Study on reduction of hexavalent chromium elution from cement-improved soil

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ABSTRACT

Hexavalent chromium may elute from a part of cement-improved soils when cement solidifications are used for the purpose of ground improvement. Particularly, the likelihood of elution increases when the type of soil is volcanic cohesive soil. Hexavalent cohesive chromium is extremely toxic to the human body. Therefore, in the above-mentioned cement solidifications, it is recommended to consider its elution when volcanic soil is used. In this study, strength and dissolution tests of hexavalent chromium are conducted on cement-improved soils in which cement solidifications and andosols are mixed. Three different waste materials (sugar syrup, burned fish bone, and rice husk ash) are used to verify their reduction properties for hexavalent chromium. According to the results of the test, the strengths of the specimens with the three different materials do not change significantly, and the improved soils maintain the required strengths. In addition, the elution amount of hexavalent chromium from the specimen mixed with a sugar syrup is lower than that from an unmixed specimen. This fact suggests that the waste syrup can reduce the elution of hexavalent chromium.

Keywords: hexavalent chromium, waste syrup, reduction, cement improved soil

1 INTRODUCTION

When a structure is to be constructed, the ground supporting it is investigated. If the ground is soft, there is a risk that the structure will be significantly deformed and the ground will liquefy. Therefore, it is necessary to improve a soft ground. There are three types of ground improvement methods: surface layer improvement method, columnar improvement method, and steel pipe pile working method. Generally, the surface layer improvement method is used, and the other two methods are employed when the former does not provide sufficient strength. In the surface improvement method, to provide strength to a soft ground, 2-m deep soil is dug and mixed with a cement-based solidification material. Hexavalent chromium exceeding the soil environmental standard value (0.05 mg/L) may be eluted from such a ground-improved soil (Kuroda et al., 2010) Hexavalent chromium is an extremely strong oxidizing agent and harmful to the human body. It causes skin and bronchial problems and is treated as a carcinogen. In the past, workers in chromic acid factories have been found to suffer from health hazards. In 2000, the former Ministry of Construction issued a notice to investigate the concentration of hexavalent chromium via an elution test when a ground was improved with a cement-based solidification material (Sakabe et al., 2012). In the previous studies summarizing the current state of hexavalent chromium elution from cement-improved soils, hexavalent chromium elution exceeding the standard value occurred from 13% of the soils that were investigated. Volcanic ash soil is a soil from which hexavalent chromium is frequently eluted. The hydration reaction is inhibited by the action of the allophane contained in volcanic ash soil, resulting in the elution of hexavalent chromium (Hosoya, 2002). Various measures are adopted to deal with this problem, for example, adsorption treatment with bamboo charcoal (Aramaki et al., 2013), acceleration of the hydration reaction with quicklime (Yoshida et al., 2017, Tsukawaki et al., 2012), and reduction treatment with sugar (Niida et al., 2015). Bamboo charcoal has the ability to adsorb hexavalent chromium. However, the adsorption treatment by it, is not effective for samples, such as volcanic cohesive soil, in which the hexavalent chromium concentration significantly exceeds the standard value. Alternatively, in the research using quicklime, the compressive strength has not been discussed sufficiently, although the elution reduction effect of hexavalent chromium is recognized. In
addition, there is a problem that the treatment process for black soil is not stable. Although the elution reduction effects of recycled roadbed materials were verified in a previous study, the effectiveness of the improved soil was not validated. Focusing on these issues, in this study, three types of waste materials are prepared, and the reduction ability for the elution of hexavalent chromium is examined by different approaches. The three types of waste materials are: rice husk ash, fish bone, and waste syrup. The cement added to each waste material is mixed with andosol, and the performance of each waste material is evaluated by the results of the dissolution and strength tests.

2 HEXAVALENT CHROMIUM IN SOIL

Hexavalent chromium rarely exists in natural rock masses, and the forms that cause environmental pollution are frequently generated artificially. The elution of hexavalent chromium by a cement-based solidification material is one form. Trivalent chromium present in a raw material is changed to hexavalent chromium by burning the former at a high temperature, when cement is produced. In the solidification processes of concrete and mortar, hexavalent chromium binds to the hydrate produced by the hydration reaction, and it is rarely eluted from them. However, when cement is used for ground improvement, hexavalent chromium can be eluted by inhibiting the formation of the hydrates depending on the type of clay mineral and organic matter. In particular, there are numerous elution cases in which volcanic ash soil is improved. This is because the allophane contained in it absorbs a large number of calcium ions and inhibits cement solidification (Henmi, 1999). Allophane is a low-crystallinity clay, which is frequently produced under soil environments affected by falling volcanic ejecta. If hexavalent chromium is eluted into a soil, there may be a risk of its flowing into groundwater. Therefore, countermeasures against the elution of hexavalent chromium are essential.

3 WASTE MATERIALS

Among the properties required for the solidification materials used for ground improvement, first, the compressive strength improvement is considered. In addition, the ability to reduce the elution of hexavalent chromium is also necessary when mixing the solidification material with volcanic ash soil. Moreover, it is desirable that the material mixed with the solidification material is inexpensive, because cement has an extremely low cost. Based on these conditions, in this study, three types of waste materials are focused.

3.1 Rice husk ash (RHA)

First, rice husk ash (RHA) is selected as a waste material. Rice husk is a food waste that is generated by threshing during rice cultivation. Two million ton of rice husk is discharged annually. In a past study, powdered rice husk and RHA were used as adsorbents for heavy metals (Samad et al., 2016), and so, a performance for hexavalent chromium adsorption is expected. It is also reported that the compressive strength of concrete is improved by mixing RHA with cement (Ishiguro, 2000). Here, the RHA used in the experiment was produced by burning the rice husk that was generated and stored at a local rice center (see Fig. 1). It is reported that the strength of RHA is increased by the presence of amorphous silica (Umeda et al., 2014). The formation of amorphous silica depends on the burning temperature. In this study, to produce amorphous silica, the burning time was 1.5 h and the burning temperature was 600 °C. The result of the analysis by the X-ray diffraction (XRD) of RHA is shown in Fig. 2. A gentle intensity peak is a property of amorphous silica, whose presence in the XRD pattern confirms the formation of amorphous silica.

![Fig.1. Rice husk ash (RHA)](image)

![Fig.2. XRD pattern of RHA](image)
Fig. 3) by some of the authors, and was employed in this study. The FbP is manufactured by burning and pulverizing the fishbones discarded at fishing ports. The adsorption of the FbP or the acceleration of the hydration reaction by the supply of calcium from the FbP contributes to the elution reduction of hexavalent chromium.

![Fishbone powder (FbP)](image)

### 3.3 Waste syrup

The third material is an expired sugar syrup. Monosaccharides such as glucose have an aldehyde group in the structure, which has a reduction action. In cement, monosaccharides undergo oxidation–reduction reactions with highly oxidizing hexavalent chromium. Thus, they can change hexavalent chromium into the harmless trivalent chromium (see Fig. 4). Gluconic acid, which is produced by the oxidation of glucose, is used as a concrete retarder and water reducing agent (Takeuchi et al., 1997). Therefore, the dispersibility of cement particles can be improved. The waste syrup used in this study contained various sugars, and tests were conducted using not only the waste syrup but also multiple types of sugars, to determine the ability of each sugar. The types of sugars were: glucose, sucrose, and allose.

![Reducibility of syrup](image)

### 4 TEST METHOD

The presence of hexavalent chromium in soil is regulated by the Soil Contamination Countermeasures Act and evaluated by the elution test of Ministry of Environment Notification No. 46. In this study, the concentration of hexavalent chromium is analyzed according to the dissolution test of Environment Notification No. 46. Alternatively, a cement solidification material is mixed with the soil to improve the strength of the ground. To determine the strength properties of the mixed waste materials, a uniaxial compression test is conducted on the specimens. The specimens are prepared in accordance with the strength test method of an improved body using a cement solidification material of the Japan Cement Association Standard (JCAS L-01: 2006). In addition, a compression test is conducted according to the uniaxial compression test method of soil (JIS A 1216). The outline of the test is shown in Fig. 5. The cement is mixed with water and used as a slurry. Based on a past study, the water–cement ratio is set as 240% when considering the moisture content of the soil (Yoneda, 2011). The cement is mixed with 100 kg per 1 m$^3$ of the soil. In addition, the waste syrup is mixed at a rate of 0.25% of the cement, and replaced with water. Besides, FbP and RHA are mixed at a rate of 3% of the cement amount and replaced with cement. The detailed test procedure is described below. Three specimens are prepared, and the test results are evaluated based on average values.

![Test method](image)
the compressive strength.
5. Approximately 4 g of the sample is collected after the compression test, 40 mL of pure water is added to it, and the mixture is shaken for 6 h.
6. After centrifugation, 25 mL of the supernatant is collected and used as the test solution.
7. The concentration of hexavalent chromium in the test solution is analyzed via diphenylcarbazide spectrophotometry.

Three specimens are prepared, and their properties are evaluated by the average value obtained from the tests.

5 TEST RESULTS

The results of the uniaxial compression and dissolution tests for each specimen are summarized in a graph. The results of experiments using sugars are compared based on the types of the sugars.

5.1 Uniaxial compression test

The results of the uniaxial compression test for each waste material are displayed in Fig. 6, and those for some sugars are shown in Fig. 7. “Blank” is a specimen to which no waste material is added. “Unimproved” denotes the specimen in which only soil is used. The compression strength and curing period of concrete are displayed in the vertical and horizontal axes, respectively. According to the result of the test, the strengths of all the specimens mixed with the cement solidification agent are improved compared to those of the “Unimproved”. In addition, the strengths of the specimen to which waste syrup is added is the highest, and the specimen after 28 days curing is significantly stronger than the “Blank”. It is assumed that the cement uniformly penetrates the soil owing to the dispersibility improvement of the cement particles by the oxidized sugar component. Therefore, it is necessary to analyze the sugar component in a test solution. However, the strengths of the specimens to which FbP is added and the RHA do not change even after 28 days of curing. This may be because both the materials absorb the water required for the hydration reaction. In the future, it can be improved by reviewing under the compounding conditions.

5.2 Uniaxial compression test (sugars)

In all the specimens with added sugar, the compressive strength increases with the passing of the curing period. However, the compressive strength of the specimens, besides that with added waste syrup, is lower than that of Blank. Accordingly, it is exhibited that the amount of cement required for the ground improvement can be reduced by mixing the waste syrup with the cement. It is considered that reducing the amount of cement may contribute not only to cost reduction but also to reducing the environmental burden. In the future, it is necessary to verify whether sufficient strength can be obtained by mixing a small amount of cement.

5.3 Elution test

The results of the elution test for each waste material and each sugar are displayed in Fig. 8 and Fig. 9, respectively. The detected concentrations of hexavalent chromium and the added materials are presented on the vertical and horizontal axes, respectively. The value in the parentheses at the top of the bar graph is the pH value of the test solution after the elution test. Based on the tests, hexavalent chromium does not elute from the soil, and the soil is weakly acid. Furthermore, the elution of hexavalent chromium decreases after 28 days; it exceeds as the reference value is eluted from both the BLANK and RHA specimens cured for 7 days. It is considered that the present hexavalent chromium is encapsulated by the sufficient hydration reaction between the cement and water. In addition, the elution concentration of hexavalent chromium is the lowest when the waste syrup is added. It is clarified that the reduction treatment is effective in the test specimen with the waste syrup. Considering the risk of hexavalent chromium flowing into groundwater, it is important to reduce the elution concentration from an early stage. However, the adsorption performances of FbP and the
RHA are not noticeable. Because the hexavalent chromium concentration in the slurry cement paste is extremely high, it is considered that sufficient adsorption performance cannot be achieved with the added amount. In the future, it is necessary to reconsider the added amount of the material and the timing of addition. It is noted that all the materials have little effect on the pH value.

5.4 Elution test (sugar)

In comparison with sugar, waste syrup has the highest reducing ability for the elution of hexavalent chromium. The elution concentration may be relatively high because sucrose is a disaccharide and not a reducing sugar. Alternatively, the test results are similar because both allose and glucose are the same monosaccharides. Besides, the pH value barely changes by the mixing of sugar.

6 CONCLUSIONS

1. The compressive strength of the specimen is the highest when the cement containing waste syrup is used as the solidifying agent. The value is approximately 1.5 times higher than that of the specimen with only cement (blank).
2. The compressive strengths of the specimens to which materials other than waste syrup are added are lower than that of the blank.
3. It is suggested that the amount of cement required for the ground improvement is reduced by mixing the waste syrup. It is necessary to verify the strength after adjusting the amount of cement.
4. Hexavalent chromium exceeding the reference value
(0.05 ppm) elutes from the blank specimen and mixing RHA after 7 days of curing. However, after curing for 28 days, hexavalent chromium exceeding the reference value does not elute from any specimen.

5. The elution concentration of hexavalent chromium is the lowest when the waste syrup is added to the specimen. In the future, it is necessary to verify the reducibility in more detail by the adjustment of the concentration of the waste syrup.

6. In the present experiment, each material is mixed in a single. The compressive strength and elution concentration may be improved by mixing different materials together. Therefore, in the future, the multiple effect should be pursued.

ACKNOWLEDGEMENTS

This work was supported by Japan Society for the Promotion of Science, the Grants-in-Aid for Scientific Research (C) (Grant number: 18J12343). Additionally, this work was under the Program for Building Regional Innovation Ecosystems (MEXT). Also, to perform this study, Nihon Kogyo Co., Ltd. provided FbP. We express our gratitude here. We would like to thank Editage (www.editage.com) for English language editing.

REFERENCES

1) Aoki, H., Yajima, T. and Koyama, T. (2007): Apatite as a marvelous biomaterial and the surface technology, Journal of The Surface Finishing Society of Japan, 58(12), 46-52 (in Japanese).

2) Aramaki, N., Amamoto, T. and Otsuru, M (2013): Applicability of bamboo charcoal to cement soil stabilization, Journal of Japan Society of Civil Engineers, Ser. C (Geosphere Engineering), 69(3), 337-349 (in Japanese).

3) Hamada, M. and Nagai, T. (1995): Inorganic components of bones fish and their advanced utilization, The Journal of Shimonoseki University of Fisheries, 43(4), 185-194 (in Japanese).

4) Henni, T. (2002): A study on the chemical properties and structure of allophane, Japanese Journal of Soil Science and Plant Nutrition, 70(3), 251-254 (in Japanese).

5) Hosoya, T. (2002): Leaching of hexavalent chromium from cementitious soil improvement, Journal of the Society of Materials Science, 51(8), 933-942 (in Japanese).

6) Ishiguro, S. (2000): Strength of mortar made with rice husk ash cement, Transactions of The Japanese Society of Irrigation, Drainage and Reclamation Engineering, 210, 799-804 (in Japanese).

7) Kuroda, Y. and Koshiishi, N. (2010): Influence of various factors on leaching of hexavalent chromium from cement concrete, Journal of Structural and Construction Engineering (Transactions of AIJ), 75(650), 715-722 (in Japanese).

8) Niida, R., Nitta, H. and Nishizaki, I. (2015): Method for reducing hexavalent chromium eluted from recycled base course material using reducing sugar, Journal of Japan Society of Civil Engineers, Ser. E1 (Pavement Engineering), 71(3), 211-216 (in Japanese).

9) Sakabe, H., Sawaya, K., Nakayama, Y. and Shiraki, O. (2012): The actual situation and tendency of the elution of hexavalent chromium from improved soil by cement –Analysis based on elution test data of three years in the past, Journal of the Society of Materials Science, 61(1), 7-10 (in Japanese).

10) Samad, A., Fukumoto, T., Dabwan, A., Katsumata, H., Suzuki, T., Furukawa, M. and Kaneco, S. (2016): Enhanced removal of arsenic from ground water by adsorption onto heat-treated rice husk, Open Journal of Inorganic Non-Metallic Materials, 6, http://dx.doi.org/10.4236/ojinm.2016.63004, 18-23.

11) Shibata, K., Yoshida, H., Iinoue, T., Matsumoto, N. and Suenaga, Y. (2019): Study on adsorption performance of food wastes for various heavy metals, International Journal of GEOMATE, 16(55), 46-52.

12) Shigeta, H., Enomoto, T. and Sugihara, T. (2013): Development of a medical grinding tool considering material properties of wet bone for minimally invasive surgery, Transactions of the Japan Society of Mechanical Engineers Series C, 79(804), 2917-2928 (in Japanese).

13) Takeuchi, T., Nagatani, S., Otsubu, N. and Banshoya, E. (1997): An experimental study on long slump retention of concrete, Doboku Gakkai Ronbunshu, 1997(571), 15-25 (in Japanese).

14) Tsukawaki, T., Kaneko, T. and Kitazono, Y. (2012): Usefulness of quicklime in stable treatment of volcanic ash clay, Japan Society of Civil Engineers Western Branch Research Presentation, III-071, 489-490 (in Japanese).

15) Umeda, J., Takaeda, R., Michiura, Y. and Kondoh, K. (2014): High-purity amorphous silica originated in rice husks of agricultural waste and utilization of concrete admixture, Journal of Smart Processing, 3(5), 323-327 (in Japanese).

16) Yoshida, M., Kitamura, T., Katsushima, H. and Kondo, K. (2017): Elution control of Cr (VI) from volcanic coarse-grained soil improved with cement, Cement Science and Concrete Technology, 71(1), 661-666 (in Japanese).

17) Yoneda, K. (2011): Examination of strength characteristics of cement solidified soil, Zenchiren technical forum 2011 Kyoto, 88, 1-2 (in Japanese).