

Inhibition of Dioxin Formation in Flue Gas by Removal of Hydrogen Chloride Using Foaming Water Glass

Isao TSUYUMOTO, Motoji KINOMURA and Kazuhiro KUZUHARA

Department of Environmental Chemistry, College of Environmental Engineering and Architecture, Kanazawa Institute of Technology, 7-1, Ohgigaoka, Nonoichi, Ishikawa 921-8501

発泡性水ガラスを利用した塩化水素除去による煙道中でのダイオキシン類生成抑制

露本伊佐男・木野村元治・葛原一大

金沢工業大学環境・建築学部環境化学科, 921-8501 石川県石川郡野々市町扇が丘 7-1

We developed a foaming water glass (FWG), a kind of alkaline sodium silicate hydrate ($\text{Na}_2\text{O} \cdot m\text{SiO}_2 \cdot n\text{H}_2\text{O}$) and applied it to a HCl remover and a dioxin inhibitor in flue of waste incinerators. HCl emissions from PVC (polyvinyl chloride) proved to decrease substantially by incinerating the PVC with the FWG, indicating that the FWG is a useful HCl remover. HCl concentrations in flues of industrial waste incinerators were also reduced with larger efficiency than the conventional calcium hydroxide particles by injecting a diluted FWG solution as a cooling water. The reduction of HCl generation led to the decrease in dioxin concentrations in flue gas and fly ash.

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1. Introduction

The primary sources of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/PCDF) emissions at present are combustion and other high-temperature processes such as municipal solid waste incinerators (MSWIs), industrial waste incinerators, crematories, electric-arc furnaces in steel-making. Because most of the waste incinerators in industrialized countries have been improved to keep stable burning over 850°C, main focus on suppression of dioxin emissions from the incinerators has been shifted to how to inhibit the de novo synthesis in flues. A number of researchers have reported that nitrogen and sulfur containing chemicals were suitable inhibitors of chlorinated dibenzo-*p*-dioxin formation on municipal incinerator fly ash.¹⁾⁻³⁾ They react with active sites on the catalytic fly ash surface to form stable complexes with metallic compounds and thereby inactivate metallic catalysts such as CuO. Addition of the compounds with lone pair electrons, e. g., those containing nitrogen or sulfur, is promising for the inhibition of the catalysts because they can easily form stable complexes with copper, iron and other transition metals.⁴⁾ Removal of raw materials for the de novo synthesis is also an effective measure to inhibit dioxin formation. HCl is one of the acidic air pollutants emitted from municipal or industrial waste incinerators, and it acts as a raw material of the de novo synthesis in flue gas. Prevention of HCl generation in the flue is essential to reduce dioxins emissions as well as to avoid air pollution. $\text{Ca}(\text{OH})_2$ is often used as a dry sorbent injected in a spray reactor to remove HCl from the flue gas.⁵⁾ The addition of calcium compounds such as limestone, calcium oxides, calcium hydroxides suppresses dioxin formation by removing HCl. However, usage of calcium compounds has disadvantage in reaction efficiency, and its 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. Moreover, the melting point of the fly ash increases with a rise in calcium content, and this gives

rise to difficulties in the ash melting process.⁶⁾ The clogging of fine particles in bag filters is also a problem in using calcium compounds in flues.

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 inhibit the dioxin formation.⁷⁾ FWG is a kind of alkaline sodium silicate hydrate ($\text{Na}_2\text{O} \cdot m\text{SiO}_2 \cdot n\text{H}_2\text{O}$) and has a special property to form a glass foam or glass balloons over about 80°C.⁷⁾ Here we present the properties of FWG as a HCl remover and investigate the potential to replace $\text{Ca}(\text{OH})_2$.

2. Materials and methods

2.1 Foaming water glass (FWG)

FWG was prepared according to our developed procedure.⁸⁾ In short, 150 g of NaOH and 20 g of NaF was dissolved in 1000 cm³ of water, and 100 g of Si lump was added into the solution at over 40°C. They reacted vigorously with the evolution of H₂ 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 mass% and 1.3-1.5 g/cm³, respectively. The solution showed high basicity at pH 12-13. Heating the FWG over 80°C yields a white glass foam just like styrene foam whose density is 0.1-0.2 g/cm³. 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 surface tensions and the viscosities of the FWG solution (40 mass%) are summarized in **Table 1**. The special property to form glass foam is assumed to be due to its peculiar surface tension and viscosity when the FWG solution is condensed around its boiling point. Raman spectroscopy indicated that the silicate ion in the FWG has a layer-structure,^{9),10)} and the peculiarity of the FWG is attributable to the layer-structure of the silicate ion.⁸⁾

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.

Table 1. Viscosity and Surface Tension of the FWG

Temperature (°C)	0	10	20	25	40	50	60
Viscosity (mPa·s)	56.5	31.0	18.5	23.0	11.0	9.5	8.0
Surface tension (mN / m)	71.0	67.3	67.5	67.6	64.7	54.8	50.4

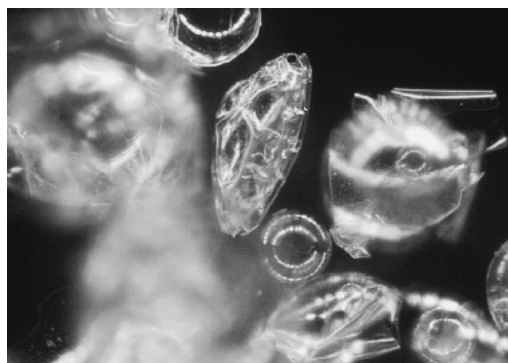


Fig. 1. Optical microscope image of microballoon formed from the FWG in a hot wind.

2.2 Performance evaluation as HCl remover in incineration of PVC

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 0.1 M 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 mass%, 5 mass%, and 10 mass% were also prepared, and the amount of HCl emission was analyzed. The possibility to suppress the HCl emission from PVC incineration by FWG was investigated.

2.3 Performance evaluation as HCl remover and dioxin inhibitor in industrial waste incinerators

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 flue gas was sampled just before the bug filter or electric precipitator. The concentrations of HCl and dioxins in the flue gas were determined according to the standard procedures (JIS K 0107).

3. Results and discussion

3.1 Performance evaluation as HCl remover in incineration of PVC

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%. Based on the assumption that 1 mol of Na in the FWG captures 1 mol of HCl by neutralization reaction, 1 g of FWG solution is calculated to capture 3.0 mmol (108 mg) of HCl. The reaction efficiency in this case was calculated at 85%. This high efficiency is owing to the foaming property that the other alkaline solutions do not have.

The secondary electron image and the X-ray fluorescence

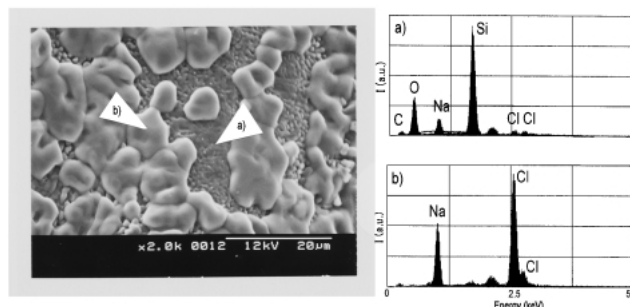


Fig. 2. SEM photograph and X-ray fluorescence microprobe analysis of the incineration residue.

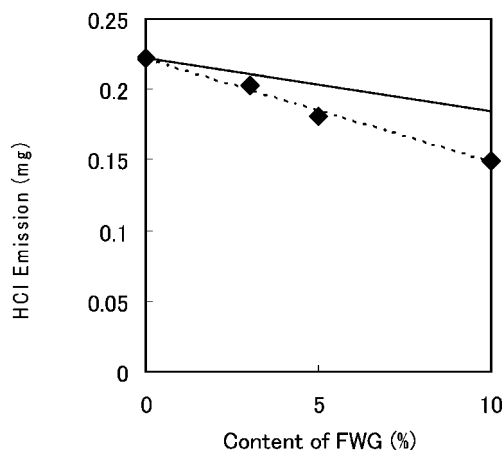


Fig. 3. Relationship between HCl emission and the content of FWG in PVC-rubber. The solid line is the theoretical line based on the assumption that 1 mol of Na in the FWG captures 1 mol of HCl gas, and the dotted line is the fitted line of the experimental values.

microprobe analysis of the incineration residue are shown in Fig. 2. NaCl generated by neutralization reaction between HCl and the FWG was observed on SiO₂ film. This demonstrates that the FWG captures HCl on SiO₂ foam by the neutralization reaction.

Figure 3 shows the result of PVC-rubber containing the FWG powder. The reduction of HCl emission was decreased linearly with increasing the content of the FWG powders. Although the linearity indicates the reaction occurred based on the chemical stoichiometry, the reaction efficiency was calculated at considerably higher value, 194% from the slope in Fig. 3. A simple interpretation of this experimental result is that 1 mol of Na in the solid FWG reduced 1.94 mol of HCl emission. This result indicates that the neutralization reaction is not the only reduction mechanism. Because it has been found that the FWG has fire retarding effect on polymers, the FWG hinders the decomposition of PVC to HCl gas, and some chloride compounds may remain in the solid residue.

We can say that the FWG is appropriate as HCl remover because of its high efficiency. Although it is technically

Table 2. Change in the Concentrations of HCl and Dioxins in the Flue Gas by Spraying the FWG. As for Incinerator C, the HCl and the Dioxins were Measured on a Different Day. Removal Efficiency is the Molar Ratio of the Reduced HCl to the Added Na of 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	HCl Reduction Ratio	Na/Cl Equivalent Ratio	Removal Efficiency	Without FWG	With FWG	
A	12	-	2268	7				900	11	0.0079
B	40	1.0	30	2	93.3 %	4.96	18.8 %	22	0.22	0.090
		0.07	23	19	17.4 %	0.45	38.4 %			
C	3300	0.6	61	44	27.9%	1.47	19.0 %		0.11	1.3
		1.2	17	11	35.3 %	10.4	3.4 %			

difficult to capture all the HCl gas from PVC by the FWG, the reaction between the FWG and HCl showed sufficient efficiency. We can expect that the addition in large excess is unnecessary as for the FWG unlike the case with Ca(OH)₂.

3.2 Performance evaluation as HCl remover and dioxin inhibitor in industrial waste incinerators

The capability of the FWG as HCl remover and the resulting reduction of dioxin formation are summarized in **Table 2**. By spraying the diluted FWG aqueous solution into the flue as a cooling water, HCl concentrations were drastically decreased as for the incinerators A and B. The removal efficiency of the incinerator B, the molar ratio of the removed HCl to the sprayed Na in FWG, was calculated at 18.8% much higher than that of the calcium hydroxide below 10%.⁶⁾ This difference is considered to be due to the shape of the sorbent like microballoons. Spraying as a cooling water is also advantageous over spraying particles because HCl gas is soluble in water and liquid-phase reactions are more efficient than gas-solid reactions.

The removal efficiencies of the incinerator C for the injection rates 0.6 g/Nm³ and 0.07 g/Nm³ were 19.0% and 38.4%, respectively, whereas that for 1.2 g/Nm³ was much lower. This drop for 1.2 g/Nm³ may be due to the low concentration of HCl gas compared to the other two. The spraying was carried out from one nozzle located at the center of the section, and thus the incinerator C with large sectional area of the flue was disadvantageous. This can be improved by the modification of the spraying technique that allows spread of the FWG all over the sectional area. The dioxins concentration in the fly ash collected in bug filters was also decreased from 4.4 ng-TEQ/g to 0.5 ng-TEQ/g similarly to those in the flue gases in Table 2. The clogging in bug 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 removers because the unreacted alkaline powders remaining in the fly ash is much less. 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. It can be said that the FWG is a promising neutralizer for acidic gases and a dioxin inhibitor in flues of the incinerators.

4. Conclusions

The foaming water glass (FWG), a kind of alkaline sodium silicate hydrate (Na₂O · mSiO₂ · nH₂O), was applied as a HCl

remover and simultaneously as a dioxin inhibitor. HCl emissions from PVC (polyvinyl chloride) incinerations were substantially decreased by dipping the PVC board in the FWG or by preparing PVC-rubber containing the FWG powder of 3 mass%–10 mass%. The reaction efficiency was in the range of 85%–194%, indicating that the FWG will be a powerful HCl remover. Full scale tests injecting a diluted FWG solution in flue at industrial waste incinerators with different capacity showed that the reaction efficiency of HCl depends on the sectional area of flues. This will be improved by modifying spraying technique in accordance with the sectional area. The removal efficiency was estimated at not less than ca. 20%. Furthermore, the clogging in bug filters does not occur, and the melting point of the fly ash in the ash-melting process decreases owing to low calcium content and high silicon content based on the phase diagram.¹¹⁾ It can be said that the FWG is a promising neutralizer for acidic gases and a dioxin inhibitor in flues instead of calcium compounds.

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