Distribution and Migration of Trace Elements during Flotation in Ge-Rich Low-Rank Coal from Wulantuga Coal Mine, Inner Mongolia, China

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ABSTRACT: The high-Ge low-rank coal in Wulantuga Coal Mine, Inner Mongolia, China, has a high utilization value due to its enrichment of critical element Ge. However, it is also enriched with toxic elements such as Be, F, As, and Hg; therefore, the coal should be cleaned before use. In this study, the flotation experiment, X-ray diffraction (XRD), X-ray fluorescence (XRF), Fourier transform infrared (FTIR) analysis, and the release experiment for the high-Ge low-rank coal from Wulantuga were carried out, and the results are as follows. (1) The total mineral content of the feed coal is higher than that of the cleaned coal and tailing, and the content of the functional group −OH is also increased, indicating that the moisture in the cleaned coal is increased after flotation. (2) Argillation occurred and some minerals (dihydrate gypsum and kaolinite) and elements were released into the water during flotation, so the ash yield and the percentage of TiO₂, Al₂O₃, Fe₂O₃, MgO, and CaO of the cleaned coal and tailing are lower than those of feed coal. (3) The concentrations of elements Li, Be, F, Mn, Zn, Sr, Hg, Ti, and Pb of the cleaned coal are higher than those of tailing, indicating that these elements are more likely to occur in organic matter or fine-grained mineral embedded in organics, but the concentration of other elements such as Ge, As, Sb, and W in the cleaned coal is lower than that of tailing, suggesting that these elements are weakly associated with organics or occur in minerals. (4) After flotation, trace elements Be, Cs, Ti, Ge, Sb, and W enriched in the feed coal were removed in large quantities, while F, As, and Hg were difficult to remove; therefore, other preparation methods should be tried. (5) The release experiment showed that the release rate of chalcophile and siderophile elements and rare earth elements and yttrium (REY) is relatively higher. In addition to those of Be, Ga, Sr, and Cs, the release rate of most elements is relatively low.

INTRODUCTION

Coal is one of the main energy sources in China. With the increasing consumption of coal resources, the efficient utilization of low-rank coal should be greatly strengthened. Low-rank coal in China is mainly distributed in North China, with the eastern region of Inner Mongolia having the largest low-rank coal resources. In China, low-rank coal is mainly used for power generation and the coal ash can also be used as a raw material for extracting critical elements such as Ge, Ga, U, V, and rare earth elements and yttrium (REY). Previous studies have shown that low-rank coal in Wulantuga Coal Mine is highly enriched with trace elements Be, F, Ge, As, and Hg and the concentration of Ge is of industrial grade. However, the toxic trace elements Be, F, As, and Hg are released into the environment during combustion. Therefore, whether from the perspective of the utilization of critical elements or environmental protection, the low-rank coal from Wulantuga should be cleaned before use.

Flotation is an effective method for industrial coal preparation. Flotation can separate minerals from coal according to the surface property difference between coal and minerals. Duan et al. studied the removal of toxic elements via the flotation of high-sulfur coal in Southwestern China and found that flotation was an effective way to remove toxic elements from coal. Liu et al. found that Hg was obviously removed from fine coal by combined flotation and gravity separation approaches. Zhou et al. found that the removal rate of arsenic in coal by flotation was higher than that by gravity separation. Different from the high-rank coal, the low-rank coal contains more hydroxyl, carboxyl, and carbonyl hydrophilic groups, which accounts for its high porosity and poor floatability. In addition, low-rank coal may undergo argillation during flotation, but the mechanism of the migration of trace elements in the process of flotation is not clear. In this study, the low-rank coal from the Wulantaga coal mine, Inner Mongolia,
China, was selected as a research object. The study of the differences of various functional groups before and after flotation, and the migration and release of toxic elements in the low-rank coal during flotation can provide a scientific basis for environmental protection and effective utilization of valuable elements.

**SAMPLE AND METHODS**

Wulantuga Coal Mine is located in the southwestern part of the Shengli coalfield, Inner Mongolia, China. The feed coal sample was collected from Wulantuga Coal Mine belonging to the Shengli Formation of the Lower Cretaceous.

Proximate analysis (moisture, ash, and volatile matter) was conducted following ASTM Standards D3173-11,26 D3174-11,27 and D3175-11,28 respectively. The total sulfur and forms of sulfur were determined following ASTM Standards D3177-02,29 D3178-02,30 and D2492-02,30 respectively. Fluorine was determined by pyrohydrolysis combined with an ion-selective electrode following the ASTM method D 5987-96.31 Arenic and Hg were measured by atomic fluorescence spectrometry (ASF2202), and Se was determined by atomic fluorescence spectrometry (LC-6500). The other elements were determined by inductively coupled plasma mass spectrometry (X Series II ICP-MS). The ICP-MS analyses and microwave digestion program for the samples followed the methods described by Dai et al.32

Coal flotation tests were performed according to the Chinese national standard GB/T 4757.33 Deionized water and 50 g of coal samples (<0.5 mm) were added into a 1.5 L single flotation cell (XFD-63) and stirred for 3 min to mix the coal slurry uniformly. Subsequently, collector (diesel), and frother (XFD-63) and stirred for 10 min at 1800 RPM, and the filtrate was obtained after filtration. The concentration of trace elements in the filtrate was determined by ICP-MS.

FTIR (Bruker, VERTEX 80v) was used to determine the functional groups of organic matter in the coal. Prior to FTIR analysis, the samples were dried and ground to less than 200 mesh, mixed with KBr, and compressed into disks. All spectra were recorded at a resolution of 4 cm\(^{-1}\) and the scans were repeated 32 times. Spectra were collected in the range of 4000–400 cm\(^{-1}\).

X-ray fluorescence (XRF) spectrometry (BRUKER S8, TIGER) was used to determine the oxides of major elements in the coal, including SiO\(_2\), TiO\(_2\), Al\(_2\)O\(_3\), FeO\(_3\), MgO, CaO, MnO, Na\(_2\)O, and K\(_2\)O. The maximum working voltage and current were 4 kV and 17 0mA, respectively. Prior to the XRF analysis, the samples were dried and ground to less than 200 mesh.

The coal samples were analyzed by XRD using a D/max-2500/PC powder diffractometer with Ni-filtered Cu Kα radiation and a scintillation detector. The XRD patterns were recorded in a 2θ interval of 2.6–70° with a step size of 0.01°. In addition, the TOPAS 4.2 software was used to conduct quantitative mineralogical analysis for X-ray diffractograms of coals.

### RESULTS AND DISCUSSION

**Coal Chemistry.** Proximate analysis, total sulfur, and forms of sulfur for the Wulantuga coal are listed in Table 1. The volatile matter content of the sample is 43.58%, indicating that the Wulantuga coal is sub-bituminous coal according to the ASTM classification.34 The Wulantuga coal is classified as a “low-ash coal” according to GB 15224.1-2004 (coal with ash yield <10% is classified as low-ash coal).35 The total sulfur content in the coal is 2.82%, suggesting it to be medium-sulfur coal according to Chou36 and GB/T 15224.2-2004 (coal with the total sulfur content of 2–3% is medium-sulfur coal).37 Sulfate sulfur is the dominant form of sulfur.

| TABLE 1. Proximate Analysis and Sulfur Analysis |
|-----------------------------------------------|
| proximate analysis (%) | sulfur analysis (%) |
| M_d  | A_d | V_daf | S_d | S_p,d | S_o,d | S_s,d |
| 11.48 | 8.81 | 43.58 | 2.82 | 0.45 | 2.11 | 0.26 |

*M, moisture; A, ash yield; V, volatile matter; S, total sulfur; S_p, pyritic sulfur; S_o, organic sulfur; ad, air-dry basis; d, dry basis; daf, dry air basis.

### Trace Elements in Coal.**

The concentration of trace elements in the Wulantuga coal (feed coal) is listed in Table 4. The concentration coefficient (CC) is the ratio of trace elements in samples investigated vs averages for world low-rank coals38 is shown in Figure 1. Based on the classification of enrichment proposed by Dai et al.,39 elements Ge, Sb, and W are unusually enriched (CC > 100); Be, F, As, and Hg are significantly enriched (10 < CC < 100); Cs and Ti are slightly enriched (2 < CC < 5); Zn, Ga, Mo, and Sn (0.5 < CC < 2) are close to their average values in world coals; and other trace elements are depleted (CC < 0.5).

**Distribution of Mineral and Organic Functional Groups during Flotation.** Quantitative mineralogical compositions of feed coal, cleaned coal, and tailing are listed in Table 2. As shown in Table 2, the percentage of mineral in the cleaned coal is the lowest, and the percentage of mineral in the feed coal is higher than that in the cleaned coal and tailing, which is consistent with the distribution of ash yield in feed coal, cleaned coal, and tailing, indicating the occurrence of argillation and the release of some minerals (dihydrate gypsum and kaolinite) into the water during flotation. Dihydrate gypsum is not detected in the cleaned coal because dihydrate gypsum is slightly soluble in water; therefore, the dihydrate gypsum in tailing is lower than that in feed coal. In addition, quartz and kaolinite in the cleaned coal and tailing are lower than that in feed coal, but the content of quartz and kaolinite in the cleaned coal is higher than that in tailing, which may be because quartz and kaolinite are mixed in the organic matter of the cleaned coal with fine-grained size. Trace amounts of pyrite were observed under electron microscopy but did not appear in the XRD pattern, possibly because it was below the detection limit of XRD.

The low-rank coal has a high content of hydroxyl, carboxyl, and carbonyl groups, so FTIR is used to study the variation in the contents of different functional groups before and after flotation. The results of the FTIR analysis of cleaned coal and feed coal are shown in Figure 2.

Infrared bands in the range of 3600–3100 cm\(^{-1}\) are attributed to the OH stretching vibrations of the coordinated water or bonded OH.40 The content of the –OH functional group in the cleaned coal is higher than that in the feed coal, indicating that
after flotation, the moisture of the cleaned coal is higher than that in the feed coal. The band occurring in the range of 3100−2800 cm\(^{-1}\) corresponds to the tensile absorption peaks of the C−H functional groups of \(-\text{CH}_3, -\text{CH}_2-,\) aliphatic, and aromatic. Bands that occur in the range of 1700−1450 cm\(^{-1}\) correspond to the stretching vibrations of aromatic C\(\equiv\)O and C\(\equiv\)C and bonded OH.\(^{41,43}\) Infrared bands in the range of 1250−900 cm\(^{-1}\) are related to the stretching vibrations of C\(\equiv\)O (carbonyl) and \(-\text{O}-\) (ether group).\(^{40,44−46}\) The flexural vibrations of H groups that lie in the range of 870−600 cm\(^{-1}\) are vibrations of aromatic nuclei and benzene rings.\(^{47}\)

Figure 2 shows that the content of the functional groups of C−H, C\(\equiv\)C, and C\(\equiv\)O in the cleaned coal is lower than that in the feed coal. An infrared band at 530 cm\(^{-1}\) is the elastic vibrations of the Si−O functional group in kaolinite and that at 462 cm\(^{-1}\) is the elastic vibrations of the Si−O functional group in quartz.\(^{45,46}\) Compared with that in the feed coal, the peak intensity of the Si−O group in the cleaned coal is lower, indicating that a part of aluminosilica minerals and quartz are removed through flotation but the content of OH in the cleaned coal is increased. This shows that the moisture of the cleaned coal increases after flotation.

### Distribution of Oxides of Major Element during Flotation.

The yield, ash yield, and percentage of oxides of major elements in the Wulantuga coal and flotation products are shown in Table 3. The total yield of the cleaned coal and tailing obtained by flotation is 84.46%. In addition, the ash yield and the percentages of TiO\(_2\), Al\(_2\)O\(_3\), Fe\(_2\)O\(_3\), MgO, and CaO in the cleaned coal and tailing are lower than those of feed coal, indicating that argillation occurs and some minerals (dihydrate gypsum and kaolinite) and elements are released into the water during flotation. The percentage of SiO\(_2\) and K\(_2\)O in the feed coal is slightly lower than that of the cleaned coal and tailing. Compared to the world coal, except for Fe\(_2\)O\(_3\), the percentage of other oxides of major elements in the Wulantuga coal are lower than that in the world coal.

### Distribution of Trace Elements in Floating Products.

The distribution of trace elements in feed coal, cleaned coal, and tailing is listed in Table 4 and shown in Figure 3.

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**Table 2. Percentages of Minerals in the Feed Coal and Floating Products (%)**

| sample     | dihydrate gypsum | quartz | kaolinite | total |
|------------|------------------|--------|-----------|-------|
| cleaned coal | bdl\(^a\)       | 4.13   | 0.89      | 5.02  |
| tailings  |        | 2.85   | 3.87      | 0.40  | 7.12  |
| feed coal |        | 4.64   | 4.23      | 1.13  | 10.00 |

\(\text{bdl, below the detection limit.}\)

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Figure 3 shows that the concentrations of Li, Be, F, Mn, Zn, Sr, Hg, Tl, and Pb in the cleaned coal are higher than those in tailing, indicating that these elements mainly occur in organic matter or fine-grained minerals embedded in organic matter. The concentrations of other trace elements such as Ge, As, Sb, and W in the cleaned coal are lower than those in tailing. Wei and Rimmer\textsuperscript{10,11} studied the mode of occurrence of Ge, As, Sb, and W by electron probe microanalysis and acid leaching and

Table 3. Yield, Ash Yield, and Percentages of Oxides of Major Elements in the Feed Coal and Floating Products (\%)\textsuperscript{a}

| sample        | yield | A\textsubscript{j} | SiO\textsubscript{2} | TiO\textsubscript{2} | Al\textsubscript{2}O\textsubscript{3} | Fe\textsubscript{2}O\textsubscript{3} | MgO | CaO | Na\textsubscript{2}O | K\textsubscript{2}O | P\textsubscript{2}O\textsubscript{5} |
|---------------|-------|-------------------|----------------------|----------------------|-----------------------------------|---------------------------------|------|-----|---------------------|---------------------|---------------------|
| cleaned coal  | 30.72 | 4.70              | 3.30                 | 0.05                 | bdll                              | 1.90                           | 0.11 | 0.18 | bdll                 | 0.075               | 0.005               |
| tailing       | 53.74 | 6.04              | 3.06                 | 0.06                 | bdll                              | 2.00                           | 0.07 | 0.15 | bdll                 | 0.051               | 0.003               |
| feed coal     | 100   | 8.81              | 2.88                 | 0.06                 | 1.09                              | 4.16                           | 0.19 | 0.53 | 0.06                 | 0.046               | 0.007               |
| world coal\textsuperscript{b} | nd    | nd                | 8.47                 | 0.33                 | 5.98                              | 4.85                           | 0.22 | 1.23 | 0.16                 | 0.19                | 0.092               |

\textsuperscript{a}bdll, below the detection limit; nd, no data. \textsuperscript{b}Ketris and Yudovich.\textsuperscript{38}

Table 4. Concentrations of Trace Elements in the Feed Coal and Floating Products (\(\mu g/g\))

| sample        | Li   | Be   | F    | Sc   | Ti   | V    | Cr   | Mn   | Co   | Ni   | Cu   | Zn   | Ga   |
|---------------|------|------|------|------|------|------|------|------|------|------|------|------|------|
| cleaned coal  | 2.91 | 6.48 | 976  | 0.42 | 146.99| 2.61 | 4.28 | 7.34 | 0.34 | 0.83 | 2.23 | 4.15 | 3.09 |
| tailing       | 2.59 | 5.00 | 822  | 0.49 | 217.72| 3.02 | 5.70 | 4.41 | 0.47 | 1.55 | 2.75 | 2.05 | 5.08 |
| feed coal     | 2.88 | 16.5 | 1014 | 1.19 | 205.71| 4.83 | 5.21 | 27.4 | 0.94 | 2.89 | 3.87 | 12.0 | 6.58 |

| sample        | Ge   | As   | Se   | Rb   | Sr   | Zr   | Nb   | Mo   | Cd   | In   | Sn   | Sb   | Cs   |
|---------------|------|------|------|------|------|------|------|------|------|------|------|------|------|
| cleaned coal  | 125.7| 326.6| <0.065| 2.17 | 24.6 | 6.19 | 0.60 | 0.65 | 0.004| 0.002| 0.26 | 30.4 | 2.40 |
| tailing       | 321.9| 485.4| 0.196 | 2.50 | 13.0 | 9.48 | 1.11 | 1.46 | 0.006| 0.002| 0.33 | 80.1 | 2.41 |
| feed coal     | 264.4| 467.0| <0.065| 2.58 | 24.5 | 7.97 | 1.00 | 1.68 | 0.019| 0.005| 0.58 | 134  | 3.78 |

| sample        | Ba   | Hf   | Ta   | W    | Hg   | Ti   | Pb   | Bi\textsuperscript{c} | Th   | U    | La   | Ce   | Pr   |
|---------------|------|------|------|------|------|------|------|------------------------|------|------|------|------|------|
| cleaned coal  | 35.0 | 0.20 | 0.012| 138  | 9.56 | 1.69 | 5.32 | 0.057                  | 0.31 | 1.91 | 2.89 | 0.32 |
| tailing       | 120  | 0.31 | 0.062| 333  | 3.56 | 0.99 | 2.70 | 0.059                  | 0.44 | 1.99 | 3.11 | 0.35 |
| feed coal     | 44.2 | 0.26 | 0.088| 278  | 5.15 | 2.36 | 6.32 | 0.029                  | 0.77 | 0.21 | 2.68 | 4.60 | 0.54 |

| sample        | Nd   | Sm   | Eu   | Gd   | Tb   | Dy   | Y    | Ho   | Er   | Tm   | Yb   | Lu   |
|---------------|------|------|------|------|------|------|------|------|------|------|------|------|
| cleaned coal  | 1.17 | 0.20 | 0.05 | 0.18 | 0.03 | 0.16 | 0.89 | 0.03 | 0.09 | 0.02 | 0.10 | 0.01 |
| tailing       | 1.27 | 0.23 | 0.08 | 0.19 | 0.03 | 0.18 | 0.95 | 0.04 | 0.11 | 0.02 | 0.11 | 0.02 |
| feed coal     | 2.16 | 0.42 | 0.09 | 0.38 | 0.06 | 2.07 | 0.07 | 0.21 | 0.04 | 0.22 | 0.03 | 0.03 |

\textsuperscript{c}Bismuth in cleaned coal and tailing was higher than that in feed coal, which may be caused by the release of trace elements from diesel collector.

Figure 3. Distribution of trace elements in the feed coal and floating products.
showed that these elements were weakly bonded to organic matter or occur in fine-ground sulfate minerals, quartz, pyrite, and other minerals. Based on the previous studies and the flotation experiment, elements Ge, As, Sb, and W are weakly bonded to organic matter or occur in fine-grained minerals. Elements Ga, Rb, Mo, Cd, In, Sn, Sb, Cs, Ta, Tl, and Pb in the cleaned coal and tailing are lower than that in feed coal because part of these elements is released into coal preparation water during flotation. Consequently, the treatment of filtrate after flotation should be strengthened, which can prevent the coal preparation wastewater from polluting the environment.

The REY in feed coal, cleaned coal, and tailing are normalized to the upper continental crust (UCC). The distribution of UCC-normalized REY is shown in Figure 4. The concentrations of REY in tailing are higher than that in the cleaned coal, indicating that REY mainly occur in minerals, but the concentrations of REY in the cleaned coal and tailing are lower than those in feed coal because part of these elements is released into coal preparation water during flotation.

Figure 3 shows that the concentrations of trace elements Be, F, Sc, V, Mn, Co, Ni, Cu, Zn, Ga, Rb, Mo, Cd, In, Sn, Sb, Cs, Ta, Tl, and Pb in the cleaned coal and tailing are lower than those in feed coal because part of these elements is released into coal preparation water during flotation. Consequently, the treatment of filtrate after flotation should be strengthened, which can prevent the coal preparation wastewater from polluting the environment.

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lower than that in feed coal, indicating that REY migrated to coal preparation wastewater during flotation.

**Removability of Trace Elements.** To study the degree of reduction of trace elements during coal preparation, the following equation was used to calculate the removability.

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

where \( R_i \) is the removability, \( c_i \) is the concentration of element \( i \) in the cleaned coal or tailing, and \( C_i \) is the concentration of element \( i \) in the feed coal. The removability of coal ash and trace elements of the cleaned coal are listed in Table 5 and shown in Figure 5. Because the concentrations of some trace elements in the cleaned coal and tailing are lower than that in the feed coal, the removability of trace elements in the cleaned coal and tailing is calculated to reflect the migration of trace elements from feed coal to the cleaned coal and tailing.

From Table 5 and Figure 5, the removability of unusually enriched elements Ge, Sb, and W in the cleaned coal is higher than 50%. The removability of significantly enriched element Be in the cleaned coal is more than 60%, and the removability of elements F and As is about 30%. The removability of the slightly enriched elements Cs and Ti is under 50%. The removability of Sc, Co, Ni, Cu, Zn, Ga, Mo, Cd, In, Sn, and Ta is higher than 50%, while Hg is enriched in the cleaned coal and the removability of other elements is lower.

The removability of a few elements such as Ti, Cr, Ge, As, Zr, Nb, Ba, Hf, W, and Bi in the tailing is lower than 0, which indicated that these elements are enriched in the tailing and occur in minerals. The removability of other elements is all higher than 0, which indicated that these elements migrated to the cleaned coal or coal preparation wastewater.

The removability of REY in the cleaned coal and tailing is shown in Figure 6. Except for the removability of a few REY (La, Ce, Pr, and Eu) below 40%, the removability of the remaining REY in the cleaned coal and tailing can reach nearly 50% or above. Because REY generally occur in the clay minerals, leading the release of some REY into the coal preparation wastewater along with the clay minerals.

**Migration of Toxic Elements during Release Experiment.** During flotation, some trace elements migrated to coal preparation wastewater, so the release experiment was carried out to quantitatively study the release of trace elements to coal preparation wastewater. The release rate of trace elements in coal is shown in Table 6. The release rate can be calculated by the following formula

\[ \text{release rate} = \left( \frac{\text{concentration of element } i \text{ in filtrate}}{\text{volume of filtrate}} \right) \times \frac{100\%}{\text{concentration of element } i \text{ in feed coal} \times \text{total content of element } i \text{ in feed coal}} \]

where \( i \) is the trace element.

As listed in Table 6, the release rates of sulfurophile and siderophile elements Sc, V, Mn, Co, Ni, Zn, Cd, and Tl into water are higher than 45%. The release rates of most REY are between 30 and 60%, and the release rates of elements Be, Ga, Sr, and Cs are also relatively high. The high release rates of these lithophile elements are because they may occur in clay minerals that are easily muddied and released to the coal preparation wastewater. The release rate of elements such as Ge, Sb, and W is low because these elements occur in organic matter or minerals, which did not undergo argillization easily.

**CONCLUSIONS**

The total mineral content of the feed coal is higher than that of the cleaned coal and the tailing, and the contents of dihydrate gypsum, quartz, and kaolinite in the cleaned coal and the tailing are lower than that in the feed coal. The contents of C–H, C═C, and C═O are reduced by flotation but that of OH is
increased, indicating that the moisture in the cleaned coal increases after flotation.

Because of the argillation and some minerals (dihydrate gypsum and kaolinite) and elements are released into water during flotation, the contents of $\text{Al}_2\text{O}_3$, $\text{Fe}_2\text{O}_3$, Mg, and Ca of the cleaned coal and the tailing are lower than that of the feed coal. The concentrations of elements Li, Be, F, Mn, Zn, Sr, Hg, Ti, and Pb are higher than that of tailing, indicating that these elements are more likely to occur in the organic matter or fine-grained minerals. The concentration of the rest elements such as Ge, As, Sb, and W in the cleaned coal is lower than that of the tailing, suggesting that these elements are weakly bonded to organic matter or occur in fine-grained minerals.

After flotation, the enriched elements Be, Ca, Ti, Ge, Sb, and W were removed in large quantities, while F, As, and Hg were difficult to remove. In view of the poor removal effect of flotation, it is suggested to use gravity separation or dry coal preparation to remove toxic elements.

During flotation, some trace elements are released into coal preparation wastewater, so it is necessary to strengthen the treatment of the filtrate after flotation to prevent the coal preparation wastewater from polluting the environment.

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Notes
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