Suppression of Dioxins Formation in Flue Gas by Removal of Hydrogen Chloride Using Foaming Water Glass

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Introduction

Hydrogen chloride (HCl) is an acidic air pollutant emitted from municipal or industrial waste incinerators, and this causes the de novo synthesis of dioxins in flue gas. It is essential to remove hydrogen chloride from the flue gas to reduce dioxins emissions as well as to avoid air pollution. Calcium hydroxide ($Ca(OH)_2$) is often used as a dry sorbent injected in a spray reactor to remove HCl from the flue gas.[1] However, usage of $Ca(OH)_2$ has disadvantage in reaction efficiency, and $Ca(OH)_2$ powder is usually injected in large excess over ten times its chemical reaction stoichiometry. This brings about the increase of fly ash and the rise in pH, which is undesirable to reduce solid wastes and to suppress the elution of amphoteric metals such as Pb, Zn, Sn.

Recently, we have developed “foaming water glass (FWG)” as a new wet sorbent for injection in a cooling tower to remove HCl and simultaneously to suppress dioxins formation.[2] FWG is a kind of sodium silicate hydrate ($l\mathrm{Na_2O}$ $m\mathrm{SiO_2}$ $n\mathrm{H_2O}$) and has a special property to form a foam over about 80 . Here we present the properties of FWG as a HCl remover and investigate the potential to replace $Ca(OH)_2$.

Methods and Materials

Foaming Water Glass (FWG)

FWG was prepared according to our developed procedure. In short, 150 g of NaOH and 20 g of NaF was dissolved in 1000 mL of water, and 100 g of Si lump was added into the solution at over 40 . They reacted vigorously with the evolution of H_2 gas, and pale yellow viscous FWG was obtained. The active ingredient concentration and the density of the solution were in the range of 35-45 % and 1.3-1.5 g/cm^3, respectively. The solution showed high basicity at pH 12-13. Heating the FWG over 80 yields a white glass foam just like styrene foam whose density is 0.1 - 0.2 g/cm^3. This glass foam is soluble in hot water, and the solution exhibits the same properties as FWG again. The FWG contains no vesicant, and the foaming gas is water vapour. The special property to form glass foam is due to its peculiar surface tension and viscosity around its boiling point. Raman spectroscopy indicated that the silicate ion in the FWG has a layer-structure, and the peculiarity of the FWG is attributable to the layer-structure of the silicate ion.

When the FWG solution is sprayed into a hot wind, microballoon or microfilm of sodium silicate is formed as shown in Fig. 1. Thus the FWG contacts with the flue gas with wide area, and higher reaction efficiency is expected.

Incineration of PVC with FWG

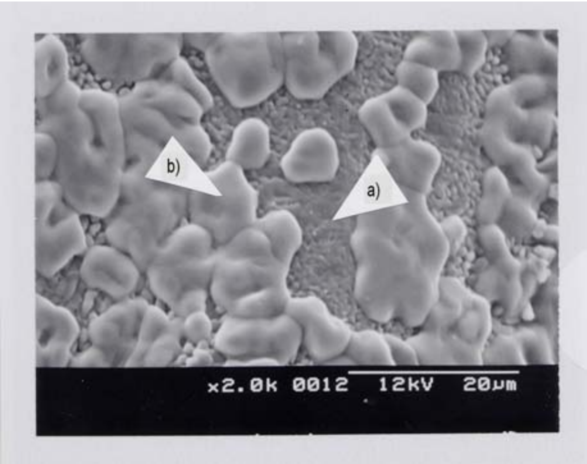
In order to check performance as HCl remover, the HCl emission was investigated when PVC (polyvinyl chloride) was incinerated with the FWG in air. 0.5 g of PVC board was dipped in the FWG and incinerated in air in a quartz tube. The emitted gas was captured in 0.1M NaOH (aq), and the concentration of Cl^- was determined by the Mohr method. The element distribution in the incineration residue was observed by SEM (scanning electron microscope) and EPMA (electron probe microanalyzer).

The PVC-rubbers containing the FWG powder of 3 wt%, 5 wt%, and 10 wt% were also prepared, and the amount of HCl emission was analyzed.

Fig. 1 Optical microscope image of microballoon formed from the FWG in a hot wind.

Spraying FWG in a Cooling Tower

Full scale tests were performed using three real industrial waste incinerators with different incineration capacity of 12 kg/h, 40 kg/h and 3300 kg/h. The FWG was diluted in water, and it was sprayed as cooling water into the flue gas just after a combustion chamber. The concentrations of HCl and dioxins in the flue gas were determined according to the standard procedures (JIS K 0107).



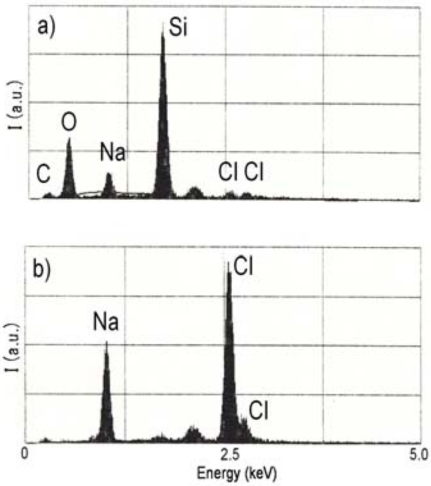


Fig. 2 SEM photograph and X-ray fluorescence microprobe analysis of the incineration residue

Results and Discussion

Incineration of PVC with FWG

The amount of HCl emitted from 0.5 g of PVC dipped with 0.5 g of FWG was determined at 0.116 g whereas that from PVC only was 0.164 g. The HCl emission was reduced by about 30 %. 0.5 g of FWG is considered to capture 1.5mmol (54mg) of HCl from the chemical reaction stoichiometry assuming that 1 mol of Na in FWG reacts with 1 mol of HCl. The reaction efficiency is calculated at 85 %. The secondary electron image and the X-ray fluorescence microprobe analysis of the incineration residue are shown in Fig. 2. NaCl generated by neutralization reaction between HCl and the FWG was observed on SiO_2 film. It was demonstrated that the FWG captures HCl on SiO_2 foam by neutralization reaction.

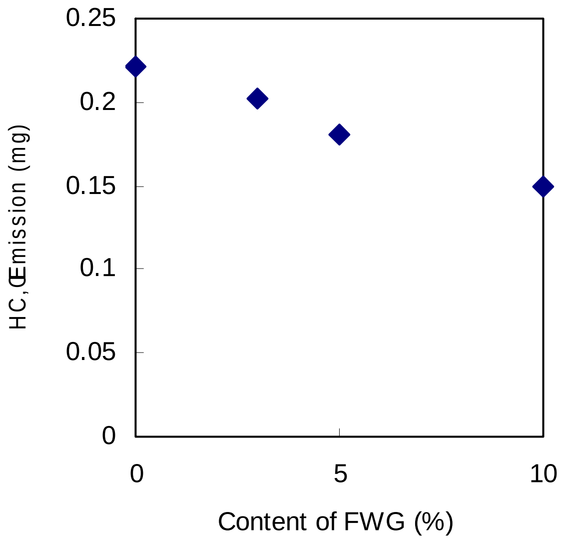


Fig. 3 Relationship between HCl emission and the content of FWG in PVC-rubber.

Fig. 3 shows the result of PVC-rubber containing the FWG powder. The reduction of HCl emission with increasing the content of the FWG powders agreed well with theoretical prediction based on the chemical reaction stoichiometry. This indicates the high reaction efficiency between the FWG powder and HCl gas.

Although it is technically difficult to capture all the HCl gas from PVC by the FWG, the reaction between the FWG and HCl showed sufficient efficiency. As for the FWG, the addition in large excess is unnecessary unlike the case with $Ca(OH)_2$.

Spraying FWG in a Cooling Tower

The capability of the FWG as HCl remover and the resulting reduction of dioxins formation are summarized in Table 1. By spraying the FWG aqueous solution into the flue instead of a cooling water, HCl concentrations were drastically deceased as for the incinerators A and B. However, since the spraying was carried out from one nozzle located at the center of the section, the removal efficiency was not so high with regard to the incinerator C with large sectional area of the flue. This can be improved by the modification of the spraying technique.

Table 1 Change in the concentrations of HCl and dioxins in the flue gas by spraying the FWG.

	Capacity (kg / h)	Injection Rate (g/Nm^3)	HCl (mg / Nm^3)		Dioxins (ng-TEQ/Nm^3)		Sectional Area of Flue (m^2)
			Without FWG	With FWG	Without FWG	With FWG	
A	12	-	2268	7	900	11	0.0079
B	40	1.0	30	2	22	0.22	0.090
C	3300	0.07	23	19			
		0.6	61	44		0.11	1.3
		1.2	17	11			

As for incinerator C, the HCl and the dioxins were measured on a different day.

The dioxins concentration in the fly ash collected in bag filters was also decreased from 4.4 ng-TEQ/g to 0.5 ng-TEQ/g. The clogging in bag filters was not observed for the FWG unlike the fine particles of $Ca(OH)_2$.

Our result indicates that HCl and dioxins emission can be controlled by spraying the FWG instead of using $Ca(OH)_2$ or activated carbon. The FWG is advantageous over the other HCl remover because unreacted powders do not remain in the fly ash owing to the high reaction efficiency. Furthermore, no extra equipment is necessary other than a cooling tower because the FWG is injected with cooling water. Thus the performance of existing incinerators is improved easily without any modification of the equipment.

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References

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