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Cr(VI) concentration from batch contact/tank leaching and column percolation test using fly ash with additives

Jin-Chun Chai[a,*], Katsutada Onitsuk[a,1], Shigenori Hayashi[b,2]

[a] Department of Civil Engineering, Saga University, Saga, Japan
[b] Institute of Lowland Technology, Saga University, Saga, Japan

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ABSTRACT

Batch contact, tank leaching and column percolation tests were conducted to investigate the Cr(VI) concentration in the solution/leachate from two fly ashes (fly ash A and B) with additives. The additives used were cement, low alkalinity additive and Ariake clay. There are several factors influencing Cr(VI) concentration in solution/leachate, namely (1) properties of solid/liquid mixture (chemical composition, pH value, etc.), (2) cementation effect, (3) amount of water in contact with the solid mass (solid/liquid ratio in case of batch contact test), and (4) adsorption characteristics of the solid particles to Cr ions. The test results indicate that fly ash A has less cementation component (CaO of 1.92%) and the amount of water in contact with the fly ash played an important role. As a result, Cr(VI) concentration from the column percolation test was much higher than that of the batch contact test. Adding Ariake clay had more effect on reducing Cr(VI) concentration for fly ash A than B because the pH value of the solution from fly ash A was lower, which provided a favorable condition for Cr(VI) ions to be reduced to Cr(III) and possibly to be adsorbed by clay particles. Fly ash B has more cementation component (7.15%) and for column percolation test, curing the sample for 1 week reduced Cr(VI) concentration significantly. The test results indicate that in engineering practice, a method which closely simulates the field condition should be selected to assess possible environmental effects and corresponding countermeasure methods.

1. Introduction

In Japan, the amount of fly ashes generated from thermal power stations was about 54 million ton/year [1]. How to treat and/or effectively use the fly ashes is an important environmental issue. One of the ways is to use them as construction material, such as for embankment construction. However, fly ashes normally contain ions of heavy metals such as Cr(VI), Cd(II), Pb(II), etc., which may have a negative effect/impact to environment [2]. To use fly ash as a construction material, its geo-environmental impact must be checked. There are three methods available to check the concentration of a target chemical component/ion in solution/leachate, namely, batch contact test, tank leaching test and column percolation test. The batch contact test represents the process of mixing a solid mass into groundwater and to check the effect of this process on groundwater. While the tank leaching test simulates a process of submerging a solid mass into groundwater, and check the effect of this solid mass to groundwater quality. The column percolation test simulates the process of percolation/seepage of water into a soil structure to investigate the effect of leachate on environment. The batch contact test is faster and is often used and it has been specified as a standard test method by Japanese Environment Agency (JEA) [3]. However, using batch contact test for solidified/stabilized substance not represents the field condition, and some times, it may give an unsafe result. Kamon et al. [4] reported that a long-term column percolation test may result in a higher concentration than a batch contact test for some chemical substance. Therefore, in practice there is a question which method will result in a more reliable and safer result.

In this study, the concentration of hexavalent chromium (Cr(VI)) in solution/leachate from two fly ashes (coal ashes), named as fly ash A and B, was investigated by batch contact, tank leaching and column percolation tests. The effect of adding cement, clayey soil (Ariake clay) and low alkalinity additive on Cr(VI) concentration is also investigated experimentally. The results are compared and the influencing factors on Cr(VI) concentration are discussed.

* Corresponding author. Tel.: +81 952 28 8580; fax: +81 952 28 8190.
E-mail addresses: chai@cc.saga-u.ac.jp (J.-C. Chai), onitsuka@nkg-net.co.jp (K. Onitsuk), hayashi@ilt.saga-u.ac.jp (S. Hayashi).
[1] Tel.: +81 952 28 2525
[2] Tel.: +81 952 28 8627; fax: +81 952 28 8189.

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2. Materials and test methods

2.1. Fly ashes

The fly ashes tested have a brand name of Blair Athol (from Blair Athol coal, Australia). Two batches of ashes were sampled at different time and their properties are different. For easy to discuss, the two batches of the samples will be designated as fly ash A and B respectively, and their chemical compositions, ignition loss, specific surface area and the density of the particles (fly ash A only) are given in Table 1. The chemical compositions were analyzed by fluorescent X-ray analysis method.

2.2. Admixtures

2.2.1. Ariake clay

There is considerable amount of waste clayey soils generated from construction sites in Japan, and mixing waste clayey soils with fly ashes provides a possible method to treat both waste clayey soils and fly ashes [5]. The clayey soil adopted to mix with the fly ashes in this study was Ariake clay with a liquid limit (w_l) of 116.6% and plastic limit (w_p) of 57.5% and clay content (<2 μm) of about 31.0%. The dominant clay mineral in the Ariake clay is smectic one [6]. The pH value of the solution from the clay/distilled water mixture with a solid/liquid ratio of 1:10 was 7.64. Unfortunately, the chemical compositions of the Ariake clay used were not measured, and the chemical compositions of an Ariake clay sample from a different location were measured and included into Table 1 as a reference.

2.2.2. Cement

The cement used is a kind of Portland cement, and its chemical compositions are listed in Table 1 (the data are provided by the manufacturer). The equilibrium Cr(VI) concentration in the solution from a batch contact test with a solid/liquid ratio of 1:10 was 0.33 mg/l and pH of 12.7.

2.2.3. Low alkalinity additive

Normally fly ash shows alkaline property and it may affect the geo-environmental condition. Low alkalinity additive has an advantage over cement on reducing alkalinity of the treated fly ash. The chemical properties of the low alkalinity additive used are given in Table 1 also (the data are provided by the manufacturer). The main content of the low alkalinity additive is gypsum ($CaSO_4$), and in chemical composition analysis, it has been separated as CaO and SO_3. In the solution from a batch contact test with a solid/liquid ratio of 1:10, no Cr(VI) was detected (lower limit of the measurement was 0.005 mg/l). The pH value reported by Kamon et al. [7] is 10.2 (although the condition of measurement was not stated, it is interpreted as standard batch contact test in Japan with a solid/liquid ratio of 1:10).

Table 1
Chemical components and other properties of the fly ashes, the cement[a], the low alkalinity additive[a] and Ariake clay[b].

Content (%)	Chemical component						
	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	K_2O
Fly ash A	60.0	21.5	10.9	1.95	1.92	0.66	0.26
Fly ash B	39.3	29.1	14.0	1.13	7.15	0.81	3.02
Cement	19.15	4.76	2.43	–	60.49	1.15	–
Low alkalinity additive	13.80	3.19	2.57	–	30.70	1.16	0.14
Ariake clay	57.4	16.9	5.3	0.7	2.0	2.2	2.0

Content (%)	Chemical component					
	P_2O_5	SO_3	Sr	Cr	Na_2O	H_2O
A	0.33	0.22	0.192	0.010	0.09	–
B	1.50	0.69	0.129	0.006	1.00	–
Cement	–	7.45	–	–	–	–
Low alkalinity additive	–	32.56	0.29	-	0.12	9.6
Ariake clay	0.1	2.4	–	–	2.6	–

Other properties	Ig. loss (%)	Specific surface area (m^2/g)	Density of particles (kg/m^3)
A	1.2	0.25	2300
B	1.4	–	–
Cement	–	0.39	3040
Low alkalinity additive	–	–	–
Ariake clay	9.0	–	–

[a] Values were provided by manufacturers.
[b] Not the same batch as used for batch contact and column percolation tests.

2.3. Method for batch contact test

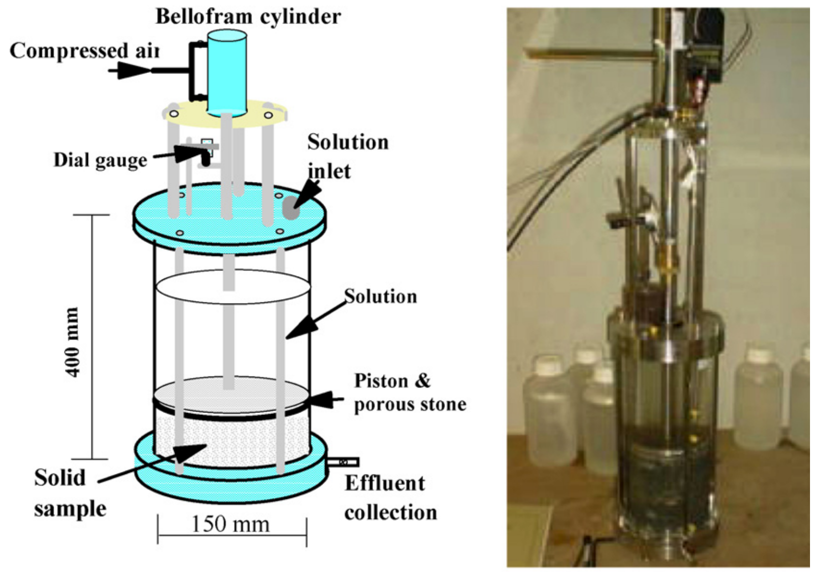
The tests were conducted basically according to the regulation of the Public Notice No. 46, JEA [3]. The solid/liquid ratio adopted was 1:10. The liquid used was distilled water and the initial pH value was adjusted to about 6 by adding hydrochloric acid. The mixture was put into 1 l glass bottles and mixed for 24 h by rotating the bottles (upside down) with a speed of 30 rpm. Due to the availability of the equipment, this mixing process is different from that described in the Public Notice No. 46, JEA. Then the solid was separated from the liquid by a centrifuge machine. After centrifuge separation, since the liquid phase was clear, no filtration was made. The concentration of Cr(VI) and pH value of the solution were measured. For all tests, Cr(VI) concentration was measured by absorptiometric method using diphenyl carbazide (JIS K 0102 65.2) [8]. pH was measured following the method specified by Japanese Geotechnical Society, JGS 0211-2000 [9].

2.4. Method for tank leaching test

The test was conducted according to the Regulation No. 49, the Ministry of Construction (currently the Ministry of Land, Infrastructure and Transport), Japan [10]. The method requires to put solid mass in blocks into distilled water with a solid/liquid ratio of 1:10 and to leave it for 28 days. Then the concentration of Cr(VI) in the solution was measured. It is required to adjust the pH value of the water to be within 5.8–6.3 initially (about 6 in this study).

2.5. Method for column percolation test

A column used is 150 mm in diameter and 400 mm in height. The samples of fly ash or its mixture were typically 20 mm thick. The samples were formed by compacting the materials inside the column. For fly ash and fly ash adding 2 and 5% cement cases, the samples were compacted at near their optimum water content of about 23% to a dry density of about 1340 kg/m^3 for fly ash A and about 1400 kg/m^3 for fly ash B. The degree of compaction was about 95% according to the method-A of JIS 1210 [11]. In cases of fly ash A with a clay/fly ash (C/F) ratio of 20:80, the fly ash and the clay mixture was directly compacted without adding additional water. The resulting water content was about 26% and dry density was about 1160 kg/m^3. In case of C/F ratio of more than 20:80, the initial water content was too high for an effective compaction, and the samples were made by consolidating the material under a pressure of 50 kPa. The device used is shown in Fig. 1. During the tests, the depth of distilled water on the top of the samples was kept as 150 mm and the leachate was collected and the concentration of Cr(VI) was measured periodically. For fly ash B plus 5% cement case, the pH value of the leachate was measured also. The flow rate was 500–600 ml/day and for the conditions adopted, a hydraulic conductivity of $(4–5) \times 10^{-8}$ m/s can be back-evaluated for the samples.



(a) Sketch of the device (b) Actual device

Fig. 1. Column percolation test device.

Table 2
List of all tests conducted.

Clay/fly ash ratio (C/F)	Cement mixed into fly ash (%)					
	Column test		Batch contact test		Tank leaching test	
	A[a]	B	A	B	A	B
0:100	0, 2, 5	2, 5	0, 2, 5	0, 5, 5[b]	0	–
20:80	2, 5		0, 2, 5	0, 5, 5[b]	2, 5	–
40:60	2, 5		0, 2, 5	0, 5, 5[b]	–	–
60:40	–		0, 2, 5	0, 5, 5[b]	–	–
80:20	–		0, 2, 5	0, 5, 5[b]	–	–

[a] A and B mean fly ash A and B respectively.
[b] 5% of low alkalinity additive.

The conditions for batch contact, tank leaching and column percolation tests are listed in Table 2.

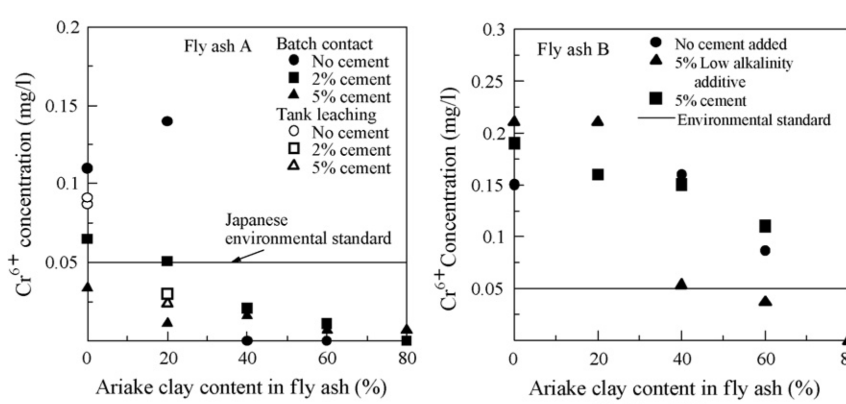
3. Test results

3.1. Results of batch contact tests

Equilibrium Cr(VI) concentration in the solution is summarized in Fig. 2(a and b) for fly ash A and B respectively, and the results are discussed in following paragraphs.

3.1.1. Comparison of the results of fly ash A and B

From chemical composition, fly ash B contains less total Cr (Table 1), but it shows higher Cr(VI) concentration in the solution. The concentration of Cr(VI) in the solution depends on the content of Cr(VI) in the solid mass, reaction characteristics (including oxidation-reduction) of Cr(VI) with solution, etc. Mohan and Pittman Jr. [12] summarized that there are two mechanisms for removing Cr(VI) from a solution, i.e. (a) adsorbing Cr(VI) into the interior surface of a adsorbent (e.g. carbon); and (b) reducing Cr(VI) to Cr(III) and adsorbing at the external surface of a adsorbent. For the conditions considered here, it is considered that the mechanism (b) has an important influence on Cr(VI) concentration. The process of reducing Cr(VI) to Cr(III) is influenced by pH and redox potential (Eh) values of a solution. Chai et al. [13] reported that the equilibrium pH value of a solution had a significant effect on the adsorption capacity of an Ariake clay to chromium (Fig. 3). Fig. 3 was produced under the assumption that reduction of Cr(VI) concentration in the solution is caused by reducing Cr(VI) to Cr(III) and then adsorbed by clay minerals. The Ariake clay tested had a plastic limit of 47.6%, and liquid limit of 109.9%. The pH value of the solution from the clay/water mixture with a ratio of 1:10 was about 8.0. The test method used for producing the results in Fig. 3 was basically the same as the batch tests in this study, but the way of



(a) Fly ash A (b) Fly ash B

Fig. 2. Cr(VI) concentration in solutions. (Batch contact and tank leaching tests). (a) Fly ash A; (b) Fly ash B.

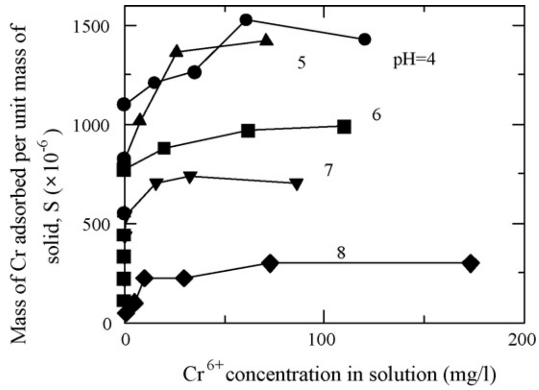


Fig. 3. Effect of pH value on Cr adsorption capacity [13].

adjusting the pH value of the solution was different. For the results in Fig. 3, the pH values of the equilibrium solution (not the initial liquid phase) were adjusted by adding hydrochloric acid. Although the range of pH values in Fig. 3 does not cover the most test conditions of this study, it has been used here to explain the tendency of the effect of pH value. Fig. 4(a and b) shows the equilibrium pH values of the solutions for fly ash A and B respectively. Note, in Fig. 4(a), the pH values for 2% and 5% the cement and C/F ratio of 20:80 batch contact tests are almost the same. It seems that fly ash B was more alkalinity than fly ash A. For batch contact tests of adding 5% the cement case, the equilibrium pH value of the solution with fly ash B is about 1 unit higher than that of fly ash A. It is considered that the difference in alkalinity can partially explain the difference on Cr(VI) concentration in the solution. Reducing Cr(VI) to Cr(III) is not only influenced by the pH value of a solution, the redox potential (Eh) of the solution also plays an important role. For fly ash B, the Eh values of the solutions were also measured and the results are imposed into the Eh–pH diagram of chromium [14] in Fig. 5. It indicates that reducing pH value from about 12 to about 10 and Eh of about 0–0.2 V, Cr(VI) (in a form of $CrO_4{}^{2-}$) [15,12] can be reduced to Cr(III) (in a form of $Cr(OH)_2{}^{+}$) [14]. The reaction can be as follows.

$$CrO_4{}^{2-} + 4H^+ + 3e \leftrightarrow Cr(OH)_2{}^+ + 2HO^- \quad (1)$$

The Eh–pH diagram for chromium also indicates that for pH value of about 12 and when Eh is less than 0 (reduction condition), Cr(VI) can be reduced to Cr(III) (in a form of $Cr(OH)_4{}^-$), and this follows standard potential reaction formula.

$$CrO_4{}^{2-} + 4H_2O + 3e \leftrightarrow Cr(OH)_4{}^- + 4OH \quad (E_0 = -0.17) \quad (2)$$

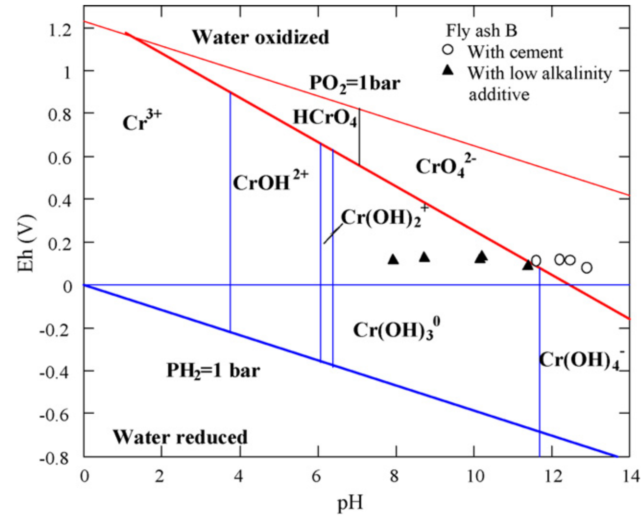


Fig. 5. Eh–pH diagram for chromium and batch test results of fly ash B.

3.1.2. Effect of adding Ariake clay

For fly ash A, increase the Ariake clay content in the fly ash reduced Cr(VI) concentration in the solution significantly. However, for fly ash B, the reduction was small. There are two possible reasons for reducing Cr(VI) concentration with the increase of the Ariake clay content. Firstly, under the condition of solid/liquid ratio of 1:10, increasing Ariake clay content means reducing the amount of the fly ash and therefore Cr(VI) in the mixture. However, if this is the only reason, Cr(VI) concentration will reduce linearly with the increase of the Ariake clay content. The results show that the reduction is nonlinear, especially for fly ash A. The second reason considered is reducing Cr(VI) to Cr(III), which is less soluble and can be adsorbed by the Ariake clay. Cr(VI) exists in anion forms of $Cr_2O_7{}^{2-}$, $CrO_4{}^{2-}$ and $HCrO_4{}^-$ cannot be directly adsorbed by clay mineral. Cr(VI) needs to be reduced to Cr(III) (cation) and then be adsorbed by clay mineral [16]. As shown in Fig. 4(a), for not adding the cement case, increasing the Ariake clay content reduced the pH value of the solution from more than 10 to 8–9. For fly ash B, the pH value of the solution of not adding the cement case was not measured. In case of adding 5% the cement, the solution of fly ash B showed a higher pH value than fly ash A, and the reduction and/or adsorption effect of Ariake clay to Cr ions might be less significant.

3.1.3. Effect of the cement

Adding the cement can increase cementation effect or some other possible chemical reaction. However, the cement used is more

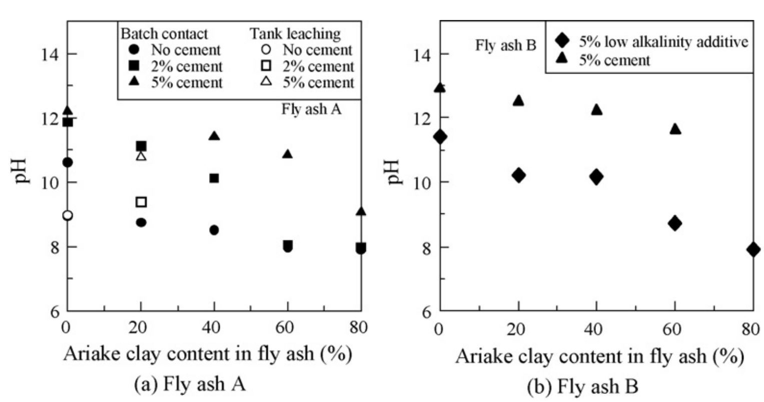


Fig. 4. pH value of solution (Batch contact and tank leaching tests). (a) Fly ash A; (b) Fly ash B.

alkalinity (pH 12.7) and contains more Cr(VI) than fly ash A and B. In terms of Cr(VI) concentration, the results show a complicated picture. For fly ash A, in cases of no and 20% the Ariake clay, adding the cement reduced Cr(VI) concentration considerably. Due to the lack of necessary chemical analysis during the tests, the exact reason is not clear. It is considered that the cementation effect might promote the aggregation of the solid particles and partially prevent dissolving of Cr(VI). However, for more than 20% the Ariake clay case, adding the cement increased the pH value of the solution, which tends to reduce the reduction and/or adsorption effect of the Ariake clay to Cr ions and resulted in a higher Cr(VI) concentration in the solution. For fly ash B, it contains 7.15% of cementation component (CaO) which is much higher than that of fly ash A (1.92%), and the cementation effect of adding 5% the cement was not significant.

3.1.4. Effect of the low alkalinity additive

Comparison of the effect of adding the cement and the low alkalinity additive was only done for fly ash B. In term of Cr(VI) concentration, there are two advantages of using the low alkalinity additive over the cement. Firstly, it does not contain Cr(VI), and secondly it has a lower alkalinity and which can promote the reduction of Cr(VI) to Cr(III). As shown in Fig. 4(b), the pH values of adding the low alkalinity additive is about 2 unit lower than that of adding the cement. Fig. 2(b) shows that when the Ariake clay content is more than 20% (pH value is less than about 10), Cr(VI) concentration reduced significantly. It seems that reduction effect and/or the adsorption effect of the Ariake clay to Cr ions played a profound role on reducing Cr(VI) concentration.

3.2. Results of tank leaching tests

Tank leaching tests for fly ash A were conducted using the samples after unconfined compression tests, which were cured for 28 days in a humid container before tests. The original samples had a size of 50 mm in diameter and 100 mm in height. After the unconfined compression test, it was broke into 4–5 pieces that were used for tank leaching tests. The results on Cr(VI) concentration and the pH values of the solution are included in Figs. 2(a) and 4(a) respectively. Ideally, the solid/liquid contact area for the tank leaching test is less than that of the corresponding batch contact test, and it may result in lower Cr(VI) concentration. Fig. 2(a) shows this tendency. However, the data are limited and scattered and a definite conclusion cannot be drawn. The pH values of the tank leaching tests were lower than the corresponding batch contact tests (Fig. 4(a)). For fly ash A alone and fly ash A plus 2% the cement with a C/F ratio of 20:80 cases, the pH values of tank leaching tests were about 1 unit lower.

3.3. Results of column percolation tests

For fly ash A, after setting the samples, the percolation tests using distilled water were started without curing the sample. For fly ash B, the effect of curing the sample was investigated. Numbers of pore volume (NPV) versus Cr(VI) concentration relationships are given in Fig. 6(a and b) for fly ash A and Fig. 7(a and b) for fly ash B respectively. NPV means the volume of the leachate collected (V_L) divided by the pore volume (volume of voids, V_V) of a sample of fly ash or fly ash mixture.

$$\mathrm{NPV} = \frac{V_\mathrm{L}}{V_\mathrm{V}}, \quad V_\mathrm{V} = n \cdot V_\mathrm{T} \tag{3}$$

where V_T is the total volume of a sample (soil layer), and n is the porosity of the sample, which can be calculated as follows:

$$n = \frac{\rho g - \gamma_\mathrm{d}}{\rho g} \tag{4}$$

where ρ is the density of solid particles, g is specific gravity, and γ_d is the dry unit weight of a soil sample. For fly ash B, ρ has not been measured and for calculating NPV, $\rho = 2300\,\mathrm{kg/m^3}$ (the same as fly ash A) was assumed. For all column percolation tests conducted, generally Cr(VI) concentration reduced with the increase of NPV. The detailed results will be presented by comparing with that of the corresponding batch contact tests. The factors affect Cr(VI) concentration in solution/leachate of batch contact and column percolation tests are as followings.

(a) Amount of water in contact with solid particles. At a given time, there is more water in contact with solid particles in the batch contact test (solid/liquid ratio of 1:10) than that of the column percolation test. For example, the compacted sample for the column percolation test had a void ratio of about 0.7, and the ratio of the solid mass of the sample to 1 NPV of leachate by weight is approximately 1:0.25, which is much larger (less water) than the solid/liquid ratio of 1:10 adopted for the batch contact test. Assuming a constant distribution coefficient (K_d), a lower solid/liquid ratio (more liquid) will result in a lower equilibrium concentration in the liquid phrase. This factor tends to increase Cr(VI) concentration of the column percolation test.

(b) Cementation effect. When particles have been cemented/bonded together, their surface area will be reduced which partially hinders the dissolving of Cr(VI) into pore water.

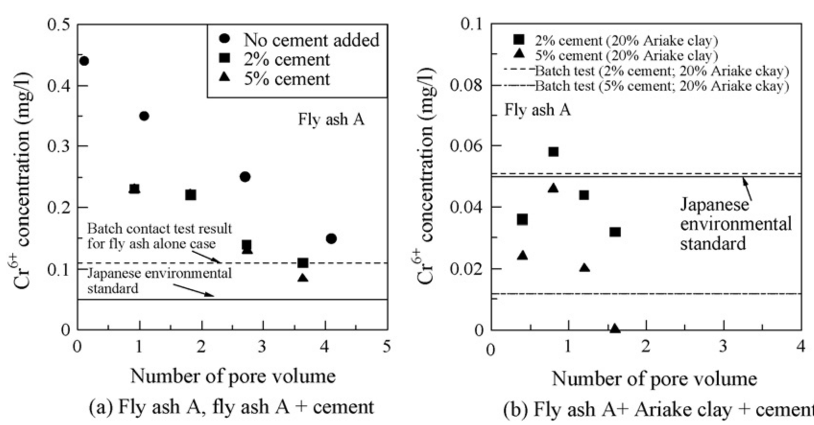


Fig. 6. Cr(VI) concentration in the leachate of column percolation test for fly ash A. (a) Fly ash A, fly ash A + cement; (b) fly ash A + cement + Ariake clay.

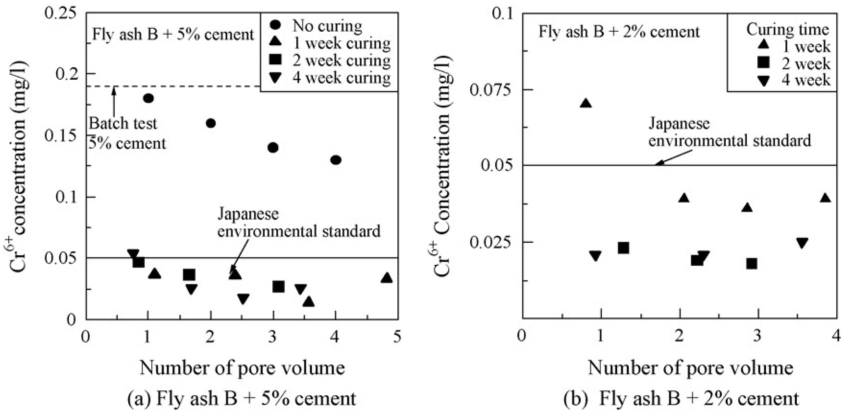


Fig. 7. Cr(VI) concentration in the leachate of column percolation test for fly ash B. (a) Fly ash B + 5% cement; (b) fly ash B + 2% cement.

Cementation effect will be more effective for the column percolation test than that for the batch contact test. This factor also tends to reduce Cr(VI) concentration in the leachate from a column percolation test.

3.3.1. Comparison of the results of fly ash A and B

For adding 5% the cement case, contrast with the results of the batch contact tests, fly ash A resulted in a higher Cr(VI) concentration than fly ash B (Fig. 6(a) and Fig. 7(a)). Although the exact reason is not clear, it is considered that the cementation effect played a role. Fly ash A has less cementation component (CaO) than fly ash B (Table 1), and therefore, the cementation effect will be less in the column tests and resulted in a higher Cr(VI) concentration. When comparing with the batch contact test results, for fly ash A alone or fly ash A plus 2–5% the cement cases, the column percolation tests resulted in much higher Cr(VI) concentrations than that of the batch contact tests. For these cases, it is believed that the amount of water in contact with the solid mass played a dominate role. However, for fly ash B, at NPV = 1, Cr(VI) concentration from the column percolation test is very close to that of the corresponding batch contact test. In this case, although the amount of water in contact with the solid at a time is much less in the column test, but column test provided a favorable condition to display cementation effect and which partially restricted the dissolving of Cr(VI) into the leachate. For both fly ash A and B, in cases of fly ash along or with 5% the cement, even at NPV of 4, Cr(VI) concentration is still higher than Japanese environmental standard (0.05 mg/l). For most of the column tests, the pH value of the leachate was not measured. The measurement was only made for fly ash B plus 5% the cement without curing case and the results are given in Fig. 8. Up to NPV of 4, pH value was about 12 and lower than that from the batch contact test of about 13.

3.3.2. Effect of Ariake clay

The column percolation test of adding the Ariake clay was only conducted for fly ash A. The results for C/F ratio of 20:80 are shown in Fig. 6(b). For case of C/F ratio of 40:60, no Cr(VI) was detected in the leachate. Comparing the results in Fig. 6(a and b) indicates that adding the Ariake clay reduced Cr(VI) concentration significantly. For adding 2 and 5% of the cement into fly ash A and then mixed with the Ariake clay with a C/F ratio of 20:80 cases, Cr(VI) concentrations from the column tests are comparable with those of from the batch contact tests (Fig. 2(a)) at about 1 NPV and then reduced with the increase of NPV. In this case, although the amount of water was less in the column percolation test, but the column test provided a favorable condition (possibly lower pH value) for reduction of Cr(VI) to Cr(III) (Fig. 5). For fly ash A, the pH value of the leachate from the column test was not measured, but referring the result of fly ash B, the pH values for the column tests are lower than that of the corresponding batch contact tests (Figs. 4(b) and 8).

3.3.3. Effect of the cement

As shown in Fig. 6(a), adding 2 and 5% the cement into fly ash A reduced Cr(VI) concentrations, and at about 1 NPV, the value was about 70% of the corresponding value of fly ash A alone. The difference between 2 and 5% of the cement cases is not obvious. However, for fly ash A and the Ariake clay mixture (C/F of 20:80), increase the cement content reduced Cr(VI) concentration considerably. It can be interpreted as a combination of cementation and reduction effects. Comparing Fig. 7(a and b) indicates that there is no obvious effect of varying the cement content from 5% to 2% for fly ash B. It can be explained that fly ash B itself contains a relatively larger amount of cementation component (CaO), and varying the cementation content from 5% to 2% did not alter the cementation effect much.

3.3.4. Effect of curing time

For fly ash B, the effect of curing on Cr(VI) concentration in the leachate was investigated and the results are given in Fig. 7(a and b). Figure 7(a) shows that curing had a significant effect on reducing Cr(VI) concentration. The most effect appeared within 1 week curing time. It is believed that the reduction is mainly due to the effect of cementation. It is the same mechanism as using stabilization/solidification method to treat a contaminated land. This result

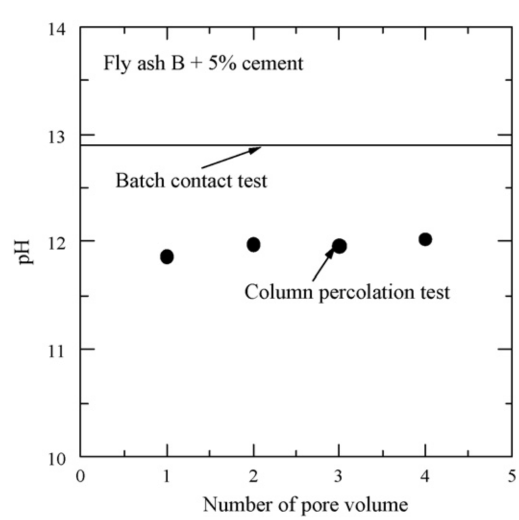


Fig. 8. Comparison of pH values from batch contact and column percolation tests.

implies that when using a fly ash plus cement as embankment fill, providing more than 1 week curing time before opening to rainfall precipitation can reduce the risk of potential environment impact.

4. Conclusion

Dissolving and/or leaching Cr(VI) from two fly ashes (fly ash A and B) with additives was investigated by batch contact, tank leaching and column percolation tests. The test results indicate that there are several factors influencing Cr(VI) concentration in a solution/leachate. The main factors are: (1) properties of solid/liquid mixture (chemical composition, pH value, etc.), (2) cementation effect, (3) amount of water in contact with the solid mass (solid/liquid ratio in case of batch contact test), and (4) adsorption characteristics of clay mineral to Cr ions. The test results indicate that Cr(VI) concentration is the result of the interaction of these factors. In engineering practice, a method closely simulates the field condition should be chosen to assess possible environment effect and corresponding countermeasure method.

Fly ash A has less cementation component, CaO (1.92% compared with 7.15% of fly ash B) and it seems that the amount of water in contact with the solid played an important role on Cr(VI) concentration. As a result, the initial Cr(VI) concentration from the column percolation test is much higher than that of the batch contact test. The solution of fly ash A had a relatively lower pH value (about 1 unit less than that of fly ash B), which provided a favorable condition for Cr(VI) to be reduced to Cr(III), which is less soluble than Cr(VI) and can be adsorbed by clay mineral, and it showed that adding the Ariake clay into the fly ash reduced Cr(VI) concentration significantly. For fly ash A, adding the cement can increase its cementation effect but increased alkalinity of the solution and resulted in a complicated reaction on Cr(VI) concentration.

Fly ash B has more cementation component, and the cementation effect played an important role on reducing Cr(VI) concentration. For the column percolation test, due to cementation effect, curing the sample for 1 week reduced Cr(VI) concentration dramatically. Fly ash B has a higher alkalinity and adding the low alkalinity additive reduced the pH value of the solution about 2 unit and resulted in a lower Cr(VI) concentration, and it is considered mainly due to the lower pH value promoted reduction of Cr(VI) to Cr(III).

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References

[1] RCUWGCM, Activity Report, Research Committee for Using Wastes as Geotechnical Construction Material (RCUWGCM), Japan, 1999.
[2] M. Kamon, T. Katsumi, Geotechnical utilization of solid waste materials and its environmental impacts, Journal of Japanese Waste Material Society 12 (3) (2001) 140–149.
[3] The Japanese Environment Agency, Environment Standards Regarding to Soil Contamination, Public Notice No. 46, 1991.
[4] M. Kamon, T. Katsumi, T. Inui, M. Castro-Cuba, Evaluating the environmental impact of using solid waste by leaching tests. Annual Report of Institute of Disaster Prevention, Kyoto University, Japan, No. 42, B-2, 1999, pp. 459–469 (in Japanese).
[5] J.-C. Chai, S. Hayashi, K. Onitsuka, Geoenvironmental and mechanical properties of a fly, in: Proceedings of Fifth International Congress on Environmental Geotechnics, vol. 2, Cardiff, UK, 2006, pp. 1305–1312.
[6] K. Ohtsubo, K. Egashira, K. Kashima, Depositional and post-depositional geochemistry, and its correlation with the geotechnical properties of marine clays in Ariake Bay, Japan, Geotechnique 45 (3) (1995) 509–523.
[7] M. Kamon, J. Jeoung, T. Inui, Alkalinity control properties of the solidified/stabilized sludge by a low alkalinity additive, Soils and Foundations, Japanese Geotechnical Society 45 (1) (2005) 87–98.
[8] Japanese Standard Association (JSA), Testing Method for Industrial Wastewater, JIS K 0102 65.2.1 (Chromium), Tokyo, Japan, 1998.
[9] Japanese Geotechnical Society (JGS), Test Method for pH of Suspended Soils, JGS 0211-2000, Tokyo, Japan, 2000.
[10] Ministry of Construction (Currently the Ministry of Land, Infrastructure and Transport), Japan, Regulation No. 49, Current Measures on Using Cement Type Ground Improvement Material and Recycling of the Improved Soils, 2000.
[11] Japan Standard Association (JSA), The Method for Soil Compaction using a Rammer, JIS A 1210, Tokyo, Japan, 1999.
[12] D. Mohan, C.U. Pittman Jr., Activated carbons and low cost adsorbents for remediation of tri-and hexavalent chromium from water, Journal of Hazardous Materials B137 (2006) 762–811.
[13] J.-C. Chai, N. Miura, K. Onitsuka, Adsorption characteristics of Ariake clays to chromium and the effect of pH-value, in: Proceedings of Ninth Australia New Zealand Conference on Geomechanics, Auckland, 2004, pp. 467–472.
[14] C. Palmer, R. Puls, Natural Attenuation of Hexavalent Chromium in Ground Water and Soils. EPA/540/S-94/505, U.S. Environmental Protection Agency Ground Water Issue, October 1994.
[15] Dionex, Determination of Cr(VI) in water, wastewater and solid waste extracts, Technical Note 26 LPN34398-01 1 M 7/96, Dionex Corporation, 1996.
[16] J.K. Mitchell, Clay-water electrolyte system, in: Chapter 7 of Fundamentals of Soil Behavior, 2nd edition, John Wiley & Sons, Inc., 1993, pp. 111–130.