

THE AFFINITY OF RARE EARTH ELEMENTS IN HUADIAN AND LUOZIGOU OIL SHALES OF CHINA

JINGRU BAI^{*}, KUNTONG SONG, KUN LI

Engineering Research Centre of Oil Shale Comprehensive Utilization, Northeast Electric Power University, Ministry of Education, Jilin 132012, P.R. China

Abstract. *Rare earth elements (REEs) are important geochemical indicators and they can provide a lot of useful pertinent information. The inorganic/organic affinity of REEs in Huadian and Luozigou oil shales from Jilin Province, China, was determined using the float-sink and acid-washing tests and sequential chemical extraction methods. The constituents of REEs were determined employing inductively coupled plasma-mass spectrometry (ICP-MS). The results of the float-sink test indicated that the concentration of REEs increased with increasing specific gravity, while during the acid-washing tests, REEs were removed from oil shale. The linear regression of REEs and ash content revealed that the majority of the elements were associated with minerals in coal. In addition, acid washing proved to influence the desorption of REEs. REEs in oil shale exist mainly in the mineral fraction, while the organic fraction plays a major role in their aggregation, especially in case of light rare earth elements (LREEs). REEs in oil shale derived from terrigenous clastic rocks when they were absorbed by organic matter or minerals.*

Keywords: *oil shale fractions, rare earth elements, inorganic/organic affinity, float-sink test, acid-washing test, sequential chemical extraction.*

1. Introduction

Rare earth elements (REEs) are important geochemical indicators, representing a rich source of pertinent information. Previously investigators dealt with REEs to provide information about coal geology, environmental science and material science [1]. Compared with analysis of trace elements in coal, investigations into REEs in coal have mainly concentrated on their mass fraction, geology and genesis of enrichment. The study of the mode of occurrence of REEs is also important in terms of determining their release ability in coal.

^{*} Corresponding author: e-mail jibjr@163.com

The float-sink test [2–9], the acid-washing test [10–11] and chemical sequential extraction methods [12–16] have been widely used in researching the mode of occurrence of trace elements in coal (inorganic/organic affinity of elements), as well as the occurrence of REEs in coal. Zhao et al. [17], employing the float-sink test, showed that REEs in coal were closely related to inorganic components, but were not correlated with water or plant source materials. Based on the results of the acid-washing test and quantifying analysis, Yang [18] found that light rare earth elements (LREEs) and heavy rare earth elements (HREEs) obeyed completely different rules of organic affinity evolution. Dai et al. [19], using a sequential chemical extraction method, studied the occurrence states of REEs in coal. The researchers discovered that the amounts of REEs in coal were mainly controlled by clay mineral content, followed by organic matter, and the elements existed mainly in combinations of silicon and aluminum compounds.

Oil shale is a fine-grained sedimentary rock, having subtle bedding and being rich in organic matter. The majority of the organic matter is oil material which is insoluble in ordinary organic solvents. Apart from the investigations by Liu [20] and Gao et al. [21] on the REEs content in Chinese Huadian oil shale, researches into the occurrence state of REEs in oil shale have rarely been reported.

In this paper, the organic/inorganic affinity of REEs in Chinese Huadian and Luozigou oil shales (resp HOS and LOS) was investigated using the float-sink and acid-washing tests and sequential chemical extraction methods. The state of occurrence of REEs in HOS and LOS was also studied. This information is important for revealing the geological formation of oil shales and establishing the rational utilization of the resources. The current research will also provide a foundation for the development of green oil shale industry.

2. Experimental

Huadian oil shale and Luozigou oil shale were selected as experimental objects. The proximate and ultimate analyses of HOS and LOS obeyed Chinese national standards “Proximate analysis of coal” (GB/T212-2001) [22] and “Ultimate analysis of coal” (GB/T467-2001) [23], respectively. The determination of calorific value of oil shales followed the Chinese National Standard “Determination of calorific value of coal” (GB/T213-2003) [24]. The analysis results (air-dry basis) are given in Table 1.

Minerals in Chinese oil shale originate mainly from continental rocks. The most common minerals in Chinese continental oil shale are quartz, feldspars, clay minerals, calcite, siderite and pyrite. Quartz belongs chiefly to terrigenous clastics, but in the nature there is also found quartz of chemical sedimentary origin. The results of X-ray diffraction analysis (XRD) of oil shale samples are presented in Table 2. The Huadian oil shale

is mainly a clay mineral, and the Luozigou oil shale is predominantly a terrigenous clastic mineral.

After digestion (HF-HClO₄-HNO₃) of oil shale samples, the content of REEs was determined using inductively coupled plasma-mass spectrometry (ICP-MS). The results of testing are given in Table 3.

Table 1. Proximate and ultimate analysis of oil shale samples

| Sample | Proximate, % | | | | Ultimate, % | | | | | | Q _{ar,net} , kJ/kg |
|--------|----------------|-----------------|-----------------|------------------|-----------------|-----------------|-----------------|-----------------|-----------------|------|--------------------------------|
| | M _t | A _{ar} | V _{ar} | FC _{ar} | C _{ar} | H _{ar} | O _{ar} | N _{ar} | S _{ar} | H/C | |
| HOS | 7.51 | 50.28 | 39.44 | 2.77 | 27.84 | 3.79 | 6.15 | 0.69 | 3.74 | 1.63 | 11539.14 |
| LOS | 2.58 | 72.24 | 20.44 | 4.74 | 13.17 | 1.55 | 9.46 | 0.59 | 0.41 | 1.41 | 5226.48 |

Note: _t – total; _{ar,net} – air-dry basis.

Table 2. X-ray analysis of oil shale samples

| Sample | The relative content of minerals, % | | | | | | | | | | | |
|--------|-------------------------------------|-----------------|----------|--------|-------|-------------------------------|-----------|-------------|-------|--------------------|----------------|--------|
| | Clay minerals | | | | | Terrigenous detrital minerals | | | | Carbonate minerals | Other minerals | |
| | Kaolinite | Montmorillonite | Smectite | Illite | Total | Quartz | Feldspars | Palgioclase | Total | Calcite | Siderite | Pyrite |
| HOS | 2 | 57 | — | — | 59 | 14 | 1 | 1 | 16 | 22 | — | 3 |
| LOS | 6 | — | 4 | 5 | 15 | 51 | 19 | 15 | 85 | — | — | — |

Note: “—” represents no data.

Table 3. The content of REEs in oil shale samples, μg/g

| Sample | La | Ce | Pr | Nd | Sm | Eu | Gd | Tb | Dy | Ho | Er | Tm | Yb | Lu |
|--------|-------|-------|------|-------|------|------|------|------|------|------|------|------|------|------|
| HOS | 23.92 | 40.77 | 5.55 | 19.57 | 3.40 | 0.76 | 3.27 | 0.50 | 2.58 | 0.51 | 1.53 | 0.25 | 1.44 | 0.22 |
| LOS | 30.86 | 64.22 | 6.88 | 26.61 | 4.97 | 1.18 | 4.61 | 0.78 | 3.75 | 0.76 | 2.15 | 0.31 | 1.96 | 0.30 |

2.1. Float-sink test

The float-sink test is one of the most effective methods to study the organic/inorganic affinity of trace elements. This approach determines the content of trace elements at different density component levels to indirectly identify their occurrence in coal.

The test carried out in this work followed the Chinese National Standard “Method for float-sink analysis of coal” (GB/T478-2008) [25]. Due to the low content of organic matter in the oil shale samples under study, the density of a liquid less than 1.4 g/cm³ set in the standard was too low to enable their analysis. Therefore in the current investigation, the liquid

density of at least 1.5 g/cm^3 was used. At the same time, in order to avoid various density separation series and low production rates of individual densities, a four-stage density separation for HOS and a five-stage density separation for LOS were performed. In the product of each density level, the contents of ash, REEs and mineral components were determined. In the test, methylene chloride (CH_2Cl_2) and carbon tetrachloride (CCl_4) were used as organic solvents (heavy liquids) to ensure the purity of analysis. The density levels of HOS samples were the following: $< 1.5 \text{ g/cm}^3$ (HD1), $1.5\text{--}1.6 \text{ g/cm}^3$ (HD2), $1.6\text{--}2.0 \text{ g/cm}^3$ (HD3) and $> 2.0 \text{ g/cm}^3$ (HD4), and those of LOS samples were: $< 1.5 \text{ g/cm}^3$ (LD1), $1.5\text{--}1.6 \text{ g/cm}^3$ (LD2), $1.6\text{--}2.0 \text{ g/cm}^3$ (LD3), $2.0\text{--}2.4 \text{ g/cm}^3$ (LD4) and $> 2.4 \text{ g/cm}^3$ (LD5).

2.2. Acid-washing test

To investigate the affinity between REEs and minerals in HOS and LOS, the samples were subjected to the ash-washing test to remove ash. Based on the results of orthogonal experiments, the most optimum liquid ratio for ash removal was 1:10 g/mL. Acid washing was carried out using acids in the order HCl-HF-HCl, the washing time was two hours [26]. The acid-washed HOS and LOS samples were labeled as HAW and LAW, respectively. The test was conducted under the following conditions: water bath temperature $75 \text{ }^\circ\text{C}$, HCl concentration 5 mol/L, HF concentration 40% and hexafluoro-silicic acid (H_2SiF_6) concentration 30%. All the chemicals were analytical grade, and demonized water was ultrapure.

2.3. Sequential chemical extraction

Sequential chemical extraction (SCE) is one of the most efficient techniques to study the occurrence of chemical elements in different materials. This approach is based on the method used to extract trace elements from soil. Recently, SCE has been widely used to investigate the mode of occurrence of trace elements in oil shale. In this study, we developed a 6-step SCE method (Table 4) to analyze the oil shale samples for trace elements contents. During SCE, the samples were processed in parallel, incorporating blank samples. The reagents used were premium grade pure or analytical pure, and water was secondary distilled water. Glass and plastic utensils were soaked overnight in a 1:1 HNO_3 solution before rinsing with secondary distilled water.

2.4. Trace elements test

The electrothermal digestion method was used to liquefy the original oil shale samples, and, after the float-sink and acid-washing tests and SCE, also the solid oil shale samples. The contents of REEs were determined using ICP-MS at the Test Center of Jilin University.

Table 4. Steps of sequential chemical extraction

| SCE step | Fraction | Extraction solution | Operation conditions |
|----------|------------------------------------|---|---|
| I | Exchangeable | MgCl ₂ (1 mol/L, pH = 7) | Shake for 4 h at room temperature |
| II | Carbonate-bound | CH ₃ COONa (1 mol/L, pH = 5) | Shake for 5 h at room temperature |
| III | Ferromanganese oxyhydroxides-bound | CH ₃ COOH (25%, 0.04 mol/L HONH ₃ Cl) | Shake for 5 h at 90 °C |
| IV | Sulfide-bound | HNO ₃ (2 mol/L) | Shake for 6 h at 90 °C |
| V | Organic matter-bound | HNO ₃ (0.02 mol/L) + H ₂ O ₂ (30%), CH ₃ COONH ₄ (3.2 mol/L, 20% HNO ₃) | Shake for 2 h at 90 °C Shake for 1 h at room temperature |
| VI | Aluminosilicate-bound | | Wet digestion |

3. Results and discussion

3.1. The content of REEs in oil shale samples of different densities

The contents of individual REEs and ash in HOS and LOS samples of different densities are given in Table 5. The experimental results demonstrated that the material balance error of ash and REEs contents in the two oil shale samples was less than 10%.

From Table 5 it can be seen that the ash contents in the 1.5 g/cm³ (HD1 and LD1) density fractions of HOS and LOS are respectively about 50% and 20% lower than those in the original samples. The ash content of the density fraction > 2.0 g/cm³ was 72.63% (HD4) and 86.76% (LD5). As the ash content of both HOS and LOS is generally high, then the fractions, which are classified as lower-density ones, also contain a certain amount of ash, while organic matter accounts for the major part of the samples.

Comparison of the experimental results for Huadian and Luozigou oil shales showed that the former yielded products in high amounts at the medium density level of the sample (HD3), whereas LOS provided high yields of products at the highest density level of the sample (LD5). This indicates that the inorganic material in HOS is mainly internal minerals, while in LOS it is predominantly external minerals.

Table 5 reveals that REEs are present in the oil shale samples of all density levels, while there are differences in the elements concentration between the samples. The total content of REEs in low-density samples of both oil shales is relatively low but in high-density samples, relatively high. This is a sign of a positive correlation between the sample density and REEs concentration.

Table 5. The yield and contents of ash and REEs in oil shale products of different densities

| Sample density level | Products yield, % | Ash, % | REE, $\mu\text{g/g}$ | | | | | | | | | | | | | |
|----------------------|-------------------|--------|----------------------|-------|------|-------|------|------|------|------|------|------|------|------|------|------|
| | | | La | Ce | Pr | Nd | Sm | Eu | Gd | Tb | Dy | Ho | Er | Tm | Yb | Lu |
| HD1 | 0.51 | 27.27 | 12.53 | 22.52 | 2.57 | 9.71 | 1.67 | 0.39 | 1.66 | 0.26 | 1.36 | 0.26 | 0.68 | 0.13 | 0.67 | 0.13 |
| HD2 | 10.00 | 36.30 | 16.11 | 28.6 | 3.24 | 12.37 | 2.18 | 0.5 | 2.09 | 0.33 | 1.67 | 0.33 | 0.85 | 0.17 | 0.81 | 0.15 |
| HD3 | 77.54 | 49.88 | 22.35 | 36.64 | 4.32 | 17.3 | 3.01 | 0.66 | 2.92 | 0.43 | 2.27 | 0.47 | 1.36 | 0.23 | 1.31 | 0.20 |
| HD4 | 11.95 | 72.63 | 37.2 | 70.43 | 7.77 | 31.4 | 5.81 | 1.26 | 5.66 | 0.79 | 4.36 | 0.86 | 2.59 | 0.41 | 2.28 | 0.36 |
| LD1 | 0.07 | 12.46 | 10.64 | 20.41 | 2.32 | 8.74 | 1.62 | 0.29 | 1.51 | 0.27 | 1.33 | 0.25 | 0.67 | 0.13 | 0.67 | 0.12 |
| LD2 | 0.38 | 29.64 | 11.44 | 21.70 | 2.47 | 9.56 | 1.76 | 0.33 | 1.79 | 0.30 | 1.52 | 0.29 | 0.80 | 0.15 | 0.81 | 0.14 |
| LD3 | 2.28 | 37.33 | 24.21 | 45.69 | 4.95 | 19.17 | 3.61 | 0.62 | 2.99 | 0.50 | 2.65 | 0.50 | 1.29 | 0.23 | 1.18 | 0.20 |
| LD4 | 19.00 | 42.58 | 30.16 | 55.42 | 6.04 | 23.61 | 4.28 | 0.90 | 3.58 | 0.57 | 3.10 | 0.59 | 1.59 | 0.28 | 1.52 | 0.23 |
| LD5 | 76.27 | 86.76 | 31.60 | 68.00 | 7.28 | 28.30 | 5.23 | 1.28 | 4.95 | 0.86 | 3.99 | 0.82 | 2.28 | 0.32 | 2.10 | 0.32 |

3.2. The content of REEs in oil shale samples after acid washing

In order to investigate the relationship between REEs aggregation and organic matter in oil shale samples, HCl and HF were used to remove the inorganic material from them. The treated samples were then washed with deionized water and dried. The contents of ash and REEs in acid-washed oil shale samples are given in Table 6. For the Huadian oil shale the ash content declined from 50.28% (HOS) to 4.13% (HAW) after acid washing. In contrast, for the Luozigou oil shale the ash content reduced from 72.24% (LOS) to 5.43% (LAW) after acid washing. For both oil shales the ash removal rate exceeded 90%. Such a decline in ash content had a significant effect on the concentration of minerals in the samples.

From Table 6 it can be seen that the content of REEs is significantly lower in the acid-washed samples than in the original ones. The table also reveals that the acid washing removed the majority of REEs, which indicates that in HOS and LOS these elements occur mainly in inorganic minerals.

Table 6. The content of ash and REEs in acid-washed oil shale samples, $\mu\text{g/g}$

| Sample | Ash, % | REEs, $\mu\text{g/g}$ | | | | | | | | | | | | | |
|--------|--------|-----------------------|-------|------|-------|------|------|------|------|------|------|------|------|------|------|
| | | La | Ce | Pr | Nd | Sm | Eu | Gd | Tb | Dy | Ho | Er | Tm | Yb | Lu |
| HOS | 50.28 | 23.92 | 40.77 | 5.55 | 19.57 | 3.40 | 0.76 | 3.27 | 0.50 | 2.58 | 0.51 | 1.53 | 0.25 | 1.44 | 0.22 |
| HAW | 4.13 | 8.18 | 13.77 | 1.84 | 6.63 | 1.15 | 0.26 | 1.39 | 0.23 | 1.43 | 0.31 | 0.97 | 0.16 | 0.91 | 0.19 |
| LOS | 72.24 | 30.86 | 64.22 | 6.88 | 26.61 | 4.97 | 1.18 | 4.61 | 0.78 | 3.75 | 0.76 | 2.15 | 0.31 | 1.96 | 0.30 |
| LAW | 5.43 | 22.40 | 35.82 | 4.60 | 15.10 | 2.59 | 0.52 | 2.47 | 0.40 | 2.29 | 0.51 | 1.69 | 0.29 | 1.90 | 0.40 |

Note: HOS – original Huadian oil shale sample; HAW – acid-washed Huadian oil shale sample; LOS – original Luozigou oil shale sample; LAW – acid-washed Luozigou oil shale sample.

3.3. Results of sequential chemical extraction

Figure 1 and Figure 2 show the results of sequential chemical extraction for HOS and LOS. It can be seen that REEs in the oil shales occur mainly in minerals, i.e. in the sulfide-bound, carbonate-bound, ferromanganese oxhydroxides-bound and aluminosilicate-bound fractions. The exchangeable fraction can generally be ignored, except for Lu (1.2%) in HOS. The REEs content in the organic matter of HOS and LOS is less than 2%, which is indicative of its very weak affinity for the elements. These results are in agreement with those obtained by Jiang et al. [27] who investigated the occurrence state of REEs in coal.

Based on the results of the float-sink test and sequential chemical extraction of the density fraction $< 1.5 \text{ g/cm}^3$, the contents of REEs in the organic matter of HOS and LOS were compared. It was observed that during SCE, the content of REEs in the organic matter of both HOS and LOS was the lowest. It is due to the fact that not all minerals can be removed from the samples during the acid washing, and, considering that the minerals content

in low-density samples is high, their REEs content is higher than that in the organic matter. After the acid washing, the samples still contained some pyrite whose affinity for REEs was stronger than that of organic matter. On the whole, organic matter had a certain affinity for REEs, but, compared with inorganic minerals, it was relatively weak. In contrast, sulfides, carbonates and iron manganese oxides had a very strong affinity for REEs.

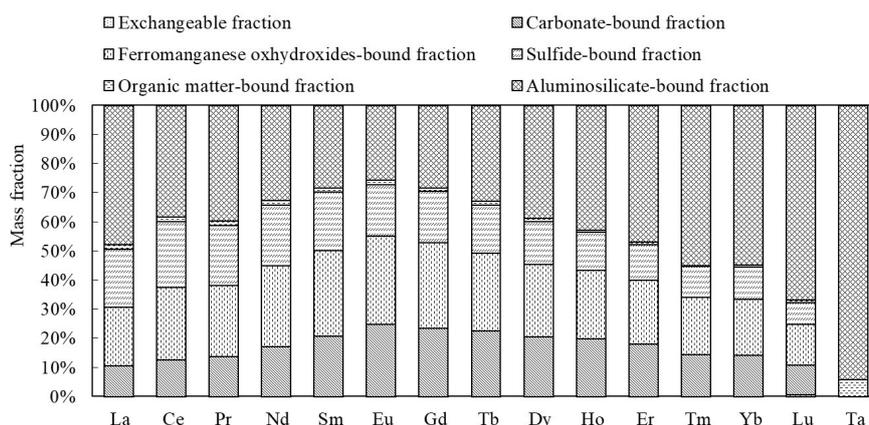


Fig. 1. Modes of occurrence of REEs in Huadian oil shale.

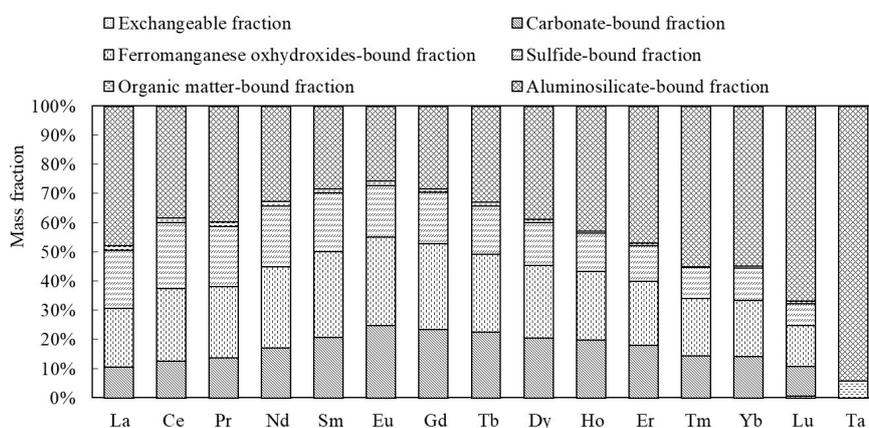


Fig. 2. Modes of occurrence of REEs in Luozigou oil shale.

3.4. The geochemical characteristics of REEs in oil shale

In order to quantitatively describe the geochemical characteristics of REEs, parameters such as ΣREE ($\Sigma\text{REE} = \text{La} + \text{Ce} + \text{Pr} + \text{Nd} + \text{Sm} + \text{Eu} + \text{Gd} +$

Tb + Dy + Ho + Er + Tm + Yb + Lu), LREE (LREE = La + Ce + Pr + Nd + Sm + Eu), and HREE (HREE = Gd + Tb + Dy + Ho + Er + Tm + Yb + Lu) were used. The ratio of LREE to HREE content was denoted as LREE/HREE. The ratio of La to Yb after chondrite standardization was expressed as La_N/Yb_N . The exceptions to chondrite standard were designated as δEu_N and δCe_N . Chondrite standardization calculations for δEu_N and δCe_N were made using Equations (1) and (2):

$$\delta Eu_N = Eu_N / (Sm_N \times Gd_N)^{1/2}, \quad (1)$$

$$\delta Ce_N = Ce_N / (La_N \times Pr_N)^{1/2}, \quad (2)$$

where Eu_N , Sm_N , Gd_N , Ce_N , La_N and Pr_N are chondrite-standardized values of an element.

In this investigation, ICP-MS was used to measure, as per the method of Zhao [28], the content of REEs in HOS and LOS.

Using the results given in Tables 5 and 6, the geochemical parameters of REEs in the oil shale samples under study were calculated (Table 7). The values of LREE/HREE in the original samples and components of each density level (HD1, HD2, HD3, HD4, LD1, LD2, LD3, LD4) were found to be higher than 8. This showed that in all the samples LREEs were more enriched than HREEs, while both underwent an obvious fractionation. This classifies HOS and LOS as oil shales of medium LREE enrichment.

The LREE/HREE values showed a tendency to first increase, and then decrease as the samples density increased. The LREE/HREE of medium-density samples was relatively high, being higher than that in the original samples. This indicated that in such samples light REEs were relatively enriched compared to heavy REEs.

Table 7. Geochemical parameters of REEs in oil shale samples

| Sample | Ash, % | Σ REE, $\mu\text{g/g}$ | LREE, $\mu\text{g/g}$ | HREE, $\mu\text{g/g}$ | LREE/HREE | La_N/Yb_N | δEu_N | δCe_N |
|--------|--------|-------------------------------|-----------------------|-----------------------|-----------|-------------|---------------|---------------|
| HD | 50.28 | 103.45 | 93.17 | 10.28 | 9.06 | 10.97 | 0.70 | 0.90 |
| LD | 72.24 | 149.30 | 134.72 | 14.58 | 9.24 | 10.40 | 0.76 | 1.03 |
| HD1 | 27.27 | 54.54 | 49.39 | 5.15 | 9.59 | 12.35 | 0.72 | 0.93 |
| HD2 | 36.30 | 69.40 | 63.00 | 6.40 | 9.84 | 13.13 | 0.72 | 0.93 |
| HD3 | 49.88 | 93.47 | 84.28 | 9.19 | 9.17 | 11.27 | 0.69 | 0.87 |
| HD4 | 72.63 | 171.18 | 153.87 | 17.31 | 8.89 | 10.77 | 0.68 | 0.97 |
| LD1 | 12.46 | 48.97 | 44.02 | 4.95 | 8.89 | 10.49 | 0.57 | 0.96 |
| LD2 | 29.64 | 53.06 | 47.26 | 5.80 | 8.15 | 9.33 | 0.57 | 0.96 |
| LD3 | 37.33 | 107.79 | 98.25 | 9.54 | 10.30 | 13.55 | 0.58 | 0.98 |
| LD4 | 42.58 | 131.87 | 120.41 | 11.46 | 10.51 | 13.10 | 0.71 | 0.96 |
| LD5 | 86.76 | 157.33 | 141.69 | 15.64 | 9.06 | 9.94 | 0.78 | 1.05 |
| HAW | 4.13 | 37.42 | 31.83 | 5.59 | 5.69 | 6.07 | 0.63 | 0.83 |
| LAW | 5.43 | 90.98 | 81.03 | 9.95 | 8.14 | 7.97 | 0.63 | 0.83 |

Note: HAW – acid-washed Huadian oil shale sample; LAW – acid-washed Luozigou oil shale sample.

After the removal of ash, the LREE/HREE values of the samples were lower than those of the original ones. This is indicative of that the effect of ash removal is stronger on the content of LREEs than on that of HREEs, which is especially noticeable in case of Huadian oil shale.

The δCe_N and δEu_N values in Table 7 give evidence of abnormally high contents of Eu and Ce in the samples of each density level and the original ones. This suggests that lake water was affected during the diagenetic process but a little, which did not cause any serious loss of Ce. This provides evidence of reducibility during the formation of the sedimentary environment, while the abnormally high Eu value is inherited from terrigenous rocks, which are usually Eu negative abnormal. This indicates that REEs in the oil shale samples studied are closely associated with terrigenous clastic rocks. The values of δEu_N and δCe_N are very similar, which is a sign of that the REEs in the samples of both HOS and LOS originate from the same source.

3.5. The source of REEs in oil shales

In Figure 3, the results presented in Table 7, the chondrite-standardized distribution of REEs in the original oil shale samples, the density of each component, and REEs contents in the acid-washed samples are illustratively summarized. The chondrite-standardized distribution curve for REEs shows that the content of components of different density levels is different. The distribution pattern of REEs in the samples is very similar to that in the original ones and is characterized by a broad and gentle V-shaped curve that is high on the right, low on the left and curves at Eu are at the bottom. From La to Eu the curve is steep, with a gentler slope. The curve for heavy rare earth elements Gd and Lu is generally gentler. This suggests that the source materials of REEs in the oil shale samples of different densities are similar. Figure 3 reveals that REEs contents in the oil shale samples as well as their inorganic composition are closely related to terrigenous source materials, and not to water or plant source materials.

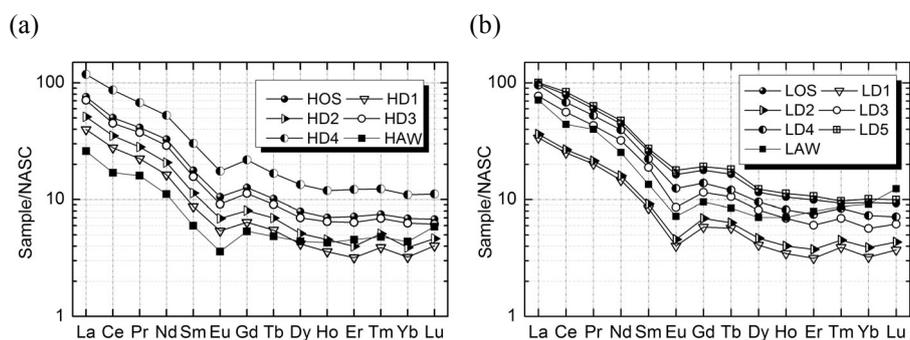


Fig. 3. NASC-normalized patterns of REEs in Huadian (a) and Luozigou (b) oil shale samples. (NASC – North American Shale Composite.)

4. Effect of organic matter on REEs aggregation in oil shale

If REEs in oil shale exist in the inorganic combination state, it means that they combine with a single mineral or are present in combination with minerals. In this work, REEs in the inorganic combination state were separated from the heavy liquid in the course of the float-sink test, while those in the organic combination state were not separated. The combined states of REEs in oil shale could then be investigated according to their content distribution in the samples of different density levels.

Figure 4 shows the relationship of Σ REE, HREE and LREE in each density fraction of the oil shale sample with its ash content. It can be seen from the figure that for the Huadian oil shale the content of REEs in each density fraction has a positive correlation with its ash content, while for the Luozigou oil shale this correlation is relatively weak. REEs in HOS and LOS are also shown to have a strong inorganic affinity.

Figure 4 also displays that in case of HOS, the content of REEs has a positive correlation with the ash content as the density increased. For LOS, the ash content increased from 12.46 to 29.64% with density level changing from < 1.5 to $1.5\text{--}1.6 \text{ g/cm}^3$, but no obvious increase in the content of REEs was observed. This is indicative of the significant role of organic matter in the aggregation of REEs. The density level change from $1.5\text{--}1.6$ to $2.0\text{--}2.4 \text{ g/cm}^3$, which reflects the role of inorganic minerals, gives evidence of their strong affinity for REEs. The density level change from $2.0\text{--}2.4$ to $> 2.4 \text{ g/cm}^3$ shows that there is no obvious increase in REEs content. This suggests that above the fraction density level of 2.4 g/cm^3 , the aggregation ability of some minerals in relation to REEs is low.

Rare earth elements are important indicators of the occurrence state of minerals, at the same time, they may be absorbed by organic matter. In addition to its ability to absorb REEs, organic matter can also aggregate the elements.

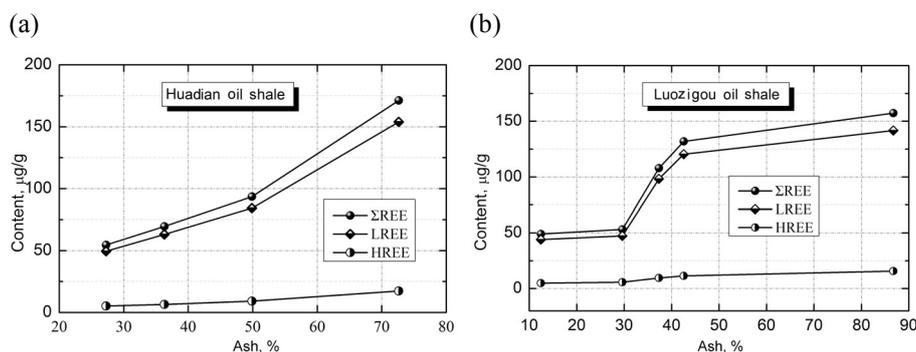


Fig. 4. Changes of REEs content in oil shale samples of different densities with ash content.

After acid washing, the high REEs content in the samples also reflected the role of organic matter in their aggregation. In order to elucidate the role of organic matter in aggregating REEs in oil shale, the ratios of HAW/HOS and LAW/LOS in the acid-washed oil shale samples were calculated. The results are presented in Table 8.

The ash content of HOS was previously noted to have declined from 50.28 to 4.13%, and that of LOS, from 72.24 to 5.43% after acid washing. The acid washing removed more than 90% of ash, while the removal of minerals was also obvious (Table 6). After the acid-washing treatment the content of ash in the samples was below 10%. Although in HAW and LAW, Σ REE was significantly lower than that in HOS and LOS, the degree of reduction was far lower than the decrease of ash content. The remaining portion of REEs cannot be explained by the combination of detrital minerals. At the same time, organic matter in oil shale plays an important role in accumulating REEs, particularly HREEs. Table 6 also reveals that the calculated δEu_N and δCe_N are similar, as are their distribution patterns. This indicates that REEs in oil shale absorbed by organics or minerals are of terrestrial origin.

Table 8. The ratio of REEs content in acid-washed oil shale samples to that in original ones

| Ratio | Ash, % | Σ REE | LREE | HREE |
|---------|--------|--------------|--------|--------|
| HAW/HOS | 0.0821 | 0.2861 | 0.2696 | 0.4398 |
| LAW/LOS | 0.0752 | 0.5418 | 0.5306 | 0.6533 |

Note: HAW – acid-washed Huadian oil shale sample; HOS – original Huadian oil shale sample; LAW – acid-washed Luozigou oil shale sample, LOS – original Luozigou oil shale sample.

5. Conclusions

The organic/inorganic affinity of rare earth elements in Huadian and Luozigou oil shales was investigated. Based on the results of the float-sink and acid-washing tests and sequential chemical extraction, the following conclusions were drawn:

1. After the float-sink test, all rare earth elements were detected in oil shale samples of each density level. Acid washing removed most of the elements from the samples. After the sequential chemical extraction, rare earth elements were detected mainly in the minerals present in the samples. The float-sink and acid-washing tests and sequential chemical extraction showed that rare earth elements in the oil shale samples under study existed mainly in inorganic minerals.
2. The contents of rare earth elements in the oil shale samples of each density level were different, as shown by their chondrite-standardized distribution curves; however, their distribution patterns were very

similar to those in the original samples. The curves represented broad and gentle V-shaped curves that were high on the left and low on the right. The curve at Eu was at the bottom, while the source materials of REEs in the oil shale samples of different densities were similar. This suggests that REEs and inorganic components in oil shales are of terrigenous origin, and are not related to either water or plant source material.

3. Organic matter in oil shales plays an important role in the aggregation of rare earth elements, especially heavy ones. At the same time, REEs in oil shales are absorbed by terrigenous organic matter or minerals.

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