Master's Thesis of Engineering

Oyster shell, zeolite, and red mud binding mechanisms and their applicability for immobilizing toxic metals in diverse contaminated scenarios

굴패각, 제올라이트 및 레드 머드 결합 메커니즘 기반 오염시나리오에 따른 독성 중금속 고정화 기술 적용가능성 평가

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Civil and Environmental Engineering Major

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지도 교수 박준범

이 논문을 공학석사 학위논문으로 제출함

2021 년 08 월

서울대학교 대학원
건설환경공학부
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세실리아의 석사 학위논문을 인준함

2021 년 08 월

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Abstract

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Oyster shell powder (OS), zeolite (Z), and red mud (RM) has elicited the attention of researchers as binders for the stabilization/ solidification technique used to remediate polluted soil. However, their immobilization performance with respect to potentially toxic metals can be affected by various factors, such as the pH of the medium, contact time, and initial heavy metal concentration. Therefore, this study seeks to investigate the performance of OS, Z and RM in stabilizing four type of contaminated soils. The batch experimental tests performed in the first binder evaluation consisted of mixed binder with the contaminated soil and measured the toxic metal concentration by using leaching tests. The second binder evaluation was set up to evaluate the best two binders from the previous evaluation facing arsenic pollution in *As*-contaminated soil by pot cultivation test and in *As*-solution by sorption batch test.

As a result, from the batch experimental tests, OS bound approximately 82% of Pb and 78% of Cu in the soil samples of silty sand from abandoned metallic mine site (Case I) and soil samples from sandy soil from a military zone (Case II), respectively. On the other hand, Z was highly effective in stabilizing Pb in highly polluted soil (handmade contaminated soil HCS, Case III) binding more than 50% of Pb at lower dosages than those of OS and RM, RM showed an instable performance when it was applied to soil with low toxic metal concentrations (Case I and II), but achieved a remarkable Pb immobilization rate at dosages over 5% in highly contaminated soil (Case III). Furthermore, the Pb-immobilization capacity of OS improved considerably when the contact time increased, after 1 day it bounded 87% of Pb and after 10 days it was 94%. This basically occurs due to OS and RM are better at driving an acidic medium to an alkaline state.

Results from the second binder evaluation indicates that Z was better binding arsenic in a soil environment (Case IV) compared to OS (up to 60%) and it can be attributed to high CEC which interact with the soil minerals, instead of the adsorption mechanism. In addition, in an aqueous solution, where the absorbent was directly in contact with *As (III)*, using a binder-to-liquid ratio of 1:5, OS and Z only reduced around 10% of *As (III)* concentration. The fit Freundlich isotherms suggested that the adsorption behavior of arsenic was single-layered on the surface for both binders.

Further experiments were conducted to observe the influence of adding OS, Z and RM in soil that later will be used as fill materials. In terms of geotechnical properties, the addition of OS increases the maximum dry unit weight, while Z and RM decrease this value, and also increase the optimum water content due to the capacity of Z and RM to hold water. Considering that samples were prepared at 95% compactness; direct shear test results showed a slight decrease in the friction angle (between 7 to 11%) and increase in its cohesion parameter.

To recommend a suitable binder for each condition scenario, the initial concentration of the toxic metal, type of toxic metal, and pH medium are recognized as the main factors that can influence the binding process. Especially when the pH medium increases after binding addition hydroxyl ions participate directly in the precipitation of metals. Also, this study showed that the binder dosage increment can be favorable to the reduction of toxic metal concentration, but further evaluation should be done to avoid secondary pollution. For example, the risk associated with RM about releasing other metalloids (water-soluble Al concentrations in RM).

Based on the results of the present study, the binders OS, Z, and RM can be used for immobilization of toxic metal through different binding mechanisms: OS by causing the precipitation of heavy metal and physical adsorption, Z by ion exchange capacity and physical adsorption, and RM by precipitation of toxic metal and ion exchange capacity. However, it is highly important to identify the limitations of its application according to each pollution scenario.

Keyword: soil remediation, leaching, chemical stabilization, low-cost materials, potentially toxic metals, sustainable solutions, pot cultivation test, sorption test.

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Chapter 1 : Introduction

1.1 Study background

Soil contaminated with toxic metals is a serious environmental issue worldwide (Hu et al. 2013, Selvi et al. 2019). Toxic metals exhibit the potential of affecting the soil–food chain, impairing soil fertility (Bünemann et al. 2018, Ma et al. 2020, Wang et al. 2020), and reducing drinking water quality (Kumar et al. 2019). Once they enter the food chain, toxic metals can trigger cell mutation, possibly causing cancer(U.S. EPA 2001). Potentially toxic metals can occur naturally or as a negative impact due to man-kind activities (Figure 1.1). Among those metals: *Pb*, *Cd*, *Cu*, *Zn,* and *As* have elicited considerable concern because they are leached from tailings and discharged directly into adjacent streams and agricultural lands (Jung 2008).

Numerous remediation techniques have been developed for remediating soil contaminated with toxic metals. They include surface capping, encapsulation, landfilling, soil flushing, soil washing, electrokinetic extraction, stabilization/solidification (S/S) (Du et al. 2010, Xia et al. 2019), vitrification, phytoremediation and bioremediation. Among these techniques, S/S has attracted the attention of many researchers due to its low-cost application while preserving the long-term stability of the stabilized soil (Babel and Kurniawan 2003, Liu et al. 2018). This technique involves the addition of binding materials (binders) to contaminated soil to stabilize and immobilize contaminants (Paria and Yuet 2006, Yakubu et al. 2018, Zhong et al. 2020) via the chemical fixation of pollutants; this process is achieved through the interactions between the hydration products of binders and contaminants or the physical adsorption of contaminants (Zheng et al. 2012, Liu et al. 2018).

The addition of lime, cement, and other cementitious binders to soil has demonstrated excellent performance in treating soil contaminated with toxic metals (Xia et al. 2017). However, stabilizing vast areas of polluted soil using cementitious materials is economically infeasible due to the cost associated with such binders. To address this issue, many researchers have investigated nature-based materials, such as chitosan, zeolite, compost, hydroxyapatite, and waste products from certain industries, including fly ash, oyster shell powder, red mud, and coal, for their potential use as binders. At present, these materials have gained popularity as binders because of their local availability and low cost (Babel and Kurniawan 2003, Zhong et al. 2020).

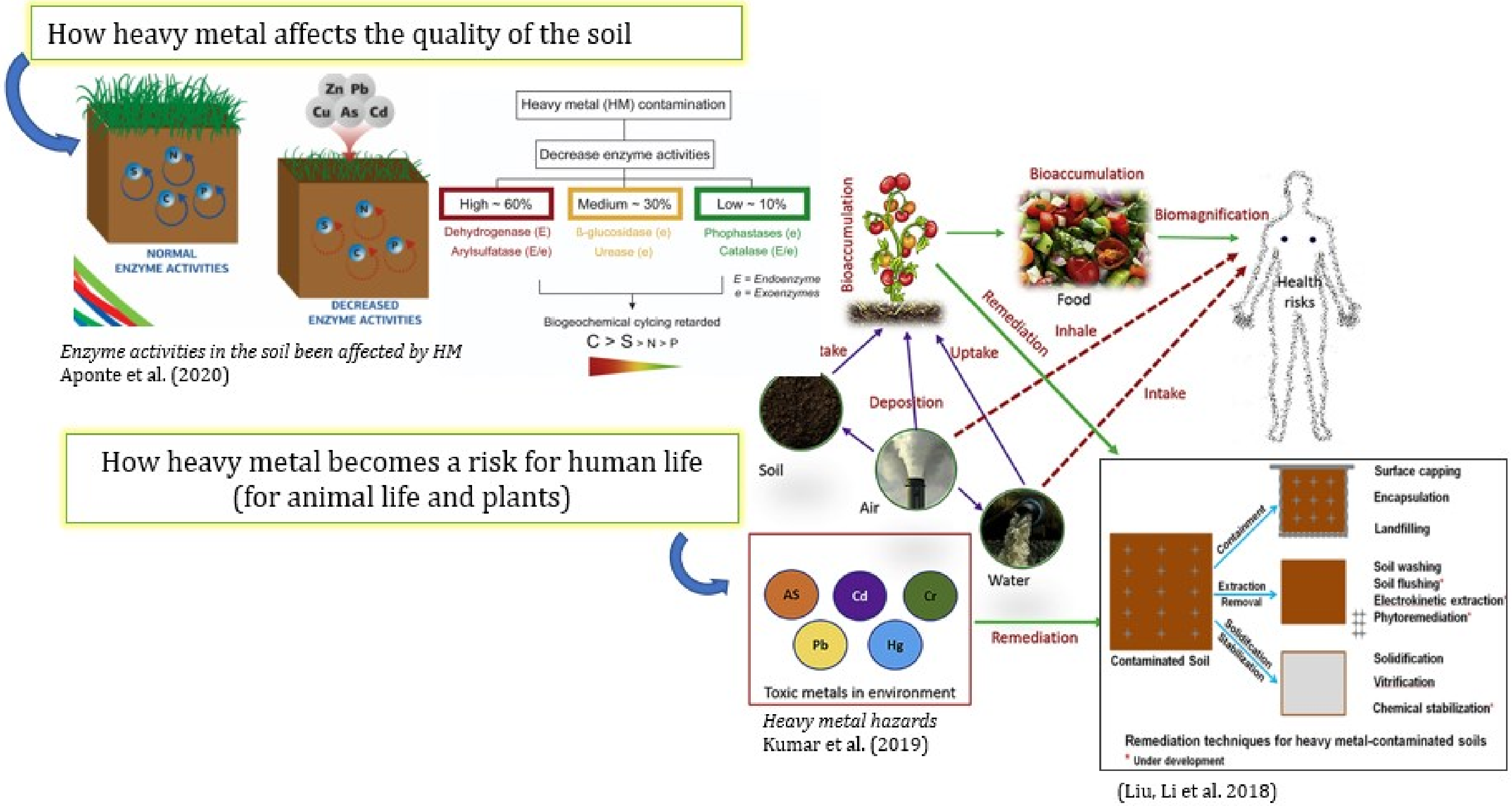

Figure 1.1 Heavy metal hazards, fate and remediation (Liu et al. 2018, Kumar et al. 2019, Aponte et al. 2020)

The primary source of pollution by toxic metals in South Korea is associated with abandoned mines (Kim et al. 2001), which was related to the extensive metal–mining activity that was developed during the early 20th century(Jung 2008) and the extension of industrial zones during the recent years (Kwon et al. 2019). According to the Korean Government report in 2015, only in Gangwon, specifically in Chungbuk, the study found that 72 of 140 abandoned metal mines have toxic metal concentrations over the Korean Standard. The areas that exceeded the standard by soil pollutant with Arsenic were 54 places, zinc 34 places, lead 28 places, cadmium 16 places, copper 12 places, and mercury were 3 places①.

For soil remediation, in-situ technologies such as a soil vapor extraction and bioventing are applied the most in South Korea. However, these are not suitable for contaminants such as toxic metal. Soil remediation techniques for toxic metals are soil washing, soil replacement, soil capping and chemical oxidation/reduction applied in lower percentages. S/S is in the category of others for In-situ technologies, according to Figure 1.2.

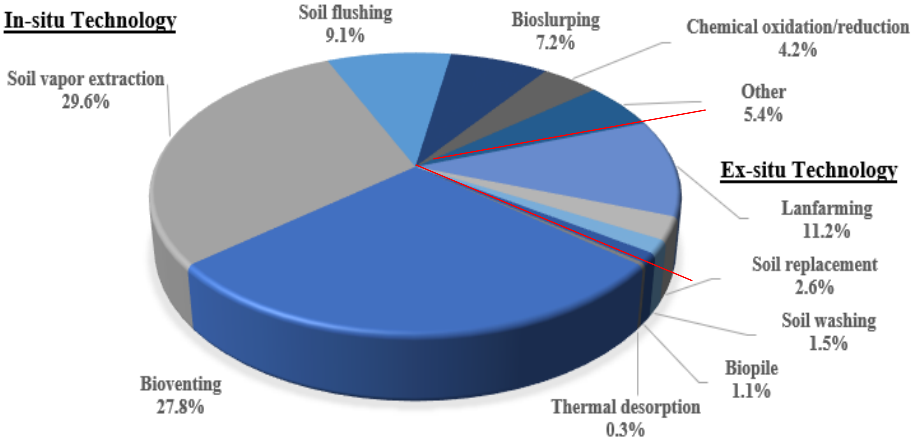

Figure 1.2 Soil remediation technologies in Soil Korea (Yang and Lee 2007)

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① 환경부 – 강원 · 충북지역 140개 폐금속광산 중 72개소에서 중금속 오염 https://www.ebn.co.kr/news/view/808547

1.2 Purpose of research

The main objectives of this thesis are to use low-cost materials derived from recycling materials (oyster shell and red mud) and zeolite, also considered as low-cost adsorbent material, as binders for immobilizing toxic metals in a variety of contaminated soil cases to evaluate their efficiency and identify the binding mechanisms associated with them. Secondary objectives are to identify the factors that can alter each binder's efficiency, such as initial concentration of the contaminant, binder dosage, contact time, and pH value in the medium. Besides, all concentration data reported in this thesis passed through a statistic evaluation using descriptive statistics and ANOVA one-way analysis.

As granular soils have a lower capacity to retain these toxic metals, the low-cost materials might chemically stabilize soils quickly before the metals leach into groundwater levels. Materials that come from recycling waste after converting them into new forms is at the same time a sustainable solution because it reduces the environmental impacts generated by improper waste management.

Therefore, the current study investigated the performance of oyster shell, zeolite, and red mud in stabilizing diverse contaminated scenarios; two of them, from real scenarios of granular contaminated soils with toxic metals concentrations close to permissible limits at a laboratory scale (Case I and Case II). Then, due to the worldwide presence of Pb pollution in soils in high concentrations (Du et al. 2014), considered evaluating the immobilization of Pb in a handmade contaminated soil with high Pb concentration (Case III). Moreover, because it is well-known that toxic metals such as Pb, Cu, Zn, Ni, and Cd have different behaviors than Arsenic in the environment, a different type of binder evaluation was set up to check its performance against arsenic.

To do this, two additional tests were implemented, one named pot cultivation test to determine the degree of effectiveness in treating an *As*-soil in soil environment and the second one named sorption batch test to simulate an As-aqueous environment.

To quantify the toxic metal concentrations before and after binder application, in this research diverse leaching tests were used. For example, the leaching test using deionized water (DI) or other extraction acid agents indicated in the toxicity leaching characteristic procedure (TCLP) and Mehlich-3 extraction procedure. The two last mentions were for measuring toxicity and bioavailability of toxic metals after applying oyster shell powder, zeolite, and red mud as binder stabilizers for immobilizing toxic metal in each soil case scenario.

Chapter 2 : Literature review

2.1 Stabilization/ Solidification

Stabilization/ Solidification (S/S) involves adding adsorbent or cement material into the soil to reduce the mobility of contaminants or exposure hazards in soil. On the field, it can be applied in-situ (direct addition of binder) or ex-situ (outside the area). In-situ stabilization can be reached by (a) conventional or chemical grouting to reduce hydraulic conductivity and/or fix contaminants such as toxic metals. Meanwhile, ex-situ stabilization could include processes such as excavation, stockpile construction, or off-site disposal (Du et al. 2010). Various amendments have been investigated for PTE immobilization in soil environments, as is observed in Figure 2.1 being sorption/ desorption reactions as well as chemical complexation with inorganic and organic ligands. They are important in controlling the potentially toxic element bioavailability, leaching, and toxicity (Violante et al. 2010, Palansooriya et al. 2020).

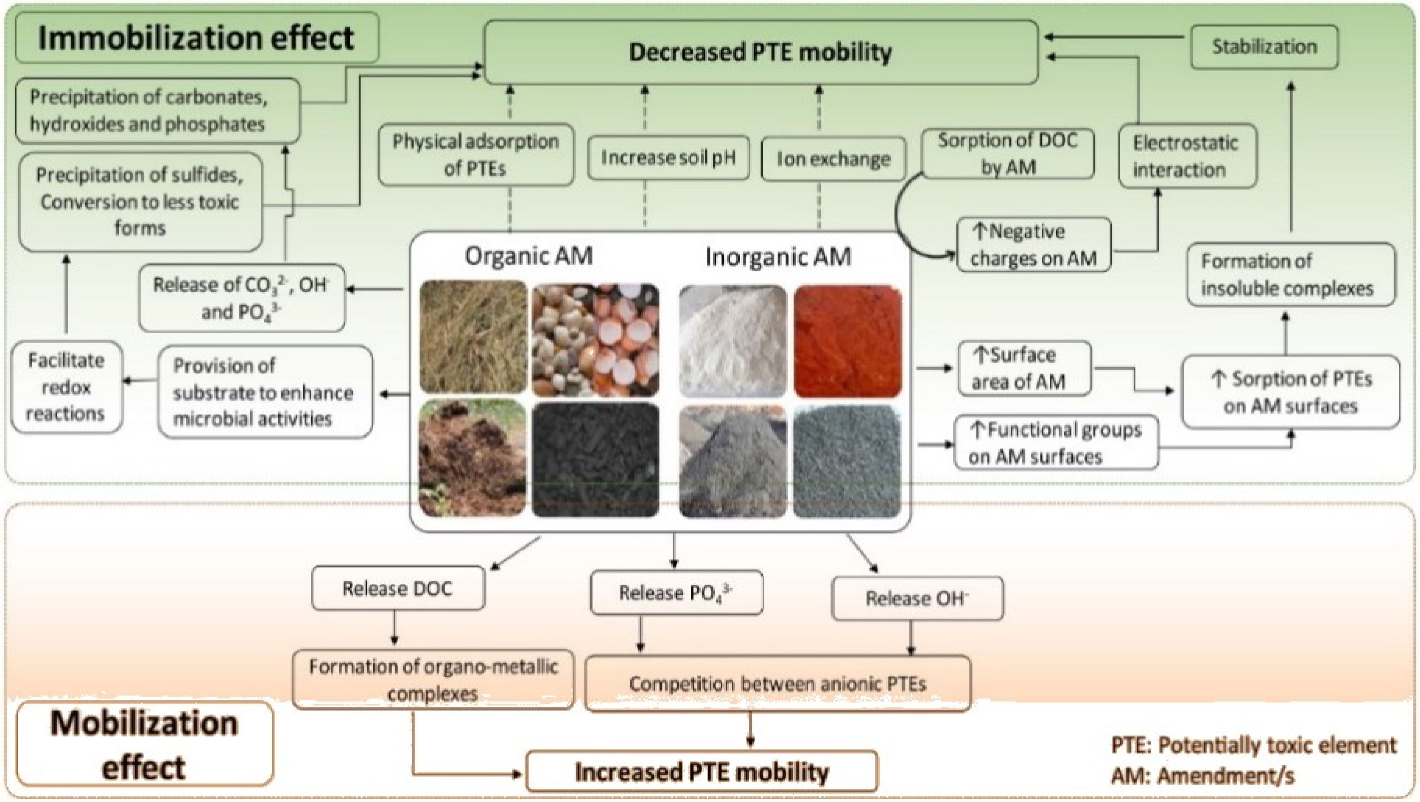


Figure 2.1 Mechanisms of PTE immobilization and mobilization from various organic and inorganic soil amendments (Palansooriya et al. 2020)

2.2 Leaching test

Leaching tests were first used for environmental assessments of waste during the early 1980s. Fallman and Aurell (1996) mentioned that leaching tests are mainly used for determining 1) the total content of a pollutant and its ability to leach under specific conditions; 2) the time-dependent release from the material by equilibrium or diffusion-controlled leaching (a column percolation test); 3) changes in geochemistry by environmental conditions, time, or by leaching; 4) how changes of the pH and redox potential during the leaching process influences the time-dependent release which can help us to determine if the material can be recycled, transformed or only be disposal.

To assess the effectiveness of each binder used in S/S, diverse methods and laboratory practices for measuring the leachability of these inorganic substances (toxic metals) from waste materials are performed. First, performing a leaching test using DI water as an extracting agent aims to quantify the concentration of the pollutant under non-aggressive conditions. Second, it is crucial to determine its potential toxicity and its bioavailability after binder addition.

According to Method 1311, Toxicity Characteristic Leaching Procedure (TCLP) is designed to determine the mobility of both organic and inorganic contaminants present in the liquid, solid and multiphasic wastes (U.S. EPA 1992). This method indicates the acetic acid CH_3COOH (pH 2.88) as the extractant agent. The solution was prepared and mixed with the sample for extraction in a relation of liquid/solid ratio (L/S) of 20:1. Like all kinds of methods, there are some limitations; for example, TCLP may not be effective for determining metal leaching potentials if the pH of the leaching solution turns alkaline during the test (Lu et al. 2019), thus pH control is essential.

Others leaching experiments such as sequential extraction can overestimate toxic metals mobility; therefore, single extraction with acetic acid can be more suitable for comparing trace metal mobility (Sahuquillo et al. 2002).

On the other hand, the Mehlich-3 method is a weak acid soil extraction procedure based on chelating agents (0.2 M CH_3COOH, 0.25 M NH_4NO_3, 15 mM NH_4F, 13 mM HNO_3, and 1.0 mM EDTA), that has the advantage of being applicable for several elements. Although it is mainly used for the determination of macronutrients (phosphorous, calcium, magnesium, and potassium) and micronutrients (copper, zinc, manganese, and iron), it was also applied to measure the bioavailability of *As*. Because Mehlich-3 (pH=2.5), consisting of several chemicals, removes *As* bound to *Fe/Al* minerals along with dissolved and adsorbed forms of As. Also, EDTA included in the Mehlich-3 solution targets organically-bound *As* fraction but may dissolve a considerable proportion (up to 20%) of *Fe/Al* from amorphous hydrous oxides. Mehlich-3 solution has been widely used to predict nutrient availability for crops (Mehlich 1984).

2.2.1 *Initial toxic metal concentrations*

The concentrations measured in leachate (mg/L) using ICP-OES after conducted TCLP extraction was converted as a fraction of mass (mg/kg) by using Eq. (1) in the Korean standard procedure ES 07400.2c (EHTI 2018).

$$\boldsymbol{C_{(\frac{mg}{kg})} = \frac{(C_1 - C_0)}{W_d} x f x V} \qquad \textbf{(Eq. 1)}$$

where

C_1: metal concentration of the analytical specimens obtained from the calibration curves (mg/L),

C_0: metal concentration of the blank solution obtained from the calibration curve (mg/L),

f: dilution rate,

V: volume of specimen container

W_d: dry weight of soil specimen

2.2.2 *Environmental regulations for toxic metals*

Regulations regarding toxic trace elements' limits can vary from one country to another. These values are based on the definition of its toxicity, corrosivity, ignitability, and reactivity. For example, the U.S. Environmental Protection Agency (USA) implements and enforces the federal statute known as the Resource Conservation and Recovery Act RCRA, which regulates the management of Hazardous wastes(U.S. EPA 2011). China regulates these limits through Soil Environmental Quality Standards for Trace Elements, a publication from the Ministry of Environmental Protection of China, Beijing, China (MEPC 2007). Meanwhile, in South Korea, the government had legislated the law on "Conservation of Soil Environment" in the mid-1990s and managed and treated hazardous wastes in contaminated sites as a remediation policy (Yang and Lee 2007). Table 2.1 resumes these limits by country and environment scenery.

Table 2.1 Permissible limits for toxic metal measuring in leachate, water, and soil

Country & Criterium	**US**	**US**	**China**	**China**	**South Korea**	**Japan**	**Canada**	**WHO**	**South Korea**	**Australia**	**Canada**	**European Union**
	Leaching from waste	**Surface water, fresh water**	**Soil Solution**	**simulation of water runoff (with DI)**	**Leaching from waste**	**Soil Solution**	**Soil Quality**	**Unpolluted Soil**	**In Soil**	**In Soil**	**In Soil**	**In Soil**
	(mg/L)						**(mg/kg)**					
Cd	1	2	1	2	0.3	0.01	22	0.8	10	3	1.4	10
Pb	5	2.5	5	0.1	3	0.01	600	85	400	300	70	200
Zn		120	100	0.01			410	50	600	200	200	250
Cu		9			3		91	36	500	100	63	150
Ni		52					89	35	200	60	50	100
As	5	-	5	0.1	1.5	0.01	12	25	75	20	12	50
Source	(U.S. EPA 2011)	(Buchman 2008)	(MEPC 2007)	(MEPC 2007)	(EHTI 2017)	(Liu et al. 2018)	(CCME 2020)	(WHO 1996)	(EHTI 2017)	(Liu et al. 2018)	(Liu et al. 2018)	(Liu et al. 2018)

* Soil Environmental Quality Standards in China (GB 5085.3-2007)

2.3 Low-cost materials

The technical feasibility of various low-cost materials with sorption properties elicits the interest of the scientific community. Instead of using absorbent, highly efficient but expensive, commercial activated carbon, many researchers explore the use of natural material locally available and the recycling/modification of waste converted into low-cost absorbents (Babel and Kurniawan 2003). The effectiveness of each material used as an adsorbent depends on the target contaminant, and each material exhibits preferences for certain metal ions.

An industrial country such as South Korea generates tons of industrial waste that requires been disposal appropriate. However, the lack of disposal areas makes waste management a challenge—for example, shells waste from the Oyster farming industry or Red Mud waste from the Alumina production. Also, other natural absorbents that are found in nature is Zeolite; the degree of fineness and mineral-chemical compositions could vary, depending on the cost associated with the production of a homogeneous material even though due to the nature of this material, it is also considered a low-cost adsorbent. Looking a cost comparison with a commercial activated carbon on average, the price is 9 US$/kg, but can also reach 22 US$/kg (Babel and Kurniawan 2003). Low-cost adsorbents are 10 times cheaper the CAC. Natural zeolite whose price is 0.04-0.90 US$/kg (Shahrokhi-Shahraki et al. 2020); the OS powder cost used in this study is between 0.5 US$/kg, the synthetic zeolite cost was 2.2 US$/kg, and RM is 0.7 US$/kg (Prices are from domestic suppliers).

2.3.1 *Oyster shell powder (OS)*

OS, a byproduct of shellfish-farming in Korea and containing a high amount of calcium carbonate $CaCO_3$ (Lee et al. 2008, Bonnard et al. 2020) can be used as a liming material in agriculture (Lee et al. 2008) or an alkaline amendment (Palansooriya et al. 2020). South Korea which is the second-largest world producer of oysters after China (Ok et al. 2010) have seen the recycling of oysters as a sustainable solution that should be explored. The oyster farming industry of South Korea produces goods for exporting overseas, around 60%, which are sold in the exemplary form of a canned, dried raw and frozen oyster. It generates a profit of over $100 million every year, and this is directly related to the volume of OS waste generated (Silva et al. 2019). The generation of OS in Ton rise from 258 150 Ton to 465 240 Ton in South Korea between the years 1997 – 2006 (Ramakrishna et al. 2018). According to Huh et al. (2016), the domestic disposal amount of waste from OS reached about 300 thousand tons. At least 50% of those amounts are not being recycled, and they are left just unattended by being field-heaped on the seaside as offshore landfill. The main environmental impact associated with the poor management of OS waste is the release of foul-smelling noxious odors. Also, OS is non-biodegradable, so they can modify local soils, natural water and affect marine ecosystems (Bonnard et al. 2020).

OS have been investigated for their interactions with toxic metal ions in an aqueous medium (Shin et al. 2014, Lu et al. 2018, Xu et al. 2019). However, only a few researchers have investigated their application into the soil (Lim et al. 2009, Jeong et al. 2013, Moon et al. 2013, Zhong et al. 2020). All the methods proposed for recycling OS suggested first collecting and then, washing by using alcohol or other acids to eliminate impurities. Then, dried and crushed until reduced the particle size (depending the proposal use). Many researchers also suggested that calcination at 800°C – 1200°C converts more calcium carbonate $CaCO_3$ to active CaO (Ok et al. 2010), which participate directly in the co-precipitation of toxic metals and adsorption of them on the surface.

2.3.2 *Zeolite (Z)*

Z corresponds to the chemical group of hydrated aluminosilicates of Sodium, Calcium, Magnesium, Potassium, and other alkaline minerals, whose formation is attributable to pyroclastic deposits. The mineral structure consists of 4 oxygen of SiO_4-4 tetrahedra, which are shared with other tetrahedra. This structure is named tectosilicate 3D structure, considered as an open structure. Due to it, Z has voids like tunnels that can loosely hold water molecules, and these tunnels can adsorb molecules smaller than tunnel diameter (Georgiannou et al. 2017).

Several kinds of research have inquired about zeolites' function in pollutant removal from water and sediment environments. Mainly, Z' sorption characteristics and cation exchange capacity have been studied extensively for their potential in removing toxic metals from water (Grant et al. 1987, Zamzow et al. 1990, Ouki and Kavannagh 1997, Erdem et al. 2004, Parades-Aguilar et al. 2020). Like OS powder, Z has not been investigated in terms of its use in remediating soil, although a few studies investigated this subject (Wen and Zeng 2018). However, it is expected that due to its similarity to clay minerals, isomorphic substitution of Si by Al in three-dimensional lattice of the zeolite is the cause of a net negative charge, which is balanced by exchangeable cations (Wingenfelder et al. 2005).

2.3.3 *Red Mud (RM)*

The increase in demand for products containing aluminum has ended up in an increase in aluminum worldwide production. RM or Bauxite residue of the Bayer process used in alumina production is classified as an industrial waste due to its strong alkalinity. The chemical composition of RM varied on the bauxite ore and the refining process, is mainly Al_2O_3, Fe_2O_3, and SiO_2. The total stockpile of RM reported in the world reached 4 billion tons (Archambo and Kawatra 2020), and the annual RM pile rate is around 140 million tons(Venkatesh et al. 2020). In South Korea, KC Co., Ltd, located in Yeongan, Jeollanam-do has generated around 300,000 tons/year of RM (KIGAM 2015). This material has been studied as intermediate cover material for 1) a waste landfill and 2) the feasibility of using it for neutralization as a potent alkaline base for acidic mineral debris (waste-rock and tailings). RM has gained popularity in remediating contaminated soils (Wang and Liu 2012); however, its application has been limited due to the health risks associated with its use (Ujaczki et al. 2015).

Chapter 3 : Materials and methods

3.1 Materials

3.1.1 *Contaminated soil*

The first binder evaluation consisted of batch experiments through leaching tests. The soil samples collected from two sites contaminated with toxic metals; Case I: soil from surroundings of an abandoned metal mining area that was classified as silty sand (SM) with fines content of 22% (denoted as "silty sand") and Case II: soil from a military service area that was classified as well-graded sand (SW) with fines content lower than 5% (denoted as "sandy soil"). The sites are respectively located at 62, 26 beon-gil, Gaegeumonjeong-ro, Gaegeum-dong, Busan, and San 65-1, Jangan-ri, Jangan-eup, Gijang-gun, Busan, South Korea.

In addition, an artificially highly Pb-contaminated soil was made using as a base the weathered granite soil from Gwanak Mountain. This case III, artificially Pb-contaminated soil was prepared following an approach like that of Martini and Shang (2018); highly contaminated soil (denoted as HCS) was made by mixing 4 kg of residual weathered soil (passed through a 2 mm mesh) classified as "well-graded sand" with Pb solution. Firstly, the sieved soil was analyzed for the presence of toxic metals. Secondly, 67 g of $PbCl_2$ was dissolved in 2 L of DI water. The solution was introduced into the soil and thoroughly mixed using an electric mixer until a homogeneous slurry was achieved. The slurry was kept at room temperature for two days and then dried at 100 °C for 24 h. Lastly, the spiked soil mixture was homogenized by diagonally flipping it 3–5 times on a plastic sheet. Overall, HCS had an initial concentration of 100× the maximum permissible level for Pb in South Korea, i.e., 3 mg/L.

The second binder evaluation involves probing the binders on an As-contaminated soil, Case IV: from an industrial zone located in Ipjang-myeon Hongcheon-ri 33-8, Chungcheong Nam-do, Cheonan-si, South Korea (denoted as “As-soil”). All the soil samples collected from the real scenario were air-dried and passed through a 2 mm mesh before preliminary analysis and experiments. Table 3.1 showed the initial toxic metal concentrations of the soil used in this study; these values have been used as a control value to measure binder efficiency.

Table 3.1 Toxic metal concentrations in leachates before binder application.

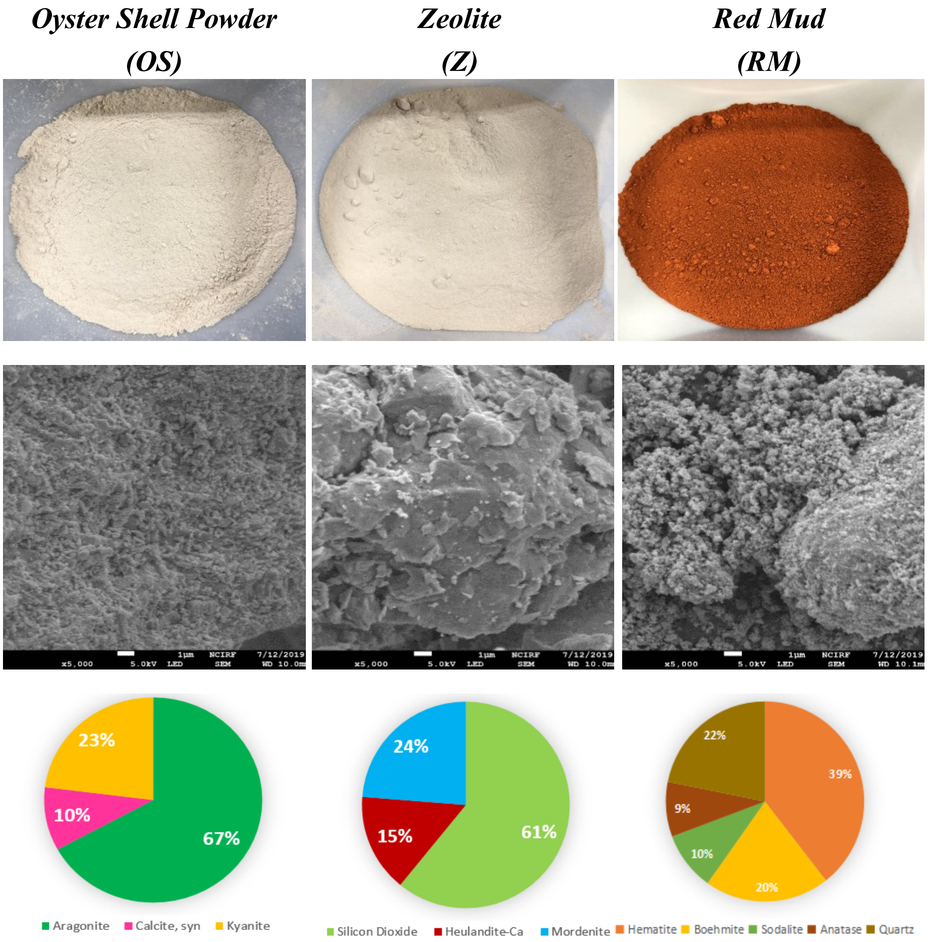
1st binder evaluation						
Source	**Extraction Method**	**Initial concentrations**				
		Pb	**Cu**	**Zn**	**Cd**	**Ni**
	DI (mg/L)	0.015	0.110	0.045	0.002	-
Case I	TCLP (mg /L)	0.639	3.954	102.784	0.316	0.432
	TCLP (mg/Kg)	12.780	79.080	2055.680	6.320	8.640
	DI (mg/L)	0.550	0.210	0.450	0.003	-
Case II	TCLP (mg/L)	0.079	2.235	10.053	0.046	-
	TCLP (mg/Kg)	1.580	44.700	201.060	0.920	-
	DI (mg/L)	301.657	0.440	-	-	
Case III	TCLP (mg/L)	159.802	0.444	-	-	-
	TCLP (mg/Kg)	3196.04	8.880	-	-	-
2nd binder evaluation						
		Pb	**Cu**	**Zn**	**Cd**	**As**
	DI (mg/L)	-	0.015	0.019	-	0.101
Case IV	TCLP (mg/L)	-	-	0.388	-	0.318
	TCLP (mg/kg)		-	7.760	-	6.360
	M-3 (mg/L)	0.445		0.560		0.637
	M-3 (mg/kg)	4.45		5.600		6.370
	Aqua regia (mg/kg)		40.653	74.454		133.77

The main physical and chemical characteristics of the soils used in this study are presented in Table 3.2.

3.1.2 *Binders*

The first binder evaluation considered the following materials: oyster shell powder (Jisan Industrial Co., Ltd., Busan, Korea), natural zeolite (Kumnong Industrial Co., Ltd., Pohang, Korea), and red mud (Sanha E&C Co., Ltd., Gyeonggi, Korea). Prior to using them as binders, all the materials were washed with DI water, dried, and sieved (through a 0.15 mm mesh). Besides, the initial pH of Red Mud was lowered to 8.5–9 prior to using 1 M HCL.

SEM-EDS (Scanning Electron Microscopy and evaluated via Energy-Dispersive X-ray Spectroscopy, model Supra 55VP, Germany), xRF, xRD, and Cation Exchange Capacity (CEC) were measured by NICEM (an analysis agency in Seoul National University). All the binders were observed by SEM-EDS to observe the structure of each binder (i.e. surface and porosity) and by XRF to determine their chemical compounds, see Figure 3.1 .and Table 3.3.



CaO – 94.59%

SiO_2 – 70.75%
Al_2O_3 – 13.93%

Fe_2O_3 – 39.47%
Al_2O3- 17.47
SiO_2 15.18

Figure 3.1 SEM analysis, quantity analysis by XRD and main chemical compounds② by XRF analysis of the binders used in the first binder evaluation

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② Information provided by the project: “중금속 오염부지 시나리오를 고려한 최적의 안정화제 개발”

For the second binder evaluation, the materials to be tested facing As-Contamination changed to Oyster Shell Powder provided by Jisan Industrial CO. Ltd, which is an agricultural amendment. Meanwhile natural Zeolite was replaced by a synthetic Zeolite 4A produced by Zeobuilder (Seoul, Korea) identified with chemical form as $Na_{12}[(AlO_2)_{12} (SiO_2)_{12}] 27H_2O)$. The chemical characteristics of these materials slightly differ from the previous ones, XRD results for these binders was performed in the Department of Chemical and Biological Engineering at Seoul National University while XRF was analyzed by NICEM. Results are shown in Figure 3.2 and Table 3.3.


Oyster Shell Powder (OS)

Zeolite 4A (Z_{4A})

CaO – 94.17%

SiO_2 – 71.73%
Al_2O_3 – 17.55%

Figure 3.2 Characteristics, texture and porosity (by SEM analysis), quantity analysis by XRD and main chemical compounds by XRF of the binders used in the second evaluation

Table 3.2 Physio-chemical properties of the contaminated soil and binders used in this study

Property	**Chemical Form**	**pH**	**Classification (USCS ASTM D 422)**	**Specific gravity (ASTM D 854)**	**Cation Exchange Capacity (meq/100g)**	**Specific Surface Area (m^2/g)**
1st binder evaluation						
Case I: Soil from Mining area	Quartz (50.46%), Calcite, Albite	8.1	SM		23.09	-
Case II: Soil from Military area	Quartz (60.79%), Muscovite, Albite	6.7	SW	2.68	10.02	-
Case III: Gwanak weathering soil	Quartz (67.35%)	7	SP	2.63	5.45	-
Oyster Shell Powder	$CaCO_3$	8.5	ML	2.69	4.42	2.13
Zeolite	SiO_2; $Ca_4(Al_8Si_{28}O_{72}).24H_2O$ $Na_4(Al_8Si_{28}O_{72}).24H_2O$	6.5	SP	2.34	7.76	44.97
Red mud	-		ML	2.45	66.81	-
2nd binder evaluation						
Case IV As-soil from Industrial zone	Quartz (67.35%), Microcline, Albite, Muscovite	7.9	SP	2.68	9.58	-
(New) Oyster Shell	$CaCO_3$	8.5	ML	2.71	4.81	-
Zeolite 4A	$Na_{12}[(AlO_2)_{12}(SiO_2)_{12}]\ 27H_2O$	10.87	ML	2.10	311*	-

Table 3.3 Chemical compositions of the silty sand soil, sandy soil and HCS; the binders, namely, oyster shell (OS), zeolite (Z) and red mud (RM) used in the 1st binder evaluation and As-soil, new oyster shell (OS*) and synthetic zeolite 4A (Z_{4A}) used in the 2nd binder evaluation, observed via X-ray fluorescence analysis.

	1st binder evaluation						**2nd binder evaluation**		
	Case I Silty sand soil③	**Case II Sandy soil③**	**Case III HCS**	**OS**	**Z**	**RM**	**Case IV: As-soil③**	**OS***	**Z_{4A}**
SiO_2	50.46	67.35	53.62	0.240	70.75	15.18	60.79	2.27	71.73
Al_2O_3	19.01	18.79	24.95	0.013	13.93	17.47	24.64	0.628	17.55
Fe_2O_3	7.98	3.34	8.41	0.033	2.75	39.47	3.1	0.517	0.006
CaO	10.68	2.96	2.33	94.59	1.61	1.99	2.5	94.17	0.09
MgO	2.81	1.36	1.51	0.550	0.91	0.23	2.19	0.545	-
MnO	0.34	0.12	0.12	0.007	0.102	0.04	-	0.036	-
ZnO	0.48	0.07	0.02	-	-	-	-	0.011	0.001
Na_2O	1.66	1.46	1.81	1.100	3.95	10.46	1.14	0.46	10.20
K_2O	3.17	3.62	3.66	0.040	3.17	0.06	4.18	0.156	0.08
P_2O_5	0.89	0.20	0.70	0.110	0.105	0.12	0.54	0.375	0.33
TiO_2	1.54	0.61	1.06	0	0.38	6.85	0.59	0.06	-
Cr_2O_5	0.34	-	-	-	-	-	-		-
SO_3	0.64	0.11	-	-	-	-	0.32	0.511	-
PbO	-	-	1.11	-	-	-	-		-
Cl	-	-	0.44	-	-	-	-	0.132	0.02
Others	-	0.01	0.26	3.317	2.343	8.13	0.01	0.129	0

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XRD performed to identify the structure of each binder in the second methodology for binder evaluation. The test was conducted in the Smart Lab by Rigaku with Cu radiation (Chemical and Biological Engineering Research Facilities at Seoul National University). The XRD patterns were collected at 2θ values in the range of 5°– 70°, with a 2θ step size of 0.02° and a count time of 4 s per step. The qualitative analyses of the XRD patterns were conducted using the Match! Version 3 (Developed by Crystal Impact launched in Germany 2021) with reference to the patterns present in the International Centre for Diffraction Data database (ICDD 2002).

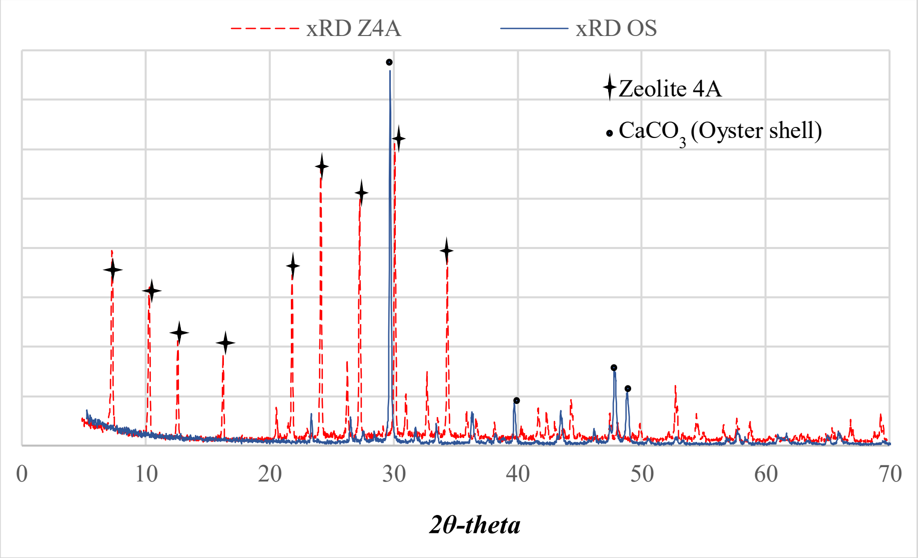


Figure 3.3 XRD analysis of OS and Z_{4A}

3.2 Experimental procedure

3.2.1 *Batch leaching experiments*

First binder evaluation consisted of batch experiments applying the binder to the contaminated and mixing them with DI water following a procedure similar to that used for leaching with DI water in HJ-557-2010 (MEPC 2010). The liquid: solid ratio (L/S) and mixing time was adjusted to obtain a homogeneous mixture of soil and binder. Firstly, a batch leaching tests with the modified DI water leaching procedure was performed on the control samples (i.e., contaminated soil without binder).

The experiment procedure is described as follows. All the samples were tested at least in duplicate.

a) The test was initiated by taking samples of 50 g of air-dried soil as the control and measuring the initial toxic metal concentrations (Pb, Cu, Zn, Cd and Ni). Then, 50 g of stabilized soil under different binder dosages per total weight (1, 3, 5, 7 and 10 wt%) was placed in a 250 mL glass flask and agitated for 2 h at 150 rpm with DI water at an L/S of 3.

b) The supernatant fluid from the previous step was extracted 8 h after step a. For silty sand soil, however, additional extractions were performed at 12, 24 and 36 h after the first extraction to evaluate the effect of contact time with the binder on soil. After the supernatant fluid was extracted, it was filtered using a 0.45μm membrane filter and then collocated in a 14 mL tube for toxic metal (Pb, Cu, Zn, Cd and Ni) concentration measurement via inductively coupled plasma optical emission spectroscopy (ICP-OES). Furthermore, pH was measured using a Thermo Scientific Orion 5-Star Plus Portable pH/ORP/ISE/Conductivity/ DO Multiparameter Meter Model Number: PH3642-2 (Beverly, MA, USA) as presented in Table 3.4.

c) The control samples (without binder) and stabilized soil (after step b, solid phase) were placed in an oven and dried at 60 °C for 24 h.

d) TCLP test was conducted on all the soil samples obtained after step c.

TCLP test was performed to measure toxic metal concentration in accordance with the U.S. EPA Method 1311 (U.S. EPA 1992, Lu et al. 2019) because CH_3COOH, as an extract reagent, achieves better harmonization during the laboratory testing of leaching compared with other reagents, such as EDTA. Furthermore, acetic acid was used as the reagent because it represents a scenario in which organic acids are found in leachates from landfills. The steps for the TCLP test are described as follows.

e) A 2 g sample (from Step c) was placed in small tubes that contained 40 mL of the extract solution (L/S = 20). Extract solution type depends on the pH of the medium.

f) After mixing thoroughly using a rotary tumbler at 30 ± 2 rpm for 18 h, the samples were allowed to settle for 12 h. Then, the supernatant fluid was extracted and filtered using a 0.45 µm membrane filter and collocated in tubes with a 14 mL capacity to measure toxic metal concentration via ICP-OES. For the HCS treated with OS, additional extractions were performed after 1 day and 10 days of mixing to evaluate the effect of contact time.

g) Lastly, the pH of the leachate was measured and reported in Table 3.5. A summary of the experiment procedure is presented as Figure 3.4.

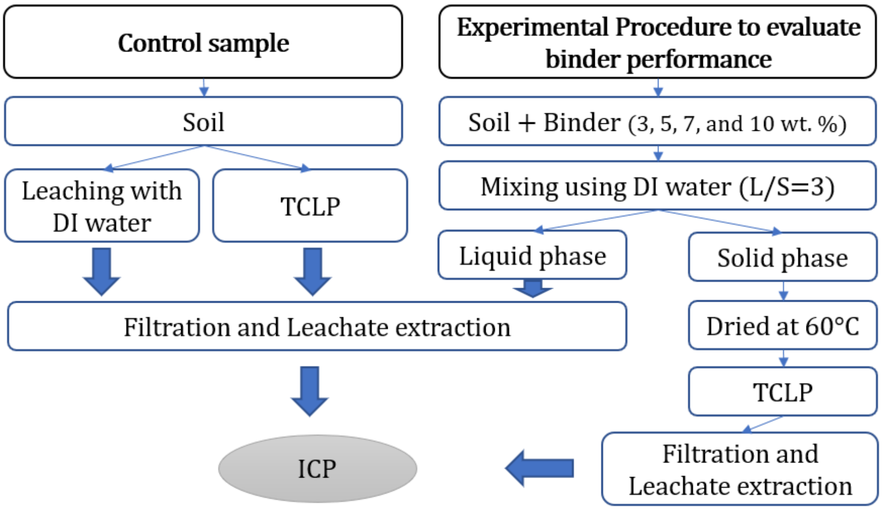


Figure 3.4 An overview of the experimental procedure

Table 3.4 pH value of the contaminated soils considered in this study after the addition of binders at various dosages.

Source	pH	Soil + Binder	1%	3%	5%	7.5%	10%
Abandoned metal mine site (silty sand soil)	8.13 ± 0.16	+ OS	7.95 ± 0.08	7.87 ± 0.06	8.01 ± 0.17		
		+ Z	7.75 ± 0.15	7.67 ± 0.16	7.62 ± 0.19		
		+ RM	7.96 ± 0.07	8.40 ± 0.21	9.03 ± 0.09		
Military service area (sandy soil)	6.70 ± 0.15	+ OS	7.59 ± 0.20	7.78 ± 0.16	7.68 ± 0.36		
		+ Z	6.37 ± 0.12	6.44 ± 0.14	6.46 ± 0.12		
		+ RM	8.04 ± 0.14	8.90 ± 0.12	9.44 ± 0.04		
HCS	4.90 ± 0.15	+ OS	7.31 ± 0.40	7.88 ± 0.12	7.65 ± 0.08	7.76 ± 0.27	7.50 ± 0.01
		+ Z	4.47 ± 0.05	4.59 ± 0.11	4.73 ± 0.04	4.94 ± 0.01	5.17 ± 0.01
		+ RM	6.24 ± 0.01	8.13 ± 0.18	8.62 ± 0.01	9.13 ± 0.10	9.61 ± 0.02

Table 3.5 pH value of the contaminated soils treated with binders after performing leaching test by TCLP.

Source	Soil + Binder	1%	3%	5%	7.5%	10%
Abandoned metal mine site (silty sand soil)	+ OS	5.22 ± 0.25	5.59 ± 0.38	6.78 ± 0.15		
	+ Z	5.12 ± 0.21	5.00 ± 0.10	5.01 ± 0.08		
	+ RM	4.99 ± 0.08	5.05 ± 0.04	4.99 ± 0.08		
Military service area (sandy soil)	+ OS	3.81 ± 0.06	4.48 ± 0.32	5.61 ± 1.16		
	+ Z	3.28 ± 0.02	5.00 ± 0.10	5.01 ± 0.08		
	+ RM	3.60 ± 0.06	3.92 ± 0.04	4.10 ± 0.02		
HCS	+ OS	5.18 ± 0.01	5.42 ± 0.03	6.35 ± 0.06	7.36 ± 0.06	7.54 ± 0.01
	+ Z	4.47 ± 0.01	4.52 ± 0.08	4.77 ± 0.11	4.88 ± 0.11	5.28 ± 0.05
	+ RM	4.75 ± 0.18	5.38 ± 0.11	6.80 ± 0.12	7.25 ± 0.08	7.98 ± 0.05

3.2.2 *Pot cultivation test in As-soil*

OS and Z probe have a positive effect on the treatment of heavy metals such as Pb, Cu, Cd, and Zn. However, *As*, has a different behavior associated to its metallic nature and its consequent anionic character (Harper and Haswell 2008). Thus, the pot cultivation test was considered as a second methodology for binder evaluation.

The pot cultivation test recreates field conditions such as moisture content (around 30%) and the lack of sun light into the ground. This aims to evaluate the binder facing As-contamination in soils. Control samples and treated soil was preserved under dark conditions in polypropylene amber wide neck round bottles. The steps are described as follow:

a) In 14 polypropylene amber wide neck round bottles of 250 ml capacity, 150 g of soil with 30% moisture content was set up in each bottle. First, 2 bottles for the control samples, and in the remaining 12 bottles, OS, Z and OS/Z was added in a proportion of 3% and 5% of the total weight. Soil, water and binder were thoroughly mixed and placed in each bottle. The experiment was conducted in duplicate for each sample.

b) Samples were collected each week starting with time control 0 (t0) immediately after mixing and then settled in the bottles. The bottles were put down in a dark space and covered to keep their temperature constant. The collection of samples continues for seven weeks (49 days).

c) After removing a small sample from each bottle, the wet soil weight was measured, then samples were carried to the oven for drying them at 60°C for 24 h. After that, moisture content was calculated.

d) Finally, bioavailability of *As* was examined by using Mehlich-3 extraction. In a flask glass of 100 ml capacity, 5 g of the sample was placed in 50 ml (L/S=10) of extraction solution, later agitated at 120 rpm for 5min with a final pH control after extraction.

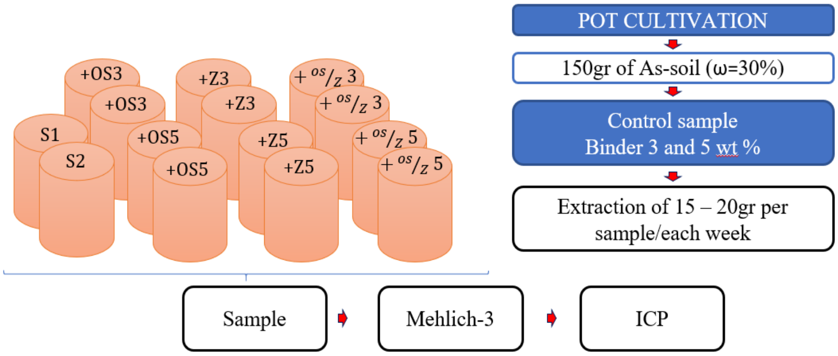


Figure 3.5 An overview of the experimental procedure of the second evaluation of the binder (tested binders on As-soil) – Pot cultivation test

3.2.3 *Sorption test in As-solution*

Complementing the binder evaluation facing *As* contamination, batch sorption experiments were conducted to evaluate the binders (OS and Z_{4A}) in an *As*-aqueous solution. It consists of evaluating the adsorption of "*As*" from a solution by an absorbent at equilibrium. Using *As*-standard solution of 1000 mg/L (As_2O_3 ▪ $NaCl_{(0.05\%)}$ ▪ HCl), authors prepared the solution of *As(III)* of 250 ppm, 100 ppm, 50 ppm and 5 ppm. For determining the adsorption capacity of each binder independently, 50mL of *As*-solution were set up in 100ml flask glass, and the binder was added at different binder-to-liquid (S/L) ratio 1:20 (2.5 g), 1:10 (5 g) and 1:5 (10 g). The suspensions were agitated at 180 rpm for 24 h, centrifuged at 3500 rpm for 20 min, and filtered by a 0.45μm membrane filter. The initial pH value for all suspensions was measured before and after binder addition by using a using a Thermo Scientific Orion Series – Model Meter 121900 (USA).

3.2.4 *Geotechnical tests*

The addition of these materials in the soil can alter some geotechnical parameters. The values of the specification to use materials as fill is suggested by the Ministry of Land, Infrastructure, and Transport of Korea. Geotechnical tests were performed to evaluate the strength of soil-binder mixtures. To identify the effects of the binder addition, the fine granular part of Gwanak weathered soil was used as blank soil for further comparisons by performing:

a) Standard compaction test

Binder was added to the soil in a proportion of 10% the total weight in the soil blank, then the compaction test was performed following the ASTM D 698 method.

Figure 3.6 Compaction test ASTM D 698

b) Direct shear test

The direct shear test was performed to evaluate the strength parameter of soil- binder mixtures. The test was performed following the ASTM D 3080 method. The mixtures were compacted with 95% of maximum dry unit weight at optimum water content determined previously in the compaction test.

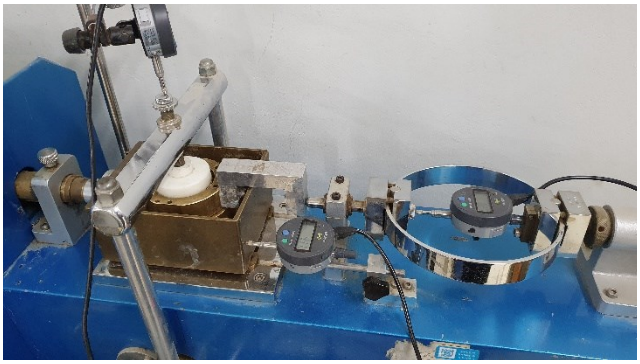


Figure 3.7 Direct shear test apparatus

Chapter 4 : Results

4.1 Batch experiments

4.1.1 *Case I: Silty Sand Soil from an Abandoned Metal Mine Site*

The silty sand soil had an initial pH between 7.97 and 8.29 due to the presence of CaO (Table 3.3). When mixed with different dosages of OS, Z and RM, the pH of the soil changed to 7.87–8.18, 7.60–7.81 and 7.89–9.12, respectively. The dosages of OS and Z exerted no significant effect on the pH of this soil, whereas RM dosage had a significant effect on pH (Table 3.4). Also, measuring the toxic metal concentrations after binder mixing with DI water at different times (0, 12, 36 and 60 h) in the leachate showed that some binder acts faster than others in reaching equilibrium, for example in the effect of OS over Pb and Zn was immediately, immobilizing up to 70% of Pb; it did not improve with increasing contact time. Zn and Cu immobilization in soils stabilized with Z and RM are dependent on the contact time (Figure 4.1).

We observed that this soil had an initial Cu concentration (Table 3.1) that exceeded the South Korean regulation value for leachate and the World Health Organization (WHO), Australian and Canadian guideline values for soil (Table 2.1). Moreover, the silty sand soil contained Cd and Zn concentrations beyond the recommended guideline values. Meanwhile Pb and Ni were below the guideline limits. After adding 5 wt% of OS, the concentration of Cu in the leachate was reduced from 3.954 mg/L to 0.937 mg/L (Figure 4.2), i.e., a reduction of 76% (Figure 4.4), which is below the Korean regulation (<3 mg/L) and the limits stipulated by WHO. Zn was reduced from 102.784 mg/L to 68.657 mg/L, which is also under relevant limits (Figure 4.2 and Figure A.1). Moreover, Cd concentration in the leachate decreased from 0.316 mg/L to 0.182 mg/L, satisfying the condition for toxic metal presence in wastewater (U.S. EPA 2011). Although the initial Pb and Ni concentrations were below the regulatory values, their concentrations were also reduced with increasing OS dosage. In the case of zeolite, a dosage of 1 wt% reduced Cu and Pb concentrations by 50%; thereafter, binder dose exerted no further effect (Figure 4.4). This phenomenon was also observed for Zn and Ni with a dosage of over 3 wt%. Furthermore, Z appeared ineffective in binding Cd in soil at any dosage (Figure 4.2 and Figure A.1). Although the leachates from the soil were stabilized with Z at concentrations below the relevant guidelines (except for Cd), the reduction was considerably lower compared with that of OS. However, the leachate from the silty sand soil mixed with RM presented a higher amount of Cd than the initial concentration, suggesting the poor adsorption of Cd by RM. A dosage of 3 wt% was effective for stabilizing Cu and Zn, whilst increasing the dosage from 3 wt% to 5 wt% yielded no significant benefit ($p > 0.05$). Like OS, the performance of red mud in binding Pb and Ni increased with dosage.

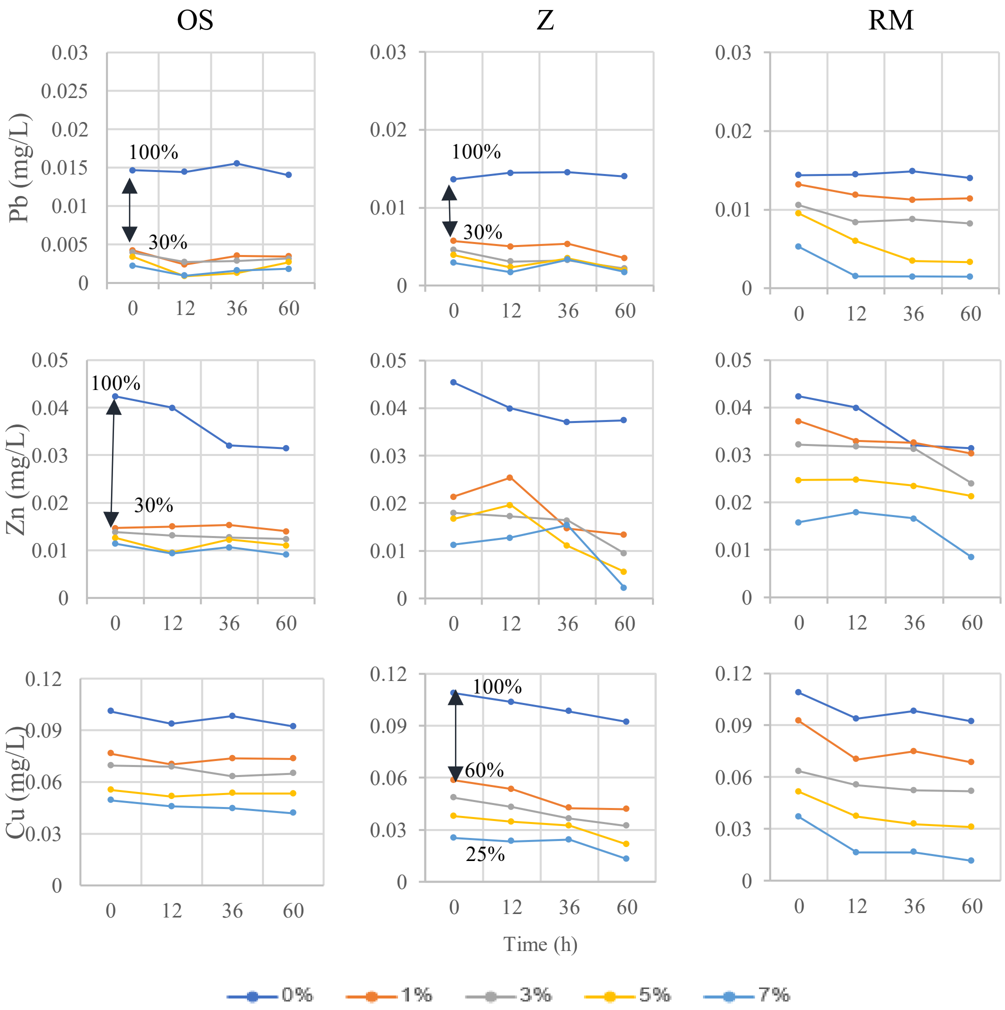


Figure 4.1 Mean toxic metal concentrations measured in the leachate at 0, 12, 36 and 60 h after mixing the binder with silty sand soil from Case I.

4.1.2 *Case II: Sandy Soil from a Military Service Area*

Meanwhile, the sandy soil had an initial pH between 6.55 and 6.85. When mixed with OS, Z and RM, pH changed to 7.59–8.04, 6.25–6.58 and 7.90–9.48, respectively (Table 3.4). The addition of OS and RM increased the pH of the medium, whereas the addition of Z reduced the pH of the medium.

Initially, the sandy soil was slightly contaminated with Zn (201.060 mg/kg) on the basis of the Korean, Canadian, Australian (<200 mg/kg) (EHTI 2017, Liu et al. 2018) and WHO (<50 mg/kg) (WHO 1996) regulations, as presented in Table 2.1. Other toxic metal concentrations were under the guideline values (Figure 4.2 and Figure A.2). Zn concentrations in the leachate were below the maximum permissible level for all the soil samples stabilized with 5 wt% dosage of any of the binders considered in this study. With a 5 wt% dosage of OS, Z and RM, lead to Zn immobilization rates of 50%, 37% and 24%, respectively, as shown in Figure 4.4. Controversially, the addition of red mud increased Pb concentration by a factor close to two, but still values are under regulatory levels. Even though, Cu was below the relevant guideline values, our findings implied that applying OS, Z and RM immobilized 86%, 42% and 37% of Cu, respectively (Figure 4.4). Overall, OS exhibited the highest immobilization rate for all the toxic metals considered in this case study.

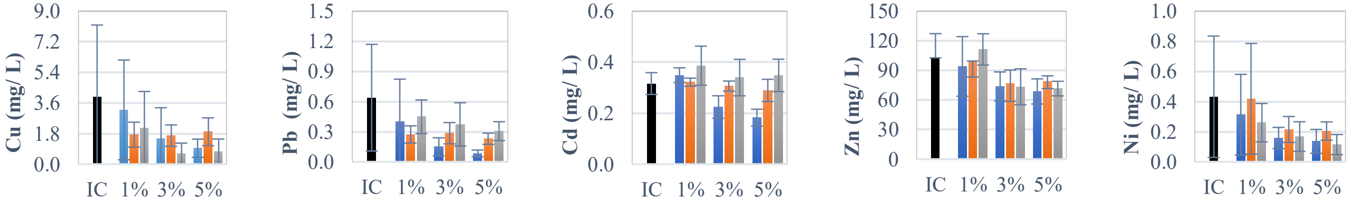
4.1.3 *Case III: Handmade Contaminated Soil (HCS)*

HCS, which is also sandy soil, had an initial pH between 4.75 and 5.05, due to the high content of lead. After mixing with OS, Z and RM, its pH changed to 6.91–7.51, 4.42–5.18 and 6.23–9.63, respectively (Table 3.4). Compared with the initial pH values, the addition of OS and RM increased the pH of HCS. By contrast, the addition of Z at dosages lower than 5% decreased pH slightly whilst dosages over 5% increased pH marginally.

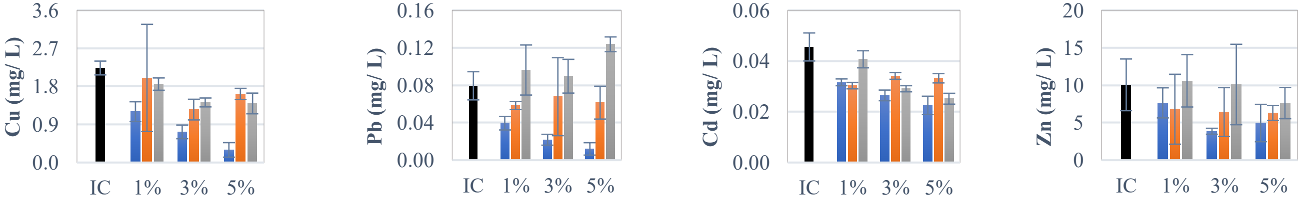
The leachate with DI water presented an initial Pb concentration of 301.65 mg/L. Conversely, the leaching test with TCLP reported a mean Pb concentration of 159.802 mg/L as the initial concentration of HCS. This value is lower than the concentrations obtained by leaching with DI water. This finding can be attributed to the aging effect (short time). The results suggested that Pb concentration can be reduced by 62% by adding 5 wt% of Z. However, the final concentration (113.825 mg/L) was still higher than Korean and international regulations (<5 mg/L, Table 2.1). Meanwhile, Pb concentration in the leachate was reduced to 269.942 mg/L (11% of Pb was immobilized) after administering OS and 177.637 mg/L (41% of Pb was immobilized) after administering RM at 5 wt% dosage (Figure 4.4). However, when dosage was increased to 10 wt%, the immobilization rate via OS addition significantly improved. By contrast, such an improvement in binder performance was not observed with Z when its dosage was increased ($p>0.05$). After adding 10 wt% of OS, Z and RM, Pb immobilization rates of 53%, 64% and 59%, respectively, were observed in Figure 4.2 and Figure A.3.

The initial Cu concentration was lower than the maximum permissible levels. However, after adding 5 wt% of OS, Z and RM, 29%, 55% and 53% of Cu, respectively, were immobilized. When dosage was increased to 10 wt%, the immobilization rates increased to 61%, 63% and 61%, respectively. Like the observations for Pb, the increment in immobilization by OS was significant when dosage was increased ($p<0.05$).

Additionally, SEM-EDS analysis was performed to observe Pb absorbed on the surface of the stabilized soil Figure 4.3.



(**a**) Case I: Abandoned metal mine site (silty sand soil)



(**b**) Case II: Military service area (sandy soil)

(**c**) Case III: Highly contaminated soils (HCS)

🟦 OS 🟧 Z ⬜ RM

Figure 4.2 Toxic metal concentrations in mg/L (from the TCLP test results of the silty sand soil, sandy soil and HCS). (IC—Initial concentration (Refer to Tables A.1 to A.3 in the appendix for the descriptive statistics of these values).

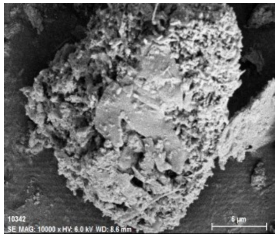
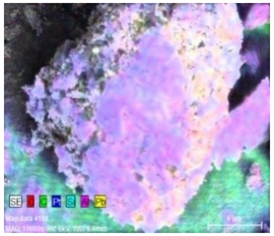
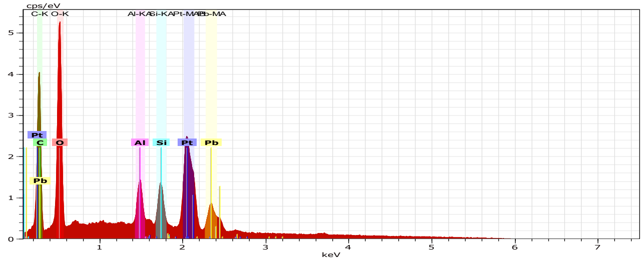
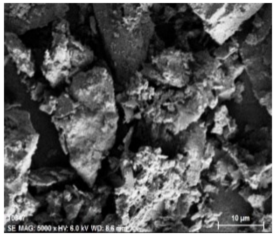
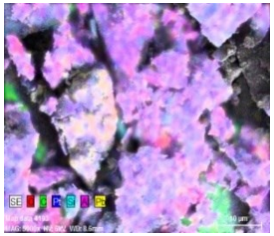
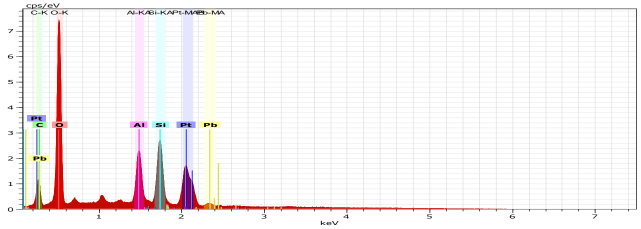
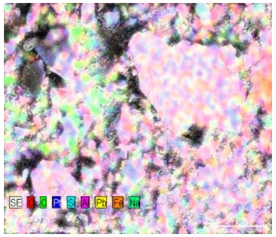
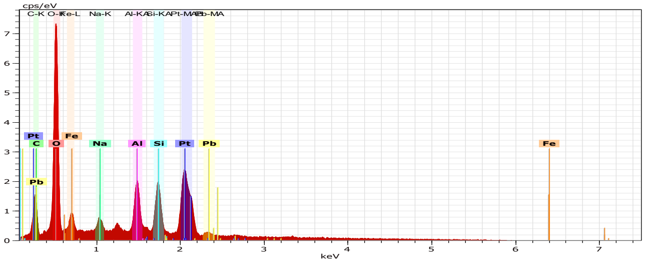
HCS + OS (10%) 10,000×			
HCS + Z (10%) 5000×			
HCS +RM (10%) 650×			

Figure 4.3 SEM–EDS analysis result for HCS treated with 10 wt% OS, Z and RM

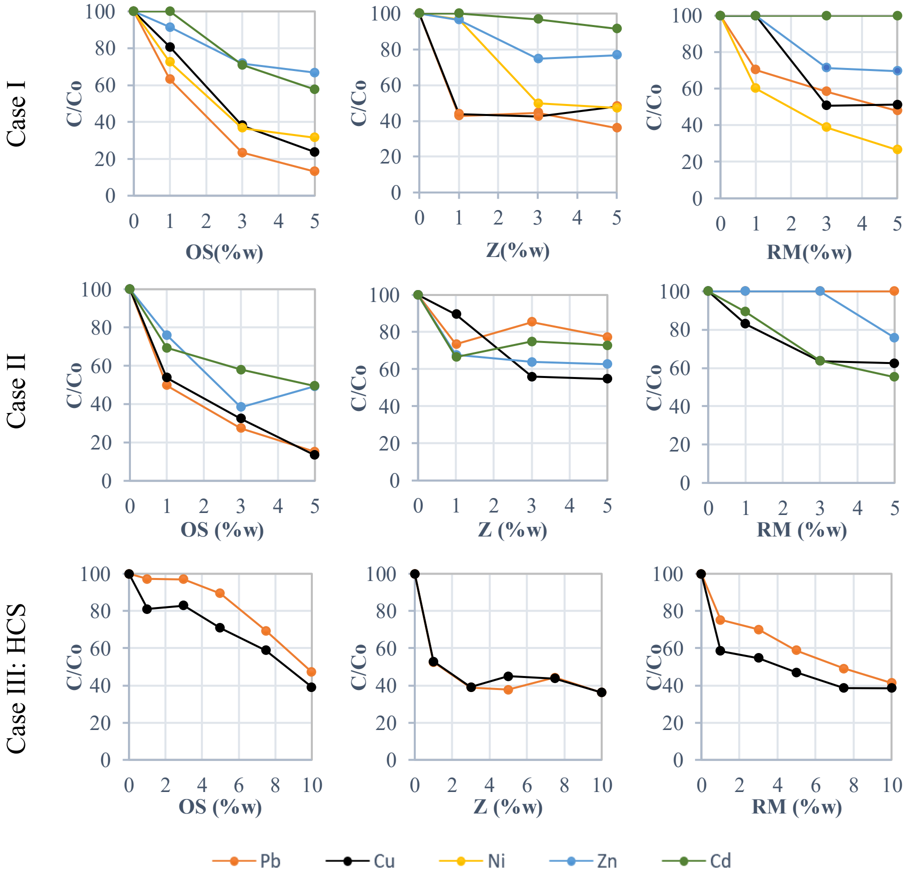


Figure 4.4 Normalized final toxic metal concentrations in the leachates of silty sand soil, sandy soil and HCS obtained through the TCLP test.

For HCS soil stabilized with OS, the high Pb concentration in the leachate was reduced to 38.769 mg/L (87% of Pb was immobilized) after 1 day of contact time and 94% of Pb was immobilized after 10 days at dosages above 5% (Figure 4.5 and Figure A.4). However, these values were still above the regulation level. When HCS was treated with OS at 10 wt%, the Pb concentration in the leachate collected after 1 day was 3.67 mg/L, which is slightly above the Korean regulation but under the maximum value of 5 mg/L stipulated by U.S. EPA. At short contact times (e.g., 12 h), OS with dosages up to 5% immobilized less than 10% of Pb. After 1 day, OS apparently reached maximum Cu and Pb stabilization because the authors did not observe any significant improvement in immobilization.

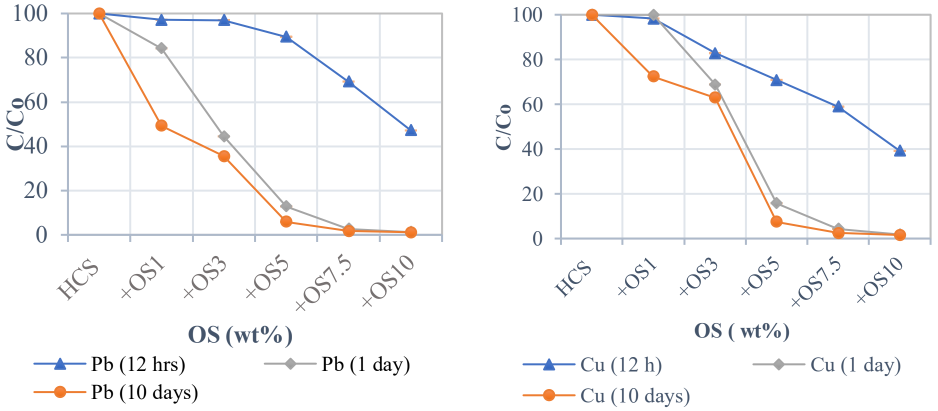


Figure 4.5 Pb and Cu concentrations in the HCS treated with OS obtained through the TCLP test at different contact times (12 h, 1 day and 10 days). Refer to Table A.4 for descriptive statistics. The number after the binder abbreviation represents mass percentage.

4.2 Pot cultivation test in case IV of As-soil

Case IV: *As*-Soil, a granular soil, had an initial *As*-concentration of 0.318 mg/L measured by TCLP test and 0.637 mg/L measured by Mehlich−3; both values are below the limits from South Korean regulation value for *As* concentration in the leachate from waste (<1.5mg/L), as well as the concentration cited by US EPA, to be considered as a hazard (<5mg/L)(U.S. EPA 2011, EHTI 2017). However, the total *As* content is 134 mg/kg determined by aqua regia extraction, while the Korean regulation also regulates the total arsenic content in soils as a maximum 75 mg/kg (EHTI 2018)

The initial water content was 30%, and it was controlled for seven weeks during the pot cultivation test. Then, the moisture content decreased slightly during the first month (4 weeks) from 30% to 28.2 ± 1.3% in soil samples, to 28.3 ± 1.7% in soil treated with OS, and to 28.4 ± 1.3% in soil treated with OS/Z, while, soil treated with Z reported a slight increase to 31.1± 2.2%. In the remaining time (3 weeks), the moisture content showed a more significant reduction attributed to the evaporation during the removal of samples. All the removed samples were dried at 70°C for 24 h prior to the Mehlich-3 extraction test (M-3 solution has pH equal to 2.5). Figure 4.6 shows the variation of the pH per time and per case. In general, all the binders increased the pH at least by 1 point and greater dosage also contributes to increasing the final pH per binder case.

The *As*-concentration measured in the soil without binder along the period of evaluation was 0.67 mg/L. After adding OS in dosage of 3% and 5%, it was reduced to 0.55mg/L and 0.48 mg/L. Then, it was reduced to 0.25 mg/L and 0.24 mg/L when 3 and 5% of Z were used. The use of the OS/Z does not represent a significant improvement in the binding process. The *As* concentration was reduced to 0.32 mg/L and 0.28 mg/L when 3% and 5% of OS/Z were added. As Figure 4.7 displays, at the end of the period, OS immobilized only 20% of *As*; meanwhile, Z immobilized 60%. The combination of OS and Z showed similar results than Z used alone; it immobilized around 50%.

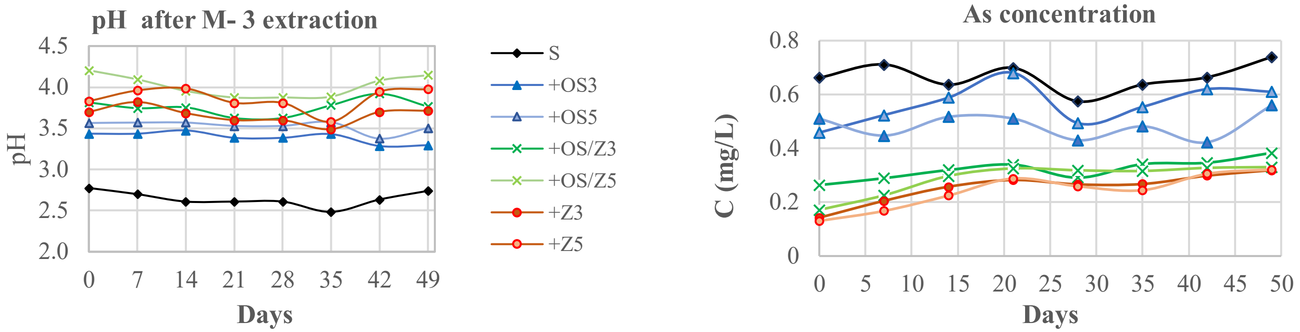


Figure 4.6 (Left) pH after Mehlich-3 extraction and (Right) *As* concentration after adding binder. Detailed statistics in Figure A.5.

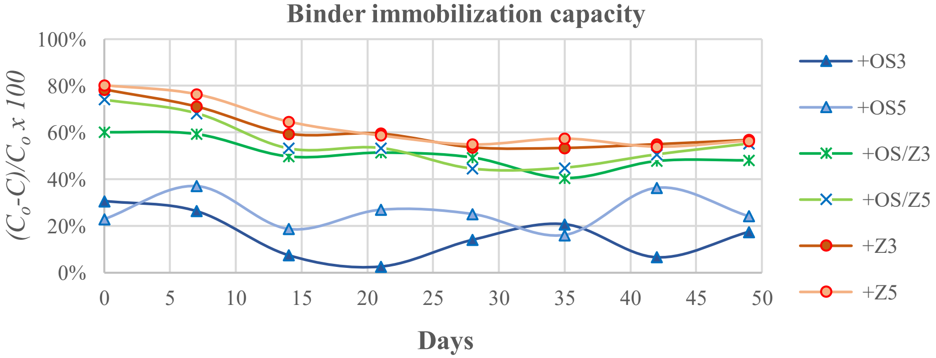


Figure 4.7 *As*-immobilization capacity of OS, Z and OS/Z

4.3 Batch Sorption Test

The most important physiochemical aspects in evaluating the adsorption process are the kinetics and equilibrium of adsorption. Equilibrium studies give the capacity of the adsorbent for specific contaminants. For example, the Freundlich model is characterized by sorption that continues as the concentration of sorbate increases in the aqueous phase. Figure 4.8(left) shows that the mass of pollutant sorbed (*As*) is proportional to the aqueous phase concentration at low sorbate concentrations and decreases as the sorbate accumulates on the sorbent surface. The fitting parameters are listed in Table 4.1. We can see that all the R^2 values were between 0.887 and 0.974, revealing that the arsenic adsorption process was suitable for modelling by the Freundlich isotherm. This indicated that the adsorption behavior of arsenic was single-layered on the surface for both binders.

The results also can be expressed as relative final concentration versus the binder-to-liquid ratio (S/L) used in this bath sorption test, as it is observed in Figure 4.8(right); using a S/L of 1/5 both binders reached only 10% of *As* removal, when the initial *As*-concentration is 100ppm. Meanwhile, the average *As*-uptaken using 1/20 was measured in concentration from 5-250ppm and 1/10 in 50-100ppm.

Table 4.1 Isotherm models, adsorption parameters for OS and Z

	Freundlich isotherm			Langmuir isotherm		
	K_F (mg/kg)	1/n	R^2	1/a	1/ab	R^2
Oyster shell	4.983	0.565	0.973	0.005	0.453	0.887
Zeolite	0.306	1.077	0.974			

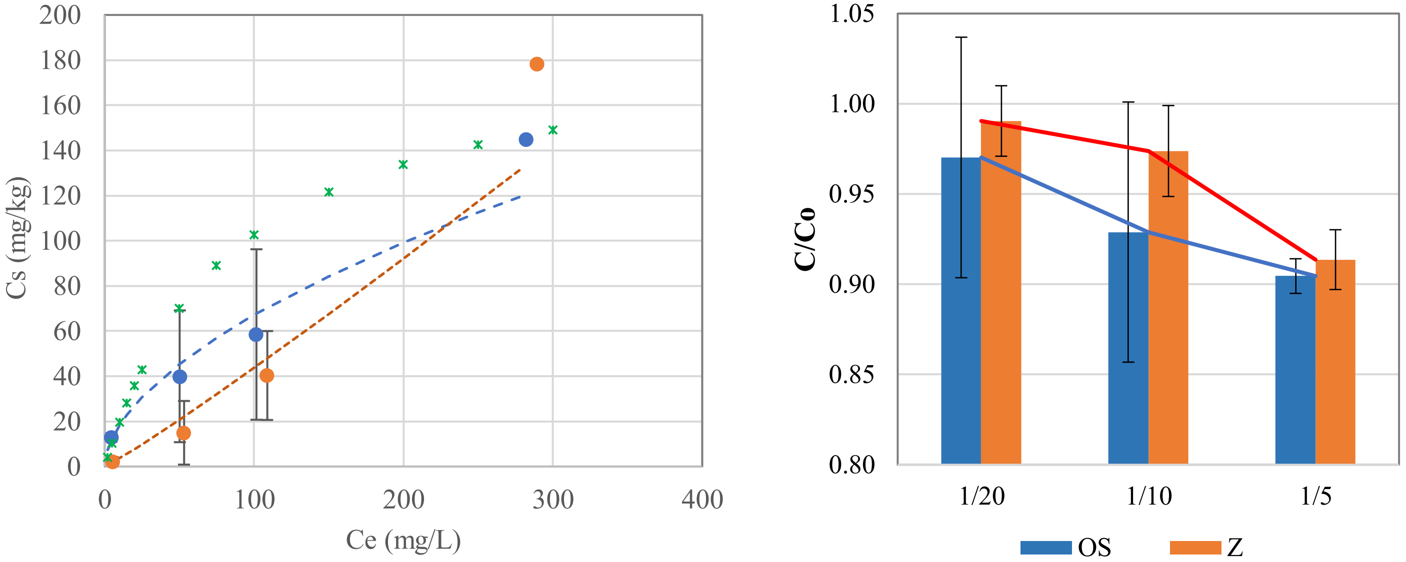


Figure 4.8 Absorption of arsenic by OS described by the Freundlich isotherm and adsorption by Z_{4A} (Left). Relative final concentration of *As* for different S/L ratio. The mean pH of the OS-solute and Z-solute were 8.61±0.10 and 10.42 ±0.04, respectively.

4.4 Geotechnical test

4.4.1 *Standard compaction test*

The compaction curves of the blank soil, and the soil after mixing with 10% of each binder are shown in Figure 4.9. From it, we can observe that the addition of OS increases the optimum water content, and also, the maximum dry unit weight slightly increases compared with the blank soil. Meanwhile, the addition of Z and RM showed a remarkable reduction of the value of the maximum dry unit weight, which will require more water for compaction. Mixtures of soil with each binder increase the fine particle making them comparable with clayey soils especially in the case of zeolite and red mud, due to its low density and higher water holding capacity. In all instances, the addition of binder in 10% reported minimum dry unit weight values over 14.71 kN/m3, which is the minimum unit weight of a material to be considered as fill soil.

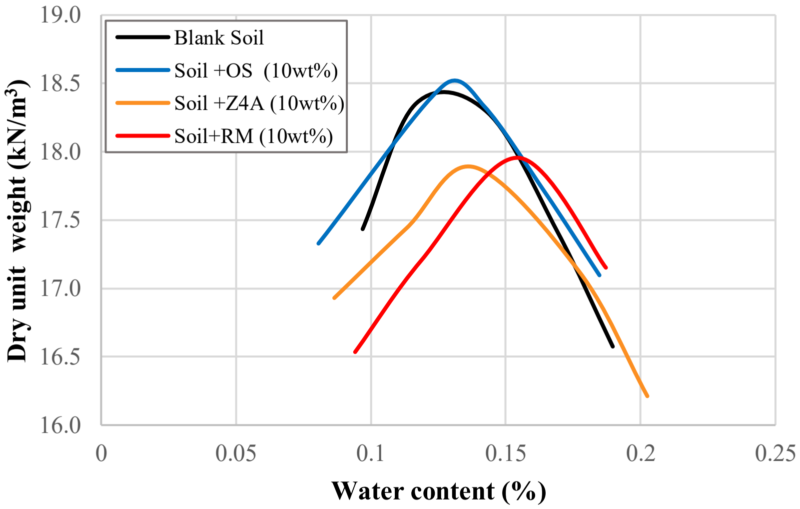


Figure 4.9 Compaction curves of soil – binder mixtures

4.4.2 *Direct shear test*

The strength parameters of the soil-binder mixtures are shown in Table 4.2. The friction angle decreased from 41.6 to 37.5 after adding 10% of OS, 36.9 after adding 10% of Z, and 38.5 after adding 10% of RM; meanwhile, the cohesion increased (Table 4.2). Kwon et al. (2019) reported similar changes after adding Z to granular soil.

Table 4.2 Shear strength parameters of soil-binder mixtures

	S	S+OS	S+Z	S+RM
Friction angle (°)	41.6°	37.5°	36.9°	38.5°
Cohesion (kPa)	14.5	21.6	24.6	22.4

Note: S – Soil base, binder addition was 10% of total weight of S.

Chapter 5 : Discussions

5.1 Batch experimental test

5.1.1 *Oyster Shell Powder*

OS demonstrated the best performance in binding nearly all the considered toxic metals, particularly Pb and Cu, for the silty sand and sandy soil samples. Furthermore, our observations suggested that the preference for sorption of OS was in the following order: $Pb^{2+} > Cu^{2+} > Zn^{2+} > Cd^{2+} > Ni^{2+}$. This order is similar to the observations of Shin et al. (2014) in their kinetic model. In addition, when HCS was treated with OS, all the samples had a pH above 7 (alkaline). $CaCO_3$ and CaO in OS were dissolved in water to produce hydroxyl ions (OH^-), increasing the pH of the medium ($CaCO_3 + H_2O \rightarrow Ca^{2+} + CO_3^{2-}$; $CO_3^{2-} + H_2O \rightarrow HCO_3 + OH^-$) (Ok et al. 2010). This alkaline condition can promote the precipitation of metals as metal hydroxides [Mn+ + n(OH) − → M (OH)n, where M denotes metal] (Ok et al. 2010, Bonnard et al. 2020), and can be linked to the reduction of toxic metals in leachate. Furthermore, the SEM–EDS analysis (Figure 4.3) showed that OS exhibited high adsorption capacity towards Pb compared with the other binders considered in this study. This finding can be attributed to ion exchange capacity (Zhong et al. 2020). The two aforementioned phenomena can justify the significant reduction ($p < 0.05$) in Pb with increased OS dosage and contact time. The number of sorption sites and reactive hydroxide ions increased with OS dosage, significantly reducing toxic metal concentrations ($p < 0.05$), as illustrated in Figures A1–A4 (descriptive statistics pertaining to the concentrations of toxic metals at different binder dosages are presented in Tables A1–A4). In the case of HCS treated with 5% OS dosage, only 30% of Cu and 10% of Pb were immobilized. When dosage was increased to 10%, sorption sites and metal precipitates were consequently increased, and immobilization rate reached up to 60% for Cu and 55% for Pb.

Furthermore, the results of Pb and Cu concentrations in the HCS leachate stabilized with OS over time. Figure 4.5 shows that better immobilization of these toxic metals can be achieved with increasing contact time. The effect of contact time seemed insignificant for dosages over 5% and the change in immobilization rate was insignificant ($p > 0.05$) for contact times beyond 1 day. This finding was also observed in silty sand soil (leaching with DI water), as illustrated in Figure 4.1. The preceding results corroborate the findings of Xu et al. (2019) and Desta (2013), who observed the roles played by the adsorption characteristics and ion exchange capacity of binders and the precipitation of ions in achieving stabilization over time. Considering that the immobilization rate was maintained without significant variation, OS can be used to stabilize a wide range of soil types; silty sand, sandy soil and HCS. Although OS exhibited good performance in binding toxic metals, the treatment of soil that is highly polluted with Pb is recommended only for industrial areas where the percolation of water can be controlled. In addition, OS contains sodium, which may be harmful to flora in excessive dosages. However, appropriate doses of OS can be used as soil amendment for agricultural soil (Lee et al. 2008, Bonnard et al. 2020).

5.1.2 *Zeolite*

In the current study, Z-treated soil had a neutral pH of approximately 6.5 and Z did not drastically change the pH of the medium. A slight increase in pH was observed when Z dosage was increased. Such pH conditions are beneficial for stabilization by Z because the major binding mechanisms of Z are adsorption and cation exchange (Ok et al. 2010, Bonnard et al. 2020).

This phenomenon can be observed in HCS soil (a slightly acidic soil) wherein Z achieved the best immobilization compared with the other binders at a contact time of 12 h. Moreover, given that the immobilization rate does not improve with dosage, we can argue that ion exchange is the primary binding mechanism of Z in our study. The surface of Z is negatively charged through the isomorphous replacement of Al^+ by Al^{3+}. This negative charge can be balanced by exchangeable cations, such as Na, K and Ca. These exchangeable cations are used in ion exchange with metals ions, such as Pb, Cd, Zn and Cu (Erdem et al. 2004, Kwon et al. 2019, Zhang et al. 2021). The number of exchangeable metal ions in soil did not change with increased dosage, and ion exchange may not occur because the activity of metal ions in the medium became considerably low. When exchangeable Pb ions are high in HCS, even a low dosage of Z (1 wt%) can bind 50% of Pb because of this high ion exchange capacity.

The leachates obtained for silty sand and sandy soil with DI water indicated that the addition of Z significantly reduced the concentrations of Pb and Cu (Figure 4.1); however, the immobilization rate was lower compared with that of OS. This result may be attributed to the low activity of the ions present in the soil. Furthermore, the final concentrations of toxic metals in the leachates of silty sand and sandy soil at 5 wt% were in the following order: Pb < Cu < Zn. This finding corroborates zeolite's selectivity for cation exchange, i.e., $Pb^{2+} > Cu^{2+} > Zn^{2+}$ (Babel and Kurniawan 2003). Zeolite can be applied to soil near military bases or industries that is contaminated with a high amount of Pb or to acidic soil. In the current study, the authors only observed the performance after a contact time of 12 h. Therefore, observing the long-term performance of zeolite is necessary because ion exchange is a reversible process in zeolite.

5.1.3 *Red Mud*

RM has an alkaline nature because of the presence of NaOH, a strong base used in producing alumina (Cui et al. 2019). The high alkalinity of red mud can increase pH drastically as we observed in this study. As shown in Figure 4.2, RM is effective for highly contaminated soil, such as HCS. Shin, et al. (Shin et al. 2014) reported that RM has a larger surface area than OS and Z, and this characteristic improves the adsorption capacity (primary components: silica, alumina and Fe_2O_3) and ion exchange capacity of this material. This characteristic may be the reason for the previous observation. Furthermore, RM can be used to precipitate soluble toxic metals in their hydroxide form. Therefore, a higher RM dosage will result in higher stabilization of Pb, as observed in Figure 4.2, particularly for HCS soil. In sandy soil, a higher Cd concentration was observed after treatment, suggesting that Cd is adsorbed poorly in a competitive environment because RM can exchange Cd ions in soil with Al compounds. RM was ineffective for soil with low contamination, such as sandy soil. In fact, the addition of RM was counterproductive, particularly in the case of Pb. This finding may be ascribed to the increase in pH and the dissolved organic carbon in soil pore water (Anton et al. 2012, Mayes et al. 2016). Dissolved organic carbon can enhance the leaching of As, Cu and Ni from RM when the latter comes in contact with organic-rich media (Ujaczki et al. 2015), such as the silty sand soil evaluated in this study.

Considering the presence of water-soluble Al concentrations in RM, biologically available Al can be released into the surrounding environment; in its acutely toxic form, i.e., $[Al(OH)_4]^-$, Al can pose considerable environmental and health hazards (Mayes et al. 2016). Therefore, the application of RM to fertilized soil is not recommended.

5.2 OS and Z as Binders for As Pollution

The As immobilization efficiency defined as the difference between final concentration and initial concentration in percentage reported that OS only reached 20%, Z_{4A} was 60% and their combination (OS/Z) was 50% from the pot cultivation test results. Meanwhile, in an aqueous solution where the absorbent was directly in contact with *As*, using a binder-to-liquid ratio of 1:5 both only reduced 10% of the initial concentration. In addition, the Freundlich isotherms fit, suggesting that the adsorption behavior of arsenic was single-layered on the surface for both binders.

Overall, OS and Z_{4A} are not a suitable binder for *As* contamination. However, the better performance of Z in the pot cultivation test can be attributed to the high cation exchange capacity, instead of the absorption mechanism.

5.3 Geotechnical properties of soil-binder mixtures

By applying the solidification and stabilization technique, the addition of a binder (solid material) into the soil was involved, which final disposition of the mixed material is left stable compacted on the field. The effect of adding 10% OS, Z and RM on a blank soil was evaluated. According to the results, the addition of OS does not affect the compaction parameter drastically compared to Z and RM, which diminished the value of the maximum dry unit weight and increased the optimum water content. However, all the results show maximum dry unit weight over the minimum 14.17 kN/m3 given in the Korean standard regulation to consider the material as fill material.

To estimate the strength parameters, all the samples were compacted at 95% to determine friction angle and cohesion by performing direct shear test. According to the results, the addition of the binder increased the cohesion from 14.5 to 21 – 25 kPa, while the friction angle was reduced between 7.5 to 11%.

Chapter 6 : Conclusions and further studies

6.1 Conclusions

The S/S technique aims to immobilize contaminants by converting them into a less soluble form (chemical stabilization) and encapsulating them by creating a durable matrix (solidification), as observed through pH measurements after mixing the binder. From the results, binder performance changed depending on the type and level of toxic metal concentration (HCS > silty sand soil > sandy soil), the pH of the final medium and the type of metal. These factors are associated with the solubility and mobilization of toxic metals. When the medium was alkaline, better binding was observed amongst all the binders, emphasizing the role of OH^- ions in aiding the precipitation of toxic metal such as Pb, Cu and Cd.

However, depending on the case, additional soil treatments might be necessary to eliminate any adverse situation that can lead into spreading the contaminant caused by the alteration of the medium (stable condition).

OS demonstrated the best performance in binding Pb and Cu in the silty sand soil (Case I) and sandy soil (Case II), and its effect was immediately observable after adding 3% of the binder to soil samples with low-to-medium contamination levels (reduction of Cd and Ni concentration was also observed). Moreover, OS proved to be a good binder even for soil with an extremely high Pb concentration (i.e., HCS in the Case III). However, higher dosages (>5%) and longer contact times (>1 day) are required to achieve the desired immobilization rates. Therefore, OS can be used to stabilize soils contaminated with of Pb and Cu.

Z is a good alternative binder for highly contaminated soils (even under acidic condition, Case III) because of its cation exchange capacity with toxic metals and sorption properties. However, no significant improvement in binding performance can be achieved with doses above 3% according to the results. In this experiment, the leaching agent was in contact for only 12 h; thus, observing the performance of zeolite in a long-term setting is recommended. RM can be used alternatively to Z. However, caution should be taken during its application because of the risk of releasing other metalloids. However, the performance of both Z and RM is not reliable compared to OS.

Binders facing As-pollution in soils (Case IV), OS* and Z_{4A} showed low rates of efficiency. Also, the evaluation in As-solution, showed poor sorption capacity (less than 10%). Thus, they are not recommended in these scenarios.

The infiltration of acid rain may decrease soil pH, leading to the mobilization of bound toxic metals. Therefore, investigating the effect of pH and conducting a column percolation test prior to suggesting any applications are recommended because most of the binders demonstrate better binding properties under alkaline conditions, particularly at low dosages.

After adding the binder into the soil, the geotechnical properties of the ground slightly change. The maximum dry unit weight and the optimum water content are important parameters used in the compaction of the fill material. Considering 95% compactness, the direct shear test shows a decrease in the friction angle after binder addition and an increase in the cohesion. Each soil is different, so before application, design engineers should conduct a complete geotechnical evaluation

6.2 Further studies

For future studies, the main suggestion is investigating whether the surface area of binders can be increased by subjecting them to high temperatures. Furthermore, biotic redox reactions, which are important for controlling the oxidation state, were not considered in the current study. Thus, how the mobilization of toxic metals is affected by such reactions requires investigation.

OS and Z used in this study does not report outstanding performance facing *As* pollution. Thus, chemical treatment modification of these binders should be necessary to increase its efficiency.

The experiments should be scaled to a column percolation test or soil boxes to help to understand and replicate the soil conditions on the field. Besides that, the geotechnical instrumentation design for monitoring leaching and preventing the spreading pollution of toxic metal should also be incorporate as part of the design for field application.

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Appendix

List of Tables A

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Table A.1 Descriptive statistics of toxic metal concentrations in the leachate obtained via TCLP from silty sand soil treated with OS, Z and RM (Case I).

		Cu				**Zn**				**Cd**				**Ni**				**Pb**			
S + OS		IC	+OS1	+OS3	+OS5	IC	+OS1	+OS3	+OS5	IC	+OS1	+OS3	+OS5	IC	+OS1	+OS3	+OS5	IC	+OS1	+OS3	+OS5
	n Samples	19	11	15	10	5	5	2	3	12	5	12	7	6	6	12	7	15	10	16	10
	Max	15.556	10.369	7.488	2.179	145.000	145.014	84.128	83.213	0.383	0.382	0.321	0.235	1.222	0.849	0.287	0.277	1.929	1.549	0.376	0.165
	Min	0.921	0.662	0.458	0.434	81.851	68.797	63.324	59.828	0.255	0.309	0.143	0.143	0.152	0.160	0.089	0.066	0.107	0.092	0.036	0.046
	Mean	3.954	3.191	1.506	0.937	102.784	94.013	73.726	68.657	0.316	0.349	0.224	0.182	0.432	0.313	0.158	0.136	0.639	0.403	0.149	0.084
	Std Dev	4.233	2.934	1.813	0.536	24.509	30.231	14.711	12.700	0.043	0.029	0.044	0.033	0.403	0.268	0.070	0.079	0.531	0.420	0.090	0.034
	Var	17.920	8.609	3.287	0.287	600.689	913.908	216.410	161.301	0.002	0.001	0.002	0.001	0.162	0.072	0.005	0.006	0.282	0.177	0.008	0.001
S + Z			+Z1	+Z3	+Z5		+Z1	+Z3	+Z5		+Z1	+Z3	+Z5		+Z1	+Z3	+Z5		+Z1	+Z3	+Z5
	n Samples		8	9	10		3	3	2		4	7	7		8	12	12		8	9	8
	Max		2.896	2.797	3.709		99.548	91.765	82.867		0.332	0.334	0.356		1.153	0.424	0.301		0.415	0.502	0.337
	Min		0.894	0.899	0.948		98.852	65.273	75.031		0.298	0.276	0.237		0.162	0.128	0.134		0.173	0.171	0.145
	Mean		1.736	1.679	1.906		99.153	76.822	78.949		0.322	0.306	0.289		0.418	0.215	0.204		0.273	0.285	0.230
	Std Dev		1.607	1.472	1.769		0.357	13.568	5.541		0.016	0.020	0.044		0.367	0.086	0.061		0.086	0.106	0.056
	Var		0.733	0.629	0.817		0.128	184.098	30.699		0.000	0.000	0.002		0.135	0.007	0.004		0.007	0.011	0.003
S + RM			+RM1	+RM3	+RM5		+RM1	+RM3	+RM5		+RM1	+RM3	+RM5		+RM1	+RM3	+RM5		+RM1	+RM3	+RM5
	n Samples		6	4	6		2	2	3		6	4	4		6	4	4		6	4	2
	Max		7.489	2.809	3.248		122.506	86.245	80.009		0.490	0.423	0.414		0.472	0.291	0.149		0.683	0.616	0.372
	Min		1.965	1.299	1.151		100.054	60.482	66.197		0.287	0.261	0.275		0.109	0.059	0.014		0.258	0.169	0.239
	Mean		4.140	2.004	2.030		111.280	73.363	71.551		0.386	0.340	0.348		0.260	0.168	0.115		0.449	0.373	0.306
	Std Dev		2.139	0.619	0.739		15.876	18.217	7.410		0.077	0.072	0.064		0.128	0.098	0.067		0.167	0.215	0.094
	Var		4.575	0.384	0.546		252.062	331.854	54.913		0.006	0.005	0.004		0.016	0.010	0.004		0.028	0.046	0.009

S – Soil sample; IC – Initial concentration; OS – Oyster shell; Z – zeolite; RM – Red mud. The number after the binder abbreviation represents mass percentage (e.g. Z3 means 3 wt% of Z).

Table A.2 Descriptive statistics of toxic metal concentrations in the leachate obtained via TCLP from sandy soil treated with OS, Z and RM (Case II)

		Cu				**Zn**				**Cd**				**Pb**			
S + OS		IC	+OS1	+OS3	+OS5	IC	+OS1	+OS3	+OS5	IC	+OS1	+OS3	+OS5	IC	+OS1	+OS3	+OS5
	n Samples	3	3	3	3	3	3	3	3	3	3	3	2	3	3	3	3
	Max	2.408	1.459	0.859	0.471	14.000	9.913	4.317	7.442	0.050	0.033	0.029	0.025	0.095	0.047	0.028	0.019
	Min	2.083	0.999	0.545	0.128	7.602	6.092	3.594	2.459	0.039	0.031	0.024	0.020	0.065	0.032	0.018	0.005
	Mean	2.235	1.203	0.725	0.298	10.053	7.648	3.858	4.956	0.046	0.032	0.026	0.023	0.079	0.039	0.022	0.012
	Std Dev	0.163	0.234	0.162	0.172	3.451	2.007	0.399	2.492	0.006	0.001	0.002	0.004	0.015	0.007	0.006	0.007
	Var	0.027	0.055	0.026	0.030	11.913	4.027	0.159	6.209	0.000	1.8E-06	4.4E-06	1.3E-05	2.3E-04	5.2E-05	3.3E-05	4.4E-05
S + Z			+Z1	+Z3	+Z5		+Z1	+Z3	+Z5		+Z1	+Z3	+Z5		+Z1	+Z3	+Z5
	n Samples		4	4	2		4	4	4		4	4	4		4	4	3
	Max		3.892	1.607	1.715		13.559	11.271	7.776		0.032	0.035	0.035		0.063	0.130	0.082
	Min		1.243	1.080	1.529		3.588	4.530	5.713		0.029	0.032	0.031		0.053	0.045	0.050
	Mean		2.000	1.251	1.622		6.799	6.419	6.302		0.030	0.034	0.033		0.058	0.068	0.061
	Std Dev		1.267	0.244	0.132		4.664	3.256	0.986		0.001	0.001	0.002		0.004	0.042	0.018
	Var		1.606	0.060	0.017		21.755	10.604	0.972		1.6E-06	1.8E-06	3.3E-06		1.8E-05	1.7E-03	3.1E-04
S + RM			+RM1	+RM3	+RM5		+RM1	+RM3	+RM5		+RM1	+RM3	+RM5		+RM1	+RM3	+RM5
	n Samples		2	3	3		3	3	3		3	3	3		3	3	3
	Max		1.957	1.513	1.677		14.592	15.847	8.907		0.044	0.030	0.028		0.127	0.108	0.132
	Min		1.751	1.306	1.229		8.139	5.227	5.213		0.038	0.028	0.023		0.077	0.071	0.117
	Mean		1.854	1.420	1.397		10.590	10.096	7.617		0.041	0.029	0.025		0.096	0.090	0.124
	Std Dev		0.145	0.105	0.244		3.494	5.364	2.084		0.003	0.001	0.002		0.027	0.018	0.008
	Var		0.021	0.011	0.060		12.211	28.777	4.343		1.1E-05	1.4E-06	4.6E-06		7.1E-04	3.2E-04	6.2E-05

S – Soil sample; IC – Initial concentration; OS – Oyster shell; Z – zeolite; RM – Red mud. The number after the binder abbreviation represents mass percentage (e.g. Z3 means 3 wt% of Z).

Table A.3 Descriptive statistics of the toxic metal concentrations in the leachate obtained via TCLP from HCS treated with OS, Z, and RM (Case III).

		Cu						**Pb**					
		HCS	+OS1	+OS3	+OS5	+OS7.5	+OS10	HCS	+OS1	+OS3	+OS5	+OS7.5	+OS10
HCS + OS	*n* Samples	9	4	2	2	2	2	4	2	2	2	2	2
	Max	0.48	0.48	0.40	0.35	0.28	0.19	175.56	299.71	321.86	295.15	215.02	144.63
	Min	0.39	0.27	0.33	0.28	0.24	0.16	145.46	286.38	263.49	244.73	202.82	139.91
	Mean	0.444	0.360	0.368	0.315	0.262	0.174	159.802	293.048	292.673	269.942	208.917	142.268
	Std Dev	0.03	0.09	0.05	0.05	0.03	0.02	12.87	9.42	41.27	35.66	8.63	3.34
	Var	0.00	0.01	0.00	0.00	0.00	0.00	165.71	88.83	1703.51	1271.35	74.44	11.15
			+Z1	+Z3	+Z5	+Z7.5	+Z10		+Z1	+Z3	+Z5	+Z7.5	Z10
HCS + Z	*n* Samples		2	2	2	2	2		2	2	2	2	2
	Max		0.26	0.19	0.22	0.20	0.17		164.61	120.78	144.40	133.76	109.28
	Min		0.21	0.16	0.18	0.19	0.15		152.47	114.16	83.25	132.56	108.53
	Mean		0.234	0.174	0.199	0.194	0.161		158.540	117.467	113.825	133.161	108.907
	Std Dev		0.03	0.02	0.03	0.00	0.02		8.59	4.68	43.24	0.85	0.53
	Var		0.00	0.00	0.00	0.00	0.00		73.71	21.90	1870.00	0.72	0.28
			+RM1	+RM3	+RM5	+RM7.5	+RM10	*IC* *	+RM1	+RM3	+RM5	+RM7.5	+RM10
HCS + RM	*n* Samples		2	2	2	2	2	*6*	2	2	2	2	2
	Max		0.27	0.26	0.22	0.17	0.20	366.99	233.18	225.13	193.65	149.88	125.03
	Min		0.25	0.23	0.19	0.17	0.15	222.93	220.05	197.36	161.63	146.14	124.25
	Mean		0.260	0.243	0.209	0.171	0.172	301.657	226.612	211.245	177.637	148.011	124.644
	Std Dev		0.02	0.02	0.02	0.00	0.04	58.40	9.29	19.63	22.64	2.64	0.55
	Var		0.00	0.00	0.00	0.00	0.00	3410.17	86.24	385.50	512.62	6.99	0.30

(* **bold**) The values shown in blue represent the results of the leaching test with DI water (initial concentrations). They are presented to provide an improved understanding of binder performance. OS – Oyster shell; Z – zeolite; RM – Red mud. The number after the binder abbreviation represents mass percentage.

Table A.4 Descriptive statistics of the toxic metal concentrations in the leachate of HCS after treatment obtained via TCLP test considering that the supernatant was extracted at different times after contact with oyster shell powder.

		Cu						Pb					
		HCS	+OS1	+OS3	+OS5	+OS7.5	+OS10	HCS	+OS1	+OS3	+OS5	+OS7.5	+OS10
HCS + OS (1day)	*n* Samples	9	4	4	4	2	2	4	2	2	2	2	2
	Max	0.48	0.63	0.35	0.10	0.02	0.01	175.56	324.58	150.25	39.85	8.51	4.05
	Min	0.39	0.33	0.25	0.04	0.02	0.01	145.46	183.93	118.13	37.68	7.57	3.27
	Mean	0.444	0.444	0.306	0.070	0.019	0.008	159.802	254.253	134.189	38.769	8.039	3.662
	Std Dev	0.03	0.13	0.05	0.03	0.00	0.00	12.87	99.45	22.71	1.53	0.66	0.55
	Var	0.00	0.02	0.00	0.00	0.00	0.00	165.71	9890.64	515.75	2.35	0.44	0.31
HCS + OS (10 days)			+OS1	+OS3	+OS5	+OS7.5	+OS10		+OS1	+OS3	+OS5	+OS7.5	+OS10
	n Samples		4	4	4	2	2		2	2	2	2	2
	Max		0.38	0.41	0.06	0.01	0.01		167.78	122.80	18.98	5.44	3.57
	Min		0.23	0.15	0.00	0.01	0.01		129.49	91.82	16.23	5.13	3.48
	Mean		0.322	0.280	0.033	0.011	0.007		148.637	107.310	17.605	5.283	3.524
	Std Dev		0.07	0.12	0.03	0.00	0.00		27.08	21.90	1.95	0.22	0.06
	Var		0.00	0.02	0.00	0.00	0.00		733.29	479.63	3.80	0.05	0.00

OS – Oyster shell. The number after the binder abbreviation represents mass percentage.

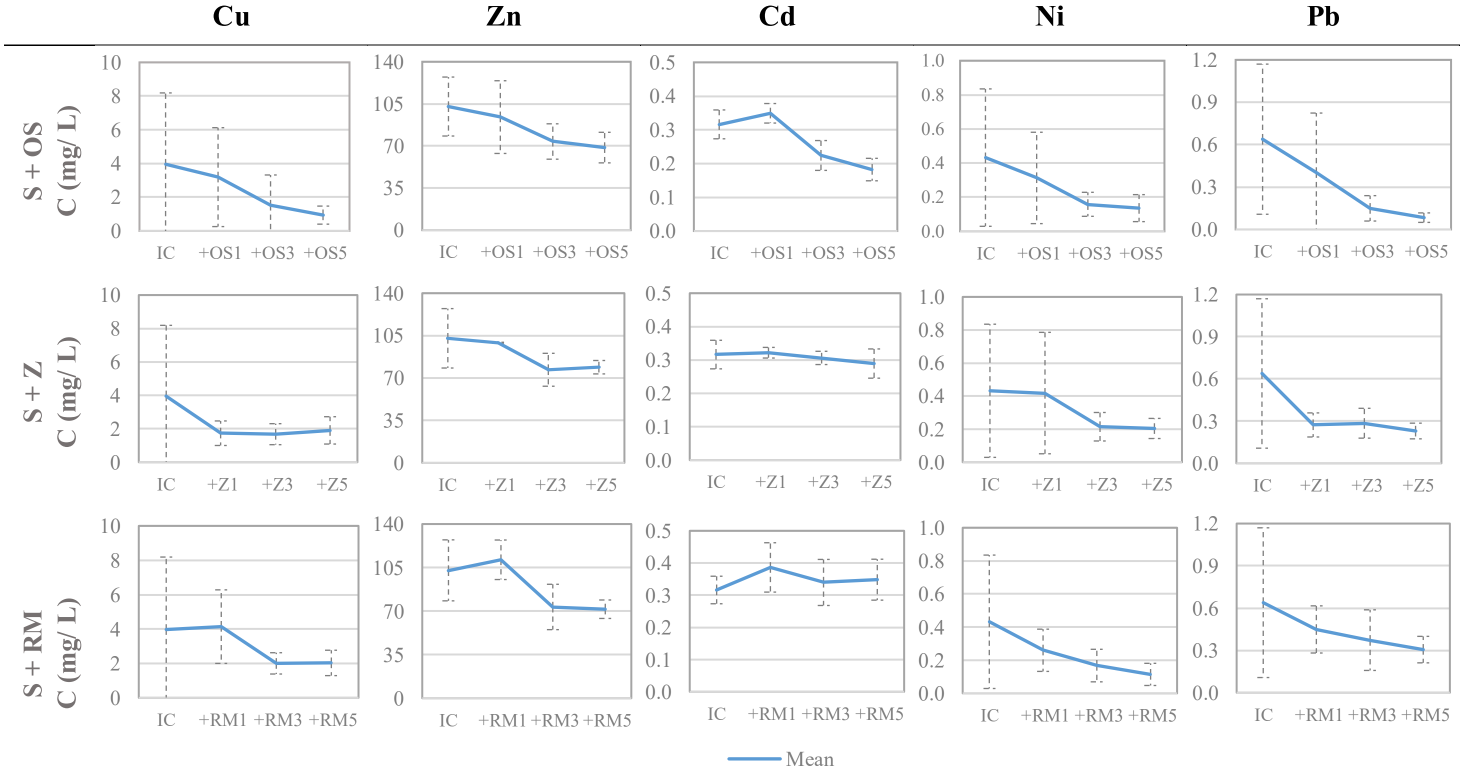

Figure A.1 Toxic metal concentrations in the leachate obtained via TCLP from the silty sand soil treated with OS, Z and RM (Case I). S – Soil sample; IC – Initial concentration. The number after the binder abbreviation represents mass percentage (e.g. Z3 means 3 wt% of Z).

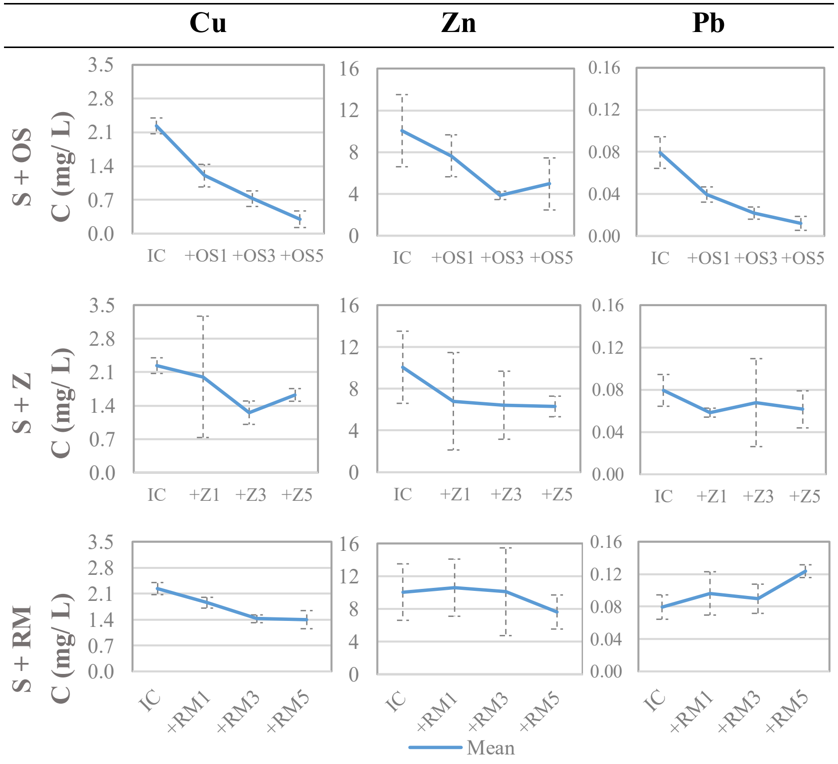

Figure A.2 Toxic metal concentrations in the leachate obtained via the TCLP test of the sandy soil treated with OS, Z and RM (Case 2). IC – Initial concentration

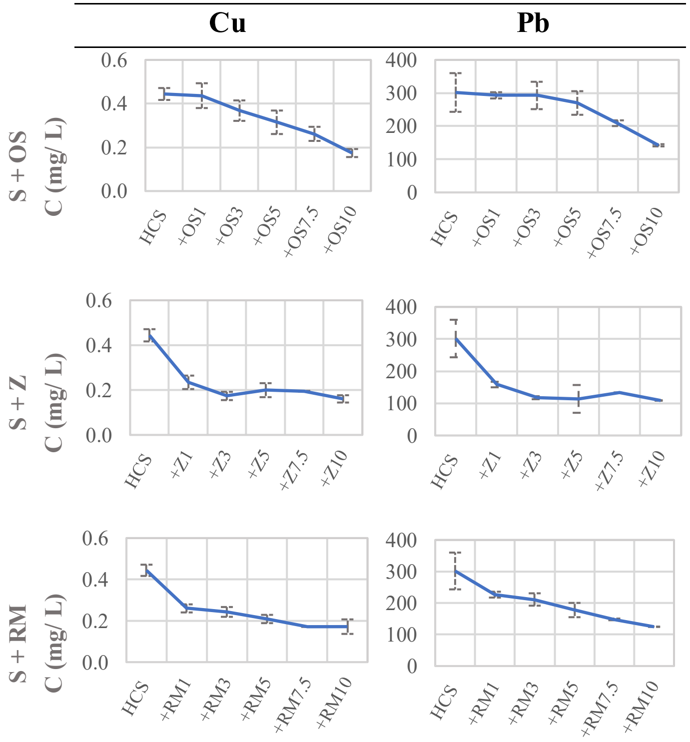

Figure A.3 Toxic metal concentrations in the leachate obtained via the TCLP test of the HCS treated with OS, Z and RM

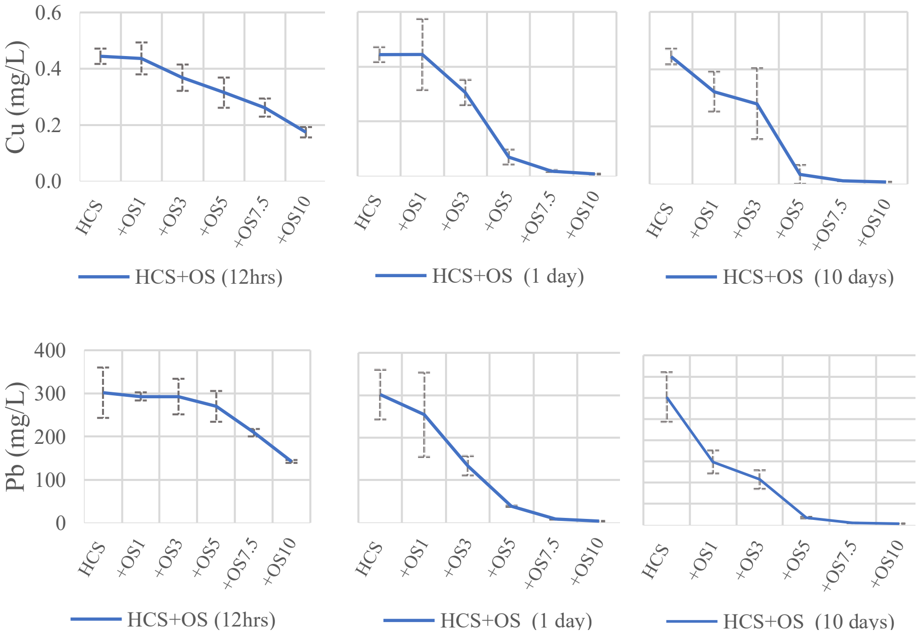

Figure A.4 Cu and Pb concentrations in the leachate obtained through the TCLP test of the HCS treated with OS at different extraction (contact) times. OS – Oyster shell. The number after the binder abbreviation represents mass percentage.

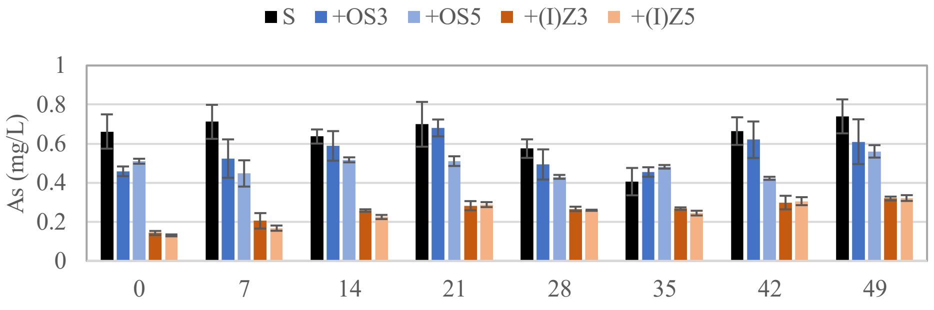

Figure A.5 Concentration of As, Pb, and Zn after binder addition in the pot cultivation test

Abstract in Korean

굴패각, 제올라이트 및 레드 머드 결합 메커니즘 기반 오염시나리오에 따른 독성 중금속 고정화 기술 적용가능성 평가

초록

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굴패각 (Oyster shell – OS), 제올라이트(Zeolite – Z), 레드 머드 (Red mud – RM)는 오염된 토양을 제어하고, 복원하는 안정화 및 고형화기법을 기반으로 하는 안정화제로 연구자들의 관심을 끌고 있다. 이러한 과정은 중금속을 고정하는 매체의 pH, 접촉 시간, 초기 중금속 농도의 영향을 받을 수 있다. 본 연구에서는 중금속 오염토양에 대한 네 가지 시나리오의 상황에서 중금속을 안정시키는 OS, Z, RM 의 성능을 조사하고자 한다. 오염토양 및 안정화제의 광물학적 특성을 규명한 후, 안정화제의 중금속 용출 저감 효율을 비교하기 위해 첫 번째 평가에서는 혼합 배치 실험을 다양한 중금속 오염토양과 혼합된 안정화제로 구성하였고, 정규추출법을 적용하여 독성 중금속 농도를 측정하였다. 두 번째 안정화제 평가는 비소오염 실내포트 토양배양실험 및 비소 흡착배치 실험을 수행한 것으로 이전 평가에서 나타난 가장 효과적인 안정화제 두 가지를 사용하였다.

혼합배치 실험에서 토양 용출법을 통한 결과를 살펴보면 OS 는 광산 현장(Case I)의 토양 샘플과 군사 지역의 모래 토양 샘플(Case II)에서 각각 Pb 의 약 82%와 Cu 의 78%를 제어/결합하였다. 반면 Z 는 오염이 심한 토양(인공오염토양 HCS, Case III)에서 Pb 를 OS, RM 보다 낮은 용량에서 50% 이상 결합시키는 데 매우 효과적이었으며, RM 은 독성금속 농도가 낮은 토양(Case I, II)에 적용했을 때 불안정한 성능을 보였다. 하지만 5% 이상으로 RM 을 사용할 때 Pb 가 고형화/안정화된 것으로 나타났다. 또한 OS 의 Pb−안정화 성능은 접촉 시간이 증가할 때 상당히 개선되었으며, 1 일 후에는 Pb 의 87%, 10 일 후에는 94%로 발현되었다. 이는 기본적으로 OS 와 RM 이 Z 에 비하여 산성 매체를 알칼리 상태로 쉽게 변화시킬 수 있기 때문으로 사료된다.

두 번째 안정화제 평가~~의~~ 결과에서는, 비소토양(Case IV)에서 Z 가 OS (최대 60 %)에 비해 비소 결합이 더 우수했으며 흡착 메커니즘 대신 토양 광물과 상호 작용하는 높은 양이온교환용량이 원인 일 수 있음을 나타낸다. 또한 흡착제가 As(III)와 직접 접촉한 수용액에서는 1: 5(결합제: 액체)을 사용하여 OS 와 Z 는 As (III) 농도의 10 % 만을 감소시켰다. Freundlich 등온선은 비소의 흡착 거동이 두 안정화제의 표면에 단일 층으로 형성된다 라는 것을 제시하였다.

안정화/고형화 법을 통해 안정화제로 사용될 토양에 OS, Z, RM 첨가의 영향을 관찰하기 위해 추가 실험을 진행하였다. 지질 공학적 측면에서 OS 를 추가하면 최대 건조 단위 중량이 증가하는 반면 Z 및 RM 은 이 값을 감소시키고 Z 및 RM 의 최적함수비를 증가시킨다. 흡착 시험 안정화제가 함유된 95 % 다짐 샘플로 직접전단시험을 수행한

결과에 따르면 내부마찰각이 7 ~ 11 % 범위에서 약간 감소하는 경향을 보였으며 점착력은 증가하는 것으로 나타났다.

각 조건 시나리오에 적합한 결합제를 선정하기 위한 실험에서 독성 중금속의 초기 농도, 독성 중금속 유형 및 pH 매체가 결합 과정에 영향을 미칠 수 있는 주요 요인으로 나타났다. 특히 안정화제를 추가 후 pH 가 증가하면 수산기 이온이 금속 침전에 직접 참여한다. 또한 본 연구는 안정화제의 용량 증가가 독성 중금속 농도 감소에 유리할 수 있음을 보여주었지만 2 차 오염을 피하기 위해 추가 평가를 수행해야한다. 예를 들면, 다른 여타의 중금속 (RM 의 수용성 Al 농도) 용출에 대한 RM 의 위험성에 대한 검토가 필요하다고 본다.

본 연구의 결과를 통하여 안정화제 OS, Z, RM 은 서로 다른 메커니즘을 통하여 중금속의 안정화 및 고형화에 사용될 수 있음을 알 수 있었으며, 특히 굴패각 (OS)은 중금속 침전 및 물리적 흡착을, Z 는 양이온교환 및 물리적 흡착이 우세한 것으로 나타났다. 독성 중금속의 침전 및 양이온교환에 의한 RM 의 기작은 오염부지에서 중금속과 결합할 수 있을 것으로 연구된다. 그러나 각 오염 시나리오에 따라 적용 한계를 파악하는 것이 매우 중요하다.

주요어: 오염토양 복원, 침출/용출, 화학적 안정화, 저가의 안정화제, 잠재적 독성 중금속, 지속가능한 해결책, 실내포트 토양배양실험, 흡착배치 실험.

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