Proceedings of the 9ICEG
9th International Congress on Environmental Geotechnics
25-28 June, 2023 | Chania, Greece

https://doi.org/10.53243/ICEG2023-323

Leaching of Cr(VI) in stabilized clay compacted with recycled concrete aggregates

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ABSTRACT

In Japan, recycled concrete aggregates (RCA) and cement-stabilized sludge (SS) from construction or demolition have been widely recycled as construction or geotechnical materials. However, these materials contained heavy metal contaminants such as hexavalent chromium (Cr(VI)). This experimental study evaluated the leaching behaviours and environmental suitability of the mixture of RCA and SS with three different compositions, which are 0:100 (RCA:SS=0:100), 20:80 (RCA:SS=20:80) and 40:60 (RCA:SS=40:60) in dry mass basis. RCA was added to improve compaction performance and mechanical properties of fine SS as well as to limit the release of Cr(VI) from the RCA. A series of experiments, including a conventional batch leaching test (BLT) and a dynamic tank leaching test (DTLT) were performed. Leaching amounts of Cr(VI) in the DTLT for compacted specimens were less than those in the BLT. Cr(VI) was undetectable from the 0:100 specimen since the purely SS had a lower leaching concentration of Cr(VI). In the DTLT, the measured apparent diffusion coefficient (D^{app}) values for Cr(VI) of the compacted specimens containing the RCA were 2.5×10^{-7} and 6.1×10^{-7}m2/s for the ratios of 40:60 and 20:80, respectively. The ratio of 40:60 exhibited lower Cr(VI) leaching than the ratio of 20:80 in spite of larger RCA content. The addition of increased RCA significantly improved the compaction performance since the variation of gradation of RCA particles in compacted SS enhanced density. Thus, the diffusive leaching of Cr(VI) from the 40:60 specimen was limited more effectively.

Keywords: Standard proctor compaction, Recycled concrete aggregates, Stabilized soil, Heavy metal contaminants, Hexavalent chromium, apparent diffusion coefficient

1 INTRODUCTION

In recent years, there has been increasing attention on reusing/recycling solid waste from demolished buildings or construction sites as construction or geotechnical materials. Various ground improvement techniques have been widely used to enhance their engineering properties (Kamon & Katsumi, 1994; Inui & Katsumi, 2009). Previous research has shown that reinforcing soil-based materials with recycled concrete aggregates (RCA) is a cost-effective and sustainable method for improving soil properties. RCA can be added to compacted clay-based materials to increase their stiffness and density, reducing deformation. For example, in landfill engineering, RCA has been added to clay mixtures as a landfill liner material to immobilize heavy metals (Li et al., 2017). In earth dam engineering, RCA has been mixed with clay soils as core materials to reduce differential settlement and increase core stiffness (Lu et al., 2021). In road engineering, RCA can be mixed with soil to improve properties such as swelling, strength, and compressibility of the sub-grade (Kianimehr et al., 2019). Although the feasibility of using RCA for improving clay-based materials has been established, most previous research has focused only on the mechanical, physical, and hydraulic properties of RCA without the use of chemical binders, except in cases where significant cohesion of soil was lost and particle segregation due to high RCA content in specimen, the soil strength was reduced (Sridharan et al.,2006; Song et al., 2012). In such cases, cement binders are necessary to maintain cohesion, moreover, cement binders are commonly used for clay improvement to mitigate undesirable characteristics such as low shear strength and high compressibility. The use of RCA in cement-treated clays reduces the amount of cement required, which is beneficial for environmental concerns (Nakayenga et al., 2021). In this research, RCA was mixed with cement-stabilized sludge (SS) to evaluate the mechanical performance and leaching of Cr(VI) from SS compacted with RCA. Both RCA and SS may contain certain amounts of heavy metal contaminants,

including Cr(VI), which is typically found in concrete materials as chromate generated from the oxidation of trivalent chromium (Cr(III)) during Portland cement clinker production (Klemm, 1994). The chemical and physical properties of chromium, such as toxicity, solubility, and sorption affinity, depend on its oxidative state and environmental conditions. For instance, Cr(III) has a higher affinity to soils and other substances, with lower solubility and toxicity compared to Cr(VI) (Macphee & Glasser, 1993). Therefore, it is crucial to determine the dissolution, sorption, and immobilization of Cr(VI) in RCA and SS, considering the environmental concerns. It has been widely reported that leaching of heavy metals from compacted clay is generally controlled by diffusion (Shackelford & Daniel, 1991; Wei et al., 2022). Hence, it is necessary to consider the migration of Cr(VI) in compacted clay in relation to diffusion. This research aims to evaluate the leaching behavior and environmental suitability of mixtures of RCA and SS with three different compositions, where the mixing ratios of RCA: SS on a dry mass basis were 0:100, 20:80, and 40:60, respectively. The goal is to improve compaction performance and mechanical properties of fine SS by adding RCA while limiting the release of Cr(VI) from RCA.

2 EXPERIMENT PROGRAMS

2.1 Materials

The clay used in this study was local Osaka clay, collected from a construction site in Osaka, Japan. The natural water content, wet unit weight and particle density were 39.6%, 1.56× 10^3 kg/m^3 and 2.69 × 10^3 kg/m^3, respectively. The liquid and plastic limits were 46.38 % and 37.45 %. RCA was generated from the other waste concrete by crushing and particle size control from site construction in Osaka, Japan (see Figure 1) and was adopted as geotechnical material. The particle density and physical colour of RCA are 2.70 × 10^3 kg/m^3 and Dark Gray.

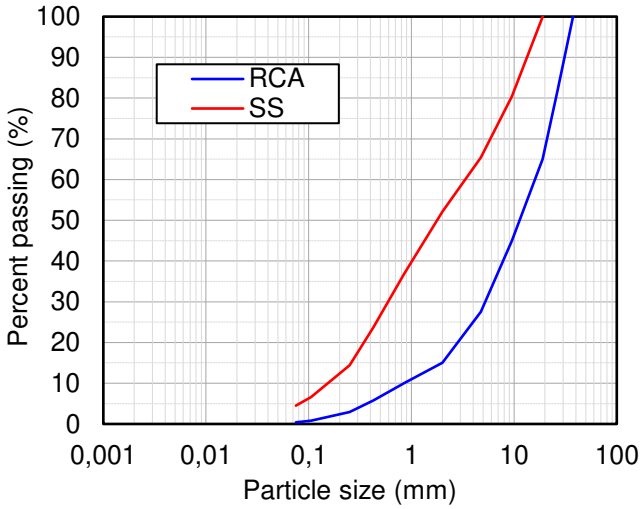

Figure 1. Grain size distributions of SS and RCA

2.2 Specimen preparation

To improve the undesirable properties of clay and prevent particle segregation of compacted SS with RCA, cement binders ranging from 50-200 kg/m^3 of wet clay volume have generally been employed for clay improvement applications, according to the guidelines set forth by the Japanese Society of Soil Mechanics and Foundation Engineering. Therefore, in this study, a cement binder of 50 kg/m^3 was used. The cement was mixed with the clay specimens using a Hobart mixer until homogeneity was achieved, and then cured for 7 days to simulate realistic site conditions. The particle density of SS was 2.74 x 10^3 kg/m^3, and the grain size distribution curve of SS is shown in Figure 1. The RCA-SS mixture was prepared using the wet mixing method, where water was evenly sprayed on the RCA-SS mixture, pre-determined by the optimum moisture content. Finally, the RCA-SS mixture was thoroughly homogenized using a spatula. The preparation of specimens for each test is presented in Table 1.

Table 1. The mixture preparations for each test

Test	Proportion of RCA:SS			
	0:100	20:80	40:60	100:0
Compaction test	✓	✓	✓	
Conventional batch leaching test	✓	✓	✓	✓
Modified tank leaching test	-	-	-	✓
Dynamic tank leaching test	✓	✓	✓	-

2.3 Standard proctor compaction test

Standard proctor compaction test was conducted following JIS A1210. For each specimen, water was added to the soil to predetermined water content. Three layers of soil were compacted into the standard mould (150 mm in diameter and 125 mm in height) using a rammer 4.5 kg and drop length of 30 cm, which creates 550 kJ/m^3.

2.4 Conventional batch leaching test

A conventional batch leaching test (BLT) was performed according to the Japanese Environmental Agency notification No.46, 1991 (JLT46), to determine Cr(VI) leaching concentrations of the RCA, the SS and the mixtures. The specimen was crushed under 2 mm of particle size. The crushed specimens were mixed with a solvent which is distilled water (pH~7) at a liquid to solid ratio (L/S) of 10 ml/g and using a shaker adjusted to approximately 200 times per minute. The solution was centrifuged at 3,000 gravitational acceleration for 20 mins., finally, filtration with a 0.45 um membrane filter. The concentrations of Cr(VI) in the leachate were determined.

2.5 Tank leaching test

Two sets of samples were prepared for the dynamic tank leaching test (DTLT) and the modified tank leaching test (MTLT). For DTLT, specimens were compacted into cylindrical PVC molds (150 mm in diameter and 125 mm in height)(see Figure 2 (left)) with maximum dry density of RCA and SS mixtures in ratios of 0:100, 20:80, and 40:60, corresponding to dry densities of 1.394× 10^3, 1.433× 10^3, and 1.55 × 10^3 kg/m^3 respectively. The specimens were covered with a polymer mesh sheet (0.45 µm opening) to prevent against erosion during leaching tests and soaked in distilled water at a liquid-to-surface area ratio of 10 ml/cm^2. For the MTLT, 500 g of granular RCA with controlled particle size, based on grain size distribution (see figure 1), was enclosed in a polymer mesh sheet (0.45 µm opening) and soaked in distilled water at a liquid-to-solid mass ratio of 10 ml/g (see Figure 2 (right)). The leachates were refreshed at cumulative times of 0.25, 1, 4, 9, 16 and 36 days. This approach was adapted from an existing tank leaching test by Inui and Katsumi (2009).

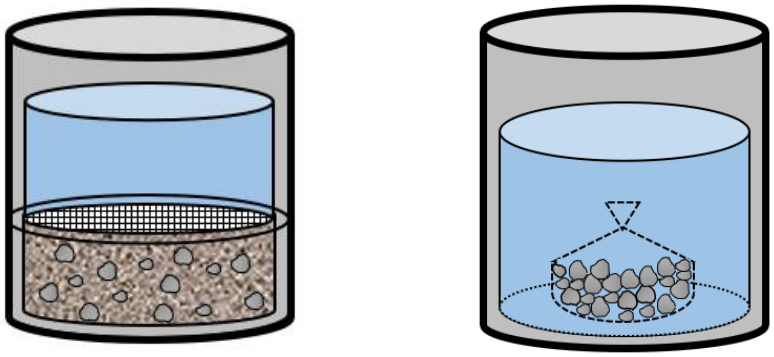

Figure 2. Schematic of the DTLT (left), and the MTLT (right)

2.6 Analytical methods

The Cr(VI) analysis was conducted using the reddish-purple 1,5-diphenylcarbohydrazide chromate complex in an acidic medium and the absorption wavelength was measured at 540 nm using the

Shimadzu UVmini-1240 UV/Visible Scanning Spectrophotometer in accordance with the Japanese Standard Association (JSA), JIS K 0102:2019.

2.7 Determination of apparent diffusion coefficient

Based on Fick's second law combined with boundary conditions of the model, the cumulative leaching mass of solute time per unit area was presented as Equation (1). (Wei et al., 2022)

$$M_t = 2\rho_d Q_0 (D^{app} t/\pi)^{0.5} \quad (1)$$

Where M_t is the cumulative leaching mass of solute per unit area (mg/m^2), Q_0 is the initial solute concentration (mg/kg) of specimens, t is the cumulative leaching time (s), D^{app} is the apparent diffusion coefficient of solute in leachate (m^2/s) and ρ_d is the dry density of specimens (kg/m^3). Taking the Equation (1) into logarithm function as shows as Equation (2).

$$\log M_t = \log[2\rho_d Q_0 (D^{app} t/\pi)^{0.5}] + 0.5 \log t \quad (2)$$

The leaching mechanisms were evaluated by linear regression analysis with the correlation of the cumulative leaching mass of solute has a linear relationship with cumulative leaching time under a logarithm function. The slope of Equation (2) can classify the leaching mechanism as follows, the slope ranges are between 0.35-0.65, the mechanism was controlled by diffusion, when the slope ranges are < 0.35, the mechanism was controlled by surface wash-off, and when the slope range is >0.65, the mechanism was controlled by dissolution. (de Groot & van der Sloot, 1992)

According to both of Equation (1) and Equation (2), M_t was calculated by the cumulative of M_i, (mg/m^2), which interprets the leaching mass of solute per unit area for each leaching interval as shown as Equation (3).

$$M_i = (C_i \times V_i)/A \quad (3)$$

Where C_i is the solute concentration in leachate for each leaching interval (mg/L), V_i is the leachate volume (L), A is the surface area exposed to leachate (m^2).

When the leaching mechanism is controlled as diffusion where the slope ranges are between 0.35 - 0.65., referring to Equation (2), the apparent diffusion coefficient of solute can then be determined in each leaching interval as follows.

$$D^{app} = \pi[M_i/(2\rho_d Q_0(\sqrt{t_i} - \sqrt{t_{i-1}})]^2 \quad (4)$$

Where D^{app} is , the apparent diffusion coefficient (m^2/s), t_i is the cumulative leaching time at the end of the current leaching interval (s), t_{i-1} is the cumulative leaching time at the end of the previous leaching interval (s). Finally, The real D^{app} was determined by taking average of the interval apparent diffusivities, and then, determined the computed uncertainty (standard deviation).

3 RESULTS AND DISCUSSIONS

3.1 Compaction characteristics

The correlation between dry density and moisture content of compacted SS with different proportions of RCA were shown in Figure 3. The results revealed that the dry densities of the compacted SS increased as the proportion of RCA in the mixture increased, while the moisture contents decreased. The improvement in compaction performance was more significant with higher proportions of RCA, suggesting that the gradation of RCA particles may have a special influence on enhancing the density of compacted SS. These results are consistent with previous research (Lu, et al., 2021).

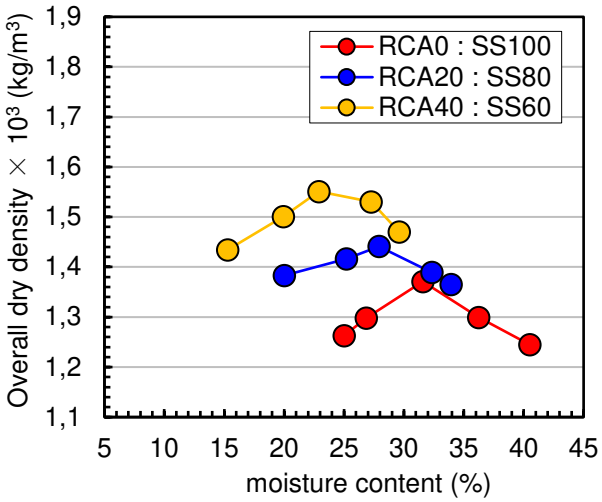

Figure 3. Compaction curve with different mixtures of RCA:SS.

3.2 Conventional batch leaching test results

Figure 4. shows the leaching amount of Cr(VI) in the BLT, which was conducted for crushed RCA and SS with under 2 mm of particle size. The Cr(VI) from purely RCA exceeded the Japanese environmental regulation (0.05 mg/L). Moreover, the 40:60 specimen was the highest concentration of Cr(VI), followed by the 20:80 and 0:100 specimens, respectively. Those results revealed that most Cr(VI) leached from RCA, since the Cr(VI) was undetectable from the 0:100 specimen.

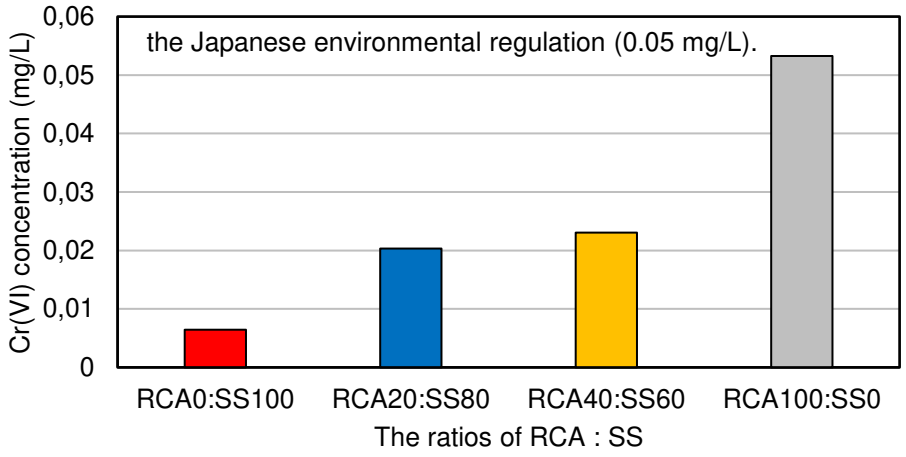

Figure 4. Cr (VI) concentration with different mixtures in the BLT

3.3 Tank leaching test results

The MTLT was conducted for granular RCA, to observe the initial leaching characteristic of Cr(VI) on purely RCA. The calculation of M_i (mg/m^2) from Equation (3) was re-calculated to M_{ii} (mg/kg), since the specimen was not monolithic (Inui & Katsumi, 2009) as follows.

$$M_{ii} = (C_i \times V_i) / m \quad (5)$$

Where m is the specimen mass (kg). The results (see Figure 5 (left)) show that the leaching amount of Cr(VI) from granular RCA decreased as cumulative time increased and stabilized at a cumulative time of 4-36 days. In the DTLT for compacted specimens (see Figure 5 (right), the ratio of 40:60 exhibited lower Cr(VI) leaching compared to the ratio of 20:80, despite having a higher RCA content due to the higher density of 40:60, which may result in effective immobilization of Cr(VI) leaching. However, Cr(VI) leaching from the 0:100 specimen was fairly similar to that from the 40:60, despite the 0:100 having the lowest density due to SS containing a lower amount of leachable Cr(VI). These results support the idea that using granular RCA can improve the compaction performance of SS, resulting in the transformation

of the granular specimen into a monolithic material that can retain heavy metal contaminants in the matrix. This finding is consistent with previous research by Li et al. (2017).

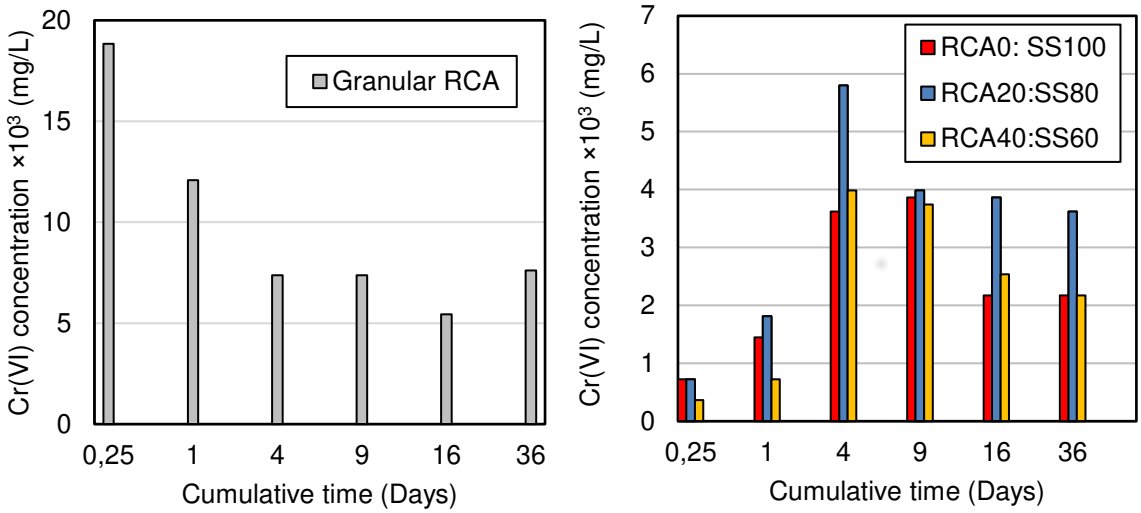

Figure 5. Cumulative mass of Cr(VI) with leaching time for the granular RCA in the MTLT (left) and the different mixtures of RCA:SS in the DTLT (right)

Variations in pH and EC of the leached amount of Cr(VI) with cumulative leaching time are shown in Figures 6 and 7. The results also show that the pH values for each specimen were around 7-10 and exhibited a fairly similar increasing trend. In the initial period, the pH values gradually increased with increasing cumulative time. In the final period, the pH values remained consistent from 4-36 days. The EC values for each specimen increased with the cumulative time, ranging from 0.25-36 days.

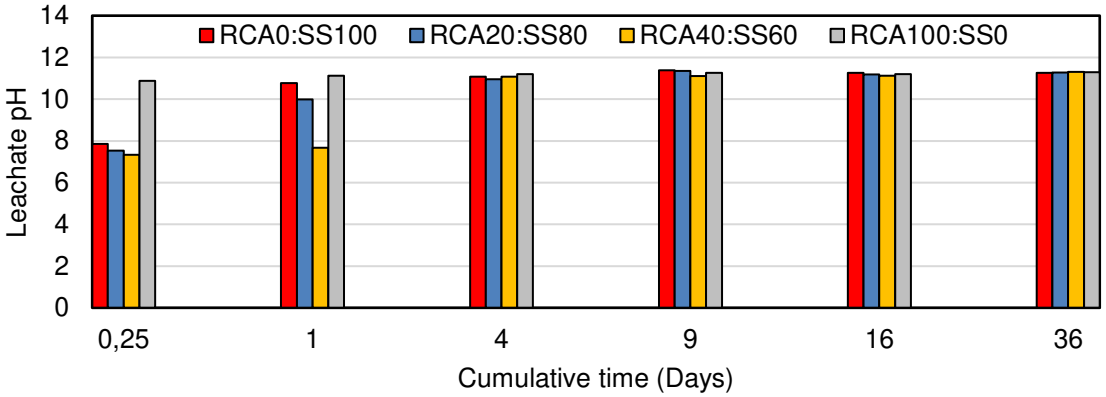

Figure 6. Leachate pH with leaching time for granular RCA in the MTLT and the different mixtures of RCA:SS in the DTLT

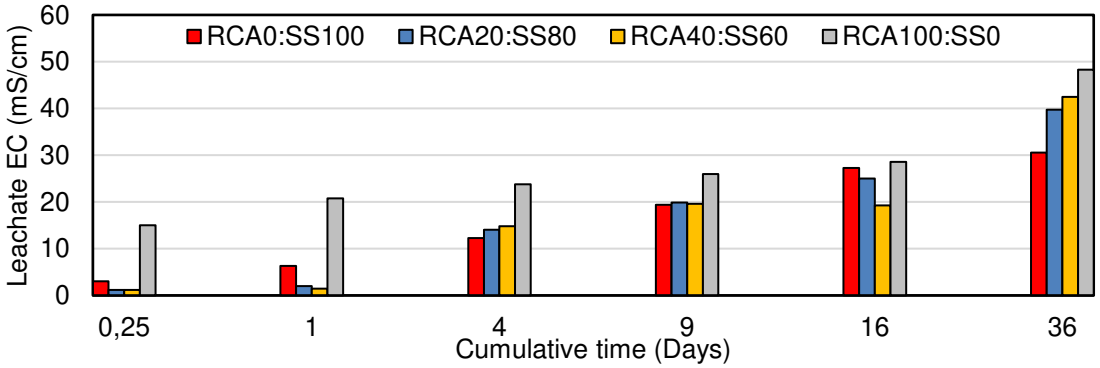

Figure 7. Leachate EC with leaching time for granular RCA in the MTLT and the different mixtures of RCA:SS in the DTLT

3.4 Apparent diffusion coefficient

The leachability results indicate a linear relationship between cumulative mass release of Cr(VI) in compacted SS with three different ratios of RCA and cumulative leaching time under logarithmic function, as shown in Table 2. According to the release mechanism determination criteria (de Groot & van der Sloot, 1992), the leaching mechanism of Cr(VI) for DTLT from the 0:100, 20:80 and 40:60 specimens was controlled by diffusion, whereas the granular RCA for MTLT was dissolved, based on Equations (4). The D^{app} is shown in Table 2, with the 40:60 ratio exhibiting the lowest D^{app}, followed by 0:100 and 20:80, respectively, despite the 40:60 having a larger RCA content. These results suggest that Cr(VI) was blocked by strong pore connectivity due to the gradation of a large amount of RCA content in the 40:60 specimen, resulting in a denser structure with more tortuous pores where Cr(VI) was restricted. On the other hand, the 20:80 specimen had poor pore connectivity, allowing for easier diffusion of Cr(VI) into the leachate. However, Cr(VI) from the 0:100 specimen was undetectable, as purely SS had a small amount of Cr(VI).

Table 2. The leaching mechanisms and apparent diffusion coefficients of the RCA:SS

Proportion (RCA:SS)	Leaching test	Element	Slope	Leaching mechanism	D^{app} (m^2/s)
0:100	DTLT	Cr (VI)	-0.5	Diffusion	3.58×10^{-7}
20:80	DTLT	Cr (VI)	-0.42	Diffusion	6.05×10^{-7}
40:60	DTLT	Cr (VI)	-0.35	Diffusion	2.53×10^{-7}
100:0	MTLT	Cr (VI)	-0.89	Dissolution	-

4 CONCLUSION

The mechanical properties and leaching characteristics of using RCA and SS as geotechnical materials for construction purposes were investigated in this study, with a focus on determining the leaching amount of Cr(VI). Compaction performance was improved with the addition of RCA particles, with the highest maximum dry density observed in the 40:60 mixture of RCA and SS, followed by 20:80 and 0:100 specimens. The leaching of Cr(VI) from RCA in the BLT exceeded Japanese environmental regulations (0.05 mg/l), whereas Cr (VI) from granular RCA in the MTLT was lower. Additionally, crushed mixtures of RCA and SS in the BLT had higher Cr(VI) leaching compared to compacted specimens in the DTLT. BLT results showed that the 40:60 mixture had the highest Cr(VI) concentration, followed by 20:80 and 0:100, respectively. However, in DTLT results, despite higher RCA content, the 20:80 mixture had the highest leaching of Cr(VI) instead of 40:60. Cr(VI) was undetectable in 0:100 and 40:60 specimens, possibly due to the stability of Cr(VI) in SS and potential immobilization in highly compacted specimens. pH values for all specimens ranged from 7-10 and increased gradually with cumulative time. EC values increased with increasing cumulative time from 0.25-36 days.

The DTLT results indicated that the leaching mechanism of compacted SS with RCA is diffusion, while the leaching mechanism of granular RCA is dissolution. D^{app} values were calculated, and the 40:60 specimen had the lowest. D^{app} value, indicating effective restriction of Cr(VI) due to a denser structure and tortuous pores. The 20:80 specimen had poor pore connectivity, resulting in easier diffusion of Cr(VI), while Cr(VI) was undetectable in the 0:100 specimen due to low Cr(VI) content in purely SS. In this study, the desorption parameters of Cr(VI) in compacted SS with RCA were neglected to avoid underestimating its diffusivity. However, further studies are needed to identify the desorption characteristics and evaluate the immobilization effect of Cr(VI) in compacted SS with RCA.

5 ACKNOWLEDGEMENTS

This work was supported by JSPS KAKENHI Grant Number 22H01590. The authors would like to thank sincerely to Dr. Katsumi Mizuno (Osaka Bentonite Association) for his valuable support for experimental works.

REFERENCES

de Groot, G.J., & van der Sloot, H.A. (1992). Determination of Leaching Characteristics of Waste Materials Leading to Environmental Product Certification. ASTM International.

Inui, T., & Katsumi, T. (2009). Environmental suitability of recycled concrete aggregates used in geotechnical applications. Proceedings of the 17th International Conference on Soil Mechanics and Geotechnical Engineering, 5.

Japanese Standard Association (JSA). (2019). Testing Method for Industrial Wastewater, JIS K 0102 (Chromium). Tokyo, Japan.

Japan Standard Association (JSA). (2020). The Method for Soil Compaction using a Rammer, JIS A 1210. Tokyo, Japan.

Kamon, M., & Katsumi, T. (1994). Civil engineering use of industrial waste in Japan. In A.S. Barasubramaniam et al. (eds), Development in Geotechnical Engineering,. Proceedings of the Symposium on Developments in Geotechnical Engineering, 265-278.

Kianimehr, M., Shourijeh, T. P., Binesh, M. S., Mohammadinia, A., & Arulrajah, A. (2019). Utilization of recycled concrete aggregates for light-stabilization of clay soils. Construction and Building Materials, 116792.

Klemm, W. (1994). Hexavalent Chromium in Portland-Cement. Cement, Concrete and Aggregates., 16, 43-47.

Li, L., Lin, C., & Zhang, Z. (2017). Utilization of shale-clay mixtures as a landfill liner material to retain heavy metals. Materials and Design, 89, 73-82.

Li, Y., Wei, M., Liu, L., Xue, Q., & Yu, B. (2020). Adsorption of toluene on various natural soils: influences of soil properties, mechanisms, and model. Science of The Total Environment, 740, 140104.

Lu, Y., Liu, S., Zhang, Y., Yang, M., Fu, Z., & Wang, L. (2021). Sustainable reuse of coarse aggregates in clay-based impervious core: Compactability and permeability. Journal of Cleaner Production, 127011.

Macphee, D.E., & Glasser, F.P. (1993). Immobilization Science of Cement Systems. MRS Bulletin, 18, 66-71.

Nakayenga, J., Cikit, A. A., Tsuchida, T. & Hata, T. (2021). Influence of stone powder content and particle size on the strength of cement-treated clay. Construction and Building Materials, 305, 124710.

Shackelford, C. D., & Daniel, D. E. (1991a). Diffusion in saturated soil. I: Background. the Journal of Geotechnical Engineering, 117(26).

Shackelford, C. D., & Daniel, D. E. (1991b). Diffusion in saturated soil. II: Results for compacted clay. Journal of Geotechnical Engineering, 117(3), 485-506.

Song, Y.-S., Kim, K.-S, & Woo, k.-S. (2012). Stability of embankments constructed from soil mixed with stone dust in quarry reclamation. Environmental Earth Sciences, 67, 285-292.

Sridharan, A., Soosan, T. G., & Jose, B. M. (2006). Shear strength studies on soil-quarry dust mixtures. Geotechnical and Geological Engineering, 24, 1163-1179.

Wei, M., Li, Y., Yu, B., Liu, L., Xue, Q., & Du, Y. (2022). Assessment of semi-dynamic leaching characteristics of lead and zinc from stabilized contaminated soil using sustainable phosphate-based binder after carbonation. Journal of Cleaner Production, 130126.