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Full Length Article

Chlorine removal from incinerator bottom ash by superheated steam

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HIGHLIGHTS

- Increasing superheated steam temperature enhances chlorine removal amount from ashes.
- Dechlorination of chloride increases in the following order: $CaCl_2$, NaCl and $MgCl_2$.
- Chlorine removal rate is controlled by diffusion of gas in the solid sample.

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ABSTRACT

In this study, the dechlorination of two kinds of incineration bottom ashes containing NaCl, $CaCl_2$ and $MgCl_2$ was investigated under various superheated steam temperatures between 408 and 693 K and a steam flow rate of 10 kg/h. The mechanism of chlorine removal from three kinds of simulated ash samples shaped into cuboid was discussed on the basis of chlorine removal rate data involving one kind of inorganic chloride. The chlorine removal amount from the incineration ashes increased with increasing superheated steam temperature, however the amount of chlorine removal depended on the composition of the incineration ashes. The amount of chlorine removal from the incineration ash containing NaCl and $CaCl_2$ was smaller than that from the ash containing NaCl and $MgCl_2$ at the same superheated steam temperature. The chlorine removal amount from the simulated ash samples with different chlorides was increased in the following order: $CaCl_2$, NaCl and $MgCl_2$. The dechlorination rate was analyzed by an unreacted core model newly applied for cuboid. It is suggested that the chlorine removal rates from the simulated samples containing SiO_2, Al_2O_3 and one of the inorganic chlorides (NaCl, $CaCl_2$ or $MgCl_2$) were controlled by the diffusion of gas in the solid sample.

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1. Introduction

Waste treatment is achieved through collecting, transporting, incinerating and landfilling in disposal sites. Effective utilization of an incineration ash [1–3] is desired in terms of recycling of resources.

One of the approaches is to use the incineration ash for a raw material of cement [4]. However, as the incineration ash contains chlorides [5,6], the steel bar or frame in a reinforced cement concrete might corrode due to a reaction between steel and chloride. Therefore, the cement standard has been set for chloride ion content [7,8], and it is necessary to remove chlorine from the incineration ash as much as possible when it is used as the cement raw material. Washing processes are generally applied to soluble inorganic chlorine separation from the incineration ash [4,9–14]. However, heavy metals in addition to chlorides are transferred to waste water, some chemical additives may be required, which causes an additional treatment cost [15,16].

On the other hands, Hase et al. [17,18] investigated organic and inorganic chlorine removals from RDF (Refuse-Derived Fuel) made from municipal solid waste by using superheated steam, and obtained the results as follows. The pyrolyzed organic chlorine by superheated steam increased with an increasing steam temperature, and the part of the pyrolyzed chlorine was changed to the inorganic chlorine, the increased amount of the inorganic chlorine had a peak value at around 500 K and then the inorganic chlorine also decreased. The chlorine removal from the incineration ash by using superheated steam might have a possibility of becoming a practice of lower treatment cost and environmental burden than the above washing method due to a low emission of waste water and easy capture of emitted gaseous chlorine, while it has another waste to capture and neutralize hydrogen chloride. However, there is few study on the inorganic chlorine removal from the incineration ash by superheated steam. Therefore, the chlorine removal behavior of two groups of the incineration ashes were investigated

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under various superheated steam temperatures and the chlorine removal mechanism was discussed based on the dechlorination behavior of three kinds of the inorganic chlorides contained in the incineration ash.

2. Experimental

2.1. Sample adjustment

Two groups of incinerator bottom ashes with a different chemical composition obtained after incinerating industrial wastes including sludge and plastic scrap by a rotary kiln of DOWA ECO-SYSTEM Co., Ltd., Okayama., Japan, were used in this study. The chemical compositions measured by fluorescent X-ray analysis are shown in Table 1. The chlorine content of ash I was 6.58 wt%, whereas that of ash II 0.75 wt%. After crushed with a blender, the granular ash sample was put into a dryer at 383 K for 24 h to remove water and adjusted by adding 2 g of ion-exchange water for 8 g of the ash so as to obtain the exact moisture content of 20%.

On the other hand, three kinds of simulated samples pressed into shapes were used to verify the chlorine removal mechanism from the chlorides involved in the incinerator bottom ashes. The pulverized material made from a single chloride, SiO_2 and Al_2O_3 was mixed and pressed into a cuboid of 8×10^{-3} m $\times$ 1.0×10^{-2} m $\times$ 8.6×10^{-2} m by a hydraulic press at a pressure of 40 MPa. Each sample contains 18.8 wt% chloride (NaCl, $CaCl_2$ or $MgCl_2$), 62.5 wt% SiO_2 and 18.7 wt% Al_2O_3. The sample porosity calculated from density and shape was 0.53 for NaCl and $CaCl_2$-containg samples and 0.54 for $MgCl_2$-containing-sample.

2.2. Experimental apparatus and procedure

Fig. 1 shows a schematic diagram of an experimental apparatus composed a boiler, superheated steam generator (Dai-ichi High Frequency Co., Ltd., Hi-Heater 2005S) and a dechlorination treatment chamber (29 $\times$ 15.4 $\times$ 21.5 cm). Steam was produced from ion-exchange water in the boiler, heated to a given temperature in the superheated steam generator and sent to the dechlorination treatment chamber. The sample was supplied on a wire gauge. Two thermocouples were set in the treatment chamber to measure, a steam temperature, T_{st} (K), and a sample temperature, T_{sp} (K). Flow rate of superheated steam was kept to 10 kg/h, steam temperature, T_{st}, was changed to 408, 493, 561, 608 and 693 K. Thus, the flow rate of superheated steam per sample weight and the average steam velocity in the treatment chamber became 5.16×10^{-4}–8.77×10^{-4} m^3/g s and 1.56×10^{-1}–2.65×10^{-1} m/s, respectively. The sample after treatment was dried at 383 K before the chlorine analysis.

Table 1
Chemical compositions of incineration ashes used for experiment (wt%).

Sample	Na	Mg	Al	Si	P	S	Cl	Ca	Fe
Ash I	8.83	7.56	7.29	26.59	1.79	5.56	6.58	6.05	5.93
Ash II	4.61	4.92	9.32	36.89	2.74	1.02	0.75	6.69	11.50

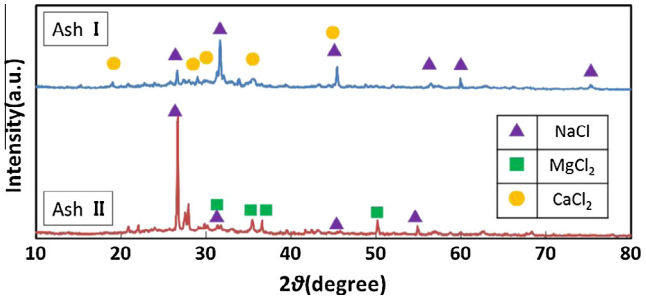

Fig. 2. XRD pattern of incineration bottom ashes used for experiment.

2.3. Chlorine analysis

In order to dissolve all of the dissolvable chlorine, chlorine in the treated sample was dissolved in hot water of 353 K for 30 min [18,19]. Liquid to sample used for analysis was 66.7–200 (mL/g). Chlorine content in the liquid was analyzed by Mercury (II) thiocyanate absorption spectrophotometry [20].

2.4. XRD analysis

The XRD pattern of two kinds of ashes was measured by an X ray diffraction apparatus (Rigaku Co., RINT 2100) as shown in Fig. 2. Ash I contained NaCl and $CaCl_2$, whereas ash II NaCl and $MgCl_2$.

3. Results and discussion

3.1. Chlorine removal behavior from incineration bottom ash

3.1.1. Chlorine removal from ash I

The chlorine removal behavior of ash I is shown in Fig. 3 where (a) the temporal change in a sample temperature, T_{sp} (K), (b) the temporal change in chlorine content, $C_{Cl}/C_{Cl,init}$, normalized by the initial chlorine content, and (c) the relationship between a chlorine removal rate, $-\Delta(C_{Cl}/C_{Cl,init})/\Delta t$ (min^{-1}) and $C_{Cl}/C_{Cl,init}$. The term of $-\Delta(C_{Cl}/C_{Cl,init})/\Delta t$ was calculated from the difference

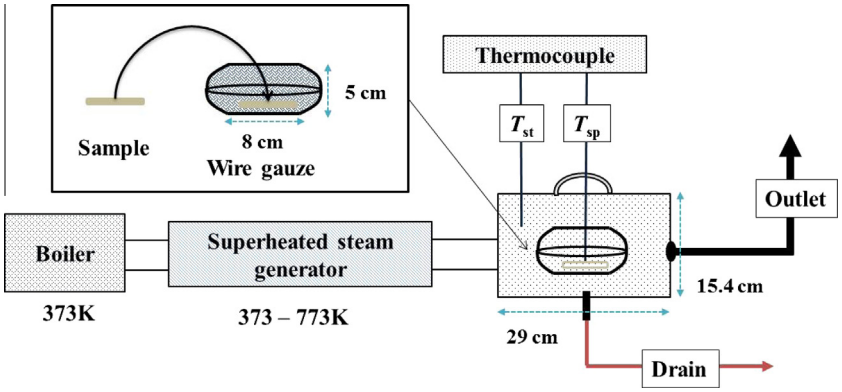

Fig. 1. Schematic diagram of experimental apparatus.

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