

Extraction of Aluminum from Combustion Ash of Coal Spoil

P. Si, X.C. Qiao, Y. Luo, X.F. Song, J.G. Yu

School of Resource and Environmental Engineering, East China University of Science and Technology, Meilong Road 130, Shanghai, China, 200237

KEYWORDS: coal spoil, combustion, aluminum, extraction, ash

INTRODUCTION

The rapid development of the global aluminum industry has led to a considerably increasing consumption of bauxite, from which alumina is mostly produced. Many aluminum producing countries including China have to import bauxite to keep the growth of native industry due to the low quality of bauxite. The costs of alumina production as well as the other aluminum-related products are correspondingly raised. Therefore, it is becoming more and more interesting to develop new alumina producing processes using non-bauxitic sources in bauxite import dependent countries.

Coal spoil (CS) is a by-product generated from the mining and beneficiation of coal. It comprises various types of minerals and rocks, associated with variable amounts of carbonaceous materials. In China, over 7, 000 million tons of CS have been accumulated and caused serious environmental problems. In most areas of China, the primary mineral in the CS is kaolinite ($\text{Al}_2\text{Si}_2\text{O}_7(\text{H}_2\text{O})_2$), which has been mostly thought to be an alternative to bauxite

The combustion of coal spoil leads to both the removal of coal content and crystal transformation of minerals, which resulted in a remarkable improvement on chemical activity of the combustion ash of coal spoil. The aluminum extraction from combustion ash is hence easier than from the uncombusted spoil. Many investigations have studied the activity of combustion ash of coal spoil and fired kaolin. Livingston W.T. et al suggested that calcination of coal spoil in the range 600~900 °C was necessary in order to obtain acceptable yields of Al using the leaching agent¹⁻². He Changling reported that the optimum calcination temperature for kaolin was 550 °C in order to increase its chemical reactivity³. The results of Kakali G. et al showed that the chemical reactivity of fired kaolin was influenced by the mineralogy of kaolin and the reactivity increased when the structure of kaolinite transformed from well-order to meta-stable phase⁴. However, the influence of combustion conditions on the reactivity of fired kaolin in the combustion ash of coal spoil has not been clearly understood.

This research investigated the aluminum extraction from combustion ash of CS (CACS) so as to recover alumina from CS. Two milled CS with particle size of less than 75 μm and 10 μm were subjected to combustion at 500, 600, 700, 800 and 900 °C. The extraction properties of combustion ash of CS under 20 wt.% hydrochloric acid have

been investigated. Thermal decompositions of CS have been also studied using X-ray diffraction, thermogravimetry analysis and Infrared spectra.

EXPERIMENTAI DETAILS

Materials

The CS was collected from Wuda Pinggou coal mine in Inner Mongolia China. The raw materials were crushed in a jaw crusher and then ground in a laboratory ball mill to totally pass through a 75 μ m sieve. Portions of the milled CS were then wet milled to less than 10 μ m in an agate mill. The two samples prepared were dried at 105 °C for 24 h in an oven. The samples with particle size of less than 75 μ m and 10 μ m were denoted as CS-a and CS-b, respectively. Figure 1 showed the X-ray diffraction (XRD) pattern of the CS. The proximate analysis and the low heating value of the CS were presented in Table 1. The chemical composition of the CS measured using X-ray fluorescence (XRF) was given in Table 2.

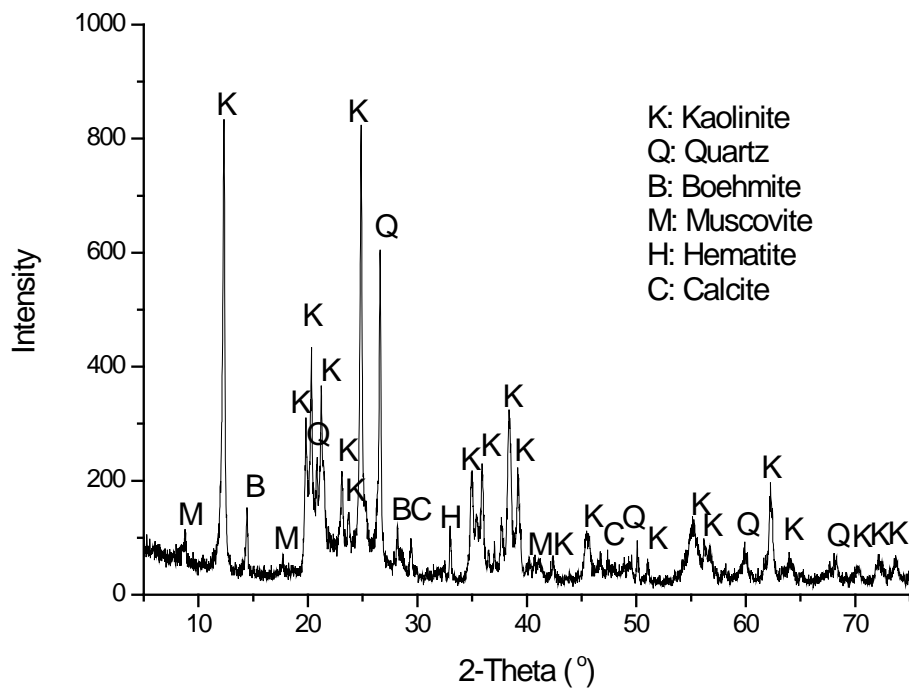


Figure 1. X-ray diffraction pattern of CS

Table 1. Proximate analysis (wt.%) and lower heating value of CS (MJ/kg).

Moisture	Ash content	Volatile matter	Fixed carbon	Lower heating value
0.6	72.5	15.01	11.89	4.45

Table 2. Chemical composition of CS (wt. %)

SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	TiO ₂	K ₂ O	CaO	SO ₃	MgO	Na ₂ O	LOI
------------------	--------------------------------	--------------------------------	------------------	------------------	-----	-----------------	-----	-------------------	-----

Thermal Analysis

An SDT Q600 instrument (TA, USA) was used for thermal analysis at air atmosphere. A sample of 20 mg was put in a corundum holder and heated at a rate of 10 °C/min.

Combustion of CS

The milled CS were loosely spread in a corundum saggar with a bed loading of 0.38 kg/m² and calcined in a muffle furnace at 500, 600, 700, 800 and 900°C for 15, 30, 60 and 120 minutes, respectively. Preheated air was blown into the furnace through an inlet on the front door and combustion gas went out through a chimney on the back. The loss on ignition (LOI) of the combustion ash of CS was measured to determine the decomposition degree of the CS, which was calculated using the following equation:

$$D = \frac{L_0 - L_1}{(1 - L_1)L_0}$$

Where D is the decomposition degree of the CS; L₀ and L₁ are the LOI of CS and calcined CS, respectively.

Procedures of aluminum leaching

5 g of each calcined CS was leached at 98 °C for 30 minutes by 25 ml of 20 wt.% hydrochloride acid in a flask fitted with a stirrer. The slurry was filtered using a Buchner funnel and the clear liquor was diluted to 250 ml for aluminum analysis using EDTA volumetry method. The reported results are the weight ratio of Al₂O₃ calculated from Al³⁺ concentration in the leachant to total Al₂O₃ in thermally treated sample.

X-ray diffraction

The crystal phases of calcined CS were determined by a D/max2550 VB/PC X-ray diffractometer (Rigaku, Japan) using a Cu target (40 kV, 450 mA, run at a 2 theta of 0.02° per step).

Infrared spectrum analysis

The infrared spectra of calcined CS over the range 4000~400 cm⁻¹ were obtained using the KBr disk method on a Nicolet 6700 Fourier transform infrared spectrometric Spectrometer (Thermo Fisher Scientific, US).

RESULTS AND DISCUSSION

Characterization of CS

The main minerals in the CS are kaolinite and quartz (Figure 1). A small amount of boehmite, muscovite , calcite and hematite are also detected. The kaolinite content is more than 90 wt.%, calculated according to the XRD patterns and the chemical composition of the CS.

The thermal analysis results in Figure 2 show that three exothermic peaks at 365, 533 and 993 °C appeared in CS-a. The first two exothermic peaks are related with the combustion of volatile matter and fixed carbon, respectively. The “993 °C” exothermic peak has been generally reported to be associated with the crystalline phase transfer of gamma-alumina or a spinel phase during the thermal treatment of kaolinite⁵⁻⁶. The three exothermic peaks of CS-b were at 350, 533 and 995 °C. The lower temperature of the first exothermic peak in CS-b indicated that the volatile matter was easier to be removed from the CS with smaller particle size. The figure 2 also showed that the decomposition of CS-b stopped at 810 °C, which was 55 °C earlier than CS-a.

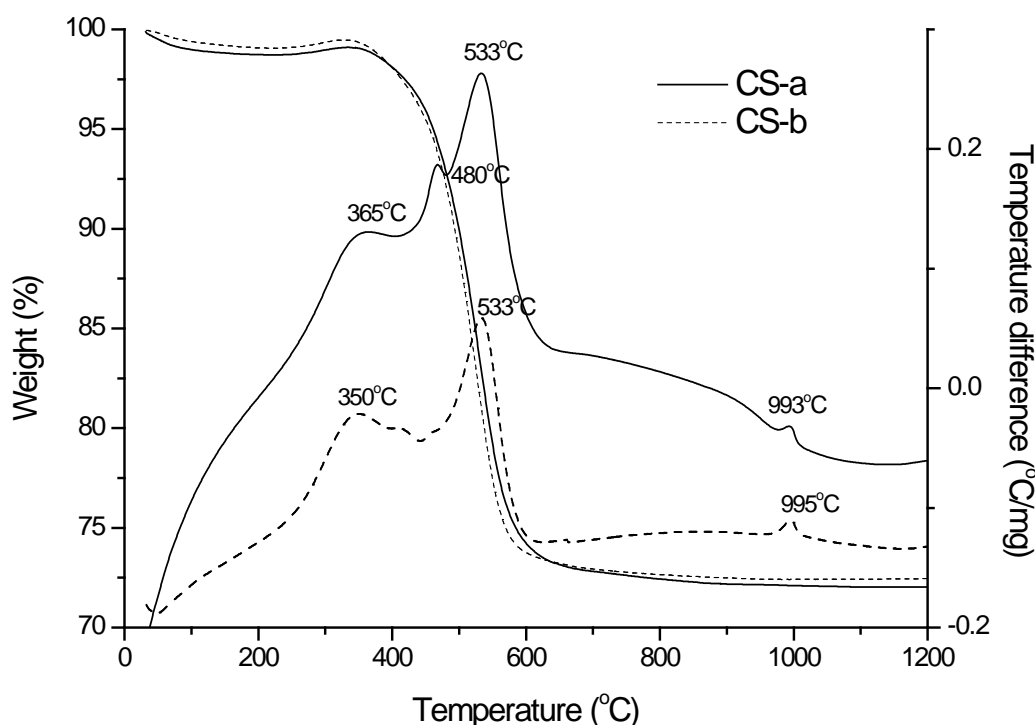


Figure 2. Thermal analysis of CS-a and CS-b

A small endothermic peak was detected in CS-a at 480 °C, which was reported to be related with the dehydroxylation of kaolinite⁷. However, it was not observed in the CS-b, which may result from the fast combustion of fixed carbon. The thermal results showed that the combustion of fixed carbon and the decomposition of kaolinite in the CS occurred simultaneously.

Leaching of aluminum

The aluminum leaching results of samples treated at different temperature are shown in Figure 3. The aluminum leaching from 500 °C calcined CS-a increased with the calcination time and was around 77 wt% after 120-minute treatment (Figure 3-a). The aluminum leaching changed little with calcination time under the treatment of 600, 700 and 800 °C, however, decreased largely at 900 °C. The treatment at 600 °C was

optimum for aluminum leaching from calcined CS-a and more than 75 wt.% aluminum was leached from calcined CS-a. The aluminum leaching from calcined CS-b showed similar characters to that of calcined CS-a (Figure 3-b). However, the aluminum extracted from calcined CS-b was 10~25 % higher than that from calcined CS-a, except at 900 °C. The optimum temperature was also 600 °C and around 80 % of aluminum was leached from calcined CS-b.

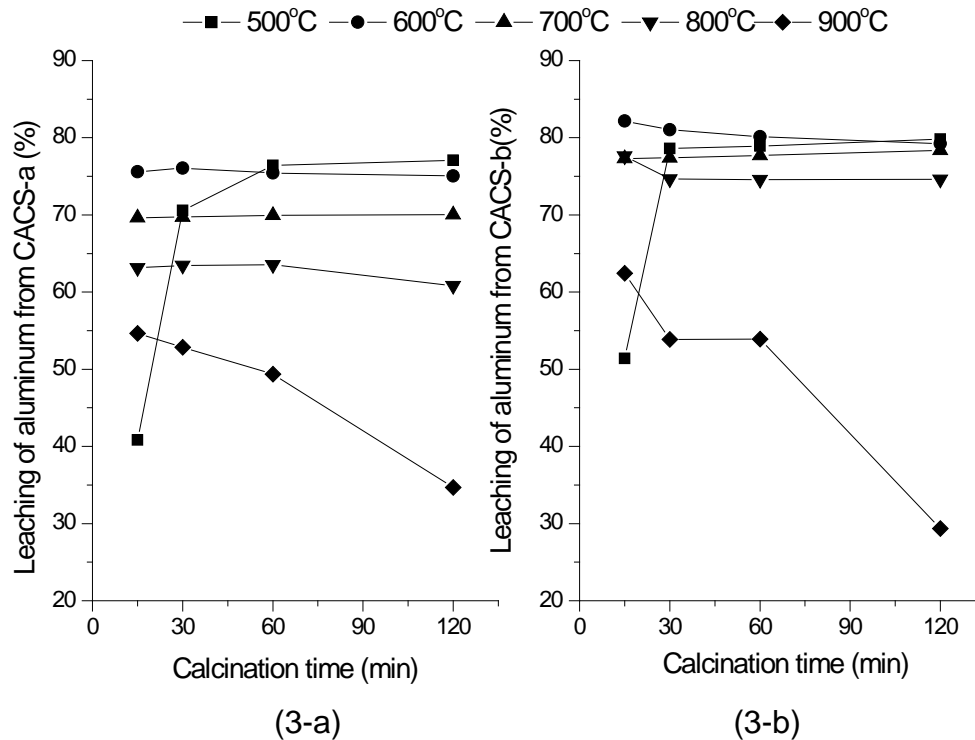


Figure 3. Leaching of aluminum from combustion ash of CS-a (3-a) and CS-b (3-b).

Decomposition of CS

The decomposition degree of CS characterized the efficiency of both the dehydroxylation of kaolinite and the combustion of coal content in the CS. The results in Figure 4 show that the decomposition degree of CS generally increased with calcination temperature and time. The decomposition degree of 500 °C calcined CS was the lowest after 15-minute treatment and then increased significantly with time. This is related with the coal combustion occurred at around 500 °C in the CS (Figure 2). The temperature of CS could increase up to 100 °C with the continuous combustion at 500 °C and the decomposition of kaolinite was hence accelerated⁸. It can be also found in Figure 4 that the decomposition of CS-b was faster than that of CS-a at 500 °C. This is attributed to the faster combustion of fixed carbon in the CS-b (Figure 2). Similar to the aluminum leaching results the difference of decomposition between CS-a and CS-b decreased with treatment temperature. Combined with the results in Figure 3 the aluminum leaching decreased when the decomposition degree was higher than 95.84 wt.%. Although more than 99 wt% of CS decomposed under the treatment of 900 °C the leaching of aluminum decreased largely. This may be related with the formation of mullite and spinel reported in previous paper⁹.

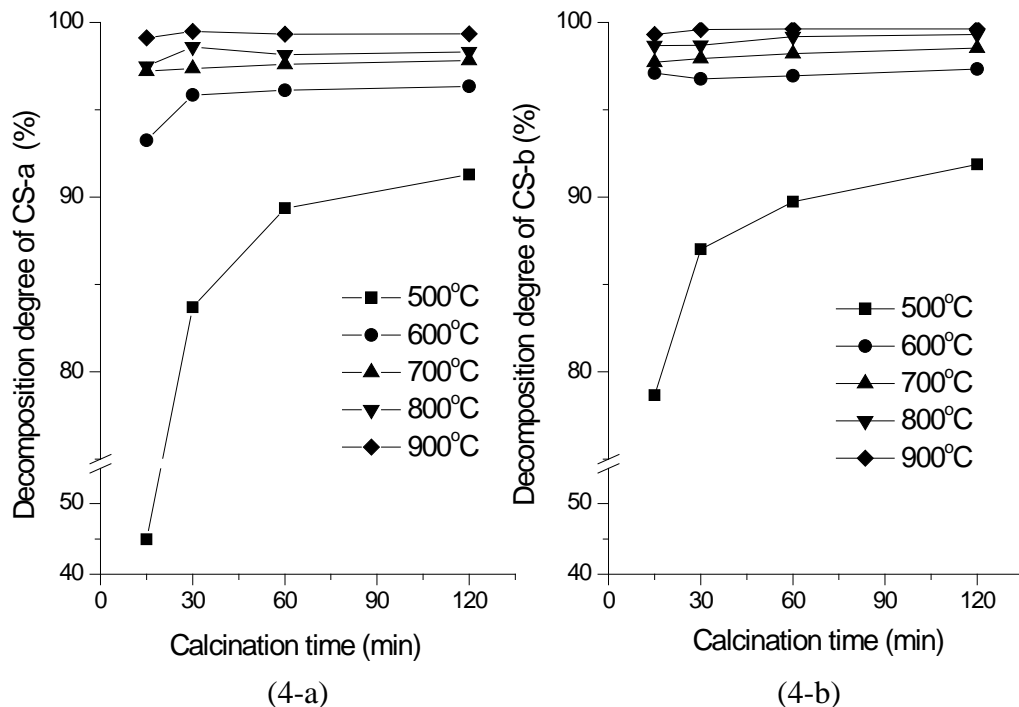
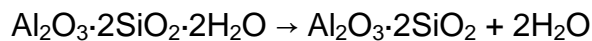


Figure 4. Decomposition degree of CS-a (4-a) and CS-b (4-b) at different temperature.

XRD analysis

The XRD patterns of combustion ash of 60-minute treated CS-a (Figure 6) showed that the kaolinite decreased with the combustion temperature and disappeared at 600 °C, which was related to the dehydroxylation of kaolinite ¹⁰.



The muscovite was dehydroxylated and the boehmite disappeared under the treatment of 500 °C for 60 minutes. The calcite was reported to be decomposed at 897 °C, however, there is no calcite detected in the CS combustion ash calcined at a temperature of higher than 700 °C. The meta-kaolinite ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) formed after dehydroxylation is amorphous phase so that it is not able to be detected by XRD ¹¹. Only quartz and a small amount of dehydroxylated muscovite appeared in the combustion ash of CS fired at 700, 800 and 900 °C. It was reported that the meta-kaolinite produced between 500 and 600 °C kept unchanged until the “980°C” exothermal reaction ¹². However, the results in Figures 5 show that the quartz peaks of calcined CS changed with the calcination temperature. The intensity of (101) quartz peak of 60-minute fired CS increased with temperature before 700 °C. This suggested that silica was formed before 980 °C during the calcination of meta-kaolinite, which was in agreement with the research of Santos H.S. ¹³ However, The intensity of (101) quartz peak decreased from 800 °C. This indicates that the silica formed during the calcination of meta-kaolinite can rejoin the reaction at 800 °C under the 60-minute treatment.

The XRD results showed that the combustion of coal content in the CS accelerated the decomposition of kaolinite and reactions between meta-kaolinite and silica.

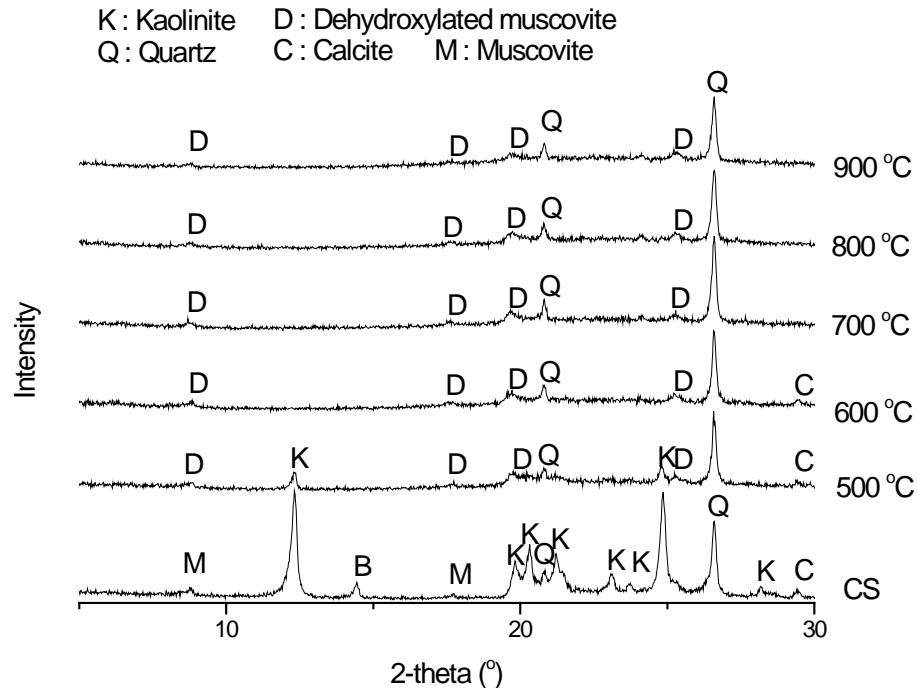


Figure 5. XRD patterns of CS combustion ash calcined for 60 mins.

IR analysis

The infrared spectra of CS-a and 60-minute combustion ash of CS-a are shown in Figure 6. The bands at 3693, 3655, 3620, 1111, 1034, 1011, 914, 794, 754, 692, 540, 470 and 430 cm^{-1} are attributed to the kaolinite¹⁴. The bands at 3693, 3655, and 3620 cm^{-1} are assigned to the hydroxyl-stretching, of which the reduction means the dehydroxylation of kaolinite in the combustion ash of CS-a¹⁵. The disappearance of bands at 914, 540 and 430 cm^{-1} and the appearance of a new band at 798.4 cm^{-1} were related with the transformation from kaolinite to meta-kaolinite¹⁶. It indicated that the kaolinite was totally converted to meta-kaolinite in the ash prepared at 600 °C, which was consistent with the XRD results. In the combustion ash the bands of kaolinite at 1111, 1034, and 1011 cm^{-1} merged to a single broad one at 1061 cm^{-1} and shifted to the shorter wavelength with the increase of calcination temperature. This is attributed to the increase in the orderliness of silicate structure which is related with the reactivity of the corresponding sample¹⁷. A new band at 559.3 cm^{-1} appeared in the CS combustion ash prepared at 600 °C. This band is reported to be assigned to amorphous $\gamma\text{-Al}_2\text{O}_3$ ¹⁴. It showed that the meta-kaolinite was decomposed to generate $\gamma\text{-Al}_2\text{O}_3$ at 600 °C for 60 minutes. Therefore, the CS combustion ash prepared at 600 °C showed higher chemical reactivity.

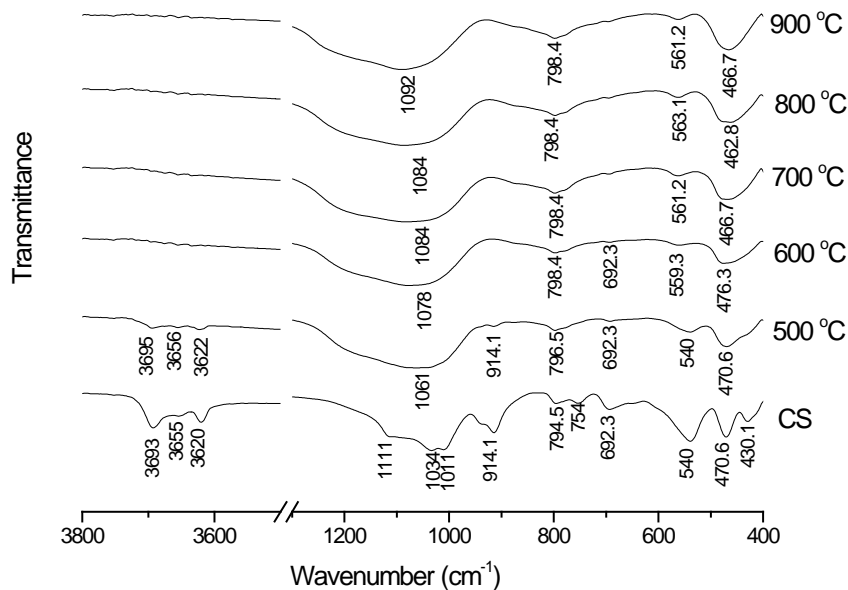


Figure 6. IR spectra of CS combustion ash calcined for 60 mins.

CONCLUSIONS

1. Combustion at 600°C was optimum for the recovery of aluminum from CS and more than 80 wt.% of aluminum was able to be leached.
2. The aluminum extraction depended on the phase transformation of kaolinite in the combustion ash of the CS. The temperature related with the formation of $\gamma\text{-Al}_2\text{O}_3$ was the up limit of calcination temperature of CS.
3. The combustion of coal content in the CS can accelerate the decomposition of kaolinite and the reactions between meta-kaolinite and silica.
4. The small particle size was helpful to elevate the chemical reactivity of CS combustion ash to acid due to the fast combustion of fixed carbon and fast decomposition of kaolinite.

ACKNOWLEDGEMENT

The work described in this paper was funded by Shanghai Pujiang Program (Project No. PJ[2007]00339), Science and technology commission of Shanghai municipality (Project No.07dz12027) and Shanghai Leading Academic Discipline Project (Project No. B506)

REFERENCES

- [1] Livingston W.R., Rogers D.A., Chapman R.J. and Bailey N.T. Hydrometallurgy, 1983, 10, p.79.

- [2] Livingston W.R., Rogers D.A., Chapman R.J. and Bailey N.T. Hydrometallurgy, 1983, 10, p.97.
- [3] He Changling, Makovicky E, Osback B. Applied clay science, 1994, 9, p165
- [4] Kakali G, Perraki T, Tsivilis S. and Badogiannis E. Applied clay science, 2001, 20, p.73
- [5] Chakraborty A.K.. Thermochemica acta. 2003, 398, p.203.
- [6] Sonuparlak B., Sarikaya M. and Aksay I.A. Journal of the American Ceramic Society. 1987, 11, p.837.
- [7] Rahier H., Wullaert B. and Mele B. Journal of thermal analysis and calorimetry, 2000, 62, p.417.
- [8] Livingston W.R., Rogers D.A., Chapman R.J. and Bailey N.T. Hydrometallurgy, 1983, 10, p.97.
- [9] Qiao X.C., Si P. and Yu J.G. Environmental science and technology, 2008, 42, p.8541.
- [10] Chakraborty A.K.. Journal of the American Ceramic Society. 1992, 7, p.2013.
- [11] MacKenzie K.J.D., Brown I.W.M., Meinhold, R.H. and Bowden. M.E. Journal of the American Ceramic Society, 1985, 6, p.293.
- [12] Chakraborty A.K.and.Ghosh D.K. 1978, 61, p.170.
- [13] Santos H.S., Campos T.W., Santos P.S.and Kiyohara P.K. Ceramic international. 2005, 31, p.1077.
- [14] Percival, H. J., Duncan, J. F., and Foster, P. K. Journal of American Ceramic Society. 1974, 2, p.57.
- [15] Frost, R. L., Kristof, J., Horvath, E., Martens, W. N. and Kloprogge, J. T. Journal of Colloid Interface Science. 2002, 2, p.350.
- [16] Rahier, H., Wullaert, B. and Van Mele, B. Journal of Thermal Analysis and Calorimetry, 2000, 2, p.417.
- [17] Mukherjee, S. and Srivastava, S. K. Fuels, 2006, 3, p.1089.