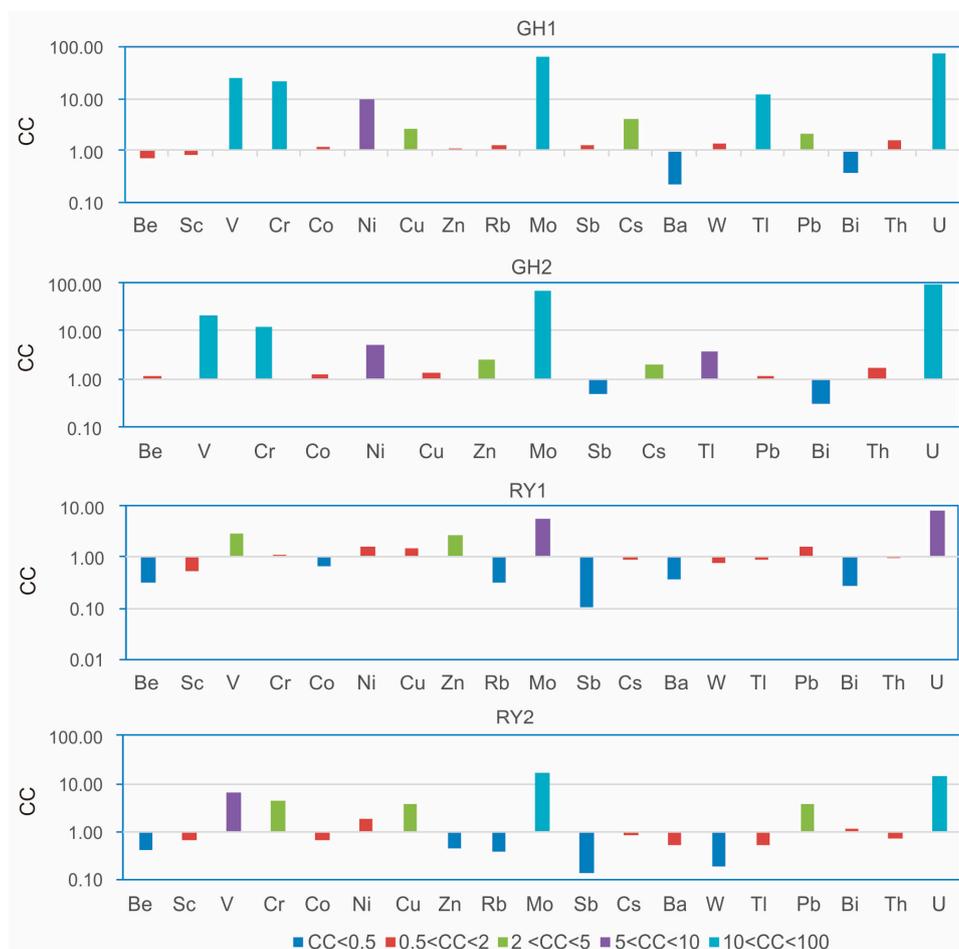


Figure 4. Concentration coefficient (CC) values for trace elements in the Ganhe and Rongyang coals.

According to the enrichment classification proposed by Dai et al. [7], elements V, Cr, Mo, and U in the Ganhe coals are all significantly enriched (i.e., $10 < \text{concentration coefficient (CC)} < 100$, CC referring to the ratio of a given trace element in an investigated sample versus the corresponding average for world hard coals reported by Ketriss and Yudovich [46]). Mo and U are enriched, while V and Zn are slightly enriched in sample RY1. In sample RY2, Mo and U are significantly enriched; V is enriched; and Cr and Pb are slightly enriched.

4.3. The Mode of Occurrence of Toxic Elements in High-U Coals from Southwestern China

4.3.1. Mineralogy

The results of our EMPA analysis of Rongyang coal are shown in Figure 5 and Table 3. These data show that U-bearing minerals include anatase, clay minerals, gadarramite, and pyrite (Figure 5), and that anatase coexists with clay minerals (Figure 5a). There are also traces of corrosion in anatase, indicating that coal has been subjected to hydrothermal fluids during syngenetic or early diagenetic stages [55]. Anatase also contains traces of Na, Mg, P, S, K, Ca, Fe, and, to a lesser extent, Cl, I, Nb, and U, and has a UO_2 content of 2.76% (Table 3: spot 1). At the same time, clay minerals contain traces of Na, Mg, S, K, and Ca (Table 3: spot 2, spot 3), while gadarramite coexists with these minerals (Figure 5b), the latter and the former of which contain UO_2 5.79% and 3.07%, respectively. Pyrite coexists with clay minerals, and they contain Na, Mg, P, K, Ca, Ti, Mn, and trace amounts of Cl, V, I, Ba, La, and U (Table 3: spot 4, spot 5). The contents of UO_2 and V_2O_5 in coexisting pyrite and clay minerals are 0.24% and 0.44%, respectively; Fe^{2+} is generally derived from the reduction of high valence Fe in clay minerals, so pyrite is often associated with these minerals [24], which also contain traces of V_2O_5 (1.19%, Table 3: spot 6).

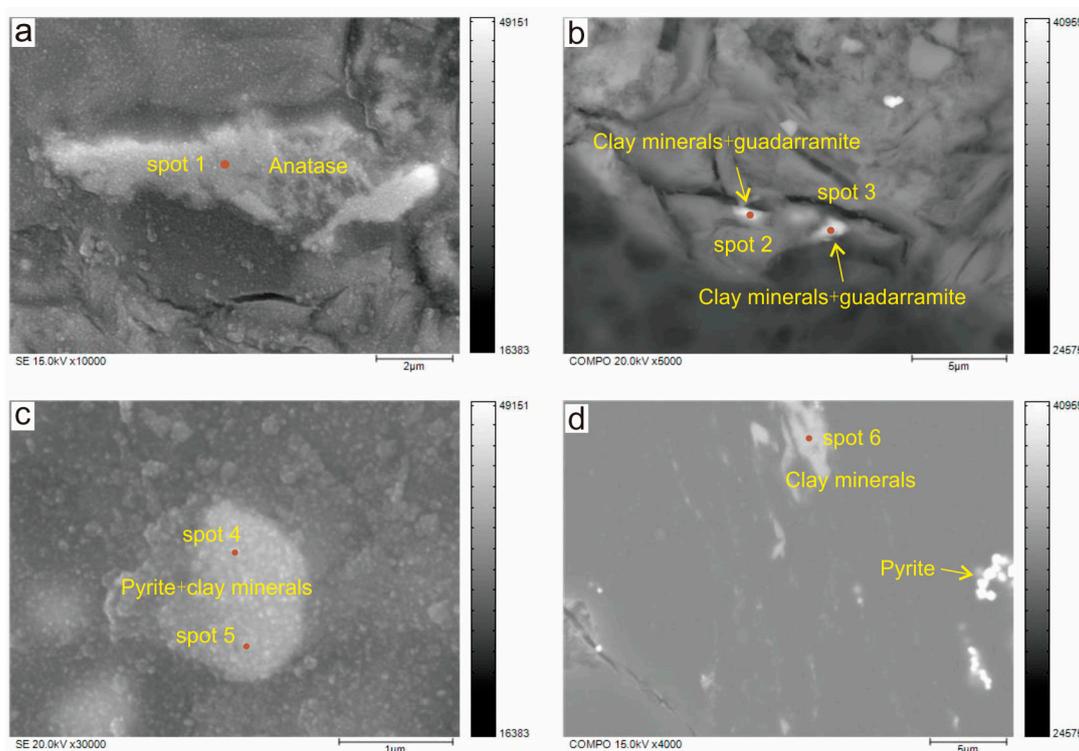


Figure 5. Minerals in the Rongyang coals: (a) anatase (EMPA, SE images); (b) mixture of gadarramite and clay minerals (EMPA, BSE images); (c) mixture of clay minerals and pyrite (EMPA, SE images); and (d) clay minerals and pyrite (EMPA, BSE images).

Table 3. EMPA results for the minerals in Figure 5 (%).

Nos.	Spot 1	Spot 2	Spot 3	Spot 4	Spot 5	Spot 6
Na ₂ O	0.19	0.46	0.38	0.29	0.29	0.35
MgO	0.12	0.29	0.35	0.42	0.44	0.24
Al ₂ O ₃	3.95	15.58	9.81	11.22	12.34	23.8
SiO ₂	12.73	55.63	35.72	35.79	42.57	63.9
P ₂ O ₅	-	-	-	3.09	1.59	-
SO ₃	1.19	1.04	5.65	20.62	15.34	6.27
Cl	-	0.14	0.62	0.1	0.11	-
K ₂ O	0.76	3.43	2.12	2.95	3.48	1.42
CaO	0.31	0.54	1.28	1.57	2.08	0.67
TiO ₂	72.37	3.70	7.67	0.19	-	-
MnO	-	-	-	-	0.3	-
V ₂ O ₅	-	-	-	-	0.44	1.19
FeO	4.36	16.12	30.04	22.29	19.58	2.19
I	0.45	-	0.55	1.07	0.94	-
BaO	-	-	-	0.16	0.08	-
La ₂ O ₃	-	-	-	-	0.41	-
Nb ₂ O ₅	0.82	-	-	-	-	-
UO ₂	2.76	3.07	5.79	0.24	-	-
Total	100	100	100	100	99.99	100

Wang et al. [56] and Xie et al. [55] found that the coals from the Yueliangtian Coalfield, adjacent to the Rongyang Coalfield, were subjected to volcanic ash, hydrothermal fluids, and seawater during syngenetic or early diagenetic stages. The elements V and U occur in syngenetic minerals and coexist with clay minerals (Figure 5). Therefore, it is probably the case that V and U are derived from U-V-Cr-Mo-rich solutions during early diagenesis. It is known that peat swamps formed in reductive environments, so the elements V, Cr, Mo, and U react with aluminum silicate minerals and coexist with clay minerals.

The areal distribution of F, Pb, Se, and Hg in framboidal pyrite is shown in Figure 6a–e. The distribution of F in pyrite shows (Figure 6b) that F content is higher closer to the central region; at the same time, Pb and Se have similar distribution pattern in pyrite, and the content of Hg is relatively low (Figure 6c–e). This areal distribution of elements shows that F, Pb, Se, and Hg occur in pyrite.

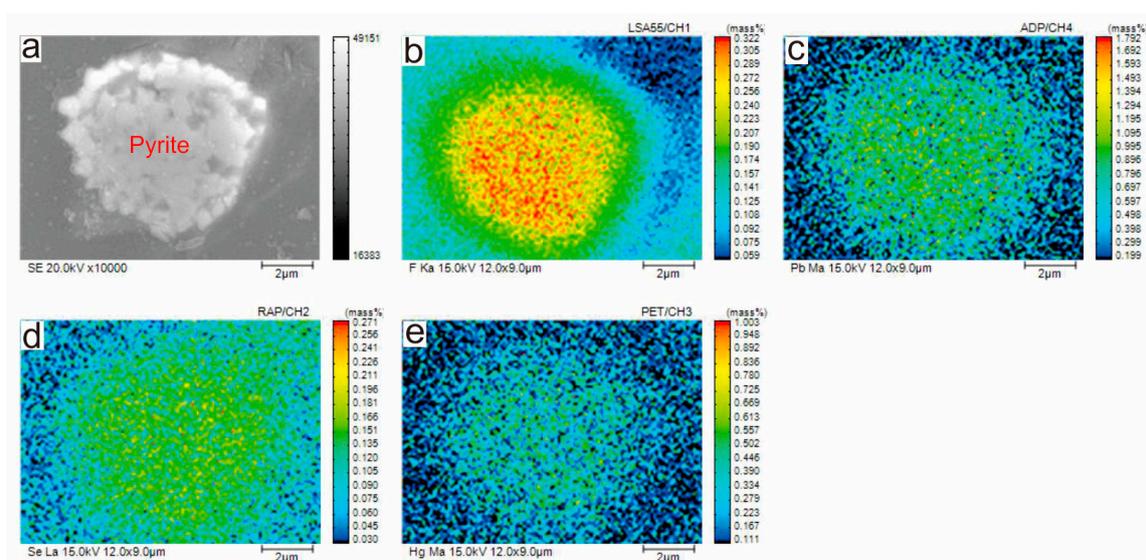


Figure 6. (a) Framboidal pyrite from Rongyang; (b–e) Energy-dispersive X-ray spectrometer elemental maps of F, Pb, Se, and Hg of (a), respectively.

The TEM analysis conducted as part of this study (Figure 7) shows that clay minerals contain the major elements Mg, Fe, S, and K, as well as traces of V and Cr, while the V also occurs in dolomite. At the same time, the particle sizes of dolomite and clay minerals are $<0.5 \mu\text{m}$ and are components of fine-grained minerals.

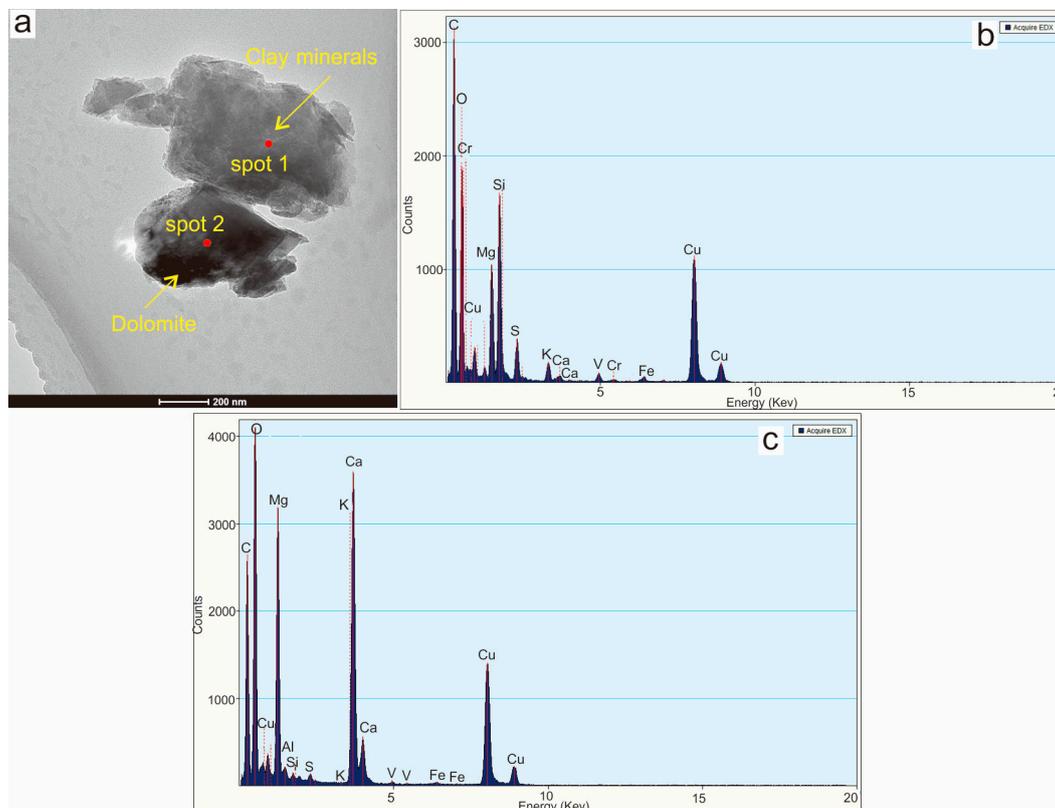


Figure 7. (a) Flotation-cleaned coal sample GH2, TEM; (b) the EDS spectrum of clay minerals in (a); and (c) the EDS spectrum of dolomite in (a).

Dai et al. [2] found that U, V, Mo, Se, and other trace elements in the Yanshan coals are derived from felsic volcanic ashes and hydrothermal fluids during syngenetic or early diagenetic stages. As the Ganhe Mine is located within the Yanshan Coalfield, while samples investigated by Dai et al. [2], as well as those present in this study, both contain a high content of organic S and are enriched in V, Cr, Mo, and U. Thus, the results presented in this study further confirmed those opinions by Dai et al. [2] that V, Cr, Mo, and U were derived from submarine exhalation.

4.3.2. The Extraction of Toxic Elements Using Dilute HCl

The toxic elements in the GH2 flotation cleaned coal sample were extracted using dilute HCl following the four methods described in Appendix A, while the extraction rate is listed in Table 4.

Table 4. The extraction rate of toxic elements from GH2 cleaned coal using HCl (%).

Method No.	Be	V	Cr	Mn	Co	Ni	Cu	Zn	Rb	Sr	Mo	Cs	Ba	U
1	6.62	10.91	3.29	11.37	14.94	21.38	10.77	38.43	1.03	35.79	36.95	4.04	9.74	9.39
2	11.82	12.67	4.32	12.02	15.29	25.09	5.56	39.32	1.93	40.15	59.05	15.17	15.62	12.35
3	10.09	14.61	7.07	18.78	16.05	32.65	44.19	57.38	3.29	48.78	58.56	13.31	23.50	12.96
4	13.62	16.35	12.97	21.22	18.34	39.13	37.30	74.72	3.77	57.01	73.76	25.31	25.25	15.10

Data show that, under acidic conditions, H^+ and metal ions adsorbed onto the surface of clay minerals will compete for the exchangeable position of clay mineral surfaces, while a component of the heavy metal ions adsorbed onto their surfaces are released, and the higher the concentration of H^+ ions, the more metal ions are released [57]. When the environment becomes extremely acidic, almost all the heavy metal ions adsorbed by clay minerals are released [57].

EMPA and TEM analyses show that V, Cr, Mo, and U all occur in clay minerals. The extraction rates of V, Cr, Mo, and U using 4 M HCl are higher than those of 2 M HCl, while the extraction rate for a 0.5-g coal sample is higher than that for a 4-g sample (Table 4). These results are due to high H^+ ion concentrations; thus, in addition to clay minerals, humus generally adsorbed Co, Ni, V, Mo, and U elements [57]. In these samples, Mo extraction rates reach 74%, indicating that most of the Mo exists in an adsorbed state, while the V, Cr, Co, Ni, and U extraction rates are not very high, suggesting that these elements are partially adsorbed, and the remainder of the component occurs in minerals, or is complexed with organic matter.

4.4. The Partitioning of Toxic Elements during the Flotation of High-U Coal from Southwestern China

4.4.1. The Distribution of Toxic Elements during Flotation

Samples RY1, RY2, GH1, and GH2 were subject to flotation; the yield, ash yield, and the content of toxic elements in flotation products are listed in Table 5. The results show that samples GH1 and GH2 have a high cleaned coal yield (~50%) and ash yields of 15.98% and 15.45%, respectively. The yield and ash yield of RY1 cleaned coal are 65.15% and 9.19%, respectively, also suggesting that the floatability of Rongyang coal is better than that of Ganhe coal. Thus, via flotation, the ash yield of RY2 cleaned coal is 3.96%, which shows that flotation can further remove minerals from coals.

The content of toxic elements in the flotation products of Ganhe and Rongyang coal are shown in Figure 8, and their distribution laws are as follows:

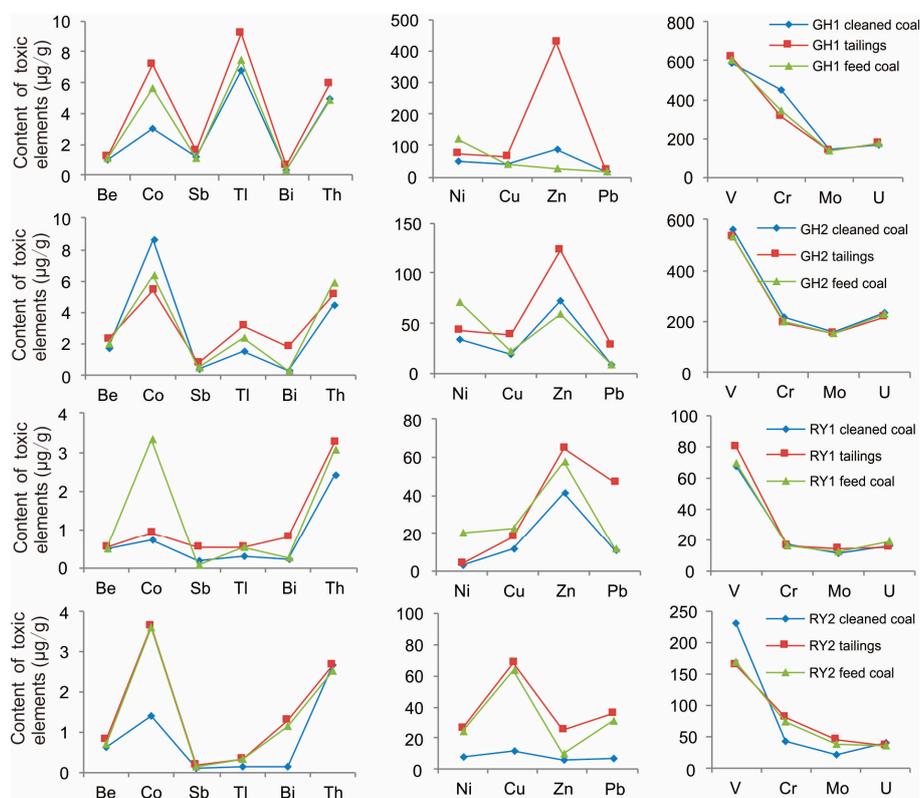


Figure 8. The contents of toxic elements in feed coal, cleaned coal, and tailings.

Table 5. The yield (%), ash yield (%), and contents of toxic trace elements in flotation products ($\mu\text{g/g}$).

Sample No.	Flotation Products	Yield	A _d	Be	V	Cr	Co	Ni	Cu	Zn *	Mo	Sb	Cs	Tl	Pb	Bi	Th	U
GH1	Cleaned coal	49.63	15.98	1.04	586	453	3.03	49.7	40.6	88.3	142	1.18	3.62	6.76	14.8	0.35	4.99	164
	Tailings	50.37	26.32	1.22	620	314	7.20	75.2	62.0	427.7	136	1.63	4.91	9.20	19.8	0.60	5.96	178
	feed coal	100	24.20	1.11	603	344	5.67	121.5	40.9	24.6	138	1.07	3.87	7.50	15.7	0.37	4.90	173
GH2	Cleaned coal	51.04	15.45	1.72	561	215	8.58	34.1	18.8	72.1	159	0.38	1.11	1.52	8.8	0.27	4.42	234
	Tailings	48.96	27.71	2.28	533	194	5.37	43.6	38.1	122.4	153	0.81	2.71	3.17	27.6	1.80	5.15	218
	Feed coal	100	23.37	1.97	532	202	6.33	70.5	22.3	59.2	153	0.45	2.01	2.34	9.4	0.31	5.85	230
RY1	Cleaned coal	65.14	9.19	0.50	67.4	16.8	0.74	3.4	11.4	41.3	11.6	0.20	0.57	0.32	11.1	0.23	2.40	16.0
	Tailings	34.86	35.59	0.55	79.9	15.9	0.92	3.6	18.0	64.4	14.1	0.55	0.92	0.55	46.6	0.81	3.25	14.9
	Feed coal	100	19.00	0.50	69.0	16.1	3.32	20.1	22.5	58.0	12.0	0.09	0.86	0.56	11.7	0.26	3.07	19.2
RY2	Cleaned coal	31.22	3.96	0.62	230	42.1	1.41	8.2	12.1	5.9	21.7	0.09	0.34	0.14	6.5	0.13	2.68	41.4
	Tailings	68.78	10.84	0.79	163	80.8	3.63	26.0	68.3	25.6	44.5	0.17	0.94	0.34	35.6	1.31	2.67	36.4
	Feed coal	100	9.12	0.69	168	73.1	3.60	24.1	63.3	10.3	38.2	0.13	0.90	0.34	30.5	1.12	2.51	37.0

* The contents of Zn in preparation products of GH1 and GH2 coals are higher than those in feed coal because of the ion exchange between coal and flotation fluids as diesel may contain Zn⁺.

- (1) The content of most toxic elements in the GH1 cleaned coal sample is lower than that in feed coal but, with the exception of Co and Ni, the contents of other elements are closer to those of feed coal. The contents of V, Cr, Mo, Th, and U in cleaned coal are higher than, or close to, those of feed coal.
- (2) Similar to the sample of GH1, the contents of most toxic elements in GH2 cleaned coal is lower than those in feed coal, while Cs and Ni have a high removal rate in cleaned coals. The contents of V, Cr, Mo, and U in cleaned coal are higher than, or near to, those of feed coal.
- (3) Due to flotation, the contents of most toxic elements (Co, Ni, Cu, Zn, Cs, Tl, and Th) in RY1 cleaned coal are lower than those in feed coal, while the contents of other elements (Be, V, Cr, Mo, and U) are closer to, or higher, than those in feed coal.
- (4) The contents of most toxic elements in RY2 cleaned coal are reduced; for example, the contents of Cr, Co, Ni, Cu, Zn, Mo, Sb, Cs, Tl, Pb, and Bi are far below those of feed coal, while the contents of V and U in cleaned coal are higher than those in feed coal.

4.4.2. The Removability of Toxic Elements by Flotation

To demonstrate the degree to which toxic elements can be reduced through flotation, Equation (1), proposed by Wang et al. [22], was used to calculate removability. In this context, if the removability value of an element is negative, then the element should be enriched in cleaned coals, indicating a poor removal effect, as follows:

$$R = (1 - c_i)/C_i \times 100\% \quad (1)$$

where R denotes removability, while c_i denotes the contents of element i in cleaned coal, and C_i refers to the content of this element in feed coal.

The removability of ash yield and trace elements in cleaned coal is listed in Figure 9 and Table 6. These data show that the removability of ash yield in the Rongyang coals are higher than those in the Ganhe coals; the contents of elements Co and Ni in sample GH1 have high removability, while the elements Ni, Cu, Sb, Cs, Tl, and Th in sample GH2 have relative high removability, and the removability of V, Cr, Mo, and U in both GH1 and GH2 is either low or negative. In addition, the removability of V, Cr, Mo, and U is low in sample RY1, while Co, Ni, Cu, Zn, Cs, and Tl exhibit high removability. The elements Cr and Mo, as well as others in RY2, have high removability; at the same time, the removability values of V and U are negative, which indicates that U and V cannot be removed by gravity separation and flotation. Although RY1 and RY2 samples are both from Rongyang, there is a significant difference between results. Most of these toxic elements have higher removability in RY2 than RY1, for it is attributed to the removal of clay from RY1 within the gravity circuit.

Table 6. The removability of toxic elements in cleaned coal via flotation (%).

Sample No.	A _d	Be	V	Cr	Co	Ni	Cu	Zn
GH1	33.97	6.84	2.93	−31.68	46.54	59.08	0.70	-
GH2	33.89	12.58	−5.36	−6.28	−35.56	51.54	15.68	−21.79
RY1	51.63	1.24	2.28	−4.30	77.56	83.01	49.24	28.79
RY2	56.62	10.17	−36.68	42.43	60.77	65.90	80.93	42.72
Sample No.	Mo	Sb	Cs	Tl	Pb	Bi	Th	U
GH1	−3.17	−10.20	6.62	9.86	5.69	3.36	−1.84	5.10
GH2	−4.13	15.53	44.93	34.90	6.48	12.08	24.44	−2.02
RY1	2.96	−120.67	33.20	42.04	5.55	10.52	21.82	16.31
RY2	43.16	35.15	62.15	58.44	78.72	88.62	−6.77	−11.88

−: Abnormal value.

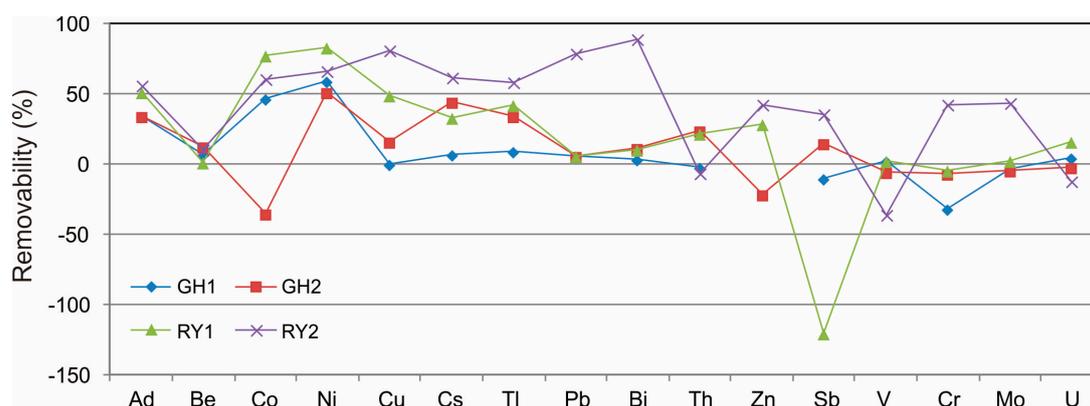


Figure 9. The removability of toxic elements in cleaned coal.

5. Conclusions

- (1) High-U coals are mainly distributed in Southwestern China, and most of them are characterized by a high content of organic S and V-Cr-Mo-U element assemblage. The correlation between V, Cr, Mo, and U is good, while the elements V, Cr, Mo, and U have a negative correlation with ash yield and a positive correlation with organic S, indicating that these elements are syngenetic in origin and mainly occur in the organic matter.
- (2) Mineralogical characteristics indicate that U in Ganhe and Rongyang coal occurs in anatase, clay minerals, gadarramite, and pyrite, while V occurs in clay minerals, pyrite, and dolomite; Cr occurs in dolomite, and F, Pb, Se, and Hg mainly occur in pyrite. These minerals are all fine-grained.
- (3) Gravity separation reveals that the contents of the enriched elements V, Cr, Mo, and U in Rongyang coal are still higher than, or close to, those of feed coal because these elements are derived from hydrothermal fluids in the stage of syngeneses or early diagenesis. At the same time, other elements (F, Mn, Zn, Pb, As, Se, and Hg) can also be efficiently removed.
- (4) Most of the elements in Ganhe and Rongyang coals can be removed by flotation, and the content of V, Cr, Mo, and U is higher than, or close to, that of feed coal. Thus, a portion of V and Cr in the cleaned coal obtained by gravity separation are removed via a flotation test, while Mo and U still cannot be removed. The results of this study show that the use of the two industrialized coal preparation methods, gravity separation, and flotation cannot effectively remove U from high-U coal.
- (5) Dilute HCl was used to extract toxic elements. The extraction rate of Mo reached 74% and indicates that most Mo exists in an adsorbed state, while V, Cr, Co, Ni, and U are partially adsorbed, and the remainder of these components occur in minerals or are complexed with organic matter. The results of this study show that the adsorbed elements V, Cr, Mo, and U can be removed using acid. As U cannot be fully removed from coal, we, therefore, suggest that use of high-U coal should be avoided.

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Conflicts of Interest: The authors declare no conflict of interest.

Appendix

The four Extract Methods are listed as follows:

Method 1: 4 g of coal is put into a centrifuge tube, then added to 30 mL of 2 M HCl for 24 h (interval ultrasonic shaking) and, finally, centrifuged;

Method 2: 4 g of coal is put into a centrifuge tube, then added to 30 mL of 4 M HCl for 24 h (interval ultrasonic shaking) and, finally, centrifuged;

Method 3: 0.5 g of coal is put into a centrifuge tube, then added to 20 mL of 2 M HCl for 24 h (interval ultrasonic shaking) and, finally, centrifuged;

Method 4: 0.5 g of coal is put into a centrifuge tube, then added to 20 mL of 4 M HCl for 24 h (interval ultrasonic shaking) and, finally, centrifuged.

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