Scientific paper

Study on Leaching of Hexavalent Chromium from Hardened Concretes Using Tank Leaching Test

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Abstract

Tank leaching tests were carried out to investigate the behavior of leaching trace elements from monolith samples. This study consists of two series, and the trace element used was hexavalent chromium.

In Series I, the influence of the leachant/surface area of the specimen (L/S ratio) on the leaching amount was investigated. The leaching amount was found to increase with the amount of worked water. This shows that any L/S ratio can be selected in the tank leaching test.

In Series II, the influence of the curing conditions of concrete on the leaching amount was investigated. In the case of concrete cured under sealed conditions, hexavalent chromium hardly leached. On the other hand, in the case of concrete dried in the room, the amount of leaching of hexavalent chromium became large. Carbonation was found to cause the decomposition of cement hydrates and the release of fixed hexavalent chromium.

The leaching of hexavalent chromium from using concrete was evaluated from these results. When water works continuously against concrete, the leaching of hexavalent chromium hardly affects the environment for water. When rainwater flows on the drying surface of concrete, the amount of leaching at the first rainfall was comparatively large, but deceased with subsequent rainfall.

1. Introduction

It is known that leaching of trace elements from hardened mortar or concrete is minimal (Takahashi 2000; Concrete Library 111 2003).

The amount of leaching depends on the fixation of trace elements by cement hydrates produced by the hydration of cement, the formation of hydroxides of trace elements in a high pH environment, or the restraint of diffusion of trace elements by the decrease of the pore volume in mortar or concrete.

The leaching behavior of trace elements from hardened mortar or concrete has widely been evaluated according to Notification No. 46 of the Environmental Agency of Japan. However, Notification No. 46, which is normally used to investigate the degree of pollution of soils, specifies that soils be sieved through a sieve with a 2 mm mesh size in order to remove small stones, etc. Therefore, application of Notification No. 46 to mortar or concrete means the preparation of samples with a particle size of less than 2 mm through crushing.

When investigating the leaching behavior of trace elements from mortar or concrete in contact with water, application of Notification No. 46 is not necessarily proper, because the mortar or concrete structures that are used are not small particles obtained through crushing.

Therefore, the authors elected to study the tank leaching test method for mortar or concrete for the purpose of investigating the behavior of leaching trace elements from mortar or concrete in water. The trace element in this paper is hexavalent chromium contained as a water-soluble constituent in cement.

2. Experiment

2.1 Tank leaching test

The procedure of the tank leaching test is shown in **Fig. 1**. The amount of leachant per unit surface area was defined as the L/S ratio. L/S = 50 means that the amount of leachant is 50 liters per 1 m^2 of surface area of specimen. The leaching was carried out without stirring the leachant. A specimen was placed in the tank and the leachant was put in the tank. After the specimen was left in the tank for the designated number of days, it was removed. The whole leachant was removed to a vessel. The specimen was then immediately placed again in the tank, completing one leaching cycle. Leaching was then repeated.

Water purified by distillation and ion-exchange was used as the leachant. The tank leaching tests were carried out at room temperature.

The leachant after leaching was filtered with a 0.45 micrometer membrane filter. The filtrate was used for analysis of chromium or hexavalent chromium. In this

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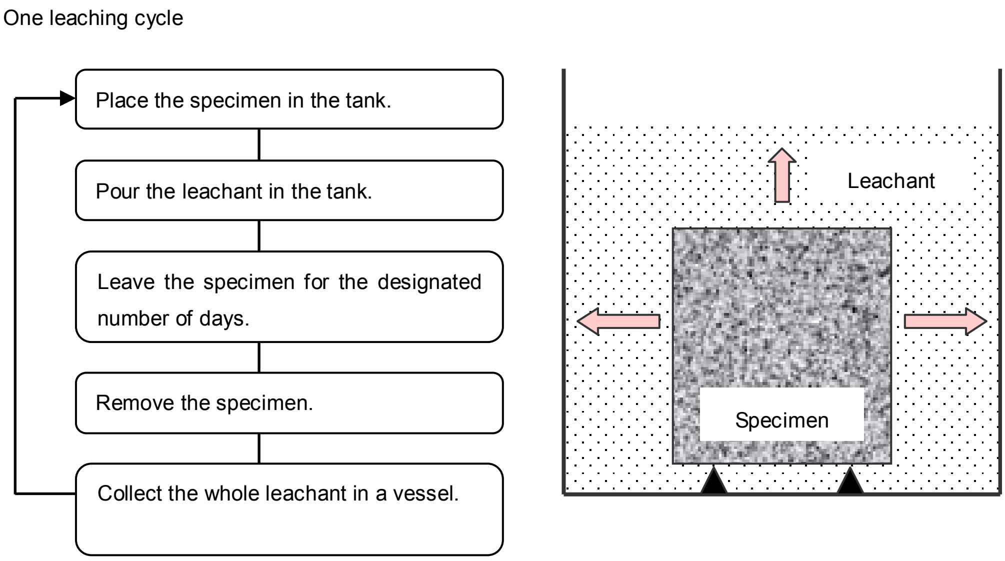

Fig. 1 Tank leaching test procedure.

paper, this filtrate is called "leachate".

The tank leaching test consisted of two series.

In Series I, the influence of L/S ratios 17, 35 and 50 on the amount of leached chromium from mortar was investigated. These L/S ratios were selected based on the leaching procedure, the size of the tank and the volume of leachant among other factors. In Series II, the influence of the curing conditions of concrete on the amount of leached hexavalent chromium from concrete was investigated at L/S = 50.

2.2 Specimens
2.2.1 Cement
Ordinary Portland cement was used in both series I and II. The contents of water-soluble hexavalent chromium in the various cement samples are shown in **Table 1**. The contents of water-soluble hexavalent chromium in cement were determined by Japan Cement Association Standard JCAS-I-51:1981. The procedure was as follows: 1 g of cement was stirred in 100 mL of purified water for 10 minutes. Immediately, the cement was filtered with 5B filter paper. The obtained filtrate was used for analysis. The amount of hexavalent chromium in the filtrate was determined by absorption spectrometry using diphenylcarbazide.

2.2.2 Specimen of mortar
The mortar specimens in Series I were prepared by the strength test method specified in JIS R 5201. The mass of cement, standard sand and water were 450 g, 1350 g and 225 g, respectively. The mixed mortar was placed in a φ 50 x 100 mm plastic form. The top of the mortar was leveled with a screed and was covered with a plastic film. These specimens were cured in a room at 20±2°C for 5 days.

Table 1 Content of water-soluble hexavalent chromium in cement.

Series	Sample number	Water-soluble hexavalent chromium (mg/kg)
I	—	14.4
II	No.1	10.3
	No.2	5.5
	No.3	6.9
	No.4	8.5
	No.5	6.0

2.2.3 Specimen of concrete
The mixture proportions of the concrete of Series II are shown in **Table 2**. The mixed concrete was placed in a φ 100 x 200 mm plastic form. The top of the concrete was leveled with a screed and was covered with a plastic film. The specimens were cured under the conditions listed in **Table 3**. The curing of II-S28-A14 was planned with the intention of determining the influence of the carbonation of concretes on leaching of hexavalent chromium.

2.3 Determination method of chromium or hexavalent chromium in leachate
The concentration of hexavalent chromium in leachate of Series I was found to be low. For this reason, the amount of chromium in the leachate was determined by means of ICP-AES, Inductively Coupled Plasma - Atomic Emission Spectrometry. In Series II, the hexavalent chromium in the leachate was determined by means of absorption spectrometry using diphenylcarbazide.

Table 2 Mixture proportions of concrete of Series II.

W/C	s/a	Unit content (kg/m^3)				
(%)	(%)	W	C	S *	G **	AEWR ***
50	41.5	170	340	736	1049	0.850

* Pit sand ** Crushed hard sandstone *** Air entraining and water-reducing admixture

Table 3 Curing conditions of concrete.

Series	Symbol	Curing
I	-	Sealing for 5 days at 20±2°C
II	II-S7	Sealing for 7 days at 20±2°C
	II-S28	Sealing for 28 days at 20±2°C
	II-S28-A14	Drying for 14 days after sealing for 28 days at 20±2°C

3. Results and discussion

3.1 Determination of L/S ratio in tank leaching test

In Series I, the influence of the L/S ratio on the amount of leached chromium from mortar was investigated.

The concentrations of chromium in leachate of Series I are shown in **Table 4**. The cumulative amounts of leached chromium from mortar are shown in **Table 5** and **Fig. 2**. In this paper, the amount of leached chromium or hexavalent chromium is expressed in milligram (mg) per surface area (m^2).

The cumulative amount of leached chromium increased with the L/S ratio. On the other hand, the concentration of chromium decreased with the L/S ratio. This suggests that the increase in the concentration of chromium in the leachant restricts diffusion of chromium from the specimen.

The cumulative leached chromium shown in **Table 5** was evaluated with the amount of work water against the surface of the specimen. When the leaching[2] at L/S = 17 ended, 17 L of leachant worked twice against the surface of specimen. Thus, the amount of work water was estimated at 34 L. Further, the leaching amount was estimated as the sum of the leaching amounts of leaching[1] and leaching[2].

The relation between the amount of leached chromium and the amount of work water is shown in **Fig. 3**.

This relation, which does not depend on the L/S ratio can be expressed with Eq. 1. This result suggests that any L/S ratio can be selected for the tank leaching test. A convenient L/S ratio is 50, because a lot of leachate is obtained and the operation is easy at this L/S ratio.

$$Y = 0.05234X^{0.6969} \tag{1}$$

where Y=Amount of leached chromium (mg/m^2), X=Amount of work water (L/m^2).

3.2 Effect of curing condition of concrete

The concentrations of hexavalent chromium in leachate of sealed curing are shown in **Table 6**. When the concretes were cured under sealed conditions, all the concentrations were less than 0.004 mg/L, the lower limit of the determination. These results show that hexavalent chromium leaches hardly from sealed curing concretes.

Table 4 Concentrations of chromium in leachate.

L/S	Concentrations of chromium in leachate (mg/L)				
	Leaching[1] 0-1 days	Leaching[2] 1-2 days	Leaching[3] 2-3 days	Leaching[4] 3-4 days	Leaching[5] 4-7 days
17	0.021	0.017	0.011	0.011	0.010
34	0.018	0.013	0.009	0.008	0.010
50	0.015	0.010	0.008	<0.008	0.008

Table 5 Cumulative leached chromium from mortar.

L/S	Cumulative leached chromium from mortar (mg/m^2)				
	1 day	2 days	3 days	4 days	7 days
17	0.357	0.646	0.833	1.020	1.190
34	0.612	1.054	1.360	1.632	1.972
50	0.750	1.250	1.650	2.050	2.450

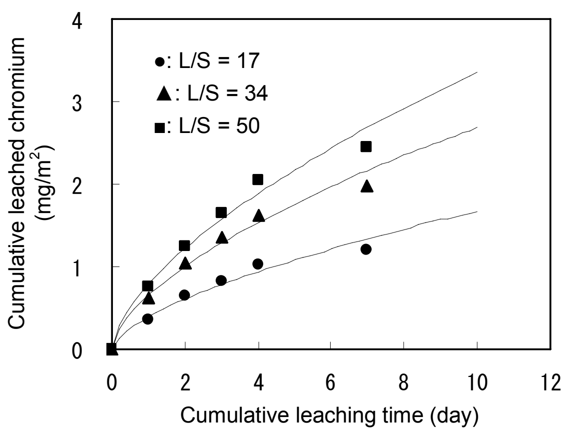

Fig. 2 Cumulative leached chromium from mortar in Series I.

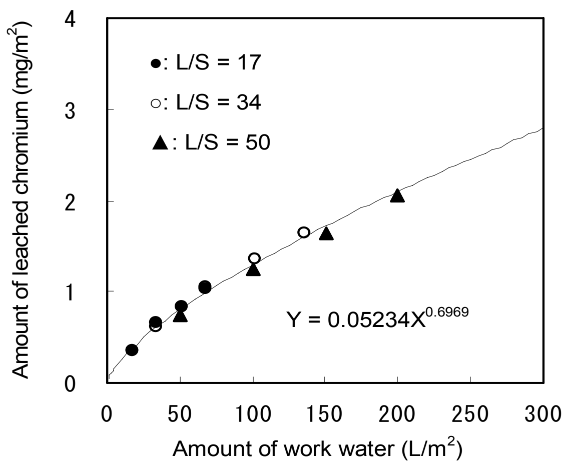

Fig. 3 Relation between amount of leached chromium and amount of work water.

The concentrations of hexavalent chromium in leachate of curing of II-S28-A14 are shown in **Table 7**. This curing condition assumed the case that the water worked on drying concrete outdoors. The concentrations of hexavalent chromium at leaching[1] were 0.035 to 0.044 mg/L. On the other hand, those at leaching[2] decreased to less than 0.010 mg/L.

These results suggest the influence of carbonation of concrete. The compressive strengths of concretes after sealed curing for 28 days were 35.1 to 37.8 MPa. Thus the depths of carbonation of concretes were considered to be almost the same. The depth of carbonation was estimated to be about 0.5mm, based on calculation from the mixture proportions and curing conditions of the concretes (Architectural Institute of Japan 2003). The amount of hexavalent chromium in the carbonated part as calculated with Eq. 2 ranged between 0.94 and 1.75 mg.

$$CR = WSC \times C \times V \quad (2)$$

where CR=Amount of hexavalent chromium in the carbonated part of concrete (mg), WSC=Content of water-soluble hexavalent chromium in cement (mg/kg), C=Unit content of cement (mg/kg), V=Volume of the carbonated part (m^3) (1m x 1m x 0.0005 m).

The amount of leached hexavalent chromium at leaching [1] ranged from 1.75 to 2.20 mg as calculated from the results in **Table 7**. From this calculation, almost all leached chromium at leaching[1] were the hexavalent chromium in the carbonated part of the concrete samples. In other words, this carbonation caused the decomposition of cement hydrates and the release of the fixed hexavalent chromium.

Table 6 Concentrations of hexavalent chromium in leachate.

Curing	Cement	Concentrations of hexavalent chromium in leachate (mg/L)			
		Leaching[1] 0-1 days	Leaching[2] 1-2 days	Leaching[3] 2-4 days	Leaching[4] 4-8 days
II-S7	All	<0.004	<0.004	<0.004	<0.004
II-S28	All	<0.004	<0.004	<0.004	<0.004

Table 7 Concentrations of hexavalent chromium in leachate of curing II-S28-A14.

Cement	Concentrations of hexavalent chromium in leachate (mg/L)			
	Leaching[1] 0-1 days	Leaching[2] 1-2 days	Leaching[3] 2-4 days	Leaching[4] 4-8 days
No.1	0.044	0.009	0.006	0.008
No.2	0.039	0.007	0.005	0.006
No.3	0.039	0.007	0.005	0.007
No.4	0.036	0.007	0.006	0.007
No.5	0.035	0.007	0.006	0.007

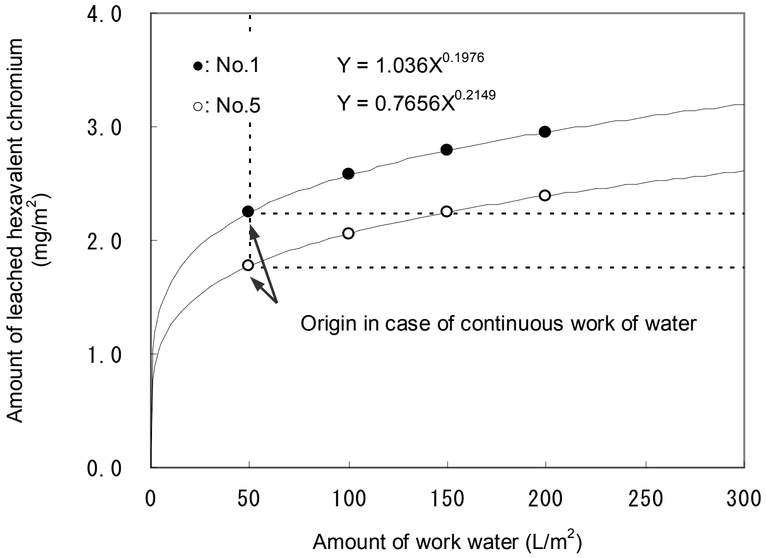

Fig. 4 Relation between amount of leached hexavalent chromium and amount of work water in Series II-S28-A14.

4. Evaluation of leaching of hexavalent chromium from concrete by means of tank leaching test

4.1 Case of continuous work of water

The piers of bridges built over rivers or lakes are in continuous contact with water. The amount of work water is generally very large and depends on the flow rate.

The relation between the amount of leached hexavalent chromium and the amount of work water on curing of II-S28-A14 is shown in **Fig. 4**. The estimation of the amount of leached hexavalent chromium and the amount of work water were carried out in the same manner as described in section 3.1.

In the case of continuous work of water, the amount of leaching at 50 L of work water was neglected because it corresponds to the leaching from drying concrete. Thus, the amount of leaching was calculated moving the origin in shown in **Fig. 4**.

The relation between the amount of leached hexavalent chromium and the content of water-soluble hexavalent chromium in cement is shown in **Fig. 5**.

The amount of leached hexavalent chromium tended to increase slightly with the contents of water-soluble hexavalent chromium in cements.

When the amount of work water was 10 L/m^2, the calculated amount of leached hexavalent chromium was 0.083mg/m^2 and the concentration was 0.008mg/L in the case of the No. 1 sample, which had the highest content of water-soluble hexavalent chromium. The concentrations of hexavalent chromium decreased with the amount of work water. From these results, it can be concluded that the leaching of hexavalent chromium hardly affects the environment in the case of continuous work of water.

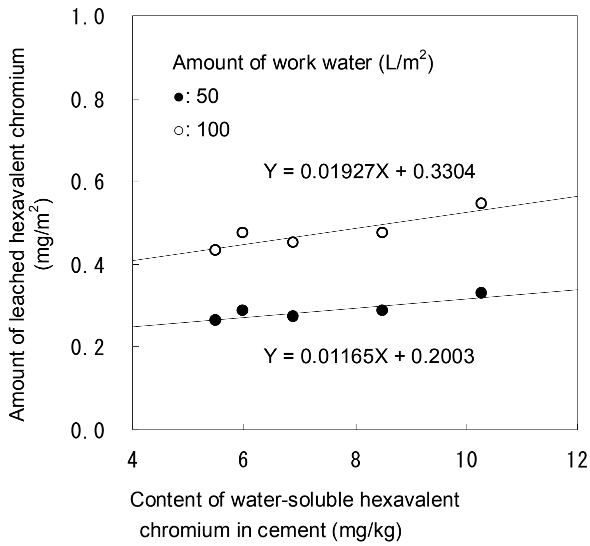

Fig. 5 Relation between amount of leached hexavalent chromium and content of water-soluble hexavalent chromium in cements in Series II-S28-A14.

4.2 Case of contact of water on dried concrete

In the case of rainfall, the concentration of hexavalent chromium in the rainwater that comes in contact with the concrete is expected to be large, because the concrete is in a dry state. And, it is considered that the concentration depend on the amount of rainfall and the length of time the water remains on the concrete surface. The concentration of hexavalent chromium in the rainwater that comes in contact with the concrete was evaluated with the simple model. The specimen used was No.1 of Series II-S28-A14.

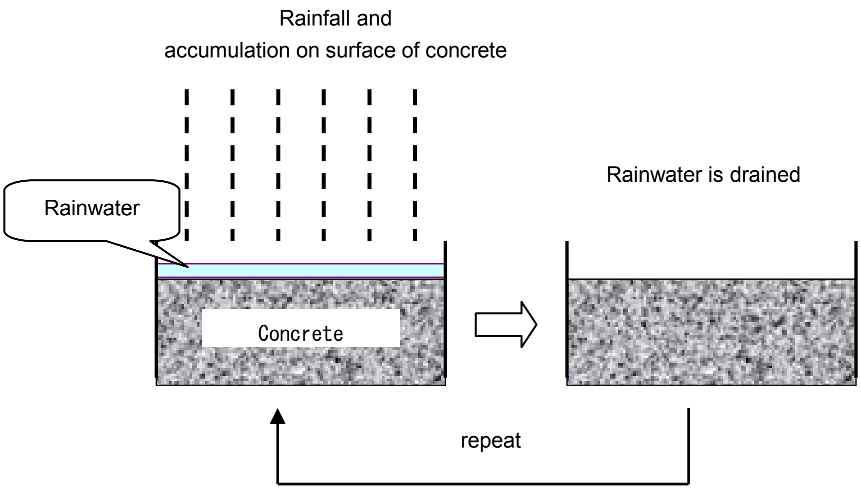

Fig. 6 Model of rainwater on surface of concrete.

The model of rainwater on the surface of concrete is shown in **Fig. 6**. The L/S ratio is not included in this model because the relation between the amount of leaching hexavalent chromium and the L/S ratio had not been determined in the case of dried concrete.

The relation between the cumulative leached hexavalent chromium and the cumulative time at L/S = 50 is shown in **Fig. 7**. This example assumes that the remaining time is one hour. The amount of leached hexavalent chromium in every hour is shown in **Fig. 8**. The amount of leached hexavalent chromium between 0 and 1 hour was 1.198 mg/m^2 and the amount of leached hexavalent chromium in eve after one hour decreased gradually. When rainfall is 1 mm/hour, the amount of rainwater is 1 L. Thus, the concentration of hexavalent chromium in the first drained water was 1.198 mg/L and that in the second drained water was 0.176 mg/L. However, there is some possibility that these concentrations were evaluated too high, because the leaching amount decreases as the L/S ratio decreases, as stated in 3.1.

A more detailed examination is necessary for the application of the tank leaching test results to actual conditions.

5. Conclusions

The tank leaching test method is deemed suitable for the evaluation of leaching trace elements from using concrete structures, based on the following findings.

(1) Cumulative leached chromium increases with the L/S ratio.

(2) The amount of leached chromium can be expressed as a function of the amount of work water. This result suggests that any L/S ratio can be selected for the tank leaching test. However, a convenient L/S ratio for the tank test is 50 from the point of view of the amount of obtained leachate and the ease of operation.

(3) The amount of leached hexavalent chromium increases with the amount of work water. On the other hand, the concentration decreases with the amount of

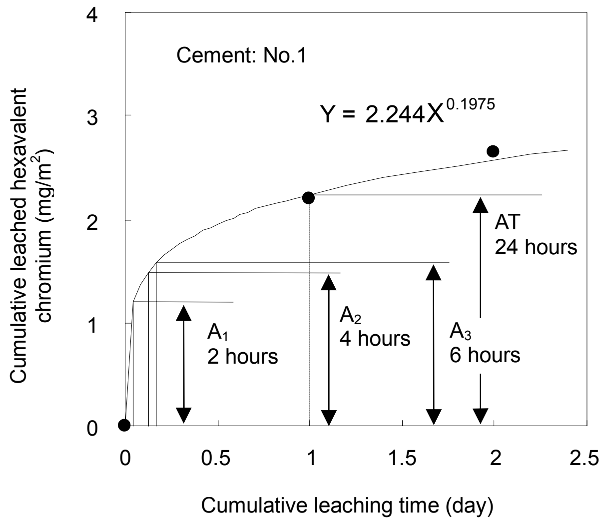

Fig. 7 Relation between cumulative leached hexavalent chromium and cumulative time at L/S = 50 in Series II-S28-A14.

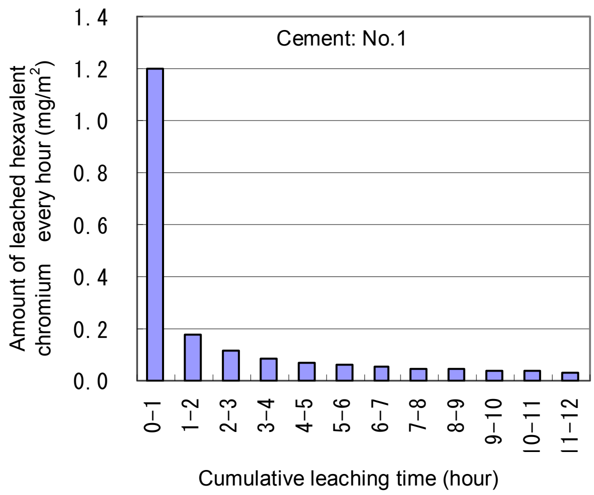

Fig. 8 Amount of leached hexavalent chromium every hour at L/S = 50 in Series II-S28-A14 (calculated from Fig. 7).

work water.
(4) When the concrete is cured under sealed conditions, hexavalent chromium hardly leaches. On the other hand, hexavalent chromium leaches easily in the case of dried and carbonated concrete.
(5) Regarding the evaluation of the concentration of hexavalent chromium in contact water, in the case of rainfall, the concentration of hexavalent chromium in the first contact rainwater is evaluated at more than 1 mg/L, but the concentration decreases rapidly with continuous rainfall.

As a final note, the tank leaching test method in this study is reflected in the JSCE Standard on Test Method for Leaching of Trace Elements from Hardened Concrete (Sugiyama *et al*. 2007).

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