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CHARACTERIZATION OF OIL SHALE PROCESSING RESIDUES AND SEPARATED PRODUCTS

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Different residues of Huadian oil shale processing were investigated. Their inorganic chemical composition and phase structural characteristics were identified by X-ray fluorescence spectrometry (XRF) and X-ray diffractometry (XRD). The influence of calcination conditions on processing residues at different ash activation degrees and impurities' leaching rates as well as the quality of obtained SiO_2 concentrate were investigated by a single-factor method. The results showed that only circular crossflow-type retorting-derived semicoke has different phase-structural characteristics at different calcination temperatures. In the range of 700–800 °C, the leaching rate of aluminum and iron reaches the maximum. To prepare SiO_2 concentrate, starting material should be calcined for 1.5 h at 700–800 °C. As a result, SiO_2 concentrate which meets the national standard of silica white will be obtained; the content of SiO_2 is 92.34% and its specific surface area 104 m^2/g. Phase structures of Fushun-type retorting residue and cogeneration power plant ash did not change dramatically at different calcination temperatures. The leaching rate of Al and Fe reached the maximum. Further calcination is unnecessary in reutilization, only removal of impurities by means of acid soaker is relevant. Fushun-type retorting residue can also be used to make SiO_2 concentrate which meets the national standard; the content of SiO_2 is 90.38%, its specific surface area is 91 m^2/g. The leaching rate of aluminum from cogeneration power plant ash is lower, and this ash cannot be used to prepare silica white meeting the national standard. It can be applied as an ingredient of cement, at brick preparation, etc. Separation and purification products are a mixture of crystalline SiO_2 and amorphous SiO_2, while the content of crystalline SiO_2 is 32.2%.

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Introduction

Oil shale is also called oil-forming shale. It belongs to solid combustible minerals. As one of the oil substitute resources, its importance has been reconsidered all around the world [1–9]. As one of the richest countries to own abundant oil shale reserves in the world, China ranks the fourth, below the United States, Estonia and Brazil. The verified reserves are 50 billion tons, mainly distributed in Huadian and Nongan of Jilin province, Maoming of Guangdong province and Fushun of Liaoning province, etc [10]. Oil shale is mainly applied to extract shale oil and burn directly for electricity generation and heat supply, however, large amounts of residue corresponding to different techniques are produced at the same time. For example, seven million tonnes of oil shale residue would be produced when the annual output of shale oil is 600,000 tonnes, which can not only cause environmental pollution, but also cause the increase in cost and impact economic benefit. Oil shale exploitation and utilization will be greatly effected as a result. At present, oil shale processing residues are usually used for producing cement or other construction materials. However, there are two ways in comprehensive utilization of oil shale residue, one is to prepare silica white with higher surplus value on the account of the residues, the other is to reduce the ash content before oil shale retorting, at which, although the eco-leveled utilization would be increased, the industrialization is hard to be realized due to low efficiency. At present, the oil shale industry lacks systematic study of oil shale residue [11–17]. In this paper, we have studied ① semicoke from circular crossflow-type retort, ② residue from Fushun-type retort, and ③ fine residue from cogeneration power plant. Their chemical composition and structural characteristics were studied systemically. Preliminary studies about the effect of calcination temperature on the leaching rate of aluminum and iron impurities in oil shale retorting semicoke showed that iron and aluminum would stay in maximum active state at 700–800 °C, and turn into acid-soluble substances, which resulted in the maximum leaching rate of iron and aluminum impurities in the ash [18]. The influence of calcination technique at different ash activation degrees and impurities' leaching rates was investigated, separated and purified products were also analyzed and characterized.

Experimental

Instruments and chemicals

PTI-C-700 X-Ray fluorescence spectrometer (XRF) was used to analyze the composition of the processing residues of oil shale; XRD-6000 X-Ray diffractometer was used to analyze the phase structure of residues and purified products; HP8453 UV spectrophotometer and chemical titration method were used for determination of leaching rate of impurities; Optima

2000 DV atomic absorption spectrophotometer was used to determine the content of copper, iron and manganese in the product which was separated and purified from oil shale residue; WSB-2 d/o was used to determine the whiteness of the separation and purification product; JW-K specific surface area analyzer was used to determine specific surface area; HITACHI (S-4800) scanning electron microscope was used for surface analysis and characterization of separated and purified products.

The oil shale residues used in this study were from Huadian oil shale processed by different techniques. Namely ① in circular crossflow-type retort (the residue was obtained at oil shale retorting under oxygen-free atmosphere, experimental temperature was 510–650 °C); ② in Fushun-type retort (the residue was obtained from the process of producing oil from oil shale under incomplete combustion conditions, experimental temperature was 800–850 °C); ③ in Huadian cogeneration power plant (the fine residue was obtained from oil shale under complete combustion in the process of electricity generation, experimental temperature was 850–950 °C).

Inorganic composition analysis and XRD analysis of the three residues of oil shale

The three residues of oil shale were calcined at first. The samples of oil shale residues (particle size 0.3 mm) 2–4 g were put into a muffle furnace and calcined at 500–550 °C for four hours in aerobic environment. After organic substances were removed, the residue turned to pale yellowish from black. X-Ray Fluorescence spectra (XRF) were taken to analyze the composition of residues, and X-ray diffraction was used to analyze their phase structure.

Activation of aluminum, iron and other impurities in the residue by calcination

Certain amounts of oil shale residues (particle size 0.3 mm) were weighed and calcined at certain temperatures in a muffle furnace (the temperature rise speed was 500 °C/h) for a certain period of time. Cooled residues were analysed by XRD to study the effect of different temperatures and times on activation in order to remove aluminum and iron for separation and purification.

Removal of impurities by means of acid soaking, and determination of leaching rate of aluminum and iron

The calcined ash was leached with 50% sulfuric acid solution at 90 °C for 1.5 h in a thermostatic water-bath (liquid-solid ratio 5:1), the leached residue was separated by hot filtration and washed to neutral. Leaching rate of impurities (m_i/M_i) was determined by determination the content of iron and aluminum in the filtrate m_i and dividing it by original amounts of them in the residue M_i. The filtered cake was dried in a dry box at 105 °C for 1 h and bright yellow powder was obtained. The color is due to the presence of titanium.

Removal of Ti by ammonium sulfate

In this work, Ti was removed by ammonium sulfate to enhance the whiteness. The powder was ground and mixed with a certain amount of ammonium sulfate, calcined at 560 °C for 2 h in a muffle furnace (the temperature rise speed was 500 °C/h), and then removed, cooled to the room temperature. The product $(NH_4)_2TiO(SO_4)_2$ was a bouffant white clinker with low integrate hardness. It was dissolved in H_2SO_4 of the concentrate of 50% in beaker after having been pulverized under pressure. A small amount of oxydol was added to avoid hydrolysis of titanium. After complete dissolution, the suspension was held for 1–1.5 h, filtered, the filter cake was washed to neutral by deionized water, dried at 120 °C for 3 h, and white powder obtained after calcination and dehydration at 400 °C for 4 h is SiO_2 concentrate obtained through separation and purification.

Analysis and characterization of the product of separation and purification

The SiO_2 concentrates obtained at separation and purification of the three residues were analyzed and characterized. The content of SiO_2, the absorption value of DBP (dibutyl phthalate), as well as total content of copper, iron, and manganese were determined with reference to chemical industry standard HG/T3065-1999 (silica white) of People's Republic of China, whiteness was determined by WSB, specific surface area was measured by specific surface area analyzer, and the morphological characteristics were characterized by XRD and SEM.

Results and discussion

Inorganic composition of oil shale residue obtained using different techniques

X-ray fluorescence spectra were taken to analyze the inorganic composition of three pretreated residues of oil shale, the results are shown in Table 1. From Table 1 we can find that SiO_2 content of different residues is high exceeding 50%. At the same time, we find that Al_2O_3 content ranges from 16.8% to 20.0%, and Fe_2O_3 content is about 9%. Extraction of Al from the residue favors the application performance of products (HG/T3065-1999 provides Fe, mg/kg $\leq$1000). SiO_2 concentrate can be obtained after the removal of aluminum, iron and other impurities.

Table 1. **XRF analysis of different residues of Huadian oil shale**

Composition	Content, %		
	①	②	③
SiO_2	56.6	53.5	56.3
Al_2O_3	20.0	16.8	18.0
Fe_2O_3	9.10	9.67	8.68
CaO	5.34	11.2	9.30
SO_3	2.29	2.09	0.944
MgO	1.99	2.34	2.25
K_2O	1.97	1.97	1.97
Na_2O	1.05	0.622	0.805
TiO_2	0.998	0.844	0.836
MnO	0.171	0.283	0.219
P_2O_5	0.156	0.356	0.326
BaO	0.0914	0.113	0.126
SrO	0.0635	0.101	0.0979
Cl	0.0490	0.0485	0.0342
ZrO_2	0.0275	0.0234	0.0233
ZnO	0.0225	0.0271	0.0295
NiO	0.0173	0.0131	0.0152
CuO	0.0172	0.0237	0.0158

① Semicoke from circular crossflow-type retort
② Residue from Fushun-type retort
③ Residue from cogeneration power plant

Influence of calcination temperature on activation degree and leaching rate of Al and Fe in the residue of oil shale

X-Ray diffraction charts of the residues of oil shale obtained at different techniques, calcined and activated at 600, 700, 800 and 850 °C, respectively, are shown in Figs. 1–3. Using acid leaching of the impurities, we have determined the leaching rate of aluminum and iron in the filtrate and three groups of curves of the three residues are shown in Figs. 4–6.

The residue of oil shale originates from kaolinic shale, its initial main mineral is platy kaolinite, which experiences varying degree of decomposition at different calcination temperatures. We must activate aluminum in oil shale residue before its removal, that is to convert inactive hexacoordinate aluminum in the residue into the active quadridentate or five-coordinate aluminum in order to become an acid-soluble material for leaching. The usual approach is calcination. The removal of iron impurity proceeds in the same way, it is made acid-soluble by means of calcination under appropriate conditions so as to remove impurities (Fe, Al) and remnant black carbon by means of acid soaking at the same time. So, it is essential to study the influence of calcination conditions on the activation degree and leaching rate of iron and aluminum in the residue of oil shale so as to determine the best activation technique. In this paper we have used a single-factor method to investigate the effect of calcination temperature and calcination time. Comparing Figures 1–3, we can find that only the semicoke of circular

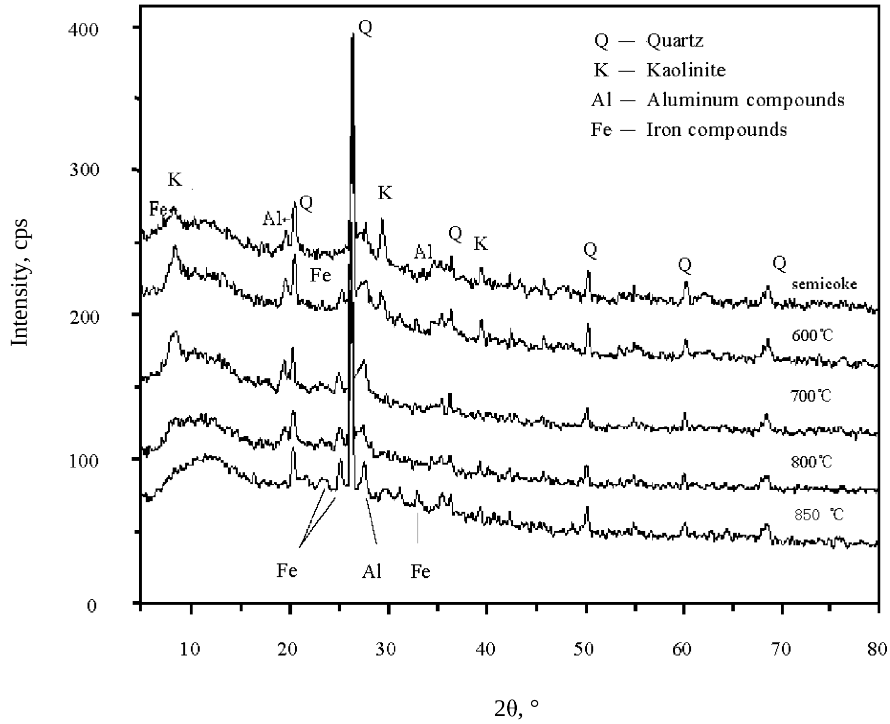

Fig. 1. XRD chart of circular retorting-derived residue calcined at various temperatures.

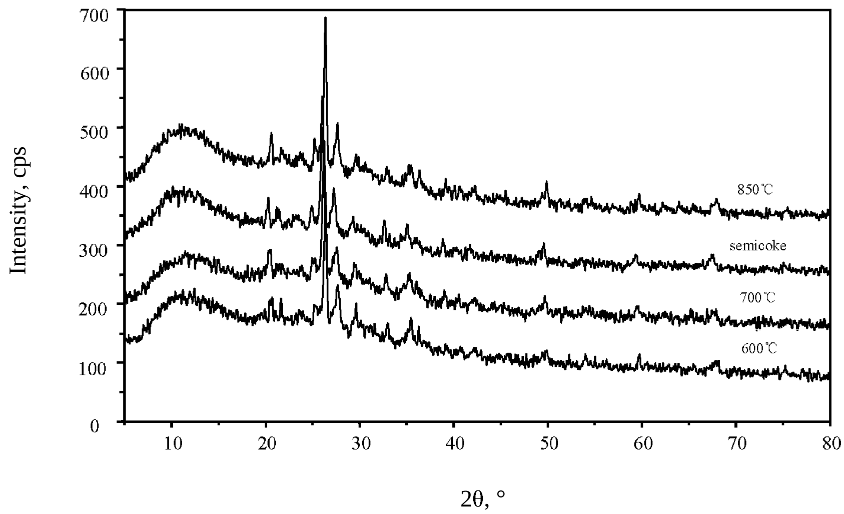

Fig. 2. XRD chart of Fushun-type retorting residue calcined at various temperatures.

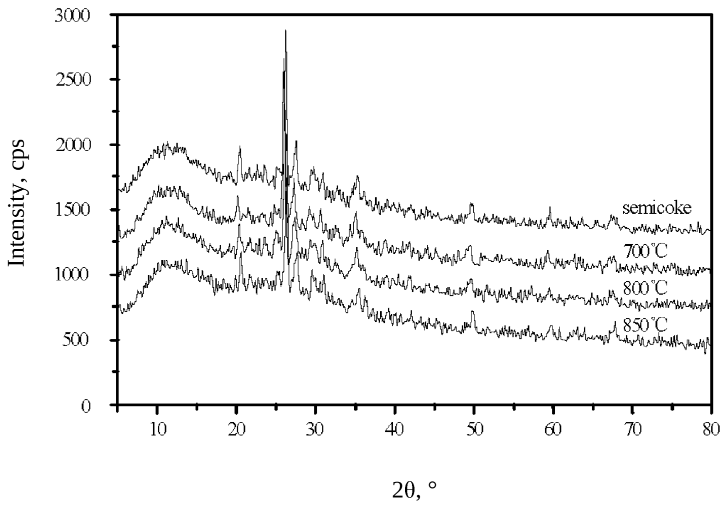

Fig. 3. XRD chart of ash from cogeneration plant calcined at various temperatures.

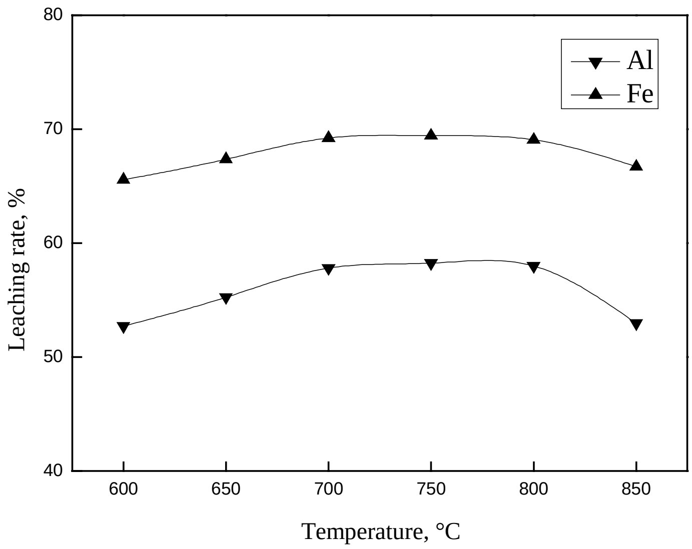

Fig. 4. Influence of calcination temperature of circular retort semicoke on leaching rate of Al and Fe.

crossflow-type retort shows different XRD charts at different temperatures (Fig. 1). Within the temperature range of 510–650 °C, there is some kaolinite still not fully decomposed, and Fe, Al are not activated. Kaolinite decomposes continuously by means of calcination with the increase in temperature, Fe and Al are activated to form acid-soluble material and are leached out. When the temperature reaches 700 °C, kaolinite decomposes completely, active states of iron and aluminum as well as their leaching rate reach their maximum degree. When the temperature exceeds 800 °C, aluminum and iron convert to a new unactivated crystalloid which is

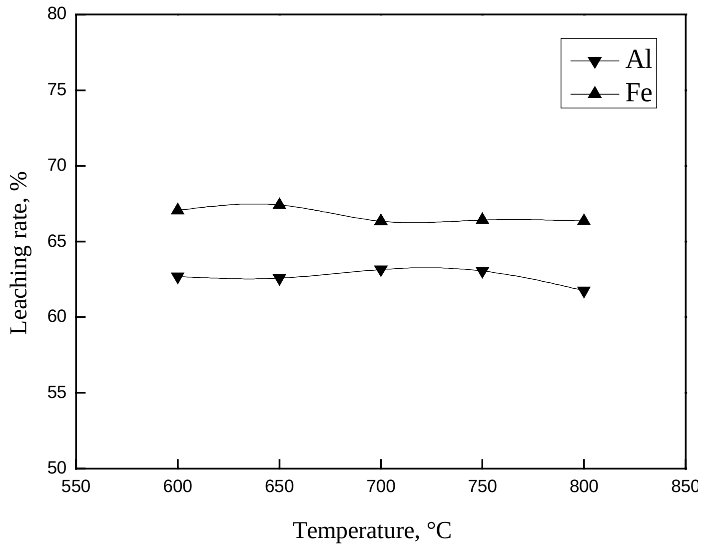

Fig. 5. Influence of calcination temperature of Fushun-type retorting residue on leaching rate of Al and Fe.

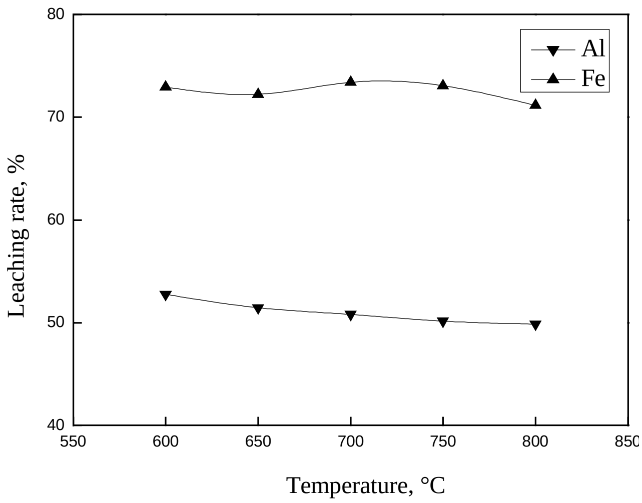

Fig. 6. Influence of calcination temperature of residue from cogeneration plant on leaching rate of Al and Fe.

insoluble in acid and makes the leaching rate of both of metals to decrease. The highest temperature of residue of Fushun-type retort investigated was 800–850 °C (incomplete combustion in the process of oil production); cogeneration power plant fine residue was obtained at temperatures of 900–950 °C (complete combustion). From Fig. 2 and Fig. 3 we can see that kaolinite is completely decomposed in both of residues, so the XRD charts corresponding to different calcination temperatures show nearly no changes, active states of iron and aluminum as well as their leaching rates reach their maximum degree, but the leaching rate of aluminum from cogeneration power plant fine residue is low (about 50%), owing to which a higher temperature is needed to make aluminum to convert into the silicon spinel and mullite phase. The results showed that the influence of calcination temperature on leaching rate of circular crossflow-type retorting-derived semicoke is highest (Fig. 4), the leaching rate of aluminum and iron gradually increased with the increase in calcination temperature. Within the range of 700–800 °C, iron and aluminum both reach the maximum leaching rate (the highest leaching rate of aluminum nearly 60%, while that of iron nearly 70%). When the temperature exceeds 800 °C, leaching rate begins to drop. While the influence of calcination temperature on the leaching rate of Fushun-type retorting residue (Fig. 5) and cogeneration power plant fine residue (Fig. 6) is less. Fushun-type retorting residue basically maintains the leaching rate of iron in an average of 70%, and that of aluminum is in average about 60%. The leaching rate of iron from the cogeneration power plant fine residue is about 70%, while the leaching rate of aluminum has declined, with an average of 50%. Therefore, in order to remove aluminum and iron in this three kinds of residues by means of acid soaking, circular crossflow-type retorting-derived semicoke should be calcined at 700–800 °C before impurities removal, while Fushun-type retorting residue and cogeneration power plant fine residue can be acid leached without calcination.

Figures 4–6 also show that the leaching rate of iron from the residues is higher than that of aluminum, while the content of aluminum in the composition of residue is higher than that of iron, that is because most of iron in oil shale is in the crystalline form of $Fe_2(CO_3)_3$ and becomes acid-soluble through different technique process, so the leaching rate is high; most of aluminum in oil shale is in the crystalline form of $Na_2Al_2Si_3O_{10}$, about 40% of it turns into metakaolinite ($Al_2O_3{\cdot}2SiO_2$) and silicon spinel ($Al_2O_3{\cdot}3SiO_2$), and little material is in acid-soluble state at different techniques, so the leaching rate of Al is relatively small.

Influence of calcination time on leaching rate of aluminum and iron

In order to study the influence of calcination time on the leaching rate of aluminum and iron, circular crossflow-type retorting-derived semicoke of Huadian oil shale was calcined for different times. The impurities were removed by means of acid soaking, the leaching rate of Fe and Al were determined, with the results shown in Fig. 7. As can be seen from Fig. 7, the leaching rate of Fe and Al both increased with calcination time increasing. When the time reaches 1.0 h, leaching rate of Fe reaches its maximum, while when the time exceeds 1.5 h, leaching rate of Al reaches the maximum, that is because the activation of aluminum is more difficult. So 1.5 h is the optimal time.

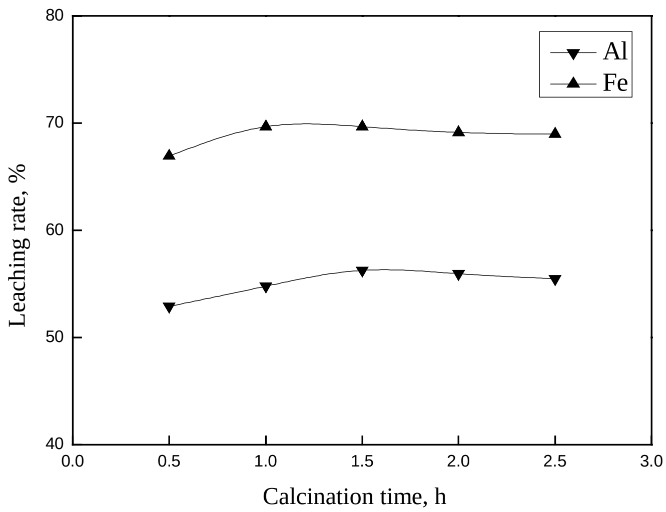

Fig. 7. Influence of calcination time of circular retorting semicoke on leaching rates of Al and Fe.

Performance test and characterization of the product of separation and purification

After the three residue of Huadian oil shale were calcined, separated and purified, as a result, three SiO_2 concentrates I, II, III were obtained and performance test performed respectively, the results are shown in Table 2.

Description of Table 2: the performances of the products which were obtained from circular crossflow-type retorting-derived semicoke and Fushun-type retorting residue of Huadian oil shale are good, furthermore, the indices of the product of the circular crossflow-type retort semicoke are better than those of the Fushun-type retort residue, the content of silicon dioxide are 92.34% and 90.38%, specific surface areas are 104 m^2/g and 91 m^2/g, reaching the E-class (71–105 m^2/g). So, these two SiO_2 concentrates can be used in the field of fine chemicals. While the characteristics of the product obtained from cogeneration power plant fine residue are below the national standard. As a result of low rate of impurities' removal, the content of silicon dioxide is only 87.39%, lower than the national standard (90%). In particular, the contents of Cu, Fe, Mn exceed quota and affect its application performance, so this product can only be used as an ingredient of cement, brick and so on.

Table 2. **All indices of separation and purification products from the three residues**

Testing item	I[1]	II[2]	III[3]	HG/T3065-1999
SiO_2, %	92.34	90.38	87.39	≥90
DBP, cm^3/g	2.50	2.10	1.80	2.0~3.50
Cu, mg/kg	14.61	24.00	34.50	≤30
Fe, mg/kg	203.40	873.80	1444.90	≤1000
Mn, mg/kg	21.50	46.50	153.50	≤50
Specific surface, m^2/g	104 (E)	91 (E)	63 (F)	E 71–105 F ≤70
Whiteness	73.90	66.70	65.40	76.4

[1] Products from circular crossflow-type retorting-derived semicoke
[2] Products from Fushun-type retorting residue
[3] Products from cogeneration power plant ash

SiO_2 concentrates which were obtained at separation and purification of circular crossflow-type retorting-derived semicoke of Huadian oil shale are characterized by the XRD chart as shown in Fig. 8. As can be seen from the chart, SiO_2 concentrate is a mixture of crystalline SiO_2 and amorphous SiO_2 ($2\theta = 20°–30°$), the content of crystalline SiO_2 is 32.2%, which was calculated by means of comparing the peak area with the XRD chart of the standard sample (crystalline SiO_2 and amorphous SiO_2 mixed in proportion).

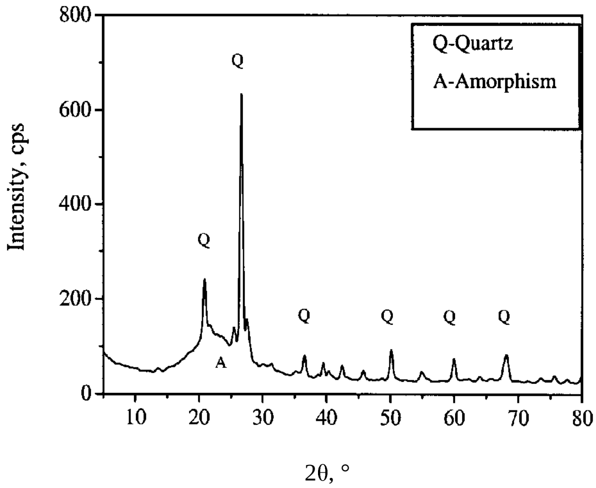

Fig. 8. XRD chart of separation and purification products.

Conclusions

1. Circular crossflow-type retorting-derived semicoke, Fushun-type retorting residue and Huadian cogeneration power plant fine residue are residues corresponding to different techniques characterized by different characteristics. Only the first one – semicoke – shows different XRD charts at different calcination temperatures, and the influence of calcination temperature on the leaching rate of iron and aluminum is high. At a temperature within the optimal temperature range of 700–800 °C, kaolinite decomposes completely, active states of iron and aluminum as well as their leaching rates can reach the maximum degree. While the XRD chart of Fushun-type retorting residue and cogeneration power plant ash have nearly no changes at different calcination temperatures, iron and aluminum reach the maximum of active state and leaching rate, and the influence of calcination temperature on them is low.
2. The content of Al_2O_3 (16.8–20.0%) is higher than that of Fe_2O_3 (8.7%–9.7%) while the leaching rate of iron (about 70%) higher than that of aluminum (50–60%).
3. After the three residues were calcined, separated and purified, products I, II, III were obtained. Their characters differed too much. The SiO_2 concentrates from circular crossflow-type retorting-derived semicoke and Fushun-type retorting residue contain 92.34% and 90.38% SiO_2, all other indices meet the national standard. While the content of SiO_2 from cogeneration power plant fine ash is only 87.39%, less than 90%. The contents of Cu, Fe, Mn exceed quota and do not meet the national standard. So it can only be used as ingredient of cement, brick and so on.
4. X-Ray diffraction is used to analyze the separated and purified products from the calcined semicoke derived from the circular cross-type retorted Huadian oil shale. The results show that it is a mixture of crystalline SiO_2 and amorphous SiO_2, the content of crystalline SiO_2 is 32.2%.

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