INTRODUCTION

Many coals in southwestern China are characterized by a high sulfur (S) content. These high-S coals are usually enriched with uranium (U). Uranium is a naturally radioactive element, and the ultrafine particles released from U-rich coals during combustion can have potentially adverse effects on human health. Coal preparation is one effective approach to reducing environmental pollution from toxic elements. At present, the most widely applied method of removing toxic elements from coal is gravity separation. However, there are few studies on the removal of toxic elements from coal by flotation.
characterized by their high S and U contents. Our previous work has shown that Rongyang coals are characterized specifically by high pyritic S contents and elevated concentrations of the trace elements U, vanadium (V), chromium (Cr), cobalt (Co), copper (Cu), selenium (Se), and molybdenum (Mo) due to marine influence and exposure to hydrothermal fluids during syngenetic or early diagenetic stages. Because U, V, Cr, and Mo primarily occur in organic matter and in fine-grained minerals, these elements cannot be removed from coal by gravity separation and flotation. In order to effectively remove these toxic elements from the Rongyang high-U coals, stepped release flotation and acid leaching were conducted in this study. Furthermore, the removal of toxic elements from high-U coal is of great significance to environmental protection.

2 | GEOLOGICAL SETTING

Rongyang Mine is located in the southwestern part of Guizhou Province, southwestern China (Figure 1). The coal-bearing stratum in the mine field is the Upper Permian Longtan Formation, which has a thickness of 230 m. The Longtan Formation has a disconformable contact with the underlying Middle Permian Maokou Formation and is conformably overlain by the Late Permian Changxing Formation. The Longtan Formation is mainly composed of siltstone, chert, limestone, mudstone, shale, and coal seams and contains fossils including brachiopods, pteridophyte, and ferns. The Kangdian Upland was the dominant sediment-source region for the Late Permian coals from western Guizhou, eastern Yunnan, south Sichuan, and Chongqing. The Late Permian Longtan Formation coal was formed in a tidal flat environment on an open carbonate platform.

3 | MATERIALS AND METHODS

3.1 | Sample background

Samples were collected from the coal-bearing Upper Permian Longtan Formation. The volatile content of Rongyang coals is 8.90%, and the ash yield is 19%. The total S content is 5.44%, which is dominated by pyritic S (4.19% total or 77.02% of the S content), followed by organic S and sulfate (SO₄), indicating that the Rongyang coal is a medium-ash and high-S anthracite.

3.2 | Stepped release flotation

Stepped release flotation testing was performed according to the Chinese Ministry of Coal Industry standard MT 144-86. The 1.5-L single flotation cell (XFD-63) was used for stepped release flotation. In the stepped release analysis, coal slime was separated by one-stage roughing and multi-stage cleaning, after which flotation products with different ash contents were obtained. Samples were initially crushed to <0.5 mm for testing. Flotation conditions for Rongyang coal were an impeller speed of 1800 revolutions/min, a pulp concentration of 100 g/L, and an aeration quantity of 0.25 m³/m²/min. Diesel was used as a collector with a content of 800 g/t.
and octanol was used as a frother with a content of 400 g/t. The stepped release flotation test followed the procedures shown in Figure 2.

3.3 | Mineralogical analyses

A Leitz MPVIII optical microscopy was used for mineral observation, and the images were captured using white-light reflectance microscopy.

3.4 | Acid leaching

The leaching method used in this study is based on those presented by Fisher et al., Qin et al., and Duan et al. Coal samples were ground to <200 mesh (75 μm). Two coal samples (3 g each) were leached by 40 mL of 2 mol/L HCl and 4 mol/L HCl for 24 hours (interval of ultrasonic shaking), respectively. After extraction, the coal samples were centrifuged for 20 minutes at 5000 r/min to separate solids from the solution. The supernatant was removed and then diluted to determine trace element contents by inductively coupled plasma mass spectrometer (ICP-MS; Thermal Fisher, X Series II). Finally, the rate of extraction of toxic elements by dilute HCl was calculated.

3.5 | Trace elements

All samples were crushed and ground to <75 μm. ICP-MS was then used to determine the concentrations of trace elements in the samples, with the exception of mercury (Hg) and fluorine (F). Samples were digested for ICP-MS using an UltraCLAVE microwave high-pressure reactor (Milestone). Digestion reagents were 2 mL of 40% (v/v) hydrogen fluoride (HF) and 5 mL of 65% (v/v) nitric acid (HNO₃) for the coal samples, and 5 mL of 40% (v/v) HF and 2 mL of 65% (v/v) HNO₃ for coal-related material samples. The procedures for ICP-MS analysis of coal and coal-related material microwave digestion were based on the methods described by Dai et al. Concentrations of arsenic (As) and Se were determined using an ICP-MS system equipped with automated, third-generation collision-cell technology (CCTED), as outlined by Li et al., which effectively diminishes the spectral interference of the argon (Ar)-based polyatomic ions ⁴⁰Ar⁴⁰Cl (chlorine) and ⁴⁰Ar³⁸Ar to ⁷⁵As and ⁷⁸Se, respectively. Hg concentrations were determined using a Milestone DMA-80 Hg analyzer, following the method outlined by Dai et al. F concentrations were measured by pyrohydrolysis with an ion-selective electrode in accordance with ASTM D5987-96.

4 | RESULTS

4.1 | Mode of occurrence of fine-grained minerals

The optical microscopy observations found that minerals in Rongyang coals are mainly composed of pyrite and clay minerals. It is consistent with the results obtained from the XRD data. There are a large amount of fine-grained clay minerals and pyrite existing in Rongyang coals (Figure 3). Wang et al. considered that fine-grained pyrite is generally <10 μm in size. The sizes of these fine-grained minerals in Rongyang coals are in the range of 1-10 μm. The fine-grained clay minerals are occurring in colloidetinite (Figure 3a) and discrete in cavities of fusinite (Figure 3b). The fine-grained pyrite is partly disseminated (speckles) in colotelinite (Figure 3c), but another part of fine-grained pyrite occurs in fusinite coexisting with clay minerals (Figure 3d). Duan et al. found that U occurs in fine-grained pyrite, clay minerals, and anatase, which coexists with fine-grained pyrite or clay minerals. In addition, U is also associated with organic component. These fine-grained minerals are difficult to be liberated from coals.

4.2 | Migration characteristics of toxic elements during stepped release flotation

The yield, ash yield (A_d), and content of toxic elements in the products of stepped release flotation are shown in both Table 1 and Figure 4. The yield of Product 1 was too low to determine the content of trace elements. Therefore, the migration patterns of trace elements during stepped release flotation could only be evaluated in general terms. The
distributions of trace elements in stepped release flotation products were as follows:

1. Compared with the products from stepped release flotation, toxic elements (except U and Mo) exhibited the lowest contents in cleaned coals. The occurrence of beryllium (Be), F, V, Cr, cadmium (Cd), barium (Ba), tungsten (W), cesium (Cs), and thallium (Tl) in the flotation products exhibited a similar trend as ash yield. Most elements (except Cr, Ni, Sc, Sb, Hg, Bi, Th, and U) maintained their highest content in Product 1. With an increased number of cleaning stages, the content of toxic elements in the products decreased, indicating that multistage cleaning helped to remove these elements from the cleaned coals.

2. The elements Co, nickel (Ni), Cu, As, Se, antimony (Sb), bismuth (Bi), and Hg exhibited a similar trend in the flotation products. The elements scandium (Sc), Co, Ni, Cu, As, Sb, Bi, and Hg exhibited their lowest contents in cleaned coals. With an increase in the number of cleaning stages, the content of toxic elements in the tailings increased. Unlike Co, Ni, Cu, As, Se, and Hg, the elements zinc (Zn), Sb, lead (Pb), and thorium (Th) exhibited their highest contents in Product 2, but their contents gradually reduced in Product 3, revealing that Zn, Sb, Pb, and Th need more than two stages of cleaning.
3. The distributions of U and Mo in the flotation products were different from all other elements. The contents of U and Mo in cleaned coals were higher than in most of the other products, of which Product 1 had the lowest content. The content of U in feed coal was higher than in cleaned coal and flotation products, which indicates that a part of U was released into washing water.

4.3 | The removability of toxic elements by stepped release flotation

To demonstrate the degree to which toxic elements can be removed through stepped release flotation. Equation 1, proposed by Wang et al., was used to calculate removability.

\[
R = \frac{1 - c_i}{C_i} \times 100\%,
\]  

where \( R \) denotes removability, \( c_i \) 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 toxic elements in cleaned coals via stepped release flotation, flotation, and gravity separation is shown in both Table 2 and Figure 5. Through stepped release flotation, the removability of V, Cr, and Mo is negative, but the removability of U is 25.67%, indicating that a portion of U can be removed, but V, Cr, and Mo cannot be removed by stepped release flotation. Moreover, most of the thiophilic and siderophile elements, such as Co, Ni, Zn, As, Rb, Cd, and Sb, also exhibit a high removability. Compared to simple flotation, and excepting Co, Ni, Cu, and Th, most elements may be better removed by stepped release flotation. When compared with gravity separation, V, Cr, and Mo exhibit a higher removability by flotation, but F, Cu, As, Se, Cd, Sb, Ba, Hg, Tl, and Pb have higher removability by gravity separation. The removability of U
by stepped release flotation was higher than that by gravity separation and flotation. The results indicate that thiophilic elements may be better removed by gravity separation than by stepped release flotation.

### 4.4 Leaching of toxic elements by dilute HCl

As shown in Figure 5, the removability of most of the toxic elements is relatively low. In order to fully remove these elements, the cleaned coals were leached by dilute HCl. The reduction rates of toxic elements from cleaned coals via stepped release flotation using 2 and 4 mol/L dilute HCl are listed in Table 3. As shown in Table 4, the reduction rates of V, Cr, Mo, and U using 4 mol/L HCl were higher than those using 2 mol/L HCl.

The highest reduction rate obtained for V was 2.82%, while the reduction rates of Cr, Mo, and U exceeded 15%. The acid leaching of thiophilic and siderophile elements Co, Ni, Zn, As, Cd, and Pb was relatively high. However, the leaching rates of the lithophile elements Sc, Rb, Ba, and Tl were lower, which suggests that the thiophilic and siderophile elements were much easily removed by acid than that of lithophile elements.
DISCUSSION

5.1 | Comparison of Chinese coals with world hard coals

As listed in Table 4, the contents of the elements Be, F, Sc, V, Cr, Co, Ni, Cu, Zn, As, Se, Mo, Hg, Tl, Pb, and U in cleaned coals, which were obtained by stepped release flotation, are lower than the average for both Chinese and world hard coals. However, the contents of Sc, V, Cr, Cu, Zn, As, Se, Mo, Hg, Tl, Pb, and U in cleaned coals are still higher than the average for Chinese and world hard coals. The concentrations of trace elements in cleaned coals by stepped release flotation, in comparison with the average values for world hard coals, are shown in Figure 6.

According to the classification scheme for elemental enrichment proposed by Dai et al., Mo and U are significantly enriched (10 < CC < 100), Sc, V, and Se are enriched (5 < CC < 10), Cu and Hg are slightly enriched (2 < CC < 5), and Be, F, Rb, and Sb are depleted (CC < 0.5). The remaining elements (0.5 < CC < 2) are close to the average for the world hard coals reported on by Ketris and Yudovich. The results indicate that Sc, V, Cu, Se, Mo, Hg, and U cannot be fully removed through stepped release flotation.

5.2 | The relationship between modes of occurrence and removal of toxic elements

Stepped release flotation uses differences in surface properties to separate minerals from coal; elements Sc, Co, Ni, Cu, Zn, Cd, Sb, Pb, As, Se, Sb, Bi, and Hg mainly occurred in pyrite, while elements Be, F, V, Cr, Ba, W, Cs, and Tl dominantly occur within clay minerals, or other minerals, or organic matter. Thus, the distributions of Sc, Co, Ni, Cu, Zn, Sb, Pb, As, Se, Sb, Bi, and Hg in the products of stepped release flotation are different from those elements Be, F, V, Cr, Ba, W, Cs, and Tl. Because U and Mo are associated with organic matter and occur in fine-grained minerals, especially clay minerals and pyrite, the distributions of U and Mo in the flotation products were different from all other elements. The removability of toxic elements by stepped release flotation and removal rate by acid leaching are closely related to their mode of occurrence. Most of the thiiophilic and siderophile elements Co, Ni, Cu, Zn, Cd, Sb, As, Se, Sb, and Bi have the higher removability than those of lithophile elements Be, F, V, Cr, and Tl. The acid leaching results illustrate that small amounts of V, Cr, Mo, and U can be removed, which due to these elements are mainly associated with organic matter or occur in fine-grained minerals.
minerals encased by organic matter. 23,24 The removal rate of the thiophilic and siderophilic elements Co, Ni, Cu, Zn, As, Cd, and Pb is higher than that of the lithophile elements Sc, Rb, Ba, and Tl.

6 | CONCLUSIONS

1. Stepped release flotation analyses revealed that the multistage cleaning helps to separate toxic elements from cleaned coals.
2. The removal of toxic elements by stepped release and acid leaching is closely related to their mode of occurrence. Vanadium, Cr, Mo, and U were difficult to be removed as they are mainly associated with organic matter or occur in fine-grained minerals. Cobalt, Ni, Cu, Zn, Cd, Sb, As, Se, Sb, and Bi, which occur in pyrite, are much easily removed than Be, F, V, Cr, and Ti which mainly occur in clay minerals and are associated with organic matter.
3. Compared to flotation, most elements are better removed by stepped release flotation. In comparison with gravity separation, U has a higher removability by stepped release flotation, while the removal effect of thiiophilic element by gravity separation is greater than by flotation.
4. Compared to world hard coals, toxic elements Sc, V, Cu, Se, Mo, Hg, and U are still enriched in cleaned coals, indicating that Se, V, Cu, Se, Mo, Hg, and U cannot be fully removed through stepped release flotation.

ACKNOWLEDGMENTS

This study was supported by the National Natural Science Foundation of China (Nos. 41572145, 41802182) and China Postdoctoral Science Foundation–funded project (2018M632412).

ORCID

Piaopiao Duan https://orcid.org/0000-0003-4558-1358

REFERENCES

1. Chou CL. Sulfur in coals: a review of geochemistry and origins. Int J Coal Geol. 2012;100:1-13.
2. Dai S, Yan X, Ward CR, et al. Valuable elements in Chinese coals: a review. Int Geol Rev. 2016;60:1-31.
3. Dai S, Finkelman RB. Coal as a promising source of critical elements: progress and future prospects. Int J Coal Geol. 2017;186:155-164.
4. Melo D, Burkart W. Uranium-environmental pollution and health effects. Encyclopedia Environ Health. 2011;2:526-533.
5. Wang X, Feng Q, Fang T, Liu J, Liu G. Geochemical characteristics of uranium in medium to high sulfur coals from Eastern Yunnan, China. J China Coal Soc. 2015;40:2451-2457 (In Chinese).
6. Liu C, Zhou C, Cong L, et al. Removal of mercury from fine coal based on combined coal processing approaches. Energy Fuels. 2017;31:12951-12958.
7. Liu C, Zhou C, Zhang N, Pan J. Release behavior of Se from coal into aqueous solution. Energy Fuels. 2018;32:2582-2587.
8. Luo G, Ma J, Han J, Yao H, et al. Hg occurrence in coal and its removal before coal utilization. Fuel. 2013;104(104):70-76.
9. Pan J, Zhou C, Cong L, et al. Mercury in Chinese coals: modes of occurrence and its removal statistical laws during coal separation. Energy Fuels. 2016;31:986-995.
10. Xie H, Nie A. The modes of occurrence and washing floatation characteristic of arsenic in coal from Western Guizhou. J China Coal Soc. 2010;35(1):117-121 (in Chinese with English abstract).
11. Cheng W, Zhang Q, Yang R, Tian Y. Occurrence modes and cleaning potential of sulfur and some trace elements in a high-sulfur coal from Pu'an coalfield, SW Guizhou, China. Environ Earth Sci. 2013;72(1): 35-46.
12. Kolker A, Senior C, Alphen CV, Koenig A., Gebo N. Mercury and trace element distribution in density separates of a South African Highveld (#4) coal: implications for mercury reduction and preparation of export coal. Int J Coal Geol. 2016;170:7-13.
13. Wang W, Qin Y, Sang S, et al. Partitioning of minerals and elements during preparation of Taixi coal, China. Fuel. 2006;85(1):57-67.
14. Wang W, Qin Y, Wei C, Li Z, Guo Y, Zhu Y. Partitioning of elements and macerals during preparation of Antaibao coal. Int J Coal Geol. 2008;68(3-4): 223-232.
15. Wang W, Qin Y, Wang J, Li J. Partitioning of hazardous trace elements during coal preparation. Proce Earth Planet Sci. 2009;1:1: 838-844.
16. Wang W, Qin Y. Partitioning of Hazardous Elements and Minerals During Coal Cleaning. Xuzhou: China University of Mining and Technology Press; 2011 (in Chinese).
17. Song D, Zhang X, Zhang J, Zheng C. Migration characteristics of hazardous trace elements in coal in the process of flotation. J China Coal Soc. 2010;35:1170-1176 (In Chinese).
18. Wang L. The study on removal of trace elements in coal by coal preparation. Clean Coal Technol. 2007;13(3):13-17 (in Chinese).
19. Duan P, Wang W, Liu X, Qiang F, Sang S, Xu S. Distribution of As, Hg and other trace elements in different size and density fractions of the Reshuihe high-sulfur coal, Yunnan Province, China. Int J Coal Geol. 2017;173:129-141.
20. Pan J, Zhou C, Zhang N, Liu C, Tang M, Cao S. Arsenic in coal: modes of occurrence and reduction via coal preparation - a case study. Int J Coal Prep Util. 2017. https://doi.org/10.1080/19392699.2017.1411348.
21. Zhou C, Liu C, Zhang N, Cong L, Pan J, Peng C. Fluorine in coal: the modes of occurrence and its removability by froth flotation. Int J Coal Prep Util. 2016;38;149-161.
22. Zhou C, Zhang N, Peng C, Cong L, Ouyang C, Han R. Arsenic in coal: modes of occurrence, distribution in different fractions, and partitioning behavior during coal separation—a case study. Energy Fuels. 2016;30:3233-3240.
23. Duan P, Wang W, Sang S, Qian F, Shao P, Zhao X. Partitioning of hazardous elements during preparation of high-uranium coal from Rongyang, Guizhou, China. J Geochem Explor. 2018;185:81-92.
24. Duan P, Wang W, Sang S, et al. Geochemistry of toxic elements and their removal via the preparation of high-uranium coal in southwestern China. Minerals. 2018;8:83.
25. China Coal Geology Bureau. *Sedimentary Environments and Coal Accumulation of Late Permian Coal Formation in Western Guizhou, Southern Sichuan, and Eastern Yunnan, China*. Chongqing: Chongqing University Press; 1996:156-216 (in Chinese with English abstract).

26. Dai S, Ren D, Chou CL, Finkelman RB, Seredin VV, Zhou Y. Geochemistry of trace elements in Chinese coals: a review of abundances, genetic types, impacts on human health, and industrial utilization. *Int J Coal Geol*. 2012;94:3-21.

27. Xu B, He M. *Guizhou Coalfield Geology*. Xuzhou: China University of Mining and Technology Press; 2003 (in Chinese).

28. Chinese Ministry of Coal Industry standard MT 144-86. Coal preparation laboratory of stepped releasing flotation test. 1986 (in Chinese).

29. Fisher QJ, Cliff RA, Dodson MH. U-Pb systematics of an upper Carboniferous black shale from South Yorkshire, UK. *Chem Geol*. 2003;194:331-347.

30. Qin Y, Zhang W, Peng P, Zhou Z. Occurrence and concentration of uranium in the hydrocarbon source rocks of Chang 7 member of Yanchang Formation, Ordos Basin. *Acta Petrol Sinc*. 2009;25:2469-2476 (in Chinese).

31. Dai S, Wang X, Zhou Y, et al. Chemical and mineralogical compositions of silicic, mafic, and alkali tonsteins in the late Permian coals from the Songzao Coalfield, Chongqing, Southwest China. *Chem Geol*. 2011;282(1-2):29-44.

32. Li X, Dai S, Zhang W, Li T, Zheng X, Chen W. Determination of As and Se in coal and coal combustion products using closed vessel microwave digestion and collision/reaction cell technology (CCT) of inductively coupled plasma mass spectrometry (ICP-MS). *Int J Coal Geol*. 2014;124:1-4.

33. Dai S, Liu J, Ward CR, et al. Petrological, geochemical, and mineralogical compositions of the low-Ge coals from the Shengli Coalfield, China: a comparative study with Ge-rich coals and a formation model for coal-hosted Ge ore deposit. *Ore Geol Rev*. 2015;71:318-349.

34. ASTM Standard D5987-96. *Standard Test Method for Total Fluorine in Coal and Coke by Pyrohydrolytic Extraction and Ion Selective Electrode or Ion Chromatograph Methods*. West Conshohocken, PA: ASTM International; 2002 (Reapproved 2007).

35. Wang W, Sang S, Bian Z, et al. Fine-grained pyrite in some Chinese coals. *Energy Explor Exploit*. 2016;34(4):543-560.

36. Ketris MP, Yudovich YE. Estimations of Clarkes for carbonaceous biolithes: world average for trace element contents in black shales and coals. *Int J Coal Geol*. 2009;78:135-148.

37. Dai S, Seredin VV, Ward CR, et al. Enrichment of U-Se-Mo-Re-V in coals preserved within marine carbonate successions: Geochemical and mineralogical data from the Late Permian Guiding Coalfield, Guizhou, China. *Miner. Depos*. 2015;50:159-186.

38. Ren D, Zhao F, Dai S, Zhang J, Luo K. *Geochemistry of Trace Elements in Coal*. Beijing: Science Press; 2006 (in Chinese).

39. An Y, Chen Y, Zhang S, Li S, Lai C. New Discovery of Post-magmatic Pyrite in Natural Coke at Yangliu Coalmine, Northern Chinaa. *Acta Geol Sin*. 2018;92(6):2436-2437.

40. An Y, Liu L, Wang M, et al. Source and Enrichment of Toxic Elements in Coal Seams around Mafic Intrusions: Constraints from Pyrites in the Yuandian Coal Mine in Anhui, Eastern China. *Minerals*. 2018;8(4):164.

41. Li W, Tang Y, Deng X, Yu X, Jiang S. Geochemistry of the trace elements in the high-organic-sulfur coals from Chenxi coalfield. *J. China Coal Soc*. 2013;38:1223-1227.

---

**How to cite this article:** Duan P, Wang W, Sang S, Ma M, Wang J, Zhang W. Modes of occurrence and removal of toxic elements from high-uranium coals of Rongyang Mine by stepped release flotation. *Energy Sci Eng*. 2019;7:1678-1686. [https://doi.org/10.1002/ese3.384](https://doi.org/10.1002/ese3.384)