

# ***Advanced Gas Cleaning Technology***

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# DEVELOPMENT OF SORBENTS FOR HEAVY METAL REMOVAL UNDER HIGH TEMPERATURE CONDITION

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## ABSTRACT

To develop the emission control technology of hazardous gas and trace heavy metals coal and/or biomass gasification gas in high temperature condition, we have studied the mechanism on capturing metals by sorbent particles. Various kinds of sorbent particles are prepared. Mineral matter, inorganic matter and Ca compounds are mixed for the sorbents. The sorbent particles containing compound A mainly had maximum adsorption. The surface of the sorbent was analyzed by SEM and XPS, and control factors of adsorption were investigated. This paper reports some results concerning sorbent performance.

## INTRODUCTION

Increase of energy conversion efficiency and utilization of renewable energy such as available waste and biomass as a fuel are effective on CO<sub>2</sub> reduction. However, combustion and gasification processes of them at high temperature exhaust corrosive gases and toxic heavy metals, emissions of which cause corrosion of heat exchanger tubes, resulting in low heat recovery in low temperature condition. Additionally, emission control of toxic metals from industrial and municipal solid wastes is also important to reduce an environmental impact because the concentration of hazardous compounds is relatively higher in comparison with fossil fuels such as coal.

We have been investigating on a gas cleanup system consisting of getter particles and a ceramic filter as a technology with simultaneous removing multi-component of corrosive gases and toxic metals at high temperature. Before confirming the performance of the gas cleanup system by a pilot test plant with a circulating fluidized bed and a honeycomb ceramic filter for sewage sludge, we investigated performance of the getter particle as a sorbent and condition increasing the removal efficiency.

## EXPERIMENTAL

### Experimental equipment

Experimental equipment used in this study is shown in Fig.1. A reactor tube (20 mm $\phi$  $\times$ 400 mm) is made of quartz and it is separable into three parts. A quartz basket (10 mm $\phi$  $\times$ 10 mm for single metal system, 15 mm $\phi$  $\times$ 10 mm for multi-metal system) filled with the source of heavy metals to be vaporized, is suspended at the center of the reactor. Sorbent particles are spread over a silica paper fixed by a ceramic frame at the bottom of the reactor. This sorbent layer is 100 mm apart from the quartz basket and works as a packed bed to capture vapor heavy metals. Air flow rate into the reactor is controlled to be constant at 1.5 L/min, using flow meter (RK-1250 KOFLOC) connected with the inlet of the reactor. Pressure in the reactor is kept constant by adjusting pressure drop between the reactor exit and a vacuum pump with a needle valve. In estimating the effect of moisture on the performance of heavy metal removal, carrier gas flow through water bubbler connected with the reactor inlet. The moisture

content in gas depends on the saturated vapor pressure that can be controlled by changing the temperature of water bath. K- type thermocouple is set close to the reactor wall, and the temperature in the reactor is controlled with the temperature control device (KP-1200 CHINO).

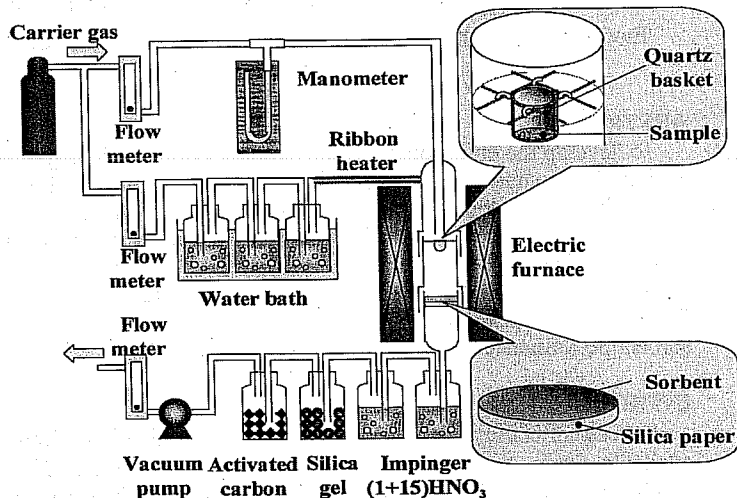


Fig. 1 Diagram of experimental equipment

#### Experimental conditions

Experimental conditions are summarized in Table 1. Sources of vaporized heavy metals, mineral sorbent and gas condition were varied as experimental parameters in this study. Composition of minerals used as sorbent is shown in Table 2. As a result of many previous studies, kaolinite is known to be effective for sodium, cadmium, zinc and lead capturing [2-7]. Kaolinite is a clay mineral and belongs to aluminosilicate group. Limestone was expected to be applied to remove many kinds of hazardous compounds simultaneously because it is a typical reagent to remove sulfur dioxide and hydrogen chloride. These minerals were crushed in a mortar, and screened to the particle size of 75 -175 $\mu$ m.

Table 1 Experimental conditions

Temperature, K	1073
Source of vapor heavy metals	ZnCl <sub>2</sub> PbCl <sub>2</sub> CdCl <sub>2</sub> NaCl
The amount of the source, set in the reactor, mol	Single metal system 0.001 Multi- metal system 0.001 of each metal total 0.003
Tested sorbent	Kaolinite, Silica, Hydrated lime Calcium carbonate
Weight of sorbent, g	1.0
Gas condition	N <sub>2</sub> 12% H <sub>2</sub> O + N <sub>2</sub>

**Table 2 Composition of kaolinite [%]**

	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	Ignition loss
kaolinite	54.1	35.4	0.21	13.4

**Table 3 Composition of getter particles [%]**

Getter	Kaolinite	Silica	Hydrated lime	Calcium carbonate
GetterA	27.7	15.2	57.1	
GetterB	15	15		70
GetterC	15	15		70

### Experimental Procedure

Heavy metals and sorbent particulates were weighed in the balance, and placed into the reactor in advance. A movable electric furnace heated to 1073 K beforehand was shifted closer to the reactor. It allowed rapid heating of the reactor in a few minutes. Vapor heavy metals emitted from the quartz basket flowed downward in the reactor with carrier gas stream, and a part of them were captured by sorbent particulates when they passed through the packed bed on the bottom of the reactor. Reaction time was counted from the moment when the reactor began to be heated up by the movement of the electric furnace. For the test under single metal condition, 0.001 mol chloride of each heavy metal was filled in the quartz basket as the source of vapor heavy metal. On the other hand, for the test under multi-metal coexisting condition, every 0.001 mol chloride of lead, cadmium and zinc (total 0.003 mol) were filled in the quartz basket. Partitions were prepared in the quartz basket so that three chlorides could not be blended together under melting condition. Schematic view of the quartz basket is shown in Fig. 1. Due to this basket structure, vapor heavy metals of three chlorides was separately emitted from basket and mixed with each other in gaseous phase in carrier gas. Sorbent particulates extracted from the reactor after tests for capturing heavy metals were dissolved in HNO<sub>3</sub>/HCl/HF mixture, and each metal in acid solution was measured via an atomic adsorption spectrometer (AA - 6800 SHIMADZU) to estimate the content of each metal captured by the sorbent.

### RESULTS AND DISCUSSION

Low boiling point compounds such as including alkali and chloride are easy to deposit to heat exchanger tubes in the cooling process after combustion, which promotes the alkali corrosion attacking. In this study, individual removal efficiencies of sodium as a representative alkali and zinc as a toxic metal were compared among several of mono-sorbent. Performance of each sorbent to capture sodium and zinc is shown in Fig. 2 and 3, respectively. From these figures, it can be seen that kaolinite is the most effective as a sorbent to capture both alkali and metal. Silica and calcium including limestone are not so ineffective to produce some alkali compound at 1073K. On the other hand, silica and limestone are ineffective to capture the metal as zinc. Existence of steam gas as shown in Fig. 3 increases captured amount of metal by transform of chloride to hydro chloride, which could increase with the steam gas concentration [1].

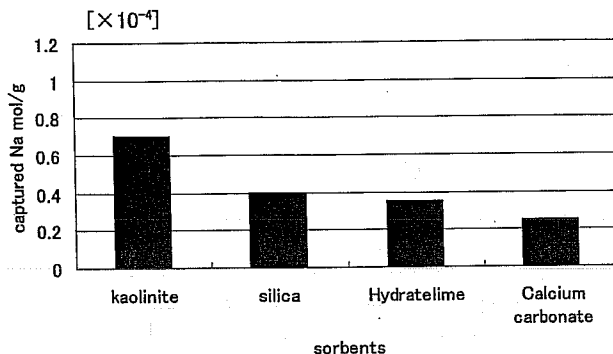


Fig. 2 Molar amounts of sodium captured by original sorbent of 1 g.

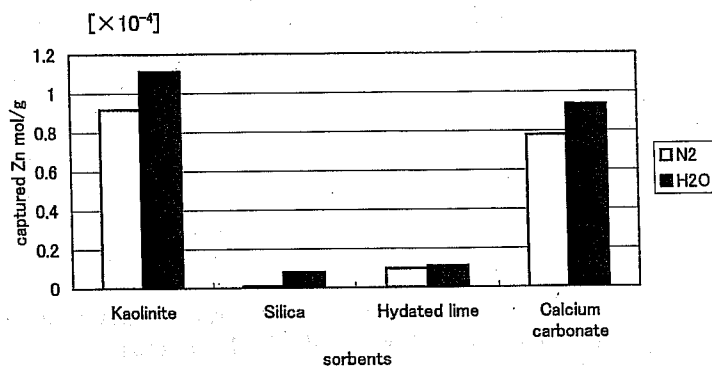
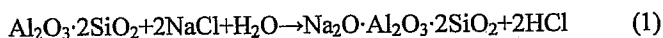


Fig. 3 Mole amounts of zinc captured by original sorbent of 1 g.

To clear the capturing mechanism of metals, especially of sodium as alkali, we observed the surface state by a Scanning Electron Microscope (SEM). From the SEM photographs shown in Figs. 4-1 and 4-2, the surface of the kaolinite sorbent after captured sodium seems to vitrify or to be wet. It suggests that the sodium would be captured by chemical adsorption of the kaolinite of Eq (1)[2, 3].



The capturing mechanism of other metals such as zinc, cadmium and lead would be also described by Eq.(1) as the metal chloride instead of sodium chloride. Furthermore, the chemical morphology was analyzed with Electron Spectroscopy for Chemical Analysis (ESCA). The results of Figs. 5-1 and 5-2 indicate that the kaolinite sorbent after captured sodium has an additional peak of No.3 at 58.1 eV. It suggests that adsorption reaction of sodium by kaolinite produce a different compounds from Na<sub>2</sub>O of Eq.(1). The result of Fig. 5-1 means that the original kaolinite before experiment had a little of sodium compounds.

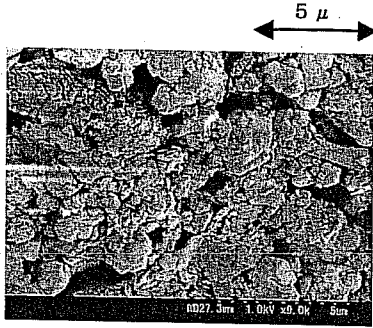


Fig.4-1 Surface of kaolinite before capturing sodium (5000 倍)

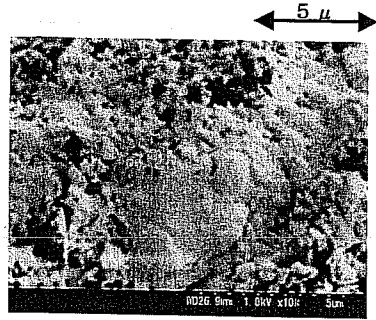


Fig.4-2 Surface of kaolinite after capturing sodium (5000 倍)

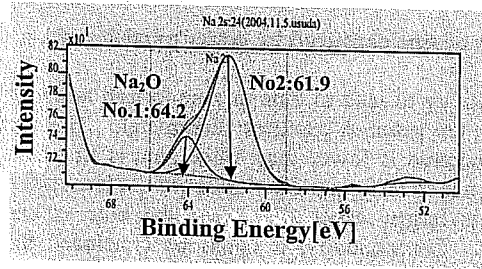


Fig.5-1 Surface of kaolinite before capturing sodium

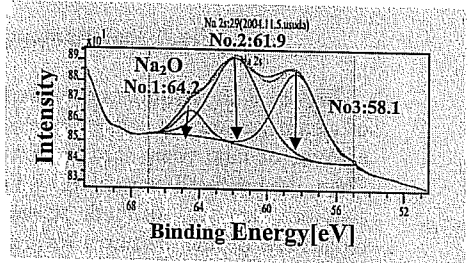


Fig.5-2 Surface of kaolinite after capturing sodium

Based on the performance of sorbent, we produced a granulated getter particles by mixing the calcia and silica to capture efficiently corrosive gases of sulfur dioxide and hydrogen chloride with the kaolinite sorbent. The performance of getter particles with multiple sorbents was investigated. The molar amounts of captured sodium and zinc per getter particles of 1 g at 1073K are shown in Fig. 6 and 7, respectively. It can be seen that the getter-A keeps the performance of original kaolinite sorbent for both sodium and zinc. When a calcium source was changed from the limestone to calcium carbonate and the calcium percentage in the getter was increased, the amount of captured metal was decreased. The influence of existence of steam gas on the capturing efficiency of the getter particles was also confirmed to be similar to the kaolinite used as a single sorbent in Fig. 3.

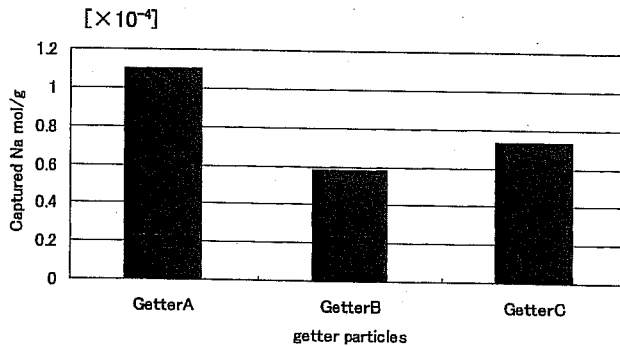


Fig. 6 Molar amounts of sodium captured by getter particles of 1 g.

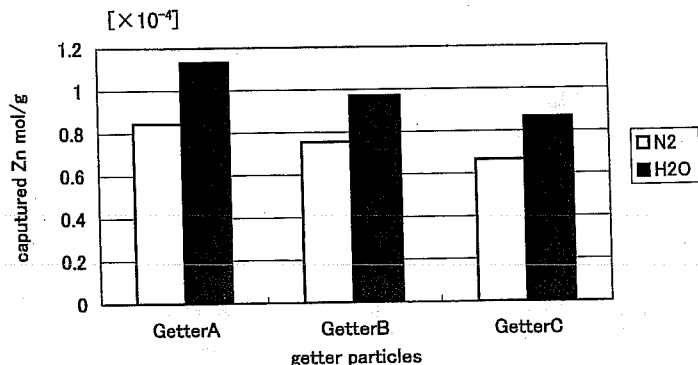


Fig. 7 Molar amounts of zinc captured by getter particles of 1 g.

Figure 8 shows influence of selectivity of lead to zinc or zinc to lead and influence of steam gas on the selectivity when the getter-A captures each metal. The captured amount of zinc when lead is first captured is lower than when zinc is first captured. Then, the captured amount of lead is not so different. The influence of steam gas on the captured amounts of both metals is larger, especially when the zinc is captured regardless of the existence of lead. Consequently, it could be concluded that the getter-A or kaolinite would prefer zinc to lead.

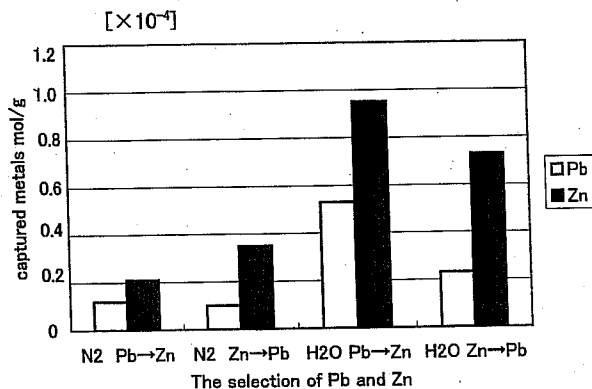


Fig. 8 Influence of simultaneous capturing and atmosphere when vaporizing three kinds of metals



Based on above experimental results, getter-A was applied to the pilot plant test. The pilot plant is consisted of a circulating fluidized bed furnace and a honeycomb ceramic filter. In this pilot plant tests, first each corrosive gas or metal compound was individually fed into the down stream of furnace, secondly multi-component was fed and finally the multi-component and sewage sludge were simultaneously fed. The results shown in Fig. 9 suggest that the cleanup system is useful to remove the multi-component of toxic heavy metals and corrosive gases of hydrogen chloride and sulfur dioxide simultaneously in high temperature condition. However, as predicted from the small fixed bed reactor test, it seems to be difficult to capture the lead in multi-component although lead of single component is efficiently captured.

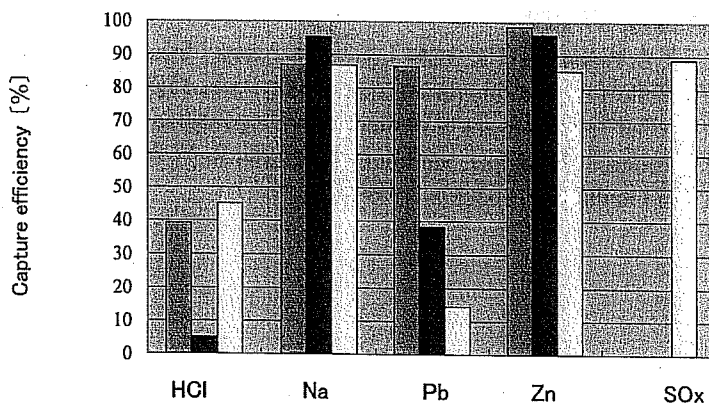


Fig. 9 Removal efficiency by the pilot test plant, a) :single component, b) :multi-component, c) :multi-component and sewage sludge

## CONCLUSIONS

In this study, the capturing performance of heavy metal by mineral sorbent such as kaolinite and limestone was experimentally investigated in both single metal and multi-metal coexisting systems. Chlorides of lead, cadmium, zinc and sodium were supplied as a source of vaped heavy metals. The effect of steam in gas on the capturing performance was also tested. Consequently, following conclusions were obtained;

- 1) Kaolinite as a mineral sorbent provides the highest capturing performance of sodium and toxic heavy metals, which can be enhanced by existence of steam gas.
- 2) Getter-A consisting of kaolinite and a mixture of calcia and silica keeps the capturing performance of the kaolinite itself for a single component of metal.
- 3) Getter-A is totally effective on capturing multi-component of metals and the capturing performance is higher as zinc, cadmium and lead in order.
- 4) A flue gas cleanup system with the getter-A and a ceramic filter is usefule to capture the multi-component hazardous gas at high temperature.

## ACKNOWLEDGEMENT

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