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The removal of unburned carbon from fly ash using cold plasma

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This study examines the effect of removing unburned carbon from fly ash depending on the treatment time associated with the cold plasma conditions and the characteristics of the fly ash powder during the process. The optimum conditions for the cold plasma process at the substrate temperature of 150 included the gas type of O_2, 200 W power, gas flow of 50 sccm, and the one-time treatment time of 10 minutes. Moreover, under these conditions, the loss on ignition of fly ash decreased from 5.8% to 1.0%. The loss on ignition decreased to 0.1% when the process was implemented eight times (10 minutes × 8 cycles) under optimum conditions. As unburned carbon was removed from the fly ash during the cold plasma process, the BET specific surface area decreased from 5,809 m^2/kg to 1,597 m^2/kg, whereas the mean particle size decreased from 15.5 μm to 11.7 μm and the particle-size distribution narrowed. The unburned carbon particles became smaller in size as their micro-pores eliminated in the plasma process, but there were no changes in size or shape to the ash particles.

Key words: Unburned carbon, Fly ash, Cold plasma, Loss on ignition.

Introduction

Using fly ash as a mineral admixture improves workability of concrete and is effective for restraining cracks that result from decreasing heat of hydration [1-3]. However, the unburned carbon in fly ash adsorbs the air-entraining agents during the concrete-mixing process, causing difficulty in the management of concrete's slump and air content [4-6]. Thus, reduction of the unburned carbon content in fly ash will to a certain degree help to improve the use of fly ash as a concrete mineral admixture.

Methods of removing unburned carbon from fly ash include air classification [7], electrostatic separation [8], and flotation [9]. Air classification is presently the preferred and widely used method in industries. It classifies the unburned carbon particles using centrifugal forces generated by pneumatics. Unburned carbon particles can be divided into two types depending on their sizes: The imperfect combustion of carbon particles generates large (mainly > 200) unburned carbon particles, while volatile compounds generate small (mainly < 5 μm) particles [10]. Air classification and electrostatic separation are appropriate for removing large unburned carbon particles but not for removing small ones. The flotation method can remove small unburned carbon particles. However, using this method increases manufacturing costs because it requires the use of foaming agents or the addition of a drying process. Air classification is effective for particle sizes of up to 30-45 μm. This allows the classifying of unburned carbon content to some degree because, in general, there is less unburned carbon content in small fly ash particles. However, the density of unburned carbon is relatively lower than that of ash particle. Moreover, unburned carbon is porous and, therefore, brittle in character. It often gets pulverized and becomes smaller, then joining the ranks of smaller particles. Another problem with unburned carbon is that it collides with other particles and gets refined while spinning in the classifier. All of these characteristics limit the ability of air classification to remove unburned carbon from fly ash.

Plasma, also called the fourth state of material, is composed of electrons, free radicals, positive ions, and neutral atoms and molecules. It is electrically neutral and can be divided into two types: thermal and cold plasma. Thermal plasma is generally made using plasma torches [11]. In thermal plasma, the electrons and atoms are in thermal equilibrium with no temperature differences. It takes high electric energy to reach this state. Thermal plasma is used for tasks such as welding, cutting, incineration, and coating. Cold plasma can easily be made using low energy under relatively low pressure conditions [12]. The temperature of the reacting gas is similar to that of the atmosphere, but the electron temperature is 10 to 100 times higher. Cold plasma creates reactants that are highly catalytic, facilitating chemical reactions that would otherwise be difficult to realize. The reactants result from the ionization of atoms or molecules by the electrons' kinetic energy. These reactants are composed of ions, including free radicals, as well as electrons, ultraviolet rays, and excited atoms. Cold plasma usually takes the form of glow discharge under low pressure. It is mainly used for etching, coating, and the surface treatment of

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semiconductor substrates.

This study deduces plasma process conditions that can reduce the unburned carbon content of fly ash to less than 1.0% using cold plasma technology and examines the effects of the decrease of unburned carbon and the powder characteristics depending on the plasma treatment time.

Experimental

Fly ash

Fly ash used in the experiment was from a pulverized coal firing boiler at Boryeong Power Station in Korea. Its loss on ignition was 5.8%, its Blaine specific surface area was 440 m^2/kg, and its density was 2.2 g/cm^3. As Table 1 shows, it had a typical class F chemical composition according to ASTM C618. According to the XRD results in Fig. 1 shows that its hallow feature was evident in the glass phase with main crystalline phase α-quartz, mullite, and a small amount of magnetite. The FE-SEM observation of the fly ash particles showed that they were mostly globular in shape with irregular particles and porous unburned carbon particles here and there (Fig. 2).

Plasma equipment

There are two types of plasma sources: inductively coupled plasma (ICP) and capacitively coupled plasma (CCP) [13]. In an ICP, which is capable of producing high-density plasma, coils are supplied with alternating current voltage to create plasma. A CCP is a plasma source that supplies direct or alternating current. It creates unvarying, though not high-density, plasma and

Table 1. Chemical composition of fly ash (mass%).

LOI	SiO_2	Al_2O_3	Fe_2O_3	CaO	TiO_2	MgO	SO_3	K_2O	Etc	Total
5.8	51.3	21.7	8.0	3.8	1.4	1.0	1.1	2.4	3.5	100

*LOI: Loss on ignition.

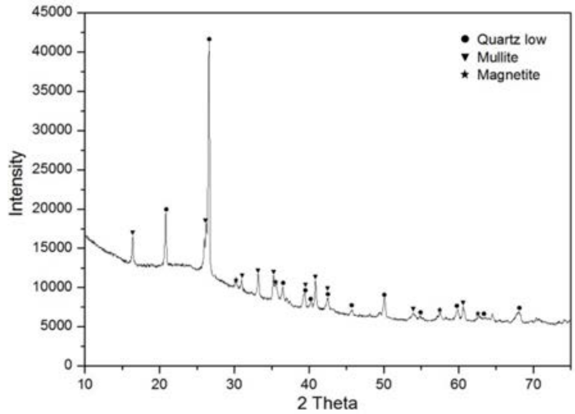


Fig. 1. XRD pattern of fly ash.

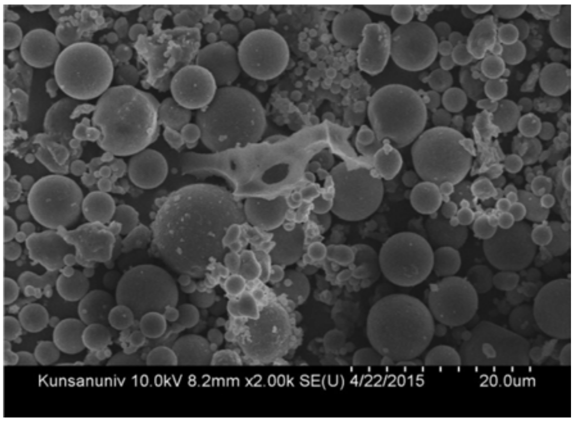
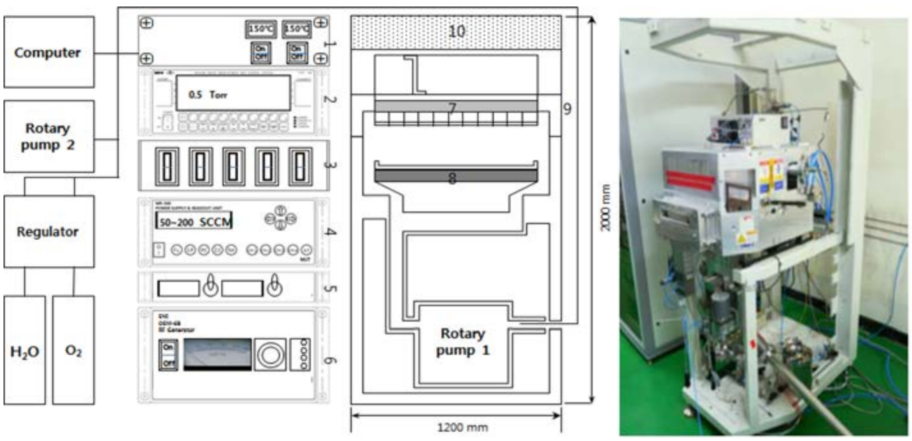


Fig. 2. SEM image of raw fly ash.



(a) Schematic diagram (b) Exterior

1: Substrate temp. controller, 2: Vacuum gauge controller , 3: Circuit breaker, 4: Power supply & readout unit, 5: Auto matching controller, 6: RF controller, 7: Plasma shower head(30 cm), 8: Substrate , 9: Vacuum chamber, 10: Cooling fan

Fig. 3. Cold plasma equipment.

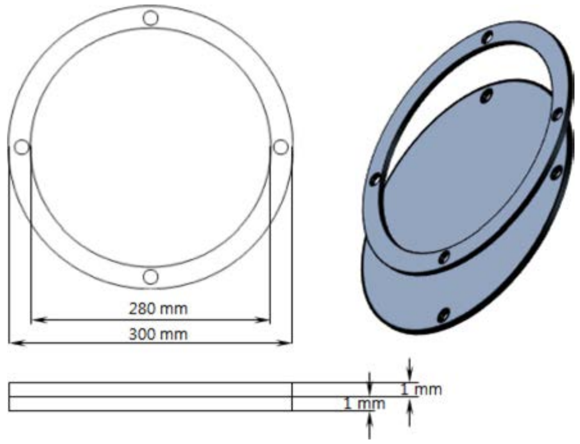


Fig. 4. Sample container and guide.

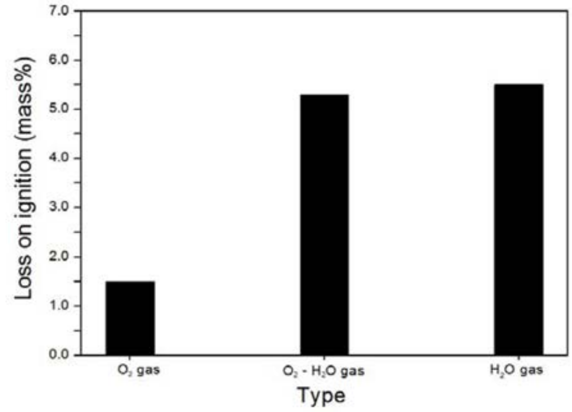


Fig. 5. Influence of gas type on loss on ignition.

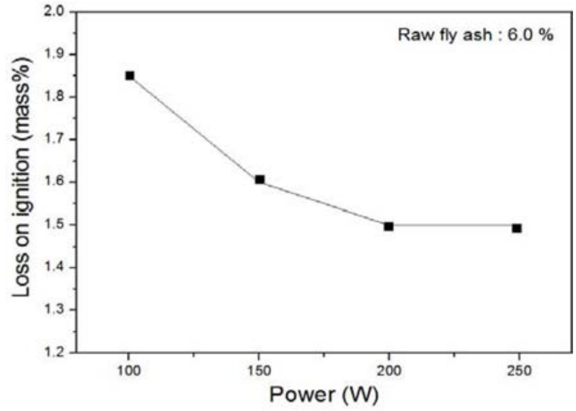


Fig. 6. Influence of plasma power on loss on ignition.

evenly distributes it over a broad area. Therefore, it is appropriate for the purpose of this study, in which the powdered specimen in the container has to be distributed evenly.

The MKS Co. Type 146 vacuum gauge and controller apparatus was used for the process, with the vacuum level initially at 10^{-3} torr and then at 0.5 torr. The radio frequency (RF) value was 13.56 MHz since fly ash is a nonconductor. The temperature nof the substrate on which the specimen container was placed within the vacuum chamber was set at 150 ^{o}C.

Three types of gas O_2, H_2O, H_2O-O_2 (50 : 50) were put in the plasma apparatus. A drawing and a photo of the resulting apparatus are shown in Fig. 3. Fly ash (10 g) was spread in a thin, uniform layer on a 1-mm-thick silicon wafer, which was fixed with guides, to help the plasma reach further inside (Fig. 4). Then the silicon wafer was put in the plasma apparatus for the experiment to remove the unburned carbon.

Testing the physicochemical properties of fly ash

Before and after the plasma treatment, the loss on ignition, BET specific surface area (Microtrac Co. Adsotrac DN-04), and particle size distribution (Microtrack-9320 HRA) of the fly ash were measured. In addition, SEM-EDS (Hitachi Co. S-4800 and Horiba Co. EX-250, respectively) was used to analyze the particle shapes and local elements. The degree of unburned carbon removal was evaluated based on the loss on ignition, which was measured by heating the fly ash from 950 ^{o}C until it weighed a constant amount according to KS L 5405.

Results and Discussion

Influence of gas types and power

Gas types are among the most important variables in the plasma process. This study selected three types of gas O_2, H_2O, H_2O-O_2 (50 : 50) for the experiment. The settings of the other variables follow: pressure was set at 0.5 torr, power at 150 W, gas flow at 100 sccm, and one-time treatment time at 10 min. Moreover, the treatment process was implemented thrice. Fig. 5 shows the loss on ignition of the plasma-treated fly ash for each gas type. The value for O_2 was the smallest at 1.5%. In comparison, O_2-H_2O gave a value of 5.3%, whereas H_2O gave a value of 5.5%. These results are assumed to follow from the fact that O_2 gas plasma is very responsive in its oxidation of unburned carbon and H_2O gas plasma is less responsive. Thus, the latter removes less unburned carbon content.

Plasma power was tested with the gas type of O_2 at 100 W, 150 W, 200 W, and 250 W. The other conditions were the same as those used in the per-gas-type experiments. The variations in the loss on ignition of the plasma-treated fly ash due to the different power levels are illustrated in Fig. 6. The effects of removal increased with the power, and the loss on ignition at 200 W was 1.5%, showing a 4.5% decrease compared to the untreated fly ash. However, sparks occurred in the chamber at 250 W, showing a treatment effect similar to that at 200 W. Therefore, the optimum power condition was deduced to be 200 W.

Influence of treatment time and the amount of gas

Each plasma was treated three times in the following plasma conditions: gas type of O_2, power of 200 W, gas flow of 100 sccm, and one-time treatment time set at

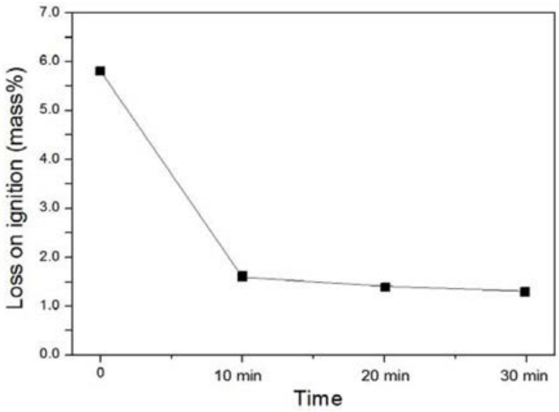


Fig. 7. Influence of plasma treat time on loss on ignition.

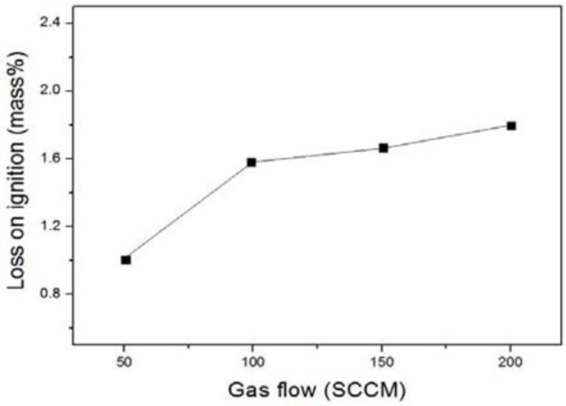


Fig. 8. Influence of gas flow rate on loss on ignition.

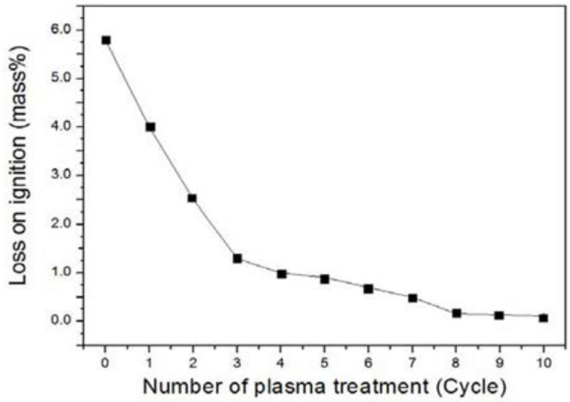


Fig. 9. Influence of cycle of plasma treatment on loss on ignition.

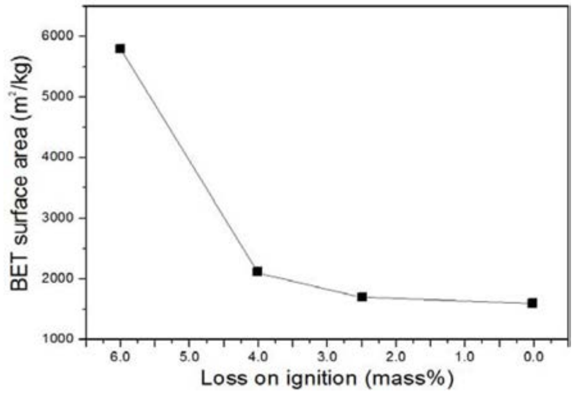


Fig. 10. BET specific surface area according to loss on ignition.

10, 20, and 30 min., respectively. The results are shown in Fig. 7. The loss on ignition was 1.6% for the treatment time of 10 min., 1.4% for 20 min., and 1.3% for 30 min. This indicated that the removal effects increased in proportion to the rise in treatment time. However, the efficiency of removal decreased with the rise in treatment time. Therefore, the time for one-time treatment was set at 10 min. in the following experiments.

Each plasma was treated three times in the following plasma conditions: gas type of O_2, power of 200 W, a varying gas flow of 50, 100, 150, or 200 sccm, and the one-time treatment time of 10 min. The loss on ignition varied with the gas flow as shown in Fig 8: As the gas flow decreased, the effect of the removal of unburned carbon increased. The loss on ignition was 1.0% at the gas flow of 50 sccm. This result was interpreted as an indication that the response rate increased because the lower gas flow resulted in the reacting radicals staying longer on the unburned carbon surfaces.

Judging from the results, the optimum process conditions for this experiment included the O_2 gas type, 200 W of power, gas flow of 50 sccm, and the one-time treatment time of 10 min.

The effect of the removal of unburned carbon according to the number of treatments

Another experiment was conducted to improve the rate of removing unburned carbon by increasing the number of plasma treatments. This time, the plasma process conditions included the following: gas type of O_2, 200 W of power, gas flow of 50 sccm, and the one-time treatment time of 10 min. The fly ash specimen was turned upside down and plasma-treated again after the 10 min treatment. This process was repeated 10 times and the results are shown in Fig. 9. As illustrated in Fig. 9, the removal process can be divided into three stages according to the number of plasma treatments and the loss on ignition. Stage 1, during which the loss on ignition decreased rapidly, included the initial three treatments. The loss on ignition decreased from 6.0% to 1.3% at the third treatment, showing a removal rate of 78%. Stage 2, during which the unburned carbon was removed slowly, included treatments four to eight. The loss on ignition at the eighth treatment showed a removal rate of 0.1%, removing most of the unburned carbon content. Stage 3 included the rest of the treatments. The loss on ignition did not vary during this stage.

The powder properties of plasma treated fly ash

The relationship of loss on ignition and the BET specific surface area of plasma-treated fly ash is shown in Fig. 10. As the unburned carbon in the fly ash decreased due to the plasma treatments, the BET

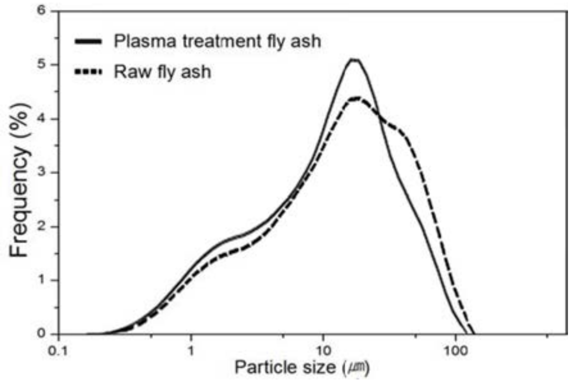


Fig. 11. Particle size distribution for fly ash before and after plasma treatment.

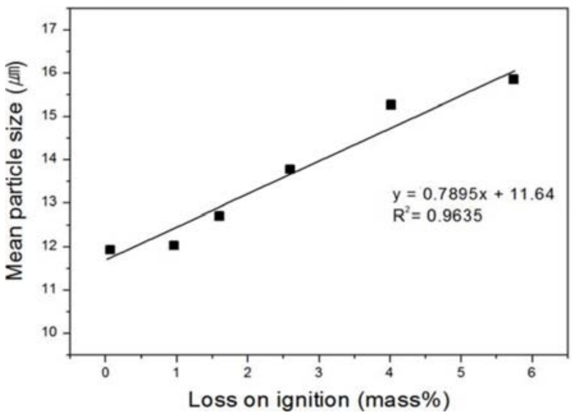


Fig. 12. Mean particle size according to loss on ignition.

specific surface area tended to decrease as well. The initial BET specific surface area of 5,809 m^2/kg (loss on ignition: 5.8%) of the fly ash specimen decreased to 1,597 m^2/kg (loss on ignition: 0.1%). Therefore, we can assume that the unburned carbon is porous with a very large specific surface area.

Fig. 11 shows the particle size distribution of the raw fly ash and that of the fly ash after being treated 10 times. The particle size distribution narrowed and the particle sizes decreased due to the treatments. This is assumed to be because the large porous particles were removed by the treatments, leaving smaller particles.

Fig. 12 shows the relationship between the loss on ignition and the mean diameter of the particles according to plasma treatments. The loss on ignition and the mean diameter are directly correlated. However, unlike the BET specific surface area, the mean diameter tended to decrease from 15.5 μm (loss on ignition: 5.8%) to 11.7 μm (loss on ignition: 0.1%) as the unburned carbon particles were removed.

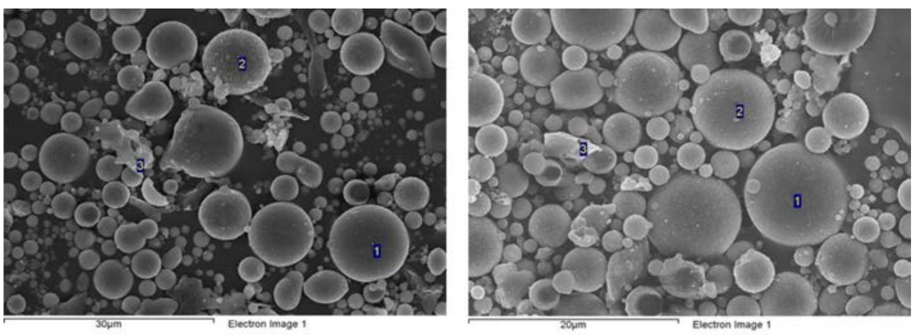
Fig. 13(a) shows SEM images of the fly ash specimen: No. 1 and 2 represent the ash particles, and No. 3 represents unburned carbon particles. When No. 3 particles were tested for elements using EDS, 74.3% carbon content was detected (Table 2). Fig. 13(b) shows SEM images of the fly ash (treated 10 times) with the loss on ignition value of 0.1%. When No. 3 particles were tested for elements using EDS, no carbon content was detected (Table 3). In addition, the effect of cold plasma treatments on the size and shape of ashes other than unburned carbon was examined. Based on the SEM images shown in Fig. 13, globular and irregularly shaped particles were observed. The results showed that cold plasma treatments did not affect the size and shape of the ash particles.

The mechanism for the removal of unburned carbon by cold plasma

The mechanism of removing unburned carbon out of fly ashes by cold plasma can be interpreted as follows. The injected oxygen goes through the reaction stipulated in formula (1) and generates oxygen radicals by electrons.

Table 2. EDS analysis of raw sample (mass%).

Point	C	O	Na	Mg	Al	Si	S	K	Ca	Ti	Fe	Cu	Total
1	–	62.5	0.6	0.6	10.5	21.2	–	1.7	–	0.4	1.2	1.3	100
2	–	65.6	2.7	0.2	10.4	18.5	–	0.8	–	0.4	1.4	–	100
3	74.3	22.5	–	0.1	0.8	1.4	0.2	–	0.1	-	0.6	–	100



(a) Raw fly ash (b) Plasma treated fly ash

Fig. 13. SEM images of fly ash before and after plasma treatment.

The oxygen radicals created this reaction moves and are adsorbed onto unburned carbon particles. In addition, oxygen reacts with electros and creates positive ions and electrons through the ionization reaction as described in formula (2). The positive ions created this way holds kinetic energy by and within an electric field and clashes with unburned carbon particles. The thermal energy generated upon clash serve as activation energy for reaction between unburned carbon and oxygen radicals, and generates CO_2 (g) as in formula (3) or (4) to remove unburned carbon.

$e^- + O_2 \rightarrow O^{\cdot} + O^{\cdot} + e^-$
(Dissociation reaction: Radical formation) (1)

$e^- + O_2 \rightarrow 2\ O^+ + 3e^-$
(Ionization reaction: Ion formation) (2)

C (Unburned carbon) + 2O$^{\cdot}$ (Adsorbed radical) $\rightarrow$
CO (g) + O$^{\cdot}$ (Adsorbed radical) CO_2(g) (3)

C (Unburned carbon) + 2O$^{\cdot}$
(Adsorbed radical) $\rightarrow$ CO_2(g) (4)

Conclusions

The optimum plasma process conditions were induced for the removal of unburned carbon content from fly ash (reducing its level to less than 1.0%) using cold plasma technology. The decrease in the effects of unburned carbon content, depending on the plasma treatment time and the particle characteristics of the carbon content, were examined. The following conclusion was drawn from the results:

1. The optimum conditions for the cold plasma process at the substrate temperature of 150 included the gas type of O_2, 200 W power, gas content of 50 sccm, and the one-time handling time of 10 min. The loss on ignition of fly ash decreased from 5.8% to 1.0%.
2. The loss on ignition decreased to 0.1% when the process was implemented 8 times (10 min $\times$ 8 cycles) under optimum conditions.
3. As unburned carbon was removed from the fly ash during the cold plasma process, the BET specific surface area decreased from 5,809 m^2/kg to 1,597 m^2/kg, whereas the mean particle size decreased from 15.5 μm to 11.7 μm and the particle size distribution narrowed.
4. The unburned carbon particles became smaller in size as their micro-pores were eliminated in the plasma process, but there were no changes in size or shape to the fly ash particles.
5. The mechanism for the removal unburned carbon out of fly ashes by cold plasma apparently generates CO_2 (g) through reaction between unburned carbon and oxygen radicals by heat energy generated as positive ions created by ionization clash with unburned carbon particles by and within an electric field after oxygen radicals generated by the injected oxygen are absorbed onto unburned carbon.

Acknowledgments

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