INFLUENCE OF CALCINATION TEMPERATURE ON LEACHING RATE OF ALUMINUM AND IRON IMPURITIES IN OIL SHALE ASH

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This work adopted 1,10-phenanthroline spectrophotometric method, complexometric titration and X-ray diffractometer (XRD) to investigate active state of aluminum and iron impurities in semicoke of Huadian oil shale which was calcinated at different temperatures and the influence of calcination temperature on leaching rate of impurities (Al, Fe) with acid. The results show that after calcination of semicoke of Huadian oil shale at 700–800 °C, iron and aluminium exist in their maximum active state and turn into materials soluble in acids, which results in their maximum leaching rate. This process is important for the removal of impurities at preparation of high-quality amorphous silica from oil shale ash.

Introduction

Residue of oil shale combustion is a solid waste which formes at oil production, burning and electricity generation from oil shale. Its main mineral is kaolinite in which the content of SiO_2 is over 50%, so we can make use of the solid waste to produce amorphous silica. Spent oil shale contains some impurities of aluminium and iron. Before producing amorphous silica, the impurities need to be removed. At present, the effective technology of impurity removal is calcination and acid leaching. The effect of acid leaching depends on the calcination degree and will influence the quality of white carbon black directly. This investigation into the influence of calcination temperature on leaching rate of impurities (Al, Fe) with acid provides a theoretical background for industrial utilization of spent oil shale.

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Experimental

Instruments, chemicals and preparation of calibration solutions

PTI-C-700 X-Ray fluorescence spectrometer; XD-32 X-Ray diffractometer and HP8453 ultraviolet spectrophotometer were used.

Semicoke of Huadian oil shale is the residue of oil shale retorting at 500–600 °C under non-air atmosphere.

Iron: ammonium ferric sulfate (0.863 g) was put into a beaker, about 100 ml of water and about 10 ml of sulfuric acid solution were added. After dissolution of sulfate, the solution was poured into a volumetric flask (1000 ml) and diluted to the scale.

EDTA: dissolved in water EDTA (3.7224 g) was carried into a volumetric flask (500 ml) and diluted to the scale.

$CuSO_4$: dissolved in water $CuSO_4$ (1.5960 g) was carried into a volumetric flask (500 ml) and diluted to the scale.

PAN indicator: is a mixture of sulfuric acid solution, ammonium sulfate, 1,10-phenanthroline solution (20%), L-ascorbic acid solution (2%) and acetic-sodium acetate buffer (pH $\approx$ 4.5).

Calcination and acid leaching

The sample of spent oil shale was ground to fine powders (<96 μm) and calcinated at different temperatures for 1.5 h. The calcined ash was leached with sulfuric acid solution of the concentration of 50–60% at 90 °C for 1–1.5 h. The leached residual ash was separated by filtration. Leaching rate of impurities was determined.

Leaching rate of impurities

Iron content determination

According to GB/T3049-86, we adopted 1,10-phenanthroline spectrophotometric method to determine the content of iron in the filtrate. Iron calibration curve was drawn as follows: iron calibration solution (50 ml) was poured into a volumetric flask (500 ml) and diluted to the scale. Samples of iron calibration solution (0, 2.00, 5.00, 10.00, 15.00, 20.00, 30.00 ml) were pipetted into volumetric flasks (100 ml), pH value was adjusted to 2 with water and hydrochloric acid, thereafter L-ascorbic acid solution (2.5 ml), buffer solution (10 ml) and 1,10-phenanthroline solution (5 ml) were added and solution was shaken up. Absorbency of solutions was measured by spectrophotometer and iron calibration curve was drawn. The measurement conditions were as follows: wavelength: 510 nm, quartz cell (1 cm) and water as reference solution.

Iron content of the filtrate was measured in the following way: the filtrate (2 ml) was taken into a volumetric flask (100 ml), water was added and adjusted to 60 ml, the aforementioned process was repeated. According to the absorbency, we can calculate and obtain the iron content of the solution.

Determination of aluminium content

The filtrate (50 ml) was put into a trigonal flask (400 ml) and some water (about 50 ml) was added. EDTA calibration solution (about 20 ml) was added, and the bulk volume was recorded. The trigonal flask was shaken and heated to 80–90 °C, then buffer solution (15 ml) was added. The temperature was kept at 80–85 °C for 3 min, PAN indicator (6–7 drops) was added, and the solution was titrated with $CuSO_4$ calibration solution. Initial yellow colour of the solution turned into sage green. The titration process was terminated when the color turned into amaranthine. The bulk volume was recorded and the concentration of Al^{3+} was calculated according to the equation of reaction $Al^{3+} + H_2Y^{2-} = AlY^- + 2H^+$.

Leaching rate of impurities

After determination of the content of iron and aluminium in the filtrate, their content (m_i) extracted from the spent oil shale is also determined. From the result of the XRF analysis of spent oil shale, we get the content of iron and aluminium (M_i) in the sample. The leaching rate of impurities is calculated using the formula m_i/M_i.

Result and discussion

Composition of spent oil shale (semicoke)

X-Ray fluorescence spectrum was used to analyze the composition of semicoke of Huadian oil shale (Table 1).

From Table 1 we can find that SiO_2 content of semicoke of Huadian oil shale is about 56.6%. It can be used to produce amorphous silica. At the same time, we find that the Fe_2O_3 content is about 9.1% and Al_2O_3 content about 20%. The impurities need to be removed.

Table. 1. **XRF analysis of Huadian oil shale semicoke**

Compound	Content, %	Compound	Content, %
SiO_2	56.6	MnO	0.171
Al_2O_3	20.0	P_2O_5	0.156
Fe_2O_3	9.10	BaO	0.0914
CaO	5.34	SrO	0.0635
SO_3	2.29	Cl	0.0490
MgO	1.99	ZrO_2	0.0275
K_2O	1.97	ZnO	0.0225
Na_2O	1.05	NiO	0.0173
TiO_2	0.998	CuO	0.0172

Influence of calcination temperature of Huadian oil shale semicoke on leaching rates of aluminium and iron

Using the aforenamed technique, we can get the leaching rate of impurities at different calcination temperatures, as shown in Fig. 1.

Figure 1 shows that leaching rates of aluminium and iron are all lower when the calcination temperature is below 700 °C. When the temperature reaches 700 °C, leaching rate reaches its maximum maintaining the rate up to 800 °C. When the temperature exceeds 800 °C, leaching rate begins to drop. So, 700–800 °C is the optimal temperature range for calcination. Within this range iron and aluminium will exist in the maximum active state enabling to reach the maximum leaching rate as a result.
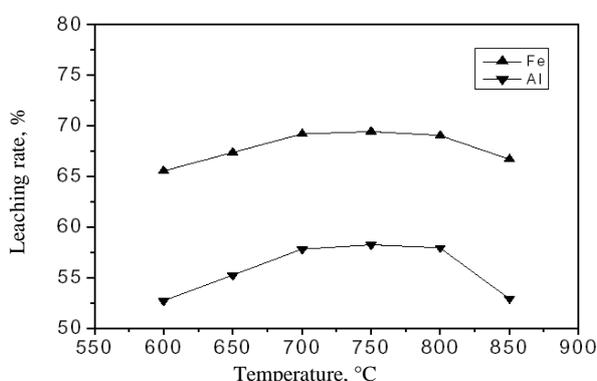
Fig. 1. Influence of calcination temperature of semicoke of Huadian oil shale on leaching rates of aluminium and iron.

Semicoke of oil shale was prepared retorting oil shale at 500–600 °C in vacuum. Compared with the original oil shale, its composition and structure have changed (Figs. 2 and 3). The structure of the semicoke is similar to that of some other kaolinites. The impurities of iron and aluminium exist in oil shale in the form of kaolinite. After retorting, some of them exist in the active state which means that the crystalloid insoluble in acids turns to the materials soluble in acids. From the X-ray diffraction patterns (Fig. 3), we find that the crystalloid structure of iron and aluminium changes ($2\theta = 30^{\circ}$) after semicoke calcination at 500 °C and 600 °C. Meanwhile, iron is more active than aluminium, so the leaching rate of iron is higher than that of aluminium. From the X-ray diffraction patterns ($2\theta = 10^{\circ}$), we find that the active states of iron and aluminium as well as their leaching rates reach the maximum degree when the calcination temperature is 700 °C. When the temperature reaches 850 °C, aluminium and iron will convert to a new unactivated crystalloid ($2\theta = 30^{\circ}$) which is insoluble in acid and makes the leaching rate of both metals drop.
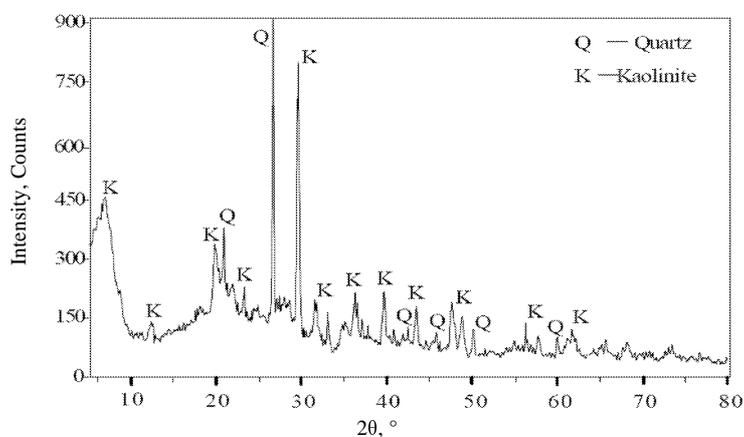
Fig. 2. XRD chart of initial Huadian oil shale.
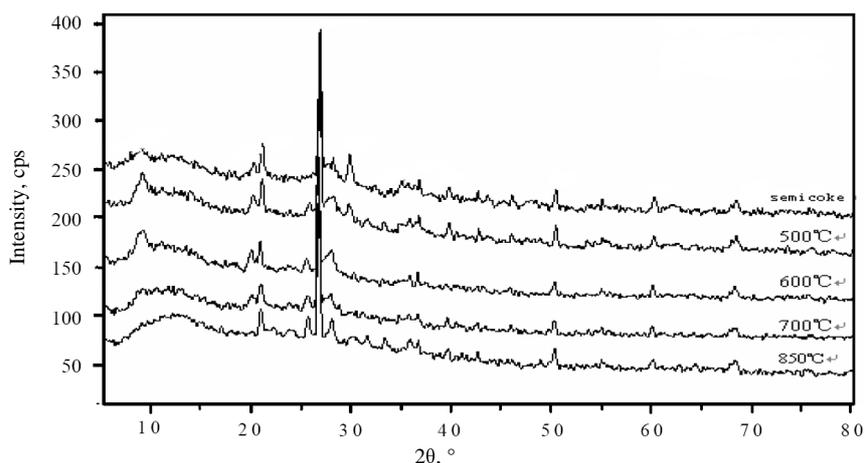
Fig. 3. XRD charts of retorting-derived residue of Huadian oil shale calcinated at various temperatures.

Conclusions

Spent oil shale contains some impurities of aluminium and iron. Before we use it to produce amorphous silica, the impurities need to be removed. The effect of acid leaching is dependent on the degree of their activity. This paper on investigation of the influence of calcination temperatures on leaching rate of aluminum and iron impurities from Huadian spent oil shale indicates that after calcination at 700–800 °C, iron and aluminium exist in the maximum active state and turn into materials soluble in acids, which results in the maximum leaching rate of iron and aluminium impurities.

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