Microwave activation of coal gangue for Al compound

Xijie Lan, Shuhong Liu, Yuan Jing
College of Environment and Chemical Engineering, Dalian Jiaotong University, Dalian, 116028
lxj@djtu.edu.cn

Abstract. The coal gangue was activated by microwave. From the results of XRD and $^{27}$Al MAS NMR, we can speculate the reactions occurred and new species were generated during the microwave activation process. Effects on power grades of microwave oven, kinds of additives, time of microwave activation, temperatures of water bath and ratio of coal gangue to additives were investigated. Much higher extraction percent of Al (>50) has been obtained with KOH as additive, ratio of coal gangue to additive is 1:2, power of microwave oven is 595W and time of microwave activation is 20 min.

1. Introduction
Coal gangue is the industrial solid residue which is discharged when coal is exploited and washed in the production of coal mine in the world. Coal gangue is one of the most industrial solid wastes. In China, annual discharge amount of coal gangue is nearly 100 million tons, the gross amount reaches more than 4 000 million tons. However, the recycling ratio of coal gangue is less than 30%, so the amount of coal gangue is increasing year by year [1-2]. Our former investigations [3-5] showed that Si or Al compound in the coal gangue can be activated by mechano-chemical activation or calcine activation.

Currently, microwave is widely used for chemical treatment process [6-8]. In this paper, microwave activation is used to improve the extraction percent of Al from the coal gangue. The characteristics of XRD and $^{27}$Al MAS NMR are investigated. The relationships between extraction percent of Al and new species are also showed.

2. Materials and methods
The coal gangue without burned was exploited from Fengmei Coal Mine, Dandong City, Liaoning Province in China. Its concentration of Al$_2$O$_3$ is 24.3%.

Microwave activation was performed in a household microwave oven, with 5 power grades, such as 0W, 119W, 465W, 595W and 700W.

The extraction percent of Al was tested under 70 centigrade degree, 10 min, 6 mol/L for HCl, ratio of solid to liquid is 1:5.

The micro appearance of microstructure was investigated by a JSM-6360LV scanning electron microscope, the sample was gilded before investigation.

The XRD was performed on an XPert PRO/PANalytical, with 40 Kv, 4mA and 20°/min.

The $^{27}$Al MAS NMR was tested on a 600MHz Avance II, 4mm H-X, 12 kHz, pi/2 was 1 us and ns was 200.
3. Results and discussions

At first, we investigate the effects on power grades of microwave oven to the extraction percent of Al when the additive is alkali. When the power is 700W, crucibles with samples in them can crack and fire. It is very dangerous to the microwave oven and the operator. When the power is 119W or 465W, the extraction percent of Al are nearly 40%, but the times of filtration are long as 4 to 3 times as the power is 595W. When the power is 0W, the extraction percent of Al is less than 3. So we focus our later researches on 595W.

The results (referring to Table 1) show that the best extraction percent of Al is 43.5 and 40.5 can be obtained if the NaOH and KOH as additives when the power is 595W, the time of microwave activation is 15 min. Acid materials and salt materials cannot be effective additives during the microwave activation process.

| Extraction percent of Al (%) | Microwave activation time (power grade=595W) |
|-----------------------------|---------------------------------------------|
|                            | 5 min | 10 min | 15 min |
| No additive                | 2.4   | 4.3    | 5.1    |
| NH₄Cl                      | 2.8   | 3.8    | 4.9    |
| NaOH                       | 38.5  | 41.5   | 43.5   |
| KOH                        | 36.7  | 37.9   | 40.5   |
| Na₂CO₃                     | 3.0   | 4.2    | 4.8    |
| NaCl                       | 3.1   | 4.3    | 5.0    |

From Fig. 1, we can see gradually increased extraction percent of Al with temperature of water bath from room temperature to 90 centigrade degrees. For the economy reasons, we chose 70 centigrade degrees as the temperature of water bath.

When we increase the ratio of solid to the additive (referring to Fig.2), we can obtain the best extraction percent of Al (~50) with KOH as the additive. To find the activation mechanisms during the microwave activation process, we characterize the coal gangue with and without activation by XRD, ²⁷Al MAS NMR and SEM methods.

There is a diffraction peak near 27 degree in the coal gangue, which is identified as SiO₂ by using PDF Card 86-2237 (referring to Fig. 3). After activation, there is a diffraction peak near 32 degree in the activated coal gangue, which is identified as K₂Si₄O₉ by using PDF Card 75-1646. The intensity of peak of new material increases with the increase of the activated time from 5 min to 20 min. The original and stable SiO₂ structure in coal gangue has been destroyed and new material (K₂Si₄O₉) has been generated.

Fig.4 is ²⁷Al MAS NMR patterns of the samples with and without activation. From the pattern of coal gangue, we can find a highest peak near 0 ppm which is identified as skeleton model Al with four-coordination. However, this material disappears after activation for 20 min that means microwave activation can change the structure in the coal gangue. More intensity peak near 60 ppm is identified as non-skeleton model Al with six-coordination. The later material is more active than the former one.
From Fig. 5 we can see the micro appearance of coal gangue without microwave activation is a kind of layers structure, that means the coal gangue is very stable. After microwave activation for 20 min with KOH as additive, the border of the coal gangue has been rounded and blearred. The phenomena indicate the stable structure has been destroyed. Much high reactive activity has been obtained. That is why more Al (>50%) can be extracted out from coal gangue after microwave activation for 20 min. The characterizations and the experiments come to an agreement.
Figure 5. Micro appearances of coal gangue without and with microwave activation for 20 min with KOH as additive

Acknowledgements
This work was financially supported by Science Research Project from Education Department, Liaoning Province, L2014175.

References
[1] Study on Countermeasures of Coal Gangue Pollution Prevention and Regional Sustainable Development of China, Applied Mechanics & Materials, 2013
[2] Effects of Coal Gangue Content on Water Movement and Solute Transport in a China Loess Plateau Soil, Clean-Soil, Air, Water, 2015
[3] Extraction of Si from Coal Gangue by Mechanochemistry Activation, Bulletin of The Chinese Ceramic Society, 2011
[4] Complex Activation of Coal Gangue to Al Compounds, Advanced Materials Research, 2012
[5] Extraction of Al from Coal Gangue by Complex Activation, Industrial Minerals and Processing, 2012
[6] Influence of Microwave Activation on the Catalytic Behavior of Pd-Au/C Catalysts Employed in the Hydrodechlorination of Tetrachloromethane, Reaction Kinetics Mechanisms & Catalysis, 2018
[7] Microwave-activated Mn-doped Zirconium Metal-organic Framework Nanocubes for Highly Effective Combination of Microwave Dynamic and Thermal Therapy Against Cancer, Acs Nano, 2018
[8] Preparation, Optimization and Characterization of Carbon Fibers Adsorbent from Cotton by Microwave Induced ZnCl₂ Activation, Science of Advanced Materials, 2018