Adsorption characteristics of Ariake clays to Cr\(^{6+}\)

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Abstract: Adsorption characteristics of 2 Ariake clays (Clay-1 and Clay-2) to Cr\(^{6+}\) were investigated by batch contact tests, advection-diffusion column tests and numerical simulation. The result revealed that adsorption characteristic of the clays to Cr\(^{6+}\) is strongly affected by pH value of solution. For the range investigated, the lower the pH value, the larger the adsorption capacity and partition coefficient, \(K_d\). From batch contact test results, a close to bilinear adsorption isotherm was observed for Clay-1 and Clay-2 with pH value of solution about 7. This phenomenon is confirmed by simulating advection-diffusion column test results. It is tentatively suggested that under an environment of pH value less than 7, both Clay-1 and Clay-2 can serve as liners for Cr\(^{6+}\) solution.

Keywords: adsorption, batch contact test, column test, clay liner, advection-diffusion analysis

1. Introduction
Chromium is one of heavy metals causing ground contamination. In Japan, a large number of Cr\(^{6+}\) contaminated sites existed, which caused by mining in past and some factories dealing with chromium recently. For example, one site in Saga, Japan, where the measured maximum Cr\(^{6+}\) concentration in groundwater was 36 ppm, which is 720 times of Japanese environmental standard (<0.05 ppm). Cleanup contaminated ground is a very costly process. Therefore, preventing newly contamination of ground is an urgent task of geoenvironmental engineering.

Containing contaminants by a barrier system, such as clay liner, is one of techniques to prevent ground contamination. In this study, adsorption behavior of Cr\(^{6+}\) in Ariake clay has been investigated by batch contact tests, advection-diffusion column tests, as well as advection-diffusion simulation. This paper presents the test and analysis results. The application of the test results to design clay barrier system is also discussed.

2. Properties of Ariake clay used
Two types of Ariake clay samples were used for batch contact tests, and the undisturbed samples of one of the clays were used for advection-diffusion column tests. The basic physicochemical properties of the clays are listed in Table 1. Cation exchange capacity (CEC) was measured by semi-micro Schollenberger method; specific surface was measured by BET (Brunauer, Emmett, Teller) method; and organic content by ignition loss method. For the undisturbed sample, the void ratio was about 3.0 (under a consolidation pressure of 50 kPa). Hydraulic conductivity was back calculated from consolidation test with a value of about 1.0×10\(^{-9}\) m/s.

Table 1 Basic physicochemical properties of Ariake clay used

<table>
<thead>
<tr>
<th>Soil</th>
<th>(W_p)</th>
<th>(W_l)</th>
<th>CEC (meq/100g)</th>
<th>Specific Surface (S) (m(^2)/g)</th>
<th>Organic Content, (f_{oc}) (%)</th>
</tr>
</thead>
<tbody>
<tr>
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<td></td>
</tr>
</tbody>
</table>


3. **Batch contact test**

Test procedure and conditions

Batch contact test were used to determine the adsorption coefficient of \( \text{Cr}^{6+} \) in Ariake clay. The tests were conducted following the ASTM standard D4646-87 (ASTM, 1993). However, comparison tests showed that for \( \text{Cr}^{6+} \), the result of mixing 6 hours was identical to that of 24 hours, and the adopted mixing time was 6 hours. Mixing device is shown in Fig. 1. The rotation speed used was 30 rpm. \( \text{Cr}^{6+} \) solution was made using potassium dichromate (\( K_2\text{Cr}_2\text{O}_7 \)) solution. 1/60 M standard solution was diluted to desired concentration by distilled water. Concentration of \( \text{Cr}^{6+} \) solution was varied from 5 ppm to 300 ppm. Adopted solid to liquid ratio was 1:10 by weight. 1l glass bottles were used. After mixing, a centrifuge (4000 rpm with a ram length of 100 mm) was used to separate solution and soil. Items measured are \( \text{Cr}^{5+} \) concentration, pH and conductivity of balanced solution.

**Test results**

Test results are summarized in Table 2. Their adsorption isotherms are depicted in Fig. 2. It can be seen that Clay-1 has a much stronger adsorption capacity for \( \text{Cr}^{5+} \) than Clay-2. Although the data are scatter, generally non-linear adsorption characteristics of the clay to \( \text{Cr}^{5+} \) can be seen. For Clay-1, when balanced solution concentration (\( C \)) is less than about 3 ppm, a close to linear isotherm can be observed with a partition coefficient \( K_d \approx 250 \text{ ml/g} \). However, when \( C \) is larger than about 3 ppm, amount of adsorbed chromium seems not changed much with increasing of solution concentration. For Clay-2, a partition coefficient of about 20 ml/g can be estimated and it is about 8% of that of Clay-1.

<table>
<thead>
<tr>
<th>Clay-1</th>
<th>Clay-2</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Source Concentration</strong></td>
<td><strong>Concentration</strong></td>
</tr>
<tr>
<td>( C_1 ) (ppm)</td>
<td>( C_2 ) (ppm)</td>
</tr>
<tr>
<td>50</td>
<td>0</td>
</tr>
<tr>
<td>60</td>
<td>0</td>
</tr>
<tr>
<td>70</td>
<td>1.8</td>
</tr>
<tr>
<td>80</td>
<td>2.8</td>
</tr>
<tr>
<td>100</td>
<td>6.8</td>
</tr>
<tr>
<td>150</td>
<td>81.0</td>
</tr>
<tr>
<td>200</td>
<td>130.0</td>
</tr>
<tr>
<td>250</td>
<td>180.0</td>
</tr>
<tr>
<td>300</td>
<td>230.0</td>
</tr>
</tbody>
</table>

For both clays, the measured physicochemical properties (Table 1) are not different much. Then there is a question on why their adsorption capacity to chromium was so much different. In water, \( K_2\text{Cr}_2\text{O}_7 \) can be resolved
into $K^+$ and $Cr_2O_7^{2-}$. $Cr_2O_7^{2-}$ is a fairly strong oxidizing agent as indicated by standard potential reaction:

$$Cr_2O_7^{2-} + 14H^+ + 6e \leftrightarrow 2Cr^{3+} + 7H_2O$$ (1)

As given in Table 2, for Clay-2, pH values of balanced solutions were from 7.97 to 8.84 and for Clay-1, pH values for balanced solution were from 5.52 to 6.36. Lower pH value means more $H^+$ ion in solution, and it is considered that reaction as indicated by Eq. 1 is more like to occur. Then, soil will adsorb $Cr^{3+}$. If the reaction of Eq. 1 cannot occur, soil cannot adsorb $Cr_2O_7^{2-}$ ion. To verify this reasoning, pH value of Clay-2 and $Cr^{6+}$ solution was adjusted to about 7 by adding hydrochloric acid. Then the batch contact tests were conducted and the results are listed in Table 3. The comparison of adsorption isotherms is given in Fig. 3.

Reducing pH value from about 8.5 to about 7 increased the adsorption capacity, especially partition coefficient significantly. Under a circumstance of pH value about 7, the adsorption behaviors of Clay-1 and Clay-2 to chromium are comparable. Although further research is needed to reveal the whole picture about the effect of pH value on adsorption characteristics of Ariake clay to chromium, these limited results indicates that when using Ariake clay as a liner for $Cr^{6+}$ solution, pH value of solution is a very important factor. As shown in Tables 2 and 3, conductivity of Clay-2 solution is about twice of that of Clay-1. It seems that conductivity does not have much effect on adsorbing $Cr^{6+}$.

### 4. Advection-diffusion column test

Although batch contact test can provide information about adsorption characteristics of soil to contaminant, the result is influenced by solid concentration (Voice et al. 1983). In fact, the diffusion/adsorption properties of contaminant in soil can be evaluated by column test better than by batch contact test. Two column tests were conducted using undisturbed Ariake Clay-1 and $Cr^{6+}$ solution.
Equipment and test procedure

Fig. 4 shows the equipment used. As illustrated in Fig. 4 (a), inner diameter of column is 150 mm and total height of 400 mm. The equipment was designed to be able to apply effective stress on top of soil sample, which is achieved using air pressure and a bellofram system. Fig. 4 (b) shows the picture of actual equipment. The procedure of the test is as follows:

1. Set soil sample. Undisturbed Ariake clay sample trimmed from a block sample with a diameter slightly larger than 150 mm and height of 75 mm was pressed into the cylinder. A cutting shoe was attached to the cylinder to perform final trim. The ceramic porous stones were placed at both top and bottom of the sample. A pressure of 50 kPa was applied to the sample. This pressure was estimated as close to the yield stress of the sample. Then the sample was left for consolidation for about 1 month.

2. Put solution. $Cr^{6+}$ solutions with an initial concentration of 20 mg/l (test No. 1) and 67 mg/l (test No. 2) were poured on top of the soil sample with a head of 150 mm. The hole for putting solution into the column was sealed by a rubber seal. Finally, the outlet valve at the bottom of the column was opened and the test started.

3. Take the measurement. Solution was sampled periodically from the sampling hole on the wall of the column by using a syringe. Both $Cr^{6+}$ and total Cr concentrations were measured. During the test, solution level in the test column was maintained by adding distilled water. The amount of water added was recorded for estimating the hydraulic conductivity of the soil column, and it is confirmed that the hydraulic conductivity of soil is about $10^{-9}$ m/s. An electric fan is used to agitate the source solution to maintain its uniformity.

4. Measure the distribution of $Cr^{6+}$ or total Cr in soil column. After termination of the tests, the soil was sliced (about 15 mm thick) and the pore solution (water) was partially separated from solid phase by centrifuge and $Cr^{6+}$ and total Cr concentration was measured.

Test results

The measured source concentration variations are depicted in Figs. 5 and 6. In the figure, $C/Co$ indicates the ratio of measured source concentration ($C$) over initial source concentration ($Co$). During the test, $Cr^{6+}$ concentration was only slightly lower than corresponding total Cr concentration. It indicates that reduction reaction in source solution
was very limited. After termination of the test, \( \text{Cr}^{6+} \) and total Cr were not detected in pore water.

If a linear reversible adsorption characteristic is assumed, with measured source concentration variation and distribution of contaminant concentration with depth in soil column, both the coefficients of diffusion and adsorption can be back evaluated. However, due to the non-linear and irreversible or partially irreversible adsorption characteristics, it is not able to precisely evaluate both parameters from the column tests. The free solution diffusion coefficient of \( \text{Cr}^{3+} \) is \( 5.94 \times 10^{-10} \text{ m}^2/\text{s} \) (Shackelford and Daniel 1991). Shackelford and Daniel (1991) reported that for fine-grained soils, the tortuosity factor \( \tau \) is 0.1 to 0.7. Assume a tortuosity factor of 0.4 for undisturbed Clay-1 sample, an effective diffusion coefficient of \( 2.38 \times 10^{-10} \text{ m}^2/\text{s} \) is resulted. If assuming the effective diffusion coefficient of \( \text{Cr}^{6+} \) is the same as \( \text{Cr}^{3+} \) and as \( 2.38 \times 10^{-10} \text{ m}^2/\text{s} \), coefficient of adsorption can be evaluated. Simulation was conducted by using Migrate (Rowe and Booker, 1988), which is based on finite layer advection-diffusion solution. The simulated results are also indicated in Figs. 5 and 6. Comparing with test data, analysis yielded a faster source concentration reduction rate at beginning and a slower reduction rate at later period. As shown in Fig. 2, for Clay-1, close to linear adsorption behavior is only for solution concentration less than about 3 ppm. When concentration is larger than 3 ppm, linear adsorption assumption with a value of 200-300 ml/g will over simulate the adsorption capacity of the soil, and resulted in a faster source concentration reduction rate. Comparing Figs. 5 and 6, at beginning period, difference between simulated and measured results in Fig. 6 is larger than that in Fig. 5. This is because the higher the initial source concentration, the more far away of the liner reversible adsorption assumption from the actual case. Then, completely reversible assumption means that when concentration in solution reduces, adsorbed contaminant will dissolve into solution again. However, actually it is not or only partially reversible. This explains simulated slower reduction rate of source concentration.

The simulated concentration distributions in soil column are shown in Figs. 7 and 8. Although no chromium was detected in pore water after the tests, due to assumed linear reversible adsorption characteristics, analysis still yields certain chromium concentration in pore water up to about 15 mm depth. This again indicates that linear sorption...
Both batch contact and advection-diffusion column test results indicated that Clay-1 has a strong adsorption capacity for \( \text{Cr}^{6+} \) (and/or \( \text{Cr}^{3+} \)). For solution concentration of \( \text{Cr}^{6+} \) larger than 3 ppm, 1.0 g of dry soil can adsorb about \( 7 \times 10^{-4} \) g chromium. In this case, 10 kN dry soil (about 1 m\(^3\) compacted clayey soil) can adsorb about 700 g chromium, which equivalent to 70 kN of 100 ppm \( \text{Cr}^{6+} \) solution.

5. Conclusions
Adsorption characteristics of 2 Ariake clays to \( \text{Cr}^{6+} \) were investigated by batch contact tests, advection-diffusion column tests and analysis. The results revealed following conclusions.

(1) Adsorption characteristic of clay to \( \text{Cr}^{6+} \) is strongly affected by pH value of solution. In case of Clay-2, reducing pH value from about 8.5 to about 7 increased its adsorption capacity, especially the partition coefficient, \( K_d \), significantly.

(2) Close to bilinear adsorption isotherm was observed for Clay-1 and Clay-2 (pH value of about 7 case) from batch contact test results. For balanced solution concentration larger than 3 ppm, a linear reversible adsorption assumption is not applicable. This phenomenon is confirmed by analyzing advection-diffusion column test results.

(3) Although further research is necessary for reveal adsorption behavior of Ariake clay to \( \text{Cr}^{6+} \) at lower pH value, it is tentatively suggested that under an environment of pH value less than 7, Clay-1 and Clay-2 investigated in this study can serve as liners for \( \text{Cr}^{6+} \) solution.

6. References

