

Characteristics of Unburned Carbon Particles Recovered from Fly Ash

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ABSTRACT

The most important and largest commercial outlet of fly ash in Korea is a replacement material for Portland cement in concrete industry. The high level of unburned carbon in ash is known to bring some malfunctions in concrete; therefore, coal ash should be refined to improve its quality. In the refining process, a lot of residual carbon is produced, and discarded currently. In the present study, to find out effective ways of the use of enriched carbon samples, the basic morphology of residual carbon in fly ash from the Boryung power station was investigated. The characterizations of unburned carbon was done by shape, size measurement and chemical analysis using scanning electron microscopy and energy dispersive x-ray spectrometer. Additionally, the physicochemical properties of unburned carbon particles obtained from fly ash were investigated. The carbon-enriched samples were liberated from fly ash by flotation method. The carbon content and chemical composition of the recovered carbon were analyzed and the ash in the sample was also examined. The unburned carbon was characterized in terms of size distribution, surface area, crystal structure and density.

INTRODUCTION

During the last few years, new products incorporating fly ash from coal combustion have been developed. Currently, fly ash has emerged from the realm of a waste to that of a resource[1]. The most important and largest commercial outlet of fly ash in Korea is a replacement material for Portland cement in concrete industry[2]. It exceeds any other single application, and has been marked increasing in the use of coal ash. However, high levels of unburned carbon in fly ash can make fly ash unsuitable for this high-value market. The high level of unburned carbon in ash is known to cause some malfunctions in concrete; therefore, coal ash should be refined to improve its quality. In

the refining process, a lot of residual carbon is extracted, and discarded currently[1~4]. The residual carbon material has been considered for use as a recycle fuel or as a low-cost absorbent. The bulk physicochemical properties of the carbon play an important role in each of these applications[2,4~6].

In the present work, the char particles and ash particles in residual carbon extracts were examined by electron microscopy and their bulk physicochemical properties were measured. Scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDS) was the major technique used in the study of the morphology and chemical composition of char and inorganic ash particles.

The chemical composition of inorganic ash particle samples are determined using Inductively Coupled Plasma Atomic Emission Spectrometer(ICP-AES). The total surface area and the average micropore size was estimated using BET isotherm model. X-ray diffraction (XRD) was also utilized on representative bulk fly ash sample and residual carbon extracts.

EXPERIMENTAL

Fly ash samples were obtained from Boryung coal-fired power plant in Korea. Overall residual carbon contents of the samples ranged from 8 to 10wt%. A wet flotation technique was used to separate and extract residual carbon from the inorganic portion of the fly ash. The process is presented in Fig. 1.

The proximate analysis of unburned carbon extracts was performed using LECO TGA601. The elemental compositions of ash samples were determined using Inductively Coupled Plasma Atomic Emission Spectrometer(ICP-AES). The morphology of the residual carbon and the nature of its association with inorganic matter were investigated by SEM (JEOL JSM6400). The samples were plasma coated with gold for secondary and backscatter electron imaging. The morphology of numerous individual particles was observed using both backscattered and secondary electron detection. The selected fly ash particles in unburned char particles were analyzed for elemental composition using EDS (Noran Series II), with spatial resolution of the order of $1 - 10^{-3}$, depending on the particle matrix composition and morphology. Electron probe conditions of 20 kV and a beam current of about 10^{-10} A were used.

The adsorption-desorption isotherms were determined for unburned carbon extract samples to determine total surface areas. The isotherms measured were interpreted by application of the well-established BET method for surface area calculation, using a

nitrogen molecule surface area of 0.162nm^2 .

The samples analyzed by XRD were prepared by grinding the carbon-rich extracts and the loose fly ash particles to the sizes between 60 and 100 mesh. X-ray diffraction analyses were performed using a Rigaku computer controlled diffractometer with an 20kW high-intensity rotating anode (Cu K α radiation). The powder diffraction patterns were referenced to the search manual of the International Center for Diffraction Data.

RESULTS AND DISCUSSION

Chemical Analysis

The carbon content was determined as-received fly ash sample using a loss on ignition (LOI) measurement. It was 8 wt%. Fixed carbon, moisture, volatile materials and ash analyses of the unburned carbon extract are presented in Table 1. The results are compared to these of active carbon which made from coconut shell. The fixed carbon component of unburned carbon extract is lower than that of active carbon. The difference is come from the content of inorganic ash.

The elemental compositions of the raw fly ash and the carbon extract are presented in Table 2. The content of aluminium is increased in ash of the carbon extract sample, but other elements are decreased. This indicates that chemical compositions of ash particles captured by residual carbon are different from these of the raw fly ash.

Size Distribution

The size of unburned carbon particles extracted by flotation ranges from submicrometer to over 600 μm . Fig. 2 summarizes the measurements of carbon-size distribution for a sample. The carbon content increases greatly with increasing size. The median size of the carbon particles is 95 μm , and 80% of the measured sample is in the range of 12 to 240 μm .

Morphology and SEM-EDS Analysis

Microscopic examination revealed that the inorganic portion of the fly ash samples consists predominantly of glassy spheres. Most of the carbon present is in the form of distinct, fused particles with an extensive macroporous structure, an example of which is seen in Fig. 3.

Fig. 3(b) is a SEM micrograph of the residual carbon extract and Fig. 3(a) that of the fly ash sample. The extract contains primarily carbon-rich particles, with isolated

distinct particles rich in inorganic matter. The carbon particles are highly macroporous, many appearing to be fragments or shells of swollen, nearly spherical or rectangular char particles. In none of the images examined did a significant fraction of the carbon appear to be encapsulated by inorganic matter.

Different structural units are identified in rectangular, vesicular, flat, lamellar, and granular, and some variation in shape within each unit is observed as shown in Fig. 4. Among the above textural components, well defined lamellar components are most easily recognized.

The inorganic-rich particles, primarily fine particles in this sample, are generally distinguishable from the low-atomic-weight carbonaceous material. Fig. 5 shows ash particles attached to unburned carbon particle. Significant amounts of fully or little fused ash particles are seen on the residual carbon particle. The ash and carbon particles can be easily signified because the brightness in SEM images is related to the local atomic weight (heavy elements appear brighter). SEM-EDS analyses in Table 3 show that the elemental compositions of the larger ash particles and submicrometer sized spheres are different. The bar-type particles consist of only aluminum and silicon, but the smaller ones have iron, calcium and potassium in addition. This is due to the contacts between different molten components in the combustion zone which are not intermixed, but formed along the boundaries of other crystallized materials. Melting points of elements and minerals are very different; therefore, the minerals containing iron or alkali elements are fully molten in combustion zone and become glassy spheres.

Thermal Treatment and Specific Surface Area

Thermal characteristics of unburned carbon were different from active carbon. Fig. 6 shows the mass reduction by combustion of unburned carbon in the range of 300 to 700 . In the case of the active carbon, the reduction of mass starts at over 300 , while the unburned carbon shows stable up to 400 . The positive slopes are appeared in the range of 400 to 600 for the unburned carbon, and 300 to 450 for the active carbon.

The total BET surface areas of unburned carbon extract and active carbon are 11 and 1,182 m²/g respectively. Heating unburned carbon to 450 leads to a significant increase in micropore surface area and micropore volume as measured with nitrogen at 77 K. This may be due to the opening up of a number of micropores in the carbon structure by the release of volatile matters. Fig. 7 shows that the apparent BET surface area after 450 -treatment is 163 m²/g. Above this temperature, the surface area is steeply decreased.

Carbon Crystalline Structure

Fig. 8 presents X-ray diffraction patterns of raw fly ash and unburned carbon extract. Both spectra show diffuse carbon band(002), but for the raw sample the peaks due to crystalline inorganic phases make detailed interpretation of the carbon diffraction patterns difficult. Close examination of the carbon extract sample spectrum reveals the absence of the three-dimensional graphitic peaks at 44.7° (101). Turbostratic structure is indicated by the diffuse nature of the (002) and (101) bands.

CONCLUSIONS

Unburned carbon morphologies and physicochemical properties are observed. The residual carbon samples show the signs of significant oxidation that has led to highly porous, fragmented particle structures. Generally the residual carbon particles are generally quite macroporous, providing good access for air to penetrate to the inside. Most of the carbon is present in distinct carbon-rich particles, whose ash content is typically 20wt%. The inorganic ash particles are usually captured by the larger carbon particles. Some ash bar or plate are attached to a carbon particle. The unburned carbon extract also have microporous surface areas of $11 \text{--} 163 \text{ m}^2 \text{ g}^{-1}$. Whereas the surface areas of residual carbon samples are lower than that of commercial active carbon made from coconut shell.

References

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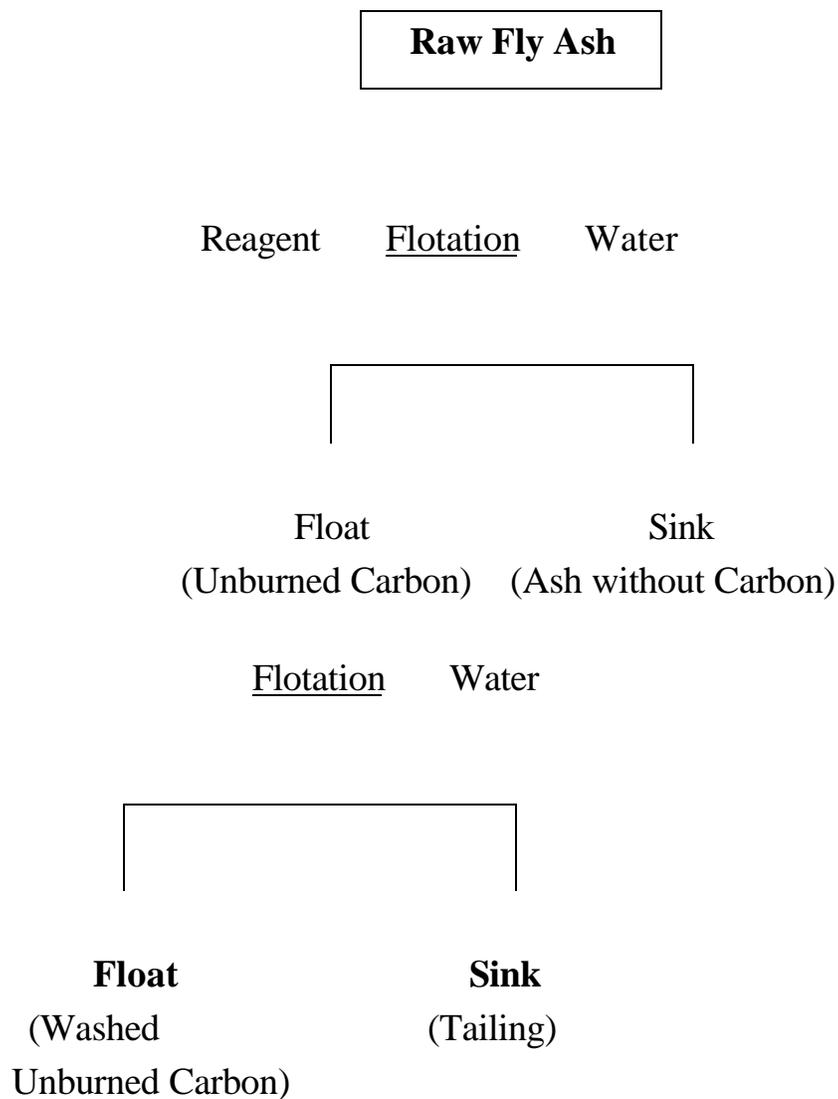


Fig. 1. The recovery process of unburned carbon.

Table 1 Proximate analysis of unburned carbon obtained from Boryung fly ash.

Composit	Fixed Carbon	Ahs ⁾	Volatile Materials ^{b)}	Moisture ^{c)}
Unburned carbon	74.7	20.9	4.44	0.93
Activated carbon ^{d)}	85.5	6.35	8.20	5.80

a) fired at 825 °C, for 2 hr, b) 7 min at 925 °C in inert environment,

c) 1hr at 107 °C, d) from coconut shell

Table 2. Chemical composition of ash samples

Composition	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	K ₂ O	Na ₂ O
Raw Fly Ash	64.5	25.1	3.69	2.87	1.13	-
Ash from unburned carbon	63.3	29.1	2.07	2.40	0.73	0.21
Ash from activated carbon	60.6	17.4	12.6	3.60	17.8	5.31

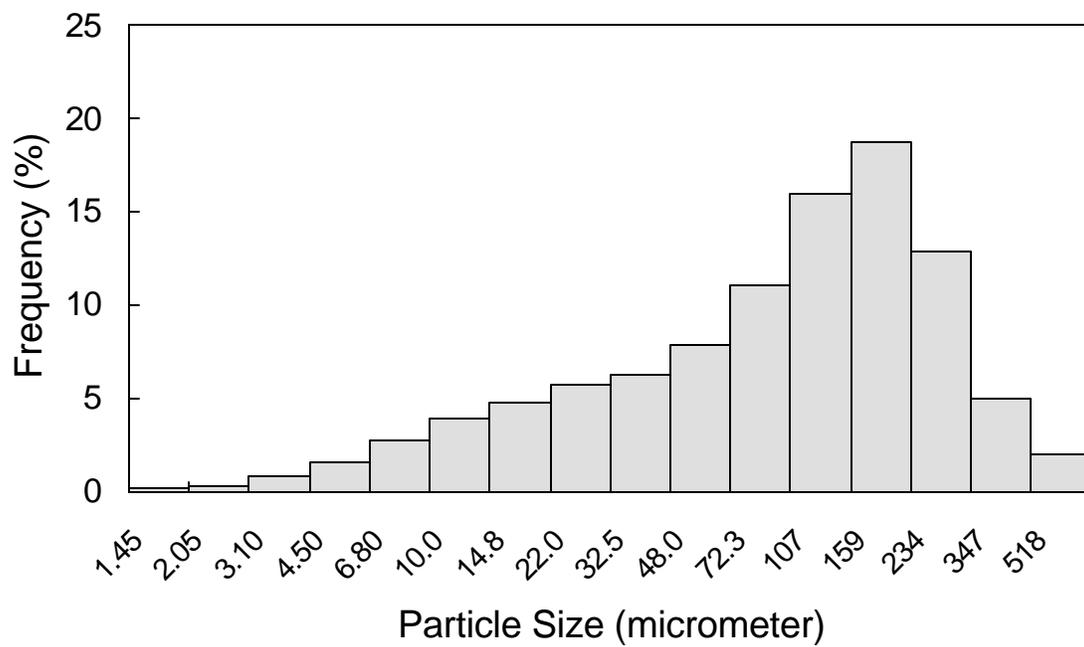
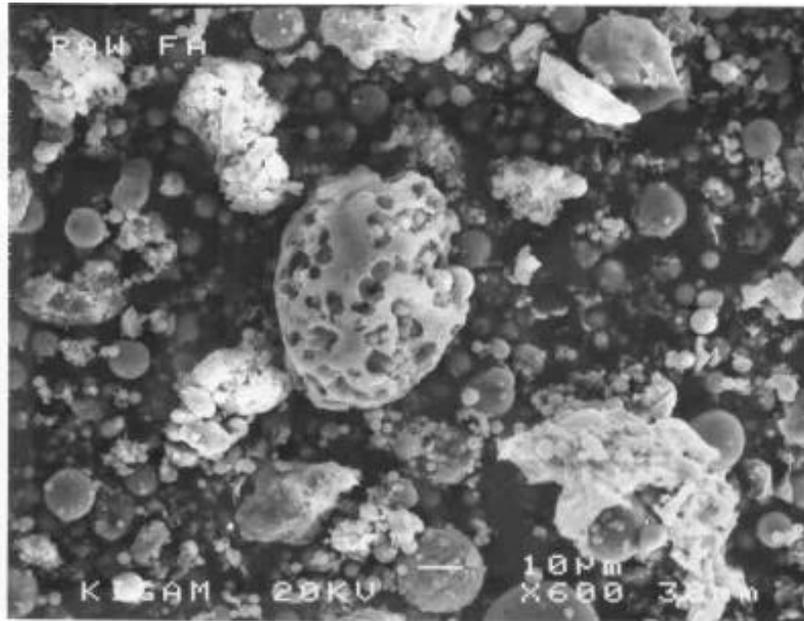
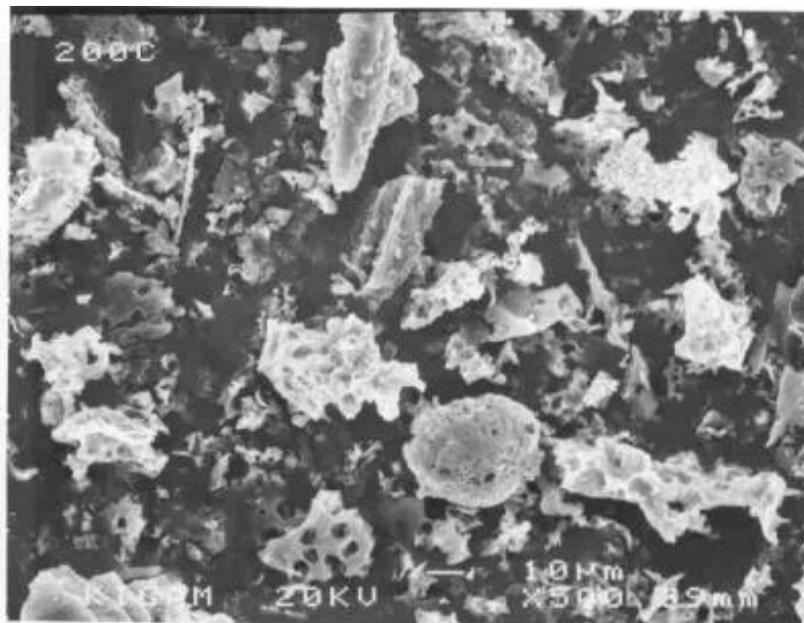


Fig. 2. Size distribution of unburned carbon extract.

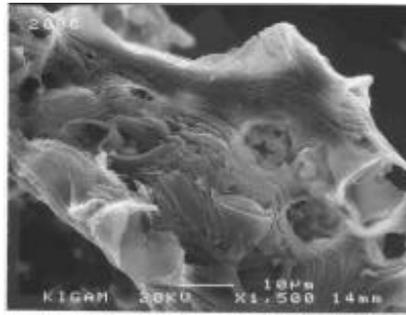


(a)

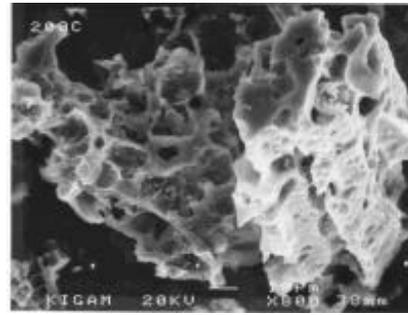


(b)

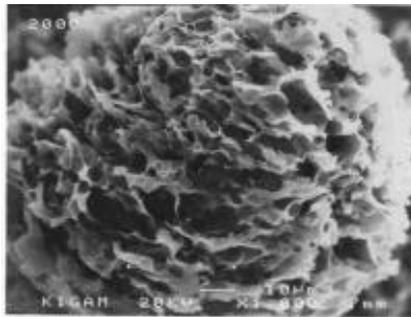
Fig. 3. SEM micrographs of fly ash and unburned carbon particles : (a) before purification (b) after purification



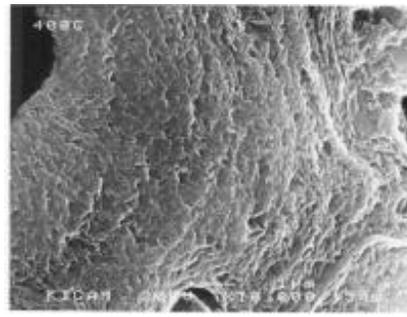
(a)



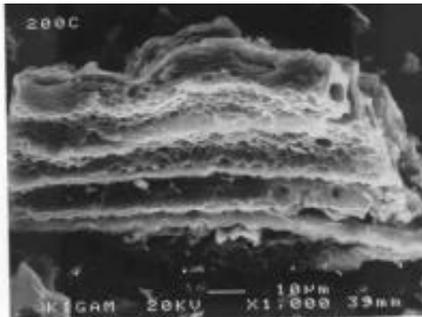
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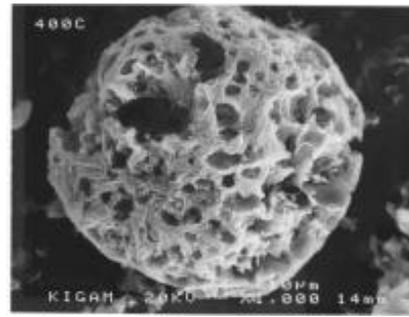
(c)



(d)



(e)



(f)

Fig. 4. SEM micrographs of some unburned carbon particles.

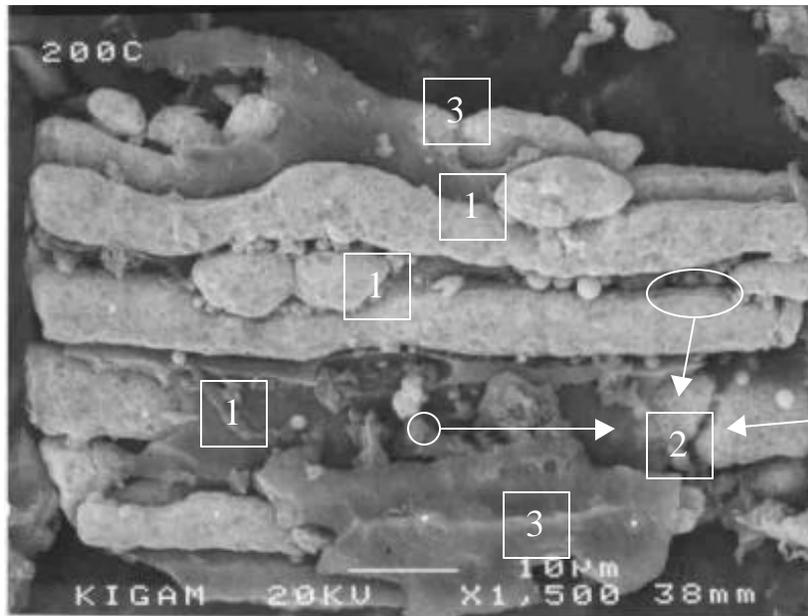


Fig. 5. Ash particles in an unburned carbon particle.

Table 3. EDX analysis of ash bars and microspheres in the unburned carbon particle in Fig. 5. (Unit : wt%)

Number	Al ₂ O ₃	SiO ₂	Fe ₂ O ₃	CaO	K ₂ O	C
1	41.7	58.3	-	-	-	-
2	30.3	61.6	4.38	2.15	1.54	-
3	-	-	-	-	-	100

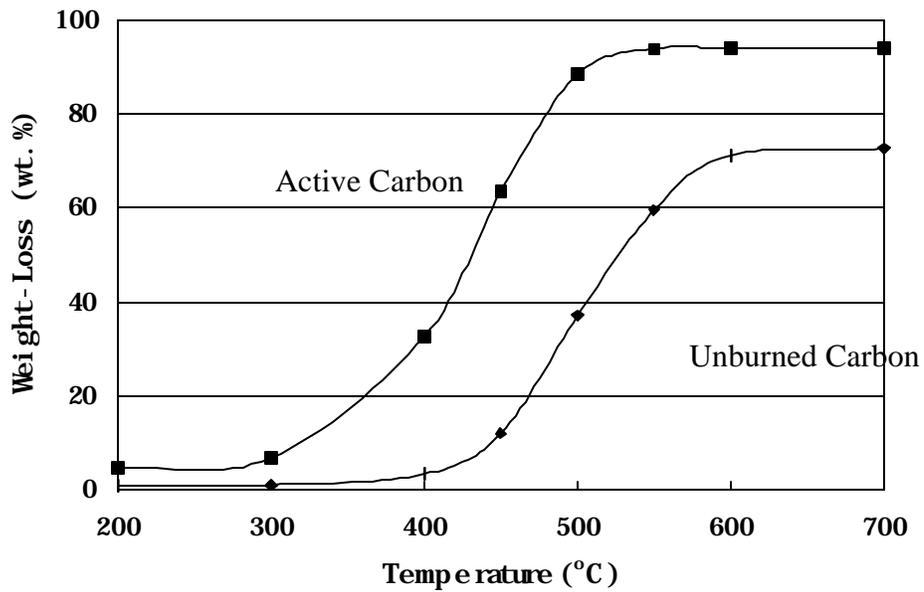


Fig. 6. Weight-loss after heat treatment for an unburned carbon sample and an active carbon sample.

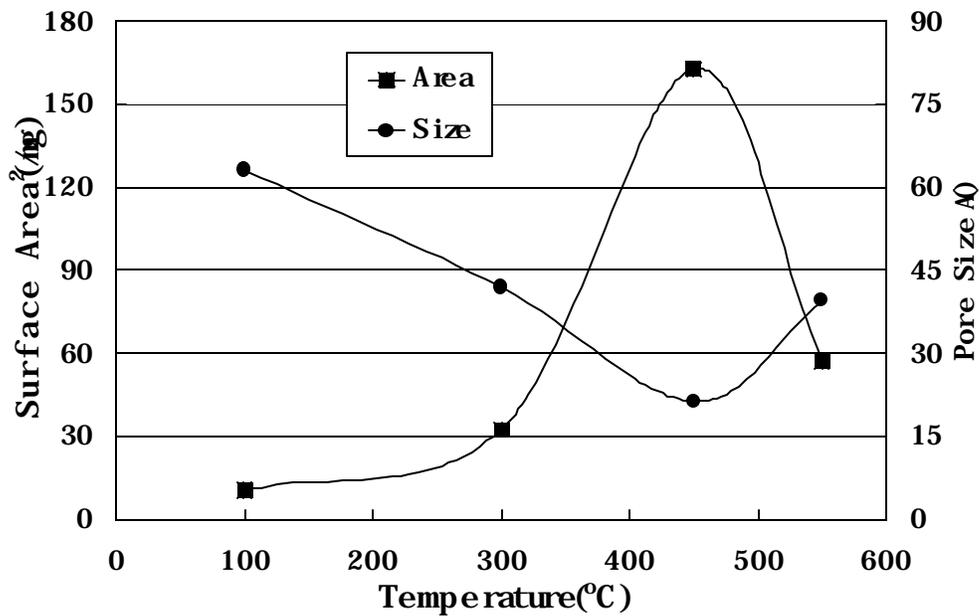


Fig. 7. BET-surface area and pore size of unburned carbon extract after heat treatment.

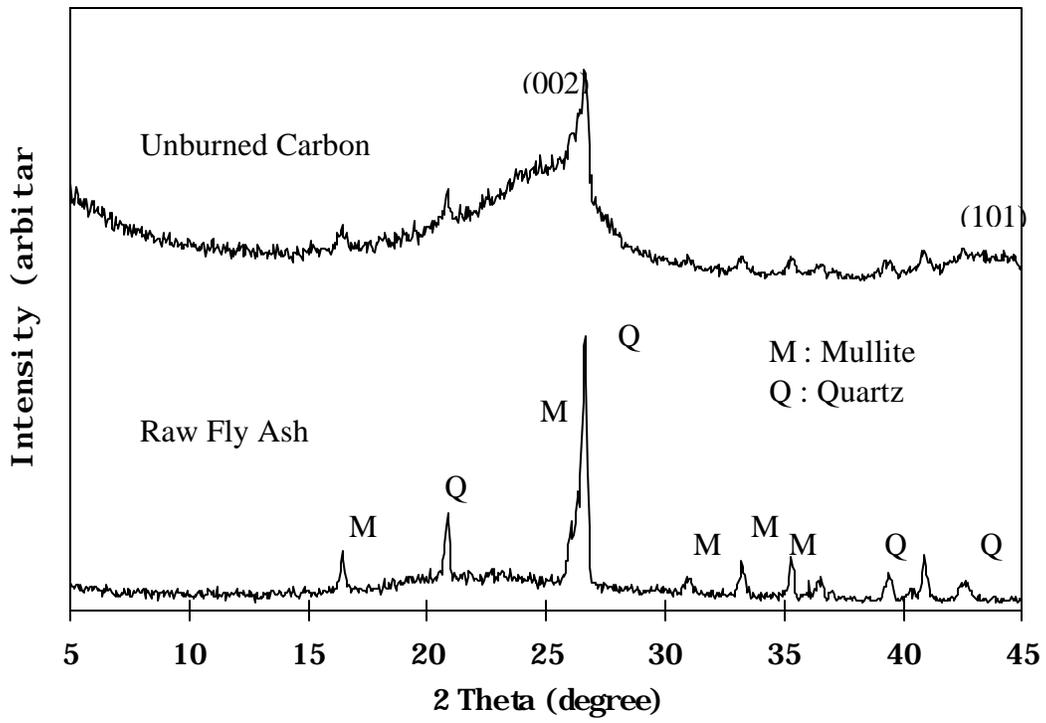


Fig. 8. X-ray diffraction patterns of unburned carbon extract and raw fly ash.