CONTROL OF DIOXIN FORMATION USING NEW SORBENT CONTAINED CALCIUM COMPOUND AS MAIN COMPONENT IN INCINERATORS

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Introduction

A large quantity of garbage has been incinerated in Japan, leading to the contamination of the environment with dioxin formed therefrom. It was reported that the dioxin concentration in exhaust gas rose with increasing Cl content [1], and the formation of dioxin was efficiently suppressed by removing HCl from the exhaust gas at temperatures of > 300 C[2] It is known that the oxidative decomposition of dioxin and/or its precursor by using a catalyst such as iron oxide is also effective.[3] We found two types of new materials, hydroxyl sodalite ($Na_8(AlSiO_4)_6(OH)_2$) [4] and hydrogrossular ($Ca_3Al_2(SiO_4)_{0.8}(OH)_{8.8}$) [4-8], as a sorbent for high-temperature HCl. The former one reacted with HCl in the exhaust gas at 400 800 C to fix chloride ions, by which dioxin formation is suppressed. The latter can also fix chloride ions in its structure and furthermore, has an ability to oxidize dioxin, by which dioxin formation is more effectively suppressed.

Calcium carbide (CaC_2) is produced from the reaction of limestone and coke at 3,000 C Calcium and magnesium compounds, iron oxide, carbon, and the others, are involved in the waste from the CaC_2 manufacturing process. Such a waste may be suitable as a sorbent for HCl, because alkaline earth metal compounds will react with HCl to fix chlorine ions. In the present study, we tried to purify the flue gas from incinerators by using this waste.

Methods and Material

The waste discharged from the CaC_2 manufacturing process was molded into the pellet with the diameter of 2 mm. Table 1 summarizes the chemical composition in the waste. The main components were CaO, MgO, SiO_2 and C and about 2 wt% Fe_2O_3 was involved.

Table 1: Chemical composition of the waste / wt%

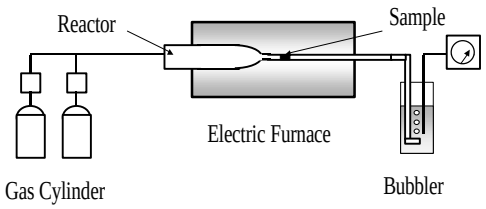
CaO	MgO	SiO_2	Al_2O_3	Fe_2O_3	K_2O	Na_2O	SO_3	C
50.08	13.13	12.31	3.83	2.04	1.57	0.47	3.53	13.04

The performance of the waste for HCl removal was evaluated by measuring the content of chlorine ions fixed in the sample. Fig.1 shows the experimental apparatus. The experimental conditions were as follows: the amount of the waste, 0.5 g; the volume of the waste packed, 10 mm in diameter×10 mm in length; reaction temperatures, 650 and 800 C; HCl concentration, 2,000 ppm with air dilution; coexisting gases, 10 % CO_2 and 10 % H_2O; gas flow rate, 200 ml/min. The HCl

supply was kept until the waste sample did not absorb it any more. The amount of chlorine ions in the waste sample was measured by XRF.

A mixture of a garbage and the waste sample, the ratio being 100 to 4 by weight, was burnt in the commercial incinerators and the concentrations of HCl and dioxin in the exhaust gas were measured. The sampling point of the exhaust gas for analysis was near the exhaust slot of the chimney. Small size incinerators of their capacity below 2,000 kg/h were used in this experiment. The garbage used was a mixture from a cloth, wood, a medical waste, papers, plastics and the others.

Fig.1 The experimental apparatus.



Results and discussion

Performance of the waste for HCl removal in the laboratory scale test

Using the model gas mixture, a laboratory scale test was carried out. Table 2 summarizes the amount of chlorine ions fixed in the waste material. Neither the reaction temperature nor the presence of both CO_2 and H_2O affected much the fixation: the extent of HCl fixation was within 12.0 - 13.7 wt% regardless of the experimental conditions varied.

Table 2: Chlorine quantity fixed in the sample

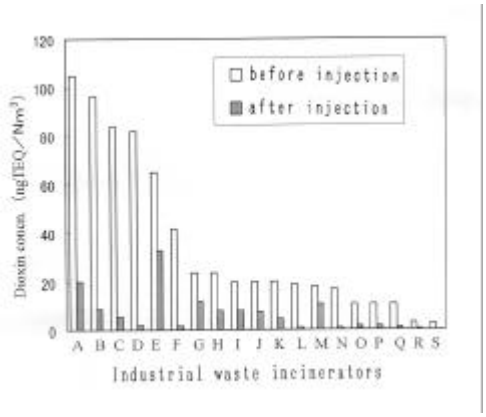
Coexistence gas		Cl quantity fixed wt%	
CO_2	H_2O	650 C	800 C
		13.7	13.3
		12.0	12.6
		12.4	12.7
		13.7	12.3

: Coexistence, : Non-coexistence

Suppression of dioxin formation in the exhaust gas

Fig. 2 shows the dioxin concentration in the exhaust gas from 19 commercial incinerators examined. The introduction of the waste sample resulted in a marked decrease in the dioxin concentration. The extent of the decrease varied from one incinerator to another. In case of the incinerator "A", which emits dioxin most pronouncedly, the concentration decreased from 105 to 21 ng-TEQ/Nm^3, while it decreased from 2.8 to 0.72 ng-TEQ/Nm^3 for the incinerator "S" with the least pronounced dioxin formation. The effect of the introduction of the waste sample on the suppression of dioxin formation was limited for the incinerator "E", from 64 to 33 ng-TEQ/Nm^3. It is interesting to note the concentration of CO varied from one incinerator

Fig.2 Dioxin concentration in exhaust before/after sample introduction.



to another. The CO concentration was lower in the incinerator suppressing dioxin formation than in that with less suppression. It is considered that the CO concentration is a measure for the atmosphere of the incinerator: a high concentration corresponds to a reducing condition, while a low one to an oxidizing condition. We can, therefore, conclude that an oxidizing condition is favorable for the suppression of dioxin formation.

For the incinerator “F”, “P” and “S”, the experimental results are summarized in Table 3. For these three incinerators, about a half HCl and 74 95% dioxin were decreased by introducing the waste sample to them. It is considered that the *de novo* synthesis of dioxin is suppressed because of the decrease in the HCl concentration in the incinerator. It is also likely that the iron oxide in the waste material can oxidize dioxin and/or dioxin precursor. [3]

Table 3: The effects of the sample on HCl fixation and dioxin formation

incinerator		F	P	S
HCl concentration (ppm)	before introduction	110	80	60
	after introduction	35	45	30
	decreasing ratio *	68 %	44 %	50 %
dioxin concentration ($ng\text{-}TEQ/Nm^3$)	before introduction	42	19	2.8
	after introduction	2.0	2.3	0.72
	dioxin restraint percentage **	95 %	88 %	74 %

* decreasing ratio = {(HCl concn. before introduction − HCl concn. after introduction) (HCl concn. before introduction)}×100

** dioxin restraint percentage = {(dioxin concn. before introduction − dioxin concn. after introduction) (dioxin concn. before introduction)}×100

Conclusion

The waste material from the CaC_2 manufacturing process, in which the oxides of Ca, Mg, Si, and Fe were involved, was tested for the fixation of HCl in it. It was found that the waste introduced in the garbage incinerator effectively decreased the amount of HCl from the incinerator, by which the formation of dioxin was highly suppressed.

References

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