Formation of Hexavalent Chromium through an Ash Drying Process

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Abstract: Hexavalent Chromium (Cr^{6+}) is one of the hazardous compounds, and a lot of pollution has been found around the waste dumping site or in the yard of chemical factory. In order to find the cause of the Cr^{6+} formation, chemical change of Chromium was investigated. In the incinerated ash, Cr^{6+} was formed by drying treatment in alkali condition. However, no formation of Cr^{6+} was found in normal soil, this difference is depends on the state of Chromium component in the waste.

Key words: Ash, drying, hexavalent chromium, formation.

1. Introduction

Hexavalent Chromium (Cr^{6+}) is one of the hazardous compound, and some pollution has been found around in Japan especially in the waste dumping site or in the yard of old chemical factory, causing a lot of soil contamination [1-4]. Almost all of these Cr^{6+} problems are considered as a pollution by-product of many chemical process. Especially leaching from cement construction material are often reported [5].

Recently, Cr^{6+} pollution from dumping area of “Ferro-silt” was reported. “Ferro-silt” is a commercial name which is formed by neutralization of the titan acidic extract. One of the causes of this pollution is (Cr^{6+})’s formation in drying process is considered [6].

Usually, 200 mg/kg to 300 mg/kg of Chromium is contained in the ash or soil. Cr^{6+} is considered, that it is formed in heat treatment from 500 °C to 700 °C [7, 8], however, Cr^{6+} formation in low Temperature was not reported. In order to find a cause of the Cr^{6+} pollution in landfill site, we investigated a Cr^{6+} formation in drying treatment at low Temperature (room Temp. to 150 °C) [9, 10].

2 Methods

2.1 Materials

In our experiment, mountain soil and incinerated ash were used. The mountain soil is an silty clay which is dug out for construction sands around the mine near the Suzuka mountain chain located in west side of Yokkaichi. Incinerated ash of sewage sludge is discharged from the sewage treatment plant in Yokkaichi city, which is incinerated in the fluid type furnace at 850 °C. Chemical compositions of the ash and mountain soil are listed in Table 1. Chromium contents in the incineration ash and mountain soil are about 800 mg/kg and 400 mg/kg (as Cr_2O_3) respectively.

2.2 Experimental Methods

20 g of ash or mountain soil was put in the evaporation dish, 20 ml of aq. NaOH solution (containing NaOH 10 g) was added, and dried at some Temp. (room Temp. to 150 °C) in a heating chamber respectively.

In order to confirm the hexavalent chromium formation, treated samples (ash and soil) were transferred into the glass beaker, and 200 ml of water (solid/liquid 1:10) was added for elution test, stirred 60 min using magnetic stirrer. After stirring, 60 min of

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Fig. 1 Experimental procedure.

Table 1 Composition of the test material.

Compositions	Sewage ash (%)	Mountain soil (%)
SiO ₂	26	62
Al ₂ O ₃	12	17
CaO	14	2.5
Fe ₂ O ₃	17	8.1
P ₂ O ₅	19	< 0.01
Cr ₂ O ₃	0.08	0.04
Others	12	10

Table 2 Cr⁶⁺ concentration in the supernatant water.

Incinerated ash (mg/L)		Mountain soil	
Non-treated	Treated	Non-treated	Treated
ND	0.42	ND	ND

ND: Non detected.

sedimentation was carried out, almost all of the ash or soil was precipitated and supernatant water became transparent. 50 ml of supernatant water was taken out from the beaker. The supernatant water was in strong alkali condition, in order to meet with analysis, supernatant water was adjusted pH < 2 by addition of dil. H₂SO₄ (about 30%), and hexavalent chromium was measured by diphenylcarbazide absorption photometry.

3. Results and Discussion

In order to confirm (Cr⁶⁺)'s formation, ash and soil were mixed with NaOH aq. solution, and dried at 105 °C, 4 h as mentioned before, and Cr⁶⁺ concentration of the supernatant water is shown in Table 2. 0.37 mg/L of Cr⁶⁺ was detected in supernatant water of dried ash, contrary, Cr⁶⁺ was not detected in the water of non-treated ash. In the case of mountain soil, Cr⁶⁺ was not detected in the treated soil and the non-treated one. These difference of the (Cr⁶⁺)'s formation in the ash

and mountain soil is considered as not dependent on the chromium concentration but the state of the chromium compound in the material. In order to identify the conditions which can form Cr⁶⁺, the relation between the concentrations of Cr⁶⁺ to the amount of alkali added to the ash, and drying Temp. was also investigated. Cr⁶⁺ formations was found in the addition rate more than 5 g NaOH (Fig. 2). At room Temp., Cr⁶⁺ was not found, and in high drying Temp. (over 100 °C), Cr⁶⁺ was found as shown in Fig. 3. With the relation of the Cr⁶⁺ concentration and drying time, high Cr⁶⁺ was found in a long drying time (Fig. 4).

These results showed the formation of Cr⁶⁺ in drying treatment, however, (Cr⁶⁺)'s formation by heating without drying should also be considered. In order to confirm this concern, (Cr⁶⁺)'s formation in wet or dry conditions was investigated.

Fig. 2 Relation of Cr⁶⁺ and NaOH addition rate.

Fig. 3 Relation of Cr⁶⁺ and drying Temp.

Fig. 4 Relation of Cr^{6+} and drying time.

Fig. 5 Cr^{6+} concentration drying.

20 g of ash was mixed with NaOH aq. solution (containing NaOH 10 g), and put into the two vessel, one was opened, and another was closed to prevent drying, and heated at 105°C , for 24 h. Cr^{6+} concentrations in the two vessels were analyzed respectively. Cr^{6+} was found in the ash of opened vessel (Fig. 5). This result showed Cr^{6+} is formed in a dry condition at this Temperature.

4. Conclusions

In order to confirm (Cr^{6+})'s formation by drying treatment, incinerated ash of sewage sludge and mountain soil were dried in alkali condition. Cr^{6+} was

found in dried ash. Contrary, elution of Cr^{6+} was not found from mountain soil, and the result depends on the state of Cr compound in materials.

Recently, recycle technology of incinerated ash or sludge is going on, however, formation of Cr^{6+} in recycle processes will be considered as an important matter.

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