minerals

Case Report

Characterization and Removal Potential of Fluorine in Lignite from a Mine in Shaanxi Province, China: A Case Study

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Abstract: Fluorine appears in coal and is released into the atmosphere upon combustion, resulting in harmful impacts on the environment and life, which needs to be removed from coal before utilization. Coal can be processed by flotation and gravity separation to reduce its fluorine content. In this study, a lignite sample from a mine in Shaanxi Province, China, was characterized using the float–sink test, sieving test, X-ray diffraction (XRD), and polarized light microscopy. Mineralogical analysis indicated that the fluorine in coal is mainly contained in Muscovite and polylithionite, and partly in pyrite. The washability and floatability analyses were employed to evaluate the extent of fluorine removal from >0.5 and <0.5 mm size fractions of lignite, respectively. Compared to the raw sample that contained 347.74 μg/g fluorine content, the proposed combination of gravity-flotation separation process decreased the fluorine content to 90.14 μg/g, which meets the requisites of coal standards.

Keywords: fluorine; occurrence; removal; gravity-flotation separation; lignite

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1. Introduction

Fluorine in coal is potentially hazardous to the environment and life [1–3]. During the coal combustion process, fluorine gets converted into gases (such as HF, SiF_4, and CF_4) and dust particles (such as SiF_6 and CaF_2), which enter into the atmospheric environment having detrimental environmental and ecological consequences [4–6]. The gaseous fluoride emissions such as CF_4, which are reported to have greenhouse potential (GWP) around 6500 times as compared to CO_2, can cause a significant greenhouse effect, while HF is multiple times more toxic to animals and plant life than SO_2 [7,8].

Interim Measures for Commercial Coal Quality Management (2014) stipulates that the maximum fluorine content of coal for commercial purposes must be less than 200 μg/g to ensure environmental protection. The fluorine content in Chinese coal ranges between 2 and 911 μg/g, and it occurs in various modes, as listed in Table 1. The majority of fluorine in coal comes from inorganic minerals. Notably, the fluorine content of different regions in China fluctuates greatly [9,10]. The fluorine content in Chinese coal is reported to follow a logarithmic normal distribution, having a range of 17–3088 mg/kg of fluorine fraction. In total, 73% of Chinese coal contains fluorine ranging from 50 to 300 mg/kg, averaging 202 mg/kg [11]. Power plants use nearly 1.76 billion tons of coal produced in China to generate electricity [12,13]. Considering the average fluorine concentration of coal at a low value of 100 μg/g, the fluorine emission from 1 t steam coal combustion into the atmosphere amounts to 8.3×10^{-5} t [14]. This can have a detrimental effect on humans, animals, and plants which is why it is important to minimize the harmful effects of fluorine generated from coal combustion.

Table 1. A summary of the fluorine content and occurrence modes in some Chinese coals.

Coal Sample	Fluorine Content (μg/g)	Fluorine Occurrence Mode	Ref.
A coal sample from Guizhou Province, China	357	Fluorine mainly occurred in residual-associated form and carbonate- and Fe/Mn-associated form.	[15]
	<200 μg/g	Most of these coals are low fluorine (<200 μg/g); however, the fluorine content of clay is as high as 1027.6 μg/g.	[16]
	715.20 (average)	The inorganic occurrence is the primary mode of occurrence of fluorine in coals from Guizhou province.	[17]
Haerwusu Surface Mine, Inner Mongolia, China	286	Boehmite and kaolinite are prime carriers of fluorine, but sometimes associated both with organic and inorganic matter.	[18,19]
Xiangning mining area, Shanxi Province, China, China	2–911	Fluorine in coal mainly exists in an inorganic bound state in forms such as fluorapatite and calcium fluoride.	[20]
Nantong coalfield, Chongqing Province, China	490 (average)	Fluorine in coals from Nantong coalfield existed in the organic and inorganic minerals simultaneously.	[21]
China coals	67.3–3145.4	Fluorine in coal mainly occurs in an inorganic form.	[22]

Various engineering measures, such as denitrification and desulfurization, can significantly reduce the amount of fluorine released during coal combustion, thereby reducing the associated environmental impacts [20]. The defluorination processes can be classified into defluorination before combustion, fluorine fixation during combustion, and flue gas defluorination after combustion [23,24]. The fluorine removal process depends on whether fluorine has an inorganic form, which is predominantly abundant, or organic form [9,20,25]. Both fluorine fixation and flue gas defluorination (the latter of which is often employed with coal-fired boilers in large power stations) can effectively remove both inorganic and organic fluorine from coal. These two methods are widely useful in particular for the removal of organic fluorine [4,14,20,26]. For coal with a higher content of inorganic fluorine, the defluorination of pulverized coal before combustion using various physical or physicochemical methods has a low operating cost compared to the other two processes [27]. As mentioned previously, the majority of fluorine in coal is in association with inorganic minerals, indicating that most of the fluorine has a strong affinity for ash materials (i.e., gangue). Thus, the commonly used coal preparation methods can be useful for the removal of fluorine from coal, such as gravity separation (physical method) and flotation (physicochemical method). Zhou et al. [15] reported that a total of 76.05% of the total fluorine was removed by froth flotation under an optimum condition. Lin et al. [20] demonstrated that froth flotation can reduce the amount of fluorine significantly. Mohanty et al. [28] found that a fine coal cleaning circuit using enhanced-gravity separation (EGS) and column flotation in a rougher–cleaner arrangement provides a more efficient reduction in ash and the trace element (i.e., Hg and Se) when compared to the results of single-stage cleaning operations. It can be implied that flotation has a high removal rate of fluorine, due to its strong interaction with ash, similar to Hg/Se.

In coal preparation plants, coal of size > 0.5 mm is commonly upgraded by gravity separation devices, such as teeter bed separators [29,30], spirals [31,32], dense medium cyclones [33,34], and jigs [35,36]. Flotation is an effective method to separate hydrophilic gangue from hydrophobic coal (<0.5 mm) [37,38]. As discussed, previous studies mainly focused on the removal of fluorine in fine coal (<0.5 mm) by using froth flotation. However, there is a lack of literature reporting the removal of fluorine in coarse coal (>0.5 mm) by using gravity separation. To bridge this gap, gravity separation as well as flotation have been utilized to remove fluorine from >0.5 and <0.5 mm coal size fractions, respectively. The first step was to study the modes of occurrence of fluorine in coal. Then, fluorine removal efficiency by gravity-separation and flotation was investigated. Finally, a flowsheet to remove fluorine from <50 mm coal was proposed.

2. Materials and Methods

2.1. Materials

Coal samples smaller than 50 mm in size were collected from a mine in Shaanxi Province, China. Sec-octyl alcohol (analytical reagent) and kerosene (commercially pure) were used as the frother and collector, respectively. Zinc chloride, benzene (carbon tetrachloride), and cyclohexane were obtained from China National Pharmaceutical Group Co., Ltd. (Beijing, China) and were used for float–sink tests.

2.2. Sieve Analysis

The sieve analysis was carried out according to Chinese Standard GB/T 477-2008 (Method for size analysis of coal) using sieves with mesh sizes of 50, 25, 13, 6, 3, 1, and 0.5 mm. The coal sample used for the sieving was air-dried under prescribed conditions. After the sieving test, the retained size fractions of 25–50, 13–25, 6–13, 3–6, 1–3, 0.5–1, and <0.5 mm were weighed. Afterwards, the sub-samples were prepared according to Chinese Standard GB/T 474-2008 (Method for preparation of coal sample). The obtained sub-samples were further used for the determination of fluorine, ash, and total sulfur content.

2.3. Float–Sink Analysis

Representative coal samples were prepared for each size fraction. Float–sink analyses were conducted according to Chinese Standard GB/T 478-2008 (Method for float and sink analysis of coal). To perform a float–sink test on >0.5 mm coal, water was mixed with pure zinc chloride (as a liquid sorting medium), to obtain a solution of a specific density. Organic heavy media with different densities were prepared to perform the float–sink test of <0.5 mm coal by mixing benzene (carbon tetrachloride) and cyclohexane.

The float–sink products were dried and weighed. After that, the sub-samples were prepared according to Chinese Standard GB/T 474-2008 (Method for preparation of coal sample) for further determination of fluorine, ash, and total sulfur content.

2.4. Batch Flotation Test

The procedure of the batch flotation test was carried out according to Chinese Standard GB/T 4757-2013 (Methods for the batch flotation testing of fine coal) using a standard laboratory RK/FD-II sub-aeration flotation cell (volume = 1.5 dm^3). The pulp with a 60 g/L solid concentration was conditioned for 3 min. The required amount of kerosene was added and conditioned for two more minutes. After that, the required amount of sec-octyl alcohol was added, and the slurry was conditioned for another 0.5 min. Then, the air valve was opened at 4.17 dm^3/ min air flow rate, and the froth was collected for 3 min. In each test, tap water was added to maintain a constant pulp level and a froth layer of 1 cm. The agitation speed was kept constant at 1900 rpm. A detailed description of the working process of the mechanical flotation cell is reported in the literature [39]. The release analysis test was performed to determine the floatability of the coking coal fines according to Chinese Standard GB/T 36167-2018 (Methods for coal preparation laboratory timed-release flotation analysis). Flotation release tests were performed based on published literature [40–42]. The flotation time was constant at 3 min for different flotation stages of release flotation. The release analysis procedure used in this study is similar to "reverse release analysis" introduced by Randolph [43], where the tailings are collected in the cleaning stage of flotation.

2.5. XRD Test

The ground sample (<0.074 mm) obtained using an XPM-φ 120 × 3 three-headed grinding machine (Nanchang Source of Mining and Metallurgy Equipment Co., Ltd., Nanchang, China) was subjected to XRD analysis using a D8 Advance X-ray diffractometer (Bruker, Germany).

2.6. Determination of Ash, Fluorine, Sulfur Contents, and Calorific Value

The proximate analysis for the determination of ash content was carried out according to Chinese Standards (Table S1) GB/T 212-2008 (Proximate analysis of coal), using a CTM100 muffle furnace (Tairui Company, Xuzhou, China). The ultimate analysis was carried out according to GB/T 31391-2015 (Ultimate analysis of coal). The total sulfur content was determined according to Chinese Standard GB/T 214-2007 (Determination of total sulfur in coal) using the CTS7000 automatic sulfur detector (Tairui Company, Xuzhou, China). The fluorine content in coal was analyzed by pyro hydrolysis/fluorine ion-selective electrode method [26] according to Chinese Standard 4633-2014 (Determination of fluorine in coal). The calorific value of coal was determined according to Chinese Standard GB/T 213-2008 (Determination of the calorific value of coal) using an auto-calorimetry instrument (CT5000, Weike Tech. Company, Xuzhou, China).

3. Results and Discussion

3.1. Mineralogical Characterization

Interim Measures for Commercial Coal Quality Management (2014) states that the maximum ash, total sulfur, and fluorine contents of coal should not exceed 30%, 1.5%, or 200 mg/g, respectively. Results of the proximate and ultimate analyses are given in Table 2. According to Chinese Standard GB/T5751-2009 (Chinese classification of coals), the coal under consideration is classified as lignite. The ash content, total sulfur content, fluorine content, and net calorific values are 38.88%, 2.95%, 241 μg/g, and 16.07 MJ/kg, respectively. Thus, the quality of this coal needs to be upgraded to meet those requirements.

Table 2. Proximate and ultimate analysis data.

Proximate Analysis (%)				Ultimate Analysis (%)					F_{ad} (μg/g)	$Q_{net.ar}$ (MJ/kg)
M_{ad}	A_d	V_{daf}	FC_d	C_{daf}	H_{daf}	O_{daf}	N_{daf}	$S_{t.d}$		
4.68	38.88	44.46	33.95	74.39	4.67	13.80	1.08	2.95	241	16.07

Note: in Table 2, M_{ad} and F_{ad} are the moisture content (M) and the fluorine content (F) in the coal on an air-dried (ad) basis; A_d and FC_d are the ash content (A) and the fixed carbon content (FC) on a dry (d) basis; V_{daf}, C_{daf}, H_{daf}, O_{daf}, N_{daf}, and $S_{t.d}$ are the carbon, hydrogen, oxygen, nitrogen and total sulfur, on dry ash-free (daf) basis, respectively; $Q_{net.ar}$ is the net calorific value (at constant pressure) as received.

The ash content, total sulfur content, and fluorine content of different size fractions are shown in Figure 1. The amount of product in each size group and their ash, sulfur, and fluorine contents and distribution are given in the Table S2. It is evident that there is a direct relation between ash and fluorine contents. As the most active non-metallic element known, fluorine has a strong oxidation affinity and can combine with almost any other to form fluoride [25]. According to previous studies [3,10,19,25,26], fluorine in coal mainly exists in the form of inorganic substances. Fluorapatite minerals may be the main occurrence mode of fluorine in coal. In addition, other inorganic substances include fluorspar, tourmaline, mica, and clay minerals.

3.2. Fluorine and Sulfur Distributions in Different Density Fractions of >0.5 mm Coal

As shown in Figure 2, the fluorine content increases significantly when the density fraction increases. This phenomenon indicates that the occurrence of fluorine in this coal sample is mainly inorganic. Figure 3 shows the relationships between ash content, total sulfur content, and fluorine content for different size fractions. For a given size fraction when the density fraction is increased the ash content increased significantly. As observed from Figure 3, the higher the ash content of the coal, the higher the content of fluorine and sulfur. According to the literature [20], fluorine in coal might be adsorbed in fluorine-containing minerals (fluorapatite) and clay minerals such as muscovite and kaolinite in ionic state. The XRD result of the high-density fraction (>2.0 g/cm^3) is shown in Figure 4. As shown in Figure 4, the main minerals are muscovite-3T, polylithionite, nimite-1MIIb, clinochlore-1MIIb, pyrite, and quartz. Fluorine mainly exists as muscovite-3T and polylithionite, while pyrite is the main form of inorganic sulfur.

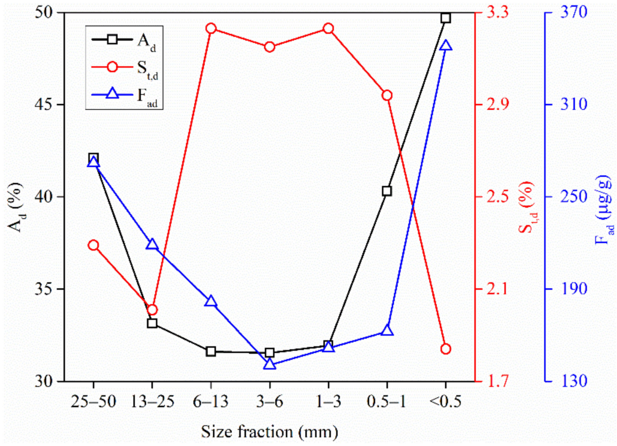

Figure 1. The ash content, total sulfur content, and fluorine content of different size fractions.

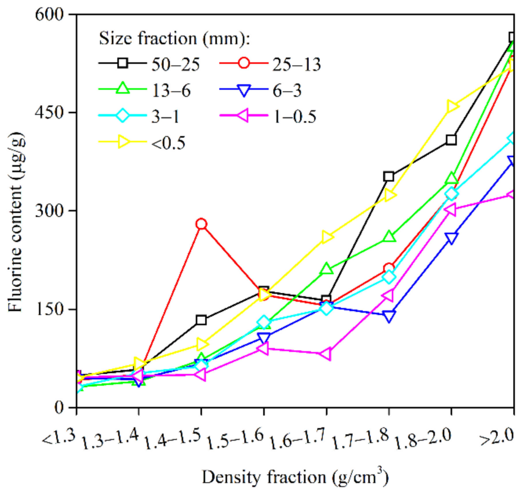

Figure 2. The fluorine content of different density fractions.

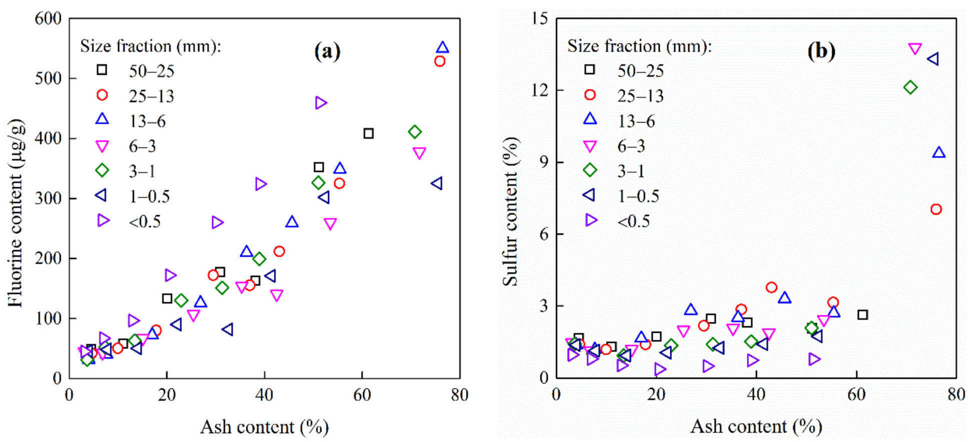

Figure 3. The relationships between ash content, total sulfur content, and fluorine content for different size fractions. (**a**) ash content vs. fluorine content; (**b**) ash content vs. total sulfur content. The high ash content corresponds to the fraction with a high density.

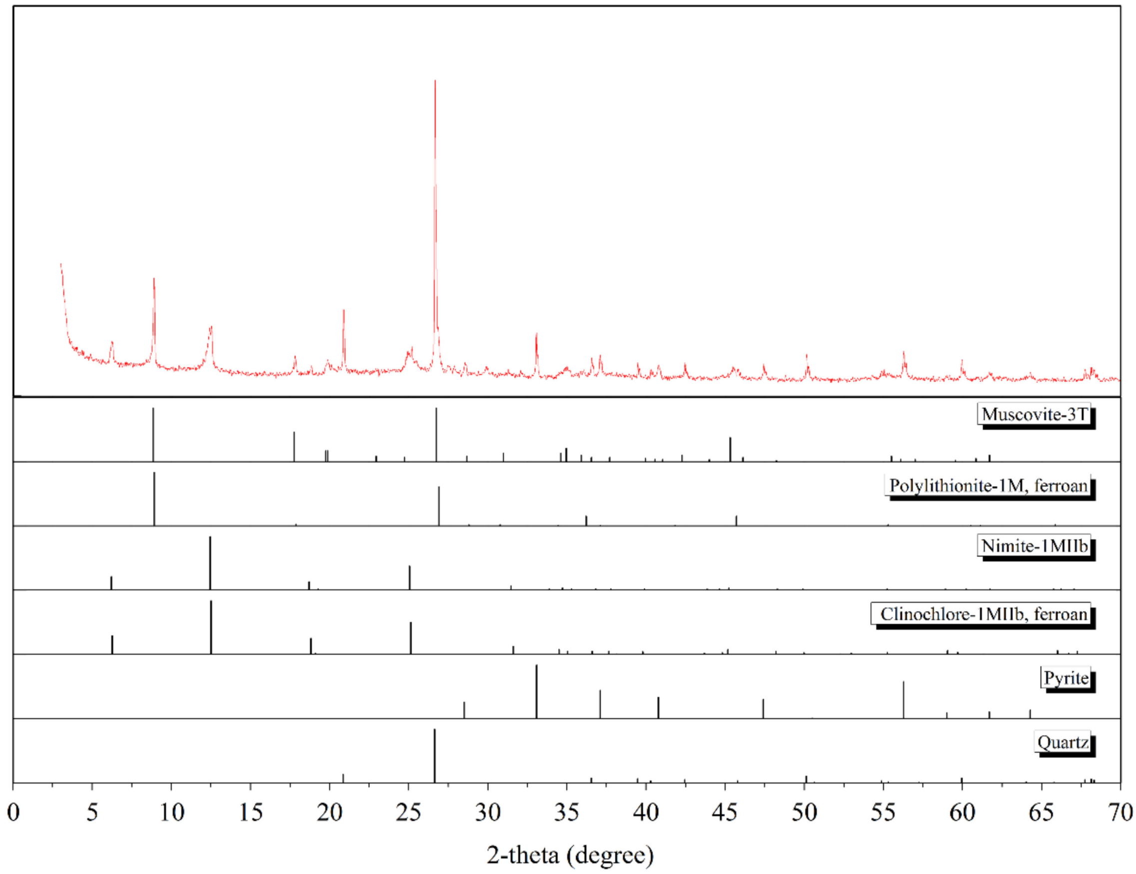

Figure 4. XRD result of the high-density fraction (>1.8 g/cm^3).

The washability curves for >0.5 mm coal are given in Figure 5. The degrees of washability of clean coal as a function of ash content and the corresponding values of fluorine, sulfur, and net calorific value in clean coal are presented in Table 3. The cumulative yield of clean coal is 72.97% when the ash content is 15%.

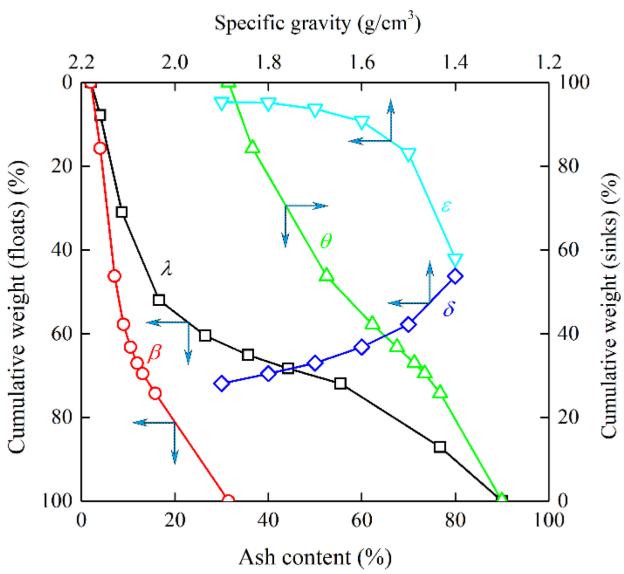

Figure 5. Classical washability curves for >0.5 mm coal. λ—primary curve; β—cumulative float curve; θ—cumulative sink curve; δ—density distribution curve; ε—near-gravity material with ±0.1 g/cm^3 specific gravity (s. g.).

Table 3. The degrees of washability of clean coal at the different given ash contents [1].

A_d (%)	Yield (%)	F_{ad} (μg/g)	$S_{t.d}$ (%)	$Q_{net.ar}$ (MJ/kg)	δ_s (g/cm^3)	$\varepsilon_{\pm 0.1}$ (%)	Degree of Washability
10.00	61.44	64.65	1.33	23.05	1.52	18.55	Moderate separation
11.00	64.70	69.00	1.37	22.73	1.59	11.04	
12.00	67.27	72.58	1.40	22.42	1.66	7.66	Simple separation
13.00	69.56	77.68	1.44	22.10	1.75	5.69	
14.00	71.18	83.39	1.46	21.80	1.80	5.31	
15.00	72.97	89.23	1.49	21.53	1.86	4.94	

[1] δ_s is the separation gravity, and $\varepsilon_{\pm 0.1}$ is the near-gravity material with ±0.1 g/cm^3 that corresponds to δ_s. The degree of washability was determined according to Chinese Standard GB/T16417-2011 (Method for evaluating the washability of coal).

3.3. Fluorine and Sulfur Distributions in Release Flotation of <0.5 mm Coal

The ash, fluorine, and sulfur contents, after release flotation tests, are shown in Figure 6. For release analysis, the kerosene dosage and the sec-Octyl alcohol dosage were 9000 and 4500 g/t, respectively. The solid concentration was 100 g/L, the airflow rate was 0.25 m^3/h, and the impeller speed was 1900 rpm. As shown in Figure 6, the fluorine content has a direct correlation with the ash content. This indicates that fluorine exists in <0.5 mm coal in the form of inorganic matter. However, results of tailings indicate that the occurrence form of sulfur is mainly organic. Classical floatability curves for <0.5 mm coal are given in Figure 7. The degrees of floatability of flotation concentrates at different given ash contents are summarized in Table 4. It can be seen that the degree of floatability is difficult-to-float for all given percentages of the ash.

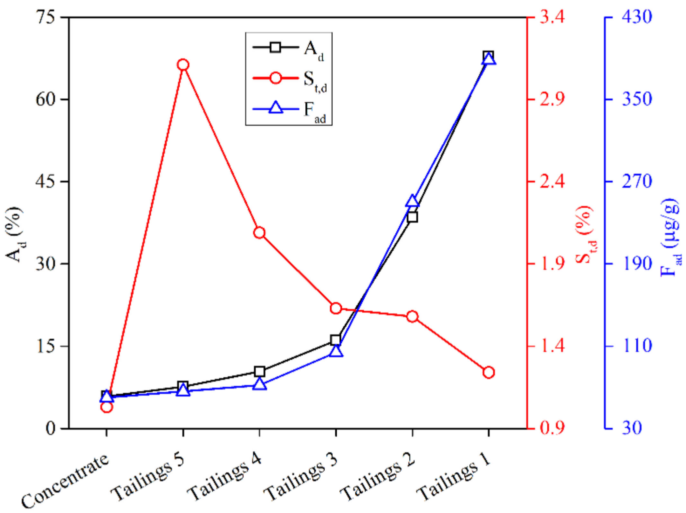

Figure 6. Ash contents, fluorine contents, sulfur contents, and net calorific values for different products of release flotation tests.

Table 4. The degrees of floatability of flotation concentrates at different given ash contents [1].

A_d (%)	Yield (%)	F_{ad} (μg/g)	$S_{t.d}$ (%)	$Q_{net.ar}$ (MJ/kg)	Combustible Recovery (%)	Degree of Floatability
10.00	27.16	79.02	1.76	23.02	48.34	Difficult-to-float
11.00	28.37	84.54	1.76	22.72	49.93	
12.00	29.72	91.41	1.75	22.44	51.72	
13.00	30.93	97.06	1.74	22.15	53.21	
14.00	32.14	103.34	1.73	21.85	54.66	
15.00	33.36	108.82	1.73	21.56	56.07	

[1] combustible recovery = *yield*. $(100 - A_{d,con})/100 - A_{d,<0.5\mathrm{mm}}$; $A_{d,con}$ is the given ash.

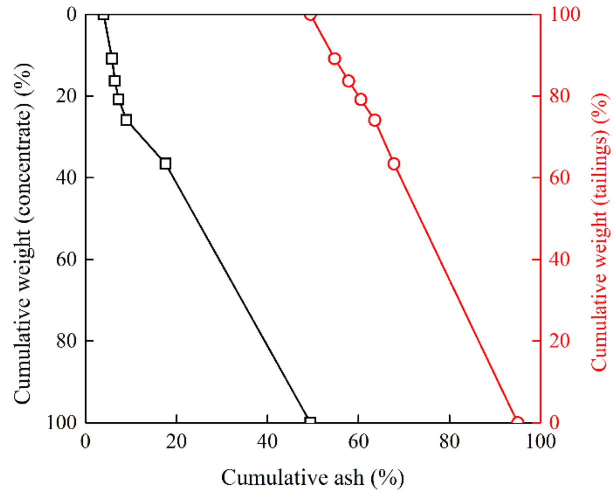

Figure 7. Classical floatability curves of <0.5 mm coal.

The flotation performance of lignite is known to be poor since several hydrophilic functional groups are present, such as hydroxyl, carboxyl, methoxyl, and carbonyl [44–46]. For the comparison, the float–sink test of <0.5 mm coal was performed. The upgrading curves can be used for the analysis of the separation process [47–50]. The comparison of float–sink and release flotation tests is given in Figure 8. The content of fluorine in clean coal increases as yields increase. It is observed that the yield of clean coal using gravity separation is higher than that of flotation separation. However, the fluorine content at a given yield (around 35%) is significantly lower than that of gravity separation, which makes the flotation technique more suited to remove fluorine from <0.5 mm size fractions.

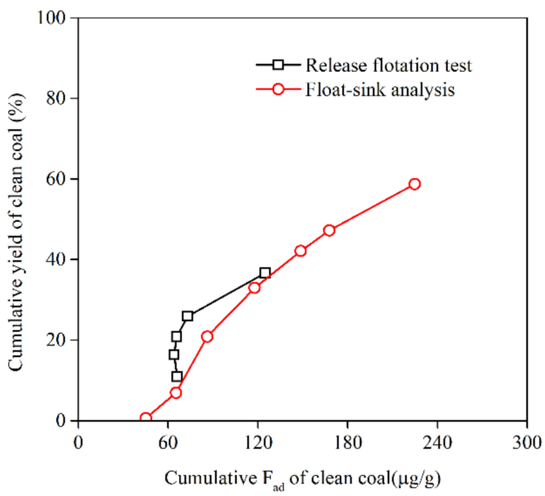

Figure 8. Comparison of upgrading curves (F_{ad} vs. yield) of <0.5 mm coal between float–sink and release flotation tests.

3.4. A Proposed Beneficiation Circuit for <50 mm Coal

It was determined that >0.5 mm coal can be straightforwardly separated using dense medium cyclones and jigs due to the degree of washability, however, for <0.5 mm the efficiency of using dense medium separation diminishes [34,51]. On the other hand, the efficiency of flotation for <0.5 mm is far greater than dense medium separation, making it more suitable for fluorine removal. It can be concluded from a simple approximation calculation (see Figure 9A) that fine coal (347.74 μg/g) can be directly mixed with coarse clean coal to obtain the final product with a qualified quality (122.14 μg/g). To further decrease the fluorine content of fine coal (see Figure 9B) flotation separation can be used before mixing it with coarse clean coal. As a result, the fluorine content in the final product is reduced down to 90.14 μg/g.

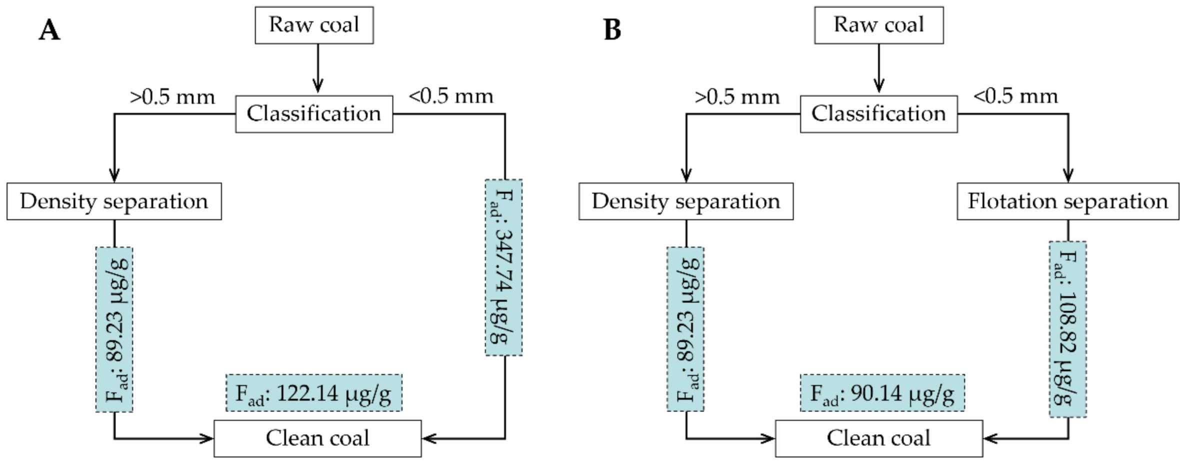

Figure 9. The proposed beneficiation circuits for <50 mm coal. (**A**) No treatment of <0.5 mm coal; (**B**) <0.5 mm coal treated by flotation separation.

4. Conclusions

In this study, gravity separation/sink–float and flotation methods were investigated for the removal of fluorine from coal (0.001–0.5 mm in size). Based on the results of proximate and ultimate analyses, the coal was classified as lignite. The results of XRD analysis showed that the majority of fluorine exists as Muscovite-3T and Polylithionite and inorganic sulfur occurs as pyrite primarily. Ash content and fluorine were found to be directly related. A qualified coal product can be obtained by gravity separation treatment of coarse coal (>0.5 mm). Considering the extent of fluorine removal, for coal <0.5 mm in size, flotation is more efficient than dense medium separation. Furthermore, the mixture of clean coarse coal (float–sink) and clean fine coal (flotation) contains significantly less fluorine than that of the mixture of clean coarse coal (float–sink) and untreated fine coal. The proposed circuit combining the float-sink–flotation process can significantly reduce the fluorine content of coal, eventually reducing fluorine emissions to the atmosphere by utilizing a fine coal fraction cleaned with flotation, covering the inefficient fluorine removal from fine coal fraction by dense medium separation.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/min12030280/s1, Table S1. List of Chinese Standards, Table S2. The amount of product in each size group and their ash, sulfur and fluorine contents and distribution. All information are mentioned in the reference [52] here in the text and in the Supplementary Material file.

Author Contributions: Conceptualization, X.B. and Y.C.; methodology, C.N. and S.Z.; software, validation, and formal analysis, G.X. (Guangqian Xu); investigation, S.Z.; resources, G.X. (Guangyuan Xie); data curation, X.B.; writing—original draft preparation, X.B., F.U.H. and M.B.; writing—review and editing and visualization, X.B., Y.C., M.B. and F.U.H.; supervision, C.N.; project administration, X.B.; funding acquisition, C.N. All authors have read and agreed to the published version of the manuscript.

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References

1. Gao, G.; Yan, B.; Yang, L. Determination of total fluorine in coal by the combustion-hydrolysis/fluoride-ion selective electrode method. *Fuel* **1984**, *63*, 1552–1555. [CrossRef]
2. Greta, E.; Dai, S.; Li, X. Fluorine in Bulgarian coals. *Int. J. Coal Geol.* **2013**, *105*, 16–23. [CrossRef]
3. Liu, G.; Zhang, H.; Gao, L.; Zheng, L.; Peng, Z. Petrological and mineralogical characterizations and chemical composition of coal ashes from power plants in Yanzhou mining district, China. *Fuel Process. Technol.* **2004**, *85*, 1635–1646. [CrossRef]
4. Liu, J.; Qi, Q.; Zhou, J.; Cao, X.; Cen, K. Distribution of fluoride in the combustion products of coal. *Huan Jing Ke Xue = Huanjing Kexue* **2003**, *24*, 127–130.
5. Sredović, I.; Rajaković, L. Pyrohydrolytic determination of fluorine in coal: A chemometric approach. *J. Hazard. Mater.* **2010**, *177*, 445–451. [CrossRef]
6. Guo, S.; Yang, J.; Liu, Z. The fate of fluorine and chlorine during thermal treatment of coals. *Environ. Sci. Technol.* **2006**, *40*, 7886–7889. [CrossRef]
7. Pisupati, S.V.; Wasco, R.S.; Scaroni, A.W. An investigation on polycyclic aromatic hydrocarbon emissions from pulverized coal combustion systems. *J. Hazard. Mater.* **2000**, *74*, 91–107. [CrossRef]
8. Thomas, G.; Fariborz, G. Effect of geological processes on coal quality and utilization potential: Review with examples from western Canada. *J. Hazard. Mater.* **2000**, *74*, 109–124. [CrossRef]
9. Luo, K.; Ren, D.; Xu, L.; Dai, S.; Cao, D.; Feng, F.; Tan, J.A. Fluorine content and distribution pattern in Chinese coals. *Int. J. Coal Geol.* **2004**, *57*, 143–149. [CrossRef]
10. Dai, S.; Ren, D. Fluorine concentration of coals in China—An estimation considering coal reserves. *Fuel* **2006**, *85*, 929–935. [CrossRef]
11. Qi, Q.J.; Yu, G.S.; Li, F.W.; LIU, J.Z.; CEN, K.F. Inorganic/organic affinity and washing floatation characteristic of fluorine in coal. *J. Liaoning Tech. Univ. Nat. Sci. Ed.* **2006**, *25*, 481–484.
12. Bu, X.; Chen, Y.; Ma, G.; Sun, Y.; Ni, C.; Xie, G. Differences in dry and wet grinding with a high solid concentration of coking coal using a laboratory conical ball mill: Breakage rate, morphological characterization, and induction time. *Adv. Powder Technol.* **2019**, *30*, 2703–2711. [CrossRef]
13. Bu, X.; Chen, Y.; Ma, G.; Sun, Y.; Ni, C.; Xie, G. Wet and dry grinding of coal in a laboratory-scale ball mill: Particle-size distributions. *Powder Technol.* **2020**, *359*, 305–313. [CrossRef]
14. Luo, K.; Xu, L.; Li, R.; Xiang, L. Fluorine emission from combustion of steam coal of North China Plate and Northwest China. *Chin. Sci. Bull.* **2002**, *47*, 1346–1350. [CrossRef]
15. Zhou, C.-C.; Liu, C.; Zhang, N.-N.; Cong, L.-F.; Pan, J.-H.; Peng, C.-B. Fluorine in Coal: The Modes of Occurrence and its Removability by Froth Flotation. *Int. J. Coal Prep. Util.* **2018**, *38*, 149–161. [CrossRef]
16. Dai, S.; Ren, D.; Ma, S. The cause of endemic fluorosis in western Guizhou Province, Southwest China. *Fuel* **2004**, *83*, 2095–2098. [CrossRef]
17. Liu, X. Evolution Of Migration Behavior of Fluofine in Coal and Sulfur-Containing Coal Molecular Structure. Ph.D. Thesis, Huazhong University of Science and Technology, Wuhan, China, 2009.
18. Wang, X.; Dai, S.; Sun, Y.; Li, D.; Zhang, W.; Zhang, Y.; Luo, Y. Modes of occurrence of fluorine in the Late Paleozoic No. 6 coal from the Haerwusu Surface Mine, Inner Mongolia, China. *Fuel* **2011**, *90*, 248–254. [CrossRef]
19. Dai, S.; Li, D.; Chou, C.-L.; Zhao, L.; Zhang, Y.; Ren, D.; Ma, Y.; Sun, Y. Mineralogy and geochemistry of boehmite-rich coals: New insights from the Haerwusu Surface Mine, Jungar Coalfield, Inner Mongolia, China. *Int. J. Coal Geol.* **2008**, *74*, 185–202. [CrossRef]
20. Guohua, L.; Qiyan, F.; Xiaoli, D.; Yahong, C.; Wenbo, L.; Hui, W.; Bo, G.; Lai, Z.; Xin, W. Geochemical characteristics of fluorine in coal within Xiangning mining area, China, and associated mitigation countermeasures. *Energy Explor. Exploit.* **2019**, *37*, 1737–1751. [CrossRef]
21. Liu, Z. The Research of Content of Distribution and Accurrence Form of Fluorine Element in Coals from Nantong Coalfield in Chongqing, China. Master's Thesis, Anhui University of Science and Technology, Huainan, China, 2016.
22. Wu, X. Fluorin Eemission Behavior and Conversion Characteristic in Industrial and Power Plant Boiler during Coal Combustion. Master's Thesis, Liaoning Technical University, Fuxin, China, 2005.
23. Prenger, F.C.; Stewart, W.F.; Hill, D.D.; Avens, L.R.; Worl, L.A.; Schake, A.; Aguero, K.J.d.; Padilla, D.D.; Tolt, T.L. *High Gradient Magnetic Separation Applied to Environmental Remediation*; Plenum Press: New York, NY, USA, 1994.
24. Liu, S.; Ye, X.; He, K.; Chen, Y.; Hu, Y. Simultaneous removal of Ni(II) and fluoride from a real flue gas desulfurization wastewater by electrocoagulation using Fe/C/Al electrode. *J. Water Reuse Desalination* **2016**, *7*, 288–297. [CrossRef]
25. Liu, X.F.; Zheng, C.G.; Song, D.Y.; Liu, J.; Zhang, J.Y. Migration behavior and washability of fluorine in Guizhou coal during cleaning process. In Proceedings of the 6th International Symposium on Coal Combustion, Wuhan, China, 1–5 December 2007; pp. 593–599.
26. Liu, D.; Sakai, Y.; Yamamoto, M.; Sadakata, M. Behavior of Fluorine in the Combustion of Chinese Coal in Small Furnaces. *Energy Fuels* **2006**, *20*, 1406–1410. [CrossRef]
27. Zhang, Z.; Yan, G.; Zhu, G.; Zhao, P.; Ma, Z.; Zhang, B. Using microwave pretreatment to improve the high-gradient magnetic-separation desulfurization of pulverized coal before combustion. *Fuel* **2020**, *274*, 117826. [CrossRef]
28. Mohanty, M.K.; Honaker, R.Q.; Mondal, K.; Paul, B.C.; Ho, K. Trace Element Reductions in Fine Coal Using Advanced Physical Cleaning. *Coal Prep.* **1998**, *19*, 195–211. [CrossRef]

29. Bu, X.; Ni, C.; Xie, G.; Peng, Y.; Ge, L.; Sha, J. Preliminary study on foreign slime for the gravity separation of coarse coal particles in a teeter bed separator. *Int. J. Miner. Processing* **2017**, *160*, 76–80. [CrossRef]
30. Galvin, K.P.; Pratten, S.J.; Nicol, S.K. Dense medium separation using a teetered bed separator. *Miner. Eng.* **1999**, *12*, 1059–1081. [CrossRef]
31. Jain, P.K. An analytical approach to explain complex flow in spiral concentrator and development of flow equations. *Miner. Eng.* **2021**, *174*, 107027. [CrossRef]
32. Ma, G.; Bu, X.; Xie, G.; Peng, Y.; Sha, J.; Xia, W.; Wu, E. Comparative Study of Separation Performance of a Spiral and Dense-medium Cyclone on Cleaning Coal. *Int. J. Coal Prep. Util.* **2021**, *41*, 108–116. [CrossRef]
33. Chen, J.; Chu, K.W.; Zou, R.P.; Yu, A.B.; Vince, A.; Barnett, G.D.; Barnett, P.J. How to optimize design and operation of dense medium cyclones in coal preparation. *Miner. Eng.* **2014**, *62*, 55–65. [CrossRef]
34. Napier-Munn, T. The dense medium cyclone—Past, present and future. *Miner. Eng.* **2018**, *116*, 107–113. [CrossRef]
35. Galvin, K.P.; Iveson, S.M. 10-Cleaning of coarse and small coal. In *The Coal Handbook: Towards Cleaner Production*; Osborne, D., Ed.; Woodhead Publishing: Cambridge, UK, 2013; Volume 1, pp. 263–300.
36. Tripathy, A.; Panda, L.; Sahoo, A.K.; Biswal, S.K.; Dwari, R.K.; Sahu, A.K. Statistical optimization study of jigging process on beneficiation of fine size high ash Indian non-coking coal. *Adv. Powder Technol.* **2016**, *27*, 1219–1224. [CrossRef]
37. Bu, X.; Xie, G.; Chen, Y.; Ni, C. The Order of Kinetic Models in Coal Fines Flotation. *Int. J. Coal Prep. Util.* **2017**, *37*, 113–123. [CrossRef]
38. Bu, X.; Zhou, S.; Danstan, J.K.; Bilal, M.; Ul Hassan, F.; Chao, N. Prediction of coal flotation performance using a modified deep neural network model including three input parameters from feed. *Energy Sources Part A Recover. Util. Environ. Eff.* **2022**, 1–13. [CrossRef]
39. Zhou, S.; Wang, X.; Bu, X.; Wang, M.; An, B.; Shao, H.; Ni, C.; Peng, Y.; Xie, G. A novel flotation technique combining carrier flotation and cavitation bubbles to enhance separation efficiency of ultra-fine particles. *Ultrason. Sonochem.* **2020**, *64*, 105005. [CrossRef]
40. Wang, X.; Bu, X.; Ni, C.; Zhou, S.; Yang, X.; Zhang, J.; Alheshibri, M.; Peng, Y.; Xie, G. Effect of scrubbing medium's particle size on scrubbing flotation performance and mineralogical characteristics of microcrystalline graphite. *Miner. Eng.* **2021**, *163*, 106766. [CrossRef]
41. Bu, X.; Zhang, T.; Peng, Y.; Xie, G.; Wu, E. Multi-Stage Flotation for the Removal of Ash from Fine Graphite Using Mechanical and Centrifugal Forces. *Minerals* **2018**, *8*, 15. [CrossRef]
42. Zhang, Q.; Niu, C.; Bu, X.; Bilal, M.; Ni, C.; Peng, Y. Enhancement of Flotation Performance of Oxidized Coal by the Mixture of Laurylamine Dipropylene Diamine and Kerosene. *Minerals* **2021**, *11*, 1271. [CrossRef]
43. Randolph, J.M. Characterizing Flotation Response: A Theoretical and Experimental Comparison of Techniques. Master's Thesis, Virginia Polytechnic Institute and State University, Blacksburg, VA, USA, 1997.
44. Xia, W.; Yang, J.; Liang, C. A short review of improvement in flotation of low rank/oxidized coals by pretreatments. *Powder Technol.* **2013**, *237*, 1–8. [CrossRef]
45. Ni, C.; Bu, X.; Xia, W.; Liu, B.; Peng, Y.; Xie, G. Improving lignite flotation performance by enhancing the froth properties using polyoxyethylene sorbitan monostearate. *Int. J. Miner. Process.* **2016**, *155*, 99–105. [CrossRef]
46. Mao, Y.; Bu, X.; Peng, Y.; Tian, F.; Xie, G. Effects of simultaneous ultrasonic treatment on the separation selectivity and flotation kinetics of high-ash lignite. *Fuel* **2020**, *259*, 116270. [CrossRef]
47. Drzymala, J.; Ahmed, H.A.M. Mathematical equations for approximation of separation results using the Fuerstenau upgrading curves. *Int. J. Miner. Process.* **2005**, *76*, 55–65. [CrossRef]
48. Drzymala, J.; Kowalczuk, P.B.; Oteng-Peprah, M.; Foszcz, D.; Muszer, A.; Henc, T.; Luszczkiewicz, A. Application of the grade-recovery curve in the batch flotation of Polish copper ore. *Miner. Eng.* **2013**, *49*, 17–23. [CrossRef]
49. Bu, X.; Zhang, T.; Chen, Y.; Xie, G.; Peng, Y. Comparative study of conventional cell and cyclonic microbubble flotation column for upgrading a difficult-to-float Chinese coking coal using statistical evaluation. *Int. J. Coal Prep. Util.* **2020**, *40*, 359–375. [CrossRef]
50. Bu, X.; Zhang, T.; Chen, Y.; Peng, Y.; Xie, G.; Wu, E. Comparison of mechanical flotation cell and cyclonic microbubble flotation column in terms of separation performance for fine graphite. *Physicochem. Probl. Miner. Process.* **2018**, *54*, 732–740. [CrossRef]
51. Paul, S.R.; Bhattacharya, S. Size by Size Separation Characteristics of a Coal Cleaning Jig. *Trans. Indian Inst. Met.* **2018**, *71*, 1439–1444. [CrossRef]
52. Chinese Standard GB/T, GBT, GB. Available online: www.ChineseStandard.net (accessed on 14 January 2022).