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공학석사 학위논문

**Evaluating properties of zeolite-soil mixture
as adsorptive fill material under industrial
zones**

산업단지 하부 지반의 흡착 성토재로써
제올라이트 토양 혼합물의 특성평가

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Abstract

Evaluating properties of zeolite-soil mixture as adsorptive fill material under industrial zones

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In the case of soil under the industrial zones, it is more vulnerable to heavy metal contamination than agricultural or residential areas due to high industrial activity. Unlike organic contamination, this heavy metal contamination does not naturally decompose by biodegradation over time and even become a source of groundwater pollution. Therefore, in this study, it is intended to reduce the spread of pollution and furthermore to prevent groundwater contamination by placing the adsorption fill layer under the industrial zone. In the case of soil under the industrial zones, sufficient bearing capacity should be provided to support the upper structure. Among the heavy metals, zinc and lead are mainly focus on this study which is prior contamination of South Korea. In this study, Zeolite, efficient sorbent for heavy metal removal, was mixed with weathered granite soil, which is commonly used as fill material in South Korea, to form an adsorptive fill layer. The geotechnical engineering characteristics of the mixture were analyzed through the standard compaction test, direct shear

test, and permeability test. As a result of the standard test, all compounds except SZ75 showed values above the regulation value. As a result of the direct shear test before and after the adsorption test, all mixtures maintained an internal friction angle of 30°. The results of the permeability test showed that hydraulic conductivity increased as the zeolite content increased. The batch test, column test, and even soil tank test were performed to test geoenvironmental engineering properties. The batch test results showed that adsorption capacity tends to increase with increasing zeolite content, and even SZ25 has a strong resistance to heavy metal desorption. The column test was performed to review the effects of flow. The result of the column adsorption test showed that the adsorption capacity of SZ25 and SZ50 showed similar value, which is believed to have affected by the hydraulic conductivity as well as adsorption ability. As with column desorption test results and batch test results, resistance to desorption increased as the zeolite content increased. The soil tank test was carried out to perform the test under more field-like conditions. The results showed that the trend that SZ25 showed about 3.5 times adsorption capability and had better resistance to desorption is similar to column result. In conclusion, SZ25 can be suggested as an optimum mixing ratio in an economical and engineering perspective. By placing the adsorption fill layer with the soil-zeolite mixture, it is expected that the area of soil contamination can be reduced and ground-water pollution can be prevented.

Keywords : heavy metal adsorption, zeolite-mixed soil, desorption, strength, industrial zone, adsorptive fill material, pilot scale test, column test

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Chapter 1. Introduction

1.1 Background

1.1.1 Industrial zones in South Korea

The industrial complex is a collection of facilities of factories or buildings related to industrial activities. Due to the high urbanization and industrialization of South Korea, the number of industrial complexes in South Korea has been increased rapidly since 2003. The number of industrial complexes in Korea is shown in Fig. 1.1 (Korea Industrial Complex Corporation, 2017). Industrial activities such as transportation, factory emission, and mining are some of the main factors of soil contamination. Among various contaminations, soil contamination has a lack of mobility unlike air or water contamination, so it remains for a long period of time. Moreover, the contaminants may even pollute groundwater which is the source of drinking water. Therefore, soil contamination with heavy metals has been considered as one of the main threats of human health because of their carcinogenic effect. Additionally, Heavy metal is not biodegradable in nature unlike organic compounds and tends to accumulate in living organisms, causing various diseases and disorders (Bailey et al., 1999, Sprynskyy et al., 2006, Oves et al., 2012; Mukwaturi and Lin, 2015). It was reported that metal oxides even have antibacterial activities (Mukwaturi and Lin, 2015). Table 1.1 shows the number of industrial zones that are contaminated. Among such soil contamination, zinc was the prior contaminant founded under industrial zones in Korea. Although nickel was second

frequently founded, it has similar mobility with zinc, so lead has chosen for the experiment. Lee and Koh investigated soil contamination of various sites at Ulsan, South Korea. The level of soil contamination was like following nonferrous metallic industrial complex > mechanic and shipbuilding industrial complex > heavy traffic area > forest area > residential area. The heavy metal concentration of the nonferrous metallic industrial complex was especially high (Lee and Koh, 2003). This trend that industrial area showed the highest concentration of soil contamination among the residential, the traffic dense and the industrial area in Daegu and Ulsan, South Korea is also reported (Lee, 2005). Jeong et al, 2015 also reported a high level of soil contamination of Korean industrial zones.

Table. 1.1 Detailed soil environmental assessment of industrial zones in South Korea, 2004-2012 (Ministry of Environment of South Korea, 2015)

Year	Industrial Area	Num	Contaminants
2004	Banwol	7	BTEX, TPH
2005	Onsan	92	Zn , Cu, Cd, Pb , As, Ni, TPH
2006	Changwon	36	Zn , Cu, Ni, TPH
	Yeosu	26	Zn , Pb , As, Ni, TPH, BTEX
2007	Ulsan Mipo	59	Cr ⁶⁺ , Fe, Zn , As, Ni, TPH, BTEX
	Sihwa	30	Zn , Cu, Ni, TPH, BTEX
	Cheongju	2	Ni, TPH
	Iksan	4	BTEX
2008	Bupyeong, Juan	39	Cu, TPH
	Jinju Sangpyeong	5	Zn
	Seonseo	47	Zn , Ni, TPH, BTEX
	W.Daegu	40	Zn , Ni, TPH, BTEX
2009	Yangsan	45	Zn , TPH, BTEX
	Dalseon	36	Zn , TPH, BTEX
	Jeonju	13	Zn , TPH
	Gumi	26	As, TPH, PCE
2010	Hanam	41	Pb , TPH, Benzene, Xylene, PCE
	Namdong	13	As, Fe, TPH, TCE
	Daegu	42	TPH
	Pohang	78	Zn , Ni, TPH, BTEX
2011	Gwangyang	9	Zn , Pb , TPH, BTEX
	Okpo	1	TPH
	Gunsan	12	Zn , As, TPH, BTEX
	Seoul (Korea Export)	2	TPH, Toluene
	Daedeok	9	Cu, Pb , TPH, Benzene
2012	Mungji-Noksan	16	Zn , Pb , TPH, Toluene
	Busan	1	PCE
	Seongnam	7	Cu, TPH
	Dasan	1	TPH
Total		739	

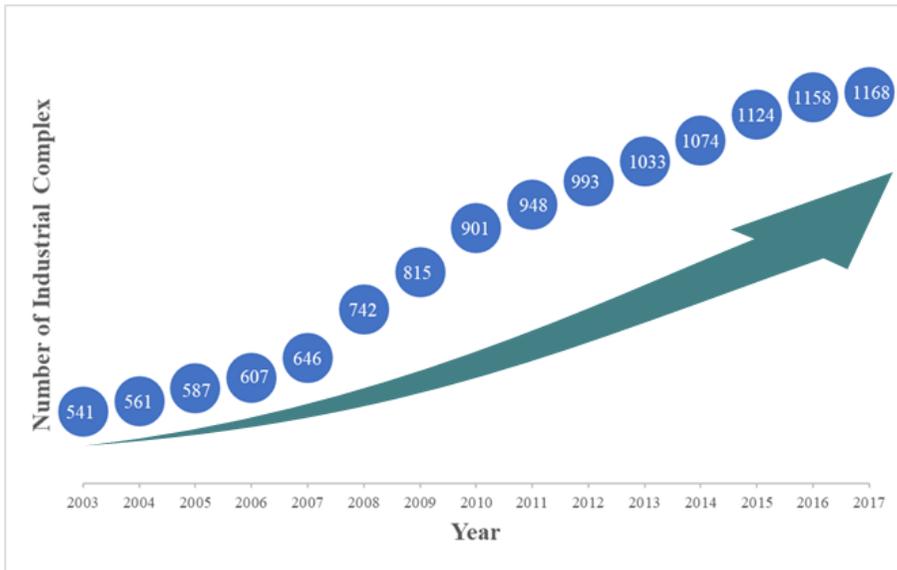


Fig. 1.1 Number of industrial complexes in South Korea (Korea Industrial Complex Corporation, 2017)

1.1.2 Heavy metal contamination under industrial zones (worldwide)

The soils under industrial zones were more vulnerable to heavy metal pollution than other sites such as agricultural, residential, or forest areas. According to Golia et al., 2008, the soil contaminations of industrial zones were generally showed a higher value than forest or agricultural areas in Greece (Fig. 1.2). The industrial zones in India were also showed highly contaminated by heavy metal (Krishna and Govil,2004, Govil et al., 2008). Fakayode and Onianwa (2002) investigated that soil around the industrial estate of Nigeria was severely polluted by heavy metal. The highest value of zinc was 307.1 mg/kg while 6.2 mg/kg of the control site. The heavy metal concentration of soil in China and Iran was reported by Li et al., 2009, Jalali and Khanlari, 2008, respectively.

Both pieces of research showed that industrial activities lead to severe environmental problems by pollution and the concentrations of zinc and lead were higher than other heavy metals. Among the researches done by various researchers, the main contaminants under industrial zones were zinc and lead.

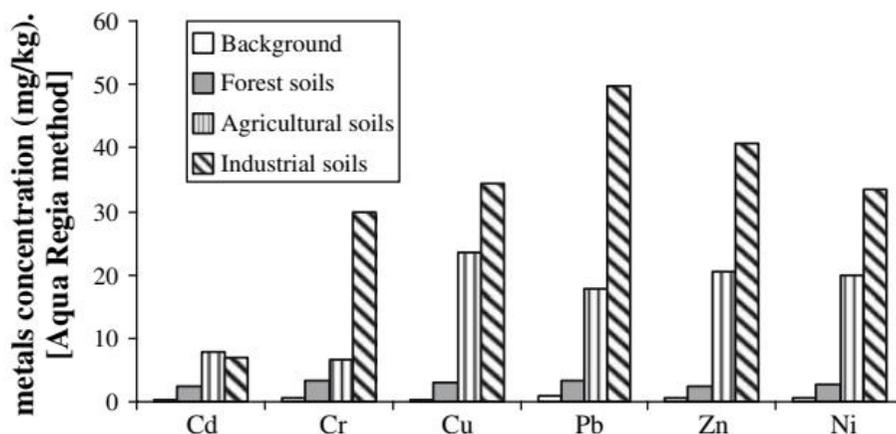


Fig. 1.2 Mean (2004 and 2005) total metal concentrations (mg/ kg) from each soil type (Golia et al., 2008)

Sampling point	Cd	Pb	Cu	Zn	Ni	Cr	Mn
S1	5.34	122.8	9.9	214.0	30.9	31.0	430.0
S2	4.31	80.6	72.0	240.0	25.6	34.0	266.0
S3	2.37	138.5	8.9	328.0	11.6	32.0	460.0
S4	2.97	175.0	25.1	236.0	13.7	28.0	274.0
S5	2.59	426.0	43.0	307.1	17.8	42.0	134.0
S6	2.76	125.1	20.3	245.7	15.2	28.6	269.4
S7	1.88	65.7	13.2	205.3	9.7	7.1	189.2
S8	1.61	70.3	9.5	211.2	11.1	16.3	247.1
S9	2.21	91.1	28.1	242.1	17.3	20.1	276.8
CTR	0.09	5.1	1.7	6.2	1.3	2.1	11.8

Fig. 1.3 Heavy metal (mg/kg) in the soil around the industrial area of Nigeria (Fakayode & Onianwa, 2002)

Soil samples	Cu	Zn	Pb	Cd
Soil heavy metal contents				
1	326.31 ± 20.19	422.41 ± 76.15	309.61 ± 50.23	2.05 ± 0.07
2	102.12 ± 21.09	443.00 ± 42.08	263.84 ± 23.43	1.32 ± 0.12
3	340.35 ± 27.61	882.46 ± 138.61	459.78 ± 21.51	2.06 ± 0.27
4	361.17 ± 37.40	774.17 ± 66.51	776.42 ± 43.46	10.96 ± 0.94
5	245.23 ± 35.50	902.31 ± 50.74	821.11 ± 48.99	11.04 ± 3.29
6	247.22 ± 19.13	739.22 ± 83.73	455.80 ± 34.40	8.12 ± 2.21
7	194.37 ± 18.76	776.92 ± 78.23	732.26 ± 63.80	9.88 ± 3.50
8	112.45 ± 16.36	543.17 ± 35.29	496.16 ± 37.00	1.29 ± 0.74
9	89.37 ± 7.70	374.83 ± 16.52	274.67 ± 21.81	1.37 ± 0.59
10	58.71 ± 11.11	245.38 ± 122.90	113.40 ± 10.67	0.76 ± 0.34
11	90.99 ± 6.75	671.71 ± 54.18	273.64 ± 32.57	2.86 ± 0.24
12	108.76 ± 13.61	502.07 ± 59.21	621.38 ± 39.11	6.48 ± 1.05
13	527.93 ± 16.67	912.45 ± 109.62	1014.11 ± 78.37	81.20 ± 11.84
14	244.83 ± 58.69	685.37 ± 103.07	524.26 ± 23.72	2.76 ± 0.57
15	182.31 ± 33.14	532.79 ± 68.20	435.15 ± 63.99	5.21 ± 1.73
16	251.71 ± 11.79	802.44 ± 59.37	512.13 ± 35.07	12.66 ± 4.35
17	257.44 ± 44.48	514.73 ± 22.14	511.77 ± 37.41	6.64 ± 1.62
18	130.58 ± 9.04	392.19 ± 28.17	255.37 ± 32.30	1.72 ± 1.22
19	104.72 ± 17.70	307.66 ± 40.39	119.41 ± 21.17	2.32 ± 1.77
20	204.60 ± 12.97	573.09 ± 27.09	433.56 ± 50.96	1.17 ± 0.32
Statistical results				
Maximum	527.93	912.45	1014.11	81.20
Minimum	58.71	245.38	113.40	0.76
Mean	209.06	599.92	470.19	8.59
Median	199.49	558.13	457.79	2.81
Background concentrations in the soils of Shenyang (Luo et al. 2003)				
	24.57	59.04	22.15	0.16

**Fig. 1.4 Heavy metal contents in soils of industrial zones, Tiexi, China
(Li et al.,2009)**

1.2 Research Concept

Since soil under industrial zones is easily exposed to heavy metal contamination, any countermeasures that can prevent further spreading is needed. In this study, the concept of an adsorptive fill layer is given to manage heavy metal pollution and prevent groundwater. Adsorptive fill material is which can reduce the area of contamination in order to decrease the cost for remediation and risk to humans. The weathered granite soil, which problems as fill material in South Korea, was used as a base material for this study. Throughout various sorbent, zeolite was chosen not only because of it's higher absorptive capacity but also it is natural mineral so it has sufficient strength than other sorbents such as oyster shell, peanut shell, or activated carbon. Generally, previous researches are focused more on adsorption, however, this study is aiming to use as fill material so this study focuses on not only adsorption but also strength parameters. Zeolite was mixed with soil to form an adsorptive fill layer. This fill layer should have enough bearing capacity to sustain industrial complexes on top of it. Since the properties that exhibit adsorption and strength are different, it is necessary to suggest the optimum mixing ratio which satisfies both regulation to use as fill material and high value of adsorption capacity. Furthermore, it is necessary that fill material should have resistance against desorption to prevent after contamination when rainfall occurs. The strength after the sorbing heavy metal was also measured to evaluate for safety.

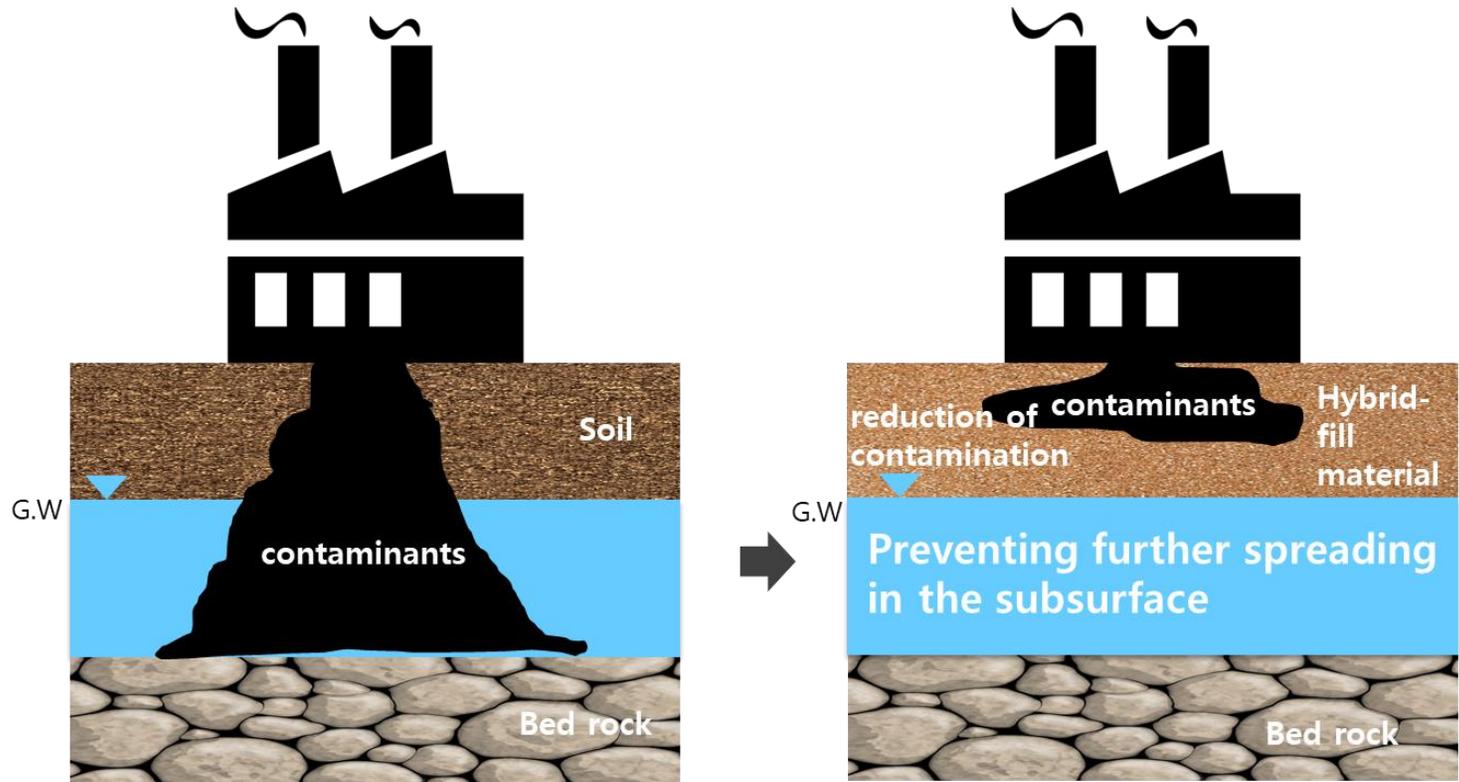


Fig. 1.5 Concept of this research

1.3 Objectives

Due to the high treatment cost of contaminated soil, it is required to reduce the area of contamination. Since the soil under the industrial is severely contaminated than other areas, this study is mainly focused on the industrial zone. The adsorptive fill layer is formed to prevent further spread of heavy metal pollution of the subsurface. The zeolite mixed soil was used as an adsorptive fill material. Substitution and mixing with the same particle size of zeolite and soil were considered, however, because those methods cannot be applied to field so mixing with weight ratio was chosen for this study. Finding the optimum mixing ratio in both economical and engineering aspects is the goal of this study. For this goal, geotechnical and geo-environmental tests were conducted to evaluate the properties of zeolite mixed soil. To evaluate the adsorption capacity of zeolite mixed soil in different conditions, batch, column, and pilot-scale tests were performed. Adsorption tests of zeolite were studied by other researchers, however, this study's mixing with soil and use as fill material is special and the comparison of size effect between column scale and pilot scale is necessary to apply this method in field scale.

Chapter 2. Literature Review

2.1 Previous research

This study was motivated by several previous research about removing heavy metal by natural zeolite, zeolite mixed materials for various objectives, and development of fill material using other material. The literature reviews of the researches were to refer to the experimental method, apparatus, and potential application of zeolite. Various researchers conducted batch and column experiments to test the heavy metal removal efficiency of natural zeolite. Natural zeolite was gathered from all over the world such as Turkey, Greece, Mongolian, and South Korea. Some researchers tested the geotechnical properties of zeolite and used zeolite as the bottom layer by mixing with bentonite. Previous researches reveal that zeolite has high adsorption capacity on heavy metal. However, previous researches are generally conducted with small the such as batch or column, so it might have a different trend on a larger scale. Thus, testing in the pilot-scale is required to apply in the field.

2.1.1 Zeolite Efficiency of removing heavy metal by batch test

Among various treatment methods, ion exchange is one of the mainly used methods in the world if effective and low-cost ion exchangers are used. Removing heavy metal ions of aqueous solution by natural zeolite have been studied by various researchers due to its low-cost and high adsorption capacity (Ćurković et al, 1997, Bailey et al, 1999, Álvarez-Ayuso et al., 2003, Cabrera et al., 2005, Motsi et al., 2009, Egashira & Habaki, 2012, Zanin et al., 2017). Zeolites in natural are commonly formed by alteration of volcanic rocks which contains glass with freshwater or seawater (Badillo-Almaraz et al., 2003). The structures of zeolite consist of three-dimensional frameworks of SiO₄ and AlO₄ tetrahedra (Meier, 1961, Xu & Van Denventer, 2000). The surface of zeolite is negatively charged by isomorphous replacement of Si⁴⁺ by Al³⁺. This negative charge is balanced by the exchangeable cation (sodium, potassium, or calcium). These exchangeable cations are used to ion exchange with heavy metal ions in solutions such as lead, cadmium, zinc, and manganese (Erdem et al., 2004, Perić et al., 2004). It was observed that heavy metal selectivity series hold by natural clinoptilolite from Greek was like following: Pb²⁺ > Cr³⁺ > Fe³⁺ ≈ Cu²⁺ (Inglezakis et al., 2003). In the research of Zamzow & Murphy (1992), the properties such as Si/Al ratio and bulk density and removal efficiency of the metal cation (Cd, Cu, Zn) of various (24) natural zeolite was investigated. The phillipsite was highest in bulk density while mordenite showed the lowest of cation uptakes. Ćurković et al. (1997) performed an adsorption batch experiment about lead and cadmium removing by natural zeolite with and without treatment. The natural zeolite experiments with 2 NaCl solution. The

result indicated that the removal efficiency by zeolite researchers as the initial concentration of metal ion increases and the uptake of metal ion had increased as temperature increases. The effect of temperature and initial concentration has in Fig. 2.1.

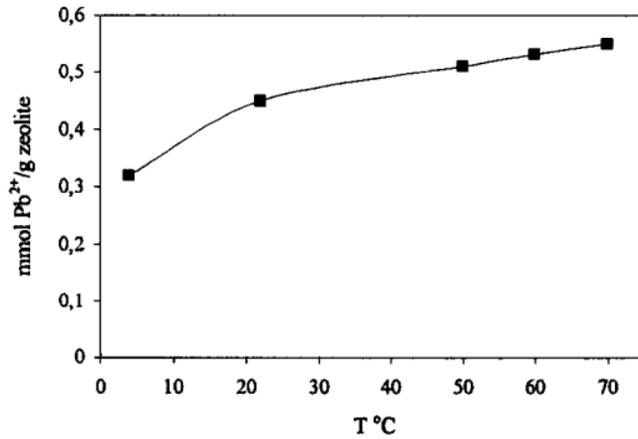


Fig. 2.1 Effect of temperature on heavy metal sorption by zeolite (Ćurković et al., 1997)

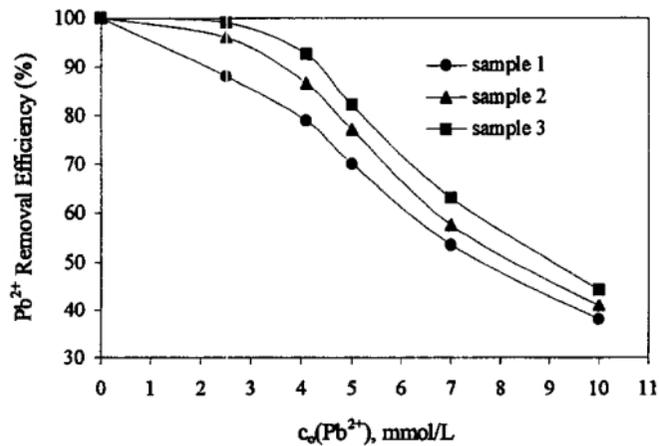


Fig. 2.2 Effect of the initial concentration of heavy metal ions on sorption by zeolite samples (Ćurković et al., 1997)

In the early 2000s, removing heavy metal ions in aqueous solution by natural zeolite had been investigated, actively. Álvarez-Ayuso et al. (2003) reported 90% of equilibrium concentration was sorbed within 1 hour of interaction. It was also mentioned that the sorption sequence of natural zeolite, Clinoptilolite for Álvarez-Ayuso's research, was like the following: Cu>Cr>Zn>Cd >Ni. In the research done by Inglezakis et al. (2003), the selectivity of natural clinoptilolite has been studied. It can be seen that in both two-component and four-component mixture solutions, the selectivity of heavy metal ions is like following: $Pb^{2+} > Fe^{3+} > Cr^{3+} \gg Cu^{2+}$. In the case of single-component solutions a selectivity order of $Pb^{2+} > Fe^{3+} > Cu^{2+} > Cr^{3+}$ may be deduced with Fig. 2.4 Test of selectivity of heavy metal ions on natural clinoptilolite. This trend for natural zeolite is also shown in the research of other researchers. Erdem et al. (2004) showed a sequence of Co>Cu>Zn>Mn while Perić et al. (2004) stated Pb>Cu>Zn. Selectivity varied as $Cu^{2+} \gg Zn^{2+} > Ni^{2+}$, with adsorption capacities comparable to those of other low-cost sorbents such as natural zeolites or bentonite. (Cabrera et al., 2005)

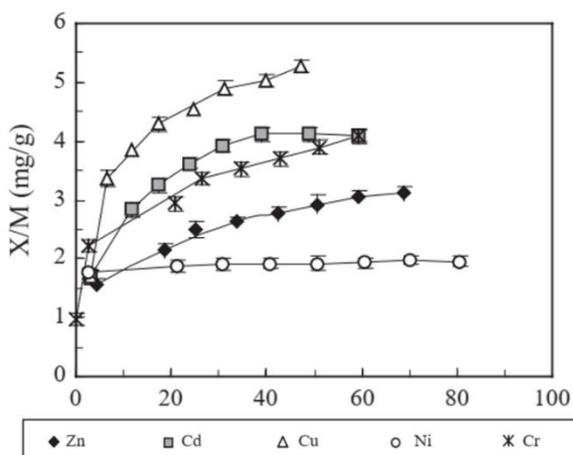


Fig. 2.3 Sorption isotherms of natural zeolite (Álvarez-Ayuso et al., 2003)

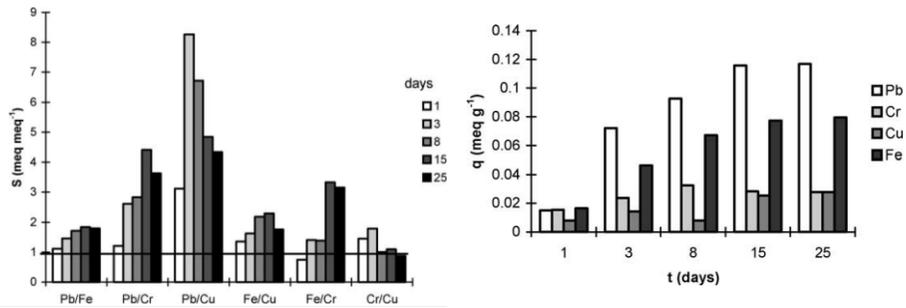


Fig. 2.4 Test of selectivity of heavy metal ions on natural clinoptilolite

(a) two-component (b) four-component (Inglezakis, et al., 2003)

The compare of sorption between single-component solution and the mixed solution was also tested by Sprynskyy et al. (2006) and Motsi et al. (2009). According to Sprynskyy et al (2006), copper, cadmium, and lead showed similar sorption even in multi-component solutions. However, nickel sorption has less occurred in a multi-component solution. This is against the research of Motsi et al. (2009) that they mentioned copper, manganese, and zinc showed less sorption in mixed solutions.

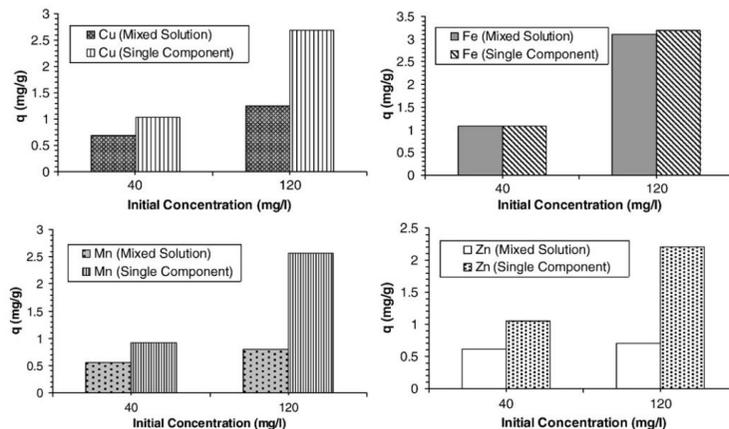


Fig. 2.5 Comparison of the adsorption of heavy metal ions from single- and multi-component solutions (Motsi et al., 2009)

2.1.2 Zeolite Efficiency of removing heavy metal by column test

The aim of this study is to use zeolite mixed soil as a fill layer. Thus, the adsorption of heavy metal inflow conditions is required. The column experiment had done by various researchers, and some of the research is referred to in this study. Previous researches are focusing to use natural zeolite as a Permeable Reactive Barrier (PRB) or bottom layer of landfill. The factors affecting the result of the column test are flow rate, initial concentration, temperature, pH, and bed height. The effect of the initial concentration of metal, temperature, and pH is equal to those of the batch experiment. Flow conditions influence exchange characteristics in columns. The saturation in the column depends on the flow rate of the solution and favored by a low flow rate. As a result, the low flow rate leads to higher adsorption capacity (Inglezakis et al., 2002, Stylianou et al., 2007). In detail, the time needed to reach the breakthrough point and the exhaustion point is longer by approximately four times for the flow of 1.0 mL/min than for the flow of 3.0 mL/min. (Medvidović, et al., 2006). The bed height is another factor affecting the column experiment. Can et al. (2010) reported that as height increases the time of breakthrough points also increased. Since the column test is modeling flow condition. The sorbents can not fully adsorb the heavy metal ions in solution, unlike batch experiments. Thus, the adsorption capacity obtained by the column test tends to have a lower value than the result of the batch test. The operating capacity obtained by the batch test and column test is different due to the flow condition of the column test (Inglezakis & Grigoropoulou, 2003).

The other case for using zeolite is the bottom layer of the landfill. Turan et al.

(2005) treated ammonia leachate from a landfill with a zeolite column system. Natural zeolite showed good performance on removing ammonia (>90%) and even increased with regeneration steps.

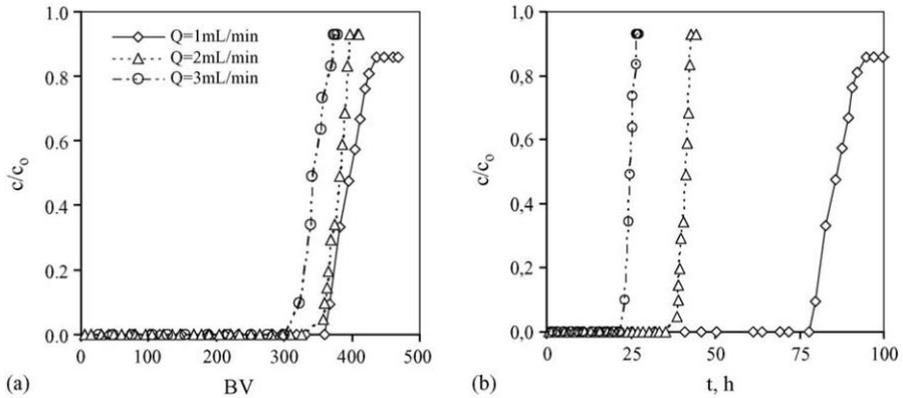


Fig. 2.6 Comparison of the breakthrough curve of different flow rate

(a) c/c_0 vs BV (b) c/c_0 vs t (Medvidović, et al., 2006).

Table. 2.1 Breakthrough points (BV of effluent) and operating capacities (meq/g), for $C/C_0=10\%$ (Inglezakis et al., 2002)

	Q(BV/h)	Fe	Cu	Cr	Pb
Breakthrough point		1.42	1.15	1.8	5.13
	15				
Operating capacity		0.053	0.084	0.104	0.210
Breakthrough point		1.27	1.18	2.32	5.47
	10				
Operating capacity		0.080	0.084	0.098	0.239
Breakthrough point		3.12	2.8	6.42	12.3
	5				
Operating capacity		0.118	0.131	0.178	0.433

2.1.3 Zeolite amended material

Zeolite amended materials have been studied for application as reactive materials due to its high adsorption capacity. Kayabali (1997) tested engineering aspects of bentonite-amended natural zeolite to use as landfill liner. The optimum water content and dry densities determined by vibration hammer were ranged from 33 to 42% and 1.16 to 1.25 t/m³. The permeability of mixture and bearing capacity was in the range of values to use as the bottom layer. Tunçan et al. (2003) mentioned that bentonite-zeolite mixture has not only low permeability but also high cation exchange capacity. Therefore, the mixtures can hold heavy metal effectively so it can act as the chemical filter. Turan & Ergun (2009) tested the zeolite-bentonite mixture to use as a liner material. The adsorption capacity of the natural zeolite-bentonite mixture increases with increasing natural zeolite rate in the mixtures which is due to higher cation exchange capacity of natural zeolite.

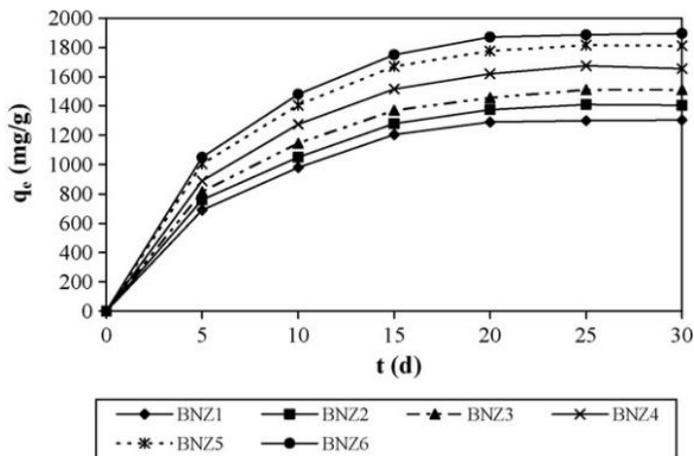


Fig. 2.7 Adsorption capacities for the removal of Cu as a function of landfilling time (Turan & Ergun, 2009)

In the research of Joanna & Kazimierz (2013), the natural zeolite is mixed with sand to use as reactive material and the removal of several heavy metals in different mixing ratios was shown. The adsorption capacity tends to increase with the higher composition of zeolite. According to the batch test, the presence of ammonium, calcium, and magnesium affected the removal of copper to decrease. The trend that as the increment of zeolite content leads to an increase of adsorption capacity is similar to the research of Turan & Ergun (2009). Therefore, it can be expected that the increase of zeolite in zeolite-soil mixture will increase the heavy metal removal efficiency, in our study.

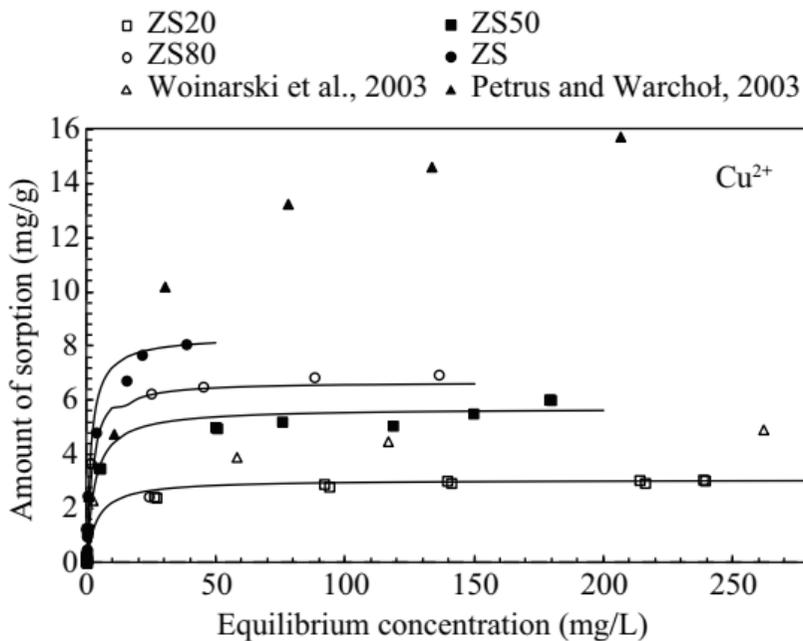


Fig. 2.8 Langmuir adsorption isotherms for the zeolite and zeolite-sand mixtures from the batch test (Joanna & Kazimierz, 2013)

2.1.4 Fill material using other material

The previous research of fill material with other materials such as lightweight fill materials or recycling waste has been focused on geotechnical properties (Shin et al., 2001, Lee et al., 2011). These researches evaluated geotechnical characteristics such as compaction, shear strength, and permeability. However, a geo-environmental characteristic such as adsorption capacity was not considered, unlike this study. Because of rapid urbanization and industrialization of South Korea, soil and groundwater contamination are one of the most crucial environmental problems. Thus, a study for preventing this pollution is needed.

Table. 2.2 The maximum dry unit weight and optimum water contents of the samples (Lee et al., 2011)

Sample	Maximum dry unit weight (kN/m³)	Optimum water content (%)
Weathered soil	18.4	14.0
Bottom ash	15.6	15.5
Residual bottom ash	13.1	18.3
Tire sherds- bottom ash mixture	11.8	-
Tire shreds-sand mixture	15.0	-
Tire shred	7.9	-

2.2 Data analysis of adsorption isotherm equilibrium test

2.2.1 Langmuir adsorption isotherm model

The Langmuir isotherm model is one of the mainly used for analyzing the adsorption isotherm test. The Langmuir model is based on the assumption that molecules (pollutants) without intermolecular interactions are ideally diluted and bound to uniform binding sites of the adsorbent. The shape of the adsorbent particles and the exact location of the binding site are not considered, but only the uniformity of the binding site is considered. However, the surface of the actual adsorbent is not uniform, and the interaction between the adsorbed molecules (adsorbents) cannot be ignored unless it is adsorbed very strongly. This model cannot be used in the case when adsorbed adsorbate covers the surface of the adsorbent completely. Therefore, the Langmuir model expresses chemical adsorption which is not large in adsorption amount and strong in adsorption intensity. The equation of the Langmuir model can plot in linear form like the following:

$$\frac{C_e}{C_s} = \frac{1}{Q_L K_L} + \frac{C_e}{Q_L}$$

Where C_s is the amount of adsorbed metal ions onto zeolite (mg/g), C_e is the equilibrium concentration of metal in solution(mg/L), Q_L is maximum sorption capacity represents monolayer coverage of sorbent, and K_L represents enthalpy of sorption which is related to the affinity.

2.2.2 *Freundlich adsorption isotherm model*

The Freundlich model is an empirical equation used to express the adsorption mechanism. Freundlich model, unlike the Langmuir model, adsorption can occur in multiple layers which means adsorption continues to occur when the concentration of sorbate increases in the aqueous phase. However, the degree of sorption is diminishing as the adsorption progresses. It is generally known that in low concentration adsorption reactions, both the Langmuir model and the Freundlich model are well suited. However, when experimenting with high concentrations, the difference can be seen clearly.

The equation of Freundlich is expressed:

$$C_s = K_F C_e^{1/n}$$

Where C_s is the amount of adsorbed metal ions onto zeolite (mg/g), C_e is the equilibrium concentration of metal in solution (mg/L), K_F is Freundlich sorption coefficient which represents the ability to absorb, and $1/n$ in numerical value that indicates the strength of adsorption. The equation can be linearized like following

$$\ln C_s = \ln K_F + \frac{1}{n} \ln C_e$$

Chapter 3. Materials & Methods

3.1 Materials

3.1.1 *Weathered soil and zeolite*

3.1.1.1 *Physical and chemical properties*

In this study, Gwanak weathered soil is used to perform characteristic of original fill material. The soils were collected from Gwanak Mountain located near Seoul National University in Korea. The soils were thoroughly mixed and air-dried for 24 hr and sieved with sieve #4. The soils were prepared with drying for 24hr under temperature 105°C in dry-oven before tested. Zeolite was taken from Kumnong company mine in Pohang. The zeolite used in the study is natural zeolite since it has economic strength than artificial zeolite. After gathered, zeolite was also prepared with drying as soil. Zeolite was mixed with the soil by weight ratio of 25%, 50%, 75%, respectively. The samples were named with its contents of zeolite. For example, SZ0 is soil, SZ100 is natural zeolite, and SZ25 is 25% zeolite and 75% soil mixed by weight ratio. The particle size distribution curves were shown in Fig. 3.1. The properties of soil and zeolite were given in Table. 3.1. The chemical composition of the materials was measured by X-ray Fluorescence Spectrometer (XRF). The specific surface area was measured by equipment based on the BET theory. Cation Exchange Capacity (CEC) was measured by NICEM which is an analysis agency in Seoul

National University. The specific surface area and CEC are one of the main factors affecting adsorption capacity to heavy metals and zeolite shows higher values of the factors than soil.

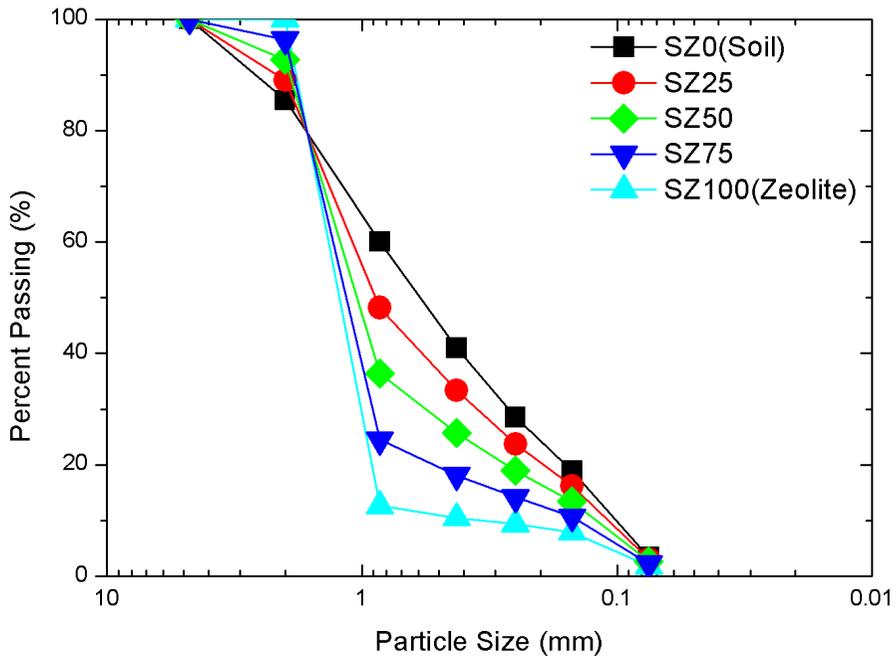


Fig. 3.1 Particle size distribution curve of soil and zeolite mixtures

Table. 3.1 Properties of Gwanak weathered soil and natural zeolite

Property	Gwanak weathered soil	Natural zeolite
pH	7.0	6.5
Classification (USUC)	SP	SP
Chemical composition	SiO ₂ - 59.55; Al ₂ O ₃ - 19.28; Na ₂ O - 1.32; Fe ₂ O ₃ - 6.68; CaO - 0.74; Na ₂ O - 1.32; K ₂ O - 2.96 LOI - 9.46	SiO ₂ - 70.87; Al ₂ O ₃ - 13.96; Na ₂ O - 2.23; Fe ₂ O ₃ - 2.72; CaO - 1.59; Na ₂ O - 3.84; K ₂ O - 3.13 LOI - 3.87
Specific Gravity	2.68	2.33
Cation Exchange Capacity (meq/100g)	9.43	69.58
Specific Surface Area	11.97	44.97

3.1.1.2 X-ray Diffractometer (XRD)

X-ray Diffractometer was performed to see the structure of the zeolite. The major mineralogical component is silicon dioxide (61%) followed by Heulandite-Ca (15.4%), Mordenite(23.8%). Heulandite-Ca and Mordenite are kinds of zeolite. The typical unit-cell formula of Heulandite is $\text{Ca}_4(\text{Al}_8\text{Si}_{28}\text{O}_{72})\cdot 24\text{H}_2\text{O}$ and $\text{Na}_4(\text{Al}_8\text{Si}_{28}\text{O}_{72})\cdot 24\text{H}_2\text{O}$ is for Mordenite. The XRD result is shown in Fig. 3.2. This XRD composition is similar to the research (Kim et al., 2015) who used zeolite from Pohang also.

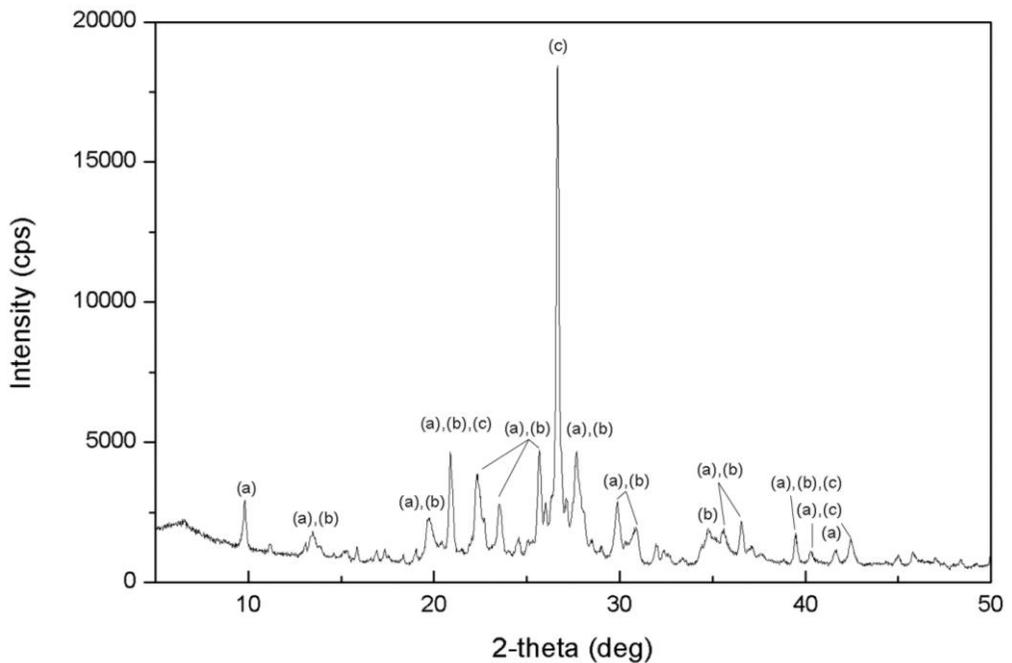


Fig. 3.2 XRD result of natural zeolite

(a) = Heulandite-Ca, (b) = Mordenite, (c) = Silicon dioxide

3.1.1.3 Scanning Electron Microscope (SEM)

SEM pictures were taken to see the close image of those soil and zeolite. Compare to the soil, zeolite seems to have a more porous structure.

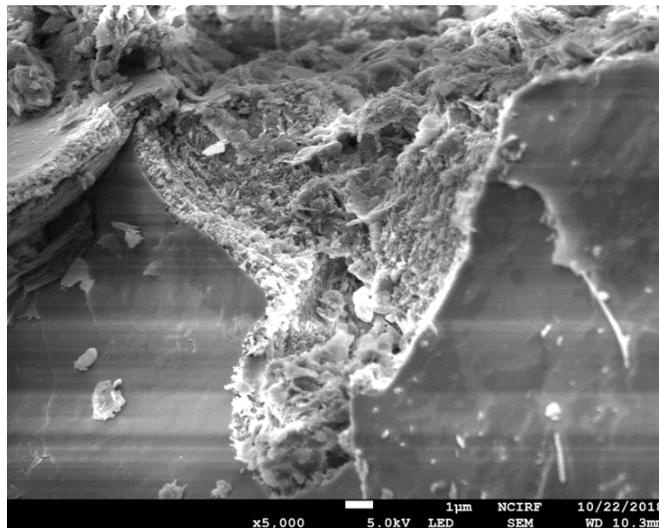


Fig. 3.3 SEM picture of soil (5000 times magnified)

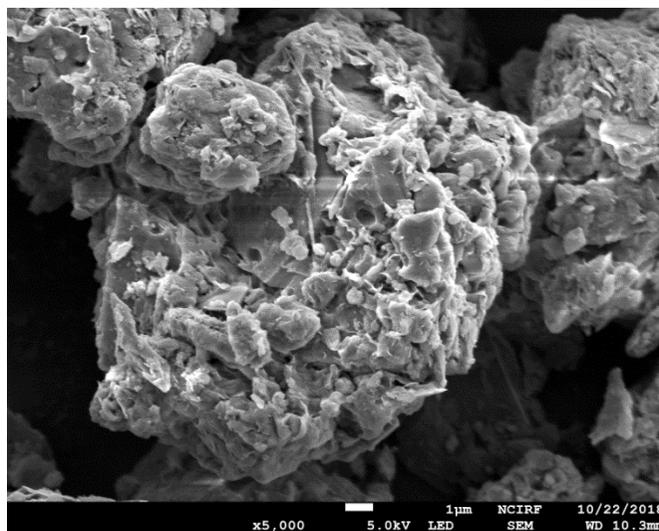


Fig. 3.4 SEM picture of natural zeolite (5000 times magnified)

3.1.2 Mixing method

By the previous research, mixing with the same particle size distribution or partial substitution was tested. In the same particle size mixing, all the mixing ratios showed a higher value of maximum dry unit than Korean regulation. For adsorption capacity, as a percent of zeolite increased the adsorption capacity increased. By partial substitution, all the sample which were substituted showed lower maximum dry unit than soil. Still, all the samples showed suitable value in maximum dry unit weight and friction angle to use as fill material in Korea. However, mixing with the same particle size or substitution is not practical to use in the real field scale. In this study, mixing with zeolite which particle size is under sieve # 40. The particle size used in this research was decided after the adsorption batch test by the particle size of zeolite. According to the adsorption test result, as particle size decreases adsorption capacity increase however, there is no big difference when the particle size becomes smaller than a certain size (sieve 40 in this research). This trend is a similar result of the research done by (Malliou et al., 1994) with clinoptilolite. Typical materials increase specific area and cation exchange capacity as particle size decrease (Helffeich and Kunin, 1963). However, the porous structure of zeolite affects specific surface and cation exchange capacity (CEC). Therefore, in the case of zeolite, the external specific surface and CEC of zeolite account for a relatively small proportion of the total specific surface area and cation exchange capacity (Guan et al., 2010). Thus, the adsorption capacity of zeolite tends to be similar under particle size of sieve # 40.

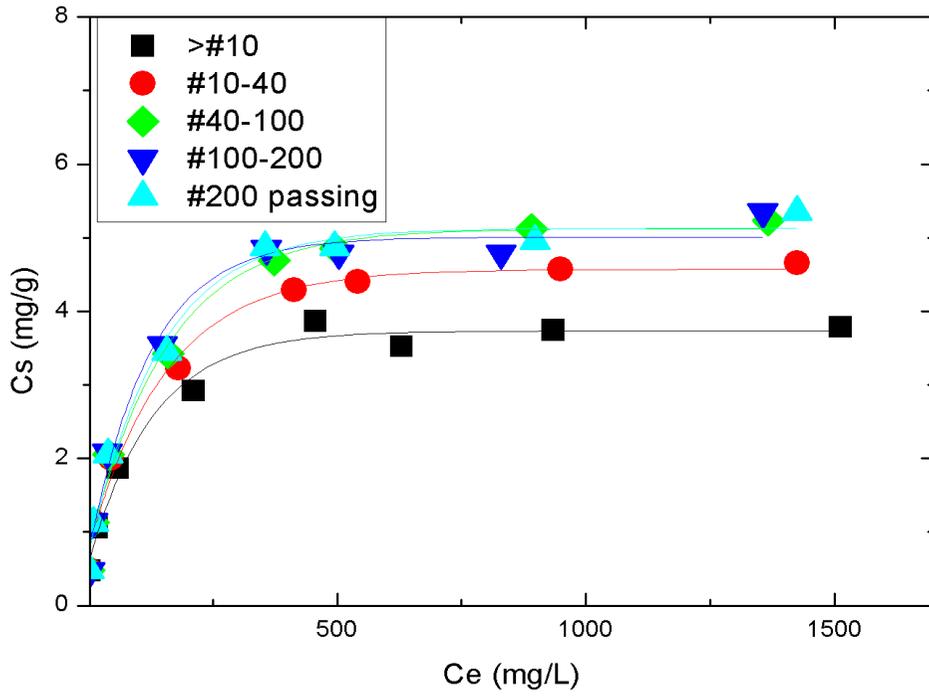


Fig. 3.5 Result of adsorption batch test for the different particle size of the zeolite

3.2 Methods

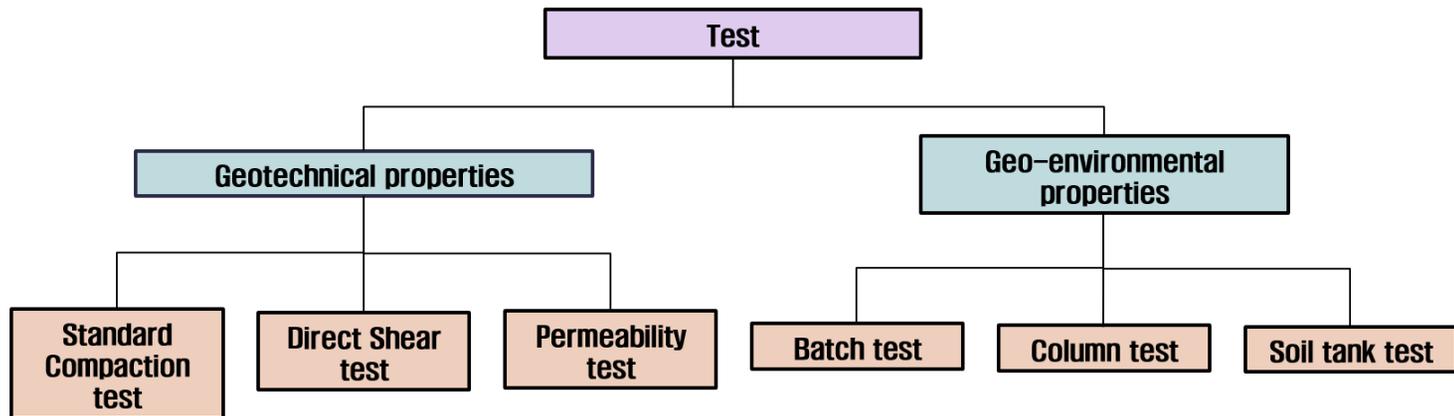


Fig. 3.6 Schematic diagram of the tests in this research

3.2.1 Geotechnical tests

The values of the specification to use as fill material is suggested by the Ministry of Load, Infrastructure, and Transport of Korea. Geotechnical tests were performed to evaluate the strength and permeability of zeolite-soil mixtures to use as fill material which satisfies the specification.

3.2.1.1 Standard compaction test

To obtain the maximum dry unit weight and optimum water content, a standard compaction test was performed with all the mixtures (SZ0, SZ25, SZ50, SZ75, SZ100). The test was followed by the ASTM D 698 method.



Fig. 3.7 Standard compaction test for zeolite-soil mixtures

3.2.1.2 *Direct shear test*

The direct shear test was performed to evaluate the strength parameter of the zeolite-soil mixtures. The test was followed by ASTM D 3080 method. The mixtures were compacted with 90% of maximum dry unit weight at optimum water content determined by the result of the compaction test. The direct shear test was performed with mixtures before and after contamination to investigate the effect of contaminants on the strength of the mixtures.



Fig. 3.8 Experimental apparatus for direct shear test

3.2.1.3 *Permeability test*

Permeability is one of the factors which can affect the contact time of sorbent and solution inflow condition. If the contact time is low, the samples cannot effectively remove heavy metal ions in the solution. Since the zeolite-soil mixtures were compacted with 90% of compactness, the permeability seems low. Therefore, the falling head test was performed instead of a constant head test. The test was followed by ASTM D5084 method.

3.2.2 *Geo-environmental tests*

3.2.2.1 *Batch tests*

The adsorption capacity of zeolite-soil mixtures to heavy metal (zinc and lead) was carried out using the batch method at first. Batch adsorption tests were performed using 4g of adsorbent with 40ml of heavy metal solution. The zinc and lead solutions were prepared with different initial concentrations. (50, 125, 250, 500, 750, 1000, 1500, 2000 mg/L). The mixtures and solution were placed in the tube and shaken for 24 hours at constant temperature (25 °C) and the solution containing the heavy metal ions was filtered, diluted, and then tested with AAS (Atomic Absorption Spectroscopy) for determining the remain heavy metal ions. The Langmuir and Freundlich isotherm equations were used to analyze the result data to determine adsorption capacity. The batch tests were conducted on mixtures with SZ0(soil), SZ25, SZ50, SZ75, and SZ100(zeolite). After adsorption tests were finished, desorption tests were performed to investigate released heavy metal ions by acid (pH4) and distilled water which is to prevent secondary contamination by adsorbed heavy metal ions. The tubes with mixtures were dried at 40 °C for 48 hours and 40ml of acid or distilled water was put into the tube. The tubes were shaken for 24 hours, filtered, and the solution was measured by AAS like the adsorption test.

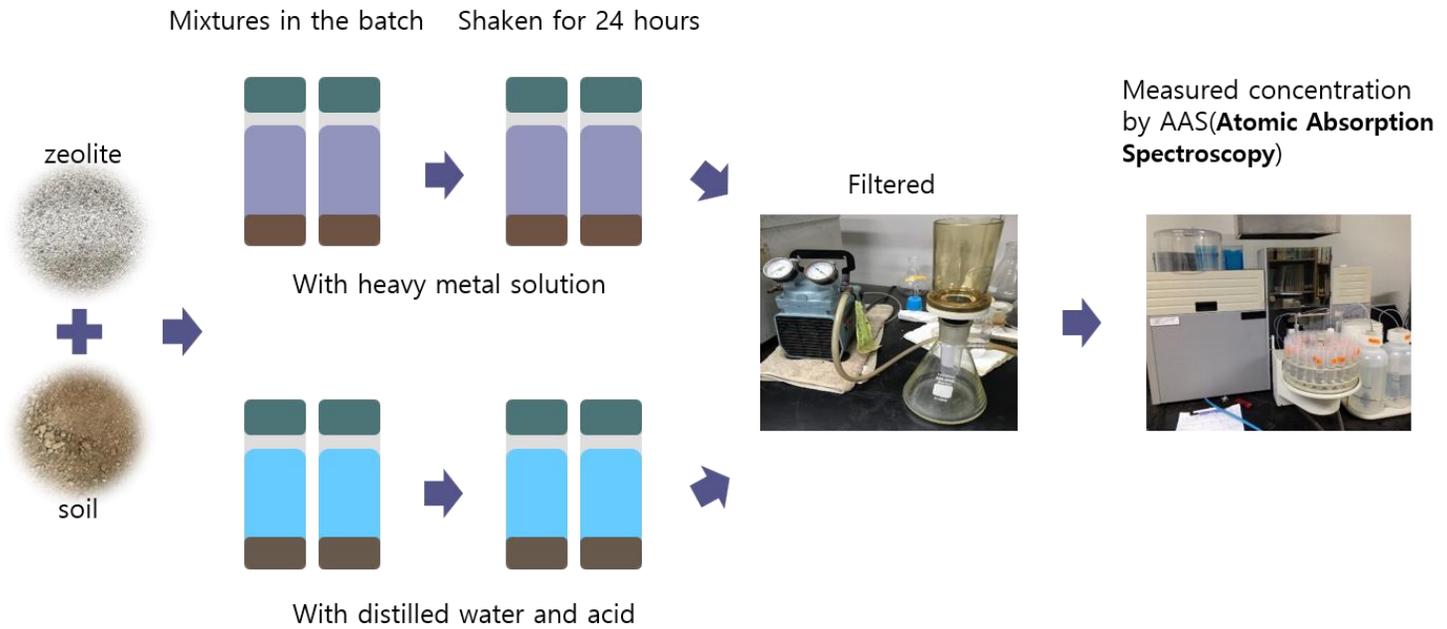


Fig. 3.9 Process of adsorption and desorption batch test

3.2.2.2 *Column test*

Experiments using columns were designed to describe the flow condition in the field. In general, when the adsorption column test is conducted, the inflow solution is injected from the bottom to assume a fully saturated condition. However, in the case of this study, an inflow solution was injected from the top to review the characteristics of the material as fill material. This reflected the formation of an unsaturated layer of the fillings on top of the underground water level. The heavy metals used in the column test are zinc. In the case of lead, the uptake of lead is too high, compared with zinc, which makes lead not suitable for flow testing. SZ75 showed lower value to use as fill material by standard compaction test so it was not tested by column test. The column was manufactured with a size of 30 cm height and 5 cm of diameter. The flow rates through the column were adjusted to 2mL/min which is the same maximum rainfall in Seoul. The column was composed of 2.5 cm of a sand layer on top and bottom and 25 cm of the adsorbent layer in the middle. The top sand layer is to distribute the solution equally to the adsorbent layer and the bottom layer is to prevent adsorbent from leakage. The picture and schematic diagram of the column are shown in Fig. 3.10. The mixtures were prepared the same mixing ratio as batch-test except for SZ75 and all the samples were compacted with 90% compactness. The concentration of zinc solution was 500mg/L and the experiment was continued until the outflow concentration reaches initial concentration. The solutions were collected every hour and measured by AAS. After finishing the adsorption test, the desorption test was also performed. The remain solution was taken out by air injection. Then distilled water was injected

flow rate with 2ml/min. Desorption test persisted until the outflow concentration becomes lower than 3mg/L which is the regulation of groundwater in Korea. The solutions were also collected every hour and measured by AAS.

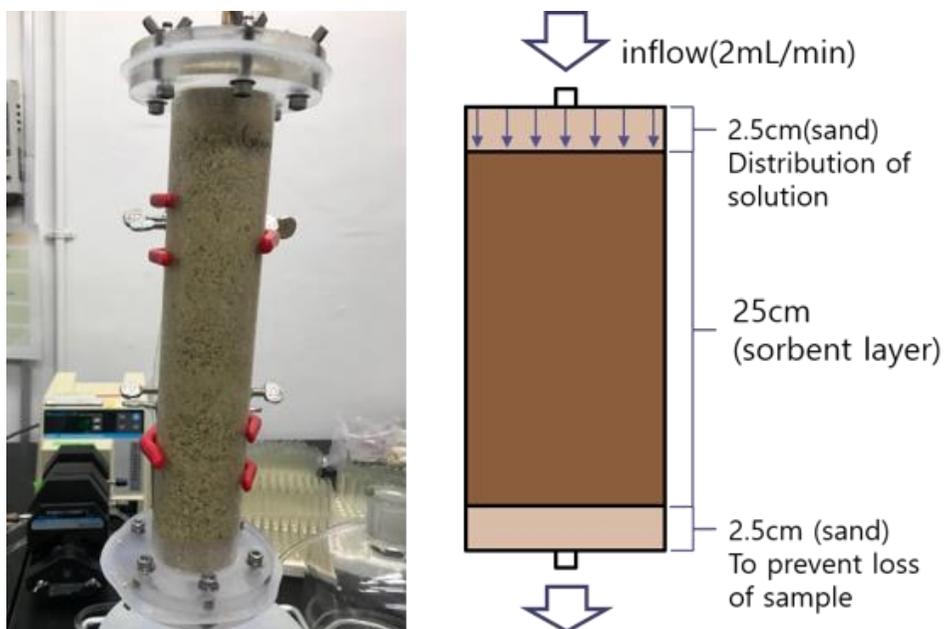


Fig. 3.10 Experimental apparatus (column) picture and schematic diagram

3.2.2.3 *Soil tank test (pilot-scale test)*

Soil tank test was conducted not only flow condition but also field condition on a larger scale than column test. Soil tank was made with steel and acrylic panels. The size of the soil tank was the width of 50x100cm and a height of 120cm. The layers of mixtures were performed the same as the column test (2.5cm of a sand layer on the top and bottom and 25cm of a sorbent layer). The picture of the soil tank is shown in Fig. 3.11 and schematic diagram of the soil tank are shown in Fig. 3.12. SZ25 and SZ0 were prepared and compacted with 90% of compactness for the soil tank test. The flow rate of the test was adjusted 130mL/min by a peristaltic pump. The concentration of zinc solution was 500mg/L and the experiment was persisted until outflow concentration equal to initial concentration. The solution coming out from soil tank was collected every hour and measured with AAS.

After the adsorption test, the samples remained for 3days for drying until no outflow comes out and distilled water was injected for 2days to test desorbed zinc ions from the samples. This cycle of drying and injecting was done for 2 times until the concentration of leachate is under 3mg/L



Fig. 3.11 Experimental apparatus (soil tank)

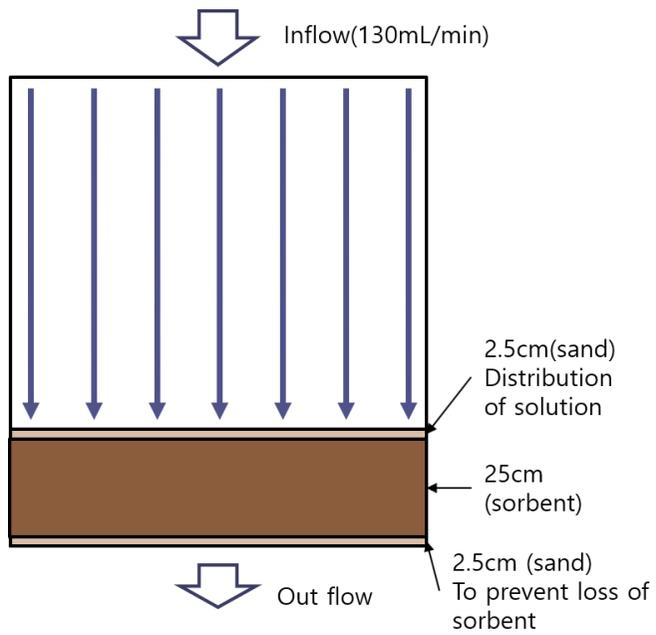


Fig. 3.12 Schematic diagram of soil tank

Chapter 4. Experimental results and discussion

4.1 Geotechnical tests

4.1.1 Standard compaction test

Fig. 4.1 Compaction curves of zeolite-soil mixtures show the result of the standard compaction test of the zeolite-soil mixtures. As the content of zeolite increases in the mixtures, the optimum water content increased and the maximum dry unit weight decreased. Mixtures with zeolite have more characteristics of clayey soils than weathered granite soil. It is due to low density and higher water holding capacity of zeolite. Mixtures except for SZ75 and SZ100 (zeolite) showed a higher maximum dry unit weight than 1.471t/m^3 , the minimum dry unit weight to use as fill material in Korea according to KDS 44 30 00. The maximum dry unit weight must show a higher value than 1.471 in 90% of compactness. The maximum dry unit weight of zeolite showed similar value with another researcher's result. (Kaya et al., 2006)

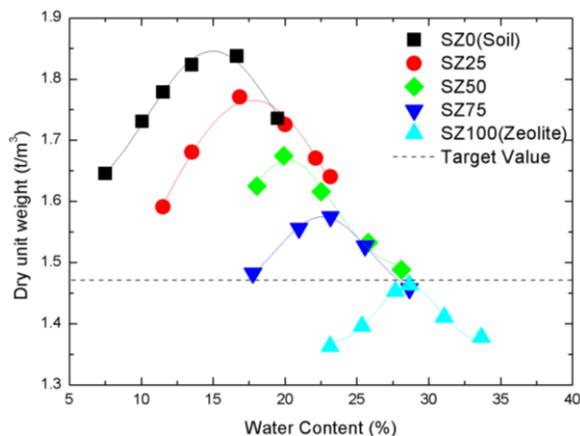


Fig. 4.1 Compaction curves of zeolite-soil mixtures

4.1.2 Direct shear test

The strength parameters of the mixtures were shown in the Table. 4.1 Shear strength parameter of zeolite-soil mixtures before column test From the result, it seems the zeolite has higher cohesion and lower friction angle than soil. In this study, it was reported that all of the mixtures showed inter friction angle value between 31.7 to 37.3 ° which is in the range of commonly used fill material in Korea according to (Lee et al. ,2011). The friction angle decreased, and cohesion increased as the content of zeolite increases. Since zeolite is classified as clay minerals, zeolite has a lower friction angle and higher cohesion than soil originally. Yukselen-Aksoy (2010) reported that the drained internal friction angles of the Bigadic zeolite and Gordes zeolite are 34 ° and 36.5 °, respectively. However, it should be noted that the properties of zeolite can vary with their source. The direct shear test of mixtures after the column test was also performed to investigate the effect of heavy metal adsorption on strength parameters. The result of the direct shear test after the column test is shown in the Table. 4.2 Shear strength parameter of zeolite-soil mixtures after column test Even after heavy metal ions are adsorbed, the strength of the mixtures showed similar value. It can be estimated that mixtures will remain stable even after adsorption and desorption of the heavy metal.

Table. 4.1 Shear strength parameter of zeolite-soil mixtures before column test

	SZ0	SZ25	SZ50	SZ75	SZ100
Friction angle(°)	40.2	37.3	35.8	31.7	31.6
Cohesion(kPa)	18.3	30.6	32.5	31.2	34.6

Table. 4.2 Shear strength parameter of zeolite-soil mixtures after column test

	SZ0	SZ25	SZ50	SZ100
Friction angle(°)	39.3	37.4	35.5	30.4
Cohesion(kPa)	22.9	28.0	34.1	42

4.1.3 Permeability test

The permeability was performed to investigate hydraulic conductivity which can use as a design parameter to use zeolite-soil mixtures as adsorptive fill layer under industrial zones. The contact time between the contaminants and the adsorbent is an important factor for adsorption, and the contact time is affected by hydraulic conductivity. The result of the permeability test is shown in the Table. 4.3. Ören et al., (2013) reported that compacted zeolite showed a hydraulic conductivity range of 8.4×10^{-3} - 1.6×10^{-5} which is dependent on the particle size of zeolite. Yukselen-Aksoy (2010) reported that the hydraulic conductivity of Bigadic zeolite and Gordes zeolite at 98.07 kPa stress are 1.65×10^{-8} and 4.09×10^{-8} cm/s, respectively. According to Kayabali (1997), the hydraulic conductivity of compacted zeolite with 5% bentonite content was 8×10^{-7} cm/s which is measured by a falling head test. The values of some researchers were lower than this study because they used zeolite with smaller particle sizes than this study. As the content of zeolite increases, hydraulic conductivity tends to increase. The results show similar results to previous studies that the permeability is proportional to D_{10}^2 (Hazen's experimental equation).

Table. 4.3 The result of permeability test of mixtures

	SZ0	SZ25	SZ50	SZ100
k(cm/s)	1.0×10^{-4}	6.0×10^{-4}	1.3×10^{-3}	2.2×10^{-3}
D_{10} (mm)	0.075	0.094	0.115	0.351

4.2 Geo-environmental tests

4.2.1 Batch test

4.2.1.1 Adsorption batch test

The results of the isothermal absorption curves of zinc and lead on the specimen mixture of zeolite and soil were shown in Fig. 4.2 and Fig. 4.3. The result analyzed by the Langmuir model and Freundlich model is shown in the Table. As shown by the graphs and tables, adsorption capacity increased as the content of zeolite increases with zinc and lead both. This seems to be due to the fact that zeolite's ability to exchange cations is relatively higher than soil samples. When comparing the adsorption graphs of lead and zinc, both soil and zeolite show that the adsorption rate of lead is far higher than that of zinc. The maximum lead uptake for the samples were higher than maximum lead uptake (SZ0 4.92mg Pb²⁺/g, SZ25 13.57mg Pb²⁺/g, SZ50 22.08mg Pb²⁺/g, SZ75 33.78mg Pb²⁺/g, SZ100 45.87mg Pb²⁺/g SZ0 2.44mg Zn²⁺/g, SZ25 4.44mg Zn²⁺/g, SZ50 4.98mg Zn²⁺/g, SZ75 5.96mg Zn²⁺/g, SZ100 8.63mg Zn²⁺/g). This is due to the smaller hydrated radius of lead is smaller than zinc, so the adsorption of lead is higher than zinc. Adsorption batch test for soil and zeolite showed a similar trend with other researchers that lead is more adsorbed by the samples (Lim, 1999, Zamzow and Murphy, 1992, Inglezakis et al,2003, Perić et al., 2004). In the case of zinc, it was found that the Freundlich model fits more than the Langmuir model. In the case of SZ0 and SZ25 of lead uptake, the Langmuir model tended to be more fitted while other mixtures and SZ100 (zeolite) are more fitted to the Freundlich equation. This is different from the results of Erdem et al. (2004) and Ören et al. (2006). They stated the Langmuir model was showed a higher correlation,

but the results of this study show that the results were more fittable by the Freundlich equation. This seems because this study conducted experiments until higher concentration (2000 mg/L) from low concentration (50mg/L) which is consistent with the results of the Shin et al (2014) who performed the test with high concentration. In the case of the batch test, the absorption capability of the zeolite-soil of heavy metal is different from the result of the column test because of the flow condition. (Inglezakis & Grigoropoulou, 2003). The effect of the reduction of the adsorption by flow condition was reviewed through the column test.

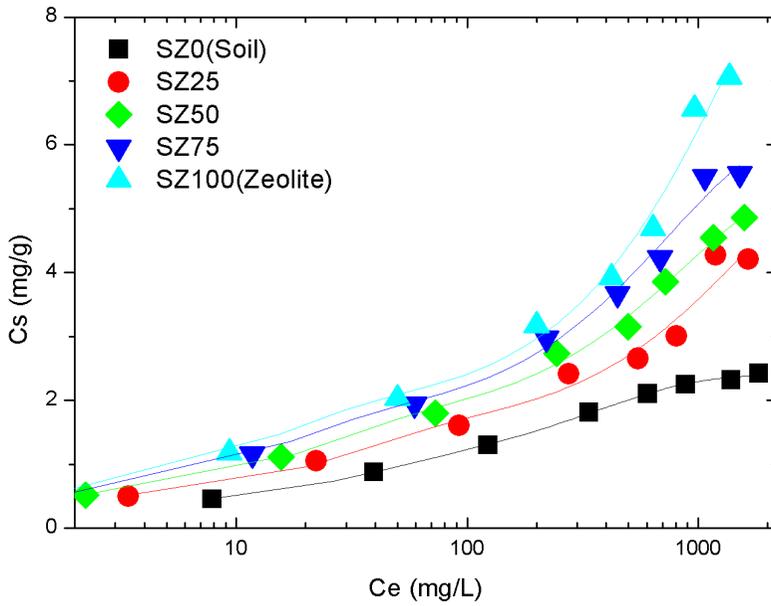


Fig. 4.2 The result of adsorption batch test with the zeolite-soil mixture in case of zinc

Table. 4.4 The result of adsorption batch test analyzes by isotherm equations (zinc)

Zinc	Langmuir model			Freundlich model		
	Q_L (mg/g)	K_L	R^2	K_F	$1/n$	R^2
SZ0	2.44	0.01	0.96	0.32	0.26	0.96
SZ25	4.44	0.00	0.86	0.36	0.33	0.96
SZ50	4.98	0.01	0.91	0.37	0.34	1.00
SZ75	5.96	0.01	0.91	0.44	0.35	0.99
SZ100	8.63	0.00	0.90	0.47	0.41	0.98

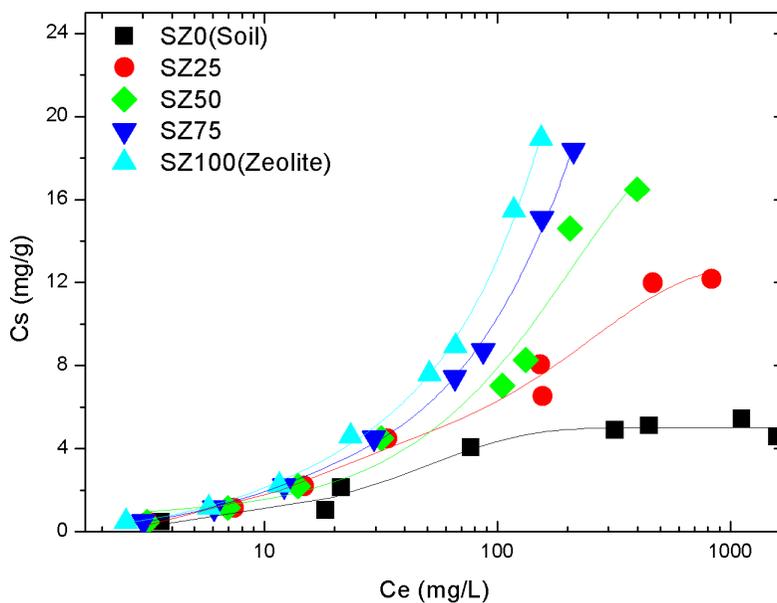


Fig. 4.3 The result of adsorption batch test with the zeolite-soil mixture in case of lead

Table. 4.5 The result of adsorption batch test analyzes by isotherm equations (lead)

Lead	Langmuir model			Freundlich model		
	Q_L (mg/g)	K_L	R^2	K_F	1/n	R^2
SZ0	4.92	0.06	0.99	0.32	0.49	0.89
SZ25	13.57	0.01	0.99	0.38	0.57	0.94
SZ50	22.08	0.01	0.90	0.28	0.71	0.97
SZ75	33.78	0.01	0.88	0.24	0.82	0.99
SZ100	45.87	0.00	0.88	0.24	0.88	0.99

4.2.1.2 *Desorption batch test*

After the adsorption test, a desorption test was conducted to evaluate the harmfulness of mixtures that adsorbed heavy metal (zinc and lead). The desorption batch test was performed with an acidic condition (pH4) and distilled water, however, the result showed a negligible difference. The desorption rate was calculated based on the adsorbed amount calculated in the adsorption test and the formula calculated is as follows.

$$\text{Desorption rate} = \frac{C_s(\text{amount desorbed})}{C_s(\text{amount adsorbed})}$$

In the case of zinc, it can be seen that the desorption rate in the case of weathered soil remained at least 5% at almost all concentrations, but in the case of mixtures, the desorption rate decreased dramatically to at least 50%. In the case of lead, a lot of desorption occurred when tested at a high concentration but reduced at low concentration, and in the case of a mixture of zeolite-soil, there was very little desorption. These test results, where lead is not more desorbed than zinc, tend to be similar to the test results presented by Martinez (2000). According to Plassard (2000), there is a large amount of desorption in the case of weathered soil, which tends to be similar to the experimental results of this study. It can be assumed that weathered soil is vulnerable to further pollution due to desorption. However, the zeolite-soil mixture can effectively reduce the risk of further contamination through the release of contaminants because it has resistance to desorption superior to that of weathered soil.

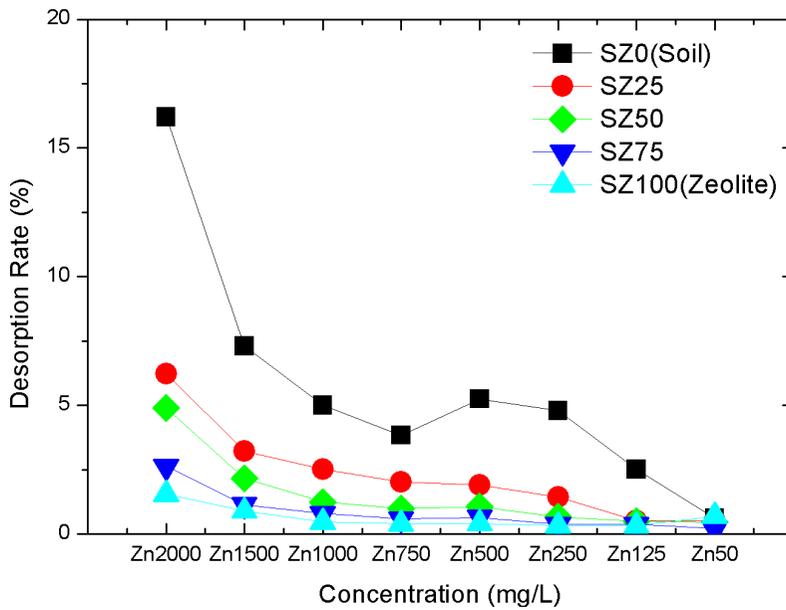


Fig. 4.4 Desorption batch test in acidic condition (pH4, zinc)

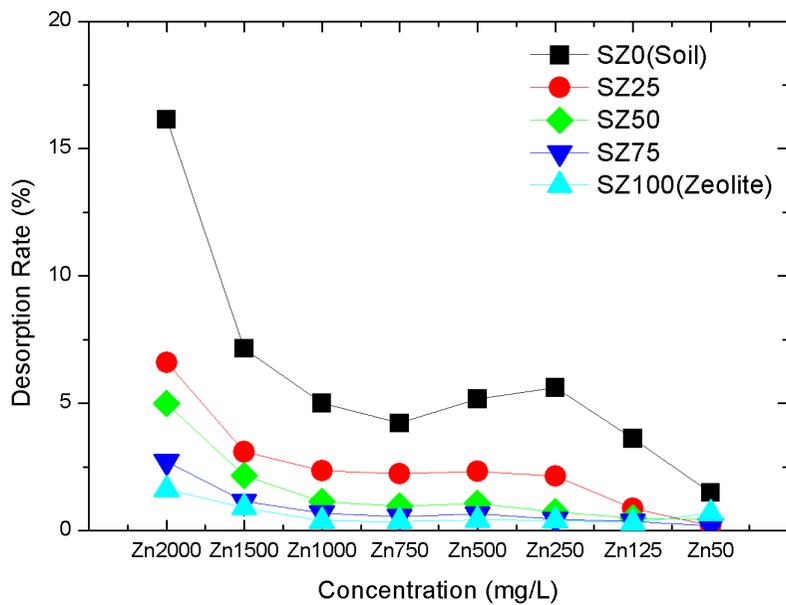


Fig. 4.5 Desorption batch test by distilled water (zinc)

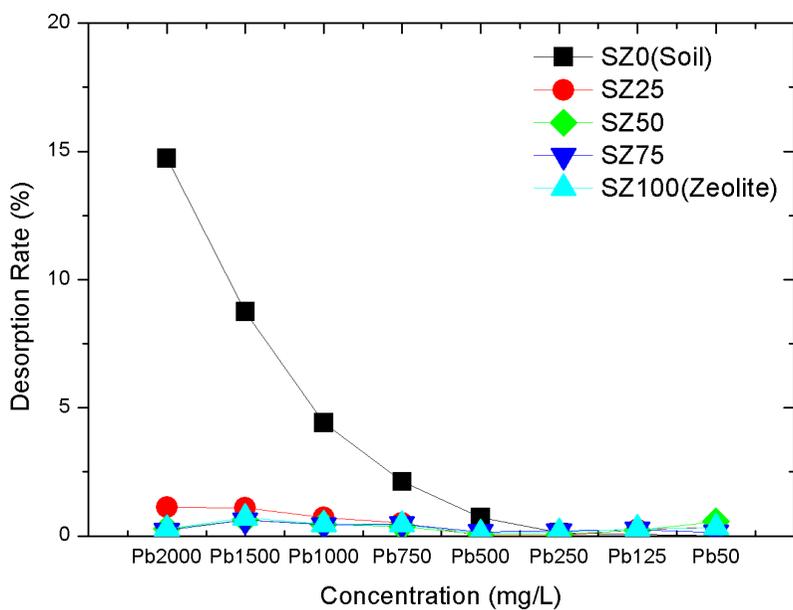


Fig. 4.6 Desorption batch test in acidic condition (pH4, lead)

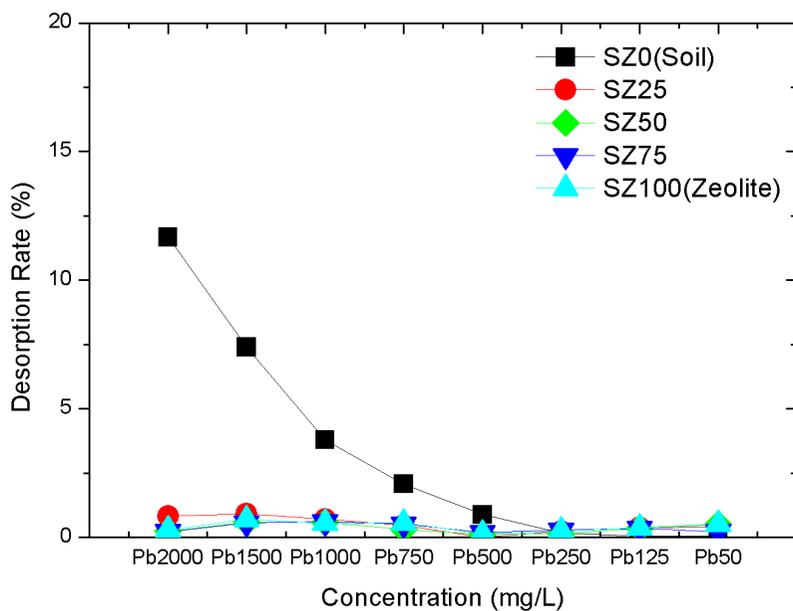


Fig. 4.7 Desorption batch test by distilled water (lead)

4.2.2 Column test

4.2.2.1 Adsorption column test

The breakthrough curves for the zeolite-soil mixtures are shown in Fig. 4.8 vs time or Fig. 4.9 pore volume, respectively. As shown in the graph against time, the SZ100 and SZ25 were reached to relative concentration (0.5) 3.5 times later than SZ0 and the leachate of SZ50 was approximately twice faster than SZ25. It can be considered that this trend of SZ25 showing higher performance of removing zinc ions than SZ50 is because of fast flow rate, and higher permeability which leads to the decrement of contact time between the sorbent, and the solution and high concentration of zinc ions. The Table. 4.6 shows the time, pore-volume, and adsorption capacity when it reaches the relative concentration of 0.5 and 0.9. The adsorption capacity was calculated by the following equation.

$$\text{Adsorption capacity} \left(\frac{\text{mg}}{\text{g}} \right) = \text{time}(\text{h}) \times \text{flow rate} \left(\frac{\text{L}}{\text{h}} \right) \times \frac{\text{inflow concentration} \left(\frac{\text{mg}}{\text{L}} \right)}{\text{total amount of sample}(\text{g})}$$

The adsorption performance was shown in the order SZ100> SZ25> SZ50>SZ0 both by table and graph. The results of the column test showed different trends from the result of the batch test. The adsorption capacity is not proportional to the content of zeolite unlike the batch test because dynamic flow and permeability prevented the samples from exhibiting the ability to remove heavy metal. According to the research of Ho & Mckay (2000) and Gode & Pehlivan (2006), it takes a certain period of time to reach the adsorption equilibrium and it is difficult to properly perform the adsorption function below a certain period of time. Stylianou et al. (2007) and Inglezakis & Grigoropoulou (2003) mentioned that a low flow rate is needed to

effectively remove heavy metals of solution. According to Darcy's law, the flow rate tends to be proportional to the hydraulic conductivity. The hydraulic conductivities of the SZ100 was almost 22 times higher than SZ0. SZ100 has high permeability and adsorption capacity at the same time, so it can not properly perform its ability to remove zinc ions. In the case of SZ50, the batch test results showed a similar adsorption capability as SZ25, but the hydraulic conductivity is about twice as large as that of SZ25. Given that the SZ50's zinc leachate is about twice as fast, adsorption is inversely proportional to the hydraulic conductivity. Malkoc & Nuhoglu (2006) suggested that the higher the concentration, the faster the outflow of heavy metals, and the faster the release of heavy metals is more occurs if the flow rate is exceeded certain values.

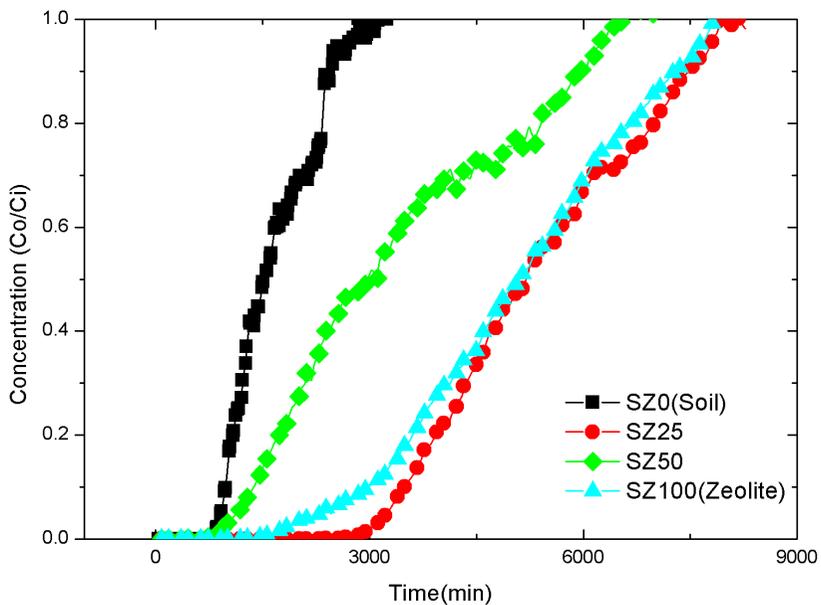


Fig. 4.8 Breakthrough curves for Zn adsorption onto the mixtures (vs time)

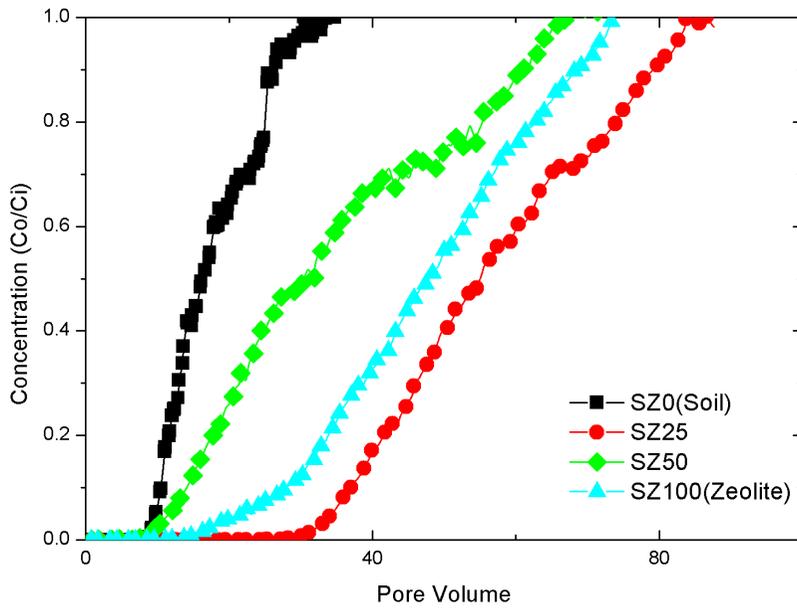


Fig. 4.9 Breakthrough curves for Zn adsorption onto the mixtures (vs pore volume)

Table. 4.6 The result of the adsorption column test and calculated adsorption capacity

Zinc	SZ0	SZ25	SZ50	SZ100
$C_0/C_i=0.5$ (pore volume)	16.1	55.2	30.5	48.2
$C_0/C_i=0.9$ (pore volume)	26.1	79.5	60.1	69.2
$C_0/C_i=0.5$ (time, min)	1504	5232	2940	5140
$C_0/C_i=0.9$ (time, min)	2486	7532	5884	7348
Adsorption capacity at relative concentration 0.5 (mg/g)	1.85	6.64	4.05	7.94
Adsorption capacity at relative concentration 0.9(mg/g)	3.01	9.58	7.95	11.35

4.2.2.2 Desorption column test

Desorption test was carried out to review of the harmfulness of the zeolite-soil mixtures adsorbed heavy metal contaminants due to the influence of flow such as rainfall. As a result of the batch test, the desorption rate difference between distilled water and acidic condition was negligible, so the experiment was conducted with distilled water and the test flow rate was carried out in the same way as the adsorption test. Fig. 4.10 and Fig. 4.11 shows the result of column desorption test vs time and pore volume, respectively. As shown in the figure, the initial zinc concentration of leachate is reducing and the time and pore volume when the concentration reaches under 3mg/L also reducing. 3mg/L is the regulation of groundwater treatment in South Korea. According to the Table. 4.7, the pore volume when SZ25 reaches under 3mg/L is about 40% less than SZ0. Even SZ25 showed resistance against desorption than SZ0(local soil). Therefore, it can be indicated that zeolite-soil mixtures with heavy metal is strong against leakage and can prevent further spreading after once adsorption occurred.

Table. 4.7 The result of desorption column test

	SZ0	SZ25	SZ50	SZ100
Reach under 3mg/L (pore volume)	25.4	15.8	10.7	6.8

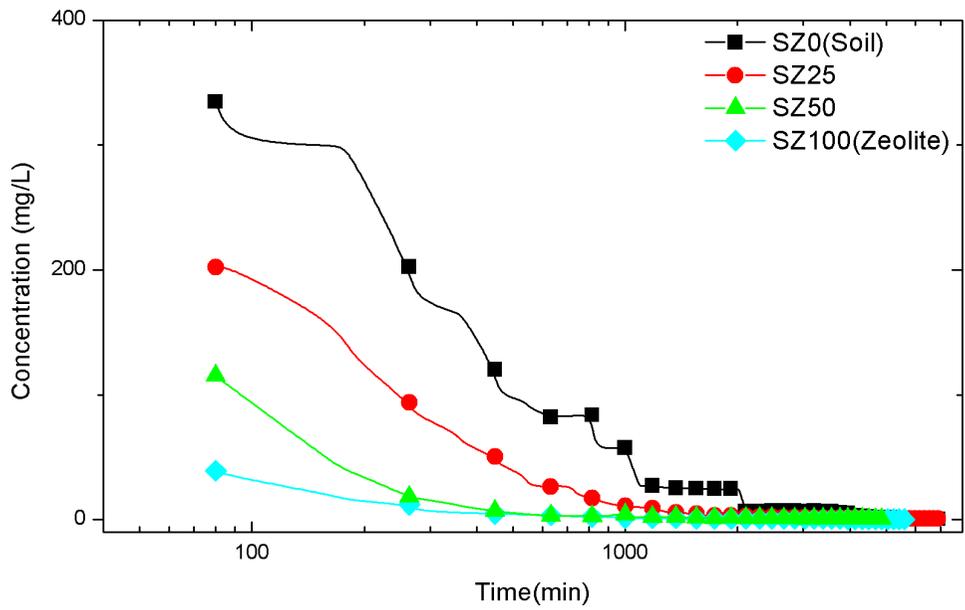


Fig. 4.10 Desorption concentration by column test (distilled water, vs time)

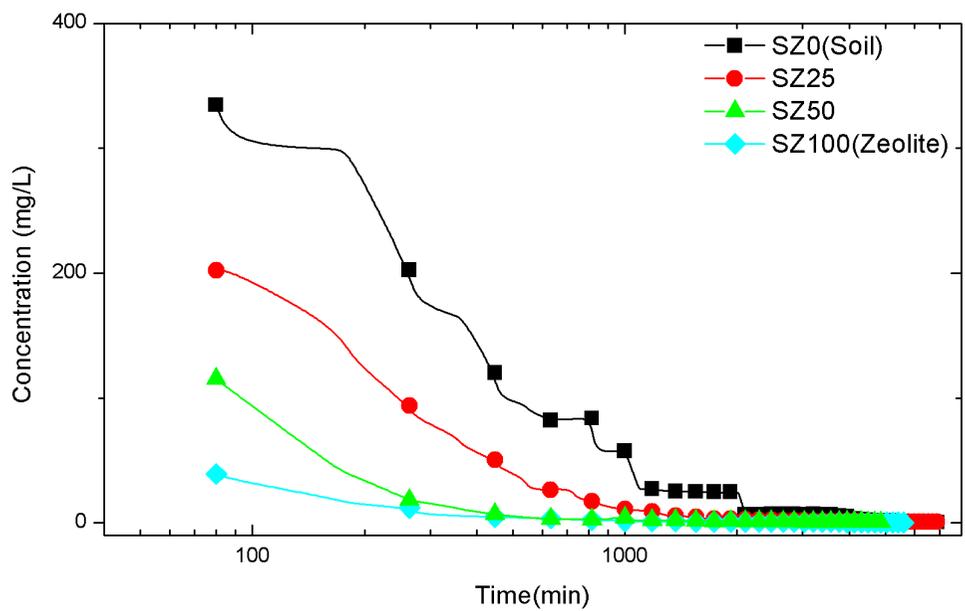


Fig. 4.11 Desorption concentration by column test (distilled water, vs time)

4.2.3 *Soil tank test (pilot-scale test)*

4.2.3.1 *Adsorption soil tank test*

The soil tank test was performed to investigate adsorption behavior in the scale more like a field than the column test. As in the economical and engineering aspect, the SZ25 showed high performance in column tests and geotechnical tests. Thus, SZ25 and SZ0(soil) are compared on the pilot scale. The breakthrough curves were shown in Fig. 4.12. Similar to the column test results performed, it can be found that SZ25 has higher adsorption capacity compared to SZ0. A relative concentration 0.9, the pore volume pass through the SZ25 were about 3.32 times larger than those of SZ0 which is similar to the value obtained by column test (3.5). The heavy metal has detected faster compare to the column test even the trend is similar. This is because the size of the soil tank is much larger than the column, so the uniformity of the pore and sample are not guaranteed. So, the solution focus on a certain pore, not all the mixture which leads to the result that the mixture could not properly show high removal efficiency that it has. Because the flow rate is faster than those of the field since the flow rate was controlled by the pump instead of the hydraulic gradient, it is a more harsh condition.

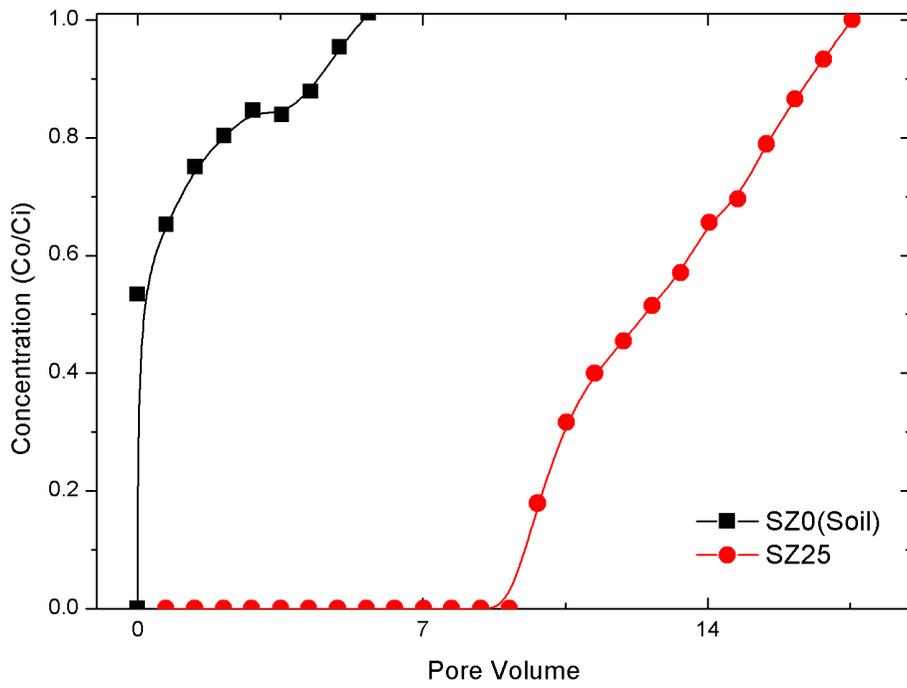


Fig. 4.12 The breakthrough curves of the soil tank test

4.2.3.2 *Desorption soil tank test*

The desorption test was carried out to review of the harmfulness of the zeolite-soil mixtures like column test. The test was conducted until no desorption occurred. In the case of SZ0, the zinc concentration of leachate was over 3mg/L in the first cycle of desorption and in the second cycle the concentration reaches under 3mg/L at pore volume of 19. In the case of SZ25, the desorption concentration reached under 3mg/L at the first cycle and no desorption had occurred in the second cycle. The leachate concentration was lower than the result of the column test. It seems because the column has a smaller diameter than the soil tank so that there is residual zinc solution in the internal pores. On the other hand, in the case of the soil tank the area is large compare to the column, so the remaining solution is less. As a result of the soil tank test and previous experiments, the zeolite-soil has resistance against desorption. Therefore, the zeolite-soil mixture is considered to be less polluted by additional outflow compared to original fill material. In the case of the SZ0, there is less resistance to desorption and vulnerable to further contamination, unlike SZ25.

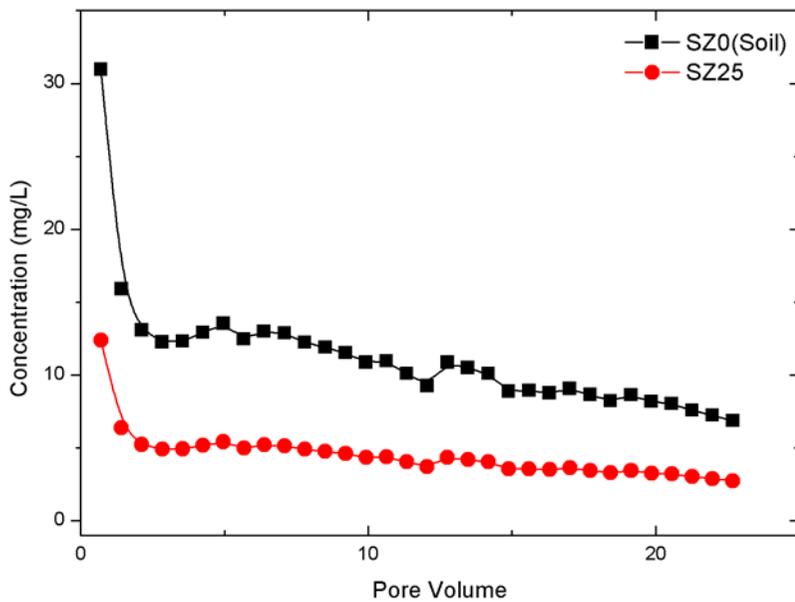


Fig. 4.13 The desorption concentration of the mixture in soil tank test (1st cycle)

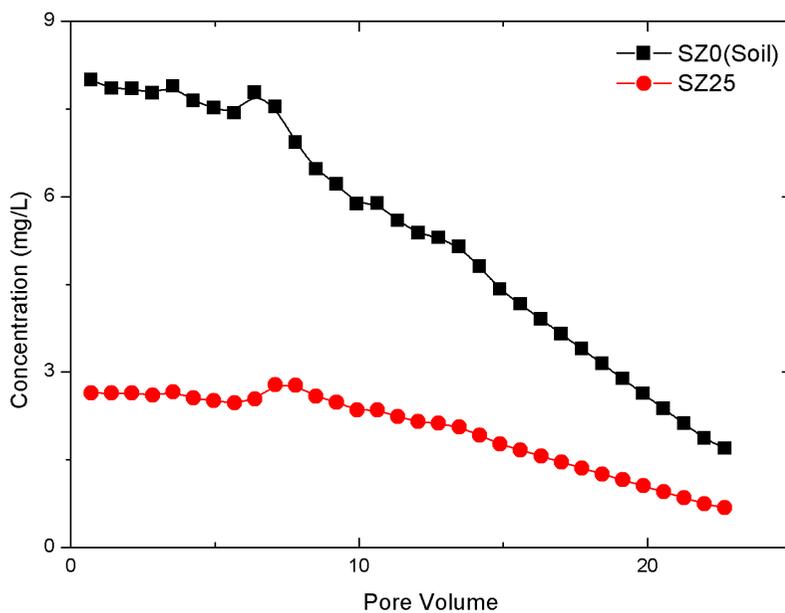


Fig. 4.14 The desorption concentration of the mixture in soil tank test (2nd cycle)

Chapter 5. Conclusion and further study

5.1.1 Conclusion

This study is aimed to develop a hybrid fill layer under industrial zones to reduce the area of contamination and prevent further spreading in the subsurface. By doing so, it is zeolite was mixed with soil to form a hybrid fill layer. The geotechnical properties were tested through standard compaction, direct shear, and permeability. The geoenvironmental properties were tested with batch, column, and in-field scale. The final goal is to find out the optimum mixing ratio in engineering and economical aspect.

The obtained results can be summarized as follows:

- 1) According to the standard compaction test, all the zeolite-soil mixtures showed a higher value than regulation except SZ75
- 2) According to the direct shear test, the result of the mixtures was in the reasonable range for fill-material (30~45°). Even after zinc adsorbed to the mixtures, the mixtures showed similar value.
- 3) According to the permeability test, as the contents of zeolite increase, the hydraulic conductivity increased which can be explained by Hazen's experimental equation.
- 4) In the case of the adsorption batch test, as the contents of zeolite increases adsorption capacity to heavy metal also increased. Lead uptake onto zeolite was higher than zinc because of its hydrated ion's diameter of lead is smaller than zinc.
- 5) In the case of the desorption batch test, the acidic condition(pH4) and distilled

water showed a similar result. Even SZ25 showed more than 50% reduction of desorption rate, which indicates that zeolite has high resistance against secondary pollution.

- 6) In the adsorption column test, SZ25 showed even higher adsorption performance than SZ50. In the desorption test, as the content of zeolite increase, the desorption concentration had been decreased.
- 7) In the pilot-scale test, adsorption trend that SZ25 showed higher adsorption capacity of about 3.5times than SZ0 is similar to the column test. In the 1st cycle of desorption test, the leachate concentration of SZ25 become lower than 3mg/L while SZ0 showed higher concentration than 3mg/L. In the 2nd cycle of desorption test, SZ25 kept leachate concentration under 3mg/L and SZ0 still has leaked zinc ions.

This study indicates that zeolite-mixed soil can be used as an adsorptive fill layer under industrial zones. The mixtures have suitable strength to use as fill material, higher performance to reduce the area of contamination than original fill material, and resistance against desorption to prevent secondary pollution. In conclusion, for geotechnical experiment as contents of zeolite increase the strength and maximum dry unit weight decrease. In the batch test results, the adsorption capacity increased as the zeolite content increased, but in the flow condition tests, the zeolite SZ25 displayed higher adsorption capability than the other mixtures. As a result, SZ25 is suggested as the optimum mixing ratio in both geotechnical and geo-environmental properties.

5.1.2 *Further study*

Since the test was performed with natural zeolite, the adsorption capacity can be limited even it is higher than soil. Thus, for further study, natural zeolite should be modified to increase the adsorption capacity. The modification by pretreatment by use of inorganic salt was studied by various researchers. Nguyen et al., (2015) suggested iron coating to increase adsorption capacity of zeolite and Han et al., (2006) showed that manganese oxide coated zeolite had higher adsorption capacity than natural zeolite. The impact of the operational and chemical pretreatment such as NaOH, CaCl₂ with various conditions like batch and column has been investigated to test the effective capacity of the clinoptilolite by Inglezakis et al., (2001).

In the case of the industrial zones, the soil can be polluted by not only heavy metals but also organic compounds such as BTEX. However, the natural zeolite is not efficient to remove those contaminants because the negatively charged surface leads to have little or no affinity for anions and exhibit low adsorption for organic compounds. A number of researchers tried to modify zeolite by binding of surfactants to the zeolite surface. Simpson & Bowman, (2009) charged the surface of zeolite with hexadecyltrimethylammonium (HDTMA) to increase the sorption of organic compounds onto zeolite.

Not only the reducing by adsorption fill layer but forming a detection system by the sensor can be an answer for preventing soil contamination. Therefore, it is necessary to such sensor system at the bottom of infrastructure to let us know when leachate occurs.

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초 록

산업단지 하부지반의 경우, 산업활동으로 인하여 다른 농업이나 주거 지역에 비해 중금속오염에 취약하다. 이러한 토양의 중금속오염은 유기 화합물에 의한 오염과 달리 시간이 지나도 자연적으로 분해가 되지 않으며 심지어 지하수 오염의 원인이 되기도 한다. 따라서, 본 연구에서는 산업단지 하부지반의 성토층에 흡착층을 배치하여 오염의 확산을 줄이고 나아가 지하수 오염을 방지하고자 한다. 산업단지 하부지반의 경우, 상부의 구조물을 지지하기 위해 충분한 지지력을 확보해야 한다. 본 연구에서는 이러한 중금속 중 한국에서 높은 빈도와 농도로 발생하는 오염물질인 아연과 납에 집중하였다. 본 연구에서는 일반적으로 성토재로 이용되는 화강 풍화토를 기반으로 중금속제거에 효율적인 제올라이트를 혼합하여 흡착성 성토재를 형성하였다. 혼합물의 지반공학적 특성은 표준 다짐시험, 직접전단시험, 투수시험을 통하여 분석하였다. 표준 다짐시험 결과, SZ75를 제외한 모든 혼합물은 규정치 이상의 값을 나타냈다. 직접전단시험을 흡착 시험 전후로 수행한 결과, 모든 혼합물들은 내부마찰각 30° 를 유지하였다. 투수시험결과, 제올라이트 함량이 증가할수록 투수계수가 증가하는 경향을 보였다. 지반환경공학적 관점에서 배치시험, 컬럼시험, 나아가 토조시험을 수행하였다. 배치시험 결과, 제올라이트 함량이 증가할수록 흡착능이 증가하는 경향을 보였으며, SZ25도 중금속 탈착에 강한 저항력이 있는 것으로 나타났다. 흐름에 의한 영향을 검토하기 위해 컬럼시험을 수행하였다. 컬럼 흡착시험

결과, SZ25와 SZ50과 비슷한 결과가 나왔으며 이는 시험에 흡착능 뿐만 아니라 투수계수도 영향을 끼친 것으로 판단된다. 컬럼 탈착시험결과, 배치시험결과와 마찬가지로 제올라이트 함량이 증가할수록 탈착에 대한 저항성이 증가했다. 보다 현장과 비슷한 조건에서 시험을 수행하고자 토조시험을 수행하였다. 토조시험결과, 컬럼시험과 비슷하게 SZ25가 SZ0보다 약 3.5배의 흡착능을 발현하였으며 탈착에 대한 저항성도 더 뛰어난 것으로 나타났다. 결과적으로 제올라이트를 25퍼센트 섞은 SZ25가 경제적, 공학적으로 최적함수비에 가까우며, 이러한 혼합물로 흡착층을 배치함으로 토양오염의 범위를 줄이고 지하수오염을 방지할 수 있을 것으로 기대된다.

주요어 : 중금속 흡착, 제올라이트 혼합토, 탈착, 강도, 산업단지, 흡착성 성토재, 파일럿 규모 실험, 컬럼 실험

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