

Evaluating the Influential Factors on Cr(VI) Leaching from Compacted Cement-Stabilized Soil through Tank Leaching Tests

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Abstract – In Japan, one commonly uses soil improvement techniques, involving the application of cement-based stabilizer, which is readily available locally and can achieve sufficient compressive strength within a short period. However, previous research has indicated potential environmental concerns associated with the use of cement stabilized soil, since cement materials contain certain amounts of hexavalent chromium (Cr(VI)). In addition, in 2022, the environmental criterion for Cr(VI) concentration in groundwater was lowered to 0.02 mg/L in Japan. Considering these conditions, a comprehensive understanding of the leaching behavior of Cr(VI) released from the cement-stabilized soil is essential for evaluating their environmental consequences. This research investigates Cr(VI) leaching from the cement-stabilized soil by conducting the tank leaching tests (TLTs), focusing on influential factors such as mixing methods (dry (DM) and wet (WM) methods), curing periods, specific surface areas of the specimens, and liquid-to-solid ratios. The results indicate that the Cr(VI) leaching concentrations of the WM specimens are much lower than those of the DM specimens of equivalent unconfined compression strength. In WM, Cr(VI) is undetectable due to specimen homogeneity and enhanced hydration of the cement. Currently, the leaching concentration after immersing specimens for 28 days is measured according to the Japanese regulation. However, this may lead to underestimation of the leaching rate of Cr(VI) concentration, as the highest leaching concentrations are observed before 28 days. Moreover, the effect of curing periods suggests that the specimens cured for 7 days exhibit higher Cr(VI) leaching concentrations than those cured for 28 days, attributed to the enhanced precipitation of Cr(VI) by hydration products such as Ca(OH)₂. A quicker leaching rate is achieved by a higher specific surface area. It is apparent that considering these effects is important to determine the appropriate regulations for the TLT.

Keywords: Tank leaching test, Hexavalent chromium, Specific surface area, Liquid-to-solid ratio

1. Introduction

Japan is one of the most seismically active countries in the world. It lies at the intersection of four tectonic plates: the Eurasian, the North American, the Pacific, and the Philippine Sea plates. Collisions and subduction among these plate causes many of the earthquakes and volcanic eruptions that have shaped the country's landscape and history. Frequently, eruptions have generated voluminous amounts of volcanic ash and soils which inundated widespread areas. In perspective of economy and practical engineering, it is reasonable to use these volcanic soils as a geo-materials. However, the geotechnical characteristics of volcanic cohesive soil has high compressibility, low cyclic strength [1]. Consequently, it becomes imperative to enhance its quality tailored to specific construction purposes. One of the most popular soil improvement technique is chemical stabilization, widely used in Japan and other countries. The commonly used stabilizer in Japan is cement-based stabilizers (mixture of cement and additives), which is locally available and can achieve sufficient compressive strength within a short period. However, previous research has reported that the use of cement-stabilized soil may have negative impacts on environmental concerns. Cement materials contain certain amounts of hexavalent chromium (Cr(VI)), and naturally occurring inert chromium (III) in raw materials (clay, limestone, etc.) used for cement clinker production oxidizes to form reactive and toxic Cr(VI) at high temperatures in cement rotary kilns [2]. Given these conditions, a comprehensive evaluation of the several factors influencing Cr(VI) released from the use of cement material is essential for evaluating their environmental consequences. One of Japanese leaching tests, as stipulated by Ministry of Construction [3] called "Tank leaching test (TLT)", involves immersing solid masses in a tank into distilled water and allowing them to remain for 28 days. However, this method can offer inappropriate estimate when evaluating only the 28 day period of the leaching test and may not accurately depict the leaching behaviour of contaminants. Numerous studies have explored the influence

on the leaching of heavy contaminants from cement-stabilized soil. For instance, the effect of hydration reaction with curing period on leaching of Cr(VI) [4], or variations in the particle size of toxic materials can yield distinct leaching patterns for heavy contaminants, as increased exposed surface area tends to generate a higher concentration of heavy metal contaminants [5]. Additionally, some research suggests that alterations in the L/S (liquid to solid) ratio can significantly influence the leaching behavior of heavy metal contaminants [6]. Therefore, the aim of this research is to investigate the leaching behaviour and influencing factors on Cr(VI) concentration through tank leaching tests.

2. Experimental Programs

2.1. Basic Properties of Materials

The volcanic cohesive soil was collected from Chiba prefecture, Kanto region, Japan. The basic properties of soil were determined, following the Japanese Geotechnical Society standards. The natural water content, wet unit weight and particle density were 92%, 1.32 g/cm³ and 2.69 g/cm³, respectively. The liquid and plastic limits were 121 % and 90 %.

A cement-based stabilizer, which was commercially available in Japan and mainly composed of ordinary Portland cement with some pozzolanic and hydration additives such as blast furnace slag and gypsum, was used as the stabilizer.

2.2. Specimen Preparation

According to the Japan International Cooperation Agency (1998), the stabilizer contents frequently used in soil improvement applications range from 50 to 200 kg/m³. Therefore, in this research, additive contents of the cement-based stabilizer were selected, corresponding to the mixing method which comprised the dry mixing method (DM) and wet mixing method (WM). For DM, 100 kg/m³ of the stabilizer was mixed with the soil at initial water content to achieve a target unconfined compression strength of 200 kPa/m² after 28 days. For WM, 200 kg/m³ of cement content was blended with water at water to cement ratio (W/C) of 0.7, then mixed with soil at initial water content to achieve the target strength. The Hobart mixer was used to ensure the water, cement and soil distributed as homogeneously as possible. It was found to be effective that the prepared mixtures via WM are much more uniform than DM. The shaped (S) and split specimen (SP), prepared under various conditions, as shown in Table 1, aimed to observe the influence of increasing specific surface areas on Cr(VI) concentration. Those specimens were crafted with density control in accordance with the JCAS L-01:2006 standard. For the S, compaction involved 12 blows, distributed across three layers within a standard mold measuring 50 mm in diameter and 100 mm in height. Regarding the SP, the specimen was divided into four specimens with a summation of 100 mm in height, namely, each with dimensions of 50 mm in diameter and 25 mm in height, resulting in 1.6 times larger specific surface area than the S. Each split specimen was compacted using 9 blows. Schematics illustrating the two specimen types are presented in Figure 1a and 1b.

Table 1: Sample preparation program.

Sample preparation program	Cement-stabilized soil							
	Shaped specimen (50×100, Dia. × H (mm))				Split specimen (50×25, Dia. × H (mm) ×4 specimens)			
Mixing method	WM (W/C =0.7)		DM		WM (W/C =0.7)		DM	
Content of the stabilizer (kg/m ³)	200		100		200		100	
Curing period (Days)	28	7	28	7	28	7	28	7
Liquid-to-Solid ratio (ml/g)	10, 5	10, 5	10, 5	10, 5	10, 5	10, 5	10, 5	10, 5

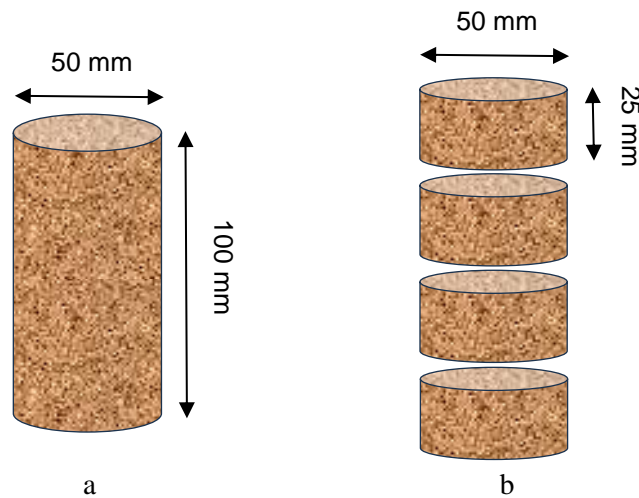


Fig. 1 Schematic of cement-stabilized soil specimens; a) shaped specimen and b) split specimen.

2.3. Unconfined Compressive Strength Test

The unconfined compressive strength (UCS) test was performed in accordance with the JGS standard. Specimens of both WM and DM were used, after curing periods of 7 and 28 days in fully-sealed condition. The UCS tests were conducted once the specified curing period was attained.

2.4. Tank Leaching Test

In this study, tests were conducted primarily to investigate Cr(VI) from cement-stabilized soil. The shaped and split specimens under various conditions were put on the polymer mesh stand in the tank and soaked into distilled water with 2 different Liquid-to-Solid ratios (L/S) as shown in Table 1. The L/S ratio was utilized instead of the Liquid-to-Surface Area ratio (L/A) found in TLT. This decision was made to account for potential variations in specimen surface area resulting from erosion under soaked conditions during the TLT. Throughout the testing period, partial leachate replacement with a solution from both specimens was adopted, rather than immersing them for 28 days as regulated by the TLT based on the Ministry of Construction (2000). The leachate was replaced partially, constituting under 10% of the total volume, at a cumulative time at 0.25, 1, 3, 7, 10, 14, 24, and 28 days continuously. The difference in leached Cr(VI) mass before and after each replacement was then calculated as a cumulative concentration, aiming to observe a comprehensive profile of Cr(VI) leaching behaviour. The collected leachate was filtered using a 0.45 μm -opening membrane filter and subsequently analyzed with the diphenylcarbazide absorption method to determine the concentration of Cr(VI).

3. Results and Discussion

3.1. UCS Test Results

The UCS results for WM and DM of specimen cured for 7 and 28 days are presented in Figure 2. It is evident that WM and DM exhibited similar strengths for similar curing periods. However, the WM exhibited higher strain than DM. The results consistently showed both WM and DM specimens have similar UCS after 28-day curing.

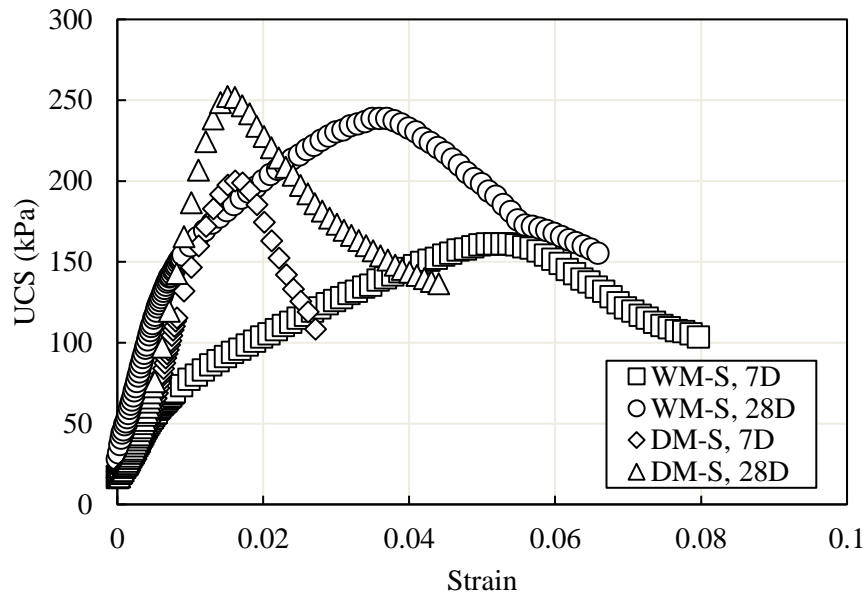


Fig 2. Streng of cement-stabilized soil with different methods and curing periods

3.2. pH and EC of Leachate

Figure 3 illustrates the pH values during leaching. For WM and DM, there was a consistent upward trend in pH, indicating the ongoing leaching of alkaline substances. The specimens of WM exhibited higher pH than those of DM, with specimens cured for 7 days showing higher pH than those cured for 28 days. This can be attributed to the higher stabilizer content of WM can generate a lot of hydration products, such as $\text{Ca}(\text{OH})_2$. During the initial 24 hours, a substantial quantity of $\text{Ca}(\text{OH})_2$, resulting from cement hydration, rapidly dissolved into the leachate. At 7 days of leaching time, the upward trend in pH became constant, signifying that the dissolution of $\text{Ca}(\text{OH})_2$ was nearing saturation. This pH change trend closely resembled findings from previous research conducted by [7].

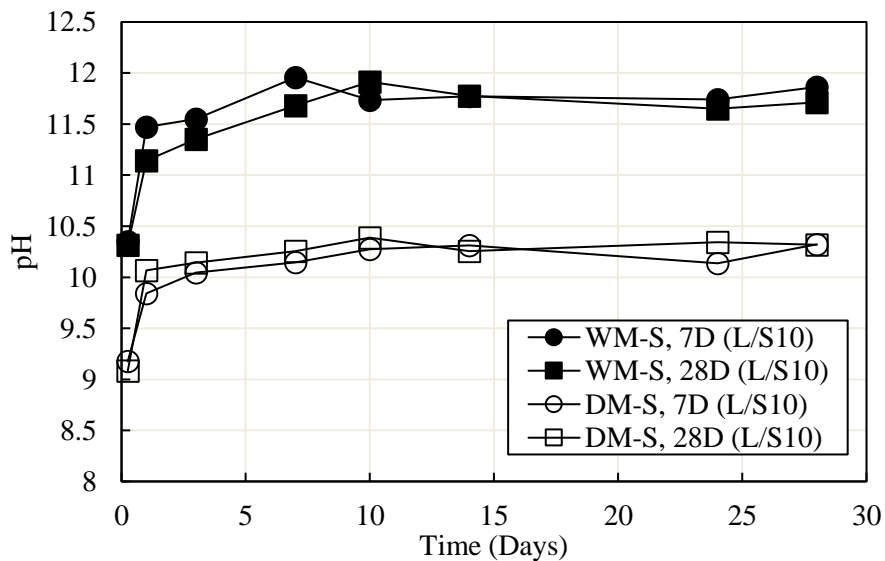


Fig. 3 leachate of pH against leaching time for WM and DM with different curing periods

Figure 4 illustrates the electrical conductivity (EC) values of the solutions from WM and DM, continuously increasing and exhibiting similar trends with the pH. The WM exhibited higher leaching of EC than DM while specimen cured for 7 days has higher leaching of EC than those 28 days. This is attributed to the fact that the specimen cured for 7 days was still in the early stages of cement hydration, suggesting that continuously generated hydration products as well as less stabilization effects tended to result in higher EC in the leachate. The specimens cured for 28 days exhibited lower EC values, as some of the soluble constituents were immobilized by final stage of hydration products.

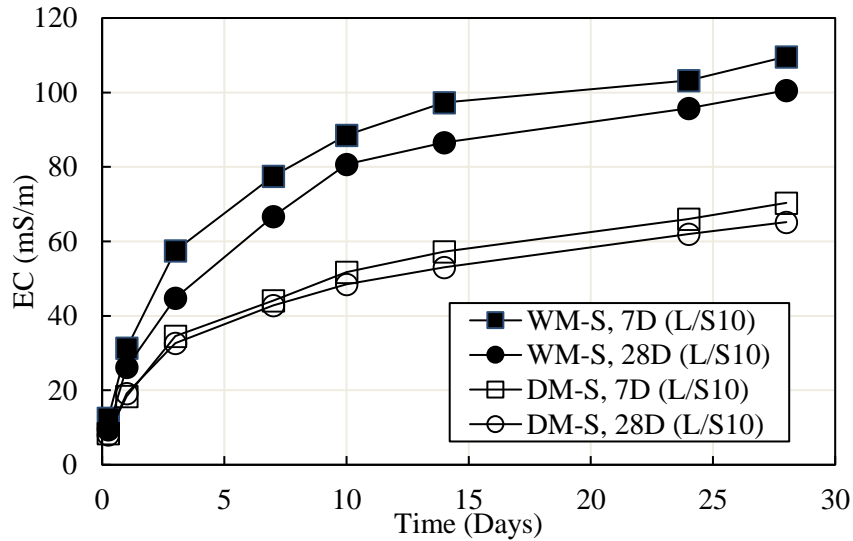


Fig. 4 leachate of EC against leaching time for WM and DM with different curing periods

3.3. Analysis of TLT Results

In this research, the different additive contents were employed, following the different mixing methods. For WM with 200 kg/m^3 of the additive content, the leaching of Cr(VI) was undetectable. It makes sense that a higher content can enhance the production of hydration reaction by wet mixing, such as $\text{Ca}(\text{OH})_2$, and creating an increased alkalinity condition. The pH of the WM exceeded 11 (See in Figure 3), whereas the most prominent species of Cr(VI) in this cement-stabilized soil was CrO_4^{2-} [8]. The reaction between Cr(VI) and cement can be explained as Eqs (1).



The $\text{Ca}(\text{OH})_2$ can reduced Cr(VI) in specimen because part of Ca^{2+} react with Cr(VI) to form calcium chromate (CaCrO_4) as a solid precipitate. For DM with 100 kg/m^3 of the additive content, The Cr(VI) concentration was detectable. This is due to the lower content compared to WM, which generates lower $\text{Ca}(\text{OH})_2$ caused by poor hydration reaction. This aligns well with the pH of DM, which is lower than 11 and lower than WM, explaining why a certain amount of Cr(VI) inside the specimen may leach out into the solution.

3.3.1. Effect of Curing Period

Figure 5 illustrates that curing periods have a significant effect on reducing Cr(VI) concentration. It is apparent that the specimens cured for 7 days exhibited higher leaching concentrations of Cr(VI) compared with those cured for 28 days. This was because the increased curing period enhanced the cementation and effectively immobilized Cr(VI) inside the specimen. This result implies that when using cement-stabilized soil as a geo-materials, providing more than 1 week curing period must be required to reduce the risk of potential environment impacts. In addition, during the 28-day leaching tests for the specimens cured for 7 and 28 days, the highest leaching concentrations were observed before 28 day in many test cases.

Conversely, the highest Cr(VI) leaching concentration occurred around 10-14 days of the leaching test, exceeding the Japanese environmental regulation limit of 0.02 mg/L for Cr(VI) leaching concentration. This indicates that the current TLT measures leaching concentration after immersing for 28 days, may lead to an underestimation of the Cr(VI) leaching concentration.

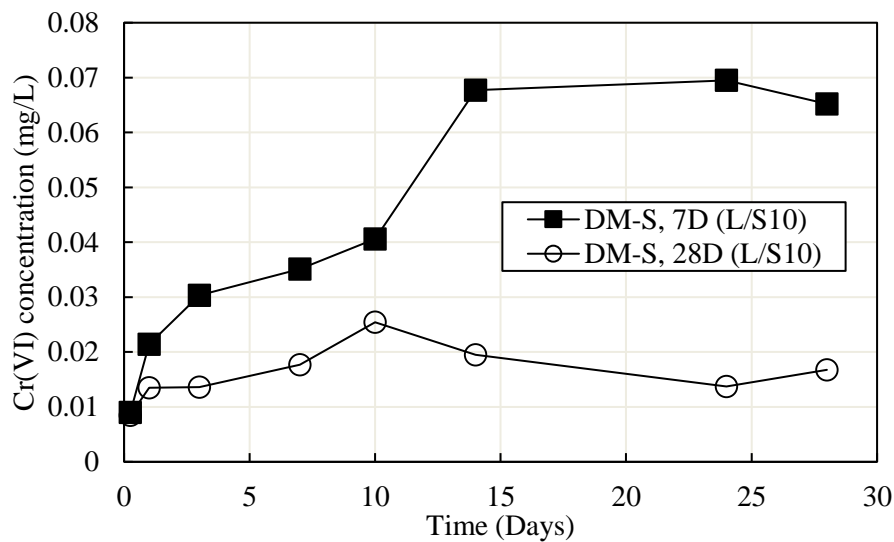


Fig. 5 Cr(VI) concentration against leaching time for cement-stabilized soil with different curing periods

3.3.2. Effect of Specific Surface Area and L/S Ratio

The TLTs were conducted on specimens cured for 28 days to investigate the influential factors on Cr(VI) leaching, considering the effect of increasing specific surface areas and different L/S ratios. Figure 6 illustrates that a higher specific surface area with lower L/S ratio resulted in the highest Cr(VI) leaching concentration, while smaller specific surface area with higher L/S ratio exhibited the lowest Cr(VI) leaching concentration. All specimens exhibited a similar trend, which can be divided into four periods. In the first period, the curves of Cr(VI) concentration abruptly increased with an increase in leaching time. In the second period, the Cr(VI) concentrations decreased with an increase in leaching time. The third period shows that the Cr(VI) concentrations tended to reach a steady stage. In the last period, the Cr(VI) curves gradually increased again with an increase in leaching time. This phenomenon between the third and fourth periods occurs because the Cr(VI) concentration starts to adsorb on the surface area of the specimen. Furthermore, for the SP specimen with L/S = 5, the highest concentration occurs at 3 days of leaching time, faster than SP and S specimens with higher L/S ratios. For the S specimen with L/S = 10, the highest concentration occurs at 10 days, slower than SP and S specimens with higher L/S ratios. These results can be concluded that the influence of increasing specific surface area with a lower L/S ratio can achieve the quicker leaching rate.

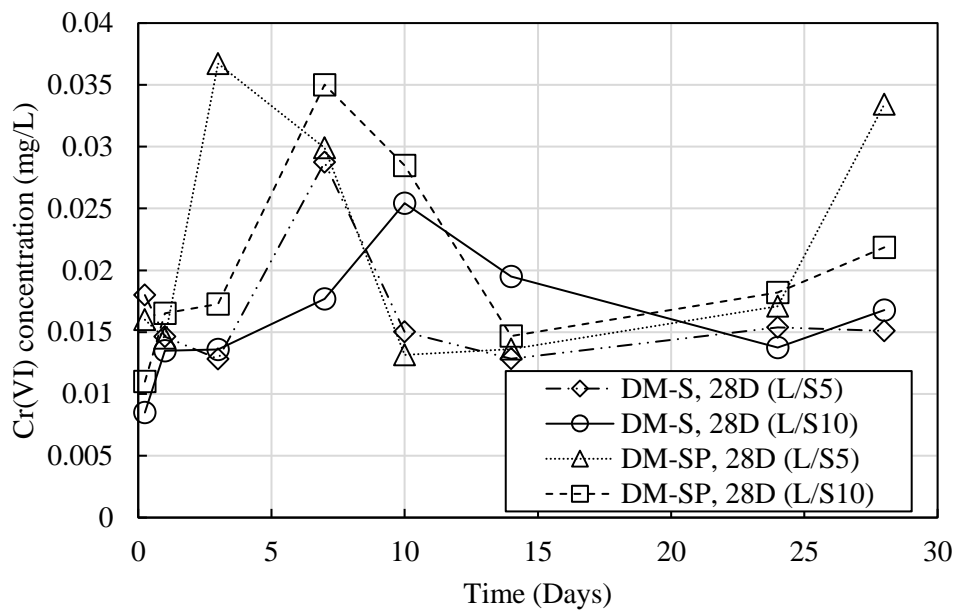


Fig. 6 Cr(VI) concentration against leaching time for cement-stabilized soil with different curing periods and L/S ratios

4. Conclusions

This research investigated Cr(VI) leaching in cement-stabilized soil, focusing on influential factors such as mixing methods, curing periods, specific surface areas, and liquid-to-solid ratios. The Cr(VI) leaching concentrations of the WM specimens are much lower than those of the DM specimens of equivalent unconfined compression strength. In WM, Cr(VI) is undetectable due to specimen homogeneity and enhanced hydration of the cement. The current TLT measures that leaching concentration is determined after immersing specimens for 28 days according to the Japanese regulation may lead to underestimation of the leaching of Cr(VI) concentration as the highest of leaching concentrations are observed before 28 days. Moreover, the effect of curing periods demonstrates the specimens cured for 7 days exhibit higher Cr(VI) leaching concentrations than those cured for 28 days, attributed to the enhanced precipitation of Cr(VI) by hydration products such as $\text{Ca}(\text{OH})_2$. This suggests that using cement-stabilized soil as a geo-materials, providing more than 1 week curing period must be required to reduce the risk of potential environment impacts. A quicker leaching rate is achieved by a higher specific surface area. It is apparent that considering these effects is important to determine the appropriate regulations for the TLT.

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References

- [1] R. P. Orense, A. Zapanta, A. Hata, and I. Towhata, "Geotechnical characteristics of volcanic soils taken from recent eruptions.," *Geotechnical & Geological Engineering*, vol. 24, pp. 129-161, 2006.
- [2] S. Bae, F. Hikaru, M. Kanematsu, C. Yoshizawa, T. Noguchi, Y. Yu, and J. Ha, "Removal of hexavalent chromium in Portland cement using ground granulated blast-furnace slag powder.," *Materials*, vol. 11, no. 1, p. 11, 2017.
- [3] Ministry of Construction (Currently the Ministry of Land, Infrastructure, Transport and Tourism), "Interim Actions on Applications of Cement and Cement-based Stabilizers to Ground Improvement and Recycling of the Stabilized Soils", 2000.

- [4] J. C. Chai, K. Onitsuk and S. Hayashi, "Cr (VI) concentration from batch contact/tank leaching and column percolation test using fly ash with additives," *Journal of hazardous materials*, vol. 166, no. 1, pp. 67-73, 2009.
- [5] T. Inui, M. Kamon, T. Katsumi and A. Kida, "Evaluating Cr (VI) leaching from recycled waste concrete aggregate using acceleration tests.," In *GeoCongress 2008: Geotechnics of Waste Management and Remediation* , pp. 280-287.
- [6] X. Y. Guo, W. T. Shi, L. I. Dong and Q. H. Tian, "Leaching behavior of metals from limonitic laterite ore by high pressure acid leaching," *Transactions of Nonferrous Metals Society of China*, vol. 21, no. 1, pp. 191-195, 2011.
- [7] Y. Sun, D. Zhang, H. Tao and Y. Yang, "The Effects of Portland and Sulphoaluminate Cements Solidification/Stabilization on Semi-Dynamic Leaching of Heavy Metal from Contaminated Sediment," *Sustainability*, vol. 14, no. 9, p. 5681, 2022.
- [8] S. Wang and C. Vipulanandan, "Solidification/stabilization of Cr (VI) with cement: Leachability and XRD analyses," *Cement and concrete research*, vol. 30, no. 3, pp. 385-389, 2000.