

LEACHING BEHAVIOR OF HEXAVALENT CHROMIUM FROM REFRACTORY BRICK UNDER HUMID ENVIRONMENT

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INTRODUCTION

In Japan, solid waste landfill is classified into three types. They are inert waste landfill, non-hazardous waste landfill, and hazardous waste landfill [1]. Among them, in hazardous waste landfill, hazardous waste which exceeds criteria for hazardous heavy metals leaching is disposed of. The hazardous waste landfill is required to be designed and constructed with robust concrete wall and base, and the top is capped. The concept of this landfill is containment of hazardous substance and eliminates the chance of reaction with water and air. In general, in non-hazardous waste landfill, various substances are subjected to many reactions and gradually stabilized. Even for hazardous heavy metals, it is known that their leaching potentials reduce due to the long-term weathering effect. But according to the concept of the hazardous waste landfill, these reactions cannot be expected. This means that the leaching potential of hazardous heavy metals will be kept forever. However, there is no guarantee that the container structure will be permanently maintained because of the impact of natural deterioration of structure or disaster.

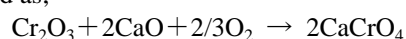
In order to prevent sudden emission of hazardous substance due to these occasions in future, some measure must be taken. There are two candidates considered to be able to achieve it. The one is multi-barrier system. To surround the site by various barrier systems such as clay barriers, impact of heavy metal to the surrounding environment can be mitigated. The other is to reduce the leaching potential of hazardous substance itself from solid waste. For incineration residue, the aging phenomenon is known to be effective for reducing the mobility of heavy metals [2]-[4]. The aging or weathering of the incineration residue is occurred by the contact with rainwater and carbon dioxide in air. As mentioned above, the hazardous waste landfill is surrounded by concrete walls and roof. The waste inside the landfill is isolated from the outside environment. This means that active control of inside circumstance is necessary to create the condition preferable for aging or weathering.

In this study, the effect of inside circumstance of the

hazardous waste landfill on the leaching behavior of harmful heavy metals was investigated. The refractory brick used in incinerator is major waste disposed of in hazardous waste landfill because of its high Cr(VI) leaching. Thus, the objective of the study is to elucidate suitable condition for reducing Cr(VI) leaching potential from the refractory brick disposed of in the hazardous waste landfill and to propose the active control method to achieve it.

MATERIALS AND METHODS

A used furnace refractory brick was obtained from a municipal solid waste melting facility and the leaching characteristics of hexavalent chromium was examined. Especially, influence of the internal circumstance of the hazardous waste landfill on its leaching was focused on. The obtained used refractory brick was rectangular parallelepipeds of about 10cm x 10cm x 20cm. It was reported that chromium in refractory bricks consists of trivalent chromium (Cr₂O₃) at the time of manufacture, but when used in the furnace, it reacts with CaO, which is the main component of slag produced by waste melting process, and changes to hexavalent chromium compound (CaCrO₄) [5]. This reaction can be expressed as;



After the refractory brick was pulverized into powder, the elemental composition, hexavalent chromium content, leaching concentration by leaching test of the Ministry of the Environment Notification No. 13 method (hereafter JLT-13), etc. were measured to grasp the characteristics of the refractory brick. However, detailed information such as elemental composition will not be shown in this paper because it will lead to product specification.

As a result of basic analysis mentioned above, it was found that trivalent chromium compound (Cr₂O₃), which is not harmful or leachable, was contained in large amounts in refractory brick. However, hexavalent chromium was generated from the reaction with slag components generated during the melting process, and this sample contained 30 mg/kg of Cr(VI). The

concentration of Cr(VI) obtained from the JLT-13 leaching test was 3 mg/L, exceeding the criteria (1.5 mg/L) for hazardous waste.

In order to prepare samples for the accelerated weathering experiment, a rectangular parallelepiped refractory brick was cut into 14 slices, and each slice was pulverized and mixed in a ball mill. This pulverizing and mixing pretreatment reduced the leaching concentration to 1/30 or less (Table 1).

Table 1. Leaching concentration of hexavalent chromium and pH before and after pulverizing and mixing

	Before	After
Cr(VI) mg/l	3	0.09
pH	8.6	7.1

This is thought to be caused by the fact that the refractory brick comes into contact with CO₂ in the atmosphere during the pulverizing and mixing process of the sample, resulting in a decrease in pH and a change in the leaching characteristics of chromium. The leaching test was also performed on each of the 14 slices, and there was little difference from the original sample. Therefore, it was suggested that a neutralization reaction progressed during mixing in the ball mill. As a result, the Cr(VI) leaching concentration was below the hazardous waste criteria, but it was subjected to the accelerated weathering experiment as it was. The pulverized refractory brick placed in a petri dish were placed in a desiccator adjusted to the circumstance that can be assumed as a hazardous waste landfill, and an accelerated weathering experiment was performed.

The four conditions shown in Table 2 were set as the circumstance conditions, including a humidified state, a completely dry state, and a gas atmosphere of air or nitrogen. Humidification conditions were achieved by placing a stainless steel tray containing water in a desiccator, and drying conditions were achieved by placing a tray containing silica gel. A sample was taken out every week, and the leaching concentration of hexavalent chromium was measured in accordance with JLT-13 method. Fig. 1 shows the status of accelerated weathering experiment. Each week, one tray of each was removed and analyzed.

Table 2. Circumstance condition set for accelerated weathering experiment

Wet/Dry	Gas condition	
Dry	N ₂	Air
Wet (humid)	N ₂	Air

RESULTS AND DISCUSSION

Fig. 2 shows the changes in the (a) pH and (b) leaching concentration of hexavalent chromium during the

accelerated weathering test of the pulverized refractory brick conducted over 10 weeks.

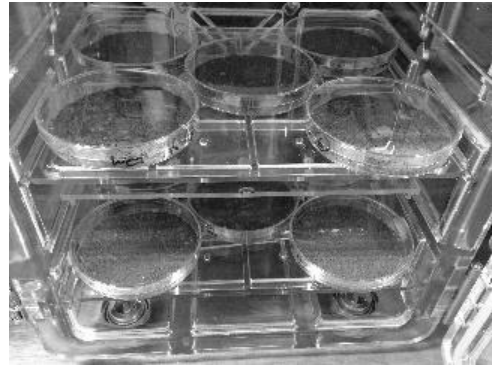


Fig. 1. Status of accelerated weathering experiment

As shown in (a), there was a significant difference in pH between dry and wet conditions. The dry conditions did not change significantly from the initial values, and the values at the start of the test were maintained within the range of 7 to 8, regardless of the gas atmosphere. On the other hand, under wet conditions, all of them were below 7, and especially under Wet (Air), they were below 6. Leaching concentration of hexavalent chromium shown in (b) also showed a significant difference between dry and wet conditions, and the leaching concentration of chromium decreased under wet conditions. In particular, under Wet (N₂) conditions, hexavalent chromium was no longer detected in all weeks after the second week.

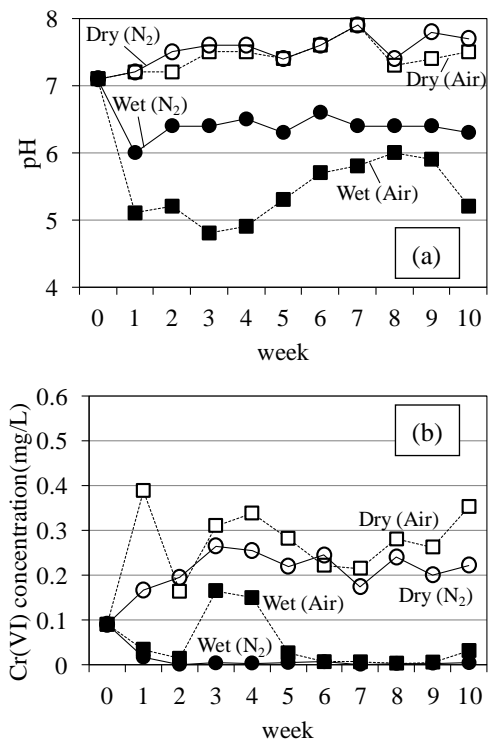


Fig. 2. Change in (a) pH and (b) hexavalent chromium

leaching concentration in accelerated weathering experiment

Although the results are not shown, pH dependent test was performed on the pulverized refractory brick to confirm whether the lowered pH reduced the leaching of hexavalent chromium. The initial addition method was adopted as the test method. As the result, no particular tendency was observed in the leaching concentration of hexavalent chromium in the pH range of 6-9. The used castable refractory (the leaching concentration of hexavalent chromium is two orders of magnitude higher than that of refractory brick) obtained at the same time from same facility was also subjected to the pH dependence test, and the leaching concentration was almost constant within the pH range of 2 to 5.

Therefore, the accelerated weathering experiment of the pulverized refractory brick was carried out again. Though the cause of the decrease in pH was not clear, tests were carried out at varying carbon dioxide concentration since it was confirmed that the leaching concentration of hexavalent chromium decreased significantly during the pulverizing and mixing process of the sample as mentioned in the experimental method. Both conditions (Table 3) were set at humid conditions, CO_2 concentrations were set at 50% and 100%, and the test period was set for 8 weeks.

Table 3. Condition of re-experiment

Run	Gas condition	Humidity
R-1	CO_2 50%, air 50%	Saturate
R-2	CO_2 100%	Saturate

The results are shown in Fig. 3. In this re-experiment as well, the leaching concentration of Cr(VI) tends to decrease with time as shown in Fig. 3(a). However, the change in pH (Fig. 3 (b)) was slight in this experiment. It was assumed that the neutralization would progress in the CO_2 atmosphere, but the pH was stabilized at around 9.5. On the other hand, the ORP (Fig. 3 (c)) decreased significantly from the first round under any CO_2 conditions. Although the results are not shown, a significant increase in ferrous ion concentration was confirmed under the condition of $\text{CO}_2 = 100\%$. Since ferrous ion is known as reducer, it seems that leaching of ferrous ion into absorbed water on refractory brick work to reduce hexavalent chromium to trivalent chromium.

For the condition of $\text{CO}_2 = 100\%$, Eh was calculated from the measured ORP, and the calculated Eh value and pH for each week were plotted on pH-Eh diagram of chromium [6] (Fig. 4) to examine the stable form of chromium in solution for each week. As can be seen in Fig. 4, Chromate ions (CrO_4^{2-}), which is hexavalent chromium compound, was in a stable form before the refractory was exposed to a moist environment. However, it was found that the stable form of

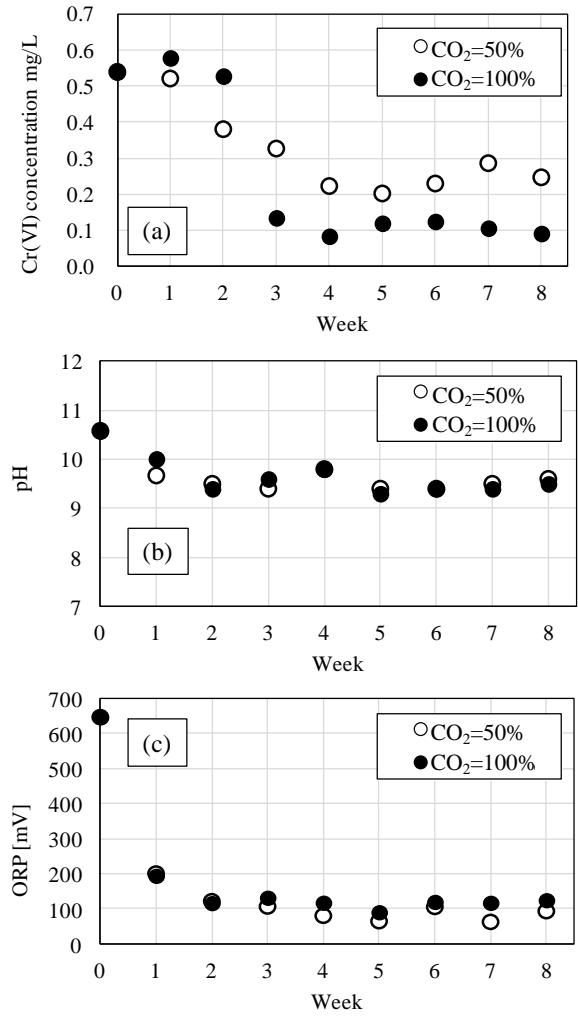


Fig. 3. Change of (a) Cr(VI) concentration, (b) pH, (c) ORP in accelerating weathering experiment done under wet condition

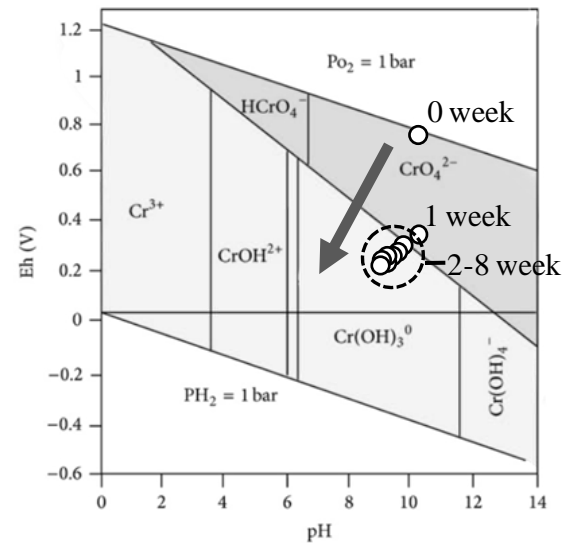


Fig. 4. Changes of chromium status at each week of weathering re-experiment

chromium after 2 weeks of exposure was chromium hydroxide ($\text{Cr}(\text{OH})_3$), which is a trivalent chromium compound. From this, an environment in which ions can be leached out into surface adsorbed water around the pulverized refractory brick particle is created due to moisture absorption in a moist environment, and gas in the environment and metal ions (such as ferrous ion) in the refractory are leached there, causing a decrease in pH and Eh. As the results, the form of chromium changed from hexavalent chromium to trivalent chromium.

This suggests that to decrease leaching concentration of hexavalent chromium from refractory brick in hazardous waste landfill, wet (humid) environments may be preferable. Fortunately, the hazardous waste landfill site is insulated from the outside environment with a concrete structure. In other words, it is considered that a concrete realization measure is to keep the humidity of the internal environment high to some extent. However, since the generation of leachate is not permitted under this structural requirement, it is essential to limit to the extent that the amount of surface adsorbed water only occurs.

REFERENCES

- [1] Ministry of Environment, Japan, Waste disposal and Recycling measures, <https://www.env.go.jp/en/recycle/manage/waste.html>
- [2] Speiser, C., Baumann, T., Niessner, R., Morphological and Chemical Characterization of Calcium-Hydrate Phases Formed in Alteration Processes of Deposited Municipal Solid Waste Incinerator Bottom Ash, *Environmental Science and Technology*, 34, 2000, pp.5030-5037.
- [3] Piantone, P., Bodenan, F., Chatelet-Snidaro, L., Mineralogical study of secondary mineral phases from weathered MSWI bottom ash: implications for the modeling and trapping of heavy metals, *Applied Geochemistry*, 19, 2004, pp.1891–1904.
- [4] Meima, J. A., Comans, R. N. J., The leaching of trace elements from municipal solid waste incinerator bottom ash at different stages of weathering, *Applied Geochemistry*, 14, 1999, pp.159-171.
- [5] Mizuhara, S., Urabe, T., Yamaguchi, A., Maeda, T., Fundamental Study on the Formation Mechanism of Hexavalent Chromium Compounds from Refractories Including Chromium Trioxide for Waste Melting Furnace, *Journal of Japan society of material cycles and waste management*, Vol.21, No.5, pp.170-177, 2010.
- [6] Palmer, C. D., and Wittbrodt, P. R., Processes Affecting the Remediation of Chromium-Contaminated Sites, *Environmental Health Perspectives*, Vol. 92, pp. 25-40, 1991.