Oil Shale, 2012, Vol. 29, No. 1, pp. 36–50
doi: 10.3176/oil.2012.1.04
ISSN 0208-189X

PREPARATION OF ALUMINA FROM RETORTING RESIDUE OF OIL SHALE

Y.-M. XU[(a)*], D.-M. HE[(b)], J.-W. SHI[(b)], J. GUAN[(b)], Q.-M. ZHANG[(b)**]

[(a)] Key Laboratory of Biochemical Engineering
The State Ethnic Affairs Commission-Ministry of Education
School of Biological Science of Dalian Nationalities University
Dalian, 116600 China

[(b)] School of Chemical Engineering of Dalian University of Technology
Dalian, 116023 China

In this research, the leaching and preparation of Al_2O_3 from retorting residue of Fushun east open-pit oil shale in China were investigated. The optimum acid leaching conditions are the following: activation temperature is 850 ºC, activation time is 1h, the particle size of the raw material is 0.074mm, the concentration of acid is 12%, the liquid to solid ratio is 5:1, reaction temperature is 100 ºC and reaction period is 1.5 h. The homogeneous chemical precipitation method was applied for the preparation of alumina. Optimum conditions for alumina preparation were determined and are as follows: reaction at 55 ºC for 1.5 h, the concentration of sodium meta aluminate is 0.4 mol/L, the dose of surfactant is 0.3%. The product can be effectively purified by washing with 25% acetic acid, and then characterized by laser particle size distribution, X-ray fluorescence spectrometry (XRF), X-ray diffraction (XRD) and scanning electron microscopy (SEM). Results prove that the product is γ- Al_2O_3 with particle diameters in the range of 0.6–0.9 μm, and its degree of purity is 98.7%.

Introduction

Alumina is one of the basic materials in high-tech fields, and it is used in space navigation, nuclear energy, metallurgy, electronics, medicine, etc, due to its excellent heat resistance, abrasion resistance and corrosion resistance properties [1–2]. Alumina can exist in any of four solid phases: β–Al_2O_3, δ–Al_2O_3, γ–Al_2O_3 and α–Al_2O_3, though it exists mainly in the α and γ forms. γ–Al_2O_3 can be used as activator and adsorption agent due to its high adsorption capacity and catalytic nature, and it can be produced from

* Corresponding author: e-mail *xym@dlnu.edu.cn*
** Corresponding author: e-mail *zhangqm@dlut.edu.cn*

bauxite [3]. Due to the limited bauxite resources, many countries turn to other resources as substitutes for preparation of alumina and many studies have been carried out on that topic [4–6]. Oil shale retorting residue contains a large amount of SiO_2 and Al_2O_3. It is a kind of renewable resource, which offers the potential of many applications [7–9]. Preparation of alumina from oil shale retorting residue in China makes oil shale residue reusable and adds value to the product, but it is also beneficial for the economy, environmental protection and society [10–11]. In this work the retorting residue of Fushun east open-pit oil shale is studied as a raw material. To determine the optimum alumina preparation conditions from this retorting residue analyses were carried out to see how the acid leaching and alumina preparation conditions influence the rate of acid leaching and particle size of the produced Al_2O_3. Characterization and analysis of the product were also carried out.

Experimental

Study of raw material

The work involves examining the retorting residue formed in oil production process using Fushun east open-pit oil shale as a raw material. The main mineral component of the raw material is platy kaolinite and there are also small amounts of impurities, such as Fe, Ti and C, associated with the kaolinite. X-ray fluorescence spectrometry was used to identify the components of raw material. Results are listed in Table 1.

From Table 1 we can see that the content of Al_2O_3 is 26% and production of alumina from the retorting residue of Fushun east open-pit oil shale is feasible.

Table 1. **XRF analysis of the ash of retorting residue of Fushun open-pit oil shale**

Constituent	Content, %	Constituent	Content, %
SiO_2	57.9	P_2O_5	0.261
Al_2O_3	26	MnO	0.12
Fe_2O_3	9.26	CuO	0.05
MgO	1.51	ZrO_2	0.0397
K_2O	1.44	ZnO	0.0214
TiO_2	1.43	SrO	0.0204
CaO	0.903	NiO	0.0202
Na_2O	0.68	SO_3	0.419

Acid leaching of alumina

A predetermined amount of oil shale retorting residue was ground and calcined at 600–900 ºC in a muffle furnace for a predetermined period of time. 15 g of calcined residue was poured into 250 mL conical flask and then

a predetermined amount of 12% HCl solution was added. The conical flask was placed into the water-bath and solution was stirred for a while. Leached residual ash was separated by filtration. The obtained filtrate was $AlCl_3$ solution. Its concentration was determined by EDTA titration of aluminium using 1-(2-pyridylazo)-2-naphthol as indicator, and the leaching rate of alumina was calculated. The influence of calcination temperature, calcination time, concentration of acid and alkali, liquid to solid ratio, reaction temperature, reaction time and particle size of raw material were determined.

Preparation and characterization of alumina

NaOH solution (10mol/L) was added to $AlCl_3$ solution obtained from acid leaching reaction. pH value was adjusted to be 13 and solution was filtered to eliminate the impurity of $Fe(OH)_3$. 20% acetic acid was added to the filtrate until pH was 11.50, liquid was transferred into three-necked flask (250 ml) and warmed-up in an ultrasonically agitated reactor for 5min. Then ethyl acetate and surfactant were added into the flask. The solution was warmed up in the ultrasonically agitated reactor for a while, taken out and filtered. The filter cake was washed by acetic acid solution to remove impurities and calcined in a muffle furnace at 900 °C for 2h. It was then dried in infrared oven for 2 h, after which alumina was obtained. The particle sizes of alumina were determined by laser particle size analyzer. The influence of reaction temperature, reaction time, concentration of $NaAlO_2$, ratio of ethyl acetate to $NaAlO_2$, reaction time and dose of surfactant on particle size of alumina were investigated. X-ray fluorescence spectrometry, X-ray diffraction and scanning electron microscopy were applied to analyze the product.

Results and discussion

Acid leaching of alumina

Influence of calcination temperature on the leaching rate of Al_2O_3

Oil shale residue with particle size of 0.074 mm was calcined in a muffle furnace at different temperatures for 1h and the changes in the subsequent leaching rate of Al_2O_3 were investigated. Results are shown in Fig. 1. The leaching rate of Al_2O_3 increased gradually from 600–850 °C, and the maximum value appeared at 850 °C after which the leaching rate decreased, which indicates that the content of acid-soluble crystals decreased above that temperature. The retorting residue shows an optimum degree of activation when calcined at 850 °C when the leaching rate reaches the maximum.

The retorting residue of raw material calcined at different temperatures was analyzed by X-ray diffraction. The spectrogram is shown in Fig. 2. We can determine the concentration of minerals in the sample from the XRD spectrogram and determine the connection between particular minerals and their temperature dependence.

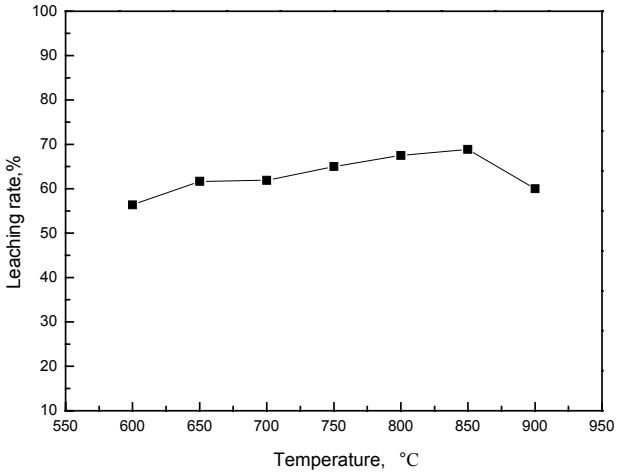

Fig. 1. Influence of calcination temperature on the leaching rate of Al_2O_3.

From Fig. 2 we can see that the diffraction peaks of the sample that was calcined at 600 °C mainly represent calcite ($CaCO_3$, 2θ = 32°) and kaolinite ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$, 2θ = 27°). Obvious changes in the intensities of peaks in the spectrograms from 600–850 °C reflect partial removal of OH^- which leads to the destruction of the crystal planes as kaolinite transforms into metkaolinite($Al_2O_3 \cdot 2SiO_2$). The diffraction peak of mullite ($3Al_2O_3 \cdot 2SiO_2$) appears at 900 °C, as an acid-insoluble crystal phase formed from partial alumina and silica. The XRD spectrogram analysis of retorting residue of Fushun east open-pit oil shale calcined at different temperatures is consistent with Fig. 1, therefore the optimum calcination temperature is 850 °C.

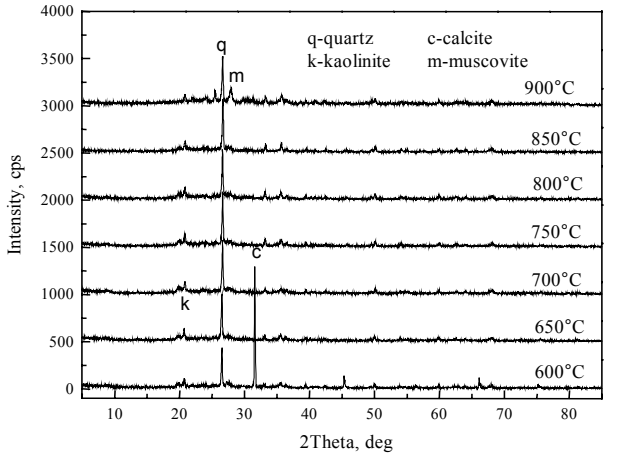

Fig. 2. XRD diffractograms of retorting residue of Fushun oil shale calcined at various temperatures.

Influence of calcination time on the leaching rate of Al_2O_3

Oil shale retorting residue with particle size of 0.074 mm was calcined in a muffle furnace at 850 °C. The influence of different calcination times on the leaching rate of Al_2O_3 were analyzed in order to determine the optimum calcination time. Results are shown in Fig. 3.

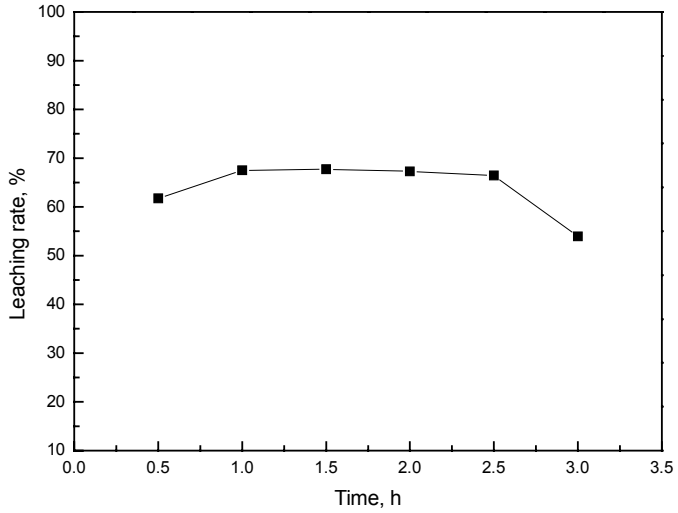

Fig. 3. Influence of calcination time on the leaching rate of Al_2O_3.

As we can see from Fig. 3, the leaching rate of alumina increases gradually from 0.5 hour up to a 1 hour calcination period. There is no obvious change in the leaching rate between 1.0 and 2.0 h of calcination, but the curve starts to decrease after 2 h of calcination. This tendency is caused by the initial increase in conversion to easily leached alumina in the retorting residue, after which retorting residue tends to agglomerate and this causes the reduction of leaching rate of Al_2O_3. 1.0 h was determined to be the optimum calcination time for leaching of alumina.

Influence of particle size on the leaching rate of Al_2O_3

The retorting residue of oil shale with different particle sizes was calcined at 850 °C for 1h to study the influence of particle size on the leaching rate of Al_2O_3. Results are shown in Fig. 4.

As shown in Fig. 4, the leaching rate of alumina reaches maximum value when the particle size is 0.074 mm. The leaching rate of alumina decreases gradually the larger the particles become because smaller particles offer greater specific surface area in contact with the liquid. This leads to the higher leaching rate. In reality there are many factors that influence the efficiency of the process. For example grinding the raw material into finer

particles will require more energy and solid-liquid separation is more complicated the smaller the solid particles, therefore, the optimum particle size of the raw material is 0.074 mm.

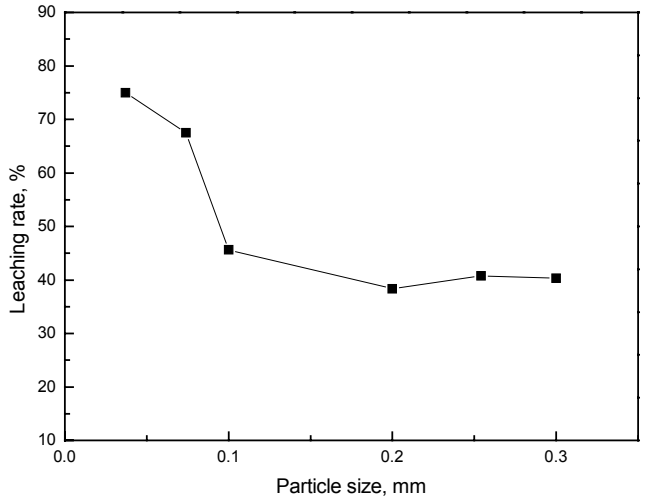

Fig. 4. Influence of particle size on the leaching rate of Al_2O_3.

Influence of reaction time on the leaching rate of Al_2O_3

Retorting residue of oil shale with average particle size of 0.074 mm was calcined in a muffle furnace at 850 °C for 1 h. The influence of different reaction times on alumina leaching rate was analyzed in order to determine the optimum reaction time. Results are shown in Fig. 5.

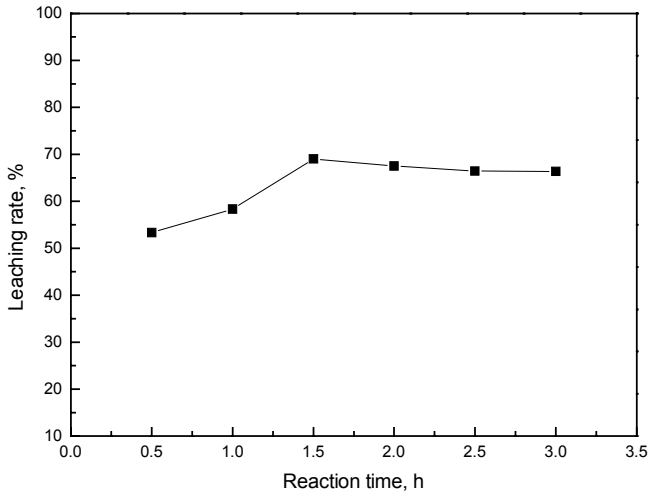

Fig. 5. Influence of reaction time on the leaching rate of Al_2O_3.

From Fig. 5 we can see that the leaching rate of alumina increases with increasing reaction time from 0.5 up to 1.5 h. The leaching rate of alumina almost does not change during the 1.5–3.0 h reaction period because activated alumina was already reacted completely after 1.5 h. Therefore the optimum reaction time is determined to be 1.5 h.

Influence of temperature on the leaching rate of Al_2O_3

The influence of reaction temperature on the leaching rate of Al_2O_3 was studied by changing temperatures during the acid leaching of alumina. Results are shown in Fig. 6.

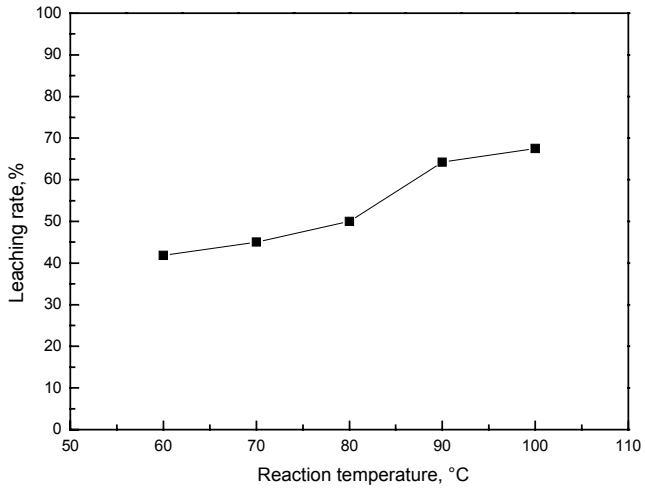

Fig. 6. Influence of temperature on the leaching rate of Al_2O_3.

As we can see from Fig. 6, the leaching rate of alumina increases in the temperature range of 60–90 ºC. The leaching rate almost does not increase when the reaction temperature is increased above 90 °C, therefore 90 °C is considered to be the optimum reaction temperature.

Influence of hydrochloric acid concentration on the leaching rate of Al_2O_3

To study the influence of hydrochloric acid concentration on the leaching rate of alumina the concentration of hydrochloric acid was changed while keeping the acid to solid ratio the same (5:1). Other parameters mentioned above were also kept the same. Results are shown in Fig. 7.

As we can see from Fig. 7, the influence of hydrochloric acid concentration on the leaching rate of alumina is significant. The leaching rate of alumina increases when hydrochloric acid concentration is increased from 2% to 12%, but there is no obvious change in the leaching rate when the

hydrochloric acid concentration is higher than 12%. Hence, the optimum hydrochloric acid concentration is considered to be 12%.

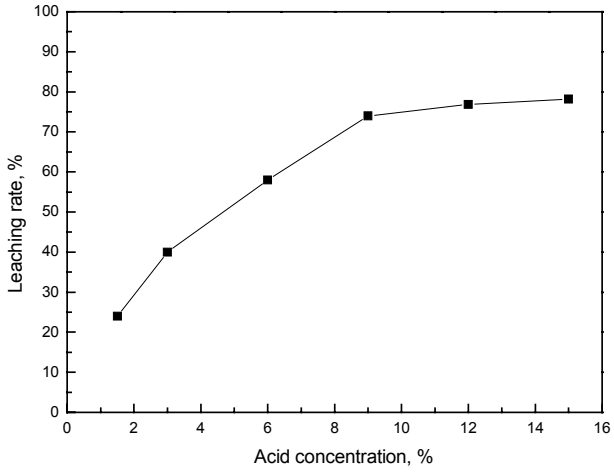

Fig. 7. Influence of hydrochloric acid concentration on the leaching rate of Al_2O_3.

Influence of liquid to solid ratio on the leaching rate of Al_2O_3

Applying the optimum conditions determined above, the optimum liquid to solid ratio was determined by changing the liquid to solid ratio, and the results are shown in Fig. 8.

As we can see from Fig. 8, higher liquid to solid ratio is associated with higher leaching rate of alumina. The leaching rate of alumina increases

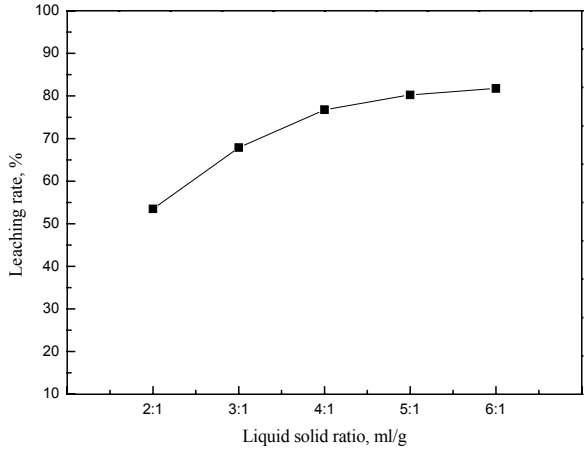

Fig. 8. Influence of liquid to solid ratio on the leaching rate of Al_2O_3.

considerably when liquid to solid ratio is below 5:1, and only a slightly increasing trend is seen when the liquid to solid ratio is higher than 5:1. Thus, the optimum liquid to solid ratio of acid leaching reaction is 5:1.

Influence of alumina preparation conditions on the particle size of alumina

Influence of reaction temperature on the particle size of Al_2O_3

Acetic ether, as a potential acidifier, was added into the solution of $NaAlO_2$ (0.3 mol/L) with 2:1 molar ratio of acetic ether to $NaAlO_2$, respectively, to initiate the reaction of alumina preparation at different temperatures and to study the influence of reaction temperature on the particle size of alumina. Results are shown in Fig. 9.

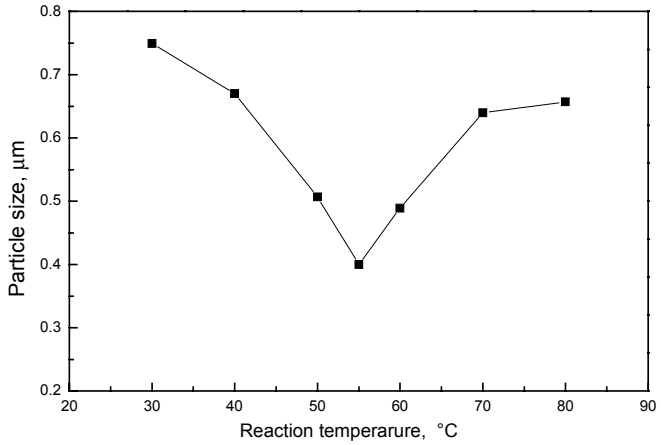

Fig. 9. Influence of reaction temperature on the particle size of Al_2O_3.

From Fig. 9 we can see that the particle size of alumina decreases when reaction temperature increases from 30–55 °C. Particle size increases when reaction temperature increases above 55 °C, so the smallest particle size was obtained at 55 °C.

Influence of $NaAlO_2$ concentration on the particle size of Al_2O_3

Regulation of $NaAlO_2$ concentration plays a key role in the homogeneous precipitation reaction. Acetic ether was added into $NaAlO_2$ solution in different concentrations with 2:1 molar ratio of acetic ether and $NaAlO_2$, respectively. Reaction took place at 55 °C. The influence of $NaAlO_2$ concentration on particle size of Al_2O_3 was studied, and results are shown in Fig. 10.

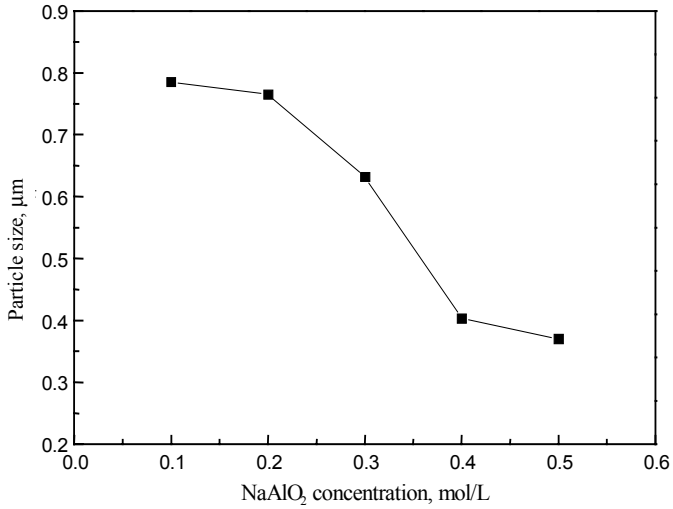

Fig. 10. Influence of $NaAlO_2$ concentration on the particle size of Al_2O_3.

The particle size of alumina decreases rapidly when the $NaAlO_2$ concentration is in the range of 0.1–0.4 mol/L. The decreasing trend becomes negligible when $NaAlO_2$ concentration increases above 0.4 mol/L. Optimum $NaAlO_2$ concentration is 0.4 mol/L.

Influence of ethyl acetate dosages on the particle size of Al_2O_3

The molar ratio of ethyl acetate to Al^{3+} was changed while keeping the reaction temperature at 55 °C and the concentration of $NaAlO_2$ 0.4 mol/L. The influence of ethyl acetate dosages on the particle size of Al_2O_3, was analyzed and results are shown in Fig. 11.

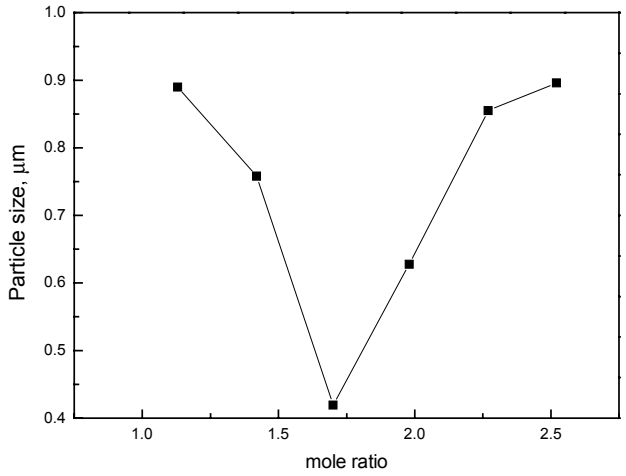

Fig. 11. Influence of ethyl acetate dosages on the particle size of Al_2O_3.

According to Fig. 11, a ratio of 1.7 yields the smallest particle size of Al_2O_3. Hence, this is determined as the optimum ethyl acetate dosage.

Influence of reaction time on the particle size of Al_2O_3

Influence of reaction time on the particle size of Al_2O_3 was investigated by conducting a series of experiments with different reaction times at 55 °C while the concentration of $NaAlO_2$ and molar ratio of ethyl acetate to Al^{3+} were kept constant (0.4 mol/L and 1.7, respectively). Results are shown in Fig. 12.

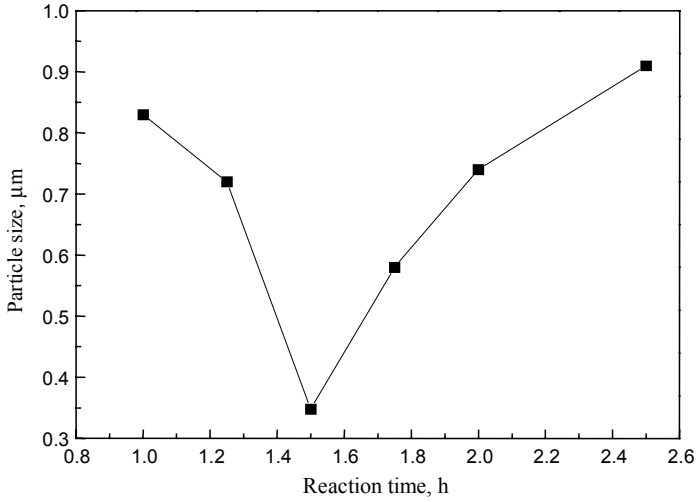

Fig. 12. Influence of reaction temperature on the particle size of Al_2O_3.

Figure 12 shows that particle size of Al_2O_3 decreases between 1.0–1.5 h reaction time and then increases when the reaction time lasts longer than 1.5 hours. Hence, optimum reaction time was determined to be 1.5 h.

Influence of surfactant dosages on the particle size of Al_2O_3

Lauryl trimethyl ammonium bromide was added into the reaction system under the optimum conditions described above for the investigation of the influence of surfactant dosages on the particle size of Al_2O_3. Results are shown in Fig. 13.

One can see in Fig. 13 that the maximum size of alumina particle is 0.5 μm and the size is smallest when the surfactant dosage is 0.3%. Lyophilic groups of lauryl trimethyl ammonium bromide can be absorbed on the particle surface forming a hydrophilic membrane with strong hydrogen bonds. It causes a sharp increase in repulsive potential energy between particles keeping them from agglomeration. As a result, particle size decreases. An increase in the concentration of hydrophobic groups favors

agglomeration of particles, resulting in an increase in particle size. So, the 0.3%-dosage of surfactant seemes to be optimum to get the smallest particle size.

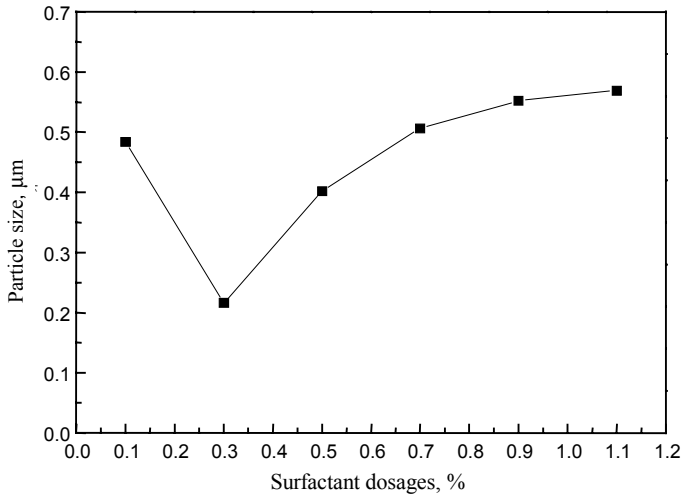

Fig. 13. Influence of surfactant dosages on the particle size of Al_2O_3.

Product analysis

Aluminium hydrate produced under optimum conditions was calcined in a muffle furnace at 900 °C for 2 h and transformed into alumina, for which the results of alumina analysis are shown below.

Particle size of the product

Alumina is a kind of white powder. The average particle size is 0.75 μm. Analyses were made by laser particle size analyzer (BT-9300H, China).

Product purity analysis

X-ray fluorescence spectrometer (SRS3400, Germany) was applied to analyze the purity of the product. Results are shown in Table 2. Purity of the product is 98.7%.

Table 2. **Purity analysis of alumina**

Constituent	Content, %	Constituent	Content, %
Al_2O_3	98.70	SO_3	0.0090
Na_2O	0.69	SiO_2	0.060
Cl	0.50	K_2O	0.020
P_2O_5	0.014	Others	0.0070

XRD analysis of the product

Figure 14 shows the results of the product analysis by X-ray diffractometer (D/MAX-2400, Japan). Diffraction peaks of γ- Al_2O_3 appear at 22°, 32°, 37°, 45°, 60° and 66°, which indicate that the product is γ- Al_2O_3.

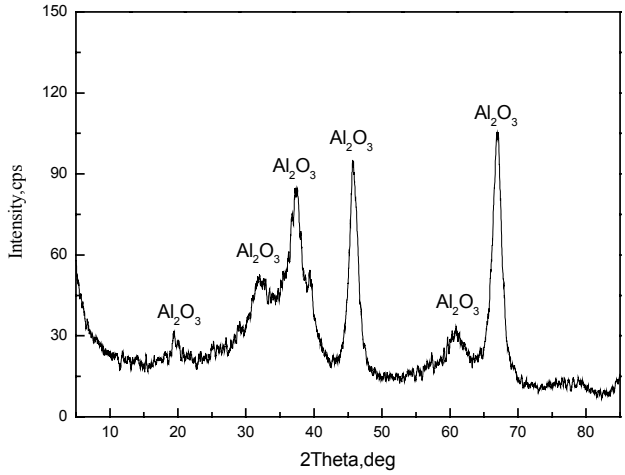

Fig. 14. XRD chart of the product.

SEM analysis of the product

Scanning electron microscopy for the product was conducted using scanning electron microscope model HITACHI S-4800 (Japan). Results are shown in Fig. 15.

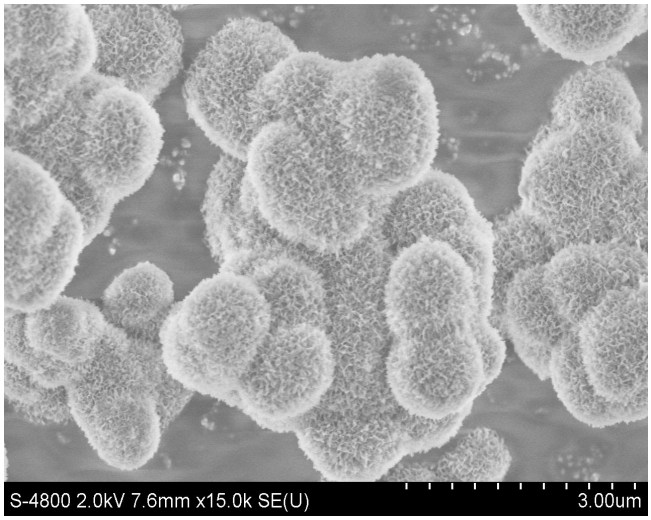

Fig. 15. SEM image of the product.

Figure 15 shows clearly that the formed alumina particles were almost spherical, with particle size of 0.6–0.9 μm.

4 CONCLUSIONS

(1) The optimum technical conditions for acid leaching of alumina from the retorting residue of Fushun open-pit oil shale are the following: activation temperature is 850 ºC, activation time is 1h, granularity of raw material is 0.074 mm, concentration of acid is 12%, liquid to solid ratio is 5:1, reaction temperature is 100 ºC and reaction period is 1.5 h. The maximum leaching rate is 81.75%.

(2) Alumina was prepared by homogeneous chemical precipitation. Optimum technological conditions of alumina preparation were determined. The reaction conditions are the following: the reaction temperature is 55 ºC, reaction time is 1.5 h, concentration of sodium meta aluminate is 0.4 mol/L and the dosage of surfactant is 0.3%.

(3) The product was analyzed by laser particle size analyzer, X-ray fluorescence spectrometer, X-ray diffractometer and scanning electron microscope. Results show that product is γ- Al_2O_3. Purity of the product is 98.7% and particle size is 0.6–0.9 μm.

(4) The recovery rate of alumina is 20.8% at the optimum process conditions.

REFERENCES

1. *An, B. C., Wang, W. Y., Ji, G. J., Gan, S. C., Gao, G. M., Xu, J. J., Li, G. G.* Preparation of nano-sized α-Al_2O_3 from oil shale ash // Energy. 2010. Vol. 35, No. 1. P. 45–49.
2. *Chen, Q. Y., Wu, X. W., Bai, Y. G.* // China Powder Science and Technology. 2003. No. 8. P. 16–18 [in Chinese].
3. *Liu, Q., Wang, A. Q., Wang, X. H., Gao, P., Wang, X. D., Zhang, T.* Synthesis, characterization and catalytic applications of mesoporous γ-alumina from boehmite sol // Micropor. Mesopor. Mat. 2008. Vol. 111, No. 1–3. P. 323–333.
4. *Xu, Y. M., He, D. M., Wang, D. M., Lian, Y. H., Guan, J., Zhang, Q. M.* Influence of calcination temperature on leaching rate of aluminium and iron impurities in oil shale ash // Oil Shale. 2009. Vol. 26, No. 2. P. 163–168.
5. *Feng, Z. Y., Li, Y., Xue, X. X.* Preparation of alumina and silica white from oil shale residue // Mining and Metall Urgical Engineering. 2008. Vol. 28, No. 4. P. 53–57 [in Chinese].
6. *Arro, H, Prikk, A, Pihu, T., Öpik, I.* Utilization of semi-coke of Estonian shale oil industry // Oil Shale. 2002. Vol. 19, No. 2. P. 117–125.
7. *Li, Y., Xue, X. X., Feng, Z. Y.* Preparation of precipitated silica from oil shale residue // Journal of Process Engineering. 2007. Vol. 7, No. 4. P. 751–754 [in Chinese].

8. *Jiang, X. M., Han, X. X., Cui, Z. G.* Progress and recent utilization trends in combustion of Chinese oil shale // Prog. Energ. Combust. 2007. Vol. 33, No. 6. P. 552–579.
9. *Trikkel, A, Kuusik, R., Martins, A., Pihu, T., Stencel, J. M.* Utilization of Estonian oil shale semicoke // Fuel Process. Technol. 2008. Vol. 89, No. 8. P. 756–763.
10. *Xu, Y. M., He, D. M., Jiang, H.M., Lian, Y. H., Zhang, W., Guan, J., Zhang, Q. M.* Characterization of oil shale processing residues and separated products // Oil Shale. 2009. Vol. 26, No. 4. P. 500–512.
11. *Gao, G. M., Zou, H. F., Gan, S. C., Liu, Z. J., An, B. C., Xu, J. J., Li, G. H.* Preparation and properties of silica nanoparticles from oil shale ash // Powder Technol. 2009. Vol. 191. P. 47–51.

Presented by J. Hilger
Received April 11, 2011