

Regeneration of Coal Ash as a High Capacity Acid Gas Sorbent

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A large amount of coal ashes which contained about 5-40% CaO is still pooled in the stocking yard without reuse. In order to extend coal ash utilization, the present work was concerned with application of coal ash to the removal of such acid gaseous as hydrogen chloride by chemical reaction. The several improvements of reactivity of coal ash toward low temperature HCl removal were carried out. The product after slaking with water was identified as Ca(OH)₂ by XRD. Slaking of coal ash enhanced the formation of crystallized Ca(OH)₂ and increases in surface area of coal ash samples.

The reaction experiments between hydrogen chloride and lime involved in coal ash was carried out by employing fixed bed reactor under simulated flue gas conditions. The experiments were conducted with 1000ppm hydrogen chloride at 200°C. The ultimate conversion value of slaked coal ash sorbent remarkably increased by slaking.

Key words; Coal ash; recycle; Acid gas removal; HCl; Ca-compound

1. INTRODUCTION

Resource reuse of coal ash generated from coal combustors is one of the most important issues of coal utilization plant waste management. For example, estimates for the generation of coal ash are 720×10^6 tones per year in Japan. The majority of this coal ash is discharged from pulverized coal combustor (PCC) and fluidized bed coal combustor (FBCC). Some were used as cement or pavement materials, and others were discharged as waste for reclaiming land from sea. Since coal ash contains 5-40% CaO, coal ash waste could be used as raw material for acid gas absorbent.

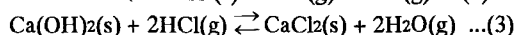
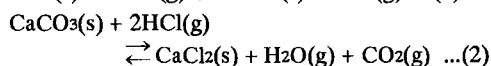
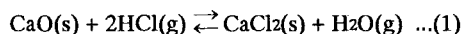
The reactions between hydrogen chloride and Ca-compounds to form calcium chloride are potentially important for various technical processes such as the removal of HCl from waste combustion flue gases. The present investigation was undertaken with the aim of studying application of coal ash toward low temperature HCl gas removal. Current methods of HCl removal often use dry Ca-compounds such as slaked lime injected at 150-200°C in the pre-bagfilter region of waste incineration.

This work examined the reactivity between Ca-compounds involved in coal ash and HCl with the intent of providing information useful toward

optimizing the removal of HCl from flue gas.

Coal ash contains CaCO₃, CaO, Ca(OH)₂ (free-lime compounds), C₂S, C₃A, CaSO₄ in its crystallized form.

Therefore the following binding reactions are important for HCl removal:



Petrini et al. (1979) studied reaction between CaCO₃ and HCl by using fixed bed reactor in the range

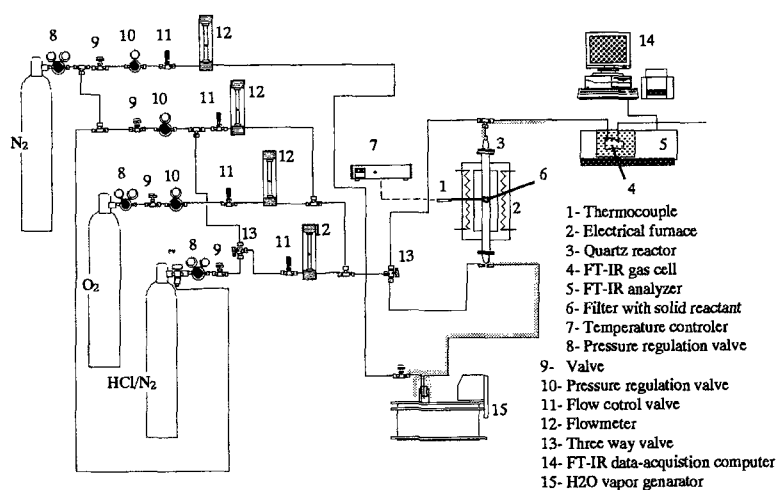


Fig. 1 Schematic diagram of experimental apparatus.

of 350-600°C. The final conversion was low at low temperatures. The progress of reaction was influenced by blockage of the pores in the low-porosity CaCO₃ by product layer of CaCl₂. Karlsson et al. (1981) reported HCl removal by Ca(OH)₂ from 150 to 400°C. A maximum conversion of 55% was possible for the removal of HCl. In addition, D. Schmal et al. (1989) studied the properties of some calcium-based sorbent at varying waste incinerator temperatures. This finding indicated that Ca(OH)₂ and alcohol hydrate Ca(OH)₂ were useful below 400°C. Moreover, high temperature generation of CaO crystal causes sintering and limiting its surface area to less than 10 m²/g.

Coal ashes contain Ca components mainly derived from coal mineral or de-SO₂ reagent injected into coal combustor. Then the Ca compound was heated above 850°C, to convert into Si-Al-Ca-O material phases and into free lime which has a low surface area. Previously, the researchers studied reaction between Ca compounds involved in coal ash and HCl by using TGA. TGA results indicated that the molted Si-Ca materials on coal ash particles did not react with HCl. Observed ultimate conversion values at low temperatures were under 5%.

In this work, several improvements were carried out on the properties of Ca compounds lime found in coal ashes as free for low temperature HCl removal.

Table I Chemical Composition of Coal Ash (Ignited Base).

Wt %	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O
FBC ash ①	47.2	21.6	1.30	9.99	2.03	0.09	0.83
FBC ash ②	30.8	13.1	5.19	22.6	0.93	0.11	0.83
FBC ash ③	24.3	13.7	6.98	45.5	0.65	0.05	0.61

2. EXPERIMENTAL

All reactivity tests were conducted by using fixed bed reactor shown in Figure 1. During sample preparation, 0.40g sample was evenly distributed on a glass filter, then was placed in the electrical furnace.

The test temperatures were monitored by a type K (C/A) thermocouple on the outer wall just beside the sample bed.

The test gas introduced in the reactor is made by mixing commercial HCl / N₂ gas (1%) and balance N₂. During the reaction time, HCl concentration in reacted flue gas flowing out of the reactor was continuously measured using Fourier Transform Infrared Spectrophotometer (FTIR-8700, SHIMADZU).

Table II Sample table.

Coal ash	Treatment
FBC ash ①	(raw) water hydrate
FBC ash ②	(raw) water hydrate
FBC ash ③	(raw) water hydrate PG* 5% aq. hydrate Et-OH** 50% aq. hydrate

*PG Polyethylene Glycol, **Et-OH Ethanol

The specific surface area was measured by nitrogen adsorption based on the Brunauer-Emmett-Taller (BET)

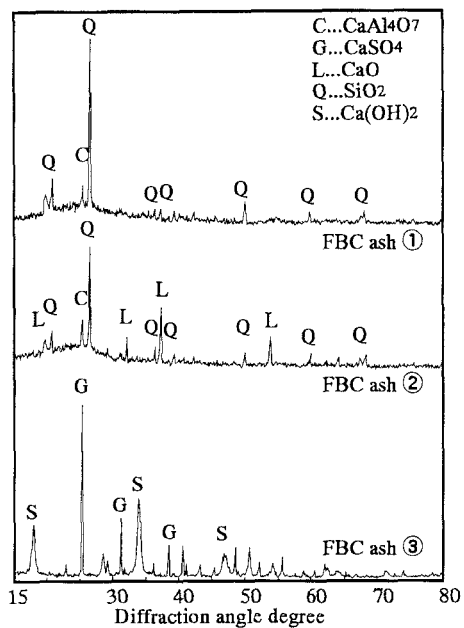


Fig.2 XRD patterns of raw FBC ashes (①-③).

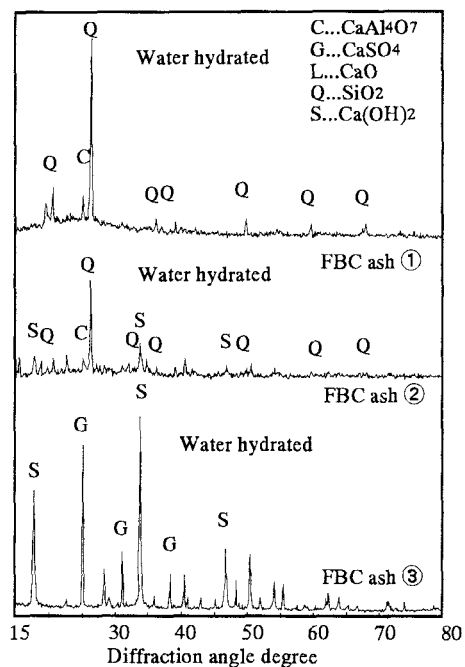


Fig.3 XRD patterns of slaked FBC ashes (①-③).

method for the sample dried and degassed at 150°C. XRD patterns were recorded on a RIGAKU RINT system for the powdered samples less than 100 μm with Cu K α radiation in the range of diffraction angle (2θ) 20-80°. The used samples were coal ash of various calcium contents (9.99-45.5%, Table I). The experimental conditions for the sorbent preparation are summarized in Table II. Prior to the slaking treatment, samples were heated at 800°C for 6 hours to decompose volatile materials.

3. RESULTS AND DISCUSSION

3.1 X-Ray Diffraction.

The results of the XRD analysis for raw coal ashes are shown in figure 2. Distinctive patterns of SiO₂ (Q), CaSO₄ (G), Ca(OH)₂ (S), CaAl₂O₇(C) and CaO (L) were observed as a result of low temperature combustion in FBC (850°C). It was considered that molten materials could not exist below 1000°C in FBC, and the crystal phases of coal mineral and fluidized bed medium material of CaCO₃ (CaO) could be left in the ash structure. CaO (L) and Ca(OH)₂ (S) phases were not present in the XRD pattern of FBC ash ① which contained low Ca content (CaO: 9.99%). The peaks for CaO were found in the pattern of FBC ash ② (CaO: 22.6%). It was assumed that Ca(OH)₂ observed in the pattern of FBC ash ③ (CaO: 45.5%) were generated after discharging from FBC. The intensity of the peaks of SiO₂ increased with the decrease of CaO content.

XRD patterns for the slaked ash having different compositions are shown in figure 3. The XRD peaks ascribed to hydrates were not observed in FBC ash ① that contain less than 10% CaO. With FBC ash ② and ③ that contain more than 20% Ca contents, the formation of Ca(OH)₂ was observable. The width of diffraction peaks of generated Ca(OH)₂ was narrow and the diffraction intensity was increased. As a result, slaking coal ash enhances the formation of crystallized Ca(OH)₂.

3.2 Morphological Observation by SEM

Figure 4a presents a SEM photomicrograph of raw coal ash ③. The SEM micrograph of slaked coal ash ③ indicated that the sorbent as agglomerated apparent submicrometer particles of random with grain size less than 3 μm (figure 4b). The photomicrograph of raw ash also show the similar structures, however the discrete grain sizes were less than 1 μm , and figure 4a show necking between adjacent grains. The slaking operation is clearly associated with the formation of the more crystalline structure of Ca(OH)₂. This results agreed with the results of XRD.

3.3 Surface Area Distribution

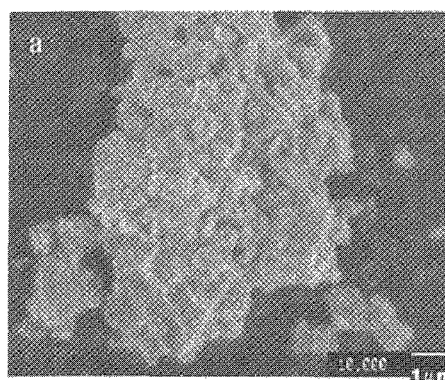


Fig. 4a SEM photograph of source FBC ash ③

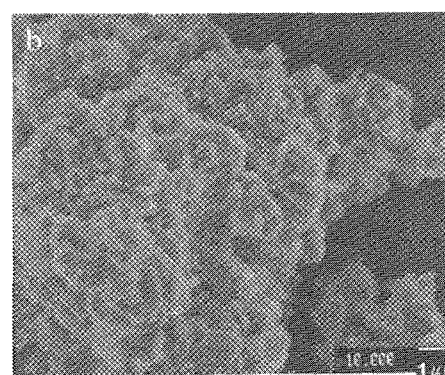


Fig. 4b SEM photograph of Slaked FBC ash ③

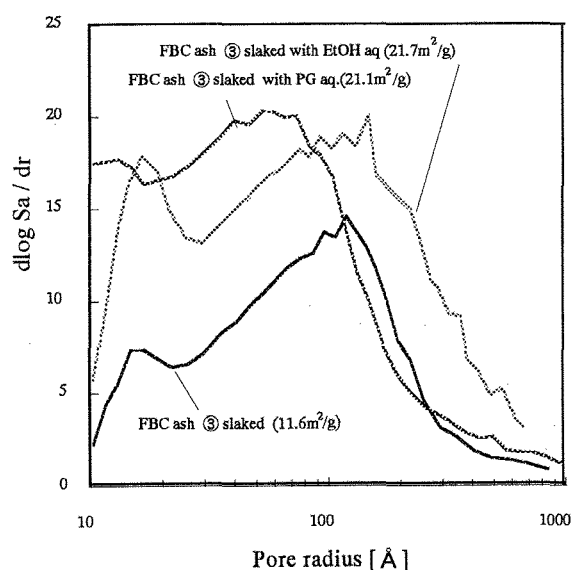


Fig. 5 Effect of treatment of raw FBC ash ③ (4.13m²/g) on surface area distribution.

Figure 5 represents the specific surface area distribution curves in FBC ash ③ at different slaking conditions. This figure clearly shows the increase in the surface area with slaking. The BET surface area increased in the following order:

Raw FBC ash ③ ($4.13\text{m}^2/\text{g}$) < Water hydrated FBC ash ③ ($11.6\text{m}^2/\text{g}$) < Polyethylene Glycol(PG) hydrated FBC ash ③ ($21.1\text{m}^2/\text{g}$) < Ethanol(Et-OH) hydrated FBC ash ③ ($21.7\text{m}^2/\text{g}$)

A remarkable increase in the pore surface area from 10 to 100 nm was observed for PG hydrate FBC ash ③ sample. As this small pores contributed to the most of the total surface area of PG hydrate sample. Although the Et-OH hydrate sample did not differ from the water slaked sample in the shape of the distribution curves, larger surface areas are observed significantly at all pore radii.

3.4 Hydration Effects

The hydration effects of each coal ash samples on conversion curves for HCl reaction are shown in figure 6. For the case of raw FBC ash ② and ③, it was indicated that the initial rate and ultimate conversion of chlorination reaction increased with the slaking treatment. The reaction stopped after a short period of time (4-20min), with maximum conversion of CaO of 3% and 11%. With the slaking treatment, the conversion values after 60 min were increased to more than 20 and 37%. Thus, the slaking of ashes affects the final CaO conversion value. No significant differences were observed between raw and slaked FBC coal ash ①.

3.5 Additives

Figure 7 shows the chlorination conversion curves in raw, water hydrate, PG hydrate, and Et-OH hydrate coal ash ③ samples. It was clearly observed that the ultimate CaO conversion were increased from 11% to 37%, 40% and 46% by application of each treatment for coal ash. With the Et-OH hydrate sample, the higher conversion was observed than that of PG hydrate sample. For larger pores (>100nm), the associated surface area in PG hydrate ash was lower than that in Et-OH hydrate ash, which may explain the higher ultimate CaO conversion of Et-OH hydrate ash.

4. CONCLUSION

As the result of a relatively simple hydration treatment, coal ash can be converted to a sorbent containing $\text{Ca}(\text{OH})_2$ with high capacity toward HCl removal at low temperatures. Increases in the amount of Ca contained in coal ash resulted in generation of $\text{Ca}(\text{OH})_2$ crystal phase. Indeed, this is supportive of SEM evidence. While the formation of $\text{Ca}(\text{OH})_2$ was

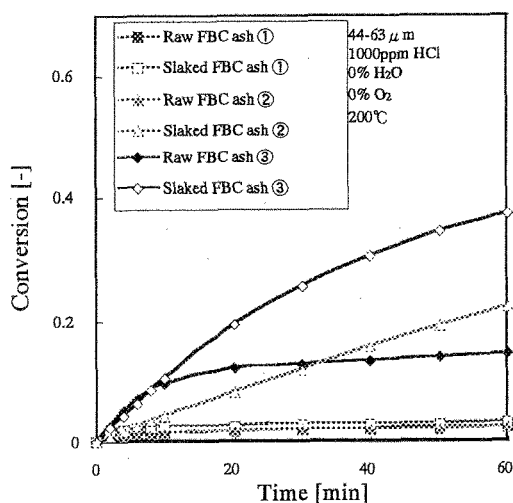


Fig.6 Conversion curves of FBC ash for HCl removal.

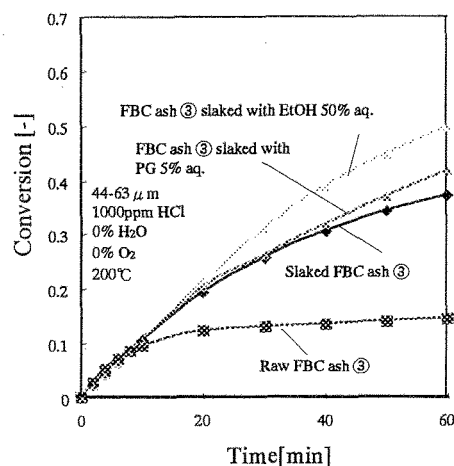


Fig.7 Conversion curves of Slaked FBC ash ③ for HCl removal.

contribute to the increase of surface area of coal ash. As a result, the capacities of HCl sorption of slaked ash were increased compared with that of raw ash. The application of alcohol hydration method enhance to increase the HCl sorption capacity of coal ash as the result of increasing in surface area.

5. LITERATURE CITED

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(Received December 16, 1999; accepted February 7, 2000)