

High Temperature HCl Removal Using Coal Ashes

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Coal ashes from fluidized bed combustors (FBC) were investigated for a HCl gas absorbent under dry high-temperature condition in terms of metal components involved. It was found that the HCl-sorption capacity of coal ashes differed corresponding to the position where ash was discharged from FBC. It was found that the absorption rate of coal ashes toward HCl was almost similar to that of CaO which was involved in coal ash as desulfurization agent. The bottom ash showed a higher HCl absorption capacity than that of the fly ashes. The difference in reactivity between the bottom ash and the fly ash may be caused by the complicated factors of gas components and temperature in flue. The fundamental characteristics of coal ash for HCl absorption were related to physical structural parameters, such as specific surface area. The absorption capacity and absorption rate of CaO were influenced by the incineration condition of CaCO₃. The applicability of coal ashes was then examined for high temperature HCl removal with the CaO calcined of Ca(OH)₂ and CaCO₃ respectively. Activation energy of 12kJ/mol was apparently obtained for coal ashes.

Key words: HCl, gas cleaning, coal ash, waste treatment

1. INTRODUCTION

Because of the negative effects of HCl vapor on air quality and erosion of the incinerator, it is necessary to remove HCl vapor from municipal waste incinerator flue gas. HCl is generally removed by injecting Ca-based compounds such as CaO and Ca(OH)₂ at high temperature. However, a large amount of Ca-based sorbent derived from natural lime stone has so far been consumed for dry acid gas removal.

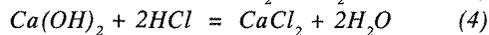
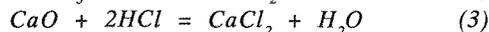
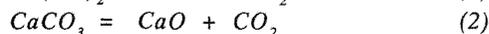
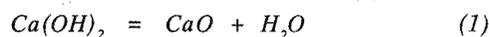
On the other hand, coal ashes are discharged from coal combustors over 7.2 million ton, and dumped into land fills about 2.1 million ton in 1996 in Japan. The coal ash contains some kinds of metal components which may be utilized as acid gas absorbent. The main target of the present work is to call attention to a reuse of the coal ash for controlling HCl emissions. Our research is also focused on the possibility of using the coal ash as an alternative dry absorbent.

2. REACTION SCHEME

Coal ash from coal combustor contains various kinds of metal components of hydroxides, carbonates and oxides, depending on the condition exposed to the atmosphere including water vapor and CO₂. This might therefore cause complicated reaction schemes of the involved metal components to HCl, when coal ash is injected into the reaction surroundings such as high-temperature flue gas.

Reaction(3) is considered to proceed when CaO is formed by the reactions (1) and (2), if the metal component involved in coal ash is specified by

calcium. Reaction (4) is dominant when the temperature is below 573K. The rate of reaction (5) seems to be low to that of reaction(3).



Since Ca(OH)₂ and CaCO₃ are considered to decompose at temperature range of 573-973K, this may cause physical and chemical changes in structure of coal ash, which may lead to the uncertain reaction behavior between calcium oxide and HCl. In general, calcination condition affects surface area and pore volume in coal ash, which mostly influence on the reaction capacity. As for the above reactions (1) and (2), dehydration of Ca(OH)₂ occurs mainly above 673K, and the decarbonation of CaCO₃ takes place at more than 923K. Thermodynamic information shows that CaCl₂ could not present above 923K under the condition of 2000ppm HCl concentration. This means that CaO produced from Ca(OH)₂ is a principal absorbent of HCl when coal ash is used for the removal of HCl in flue gas in the range of 523-923K.

It should be noted that there exists some other trace metals in coal ash which might react with HCl to some extent. In this case, the effect of the these elements on HCl removal should also be taken into consideration.

3. EXPERIMENTAL SECTION

3.1 Samples

The sorbents used in our research were seven kinds of fly ashes derived from various coals. Two sets of fly ash and bottom ash were tested to compare each other. The chemical compositions of these ashes are shown in Table I.

3.2 Sample analysis

Table I, Chemical composition of coal ashes.[wt%]

	CaO	MgO	Fe ₂ O ₃	Na ₂ O	K ₂ O	SiO ₂	Al ₂ O ₃	Unburnt carbon
Fly ash-A	26.2	0.37	2.12	0.37	0.46	51.5	13.8	36.2
Fly ash-B	23.9	0.80	1.20	0.80	0.14	45.7	21.4	12.8
Fly ash-C	26.9	0.83	2.88	0.83	0.06	36.3	24.0	22.0
Fly ash-D	12.8	0.53	3.73	0.53	0.30	46.1	27.8	16.1
Fly ash-E	20.3	0.44	2.73	0.44	0.54	51.6	18.0	26.2
Fly ash-F	9.99	2.03	1.30	0.09	0.56	47.2	21.6	8.09
Fly ash-G	22.5	0.84	5.20	1.12	1.14	48.1	13.5	---
Bottom ash-F	44.1	0.65	6.98	0.05	0.61	24.3	13.7	3.14
Bottom ash-G	12.7	0.97	3.80	0.92	1.07	54.9	19.0	---

(Coal ashes discharged from FBC)

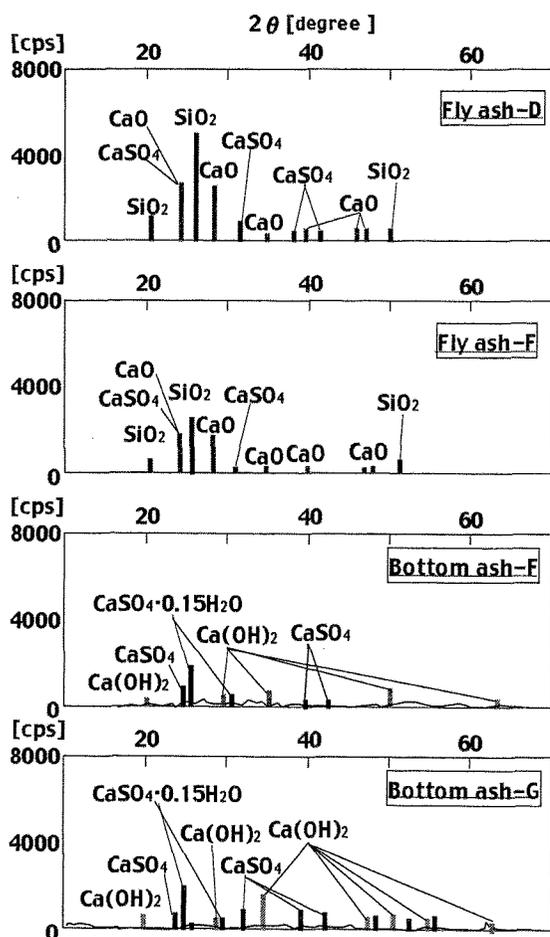


Fig. 1, Typical XRD patterns of chlorinated coal ashes.

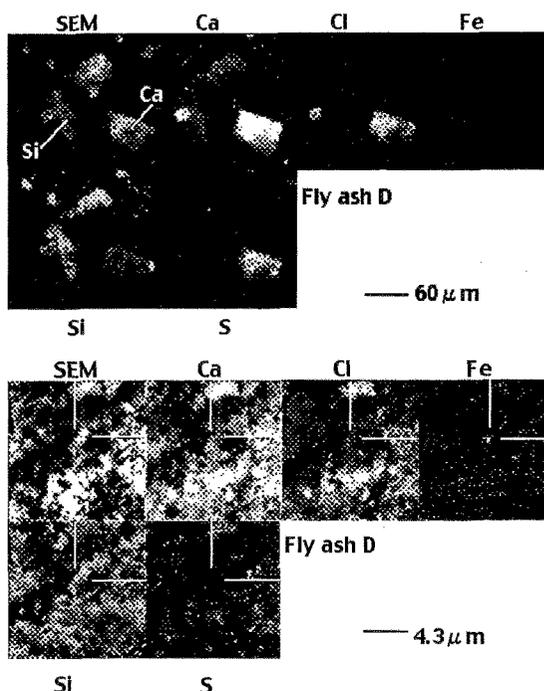


Fig. 2, XRD photo of fly ash-D chlorinated with 2000ppm HCl at 773K, and its respective EDS scanning results of Ca, Cl, Fe, Si and S species.

The compositions of coal ashes were analyzed to determine the metal compounds involved. Fig. 1 shows the typical XRD patterns of four kinds of FBC ashes. A XRD pattern resulted in the fly ash such as SiO₂, CaSO₄, and CaO. Calcium component involved in FBC ashes was mainly derived from CaCO₃ as a desulfurization agent. CaCO₃ is decomposed to CaO at temperature range 873K to 1073 K in FBC. This CaO partly absorbed SO₂ discharged from coal combustion. The unreacted CaO will also react with H₂O and CO₂ in the flue gas when the ash was collected in the scrubber, therefore another XRD result of fly ashes shows a little Ca(OH)₂ and CaCO₃. On the other hand, since bottom ashes are discharged from bottom of FBC and dumped into water tank, generally bottom ash contained much more Ca(OH)₂.

SEM / EDS micrographs of fly ash-D are shown in the Fig. 2. The resulted Ca, S and Cl were observed in similar positions, while Si and Fe species exist in different positions. It was assumed that the occurrence of chlorine as CaCl₂ existed in the chlorinated ashes, and a part of Ca had combined with S to form CaSO₄. It was found that unreacted CaO derive from desulfurization agent dominated dechlorination reaction.

3.3 Apparatus

A Thermogravimetric Analyzer was employed for all reaction experiments (Fig. 3). In a typical TGA run, a relatively small sample of about 0.3-0.7 mg was evenly distributed as a thin layer in a Pt sample cup to ensure differential operation and reduce the external resistance.

This sample was first heated up to the predetermined

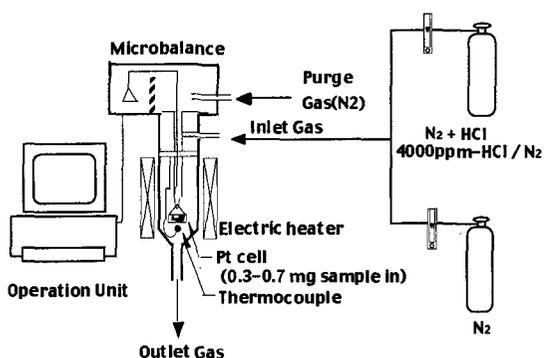


Fig. 3, Schematic diagram of the TGA apparatus.

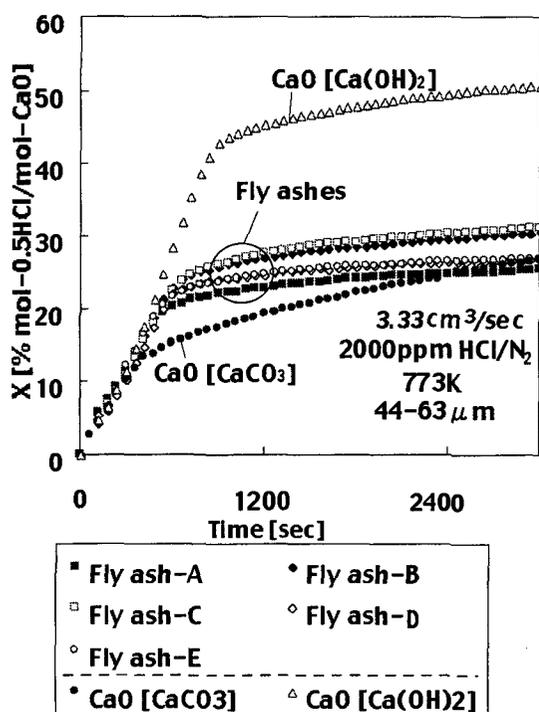


Fig. 4, Reactivity of fly ashes derived from various coal toward 2000ppm HCl at 773K.

reaction temperature at heating rate of 50K/min in N₂ flowing at 3.33cm³/sec. The chlorination experiments were carried out at temperature range from 573 to 773K with a total gas flow rate of 3.33cm³/sec containing 2000ppm HCl with N₂.

3.4 Comparison of FBC Ashes from Different Coals

In our research, five kinds of FBC fly ash samples derived from various coals. Using Equation (6), reactivities X of the five type of coal ashes from different coal, to 2000ppm HCl at 773K were computed and plotted against the reaction time as shown in Fig. 4. It was found that the reaction rate with HCl absorption with FBC fly ashes was almost similar to that of CaO which was excessively involved in coal ash as desulfurization agent, and the HCl-capacity was about 20-30%. This difference was

$$\text{Conversion } X [\%] = \frac{\Delta W / W_0}{(M_{CaCl_2} - M_{CaO}) / M_{CaO}} \times 100 \quad (6)$$

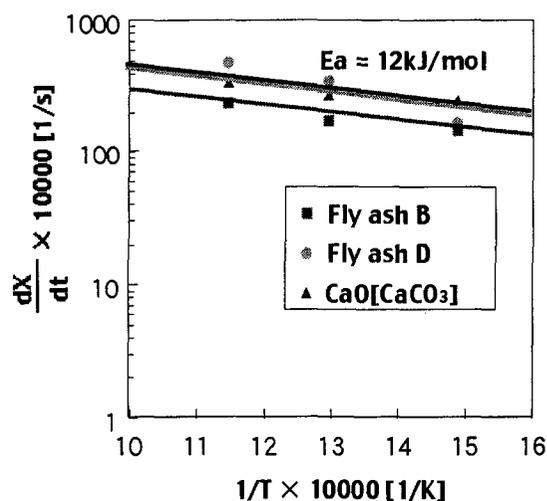


Fig. 5, Chlorination rate change with temperature at 2000ppm HCl.

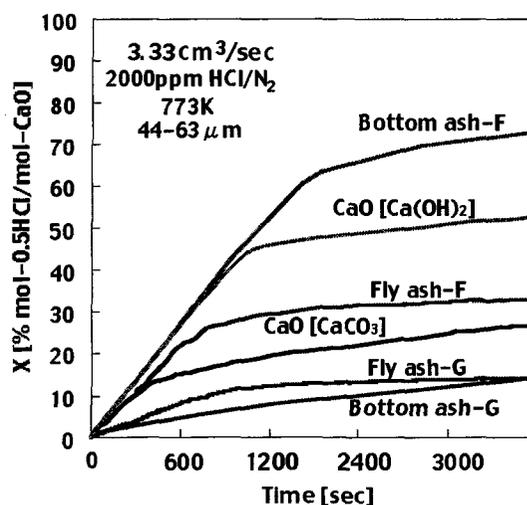


Fig. 6, Sorption curves of bottom ashes, fly ashes and Ca-based compounds.

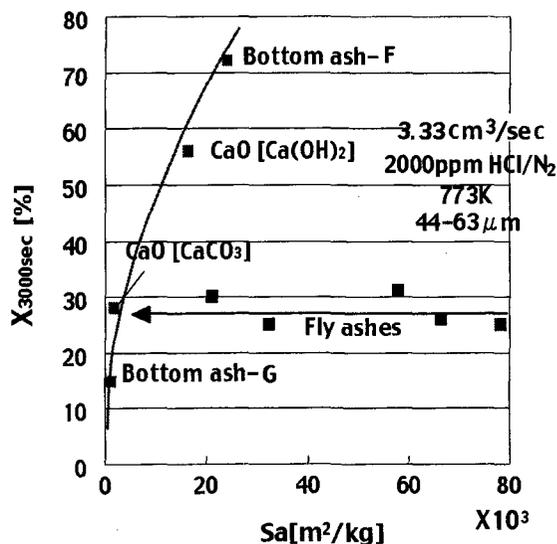


Fig. 7, Effect of specific surface area of coal ashes on CaO conversion into CaCl₂.

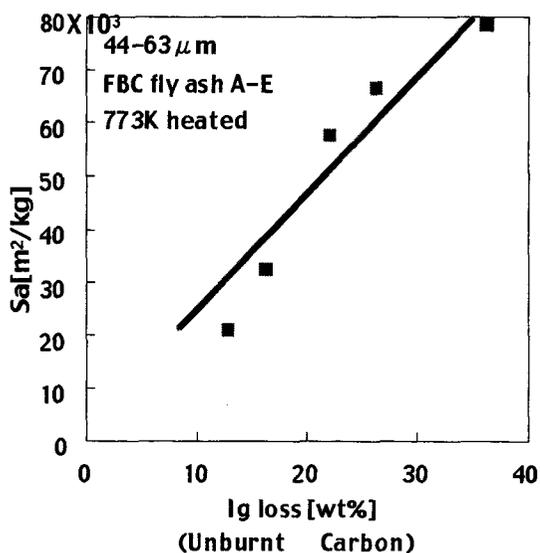


Fig. 8, Relation between unburnt carbon content and average surface area of coal burnt ash.

suspected to correspond to the difference of condition of coal ash discharged. In comparison with $\text{Ca}(\text{OH})_2$, the HCl-capacity of the fly ashes was lower, and it was similar to that of CaO derived from CaCO_3 .

3.5 Temperature Effect

The effect of chlorination temperature on the HCl-capacity of two types of fly ashes is shown in Fig. 5. The initial reactivity was found to increase with increasing chlorination temperature for all ashes. The apparent activation energies for chlorination of these ashes were about 12kJ/mol, which is equivalent to the value for chlorination of CaO prepared at 1123K from CaCO_3 which was originally injected into coal combustor as desulfurization agent. The activation energies between the temperature of 773 and 923K were observed by Walters and Daoudi(1991)[3], and they were observed between 0 and 22kJ/mol when the HCl absorption rates were governed by chemical reaction. In this work, it is found that the absorption rates of coal ashes were equivalent to the value of the pure CaO. Therefore coal ash sorbents can be used as the sorbents for dry-sorbent injection method.

3.6 Comparison between Fly Ashes and Bottom Ashes

Fig. 6 shows the difference between bottom ashes and fly ashes in reactivities toward HCl removal. It is seen that the conversion of bottom ashes is equal or better than that of fly ashes. Bottom ashes were a medium of FBC, which was pitch out from the bottom of FBC, these contain high $\text{Ca}(\text{OH})_2$ component compared with fly ashes. Therefore, it is to be noted that somewhat CaO derived from $\text{Ca}(\text{OH})_2$ involves in the removal of HCl at high temperature.

3.7 Effect of Physical Condition on Dechlorination Reaction

The effect of surface area of bottom ashes on conversion is showed in Fig. 7. Since $\text{Ca}(\text{OH})_2$ decompose firstly at reaction temperature above 653K, it is seen that the resulting calcium oxide is more porous and higher surface area than that of the original $\text{Ca}(\text{OH})_2$ at 773K. On the other hand, fly ashes mainly contain the unreacted CaO as the end of desulfurization, although this CaO generally has lower surface area than that of CaO derived from $\text{Ca}(\text{OH})_2$ at 773K. However Fig.7 shows that the fly ashes have 4-10 time larger surface area than that of bottom ashes apparently. This can be explained by the unburnt residue of coal involved in fly ashes (Fig. 8). It is assume that, in fact, the surface area of fly ash contributing to the reaction was smaller than that of bottom ash, and it was assumed that its value correspond to that of CaO derived from CaCO_3 . However, it is conducted that the fly ash can be used effectively as HCl sorbent by improving the physical structure of CaO.

4. CONCLUSIONS

From the current experiment results, it can be summarized as follows:

Coal ashes, which involved Ca-derived compounds such as $\text{Ca}(\text{OH})_2$ and CaO, can be employed as HCl sorbents. The calcium component which dominate the removal of HCl must be derived from CaCO_3 as desulfurization agent.

The HCl-capacity of fly ashes was lower than that of bottom ash because of structural difference, and it may be come from the difference of Ca compound involved in each ashes. It should be concluded that the reactivities of the employed fly ashes can be improved by increasing the surface area, depending on the pretreatment.

The activation energy for chlorination of ashes obtained below 873K was about 12kJ/mol, being equivalent to that of CaO derived from CaCO_3 .

5. NOMENCLATURE

ΔW [kg]:	the weight gain of the slag upon chlorination
W_0 [kg]:	the initial weight of coal burnt ash
ω_{CaO} [-]:	the weight fraction of CaO in coal burnt ash
M_{CaO} [kg/mol]:	the molecular weight of CaO
M_{CaCl_2} [kg/mol]:	the molecular weight of CaCl_2
X [%]:	CaO conversion into CaCl_2
S_a [m ² /kg]:	specific surface area
t [sec]:	reaction time

6. REFERENCES

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