Soil Amended with Calcium-Magnesium Immobilizing Agent against Natural Arsenic Contamination

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ABSTRACT

This geo-environmental study aims to evaluate the feasibility of decomposed granite soil amended with calcium-magnesium (Ca-Mg) composite powder as a constituent material for sorption layer method against natural arsenic contamination. The objectives of this research are: (1) to investigate the hydraulic performance including long-term variation of hydraulic conductivity, (2) to evaluate the sorption performance through both batch sorption tests and up-flow column percolation tests, and (3) to study the time-dependent sorption behavior and sorption mechanisms involved.

Excavated soils and rocks containing heavy metal(loid)s from geogenic sources are usually generated in huge volumes at construction sites. Leaching of heavy metal(loid)s with low concentrations but higher than the environmental standards after excavation is a major environmental concern. A sorption layer method, which utilizes a permeable soil layer with sorption capacity in the bottom of embankment to retain the chemicals of concern dissolved in leachate, was developed as a cost-effective countermeasure to treat and reuse such soils and rocks. Clean host soil amended with heavy metal-immobilizing agents is often used as the sorption layer material to strengthen its sorption performance. Ca-Mg composite agent has a broad range of sorption capacity on heavy metal(loid)s derived from natural resources. It is a promising material to be applied in sorption layer method.

Hydraulic performance of soil-agent mixture was evaluated through hydraulic conductivity test with different mix proportions, curing periods and hydraulic gradients. Hydraulic conductivity maintains at around 1×10^{-6} m/s. Initial addition of Ca-Mg composite by 3% slightly increases the hydraulic conductivity of decomposed granite soil. Further addition of agent up to 5% has little influence. Hydraulic gradient of 1 and 5 has no obvious effect on the hydraulic conductivity. Specimens cured at 7 days shows relatively higher hydraulic conductivity than specimens without curing. No obvious effect was confirmed for a longer curing period at 28 days. Long-term hydraulic performance was studied using permeant of arsenic solution. Relatively stable hydraulic conductivity can be maintained until pore volumes of flow over 100 and hydraulic conductivity starts gradually decreasing.

Sorption performance increases with mix proportion in batch sorption test. Soil-agent mixture was added into arsenic solution with initial concentration of 0.1 to 10 mg/L at liquid/solid (L/S) ratio of 20 and shaking for 24 hours. Sorption amount of arsenic on

soil-agent mixture under a hypothetic equilibrium concentration of 0.01 mg/L increases by 10 times by amendment of Ca-Mg agent in 3%. Further addition of 5% Ca-Mg agent increases the performance by 15 times and removal ratio of arsenic in solution by soil-agent mixture was over 95%. Up-flow column test under contact time of 24 hours showed consistent results with batch test within L/S ratio of 100. For pure decomposed granite soil specimen, higher sorption performance was exhibited in column test than the results of batch test, probably due to the higher concentration of Ca^{2+} in the solution. Curing shows no obvious effect on sorption performance in both batch and column tests.

Time-dependent sorption behavior was studied in batch sorption test firstly for specimen with mixing proportion of 5% and curing period of 7days. Shaking time of 1, 4, 12 and 24 hours was applied and sorption performance increases with longer contact time. Effect of contact time becomes less obvious when initial concentration is relatively low. Up-flow column percolation tests were conducted applying different flow rates controlled by peristaltic pumps. In early permeation stage, sorption performance under longer contact time is stronger. However, sorption capacity is higher in shorter contact time after long term permeation. Leaching of magnesium from soil-agent mixture into solution is obviously affected by different contact time and leaching of calcium is also slightly affected. Higher leaching concentrations of Mg^{2+} and Ca^{2+} in the effluent under longer contact time probably results in lower acid buffering capacity and sorption performance of the specimens. Decreasing pH and dissolution of $Mg(OH)_2$ after long term permeation might lead to total lower sorption capacity in the column test under longer contact time.

By assuming a simplified site condition of a sorption layer method, hydraulic and sorption performance were evaluated using the experimental results obtained in the study. Analysis results suggest that stable hydraulic conductivity can be maintain for at least 20 years and leaching concentration of arsenic might reach to the environment standard after 30 years, suggesting that decomposed granite soil amended with Ca-Mg composite powder is a promising material for the application of sorption layer method.

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CHAPTER 1

Introduction

1.1 General remarks

Proper management and effective utilization of excavated soils and rocks with natural contamination has been a challenging subject in recent years. On one hand, proactive reuse of these soils and rocks instead of direct disposal is very necessary considering their huge generation amount. On the other hand, risk of contaminants leaching needs to be carefully handled while utilizing these soils and rocks such as land reclamation or backfill in the embankment. Development of cost-effective countermeasures to properly treat and reuse huge amount of excavated soils and rocks with low-level leaching concentrations is a fundamental part contributes to achieving sustainable development and establishing of a recycling-based society.

Geologic strata containing relatively high concentrations of heavy metals and/or metalloids from geogenic sources are widely distributed in the world, which is resulted from several phenomena such as formation of metallic minerals by hydrothermal alternation process or accumulation of metals from spring water. Various cases concerning different kinds of elements were reported in China (Li et al. 2017), Italy (Cremisini and Armiento 2016), USA (Gonzalez et al. 2005), India (Singh et al. 2003), Switzerland (Nowack et al. 2001) and so on, covers almost all the continents on the earth.

If construction projects are conducted in these areas, physical and chemical conditions of soils and rocks including particle size, pH condition, redox potential, forms of metals will change due to excavation in combination with exposure to air and water, which might lead to the leaching of heavy metal(loid)s to the surrounding environment and raise the risk of contamination threatening human health (Tatsuhara et al. 2011).

Facts in two aspects aroused the attention of excavated soils and rocks with natural contamination in recent years in Japan. Firstly, the excavation amount is large in urban development and infrastructure construction. Large-scale construction projects such as subways and road networks in urban area or expressways and railways in mountainous area involve huge amounts of tunnel excavation and other underground excavations. According to the statistics summarized by Ministry of Land, Infrastructure, Transport and Tourism of Japan

(MLIT), amounts of excavated soils and rocks in some tunnel construction projects conducted in Japan were as large as hundreds of thousands of m^3 as shown Table 1.1, which summarized several construction projects involving tunnel excavation and generating soils with natural contamination. Reuse of excavated soils and rocks must be taken into consideration instead of direct disposal due to the limited landfill capacity. Secondly, such soils and rocks are required to be treated properly based on the related laws and regulations. According to the Soil Contamination Countermeasure Law (SCCL) issued by the Ministry of the Environment of Japan (MOE) in 2003 and amended in 2010, some naturally contaminated soils should be treated in the assigned facilities if they are subjected to leaching concentrations exceeding the standard values. For soils and rocks which are not regulated in the SCCL, the Ministry of Land, Infrastructure, Transport and Tourism of Japan (MLIT) issued the "Technical Manual on the Countermeasures against Soils and Rocks Containing Natural-Derived Heavy Metals in Construction Works" (MLIT, 2010) to give specific instructions on how to test and treat them.

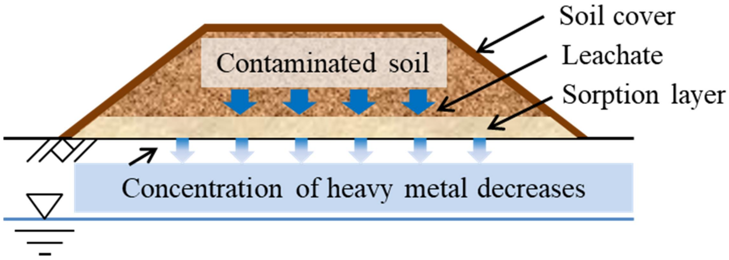
Leaching behavior of heavy metal(loid)s derived from nature resources were studied by several researchers for both soils (Cui et al. 2018, Li et al. 2017, 2018) and rocks (Tabelin et al. 2014, 2017). It was suggested that the leaching concentrations were only 2-3 times higher (or just slightly higher in some cases) than regulatory limits. These concentration levels were relatively low compared to those of anthropogenic contaminations. Based on the nature of these soils and rocks, development of cost-effective countermeasures is a more reasonable solution to treat soils and rocks with huge excavation amounts and low-level leaching concentrations (Katsumi 2015).

Table 1.1 Construction projects generating soils with natural contamination in Japan

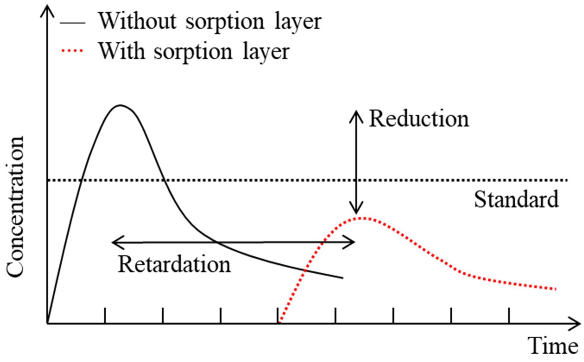
Project	Contaminants	Soil volume	Reference
Nakagoshi Tunnel, Hokkaido	As	800,000 m^3	Fuji et al. (2005)
Hakkoda Tunnel, Aomori	As, Pb, Cd, Se	540,000 m^3	Sasaki et al. (2005)
Subway Tozai line, Sendai	As, Cd, F, Pb, Se	400,000 m^3	Tanihata et al. (2010)
Odatekita-Kosaka Tunnel, Akita	Se, As, F	900,000 m^3	Hosokawa et al. (2007)

Sorption layer method is a recently developed countermeasure based on this aim (Technical Committee of Environmental Conservation Technology Association, Hokkaido 2012). This method utilizes a permeable soil layer with sorption capacity at the bottom of an embankment. Contaminants of concern are attenuated by a constituent material of the sorption layer during the flow of leachate through the sorption layer. Rainfall is prevented from entering the embankment by the soil cover to avoid generating more leachate (Fig. 1.1a). The highest concentration of specific contaminant is expected to be reduced and the time when the concentration reaches to its peak value could be retarded (Fig. 1.1b).

The basic idea of sorption layer method is to seize and retain the contaminants of concern. The definitive aim is not to completely block the contaminants, but to lower their concentrations to an acceptable level. It is applied together with risk assessment, modeling and monitoring to avoid environmental impact on certain assessment spot.



(a) Schematic diagram of sorption layer



(b) Expected effect of sorption layer (Revised from Igarashi and Mikami 2004)

Fig. 1.1 Conception of sorption layer method

Construction of the sorption layer is relatively simple, which usually consists of mixing and laying the layers with proper compaction (Fig. 1.2). Compared to the most common containment method using the geomembrane sheet, embankment with the sorption layer is more stable without any possible slip at the geomembrane-soil interface at steeper angles (e.g. Fleming et al. 2006). In addition, it provides better workability since the damage to geomembrane sheets during compaction due to direct contact with coarse gravels would not occur (e.g. Fox et al. 2014), and there would be less need for additional facilities to treat the leachate. One modified sorption layer method is chosen by MOE in 2017 as the low cost and low environmental impact soil contamination countermeasure technology, suggesting that containment using the sorption layer seems therefore promising and more appropriate for naturally contaminated soils with huge volumes and relatively lower leaching concentrations, compared to other remediation methods, which are mainly developed for highly contaminated soils with smaller volumes.

Selection and design of an appropriate constituent material is a fundamental step to achieve a successful sorption layer method. One of the promising constituent materials is local soil, which is easily available at construction sites. Its mechanical properties and sorption performance can be improved by adding some stabilizing and/or immobilizing agents, such as cement based materials, calcium composite materials and magnesium oxide (Inui et al. 2013). A Ca-Mg composite agent, once evaluated as an immobilizing agent in previous study (Bobea et al. 2012), is also a promising material to be applied in sorption layer methods for its sorption performance. This agent is manufactured through mixing powdered calcinations of

Fig. 1.2 Construction site of sorption layer method (Technical Committee of Environmental Conservation Technology Association, Hokkaido 2012)

dolomite-based natural mineral with special additives. Its composition is similar to the natural mineral of dolomite, which was proved to be capable of adsorbing both cation such as cadmium (Cd) (Kocaoba 2007) and anion such as boron (B) (Sasaki et al. 2013) or arsenic (As) (Ayoub and Mehawej 2007). Sorption performance was also confirmed for other elements such as lead (Pb), (Pehlivan et al. 2009, Irani et al. 2011), hexavalent chromium (Cr (VI)) (Stefaniak et al. 1999, Albadarin et al. 2012) and fluoride (F) (Sasaki et al. 2013, Chaudhary and Prasad 2015). These studies had covered 6 out of 8 elements which are naturally contained in soils and rocks and regulated in Japan according to the SCCL (Cd, Pb, Cr(VI), As, Hg, Se, F, B and their chemical compounds), suggesting that dolomite-based material has a broad range of sorption capacity on heavy metal(loid)s derived from natural resources.

Besides basic sorption properties of various elements, several studies were conducted to further study its sorption mechanisms. Taking arsenic for an example, precipitation of arsenic oxide and arsenic carbonate was suggested as the sorption process of a charred dolomite (Salameh et al. 2015) and 60% of sorbed arsenic by a half-burnt dolomite appeared as slightly soluble mineral (Naruse et al. 2014). For natural material such as soil, it was revealed that sorption of arsenic is associated primarily with the presence of Fe hydroxides (Wang and Mulligan, 2006).

These studies only focused on sorption performance of single dolomite-based materials and limited studies use it as an amendment for natural soil. Application of this kind of soil mixture to a constituent material for sorption layer has not been widely considered. Sorption performance of the mixture needs to be evaluated since interactions of different properties of materials and sorption mechanisms are not clear. In addition, hydraulic performance of the mixture, which is another basic property of the sorption layer, should be evaluated to assure that the permeability is still acceptable after mixing the Ca-Mg composite agent.

1.2 Objectives and scope

The objective of this study is to evaluate the feasibility of the Ca-Mg composite powder mixing with decomposed granite soil, as a constituent material for the sorption layer method. Hydraulic and sorption performance, as well as the time dependent sorption behavior of the soil-agent mixture was evaluated.

It should be noticed that there is very limited fail-safe option for sorption layer method. Once concentrations of contaminants exceeding the design value are detected in the monitoring well, the surrounding environment would have been contaminated. Thus, the performance evaluation is vital in the initial stage.

Hydraulic performance of the layer material is crucial because it affects flow conditions of the leachate inside the sorption layer which is influential to sorption process. A certain range of hydraulic conductivity should be maintained to ensure that the leachate can flow through the layer continuously as expected while a contact time is long enough for contaminants to be attenuated. Sorption performance is another important issue because sorption capacity should be large enough for the total leaching amount and concentrations of the contaminants at the bottom boundary of the sorption layer should be remained acceptable in a whole service life.

Since sorption layer method allows leachate to flow through the layer, contact time between leachate and sorption layer, is the fundamental factor for the performance evaluation. Sorption performance and mechanism with different contact time in sorption layer method is quite important for the risk assessment and modeling process. Thus, initial time-dependent sorption behavior was also evaluated.

Arsenic was selected as the target element in this study since it is one of the contaminants most frequently contained in naturally contaminated soils and rocks (Shima et al. 2009). Hydraulic performance was evaluated by hydraulic conductivity tests and sorption performance was evaluated through both batch sorption tests and up-flow percolation column tests. Effects of mix proportion and curing period of the mixture on the hydraulic and sorption performances were evaluated based on the testing results.

1.3 Outline of the dissertation

This thesis consists of 7 chapters. The constitution of the thesis is shown in Figure 1.3, and the experimental methodologies applied for this study are shown in Table 1.2.

In this chapter (Chapter 1), the objectives and the contents of the thesis are clarified. General background information related to excavated soils and rocks with natural contamination is presented. Fundamental information of sorption layer method as a cost-effective countermeasure and Ca-Mg composite powder-soil mixture as a promising constituent layer material is described.

In Chapter 2, literature review of the origin of natural contamination and its leaching behavior from excavated soils and rocks is presented and nature contamination of arsenic in Japan is highlighted. Then, administrative status together with information related to sorption

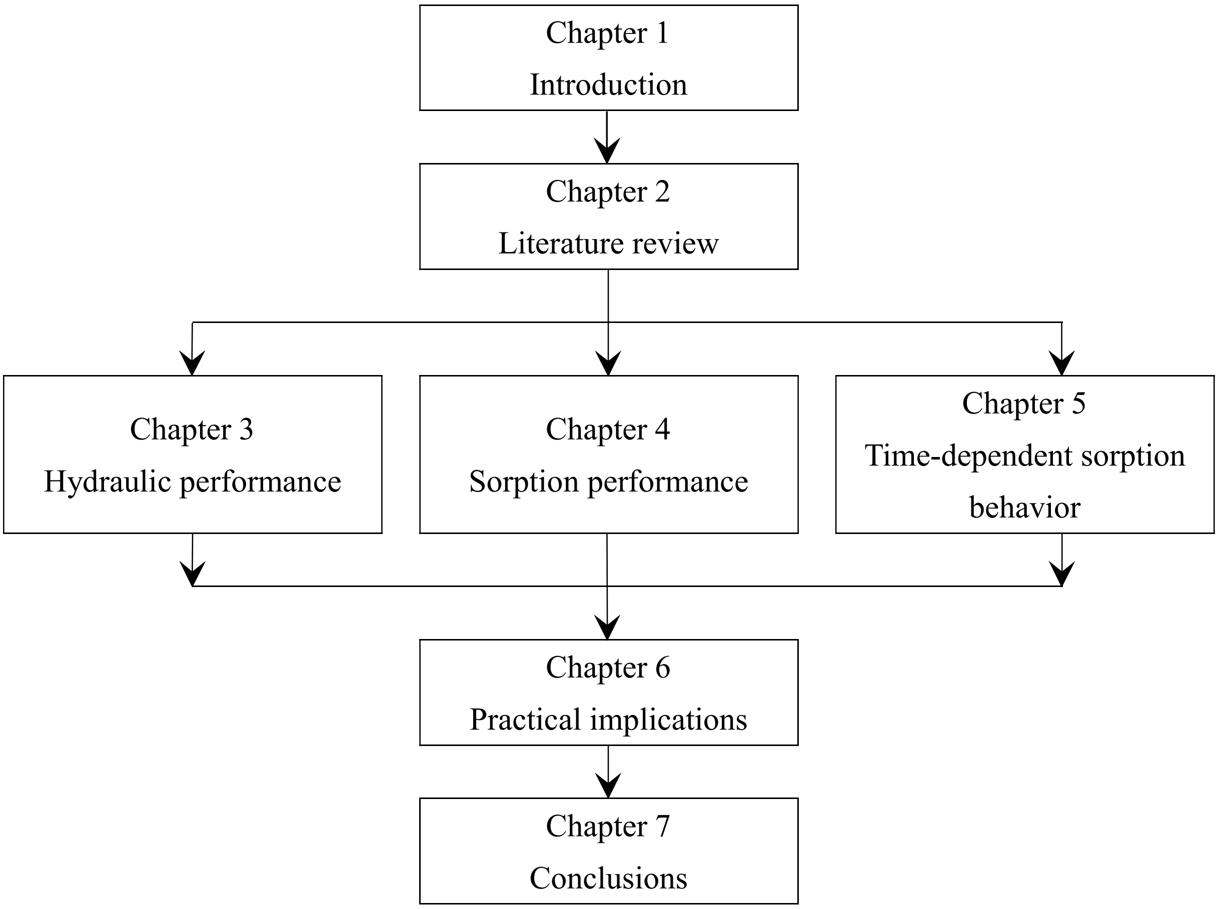


Fig. 1.3 Outline of dissertation

layer method is reviewed. Basic properties of material used in this study, decomposed granite soil as parent material and Ca-Mg composite powder as immobilizing agent is also reviewed.

In Chapter 3, hydraulic performance of soil-agent mixture is studied in three stages. In stage 1, effect of mix proportion on hydraulic conductivity is evaluated. In stage 2, a lower hydraulic gradient and a longer curing period, which is more realistic in the actual site, is applied the their effect is evaluated. In stage 3, long-term hydraulic performance combined with arsenic sorption was evaluated.

In Chapter 4, sorption performance of the Ca-Mg composite agent for arsenic is evaluated by a series of batch sorption tests firstly. It is further evaluated based on the result of up-flow column tests, which is considered more representative of practical application. Effect of curing period is evaluated and experimental results of batch and column tests are compared to study the difference between two tests.

In Chapter 5, time-dependent sorption behavior is evaluated by batch sorption tests applying different shaking time and up-flow column tests applying different flow rates. Effluent concentrations of As and other cations such as Ca and Mg together with pH and EC values under four different contact time was studied. Permeant of distilled water was also applied to compare with the result of sorption test and study the sorption mechanism.

In Chapter 6, practical implications are described based on experimental results obtained in each chapter in terms of long-term hydraulic performance, solute transport analysis and design considerations.

In Chapter 7, conclusions and future scope are presented.

Table 1.2 Experimental methodologies applied in this study

Chapter	Experimental methodologies	Evaluation approach
3	Hydraulic conductivity test	Effect of mix proportion Effect of hydraulic gradient Effect of curing period Long-term hydraulic performance
4	Batch sorption test Up-flow column test	Effect of curing period Comparison of batch and column test
5	Batch sorption test Up-flow column test	Time-dependent sorption behavior Sorption mechanism

CHAPTER 2

Background

2.1 General remarks

Arsenic is one of the major chemicals of concern related to the contamination of groundwater by nature resources. Based on the results of groundwater quality investigation conducted by Ministry of the Environment, Japan (MOE) till 2016, contamination cases of groundwater caused by heavy metal and metalloids has kept increasing in the recent 20 years as shown in Fig. 2.1. Natural contamination was the main cause for 85% for these cases and arsenic was one of the contaminants in 70% (796/1127) of the natural contamination cases as listed in Table 2.1.

As a matter of fact, natural contamination of arsenic is worldwide concern. Cases of groundwater contamination have been reported in many countries such as Bangladesh (Ahmed et al., 2004), Australia (Appleyard et al., 2006), Greece (Kouras et al., 2007) and Canada (Wang and Mulligan, 2006). It can be easily imagined that if construction work is carried out in these areas, leaching of arsenic from excavated soils and rocks can be hardly

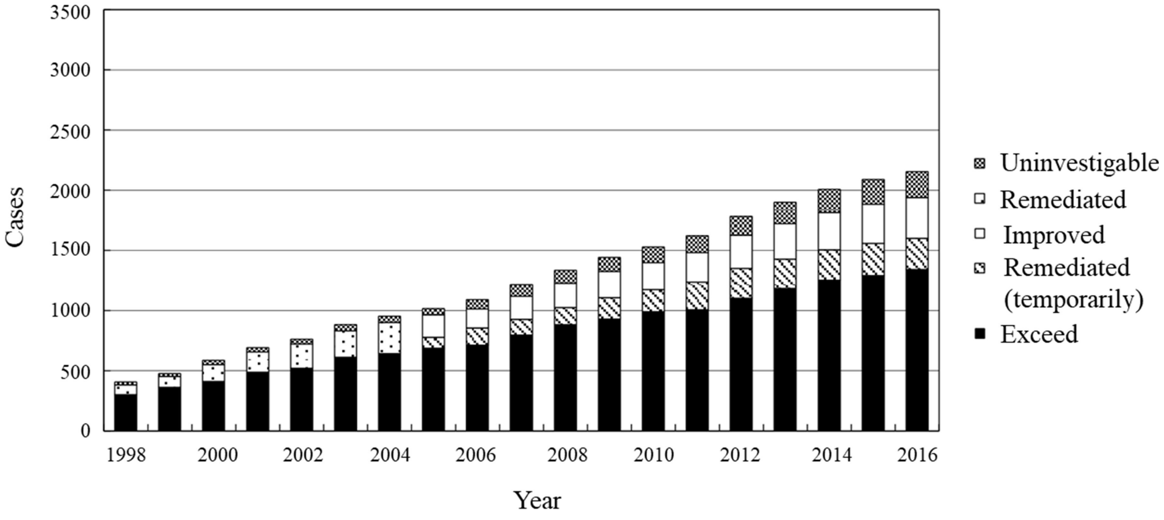


Fig. 2.1 Increasing of groundwater contamination caused by heavy metal(loid)s

(Revised from Environmental Management Bureau, Ministry of the Environment, 2017)

Table 2.1 Resources of heavy metal(loid)s for groundwater contamination (MOE 2017)

Total cases	Natural cause	As involved	Industry cause	Other causes
1335	1127 (84%)	796	157 (12%)	59 (4%)

avoided and proper management is necessary to control the risk of environmental contamination.

Based on the nature of excavated soils and rocks with natural contamination, cost-effective countermeasure such as sorption layer method is very promising. Both technical and administrative aspects are important to pursue such measures. Among technical aspects, evaluation of leaching behavior of heavy metals and metalloids from the soils is primarily important, while evaluating whether attenuation capacity of underlying soil layer functions against the leaching potential obtained is another important aspect (Kasumi et al. 2019).

Many researches have been conducted on the treatment of arsenic contamination involved different technologies such as stabilization/solidification, permeable reactive barrier, cut-off wall or some modified bottom barrier. For the sorption layer method, most researchers focus on the sorption capacity of the layer materials, which is the most fundamental issue to be studied. As for the material used in this study, several studies have been conducted to study the basic properties of decomposed granite soil as well as Ca-Mg composite. However, studies about the soil-agent mixture are rare.

In this chapter, the background information of excavated soils and rocks with natural contamination is described in section 2.2. Previous studies on the generation of excavated soils and rocks and the leaching behavior of arsenic are reviewed. In section 2.3, the administrative aspect, together with existing technology against contamination of arsenic are introduced. Previous studies conducted on the performance evaluation of sorption layer method are discussed in section 2.4. Studies on the basic characteristic of decomposed granite soil and Ca-Mg composite are described in section 2.5, including the mechanical and hydraulic performance, sorption mechanism for As and Pb, etc.

2.2 Natural contamination of arsenic

Heavy metal and metalloids such as arsenic (As), lead (Pb), mercury (Hg), fluorine (F) and boron (B) widely exists in the earth's crust. Crust abundance of these elements in global crust, continental crust and the Japanese islands was presented in Table 2.2. Concentrations of arsenic and lead in the Japanese islands are three times higher than the global average value. Islands of

Table 2.2 Crustal abundance of arsenic, lead, mercury, fluorine, boron (mg/kg) (Ministry of Land, Infrastructure, Transport and Tourism, Japan 2010)

Elements	Crustal abundance		
	Global crust	Continental crust	The Japanese islands crust
As	1.8	1	6.5-7.1
Pb	13	8	16.9
F	625	625	−
B	10	10	−
Hg	0.08	0.08	−

Japan are located in the circum-Pacific earthquake belt where the Eurasian and Pacific Plates connect and geological activities such as volcanic action and diastrophism have been active. Processes such as hydrothermal, physical and chemical phenomena resulted in higher concentration of heavy metals and metalloids in soils and rocks.

Trivalent arsenic usually exists in stratum and bedrock which is high toxicity. In surface soil and water, arsenic usually exists in pentavalent oxidized status. Masuda (2000) summarized the content of arsenic in rocks and soils as shown in Table 2.3. Content of arsenic in hydrothermal ore deposits which contain pyrite can be as high as 20,000 mg/L and the content in lacustrine sediment is as high as 13,000 mg/L.

Tatsuhara et al. (2011) and Shimada (2009) studied the leaching behavior of arsenic and three main mechanisms can be summarized based on their conclusions. First mechanism is the oxidative decomposition of pyrite. Second mechanism is the reductive decomposition of iron hydroxide. Third mechanism is desorption of arsenic from iron hydroxide and clay minerals in the sedimentary layer due to the change of pH and redox state.

Table 2.3 Content of arsenic in rocks and minerals (Masuda 2000)

Rock and soil type	Content (mg/L)	Rock and soil type	Content (mg/L)
Arenite	0.6 - 120	Galena	0 - 10,000
Pelite	0.3 - 500	Sphalerite	0 - 10,000
Iron rich sedimentary rocks	1 - 2,900	Chalcopyrite	< 80 - 5,000
River and sediment	< 1- 13,000	Pyrites	0 - 20,000
Soils	0.4 - 100	Jarosite	> 1,000

Several chemical reactions can be used to describe the oxidation process of pyrite. Due to the excavation in the construction work, pyrite is exposed to oxygen and water and oxidation process happens as follows:

$$2FeS_2 + 7O_2 + 2H_2O \rightarrow 2Fe^{2+} + 4SO_4^{2-} + 4H^+ \qquad (2.1)$$

Pyrites dissolves and pH of the water decreases due to the generation of H_2SO_4. If there is existence of thiobacillus ferrooxidans in the environment, much of the ferrous iron will oxidize to ferric ions as the following reaction:

$$4Fe^{2+} + O_2 + 4H^+ \rightarrow 4Fe^{3+} + 2H_2O \qquad (2.2)$$

At pH value between 2.3 and 3.5, ferric ions precipitate as $Fe(OH)_3$:

$$Fe^{3+} + 3OH^- \rightarrow Fe(OH)_3 \qquad (2.3)$$

At the same time, ferric ions which do not precipitate will oxidize additional pyrite in the solution based on the following reaction:

$$FeS_2 + 14 Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \qquad (2.4)$$

Since pyrites keep dissolve in the water due to oxidation, arsenic contained inside of the pyrite will also leach into the environment.

Arsenic dissolved in surface water and shallow groundwater due to the erosion of rocks behaviors as anion such as $H_2AsO_4^-$ and $HAsO_4^{2-}$. Particle surface of iron hydroxide minerals in colloid states are electropositive. Thus, arsenic can be adsorbed on the iron hydroxide because of the electrostatic attraction. However, if the water environment greatly changes such as decreasing in redox potential (Eh) or increasing in pH, desorption of arsenic into the environment will be triggered.

For example, if the oxygen in the water is consumed by organic matter, which decreases Eh, reductive decomposition of iron hydroxide will happen and arsenic ion can no longer be adsorbed. In addition, decomposition of organic matter and calcite consumes the hydrogen ion in the water, which increases pH. Surface charge of the iron hydroxide will keep decreasing until minus, finally lose the ability to fix arsenic ion. The situation of clay minerals is similar to the iron hydroxide. The surface charge of clay minerals will change with the pH of the solution. And desorption of arsenic will happen when the pH of the environment reaches to the point of zero charge.

Tabelin et al. (2009) studied the mechanism of arsenic and lead releasing from hydrothermally altered rock. The effects of pH, dissolved oxygen, redox conditions, and mixing ratio of different rocks on the leaching behaviors of As and Pb were evaluated. The leaching of As was highly pH dependent, with higher mobilization in the acidic and alkaline regions. Leaching was also higher under strongly reducing conditions. To minimize leaching of both As and Pb, the pH must be maintained in the circumneutral region. To minimize pyrite oxidation and reductive dissolution, the redox potential should be maintained at mildly oxidizing or mildly reducing conditions and attention should be paid to the removal of dissolved oxygen.

Tabelin et al. (2010) conducted in-situ experiments to study the factors affecting arsenic mobility. Four impoundments were built on site with rectangular base, truncated-pyramid structures. The results indicated that seasonal variations in temperature, O_2 concentration and volumetric water content in the impoundments strongly influenced arsenic leaching. The use of a silty soil cover of low permeability effectively lowered the As concentration in the porewater. However, it was not efficient enough to reduce the leaching of As because the conditions inside the impoundment could be dynamic. A bottom As-adsorption layer would be helpful to immobilize leached As from the waste rock.

2.3 Countermeasures for natural contamination

Several countermeasures were developed based on different mechanisms to treat excavated soils and rocks with natural contamination. Containment method utilizes geomembrane sheet and leachate treating facilities to prevent the leaching into surrounding environment. Immobilization method mixes contaminated soils with solidification/stabilization (S/S) agents, in order to fix arsenic with materials have stronger sorption capacity. Sorption layer method utilizes a permeable soil layer lying beneath the piled soils and rocks, to retain the heavy metal contained in the leachate before it reaches to the environment.

Nozaki et al. (2013), Uematsu (2011) and Shindou et al. (2013) compared these three methods with each other. By combining the results of these studies, along with the information provided by “Technical Manual on the Countermeasures against Soils and Rocks

Containing Natural-Derived Heavy Metals in Construction Works" and "Guidelines for Investigation and Action based on the Soil Contamination Countermeasure Act", containment method using geomembrane, immobilization method using S/S agents and sorption layer method were compared in the perspectives of capability, reliability, workability and economic efficiency. The conclusions are as follows:

Capability: Containment method utilizes seepage control work and water impermeable sheet to prevent migration of the contaminants in leachate into underground water. Its direct effect and simple mechanism makes it most easily acceptable. The fact that it has been applied in many practical projects also approves its high capability. The immediate effect of immobilization method by mixing contaminated soils with S/S agents also approve it good capability. However, its impact on surrounding environment like leaching of high alkaline water or hexavalent chromium solution will affect the capability. Since sorption layer method cannot be applied when the groundwater level is high, and its performance is not fully verified, the capability this method is limit for now.

Reliability: For containment method, in case the leachate remains in piled soils or embankments, their stability are significantly affected. Once seepage control systems are damaged, leakage of the leachate will happen and affect the environment. For immobilization method, its short-term effectiveness can be verified by conducting some applicability tests. However, its long-term performance under actual environmental conditions is not fully verified and has been a main concern. For sorption layer method, since it does not allow the leachate to remain inside the embankment, it has a better stability. Once the concentration of the leachate decreases to certain level inside the embankment, there will be no more concern on the effect of damage. However, the long-term performance of sorption layer, like the stability of hydraulic conductivity in different pH environment, sorption and desorption of the heavy metal due to the effect of different anion and cation, still need to be studied.

Workability: Containment method needs additional drainage equipment to remove and treat the leachate, to lay sheet on slope and adhere sheet in winter also need high technology requirements. The work amount of previous applicability tests and latter mixing soil with S/S agent is huge for immobilization method. In addition, the curing process of solidification method, especially in winter season, also increases the complexity of the method. Sorption layer method has a relatively easy construction process, which usually consists of mixing the soil with additives and laying the layers with proper compaction. Since there are no other equipment, the maintenance requirements of sorption layer method are also simple.

Table 2.4 Comparison of different countermeasures

	Containment method (geomembrane)	Immobilization method (S/S)	Sorption layer method
Capability	excellent	good	medium
Reliability	good	medium	medium
Workability	poor	good	excellent
Economic efficiency	poor	medium	excellent

Economic efficiency: The cost for containment method is around 10,000 yen/m^2, the cost for immobilization method is around 7,000 yen/m^2 and the cost for sorption layer method is around 4,000 yen/m^2. Containment method is impossible to treat huge amount of excavated soils. In contrast, sorption layer method can greatly reduce the total cost of the project.

The comparison of these three methods are summarized in Table 2.4, the performance in different field was described in four levels: excellent, good, medium and poor.

It can be concluded that, although containment method has been mostly applied, its complex workability and high cost makes it very hard to treat excavated soils and rocks. The long-term performance and environmental compatibility of immobilization method always remains a concern. As for sorption layer method, its disadvantage is due to the lack of study to verify its capability and reliability, once the requirements of these conditions can be met, its character of simple construction, low cost and good workability will make this method act as a cost-effective countermeasure for huge amount of excavated soils and rocks.

2.4 Sorption layer method

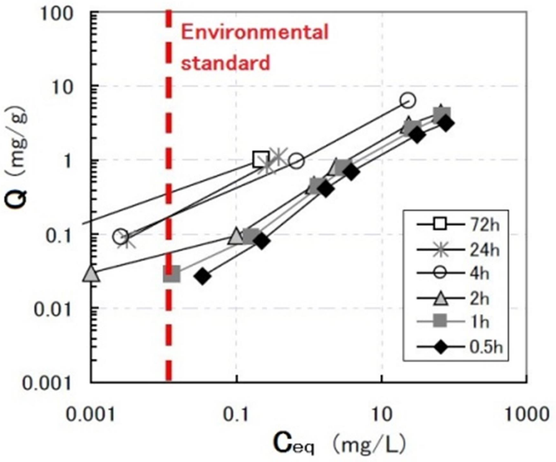
Based on the conception of sorption layer method, several studies have been conducted focused on the materials or design of sorption layer, which will be introduced as follows.

Tabelin et al. (2014) studied the ability of three natural geologic materials contain minerals like Al-/Fe oxyhydroxides/oxides to sequester As and B from aqueous solutions and the actual leachate of a hydrothermally altered rock. Results showed that the persistent alkaline pH of the leachate not only reduced adsorption but also destabilized both the geogenic and adsorbed As in the natural adsorbent. Which reflects that fact that desorption of heavy metal related with the pH environment should be carefully considered when choosing the sorption material for sorption layer.

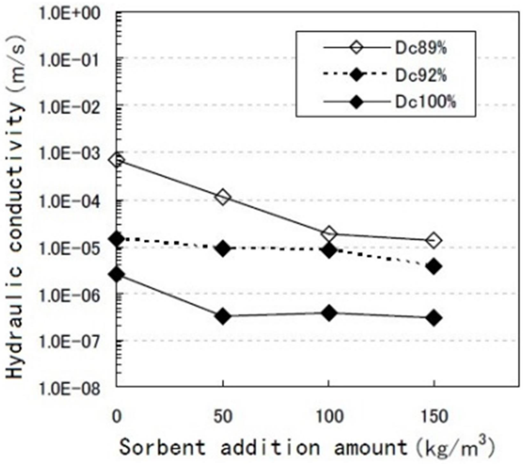
Tatsuhara et al. (2009) proposed an evaluation method for the performance of sorption material. The study conducted batch sorption test under different conditions including man-made solution with drilling core solution and different initial concentration. Results showed that sorption capacity of some materials greatly decreased in the drilling core solution, which reflects the effect of co-existing substances with arsenic in real condition should be considered when test the sorption capacity of certain material. Results also showed that sorption capacity of some material decreases when initial concentration increase, which reflects that sorption capacity of the sorption material should cover a wide range of initial concentration to make sure for the performance. At last, author pointed out four important aspects which should be considered: concentration dependence of sorption capacity, contact time, effect of co-existing substances and pH.

Nozaki et al. (2013) conducted a study based on the objective of obtaining stable quality and shorter construct period by offering base material and sorption material together. Batch sorption tests were conducted to obtain the effect of contact time and liquid/solid ratio (Fig. 2.2a). Hydraulic conductivity tests were conducted to obtain the effect of compaction degree and addition amount of sorption material (Fig. 2.2b). Column sorption test were finally conducted to verify the sorption performance of certain combination of compaction degree and addition amount (Fig. 2.2c). By obtaining the combination whose effluent concentration were under the environmental standard (e.g. Dc 92%, 100kg/m^3), the permeation time of this combination (3h) can be related with the results of time step batch test (4h case has almost the same effect with 24h case). A proper permeation time range can be obtained (at least 3h). Design factor such as hydraulic conductivity under certain layer thickness can then be obtained according to the results (for layer thickness of 50cm, hydraulic conductivity should under 8.28 × 10-6 m/s). The whole structure of the study was valuable to be referred to on how to connect the results of hydraulic conductivity test and batch sorption test and obtain initial sorption layer design factor.

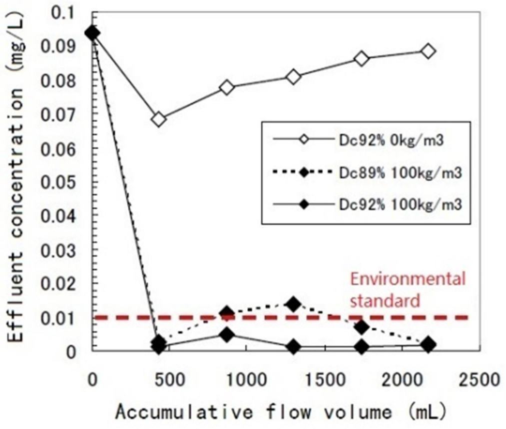
Tanaka et al. (2011) conducted column tests (Fig. 2.3) to obtain rational design of sorption layer from actual construction point of view. It is common in practical site that sorption material cannot be homogeneously distributed in the base material or the water flow inside sorption layer is not homogeneous. So, a silica sand layer was set above the sorption layer in case 2 to help exhibit the sorption capacity. Results showed that sorption equilibrium was reached after 60 hours, at the same time, the effluent concentration of arsenic in case 2 cannot be detected. Because of the flow channel dispersion effect offered by the silica sand



(a) Sorption isotherms



(b) Hydraulic conductivity



(c) Column tests results

Fig. 2.2 Experimental results of sorption layer using MgO (Nozaki et al. 2013)

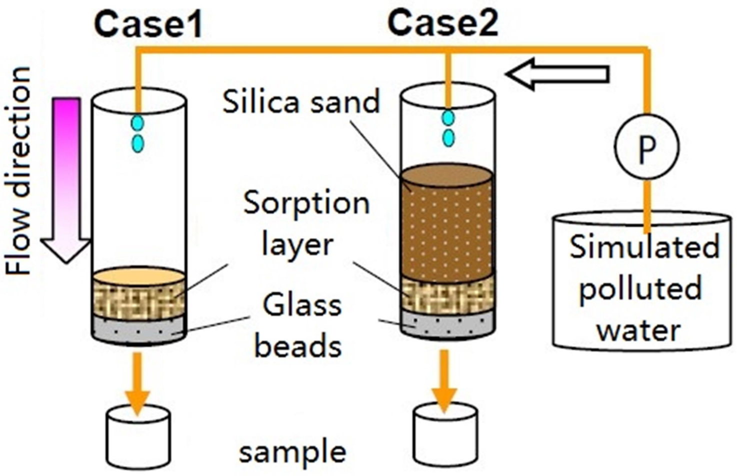


Fig. 2.3 Unsaturated column tests (Tanaka et al. 2011)

layer, sorption capacity of the sorption layer had been greatly increased without any change of the layer itself. This study shows that heterogeneity of the sorption layer and water flow should be considered in the design of sorption layer.

Toake et al. (2008) conducted two column tests on immobilizing method and sorption layer method (Fig. 2.4) using same stabilizing agent and studied the effect. In immobilizing method, 0.2% stabilizing agent was mixed with contaminated soil, which according to the results of batch sorption test, can reduce the leaching concentration of arsenic below the environmental standard. For sorption layer case, 2% stabilizing agent was mixed with 15mm clean base material. The results of the column tests were shown in Fig 2.5. It can be observed that the leaching concentration of arsenic is higher than the environmental standard, which indicated that the sorption process in column test was not as sufficient as batch test. In sorption layer method case, the concentration of arsenic was lower than the standard even after 230 hours. The first reason is that the stabilizing agent in sorption layer is higher than immobilizing method. The second reason is that stabilizing agent can contact with arsenic more sufficiently than former case. This study showed that the contact efficiency of sorption material and heavy metal is essential for the sorption effect and sorption layer method has a higher efficiency than immobilizing method.

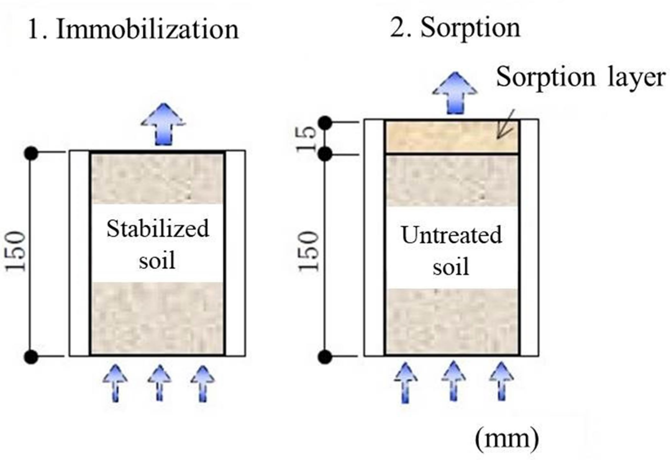


Fig. 2.4 Column tests using different countermeasures (Toake et al. 2008)

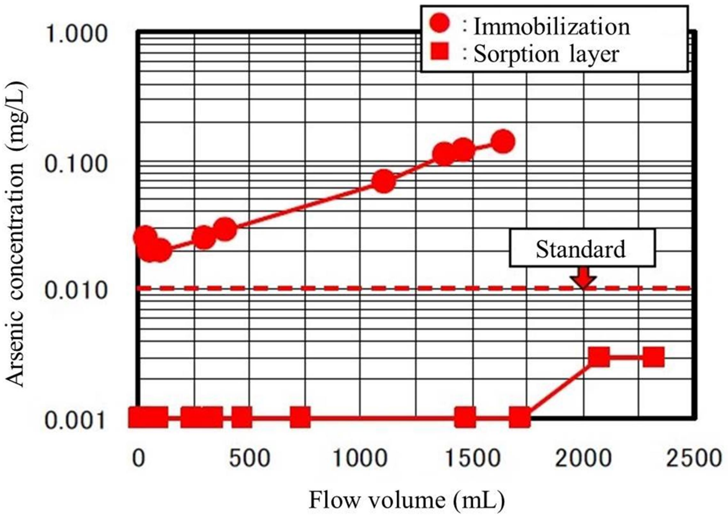


Fig. 2.5 Results of column tests using different countermeasures (Toake et al. 2008)

2.5 Performance of Ca-Mg immobilizing agent

In this study, Ca-Mg composite powder, which is developed by Sumitomo Osaka Cement Co., Ltd., Japan, is used. Sorption material used in sorption layer method should make sure that desorption of heavy metal would not happen in long term. Several studies have been conducted to study the sorption mechanism and performance of Ca-Mg immobilizing agent, which are introduced as follows.

Itaya et al. (2013) applied X-ray diffraction (XRD), X-ray fluorescence (XRF), scanning electron microscopy and energy dispersive spectroscopy (SEM-EDS) analysis on the residue after batch sorption test, explained the sorption mechanism of Ca-Mg immobilizing agent on arsenic. Author supposed that with the addition of Ca-Mg immobilizing agent, pH will increase and H_3AsO_3 will start to transfer into $H_2AsO_3^-$. As (III) will be oxidized to As (V). Precipitation of calcium arsenate will be generated according to the following chemical reactions:

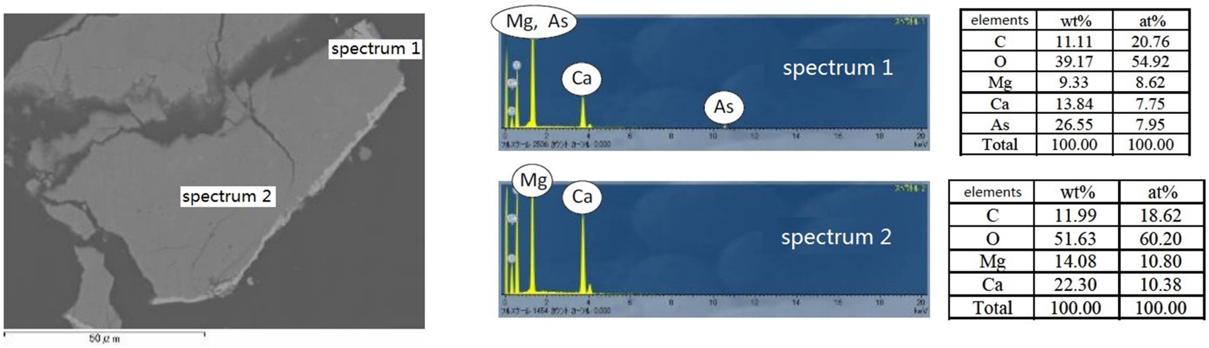
$$5Ca^{2+} + OH^- + 3AsO_4^{3-} \rightarrow Ca_5(AsO_4)_3OH\ (s) \tag{2.5}$$

$$3Ca^{2+} + 2AsO_4^{3-} + 4H_2O \rightarrow Ca_3(AsO_4)_3(H_2O)_4\ (s) \tag{2.6}$$

$$Ca^{2+} + HAsO_4^{2-} + H_2O \rightarrow CaHAsO_4(H_2O)\ (s) \tag{2.7}$$

The composograph of backscattered electron image (COMPO) and point spectrum analysis according to SEM-EDS (Fig. 2.6) showed that high percentage of arsenic, calcium and magnesium was distributed on the edge of the particle surface, which was not found inside the particle. However, XRD results (Fig. 2.7) showed that peak of calcium arsenate was not detected. So it was considered that As (III) was not transferred into As (V) and generated calcium arsenite instead. It was also shown in Fig. 2.7 that peak of magnesium hydroxide was detected while peak of magnesium arsenate was not detected. So it was speculated that the co-precipitation between arsenic and magnesium hydroxide was also one of the mechanisms to immobilize arsenic.

Kikuchi et al. (2012) conducted a study on the applicability of Ca-Mg immobilizing agent (MFX) for the sorption layer method. Batch sorption results (Table 2.5) suggested that Ca-Mg immobilizing agent has a high sorption rate covering wide initial concentration range.



elements	wt%	at%
C	11.11	20.76
O	39.17	54.92
Mg	9.33	8.62
Ca	13.84	7.75
As	26.55	7.95
Total	100.00	100.00

elements	wt%	at%
C	11.99	18.62
O	51.63	60.20
Mg	14.08	10.80
Ca	22.30	10.38
Total	100.00	100.00

Fig. 2.6 COMPO image and point spectrum analysis according to SEM-EDS (Itaya et al. 2013)

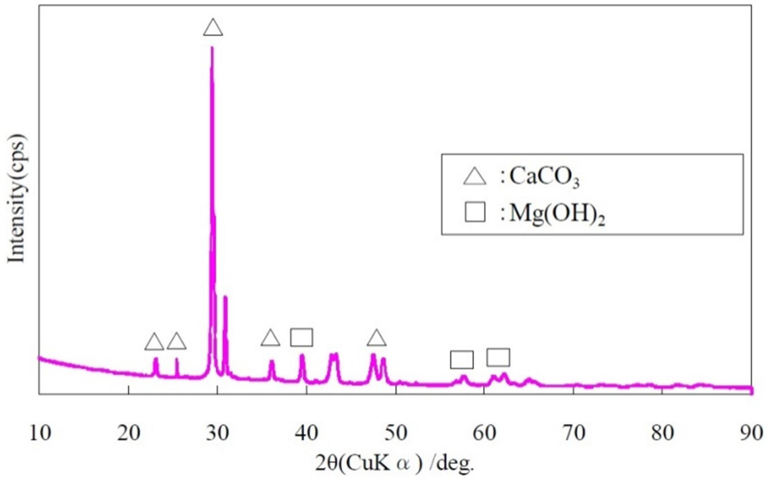


Fig. 2.7 XRD results of residue after batch sorption tests (Itaya et al. 2013)

The pH of the solution can be maintained at weak alkaline condition, which is favorable for the substances generated by sorption to keep stable. The results of repeatedly sorption test (Fig. 2.8) showed that Ca-Mg immobilizing agent has strong sorption ability and are able to exhibit sufficient sorption capacity during the initial stage of the reaction. In leaching test with acid/alkali addition, test results (Table 2.6) showed that Ca-Mg immobilizing agent has a strong ability to keep the pH of the solution in weak alkaline range, which can efficiently limits desorption happening.

In conclusion, Ca-Mg immobilizing agent can fix the heavy metal by its strong sorption ability through both precipitation of insoluble compounds and sorption onto hydration products. Its sorption ability is expected to be enough as a sorption layer to immobilize the heavy metal in the leachate passing through the sorption layer.

Table 2.5 Sorption rate and pH with different initial concentration (Kikuchi et al. 2012)

	As		Pb		F	
Initial Concentration (mg/L)	0.5 － 5	100	0.5 － 5	100	0.5 － 5	100
Removal ratio	> 99%	98.4%	> 99%	> 99%	98.4%	> 99%
pH	10.4	10.5	9.6	10.3	10.2	10.5

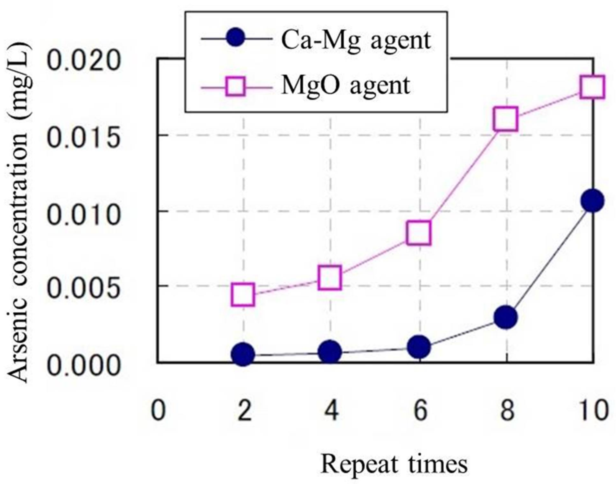


Fig. 2.8 Experimental results of repeatedly sorption test (Kikuchi et al. 2012)

Table 2.6 Leaching test results with acid/alkali addition

Initial solution	Sorption test		Leaching test			
			Acid addition		Alkali addition	
	Remove ratio	pH	Leaching amount	pH	Leaching amount	pH
As: 1mg/L	> 99%	10.4	< 0.003 mg/L	10.3	< 0.003 mg/L	11.8

CHAPTER 3

Hydraulic performance

3.1 General remarks

Hydraulic performance of sorption layer is crucial and should be preliminarily evaluated because it affects flow conditions (flow rate, retention time, etc.) of the leachate inside the layer, which is a key issue of sorption process.

Permeable is one basic concept of sorption layer method. A certain range of hydraulic conductivity should be maintained to ensure that the leachate can flow through the layer continuously as expected while a contact time is long enough for contaminants to be attenuated. At the same time, accumulation of too much leachate inside the embankment should be avoided considering the negative impact on the stability. In addition, long-term hydraulic performance is important and needs to be evaluated since the properties of layer material might be affected after long-time permeation under the interaction with chemical substance contained in the leachate. Unlike some low-permeability waste containment barrier, there are no specific regulations on the criteria of the hydraulic conductivity for a sorption layer. Thus, the evaluation in this study is more focused on a performance-based point of view rather than a product-based point of view (Katsumi et al. 2001).

There are several factors might affect the hydraulic conductivity including permeating liquid properties, soil properties and effect of chemicals (Sharma and Lewis 1994). In this study, hydraulic conductivity was measured using a flexible wall permeameter. Effect of mixing proportions and curing periods on the hydraulic conductivity is studied. Different hydraulic gradients were applied in the experiments to study their potential impact. Long-term hydraulic conductivity tests were conducted to check the performance and some potential influential factors are discussed.

In this chapter, hydraulic performance of decomposed granite soil amended with Ca-Mg composite powder is studied. In section 3.2, the properties of soil-agent mixture are described and experimental method of hydraulic conductivity test is introduced. In section 3.3, effect of mixing proportion, curing period and hydraulic gradient on the hydraulic conductivity is evaluated and the long-term hydraulic performance is discussed. Potential mechanisms which might affect the hydraulic performance are analyzed.

3.2 Materials and methods

3.2.1 Decomposed granite soil

Commercially available decomposed granite soil was used as the clean host soil. Soil particles which passed a 2 mm-opening sieve were used. Physical properties of decomposed granite soil after sieving are presented in Table 3.1. The particle density of decomposed granite soil is 2.70 g/cm^3 and pH of the soil was 9.5. The particle size distribution curve is shown in Fig. 3.1.

Table 3.1 Physical properties of decomposed granite soil under 2 mm

Items	Standard/Method	Value
Particle density	JIS A 1202	2.70 g/cm^3
Initial water content	JIS A 1203	3.8%
Particle size distribution	JIS A 1204	
Sand fraction (0.075 - 2 mm)		85.9%
Silt fraction (0.005 - 0.075 mm)		7.7%
Clay fraction (< 0.005 mm)		6.4%
Uniformity coefficient		20.2
Coefficient of curvature		3.32
pH	JGS 0211	9.5

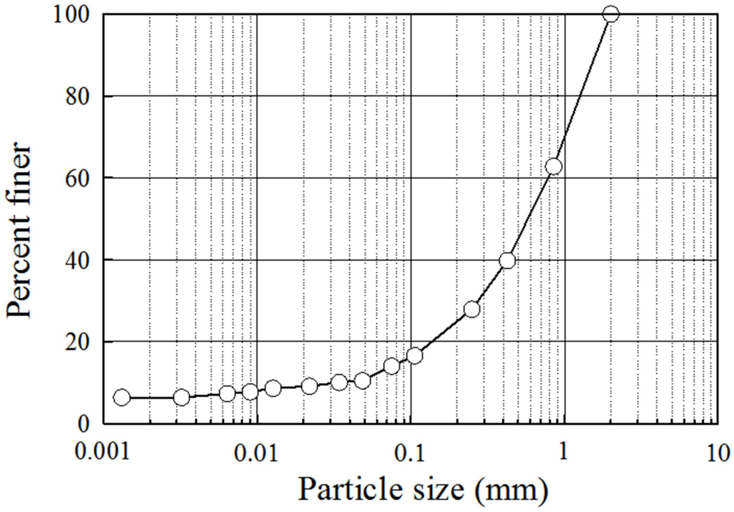


Fig. 3.1 Particle size distribution of decomposed granite soil under 2 mm

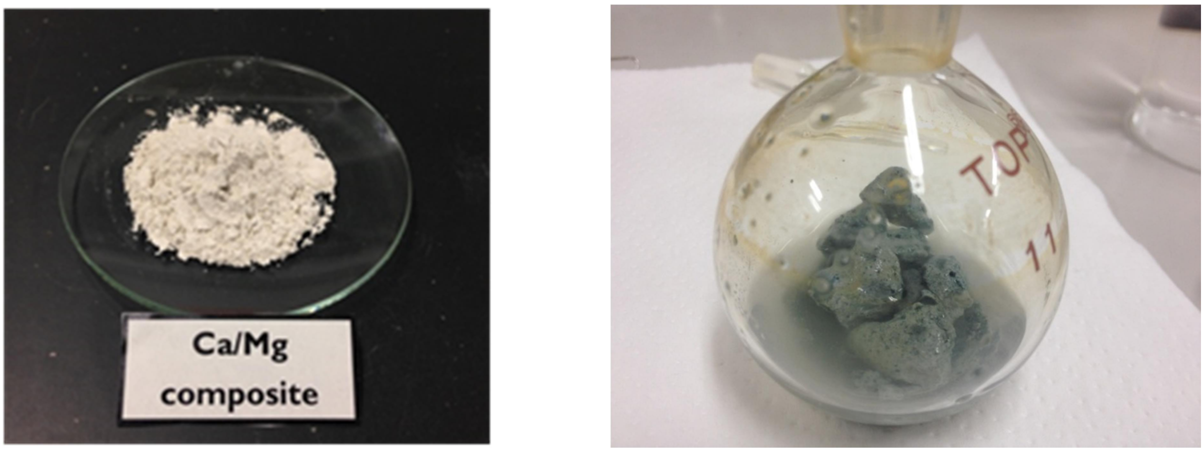
3.2.2 Ca-Mg composite powder

The immobilizing agent of Ca-Mg composite powder was obtained from Sumitomo Osaka Cement Co., Ltd. It is manufactured through mixing powdered calcinations of dolomite-based natural mineral with special additives. The main components of this agent include $CaCO_3$, $MgCO_3$, MgO and $FeSO_4$. Content of free CaO is under 0.5%. Chemical composition of the agent was determined by the test method for lime (JIS R 9011) and shown as the mass ratio of their oxide in Table 1 (The Society of Materials Science, Japan (JSMS) 2014).

It should be noticed that pure Ca-Mg composite powder reacts with water. After addition of distilled water, initial white powder showed in Fig.3.2 (a) turned into rigid agglomeration with dark green color as shown in Fig. 3.2 (b). This phenomenon is probably caused by the hydration reaction between MgO and $FeSO_4$ with water that agglomerates fine powders. Hydration products are also considered to contribute the strength development for the mixture of soil and agent. Thus, particles density test for cement using Le Chatelier Flask (JIS R5201) was used for Ca-Mg composite powder and soil-agent mixture.

Table 3.2 Properties of Ca-Mg composite powder

Items	Standard/Method	Value
Main components		$CaCO_3$, $MgCO_3$, MgO and $FeSO_4$
Bulk density	JIS R 9301(untamped)	0.90 g/cm^3
Particle density	JIS R 5201	2.79 g/cm^3
pH (25 °C)	1 g in 100 mL water, mixing 1 hour	10.3
Blaine's specific surface area	JIS R 5201	4200 cm^2/g
Moisture	5 g, dried under 110 °*C*	0.21 wt%
Component	JIS R 9011	
CaO		35.6%
MgO		19.4%
SO_3		3.98%
Fe_2O_3		3.73%
SiO_2		1.52%
Al_2O_3		0.068%
P_2O_5		0.035%
Ignition loss		33.5%



(a) Ca-Mg composite powder (b) Agglomeration after water addition

Fig. 3.2 Reaction of Ca-Mg composite powder with water

3.2.3 Preparation of the soil-agent mixture

Decomposed granite soil was dried under 105 ˚*C* for at least 24 hours by using a constant temperature oven (DNE600, Yamato, Japan). Then the soil was mixed with Ca-Mg composite powder in a mixer (KM-800, Kenmix, Japan) under the mix proportions of 0% (pure soil), 3% and 5% in dry mass basis (e.g., mix proportion of 5% = 5 g Ca-Mg composite powder per 100 g decomposed granite soil).

After the mixture was mixed homogeneously in dry state, distilled water was added to the soil-agent mixture while the mixing was continued. Addition amount of distilled water was determined based on the optimum water content obtained beforehand from the standard compaction tests following A-a method of JIS A 1210 (2009). The compaction curve of each mix proportion is shown in Figure 3.3. Considering the reaction between Ca-Mg agents with water, additional distilled water is usually added into the mixture for compensation.

Mixture of decomposed granite soil with Ca-Mg composite powder and water was subjected to compaction process immediately after homogeneous mixing. It was compacted in a cylindrical mold (*ø* 6 cm) under the compaction degree of 95%. Soils were compacted in several layers based on the specimen height and the total weight of soil compacted into the mold was calculated accordingly. A parafilm with black line showing layer height was used. Thus soils can be homogeneously compacted for each layer and the specimen can be separated from the mold easily. During compaction, surplus soil samples in the container were sealed with a polyethylene film on the top to prevent evaporation and decreasing of water content.

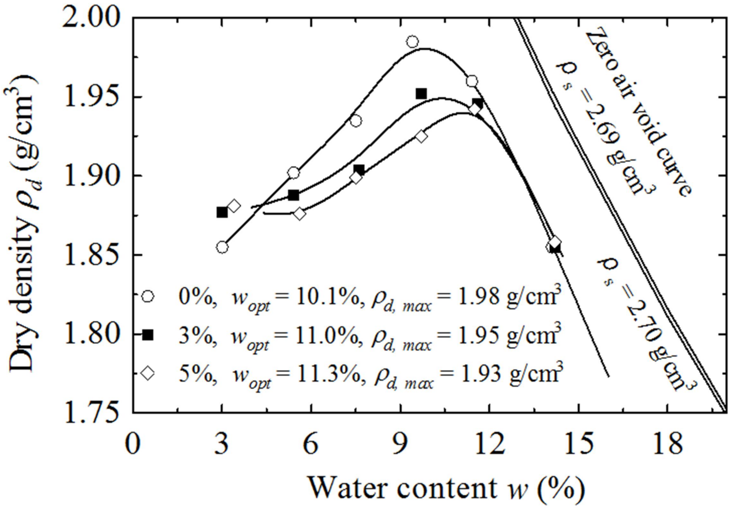


Fig. 3.3 Compaction curve of soil-agent mixture under different mix proportions

After compaction, the specimen was wrapped with cling film and kept in a sealed plastic bag for curing under constant room temperature of 20 ˚*C* and a cup of water was put inside the bag to keep humidify. The curing period was set to 0 (no curing), 7 and 28 days. Surplus soils after compaction were collected for measuring water content. Particles density test (JIS R 5201) was conducted for the soil-agent mixture oven dried for 24h and the results were summarized in Table 3.3. For different mixing proportions and curing periods, particle density is around 2.70 g/cm^3. Since the particle density of the Ca-Mg powder is 2.79 g/cm^3, it can be assumed that adding the Ca-Mg composite powder has no obvious impact on soil particles.

Table 3.3 Physical properties of soil-agent mixture

Additive content of Ca-Mg composite powder	Optimum water content (%)	Maximum dry density (g/cm^3)	Curing periods (days)	Particle density (g/cm^3)
0%	10.1	1.98	0	2.70
3%	11.0	1.95	0	2.70
			7	2.69
5%	11.3	1.93	0	2.68
			7	2.68

3.2.4 Hydraulic conductivity test

Hydraulic performance was studied in three stages. For the first stage (stage 1), effect of mix proportion on the hydraulic conductivity was evaluated. The soil-agent mixtures with the mix proportions of 0%, 3% and 5% under the curing periods of 0, 7 days were tested at a hydraulic gradient of around 5. A falling head hydraulic system was applied and the dimension of specimens was 6 cm in diameter and 7 cm in height. The cell pressure was 40 kPa. Distilled water was used as a permeant. Permeation was conducted until hydraulic conductivity values were stable and a cumulative flow volume reached 5 or more pore volumes of flow (*PVF*).

For the second stage (stage 2), the effects of different hydraulic gradient and curing period was adequately compared. A much lower constant hydraulic gradient of 1, which was more realistic in the actual site, along with a longer curing period of 28 days, was applied for specimens with the mix proportion of 5%. A constant head was maintained by using a Marriotte's bottle. The dimension of specimens was 6 cm in diameter and 5 cm in height. Distilled water was used as a permeant and permeation was conducted until the cumulative flow volume was up to 40 *PVF*s.

For the third stage (stage 3), long-term hydraulic performance combined with arsenic sorption was evaluated for the specimen with the mix proportion of 5% and 7 or 28 days-curing. The dimension of specimens was 6 cm in diameter and 2 cm in height which was consistent with the up-flow column percolation tests which will be discussed in Chapter 4 and Chapter 5. The initial hydraulic gradient was set to 2.5. Distilled water and 1 mg/L arsenic (As) solution was used as a permeant. Concentration of As in effluent was analyzed by atomic absorption spectrometry (AAS) method (AA-6800, SHIMADZU). pH value and electrical conductivity (EC) was measured using a pH/EC meter (F-55, HORIBA, Japan).

For stage 1 and stage 2, tests were conducted in duplicate. For stage 3, test was repeated for specimen with mix proportion of 5%, curing period of 28 days and permeated with arsenic solution. The whole experimental approach was summarized in Table 3.4

Flexible-wall permeameters were used for all cases based on the ASTM D 5084 "Standard Test Methods for Measurement of Hydraulic Conductivity of Saturated Porous Materials Using a Flexible Wall Permeameter" (ASTM 2010). A schematic diagram of this system with a Marriotte's bottle to maintain a constant water head is presented in Fig. 3.4.

Flexible-wall permeameter was set up by the following procedures:

1) Prepared soil-agent mixture specimen was submerged in distilled water and saturated by vacuum deaeration for 24 hours.

Table 3.4 Experimental conditions for hydraulic conductivity test

Test stage	Additive content of Ca-Mg composite powder	Curing period (days)	Test conditions
Stage 1 Effect of mix proportion	0%	0	· Falling head · ϕ 6cm × 7cm · i =5, distilled water
	3%, 5%	0, 7	
Stage 2 Effect of hydraulic gradient and curing period	5%	0, 7, 28	· Constant head · ϕ 6cm × 5cm · i =1, distilled water
Stage 3 Long-term performance	5%	7, 28	· Constant head · ϕ 6cm × 2cm · i =2.5, 1 mg/L As solution

i: hydraulic gradient

2) Specimen was taken out of the mold and set in the flexible-wall permeameter, sandwiched by porous stones (or geotextiles), filter papers, cap and pedestal. Tygon tubes which are saturated with permeants in advance are connected to the pedestal with influent channel.
3) A latex membrane with silicone grease smeared on the inner face was placed to cover the sides of the specimen to minimize the sidewall leakage. O-rings were attached around the cap and pedestal to fix the latex membrane and prevent immersion of surrounding water. Effluent channel is then connected to the cap.
4) After setting up the acrylic cylinder, tap water was introduced into the acrylic cylinder to completely soak the specimen. Air pressure was applied on the specimen via the membrane from an air compressor.

Hydraulic conductivity at 15 ℃ was used as a representative value and it was calculated using the equation 3.1 for hydraulic conductivity test applying a falling head and the equation 3.2 for hydraulic conductivity test applying a constant head.

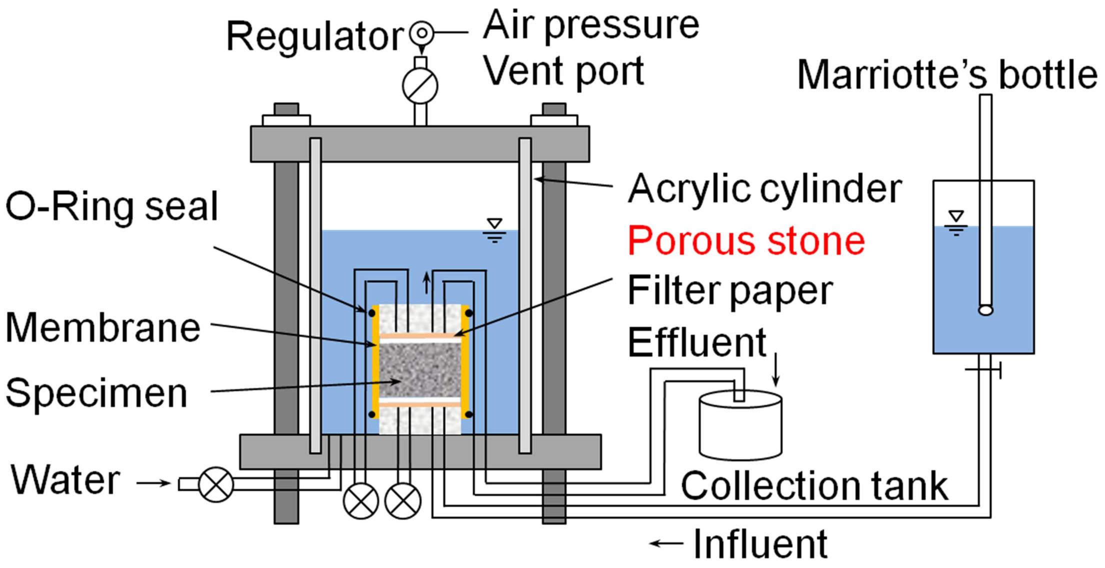


Fig. 3.4 Schematic view of a flexible-wall permeameter

$$k = \frac{\eta_T}{\eta_{15}} 2.303 \frac{aL}{A\,(t_2\text{-}t_1)} \log \frac{h_1}{h_2} \tag{3.1}$$

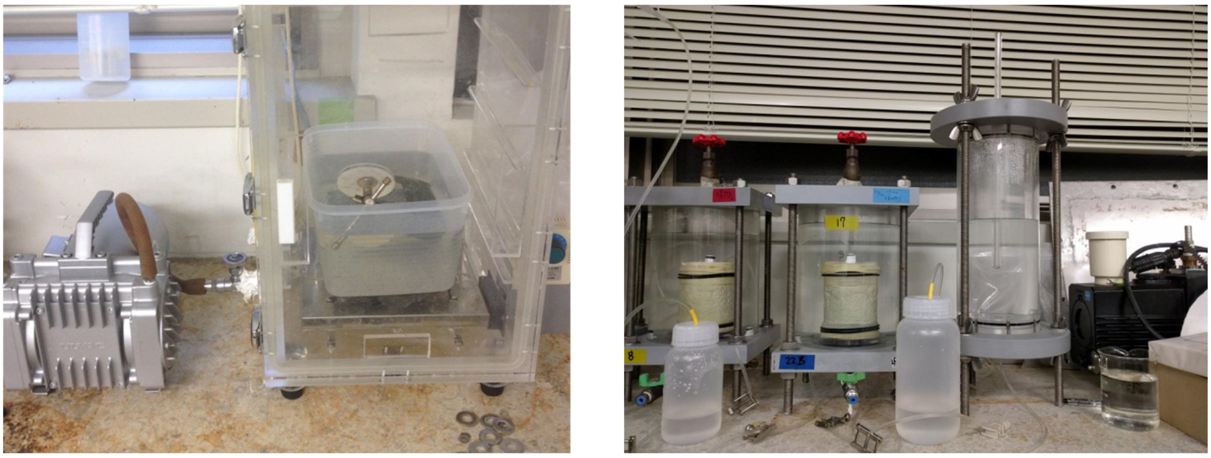
$$k = \frac{L}{h} \cdot \frac{Q}{A\,(t_2\text{-}t_1)} \tag{3.2}$$

where, k = hydraulic conductivity (m/s); a = section area of burette (cm^2); L = height of specimen (cm); A = section area of specimen (cm^2); t_1 = start time of measurement (s); t_2 = finish time of measurement (s); h_1 = initial water head level (cm); h_2 = final water head level (cm); h = constant water head level (cm); Q = outflow volume (cm^3); η_T, η_{15} = viscosity coefficient of permeant at T °*C* or 15 °*C*.

Pictures including the whole experimental procedures from specimen preparation to hydraulic conductivity test were shown in Fig. 3.5.

(a) Mixing under optimum water content (b) mold with parafilm for compaction

(c) Specimen and residue after compaction (d) Curing



(e) deaeration (f) Setting up of flexible-wall permeameter

Fig. 3.5 Experimental procedures of hydraulic conductivity test

3.3 Results and discussion

3.2.1 Stage 1: Effect of mix proportion

Hydraulic conductivity measured in stage 1 is summarized in Table 3.5 and plotted in Fig. 3.6 as a function of mix proportion. All the specimens exhibited a similar porosity and hydraulic conductivity values were within a range of 3.7×10^{-7} m/s to 1.2×10^{-6} m/s. Hydraulic conductivity of 0% case, which is decomposed granite soil without amendment of the Ca-Mg composite powder, was relatively lower than 3% and 5% cases except for one sample.

Fine soil particles were observed in the effluent of 0% cases in the initial permeation phase but not in 3% and 5% cases in spite of permeation at a same hydraulic gradient. This observation indicates that amendment of the Ca-Mg composite powder in 3% and 5% might interlock the fine particles and mitigate internal erosion. Hydration of the magnesium oxide (MgO) was considered as the main contributing process since other main components of the Ca-Mg composite powder such as $CaCO_3$ and $MgCO_3$ are slightly soluble in water. Wang and Handy (1966) suggested that $Mg(OH)_2$ generated by hydration of MgO is cementitious in nature. In addition, increase of hydraulic conductivity after lime treatment for soils such as lateritic soil (Osinubi, 1988) and clay (Nalbantoglu and Tuncer, 2001, Tran et al. 2014) was reported which was attributed to the increase of inter-aggregate pores size by the formation of coarser particles. Thus the soil-agent mixture exhibited a slightly higher hydraulic conductivity probably due to the cementation of particles of decomposed granite soil by the hydration process of MgO.

Hydraulic conductivity values of 3% and 5% cases were close to each other, which indicate that increasing the addition of the Ca-Mg composite powder has limited effects. Similar behavior was observed in the mechanical performance of amended decomposed granite soil. Unconfined compressive strength increased a little after addition of the lime (Kamon et al. 1996) or the Ca-Mg agent (Mo et al. 2014) in decomposed granite soil from 3% to 5%. It can be assumed that the interaction between soil particles and the Ca-Mg composite powder increases with increasing additive content in the initial low-additive stage, and additional agent over 3% has limited effect on soil composition or pore structure which leads to similar mechanical and hydraulic performance.

Table 3.5 Summary of hydraulic conductivity test results of stage 1

Additive content of Ca-Mg composite powder	Curing period (days)	Porosity *n*	Hydraulic conductivity *k* (m/s)
0%	0	0.307	5.4×10^{-7}
		0.308	4.7×10^{-7}
3%	0	0.319	7.1×10^{-7}
		0.310	1.1×10^{-6}
	7	0.309	8.3×10^{-7}
		0.306	7.8×10^{-7}
5%	0	0.312	3.7×10^{-7}
		0.315	8.1×10^{-7}
	7	0.310	7.9×10^{-7}
		0.315	1.2×10^{-6}

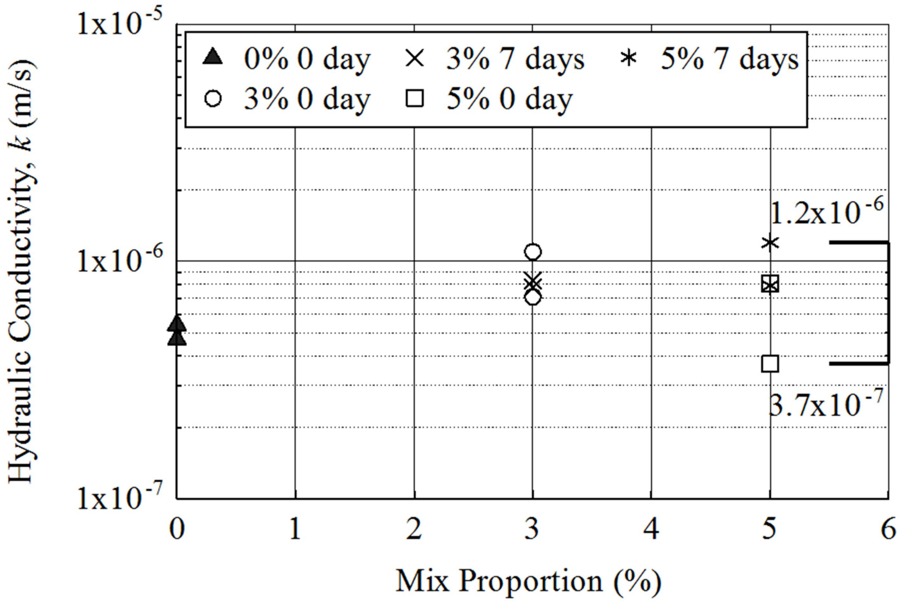


Fig. 3.6 Hydraulic conductivity of soil-agent mixture in terms of mix proportion

3.2.2 Stage 2: Effect of hydraulic gradient and curing period

In stage 1, hydraulic conductivity was measured at a hydraulic gradient of around 5, which is relatively higher than expected at the site. Considering that employment of an excessive hydraulic gradient can cause migration of fine soil particles and a reduction in hydraulic conductivity (Daniel 1984), a lower hydraulic gradient of 1 and longer permeation periods with a constant head system were applied in stage 2. Hydraulic conductivity values measured at hydraulic gradients of 5 and 1 are shown in Fig. 3.7. Similar results were obtained for both 0 and 7-day curing specimens with the mix proportion of 5% except for one specimen. The effects of the hydraulic gradient were minor, and it can be considered that a hydraulic gradient of 5 is not excessive for this mixture.

Hydraulic conductivity as a function of curing periods under a hydraulic gradient of 1 is summarized in Table 3.6 and Fig. 3.8. Hydraulic conductivity values were within a range of 7.1 × 10^{-7} m/s to 1.6 × 10^{-6} m/s. Specimens cured for 7 and 28 days exhibited similar hydraulic conductivity values, which are slightly higher than that of 0-day curing specimen. Wang and Handy (1966) suggested that the hardening of MgO in dolomitic monohydrate lime is relatively fast and is believed to contribute a lot to early strength in soil-dolomitic lime stabilization. Higher hydraulic conductivity of the cured soil-agent mixture might be attributed to the fast hydration process of MgO.

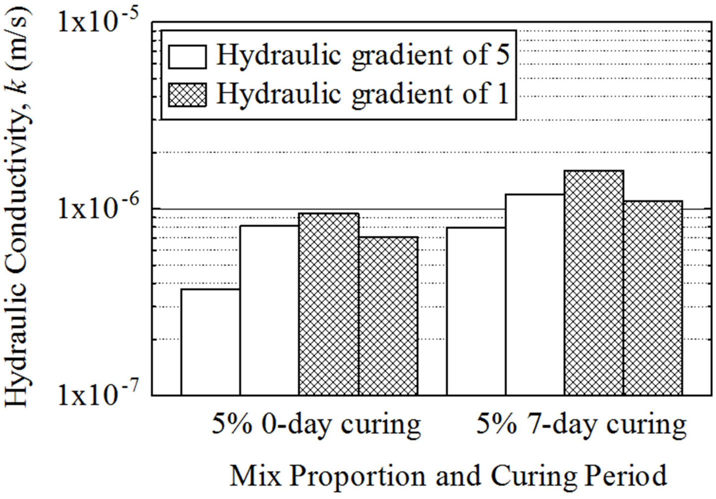


Fig. 3.7 Effect of hydraulic gradient on hydraulic conductivity

However, there is no obvious effect of longer curing period was confirmed in this study due to two potential reasons. First, the pH range offered by the Ca-Mg composite powder is around 9 to 10, which is lower than the pH favored by the pozzolanic reaction. Second, hydration products probably covered the surface of soil particles and hindered the leaching of calcium and silicate, and accordingly pozzolanic reactions were limited.

Table 3.6 Summary of hydraulic conductivity test results of stage 2

Additive content of Ca-Mg composite powder	Curing period (days)	Porosity n	Hydraulic conductivity k (m/s)
5%	0	0.310	9.5×10^{-7}
		0.309	7.1×10^{-7}
	7	0.313	1.6×10^{-6}
		0.311	1.1×10^{-6}
	28	0.318	1.6×10^{-6}
		0.311	1.4×10^{-6}

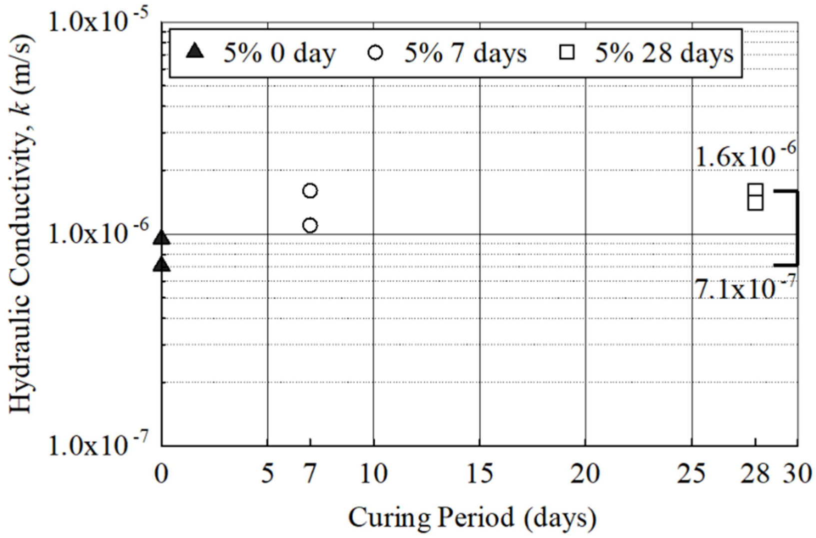


Fig. 3.8 Effect of curing period on hydraulic conductivity

3.2.3 Stage 3: Long-term performance under permeation of arsenic solution

Even though curing period up to 28 days does not significantly affect the hydraulic conductivity as shown in Fig. 3.8, long-term permeation may have a certain effect on soil structure and hydraulic performance. Thus, hydraulic conductivity change during the up-flow column sorption tests was monitored. 28-day cured specimens were tested in duplicate considering the potential interaction of hydration product with arsenic solution and their effect on the hydraulic performance. Variation of the hydraulic conductivity under permeation of 1 mg/L As solution is shown in Fig. 3.9.

For both of the specimens, hydraulic conductivity was slightly higher than 2 × 10^{-6} m/s and kept almost constant until the PVFs reached around 40, which is consistent with the results for a permeant of distilled water. However, hydraulic conductivity started decreasing after the PVFs reached 100, which was corresponding to a liquid/solid ratio (L/S) (mL/g) of approximately 20. Hydraulic conductivity was decreased to approximately 5 × 10^{-6} m/s, and after the PVFs = 200 the decreasing trend became less obvious.

McCallister and Petry (1992) reported that the permeabilities of lime-tread clays which were leached for 45 and 90 days decreased rapidly initially but approaching a slow steady decline after approximately 300 h of leaching. However, Le Runigo et al. (2009) reported that permeability of a lime-treated silt leached for 150 days did not fluctuate with circulation time and speculated that the evolution of the permeability subjected to leaching results from a competition between dissolution and precipitation processes. Despite of the different long-term hydraulic performance, both studies suggested leaching of calcium during

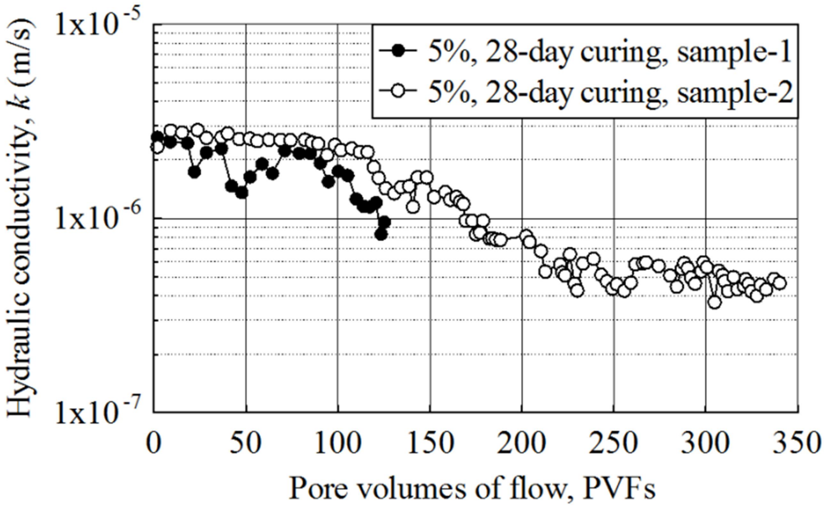


Fig. 3.9 Variation of hydraulic conductivity under permeation of 1 mg/L As solution

permeation after lime treatment. It can be assumed in this study that the hydration product of Ca-Mg composite powder might also be dissolved during the long-term permeation. Considering that the pH of effluent gradually decreased after PVFs reached 100 as shown in Fig. 3.10, which was consistent with the variation trend of hydraulic conductivity, dissolution of $Mg(OH)_2$ might happen during that period and some agglomerated particles might be flushed and obstructed the flow path.

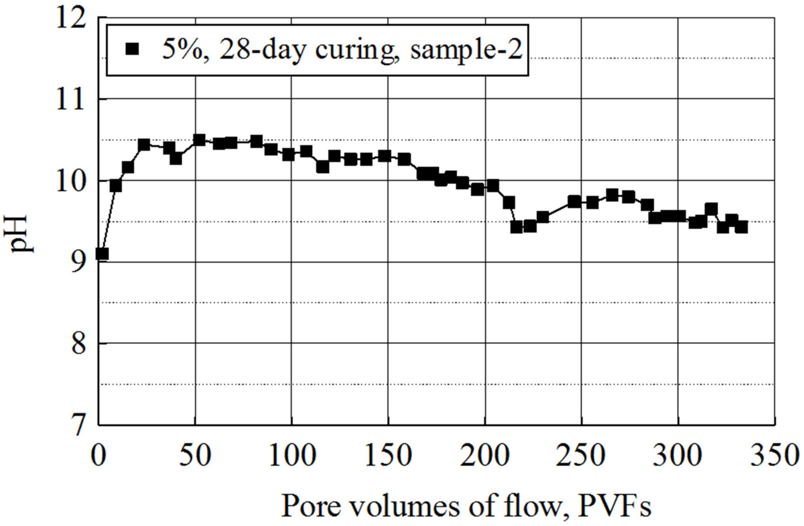


Fig. 3.10 Variation of pH of effluent under permeation of 1 mg/L As solution

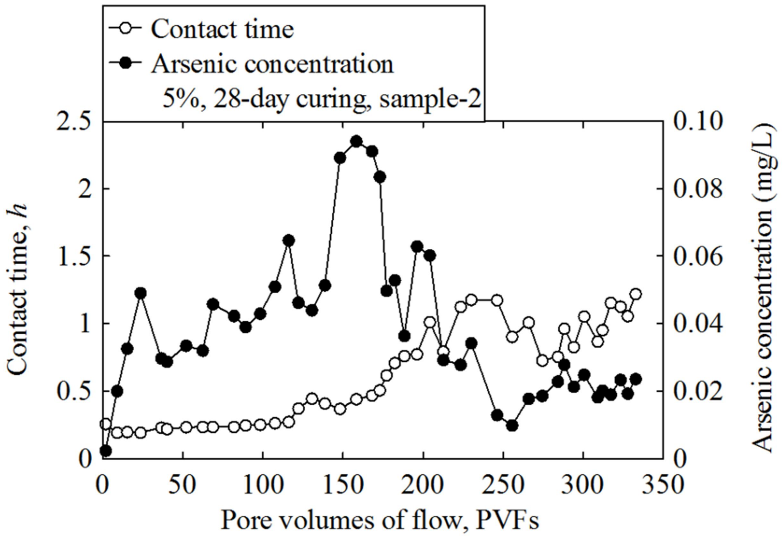


Fig. 3.11 Variation of pH of effluent under permeation of 1 mg/L As solution

In addition, low solubility substances such as $CaHAsO_3$ generated by calcium, which was released from decomposed granite soil, and arsenic in the solution might also be responsible for the decreasing of hydraulic conductivity. Arsenic concentrations of the effluent along with the contact time with specimen are shown in Fig. 3.11. Determination of contact time is described in chapter 4.2. Effluent arsenic concentration increased at the initial stage, and showed the highest concentration when the contact time started to increase, i.e. hydraulic conductivity started to decrease. Generation of precipitations probably contributed to the clogging of the flow path during this period. Effluent arsenic concentration then continuously decreased due to the longer contact time and shown increasing trend after PVFs of 250 when the hydraulic conductivity became relatively stable again. However, it should be considered that the cumulative mass of arsenic permeated into the specimen until the PVFs reached 250 was only about 6 mg, the precipitation of Ca-As related substances might be very limited and unlikely to be the major influential factor on long-term hydraulic performance.

Further research is necessary to verify the experimental results and identify the mechanisms for the decreasing hydraulic conductivity in a long term. The decreasing trend should be considered during the design of sorption layer method to prevent the sorption layer becoming less-permeable which leads to the accumulation of leachate and might seriously affect the stability of the embankment.

3.4 Conclusions for this chapter

In this chapter, hydraulic performance of decomposed granite soil amended with Ca-Mg composite powder was studied based on the results of hydraulic conductivity test. Effects of mix proportion, curing period and hydraulic gradient were evaluated and long-term hydraulic performance was discussed. The main results obtained in this chapter can be summarized as follows:

(1) Hydraulic conductivity of the soil-agent mixture was maintained at around 1×10^{-6} m/s. Initial addition of Ca-Mg composite slightly increases the hydraulic conductivity of decomposed granite soil. There is no obvious difference between the mix proportion of 3% and 5%. Further addition of Ca-Mg agent after 3% has little influence on the structure of soil-agent mixture.

(2) Fine soil particles were observed in the effluent of 0% cases in initial permeation phase but not in 3% and 5% cases during application of a same hydraulic gradient. This

observation indicates that amendment of the Ca-Mg composite powder in 3% and 5% cases might interlock the fine particles and mitigate the erosion.

(3) Hydraulic conductivity remained almost same at hydraulic gradient of 1 and hydraulic gradient of 5. Hydraulic gradient under 5 has no obvious effect.

(4) Specimens cured for 7 and 28 days exhibited similar hydraulic conductivity values, which are relatively higher than that of 0-day curing specimen. Higher hydraulic conductivity of cured soil-agent mixture might be attributed to the fast hydration process of MgO.

(5) There is no obvious effect of longer curing period confirmed in this study due to two potential reasons. First is the lower range around 9 to 10 which is not favored by the pozzolanic reaction. Second, hydration products probably covered the surface of soil particles and hindered the leaching of calcium and silicate, and accordingly pozzolanic reactions were limited.

(6) For long-term hydraulic performance, hydraulic conductivity was kept almost constant until the PVFs reached around 40 and started decreasing after the PVFs reached 100, which was corresponding to a liquid/solid ratio (L/S) (mL/g) of approximately 20. Decreasing trend became less obvious after the PVFs = 200,

(7) Dissolution of $Mg(OH)_2$ might happen during that period and some agglomerated particles might be flushed and obstructed the flow path.

CHAPTER 4

Sorption performance

4.1 General remarks

Sorption performance of materials used for sorption layer is vital and needs to be carefully evaluated to ensure that chemicals of concern can be retained by the layer and the whole method would work properly.

Ca-Mg composite powder as an immobilizing agent has been evaluated after mixing directly with contaminated soils and it was proved to be effective for both cation (Pb) and anion (As) (Bobea et al. 2012). However the process of sorption layer is quite different from conventional immobilization or stabilization practices. The agent is mixed with clean base soil first and the contaminants is retained from the leachate. How this different process affects the sorption performance needs to be studied. In addition, effects of the properties of soil-agent mixture such as mix proportion and curing periods on sorption performances should be evaluated as well. The interaction between soil and agent after mixing and its potential impact on sorption mechanisms and performances also requires investigation.

Batch equilibrium tests and column tests are generally applied to evaluate the sorption performance and to determine the solute transport parameters. Batch-test method is much quicker and can be easily conducted. Specimen particles are added into the solution and the slurry suspensions are shaken for a certain time. Compared to batch tests, Column tests are preferred, in part, because the soil density and porosity are more similar to field condition and column-test method represents a transient system which there is a flowing chemical solution (Shackelford 1994). Thus, which of the two different methods, to what extent, is more appropriate to evaluate the sorption performance needs to be studied.

In this chapter, primary sorption performance of decomposed granite soil amended with Ca-Mg composite powder is evaluated. Section 4.2 describes the procedure of preparing the soil-agent mixture and experimental methods of batch sorption test and up-flow column percolation test. In section 4.3, experimental results obtained from batch tests and column tests are presented and the effects of mix proportion and curing period are evaluated. The differences between batch tests and column tests are also discussed.

4.2 Materials and methods

4.2.1 Materials

Decomposed granite soil was used as the host soil and Ca-Mg composite powder was used as the immobilizing agent to strengthen the sorption performance. Properties of these two materials were introduced in section 3.2.1 and section 3.2.2 and the details of preparation of the soil-agent mixture were described in section 3.2.3.

For batch sorption tests and up-flow column percolation tests, the soil-agent mixture was prepared by the following procedures:

1) Sieving and drying: Decomposed granite soil was screened and soil particles under 2 mm were used. It was dried in an oven at 105 ℃ for at least 24 hours.
2) Mixing: Oven-dried decomposed granite soil was mixed with Ca-Mg composite powder under the mix proportions of 0%, 3% and 5% in dry mass basis. Distilled water was then added to adjust the water content of the mixture to its optimum water content.
3) Compaction: Soil-agent mixture was compacted in a cylindrical mold (ϕ 6 cm) immediately after homogeneous mixing. The compaction degree was set to 95%. Soil-agent mixture was compacted evenly in several layers.
4) Curing: After compaction, the specimen was wrapped with cling film and kept in a sealed plastic bag for curing under constant room temperature of 20 ℃.

After curing, specimens were taken out for batch sorption tests and up-flow column tests. Different specimen heights and curing periods were applied in these two tests and the details will be introduced in the following sections.

4.2.2 Batch sorption test

A series of batch sorption tests were firstly conducted to obtain a basic understanding of the sorption performance.

The soil-agent mixture was compacted in a cylindrical mold ($\o$ 6 cm × h 7 cm) in 3 layers with the mix proportion of 0%, 3% and 5%. For 0% and 3% cases, specimens were cured for 0 and 7 days. For 5% case, specimens were cured for 0, 7 and 28 days. After curing, specimens were extracted out of the mold and roughly crushed until the maximum diameter was under 2 mm. Arsenic solution was prepared by dissolving $NaAsO_2$ salts (procured from Nacalai tesque, Japan) in distilled water with initial concentrations of 0.1, 0.5, 1, 5 and 10 mg/L. Initial pH of each arsenic solution was not adjusted.

Table 4.1 Experimental conditions for batch sorption test

Additive content of Ca-Mg composite powder	Curing period (days)	Test conditions
0%	0	・ $NaAsO_2$ solution ・ Initial concentration: 0.1, 0.5, 1, 5 and 10 mg/L ・ L/S ratio: 20 ・ Horizontal shaking: 150 rpm for 24 hours
3%	0, 7	
5%	0, 7, 28	

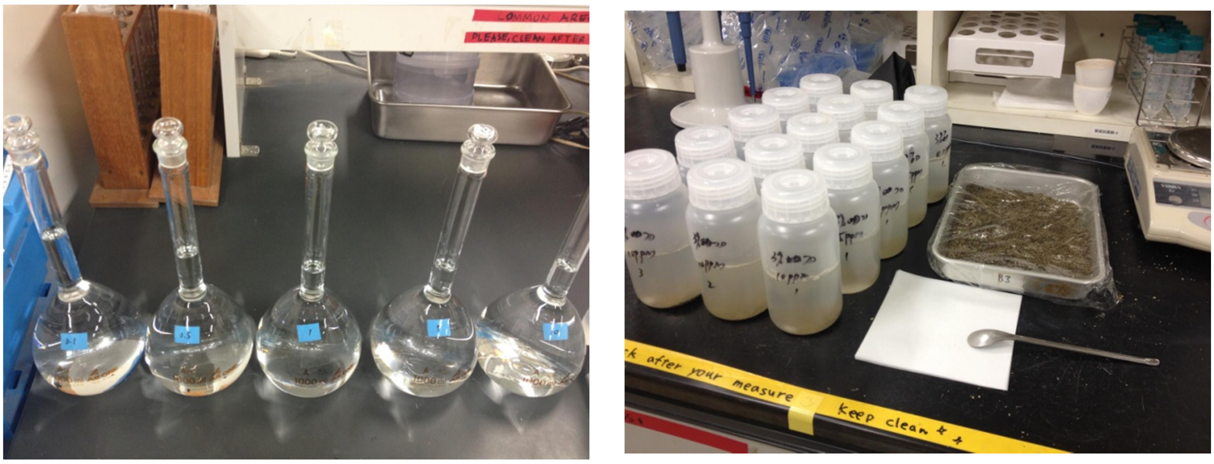
The liquid/solid ratio (L/S) (mL/g) was set to 20 and soil-agent mixture of 7 g was added into the solution of 150 mL. Samples were shaken at 150 rpm for 24 hours in horizontal direction on a shaking machine (NR-30, TAITEC, Japan). After shaking, they were left settling for 15 minutes and supernatant were taken for centrifugation under 3,000 rpm for 20 minutes (Double top centrifuge, KUBOTA, Japan). After centrifugation, solution was filtered using a 0.45 μm filter (Minisart® Syringe Filter, Sartorius). Concentrations of arsenic before and after the sorption test were analyzed by an atomic absorption spectrometry (AAS) (SHIMADAZU, AA-6800). pH value and electrical conductivity (EC) was measured using a pH/EC meter (F-55, HORIBA, Japan). Batch sorption tests were conducted in triplicate for each case. Experimental conditions for batch sorption tests were listed in Table 4.1 and photos of some major experimental steps are shown in Fig. 4.1.

4.2.3 Up-flow column percolation test

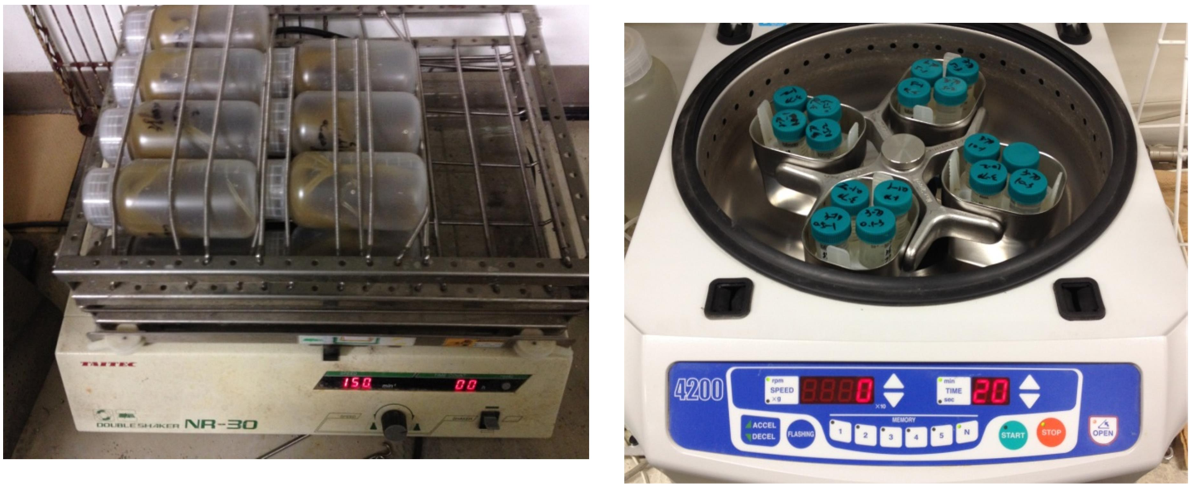
Column percolation tests were conducted to further study the sorption performance, which are considered more representative of practical application than batch tests.

Soil-agent mixture with mix proportions of 0% and 5% was compacted in a cylindrical mold (ϕ 6 cm × h 2 cm) in two layers. For 0% case, which is pure decomposed granite soil, specimen was not cured. For 5% case, specimens were cured for 7 and 28 days.

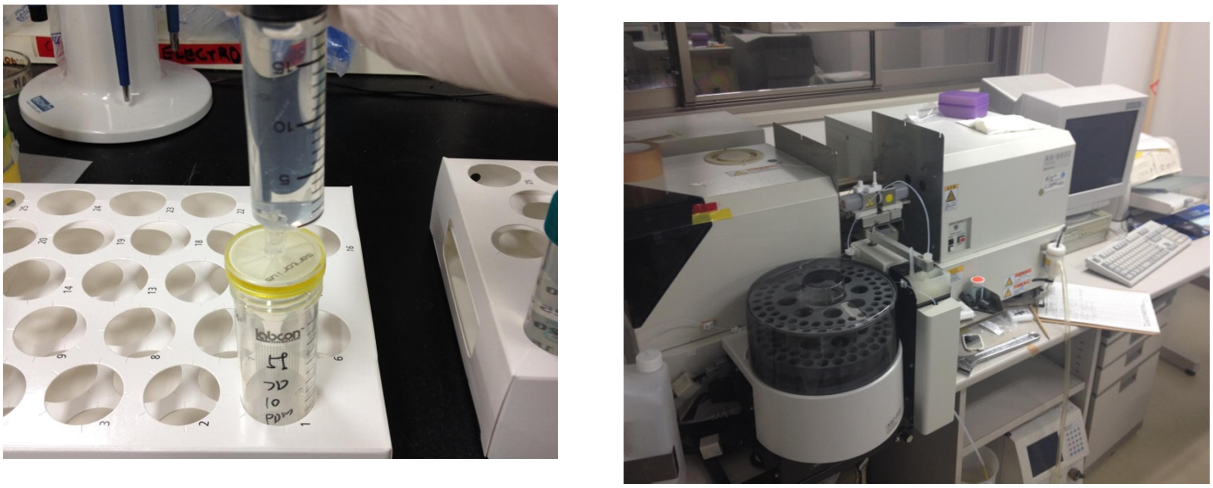
After curing, the specimen was submerged in distilled water and saturated by vacuum deaeration for 24 hours. Then, the specimen was set in a flexible-wall permeameter. The procedures are similar with hydraulic conductivity test which was described in Chapter 3.2.4. Cell pressure was set to 50 kPa. 1 mg/L arsenic solution was used as the permeant solution



(a) Preparation of As solution (b) Addition of soil-agent mixture



(c) Shaking at 150 rpm for 24 hours (d) Centrifugation under 3,000 rpm



(e) Filtration using a 0.45 μm filter (f) Analyzing As concentration using AAS

Fig. 4.1 Experimental procedures of batch sorption test and initial pH of the solution without adjustment was around 7.5. The schematic view of up-flow column percolation test is shown in Fig. 4.2.

A peristaltic pump (Thermo Fisher Scientific) was used to control the flow rate in order to achieve the same contact time with batch sorption test Contact time, T_c, was defined as the time when cumulative infiltration volume equals volume of the void of the specimen, namely pore volumes of flow (PVF) equals to one. Flow rate of the peristaltic pump, v, can be determined using the following relations:

$$PVF = \frac{Q}{V_v} = \frac{v \cdot T_c}{V_v} = 1; \;\; v = \frac{V_v}{T_c} \tag{4.1}$$

$$V_v = V - V_s = V - \frac{m_s}{\rho_s} = V - \frac{m}{\rho_s \times (1 + w / 100)} \tag{4.2}$$

where Q is cumulative volume of leachate flow (cm^3), v is flow rate of pump (cm^3/h), V_v is volume of voids, V is total mold volume (56.55 cm^3), V_s is volume of solids (cm^3), m_s is mass of solids (g), ρ_s is particle density (2.68 g/cm^3), m is wet mass of mixtures (g), w is water content (%).

During preparation of specimens, wet mass of mixtures was measured and water content was determined using surplus soil samples after compaction. Volume of voids V_v can be easily

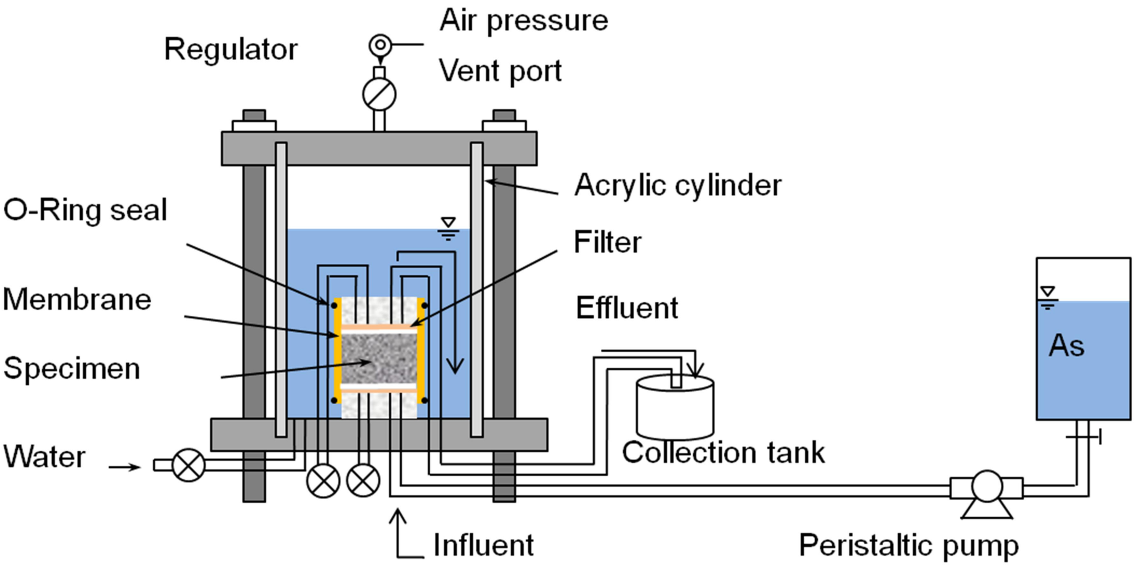


Fig. 4.2 Schematic view of up-flow column percolation test

Table 4.2 Experimental conditions for up-flow column test

Additive content of Ca-Mg composite powder	Curing period (days)	Test conditions
0%	0	・ $NaAsO_2$ solution ・ Initial concentration: 1 mg/L ・ Flow rate: 0.74 ml/h
5%	7, 28	

obtained using equation 4.2. Once contact time T_c is set, flow rate of peristaltic pump v can be calculated consequently by equation 4.1.

Contact time was set to 24 hours, which is consistent with the batch test. It should be noticed that for mix proportion of 0%, the particle density is 2.70 g/cm^3 and optimum water content is 10.1% and for mix proportion of 5%, the particle density is 2.68 g/cm^3 and optimum water content is 11.3%. The calculated flow rates of two cases were not exactly same, but the results were around 0.74 mL/h for T_c = 24 hours.

Effluent samples were collected every several pore volumes of flow and arsenic concentrations were analyzed by an atomic absorption spectrometry (AAS) method (AA-6800, SHIMADZU). Concentrations of cations such as Ca^{2+} and Mg^{2+} were analyzed by an inductively coupled plasma optical emission spectrometry (ICP-OES) (710 ICP-OES, Agilent Technologies). pH value and EC was measured using a pH/EC meter (F-55, HORIBA, Japan). Experimental conditions for up-flow column percolation tests were listed in Table 4.2.

4.3 Results and discussion

4.3.1 Batch sorption test

Arsenic removal ratio in the batch test was calculated based on the residual arsenic concentration in the solution after shaking using a following relation:

$$\text{Removal ratio (\%)} = (C_0 - C_{re}) / C_0 \times 100\% \qquad (4.3)$$

where C_0 is the initial concentration (mg/L), C_{re} is the residual arsenic concentration in the solute (mg/L).

The calculation results are shown in Fig. 4.3. The 0% case showed a certain sorption capacity for C_0 = 0.1 mg/L with the removal ratio of 77%. For C_0 = 10 mg/L, the removal ratio of 0% case dropped to 30%, suggesting an insufficient sorption capacity. For mix proportions of 3% and 5%, the removal ratio remained over 90% for all initial concentrations. The removal ratios were over 99% for C_0 = 0.1 mg/L and over 97% for C_0 = 1 mg/L for both mix proportions. For 3% case, the removal ratio decreased to 90% for C_0 = 10 mg/L meanwhile it was still over 95% for 5% case. The residual concentrations of 5% case were around 0.01 mg/L for C_0 = 1 mg/L and 0.3 mg/L for C_0 = 10 mg/L, suggesting strong sorption performance. It should be noted that the initial concentrations applied in the batch study were relatively higher than typical leaching concentrations of natural contamination for obtaining the complete sorption isotherms.

For the whole concentration ranges applied in the tests, the Freundlich model shown in Eq. (4.4) fitted the test results better than Langmuir model and was used to express the sorption isotherms in the study:

$$S = K_f C_{re}^{\,n} \tag{4.4}$$

where S is the sorption amount on the sample (mg/g), C_{re} is the residual arsenic concentration in the solute (mg/L), K_f and n are constants.

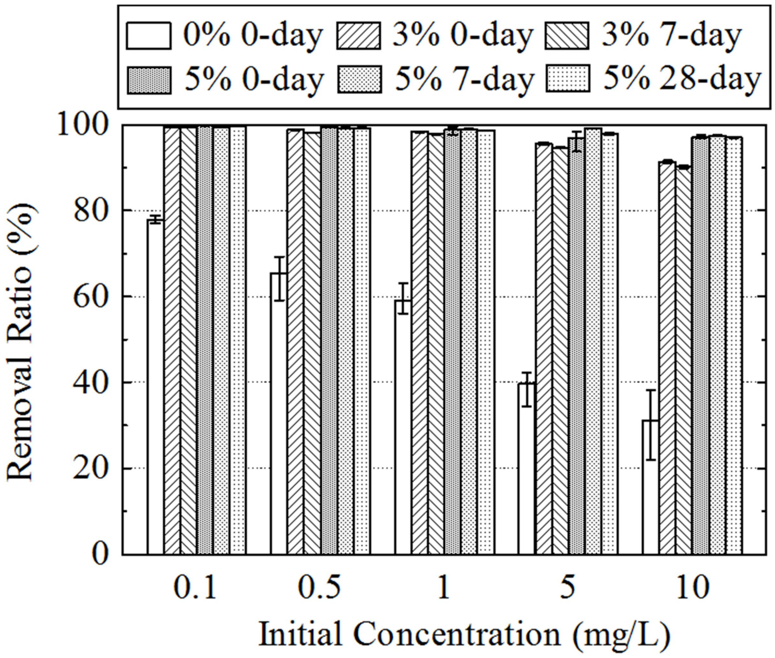
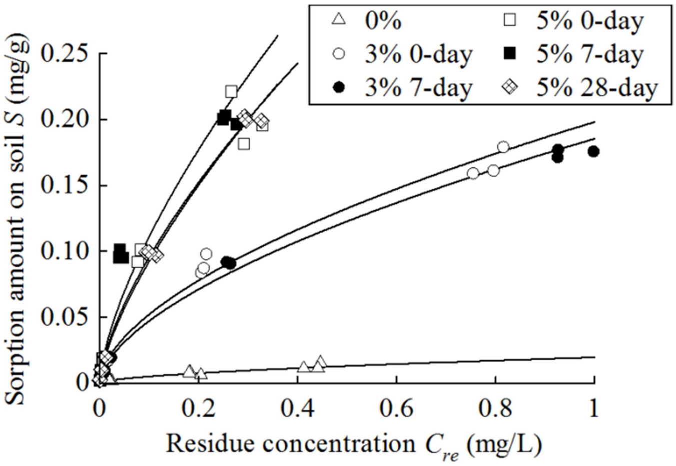


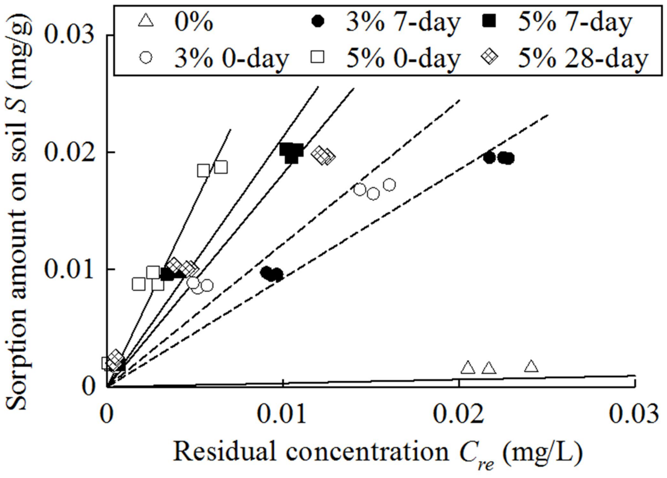
Fig. 4.3 Remove rate of each case at different initial concentration

Sorption isotherms for all the cases are shown in Fig. 4.4(a). For 0% case, residual arsenic concentrations for initial concentrations of 5 mg/L and 10 mg/L were around 3 mg/L and 7 mg/L, corresponding to sorption amounts on soil of 0.04 mg/g and 0.07 mg/g (data not showed in Fig. 4.4 (a)). Consistent results were reported by Minja and Ebina (2002) using decomposed granite soil for As(III) sorption under a same L/S ratio and initial concentration.

If the initial concentration range was narrowed to 0.1 to 1 mg/L, which corresponding to a residual concentration range up to 0.03 mg/L for mix proportions of 3% and 5% cases and 0.5 mg/L for 0% case, the Freundlich-type sorption isotherms can be simplified to linear



(a) Freundlich's sorption isotherms at initial concentration from 0.1 to 10 mg/L



(b) Linear sorption isotherms at initial concentration from 0.1 to 1 mg/L

Fig. 4.4 Sorption isotherms of different cases shape as shown in Fig. 4.4 (b). The linear sorption isotherms can be obtained by the following relation:

$$S = K_d C_{re} \tag{4.5}$$

where K_d is distribution coefficient (L/g).

Pure decomposed granite soil (0% case) exhibited lower sorption performance compared to soil-agent mixture (3% and 5% cases). Sorption performance was improved with the increasing mix proportion and the disparity is more obvious at higher concentrations compared to that at a lower concentration range.

To compare the sorption capacites of different cases, sorption amounts at a certain hypothetic equilibrium concentration was calculated using Freundlich's isotherms. An equilibrium concentration of 0.01 mg/L, which is the Japanese environmental standard of arsenic for soil and ground water quality, was applied. The fitted equations for sorption isotherms along with the calculated sorption amount are summarized in Table 4.3.

To evaluate the effect of mix design and curing period, the ratio of calculated sorption amount of soil-agent mixture (3% and 5%) under different curing period relative to that of soil (0%) is shown in Fig. 4.5.

After adding 3% of Ca-Mg composite powder, sorption performance was about 10 times higher compared to pure soil case. Sorption amount on soil of mix design of 5% is at least 1.5 times higher than that of 3%, which is almost in consistent with the increment of agent mount.

Table 4.3 Sorption isotherms and calculated sorption amount on soil

Additive content of Ca-Mg composite powder	Curing period	Fitted sorption isotherm				Sorption amount on soil (mg/g) at hypothetic equilibrium concentration of 0.01 mg/L
		Linear model	R^2	Freundlich model	R^2	
0%	0 day	$S = 0.03C_{re}$	0.95	$S = 0.019C_{re}^{0.59}$	0.87	1.3×10^{-3}
3%	0 day	$S = 1.22C_{re}$	0.95	$S = 0.20C_{re}^{0.58}$	0.99	1.4×10^{-2}
	7 days	$S = 0.93C_{re}$	0.96	$S = 0.19C_{re}^{0.59}$	0.99	1.2×10^{-2}
5%	0 day	$S = 3.13C_{re}$	0.93	$S = 0.43C_{re}^{0.62}$	0.98	2.5×10^{-2}
	7 days	$S = 2.13C_{re}$	0.98	$S = 0.52C_{re}^{0.67}$	0.99	2.4×10^{-2}
	28 days	$S = 1.82C_{re}$	0.95	$S = 0.45C_{re}^{0.67}$	0.99	2.1×10^{-2}

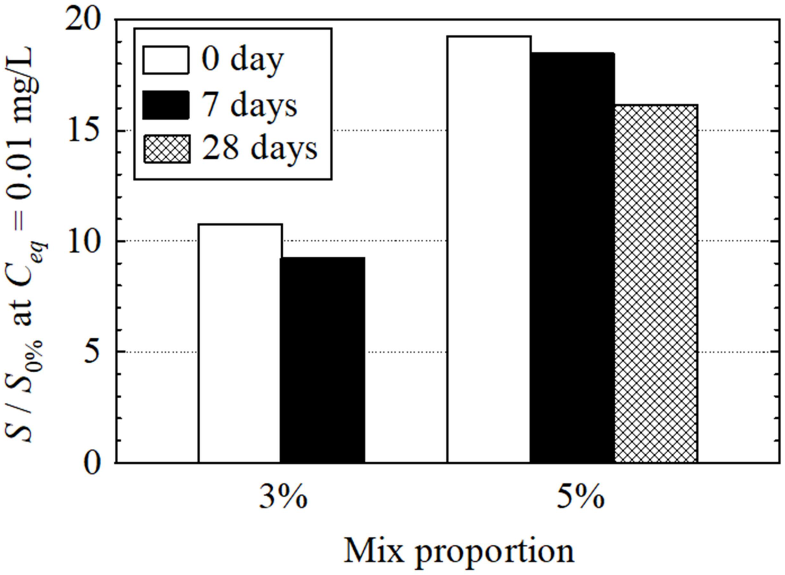


Fig. 4.5 Comparison of the ratio of sorption amount of soil-agent mixture relative to that of decomposed granite soil

Higher agent content provides more available ions in the solution which promotes the sorption of arsenic, thus exhibiting higher sorption performance. The sorption performance among different curing periods is not obvious for mix design of 3% and 5%, which implies that the effect of curing might not be reflected in batch sorption test.

For evaluating the sorption performance of soil-agent mixture further, its sorption amounts at the equilibrium concentration of 0.01 mg/L were compared with the results of some similar studies. All of these studies conducted batch sorption tests on As(III) and applied Ca-Mg composite materials as the sorbent. It should be noticed that soil-agent mixture was used in this study instead of the pure agent. Thus, the sorption amount on the agent was calculated in the comparison, assuming that sorption on the decomposed granite soil is negligible compared to sorption on the agent. For example, the average sorption amount of 5% cases was 2.3×10^{-2} mg/g on the soil-agent mixture and accordingly it was assumed that 0.46 mg/g (= 2.3×10^{-2} mg/g /0.05) was sorbed on the Ca-Mg composite powder. The results for other studies were obtained from the sorption isotherms and shown in Table 4.4.

The production process for the Ca-Mg composite powder used in this study includes calcination, grinding to powder and adding special additives. Thus, it provided a larger specific surface and more sorptive ingredients, and achieved much stronger sorption

Table 4.4 Comparison of various immobilizing agents among different studies

Material	Agent type	C_0 (mg/L)	L/S ratio	Shaking time (h)	Sorption amount on soil (mg/g)	References
Raw dolomite powder	pure	0.62	5-40	4	0.0005	Ayoub et al. 2007
Half burnt dolomite grain (0.5-2 mm)	pure	10-100	250	24	0.04	Naruse et al. 2014
Charred dolomite powder	pure	0.05- 2	1000	120	0.05	Salameh et al. 2015
Ca-Mg composite powder (same with this study)	pure	1-400	100	4	0.24	JSMS 2014
Ca-Mg composite powder	mixture	0.1-10	400	24	0.46	This study
Half burnt dolomite powder	pure	10-100	250	24	1.4	Naruse et al. 2014

performance than original raw material. Higher sorption capacity shown in this study than the same material used as a pure agent in JSMS (2014) was probably due to the longer shaking time, suggesting that sufficient contact between the agent with the object is important to exhibit sorption performance and should be carefully considered during the design of sorption layer.

4.3.2 Up-flow column percolation test

Variation of effluent arsenic concentrations of the decomposed granite soil (0% case) as a function of L/S ratio is shown in Fig. 4.6. Leaching of arsenic up to 0.1 mg/L was observed after permeation started at an initial stage of the test, which was probably caused by the preferential flow inside the specimen. Arsenic concentrations decreased afterwards, remained slightly over 0.001 mg/L until the L/S ratio of 40 and kept increasing thereafter, became relatively stable after L/S ratio of 60.

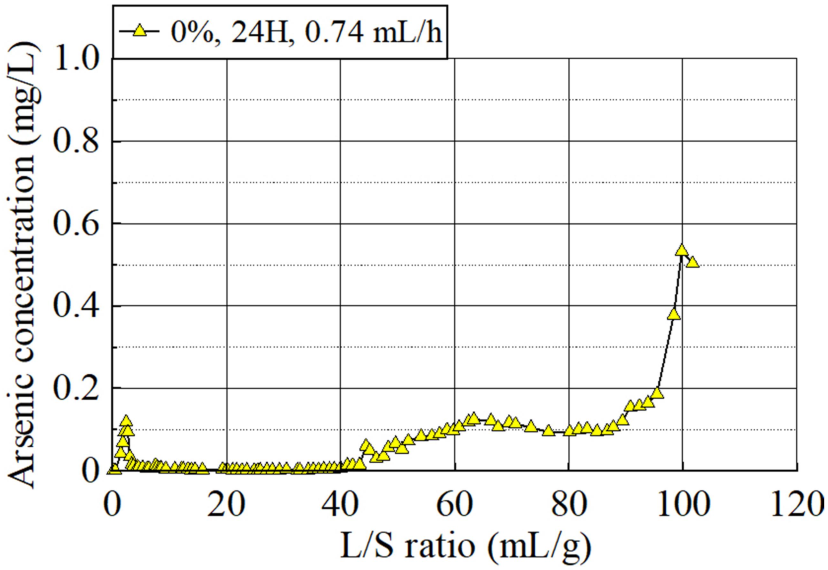


Fig. 4.6 Effluent As concentration for mix proportion of 0%, flow rate of 0.74 mL/h

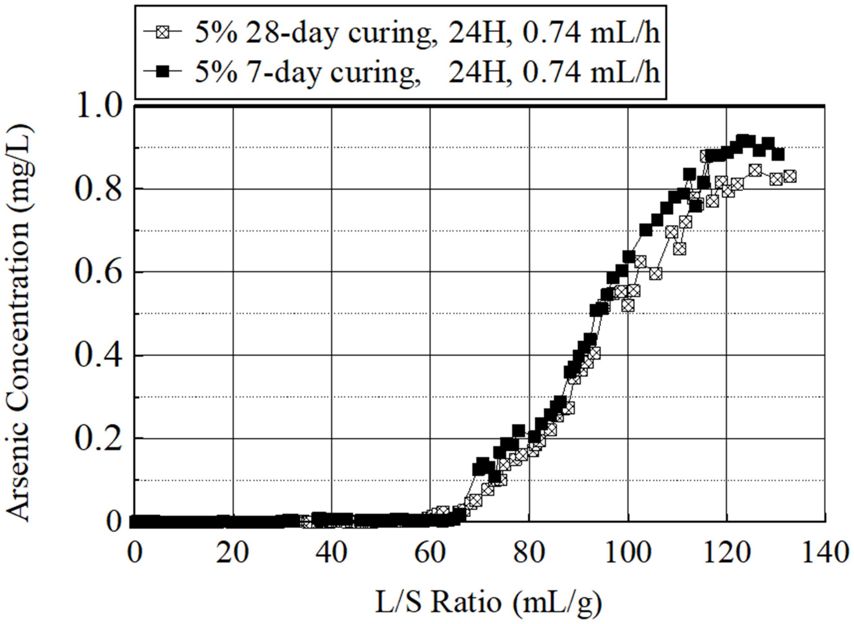


Fig. 4.7 Effluent As concentration for mix proportion of 5%

The variation trend of 0% case is discontinuity and the result is needed for verification.

For the soil-agent mixture (5% case), variations of effluent arsenic concentration as function of L/S ratio for specimen with 7 and 28–day curing under flow rate of 0.74 mL/h, which corresponds to T_c = 24 hours, the test results are shown in Fig. 4.7. No arsenic can be detected in effluent until the L/S ratio exceeded 60, which was corresponding to almost one year after permeation started. Arsenic concentration started increasing quickly after L/S ratio over 65 and almost reached to breakthrough of 1 mg/L before L/S ratio of 120. This variation trend suggested that under contact time of 24 hour in column test, soil-agent mixture of 5% can retain arsenic and keep the sorption performance for a certain time and then will lose the performance quickly, which is similar to a surface attraction phase. Once the available sorption surface is exhausted, sorption capacity will lose quickly and chemical of concern is not able to be efficiently retained.

The retardation factor, R_d, and the hydrodynamic dispersion coefficient, D, were determined by regressing the measured effluent breakthrough curve based on the following equation recommended by van Genuchten and Parker (1984) for a finite column:

$$\frac{C_e}{C_0}=\frac{1}{2}\left\{erfc\left[\frac{R_d\text{-}T}{2\sqrt{\frac{R_dT}{P_e}}}\right]+exp(P_e)erfc\left[\frac{R_d+T}{2\sqrt{\frac{R_dT}{P_e}}}\right]\right\} \tag{4.6}$$

where C_e/C_0 is concentration ratio, C_e is effluent concentration, C_0 is initial concentration, T is dimensionless time (equivalent to pore volumes of flow (PVF)) = v_st/L, v_s is seepage velocity, t is time, L is column length and P_e is Peclet number to be determined. After knowing P_e, the hydrodynamic dispersion coefficient D can be calculated for $P_e = v_sL/D$. The regressions were performed using the curve fitting functions within Kyplot®.

The regression results for the soil-agent mixture (5% case) are shown in Fig. 4.8 and the determined R_d and P_e with calculated D values are summarized in Table 4.5. For the pure decomposed granite soil (0% case), due to the discontinuity variation trend, regression could not be conducted. Fitted curves basically accorded with the measured data, suggesting that the equation (4.6) can represent the solute transport process under the condition of this study. The Peclet number obtained for all specimens are over 20, thus advection dominates the transport process. Since the hydraulic conductivity of the soil-agent mixture is relatively higher and one

Table 4.5 Summary of solute transport paramters

Mix proportion	Contact time (h)	Curing period	R_d	P_e	D (cm^2/s)	R^2
5%	24	28 days	581	37	1.22×10^{-6}	0.99
		7 days	584	27	1.66×10^{-6}	0.95

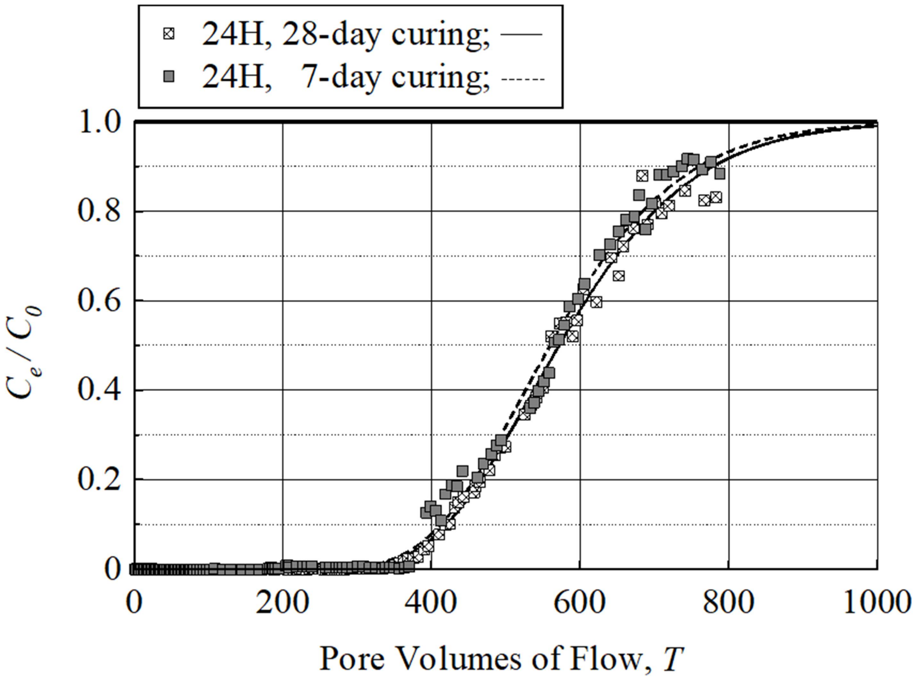


Fig. 4.8 Regression results for effluent As concentration of mix proportion of 5%

of the basic concepts of sorption layer is that it is a permeable layer, the advection-dominated process can be considered reasonable.

4.3.3 Effect of curing period

Effect of curing periods was not obvious in both batch and column tests. For batch test, there is one possible explanation related to experimental procedures. The cured specimen was crumbled and added into solution, with shaking during the test. The status was rather suspension liquid than soil column. Thus, the effect of curing including change of soil structure by agglomeration of agent and fine particles, potential generation of chemicals such as hydration products might be destructed and offset due to the procedure, which left little affection on the sorption performance and the conditions of specimens in the solution were assumed to be similar with and without curing.

In the column test, the integrity of the compacted specimens was maintained and the offset effect of curing suggested in the batch test did not occur. Considering that a longer curing period from 7 to 28 days also has no obvious effect on hydraulic conductivity, the quickly completed hydration process in the early curing phase and no-obvious pozzolanic reaction in the long term might also be responsible for the inconspicuous effect of curing on sorption. It should also be noticed that the test duration was much longer than 28 days. Since the specimen was not disturbed after assembling the apparatus and water was continuously supplied, the specimen structure might also become similar during the permeation even though slight difference might exist after curing.

4.3.4 Comparison of batch and column test

To evaluate the sorption performance in the column test comparing with the batch test, the cumulative sorption amount on soil was calculated as follows:

$$S_c = \frac{1}{m_s} \cdot \frac{Vv}{1000} \int_0^{t_{\mathrm{fin}}} (C_{in}\text{-}C_{out})\, \mathrm{d}PVF \tag{4.7}$$

where S_c is the cumulative sorption amount on unit mass of soil (mg/g), m_s is the mass of soil (g), C_{in} is the influent concentration (mg/L), C_{out} is the effluent concentration (mg/L), V_v is volume of voids, PVF is pore volumes of flow.

The cumulative sorption amounts of 0% and 5% cases under T_c = 24 hours for the column tests are shown in Fig. 4.9 along with the sorption amount in the batch test for the equivalent cases under the initial concentration of 1 mg/L, which is same with column test. The sorption amounts at L/S of 10, 20, 40, 60, 80 and 100 for both column and batch tests are summarized Table 4.6.

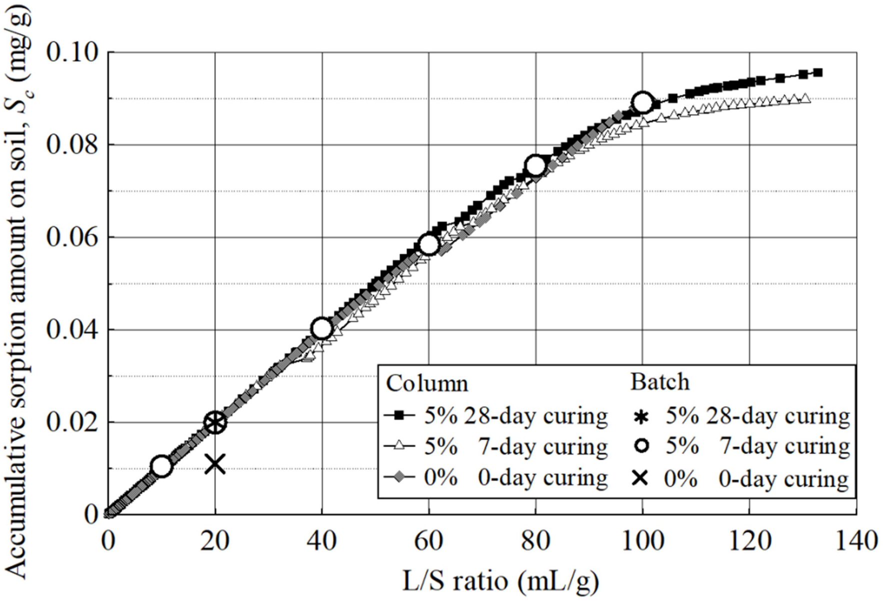


Fig. 4.9 Comparison of sorption amount of batch and column test

Table 4.6 Sorption amount on soil for batch and column test under same condition

	Sorption amount on soil (mg/g) at *L/S* = 20 and C_0 =1 mg/L	
Soil specimen	Batch test	Column test
0% 0-day curing	0.011	0.020
5% 7-day curing	0.020	0.020
5% 28-day curing	0.020	0.021

Sorption amounts of 5% cases are consistent between both of the batch test and column test, suggesting that result of column test can be reflected by the batch test which can be easily conducted under a relatively lower L/S ratio range. For 0% case, sorption amount in the column test is almost two times larger than in the batch test.

A noticeable difference between two tests is electrical conductivity (EC) values as shown in Fig. 4.10, which was not observed in 5% cases. In the column test for 0% case, the EC value decreased from over 20 mS/m to below 5 mS/m. In the batch test, the equilibrium EC value of the supernatant was below 4 mS/m. Leaching of cations was only measured in the column test and the difference of EC was assumed due to the leaching of Ca also as shown in Fig. 4.10.

Presence of Ca^{2+} ions promotes the oxidation of As(III) and immobilization of As(V) is suggested to be promoted by complexation with Ca^{2+} (Yokoyama et al. 2012). Smith et al.

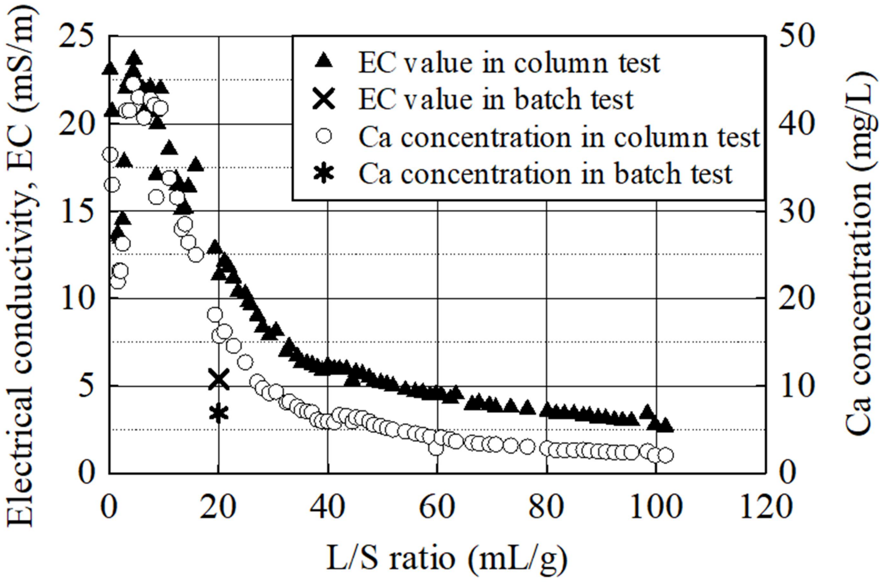


Fig. 4.10 Electrical conductivity for mix proportion of 0% case in column and batch test along with effluent Ca concentration in column test

(2002) suggested that presence of Ca^{2+} ions increased the amount of As(V) sorbed on soil though changes in the surface charge. Considering that the batch tests is a closed system and leaching of Ca^{2+} might be hindered due to the chemical equilibrium, less oxidation of As(III) to As(V) and lower Ca^{2+} concentration might result in a lower sorption amount on decomposed granite soil. Further studies need to be conducted to determine why decomposed granite soil shows higher sorption performance in column status. However, this trend is preferable since higher sorption capacity might be expected if the base material can offer more sorption capacity.

4.4 Conclusions for this chapter

In this chapter, primary sorption performance of decomposed granite soil amended with Ca-Mg composite powder was studied based on the results of both batch sorption test and up-flow column percolation test. Effects of mix proportion and curing period were evaluated and differences between batch tests and column tests were discussed. The main results obtained in this chapter can be summarized as follows:

(1) Pure decomposed granite soil shown certain sorption capacity when initial arsenic concentration (C_0) is relatively low. The arsenic removal ratio is 77% at C_0 of 0.1 mg/L, close to the performance of soil-agent mixture (99%). However, At C_0 of 10 mg/L, removal rate dropped to 30%, which is only 1/3 of the removal rate of soil-agent mixture.

(2) Addition of Ca-Mg composite powder increases the sorption performance and effect is more obvious when C_0 is high. For mix proportion of 3% and 5%, the removal rate remained over 90% for C_0 from 0.1 mg/L to 10 mg/L. The remove rates were over 99% at C_0 of 0.1 mg/L and over 97% at 1 mg/L. For 5% case, removal rate was still over 95% at C_0 of 10 mg/L. The residue concentration of 5% case was around 0.01 mg/L at C_0 of 1 mg/L and 0.3 mg/L at C_0 of 10 mg/L, suggesting strong sorption performance.

(3) The Freundlich model fitted the sorption isotherms best. If the initial concentration range was narrowed to 0.1 to 1 mg/L, the Freundlich model based sorption isotherms can be simplified to linear shape.

(4) Sorption performance increases with mix proportion in batch sorption test. Under a hypothetic equilibrium concentration of 0.01 mg/L, 3% addition of Ca-Mg composite powder increase the sorption amount of arsenic on soil for 10 times and 5% addition is at least 1.5 times higher than that of 3%, which is almost in consistent with the increment of

agent mount.

(5) Ca-Mg composite powder used in this study achieved much stronger sorption performance than original raw dolomite material. The production process for including calcination, grinding to powder and adding special additives provided larger specific surface and more sorptive ingredient.

(6) Fitted curve using advection-dispersion equation recommended by van Genuchten and Parker (1984) for a finite column basically accorded with the measured data for soil-agent mixture of 5% in column tests. The Peclet number obtained for all specimens are over 20, thus advection dominates the transport process.

(7) Effect of curing periods was not obvious in both batch and column tests. Quickly completed hydration process in the early curing phase and no-obvious pozzolanic reaction in the long term might be responsible.

(8) Sorption amount on soil is consistent between batch test and column test for 5% cases, suggesting that result of column test can be reflected by easily conducted batch test under relatively lower L/S ratio range. For pure decomposed granite soil, column test exhibited higher sorption performance than batch test, probably due to the higher concentration of Ca^{2+} in the solution.

CHAPTER 5

Time-dependent sorption behavior

5.1 General remarks

Since sorption layer method allows leachate to flow through the layer. Contact time between the chemicals of concern and the sorption material, which is affected by the flow conditions, is the fundamental factor for the performance evaluation.

Contact time is a comprehensive parameter that can reflect the effect of different factors in sorption layer method. Hydraulic conductivity might change if the mix proportion and curing period of the layer material is different, which will affect the flow rate and contact time. For the same layer material, a different design of layer thickness also leads to different contact time between the leachate and the sorption layer. Considering that water head of the leachate inside the embankment will change during the permeation, the contact time will be affected by the hydraulic gradient. In addition, some practical issues such as heterogeneity of the layer, unsaturated condition and preferential flow will finally cause a variation of contact time. Thus, all these different influential factors lead to one same focus, which is the time-dependent sorption behavior.

Understanding of sorption performance at different contact times will offer valuable information for the design considerations of the whole sorption layer system. As long as the sorption performance and corresponding contact time can be ensured, parameters such as properties of the layer material or thickness of the layer can be adjusted accordingly based on the site condition. Most previous studies focus on the adsorption kinetics study using batch method. Few studies apply long-term permeation under certain contact time using column test approach and different sorption mechanism might be involved due to different permeation time being not widely considered.

In this chapter, time-dependent sorption behavior is studied through both, batch sorption test applying different shaking time and up-flow percolation test under various flow rates. In section 5.2, the experimental approach is introduced. In section 5.3, the results of two types of tests are presented and sorption performance is evaluated. Sorption mechanism at different contact times is studied by analyzing contrastive cases conducted in column tests.

5.2 Materials and methods

5.2.1 Determination of contact time

As discussed in section 4.2.3, contact time, T_c, was defined as the time when cumulative infiltration volume Q equals to volume of voids of the layer V_v, namely pore volumes of flow (*PVF*) equals to one. Based on Darcy's law (Darcy 1856), cumulative infiltration volume of leachate flow at certain T_c can be represented using the following relation:

$$Q = k \cdot i \cdot A \cdot T_c \tag{5.1}$$

where k is hydraulic conductivity (cm/s), i is hydraulic gradient, A is section area (cm^2).

Volume of voids of a sorption layer can be represented using the following relation:

$$V_v = A \cdot L \cdot n \tag{5.2}$$

where L is the thickness of the layer (cm), n is porosity

Thus, T_c can be calculated using the following relation:

$$PVF = \frac{Q}{V_v} = \frac{k \cdot i \cdot A \cdot T_c}{A \cdot L \cdot n} = 1; \quad T_c = \frac{L \cdot n}{k \cdot i} \tag{5.3}$$

The hydraulic conductivity and the porosity are the properties of the layer material which can be obtained by other tests. If the water head and layer thickness is determined, contact time can be calculated accordingly.

For a simplified field condition assuming a constant water head (h_w) of 30 cm over a saturated sorption layer as shown in Fig. 5.1, contact time can be calculated using Eq. 5.3

Fig. 5.1 Conceptual model of a simplified field condition

Table 5.1 Calculated contact time according to different layer thickness

Water head h_w (cm)	Layer thickness L (cm)	Hydraulic gradient i	Calculated contact time T_c (h)
30	45	1.67	23.3
	30	2	12.9
	15	3	4.3
	10	4	2.2

once layer thickness is assumed. It should be noticed that water head decreases and sorption layer is considered unsaturated that in actual site. Soil-water retention capacity is expected to help sorption by retaining leachate inside the layer. However, these effects were not considered here and a relatively more conservative assumption is applied.

Assuming $k = 1\times10^{-4}$ cm/s and $n = 0.31$ which was determined according to the experimental results in Chapter 3, the calculated contact time was presented in Table 5.1 according to different layer thickness of 45, 30, 15 and 10 cm. The unit of calculated result using Eq. 5.3 should be second and was transferred to hour in the Table 5.1.

Contact time for batch sorption tests and up-flow column tests was set based on the calculation result. For batch sorption test, shaking time of 1, 4, 12 and 24 hours was applied. For up-flow column test, flow rate corresponding to T_c = 2, 4, 12 and 24 hours was applied.

5.2.2 Batch sorption test

Batch sorption test applying different contact time were conducted in triplicate for each case. The test procedures were summarized as follows:

1) Preparation of specimen: Decomposed granite soil under 2 mm was mixed with Ca-Mg composite powder with mix proportion of 5% at optimum water content. The soil-agent mixture was compacted in a cylindrical mold (ø 6 cm × h 7 cm) in 3 layers with compaction degree of 95%. Considering that the effect of curing is not obvious for sorption, a short curing period of 7 days was applied.
2) Preparation of solution: Arsenic solution with initial concentrations of 0.1, 0.5, 1, 5 and 10 mg/L was prepared by dissolving $NaAsO_2$ salts (procured from Nacalai tesque, Japan) in distilled water. 15 mL of each solution was taken out to measure the arsenic concentration before sorption. Initial pH was not adjusted and it was measured

together with EC value using a pH/EC meter (F-55, HORIBA, Japan).

3) Addition of sorbents: 7-day cured specimens were extracted out of the mold and roughly crushed until the maximum diameter was under 2 mm. The liquid/solid ratio (L/S) (mL/g) was set to 20 and soil-agent mixture of 7 g was added into the solution of 150 mL.
4) Shaking: The samples were subjected to horizontal shaking at 150 rpm for 1, 4, 12 and 24 hours on a shaking machine (NR-30, TAITEC, Japan)
5) Solid-liquid separation: After shaking, samples were left settling for 15 minutes and supernatant were taken for centrifugation under 3,000 rpm for 20 minutes in a centrifuge (Double top centrifuge, KUBOTA, Japan). After centrifugation, solution was filtered using a 0.45 μm-opening membrane filter (Minisart® Syringe Filter, Sartorius).
6) Chemical analysis: Concentrations of arsenic before and after the sorption test was analyzed by an atomic absorption spectrometry (AAS) method (AA-6800, SHIMADZU). pH and EC value after shaking was also measured.

5.2.3 Up-flow column percolation test

Time-dependent sorption behavior in up-flow column percolation tests was studied in two stages. For the first stage, sorption performance was evaluated at different contact time for a primary understanding of time-dependent sorption behavior. Specimens with proportion of 5% and curing period of 28 days were permeated with arsenic solution of 1 mg/L for T_c = 2, 4, 12 and 24 hours. In addition, specimen with mix proportion of 5% and curing period of 7 days were permeated with arsenic solution of 1 mg/L for T_c = 4 hours and 24 hours to evaluate the potential effect of curing period under different contact time.

For the second stage, repeated experiments were conducted to evaluate the results obtained in the first stage and contrast experiments were conducted to study the sorption mechanism involved in different contact time. For verification of the results, experimental cases using specimens with mix proportion of 5% and curing period of 28 days for T_c = 2 and 24 hours were repeated. For sorption mechanism study, several contrastive cases were conducted to compare the difference with and without addition of Ca-Mg composite powder and arsenic sorption. Experimental results such as arsenic concentrations in effluent, leaching of Ca^{2+} and Mg^{2+} ions and changes of pH and EC between the contrastive cases were compared.

Effect of Ca-Mg addition at different contact time was evaluated using specimens with mix proportion of 0%, which is pure decomposed granite soil, permeated with arsenic solution of 1 mg/L for T_c = 2 hours and 24 hours. Results were compared with same permeation condition using soil-agent mixture with mix proportion of 5% and curing periods of 28 days.

Distilled water was used as the permeant to establish a background leaching amount of Ca and Mg ions to help understanding the sorption mechanism. Specimens with mix proportion of 0% were permeated with distilled water for T_c = 2 hours and 24 hours.

Results were compared with contrastive cases permeated with arsenic solution to study the sorption of arsenic on decomposed granite soil. Specimens with mix proportion of 5% and curing periods of 28 days were also permeated with distilled water for contact time of 2 and 24 hours. By comparing the results with contrastive cases permeated with arsenic solution, sorption mechanism of Ca-Mg agent on arsenic is hoped to be understood. Specimens were prepared from the same soil-agent mixture used for arsenic permeation cases in order to minimize the impact of heterogeneity. The experimental approach was summarized in Table 5.2.

Table 5.2 Experimental conditions of column tests for time-dependent sorption behavior study

Test stage	Additive content of Ca-Mg composite powder	Cuing period (days)	Contact time (h)	Permeant
Stage 1 Sorption behavior	5%	28	2, 4, 12, 24	1 mg/L $NaAsO_2$ solution
		7	4, 24	
Stage 2 Verification and mechanism study	0%	0	2, 24	1 mg/L NaAsO2 solution
				Distilled water
	5%	28	2, 24	1 mg/L $NaAsO_2$ solution
				Distilled water

A photo of the up-flow column test is shown in Fig. 5.2 and experimental procedures are summarized as follows:

1) Compaction and curing: Soil-agent mixture was compacted in a cylindrical mold (ø 6 cm × h 2 cm) in two layers. The compaction degree was also set to 95%. After compaction, cling film was used to wrap the whole mold and the specimen was kept in a fully-sealed plastic bag for curing.
2) Saturation: After curing, the specimen was submerged in distilled water and saturated by vacuum deaeration for 24 hours.
3) Set of apparatus: The saturated specimen was set in a flexible-wall permeameter. It was sandwiched with filter papers, filter cloth, porous caps and pedestals, confined by a latex membrane on the side. Cell pressure was set to 50 kPa. Permeant was introduced by a peristaltic pump (Thermo Fisher Scientific). Flow rate was calculated using Eq. 4.1 and Eq. 4.2. and corresponding flow rate for contact time of 2, 4, 12 and 24 hours was set to 8.82, 4.48, 1.48 and 0.72 mL/h.
4) Chemical analysis: The effluent samples were collected every several pore volumes of flow. Arsenic concentration was analyzed by atomic absorption spectrometry (AAS) method (AA-6800, SHIMAZU) and concentration of cations such as Ca^{2+} and Mg^{2+} was analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES) (710 ICP-OES, Agilent Technologies). pH and EC value using a pH/EC meter (F-55, HORIBA, Japan).

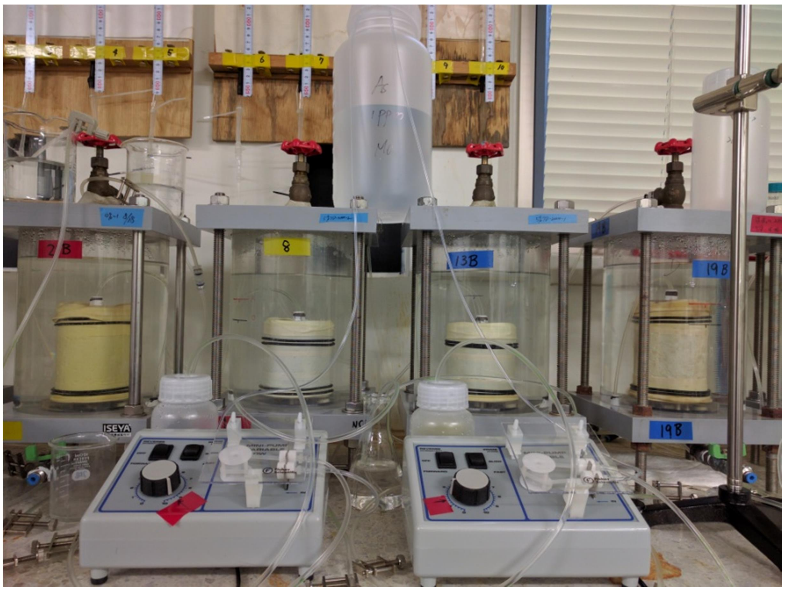


Fig. 5.2 Photo of up-flow column percolation test

5.3 Results and discussion

5.3.1 Batch sorption test

For batch sorption test, initial pH of arsenic solution without adjustment ranges from 6 to 10. Sorption isotherms of different contact time are shown in Fig. 5.3, which was determined by Freundlich equation expressed as follows:

$$S = K_f C_{re}^{\,n} \tag{5.4}$$

where S is the sorption amount on the sample (mg/g), C_{re} is the residual arsenic concentration in the solute (mg/L), K_f and n are constants.

Sorption amount under different contact time for a same hypothetic equilibrium concentration C_{eq} was calculated to compare the sorption capacity. C_{eq} of 0.01 mg/L, which is the Japanese environmental standard of arsenic for groundwater, was applied. Sorption amount was calculated as follows and shown in Fig. 5.4:

$$S = (C_0 - C_{eq}) \times V/m \tag{5.5}$$

where V is the volume of the solution (L), m is the mass of the sorbent (g), C_0 is the initial concentration of the solution (mg/L).

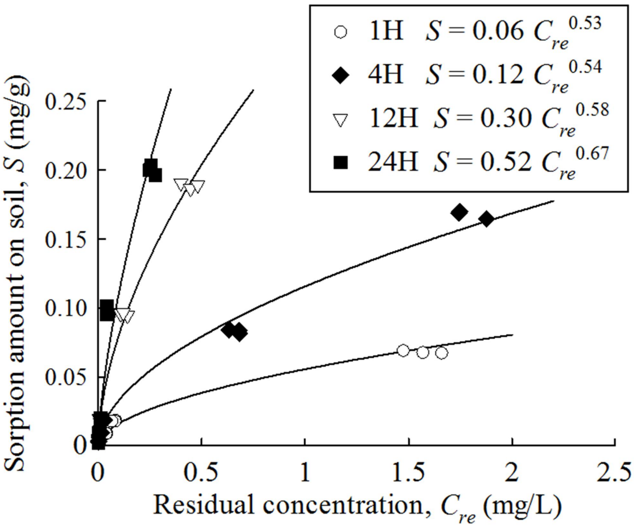


Fig. 5.3 Sorption isotherms of samples with different contact time

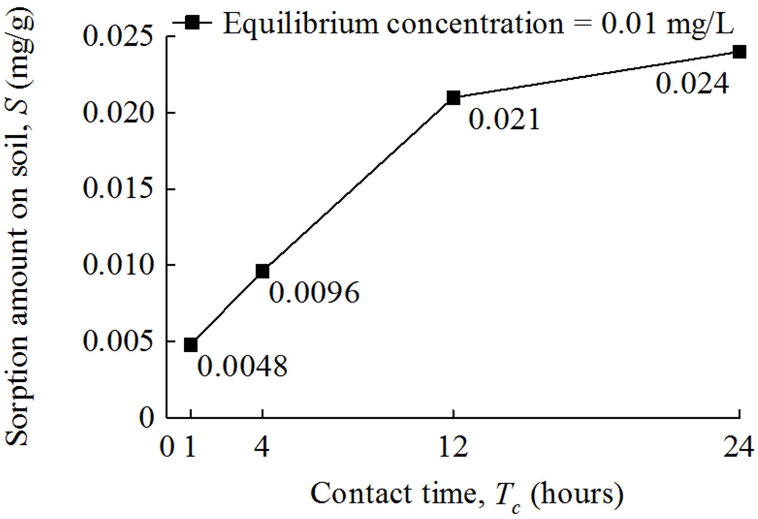


Fig. 5.4 Sorption amount with different contact time

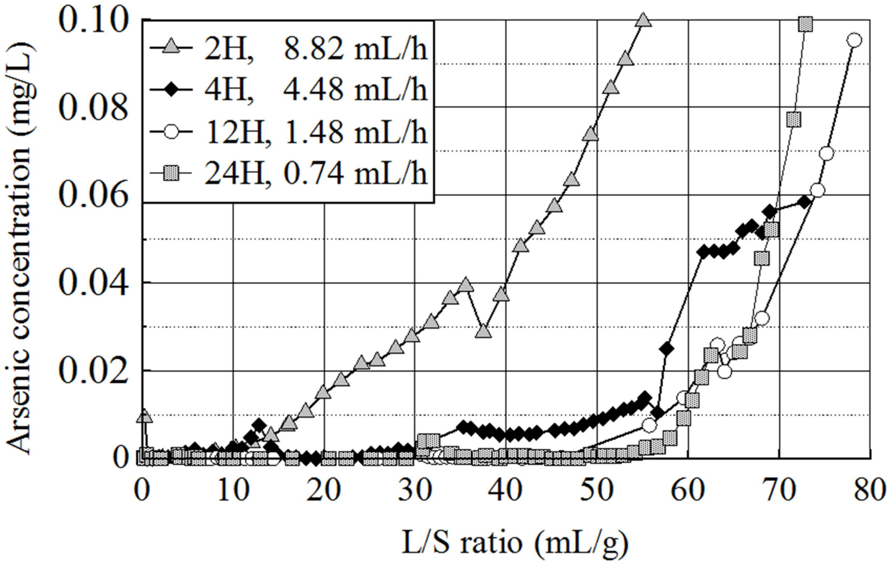
Sorption performance increases with longer shaking time because of more sufficient contact of soil-agent mixture with arsenic solution. When the equilibrium arsenic concentration is 0.01 mg/L, which corresponds to initial arsenic concentration around 1 mg/L for T_c = 12 hours and 24 hours, sorption amount was almost same. It suggests that with relatively lower initial concentration, the effect of longer contact time on sorption performance became much less obvious.

5.3.2 Up-flow column percolation test

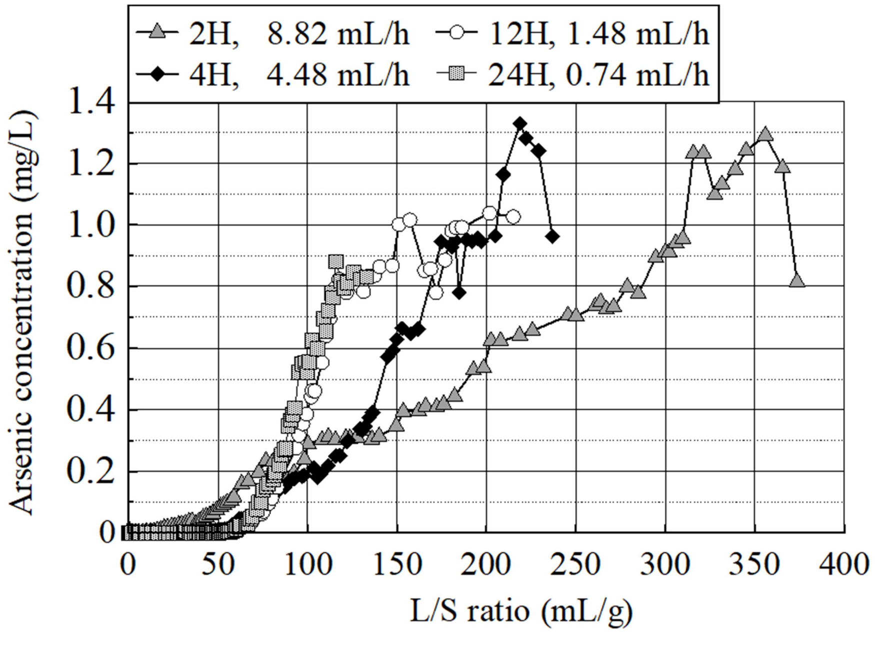
For up-flow percolation column test, effluent arsenic concentration of specimens with mixing proportion of 5%, cured for 28 days, permeated with 1 mg/L As solution under four different flow rates within liquid/solid (L/S) ratio of 80 as shown in Fig. 5.5 (a). The results for the whole permeation period are further shown in Fig. 5.5 (b).

Sorption performance during initial permeation stage is consistent with batch test. Early breakthrough was found in the case of T_c = 2 hours. Stronger and similar performance was observed in the case of T_c = 12 hours and 24 hours until L/S ratio reached to 60. However, this trend reversed in the long term. Equilibrium status was reached earlier in the cases with longer contact time.

For the specimens with 7 and 28–day curing under a flow rate of 0.74 mL/h, which corresponds to T_c = 24 hours, the test results were shown in in Fig. 5.6 (a) and the results of T_c = 4 hours (flow rate of 4.48 mL/h) are shown in Fig. 5.6 (b).

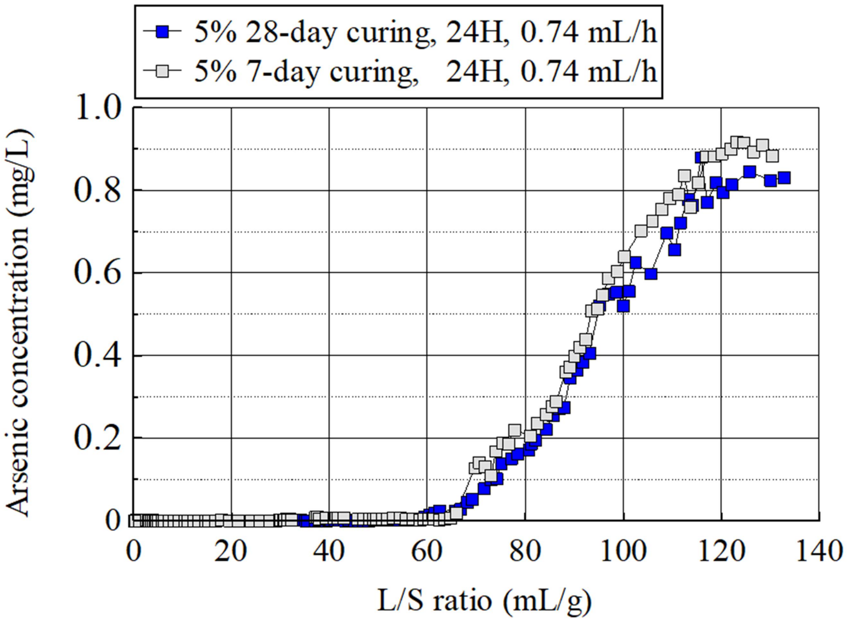


(a) Effluent As concentration of different contact time for L/S within 80

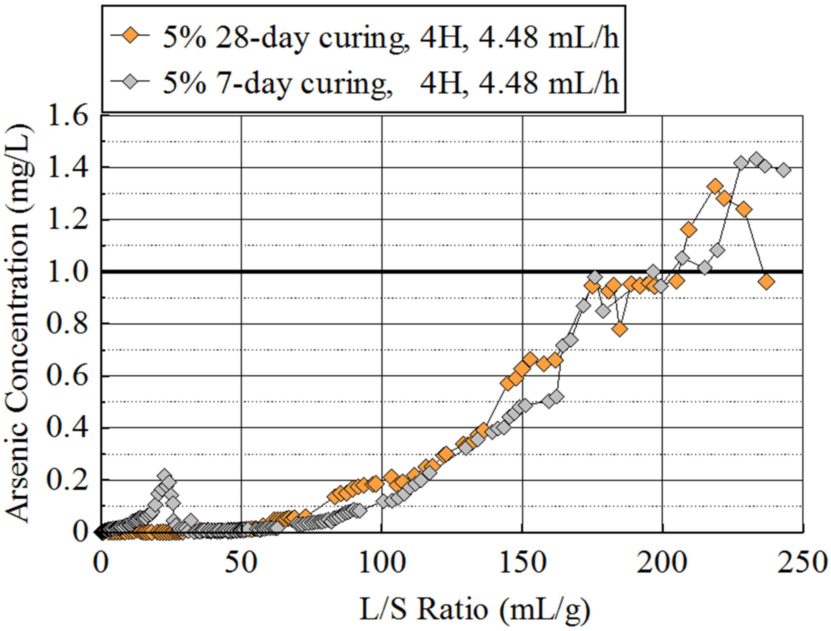


(b) Effluent As concentration of different contact time for whole permeation period

Fig. 5.5 Effluent As concentration of different contact time for 5% 28-day curing cases



(a) Effluent As concentration of 24-hour contact cases with different curing period



(b) Effluent As concentration of 4-hour contact cases with different curing period

Fig. 5.6 Effluent As concentration for specimen with 7 and 28-day curing

For the cases of T_c = 12 hours and 24 hours, no arsenic could be detected in effluent until the L/S ratio exceeded 60 and arsenic concentrations increased quickly thereafter. For the cases of T_c = 24 hours, effluent arsenic concentrations reached to 0.9 mg/L around L/S of 120. For the case of T_c = 12 hours, effluent arsenic concentrations reached to 1 mg/L at L/S of 150.

For the cases of T_c = 2 hours and 4 hours, low concentrations of arsenic could be detected in the effluent soon after permeation started and the increasing trends of effluent arsenic concentrations were more gradual compared to previous longer contact time. Effluent arsenic concentrations reached 1 mg/L at the L/S of around 180 for the cases of T_c = 4 hours and L/S around 300 for the case of T_c = 2 hours.

A clear peak shape was also observed at the early permeation stage in a breakthrough curve for the 5% 7-day curing case under T_c = 4 hours contact. For the cases of 0% and the shorter T_c cases, leaching of relatively high concentrations of arsenic soon after the permeation started should be noticed in practical applications. This early phase-leaching phenomenon was probably due to preferential flow and further study is needed for an exact explanation.

It can be observed that effluent arsenic concentrations were over the initial concentration of 1 mg/L after breakthrough point were reached for the cases of T_c = 2 hours and 4 hours, suggesting potential desorption of arsenic once sorbed might happen.

For curing periods of 7 and 28 days, variation of arsenic concentration in effluent was almost same. Effect of curing periods on sorption performance was not obvious under different contact time.

As discussed in section 4.3.2, the retardation factor, R_d, and the hydrodynamic dispersion coefficient, D, were determined by regressing the measured effluent breakthrough curve based on Eq. (4.6), which is the basic advection-dispersion equation recommended by van Genuchten and Parker (1984). The regressions were performed using the curve fitting functions within Kyplot®.

The regression results for the soil-agent mixture (5% case) are shown in Fig. 5.7 and the determined R_d and P_e with calculated D values are summarized in Table 5.3. Fitted curves basically accorded with the measured data except for the cases of T_c = 2 hours, considering the Peclet number for this case is smaller than 20 while its flow rate is the highest. The error might be caused by the relatively higher effluent arsenic concentrations in the initial permeation stage.

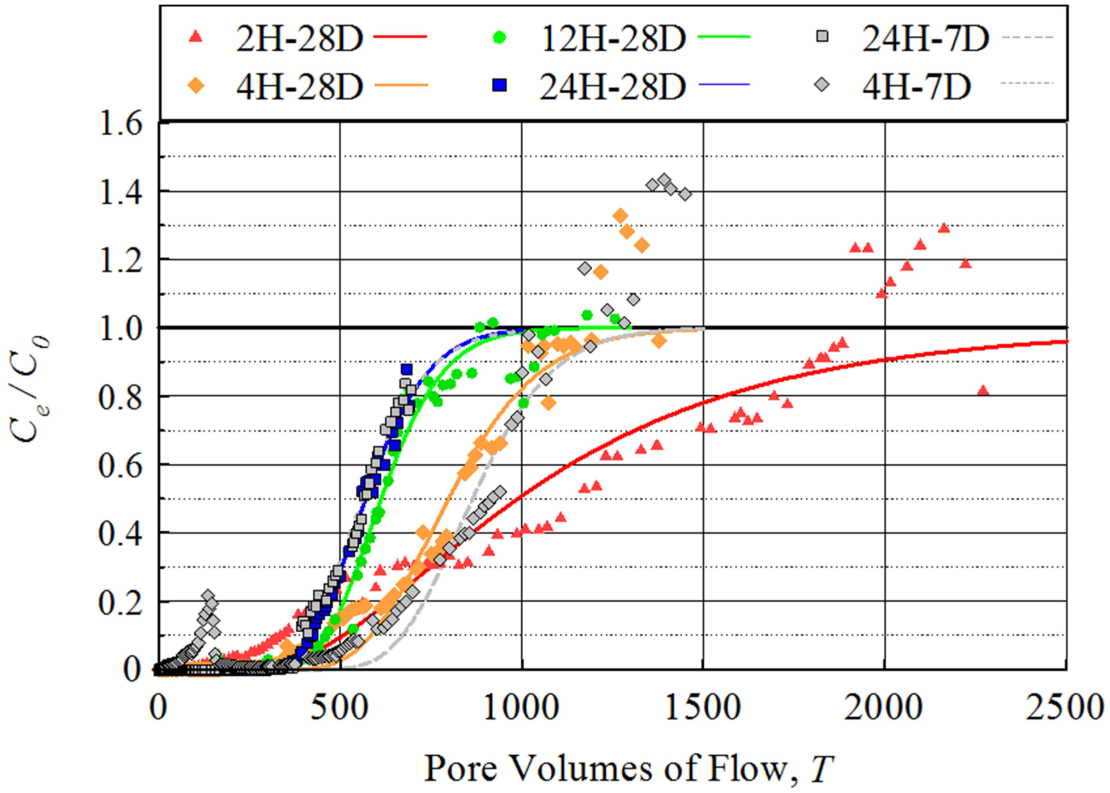


Fig. 5.7 Regression results for specimen with mix proportion of 5%

Table 5.3 Summary of solute transport paramters

Additive content of Ca-Mg composite powder	Contact time (h)	Curing period (days)	R_d	P_e	D (cm^2/s)	R^2
5%	24	28	581	37	1.22×10^{-6}	0.99
		7	584	27	1.66×10^{-6}	0.95
	12	28	627	42	2.23×10^{-6}	0.99
	4	28	823	33	8.60×10^{-6}	0.96
		7	882	50	5.66×10^{-6}	0.96
	2	28	1140	6	9.32×10^{-5}	0.92

In the column tests, retardation factors of the cases of T_c = 2 hours and 4 hours are higher than those of the cases of T_c = 12 hours and 24 hours, suggesting that the shorter contact time showed relatively stronger sorption performance. One noticeable difference is the variation trend of pH in the four different cases. For the cases with curing period of 28 days, the variation trend of pH is shown in Fig. 5.8. For the cases of T_c = 24 hours and 4 hours with different curing period, the variation trend is shown in Fig. 5.9.

For the case of T_c = 2 hours, pH gradually decreased from 10.5 and maintained relatively stable around 10 until the L/S ratio of 200. The pH was higher than 9.5 even after reaching breakthrough point. For the cases of T_c = 4 hours, pH gradually decreased from 10.5 and maintained relatively stable around 9.5 at the L/S ratio of around 60 where breakthrough of As started until the L/S ratio of 180 where effluent As concentrations were equal to the influent concentration. For the cases of T_c = 24 hours, pH dropped from 10 quickly, varied around 8 to 9, and became relatively stable around 8.5 at L/S = 60, where leaching of arsenic started. Manning and Goldberg (1997) suggested that oxidation of As(III) to As(V) occurs in solution at or above pH 9.2, which results in stronger adsorption. Yokoyama et al. (2012) reported higher interaction of As with calcite at an alkaline pH (>9) and suggested that

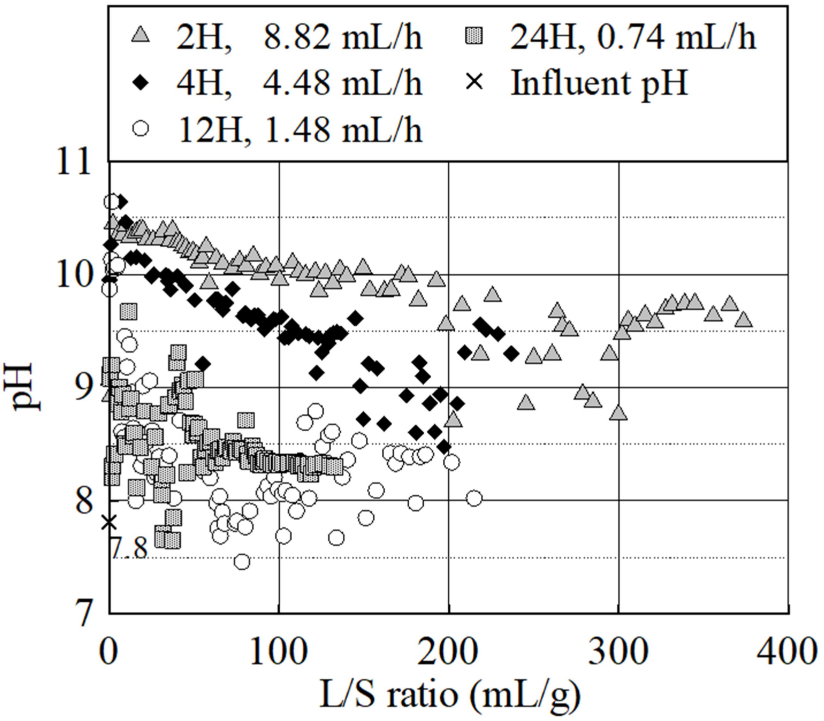


Fig. 5.8 Variation of pH for different contact time cases

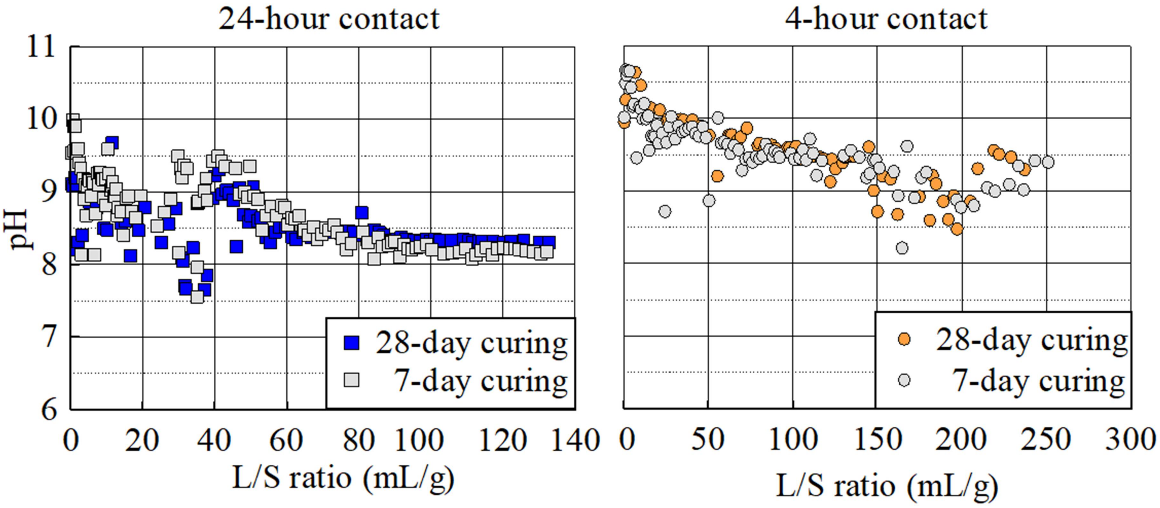


Fig. 5.9 Variation of pH for mix proportion of 5%, 24-hour and 4-hour contact

presence of Ca^{2+} promotes the oxidation of As(III). Goldberg and Glaubig (1988) also suggested the oxidation of As(III) occurred for arsenic sorption on a calcareous, montmortillonitic soil and reported that arsenate sorption increased with increasing pH. Arsenate sorption occurs primarily on soil carbonates above pH 9.

Considering that the cases of T_c = 2 hours and 4 hours in this study showed a higher pH range over 9.5, promoted oxidation of As(III) and higher sorption amount on carbonates offered by the Ca-Mg agent could be expected, which resulted in a higher sorption performance than the cases of T_c = 12 hours and 24 hours. In addition, decrease trend of pH value was much quicker under longer contact time, suggesting the acid buffering capacity lost efficacy soon and alkaline environment which favors the sorption of arsenic was unable to be maintained in the long term.

Besides of the variation trend of pH, another noticeable difference, which was the variation trend of EC, was observed after L/S ratio over 40. Variation trends of EC the cases of T_c = 2 hours, 4 hours, 12 hours and 24 hours with curing periods of 28 days were shown in Fig. 5.10. For the cases of T_c = 24 hours and 4 hours with different curing period, the variation trend is shown in Fig. 5.11.

For the case of T_c = 2 hours, EC decreased quickly in initial stage and maintained relatively stable around 5 mS/m. For the cases of T_c = 4 hours, variation trend of EC was similar. EC dropped quickly and maintained relatively stable around 6. For the cases of T_c = 24 hours, EC showed similar trend within L/S of 40. Discrete variation trend was observed

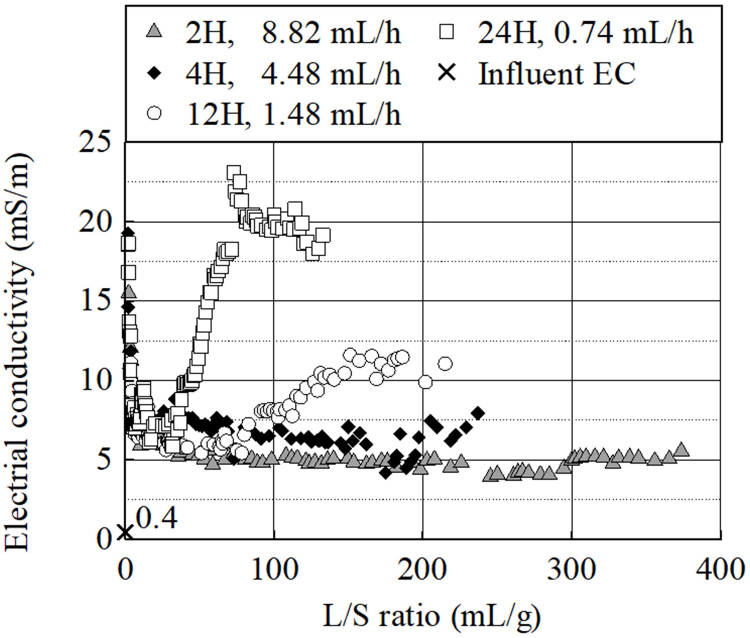


Fig. 5.10 Variation of EC for different contact time cases

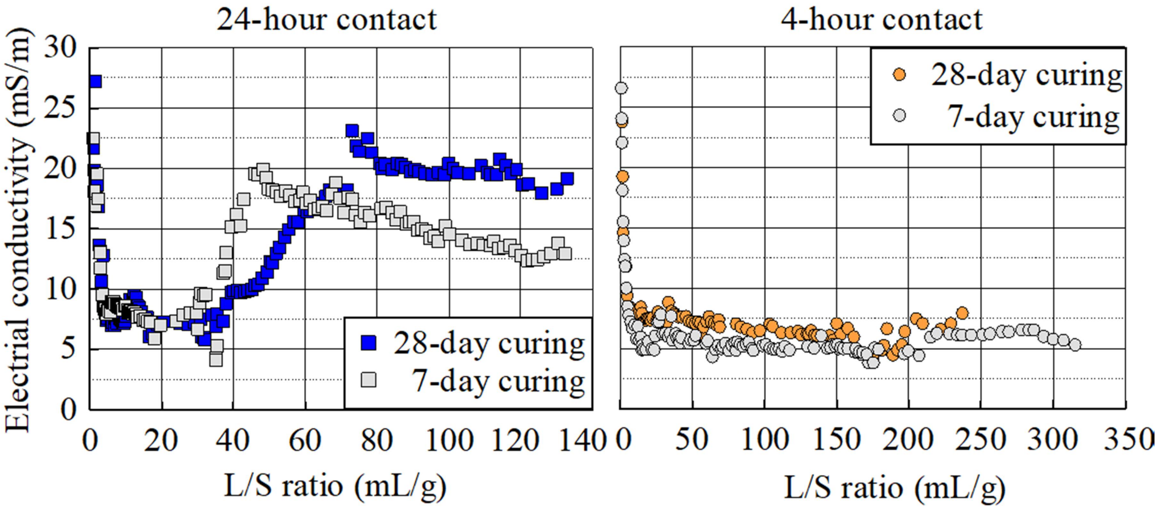


Fig. 5.11 Variation of EC for mix proportion of 5%, 24-hour and 4-hour contact

afterwards and EC started increasing and became stable again after L/S of 80 for 28-day cured specimen and L/S of 45 for 7-day cured specimen. Measurement of Mg and Ca for the cases of T_c = 12 hours and 24 hours started since then. The variation trend of Mg and Ca of different cases are shown in Fig. 5.12 and Fig. 5.13.

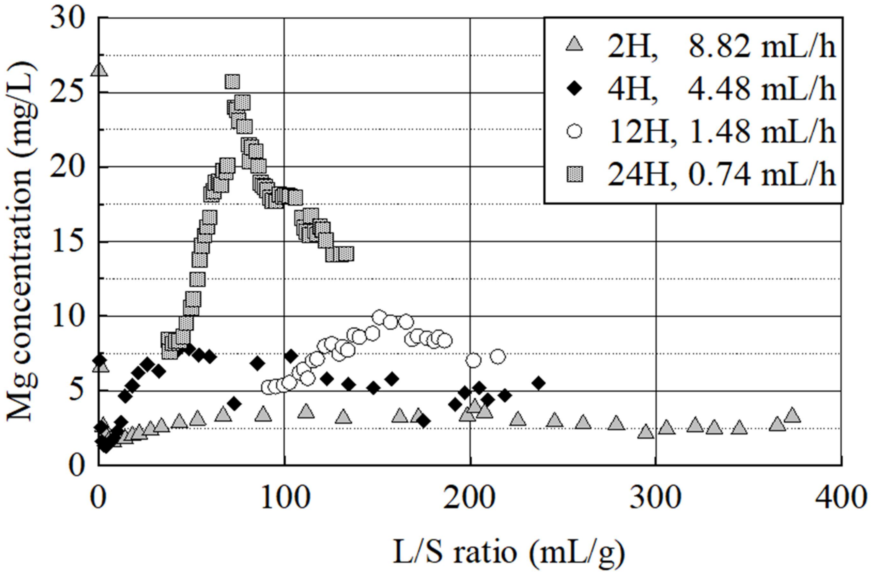


Fig. 5.12 Variation of Mg for different contact time cases

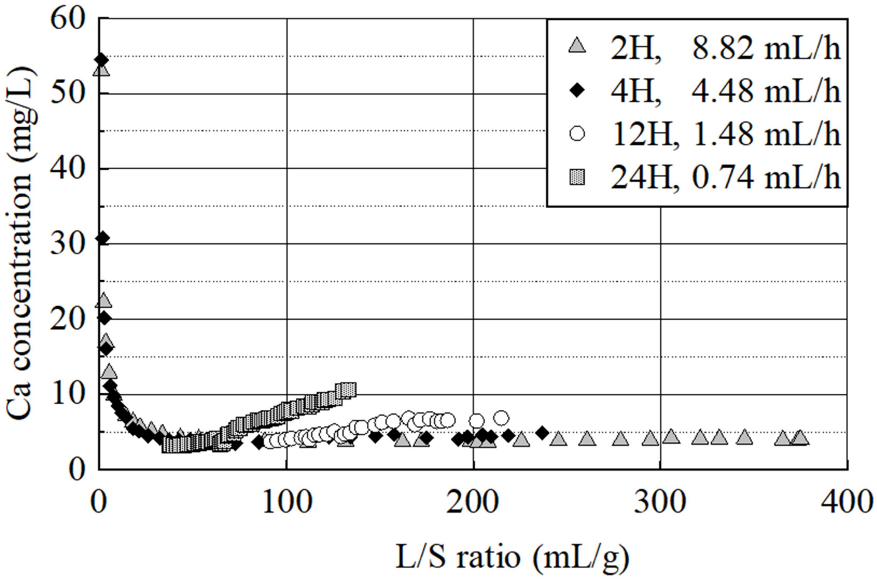
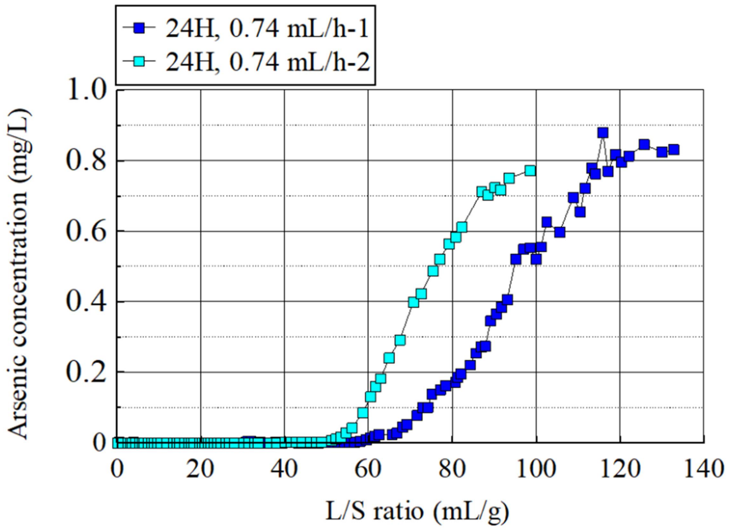


Fig. 5.13 Variation of Ca for different contact time cases

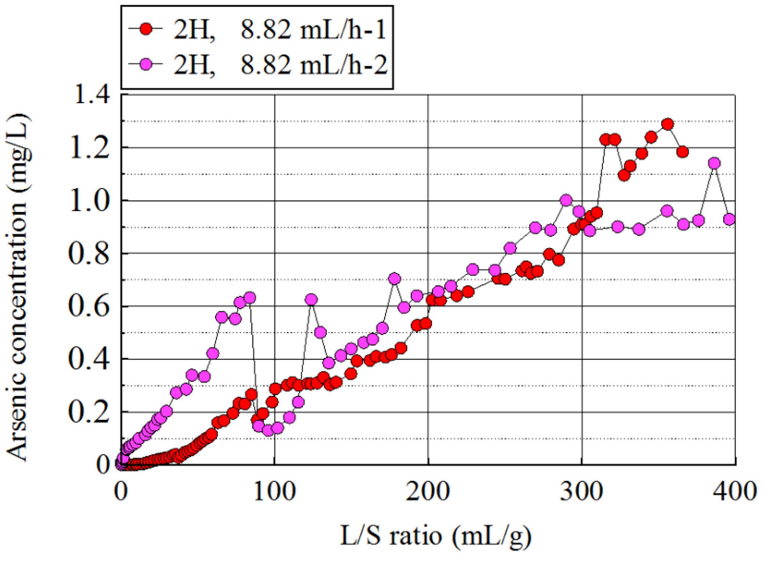
The major difference found in the effluent under various flow rates was Mg concentration. Leaching of Ca was also affected by contact time with less obvious impaction compared to the variation trend of Mg.

Mg contained in the effluent was mainly generated by the dissolution and hydrolysis of $MgCO_3$ and MgO. Due to the higher concentration of Mg^{2+}, $Mg(OH)_2$ was further precipitated. Consequently, pH value of the cases of T_c = 12 hours and 24 hours relatively decreased because of the loss of OH^- in the solution. Similar process was reported that increasing addition amount of MgO into water from 1 mg/20 mL to 50 mg/20 mL actually decrease pH from 11.3 to 10.4 (Suzuki et al. 2013).

Another concern is that precipitation might occur between magnesium and arsenic (Tabelin et al. 2013). Precipitations will accumulate on the solid surface and the available



(a) Effluent As concentration of repeated 24-hour contact cases



(b) Effluent As concentration of repeated 2-hour contact cases

Fig. 5.14 Repeated experiments for up-flow column tests sorption sites decrease. Considering that acid buffering capacity and total sorption capacity was negatively affected under longer contact time, stronger long-term sorption performance under shorter contact time can be expected as exhibited in the up-flow percolation column test.

The reverse sorption performance in the long term was out of expectation. Thus, repeated cases were conducted to for specimens with 28-day curing under T_c = 24 hours and 2 hours to verify the results. The variation of effluent concentration is shown in Fig. 5.14.

For the repeated case of T_c = 24 hours (24H-2), effluent arsenic concentration varies after L/S of 55. Even poor sorption capacity was shown in this case and the trend was consistent with the previous case. For the repeated case of T_c = 2 hours (2H-2), effluent arsenic concentration was almost same with the previous case and reached concentration of 1 mg/L around L/S of 300. Thus, the experimental results were verified. In early permeation stage, sorption performance increased with contact time up to T_c = 12 hours. Sorption performance of T_c = 12 hours and 24 hours were close. Higher sorption capacity was obtained in T_c = 2 hours and 4 hours after long term permeation.

It should be noticed that for the cases of T_c = 24 hours, no arsenic can be detected in effluent until the L/S ratio exceeded 60, which corresponds to almost one year after permeation started. For the cases of T_c = 4 hours, the progress was much faster. Low concentrations of arsenic can be detected in the effluent soon after permeation started. Effluent arsenic concentrations reached 1 mg/L at the L/S of around 180, which was corresponding to half of a year after tests started and were continued for a longer period.

Even though the cases of T_c = 24 hours reached the breakthrough point earlier in dimensionless time scale, it did show relatively stronger sorption performance in the initial stage and took a much longer realistic time than the cases of T_c = 4 hours for leaching of arsenic to start.

5.3.3 Sorption mechanism study

According to the discussion in section 5.3.2, major difference found in the effluent of different contact time was the leaching trend of Mg and Ca. Time-dependent sorption behavior was believed to be affected by the concentration of Mg and Ca in the solution along with the related variation of pH and EC.

In order to study the effect of Mg and Ca on the sorption of arsenic, first concern needs to be solved is the leaching sources of Mg and Ca. Specimen with mix proportion of 0% was permeated with arsenic solution under T_c = 2 hours and 24 hours and the experimental results were compared with 5% cases to study whether these two ions leach from Ca-Mg composite powder or from decomposed granite soil itself.

For the cases of T_c = 24 hours, variation of arsenic concentration in effluent for 0% case and two cases conducted on specimens with mix proportion of 5% was shown in Fig. 5.15. Leaching of Ca is shown in Fig. 5.16 and leaching of Mg is shown in Fig. 5.17. Concentration of Ca in 0% case is higher than in 5% cases before L/S ratio of 40 and became lower after L/S of 60. Concentration of Mg in 0% case was obviously lower than 5% cases. Thus, addition of Ca-Mg concentration increases the leaching of Mg which is to the fact that MgO was one of the reactive components of the Ca-Mg agent.

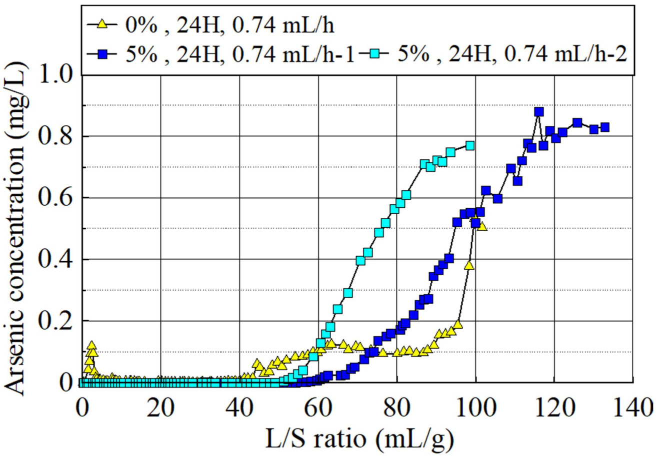


Fig. 5.15 Effluent As concentration for 0% and 5% cases under 24-hour contact

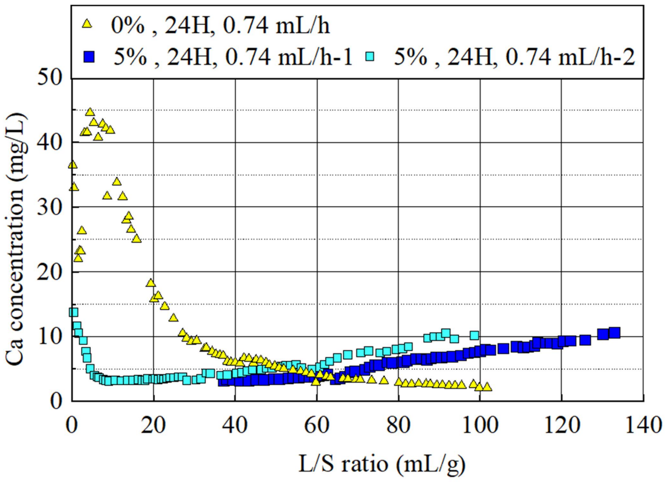


Fig. 5.16 Effluent Ca concentration for 0% and 5% cases under 24-hour contact

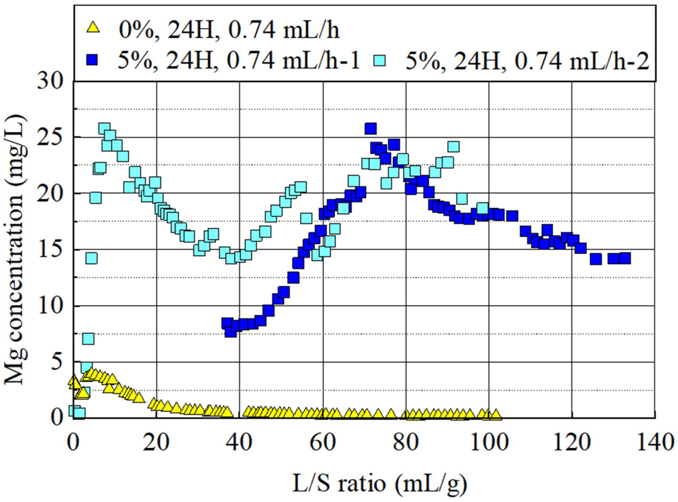


Fig. 5.18 Effluent Mg concentration for 0% and 5% cases under 24-hour contact

Variation of pH for 0% case and two cases conducted on specimens with mix proportion of 5% is shown in Fig. 5.18 and variation of EC is shown in Fig. 5.19. For 0% case, variation trend of pH and EC was consistent with leaching of Ca and Mg. Hydration of Ca and Mg in the solution increases the pH in the initial stage. pH became stable when concentration of Ca and Mg in the effluent was low. EC kept decreasing which was same with the concentration of Ca. For 5% cases, variation trend was close to leaching of Mg. Increasing leaching of Mg started when pH was lower than 9, which might be resulted from the dissolution of $Mg(OH)_2$. Variation of pH was less affected probably due to the hydration of Ca and Mg from indissolvable $CaCO_3$ and $MgCO_3$.

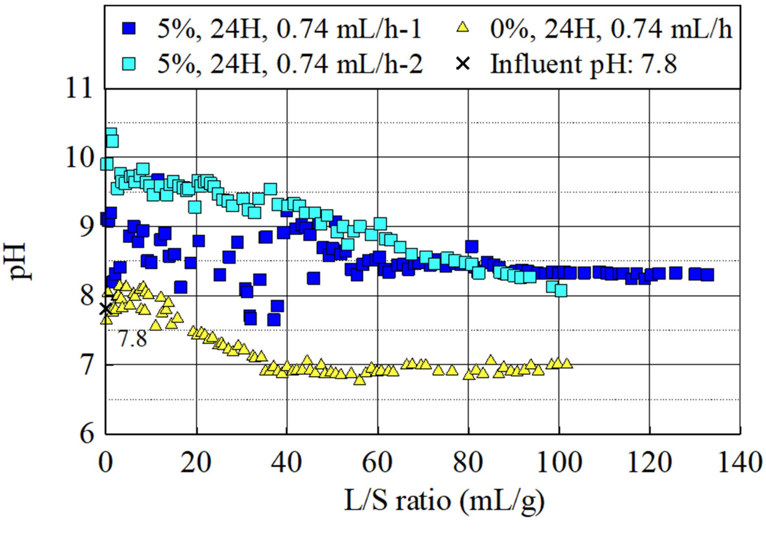


Fig. 5.17 Variation of pH for 0% and 5% cases under 24-hour contact

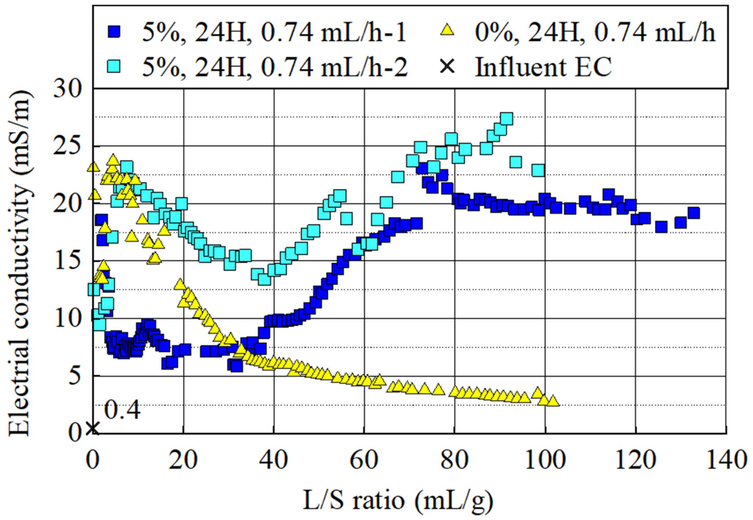


Fig. 5.19 Variation of EC for 0% and 5% cases under 24-hour contact

For the cases of T_c = 2 hours, variation of arsenic concentration in effluent for 0% case and two cases conducted on specimens with 5% was shown in Fig. 5.20. Leaching of Ca is shown in Fig. 5.12 and leaching of Mg is shown in Fig. 5.22. Effect of Ca-Mg addition on arsenic solution was more obvious under shorter T_c cases. Concentration of Ca in 0% case is same with 5% cases and much lower compared to the cases of T_c = 24 hours. Concentration of Mg in 0% case was lower than 5% cases and variation trend was different. An increasing trend in the initial stage was not observed. Limited leaching of Ca and Mg in 0% cases probably resulted in the low sorption performance.

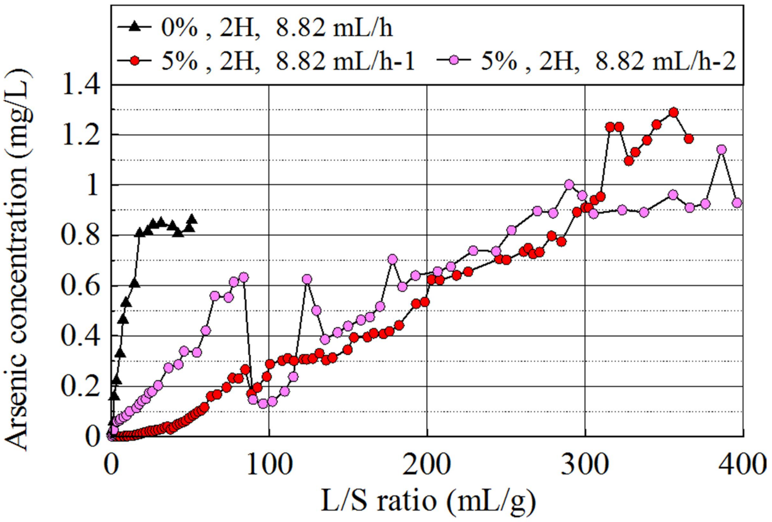


Fig. 5.20 Effluent As concentration for 0% and 5% cases under 2-hour contact

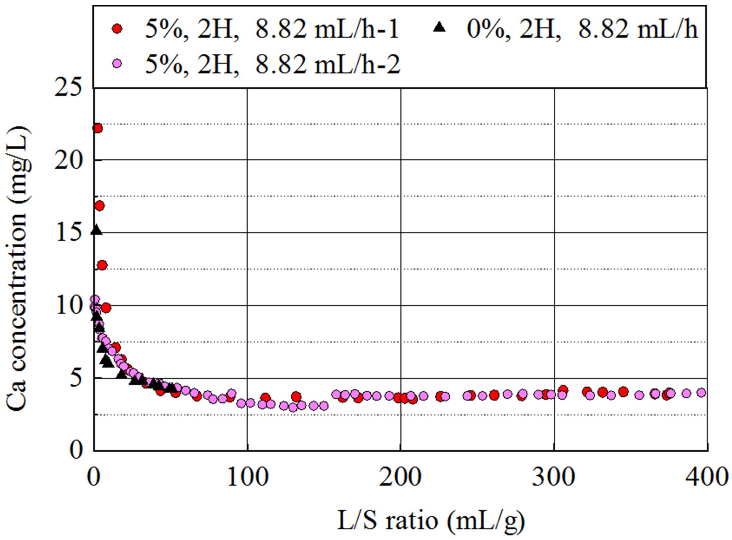


Fig. 5.21 Effluent Ca concentration for 0% and 5% cases under 2-hour contact

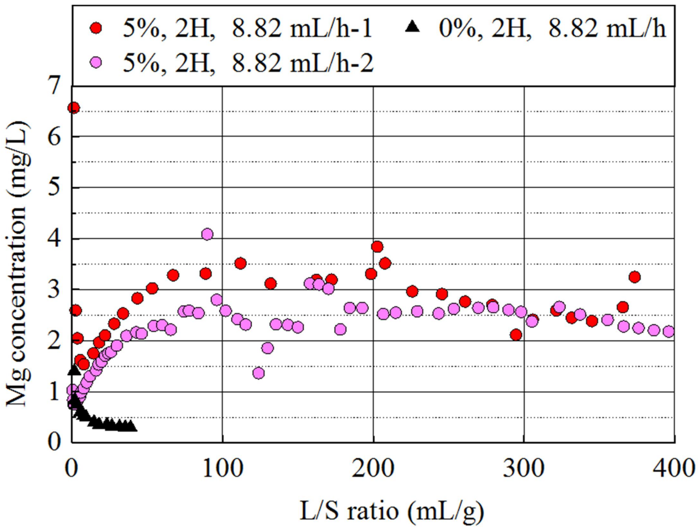


Fig. 5.22 Effluent Mg concentration for 0% and 5% cases under 2-hour contact

Variation of pH for 0% case and two cases conducted on specimens with 5% was shown in Fig. 5.23 and variation of EC is shown in Fig. 5.24. For 0% case, variation trend of EC was consistent with leaching of Ca and Mg and variation of pH was not obviously affected. Higher pH in 5% cases was probably due to the low leaching concentration of Ca and Mg thus more of them can be involved in hydration and maintain a higher pH for long term. Since pH was always higher than 9 for 5% cases, less dissolution of $Mg(OH)_2$ might lead to a low leaching concentration of Mg.

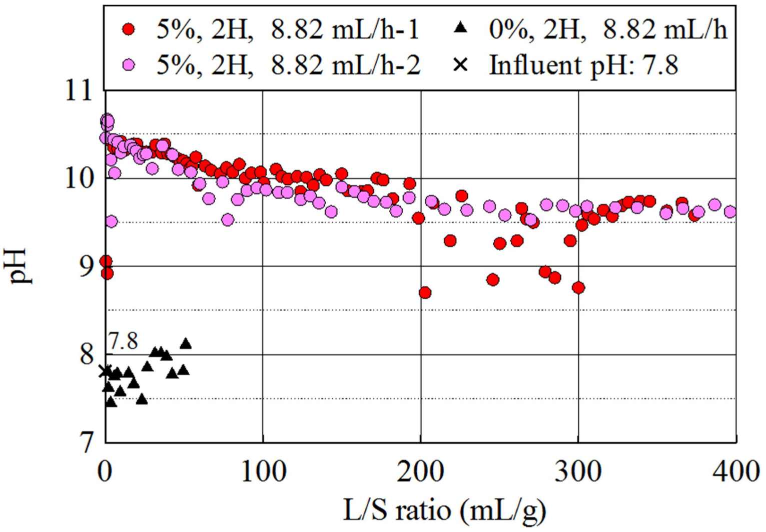


Fig. 5.23 Variation of pH for 0% and 5% cases under 2-hour contact

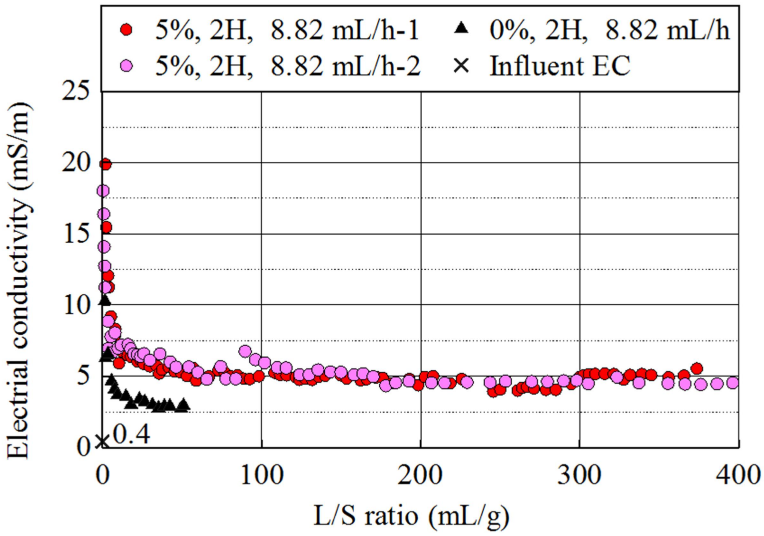


Fig. 5.24 Variation of EC for 0% and 5% cases under 2-hour contact

For 5% cases under shorted contact time, the long-term reversed sorption performance was assumed to be attributed to the higher pH buffering capacity and low leaching of Ca and Mg, which will benefit the sorption of arsenic in the specimen.

Ca and Mg ions affect the sorption of arsenic in two ways. First, they affect the pH buffering capacity and a preferable pH range is important for the sorption of arsenic. Second, Ca and Mg are directly involved in the sorption of arsenic. Surface attraction of arsenic on the hydration product of MgO is one mechanism and Ca promots oxidation of As(III) to As(V) and sorption on carbonates offered by the Ca-Mg agent. Thus, leaching of Ca and Mg ions is the main affecting factor on the sorption performance of arsenic.

Distilled water was used as permeant to compare with the condition under arsenic sorption to further study the leaching behavior of Ca and Mg ions and its correlation with arsenic sorption.

For the cases of T_c = 24 hours, variation of Ca and Mg concentration in effluent for mix proportion of 5% with and without sorption is shown in Fig. 5.25 and Fig. 5.26.

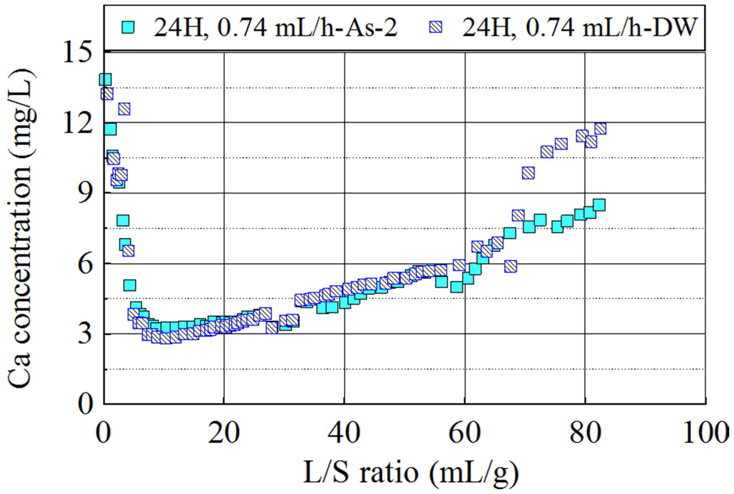


Fig. 5.25 Effluent Ca concentration for 5%, 24-hour contact with and without sorption

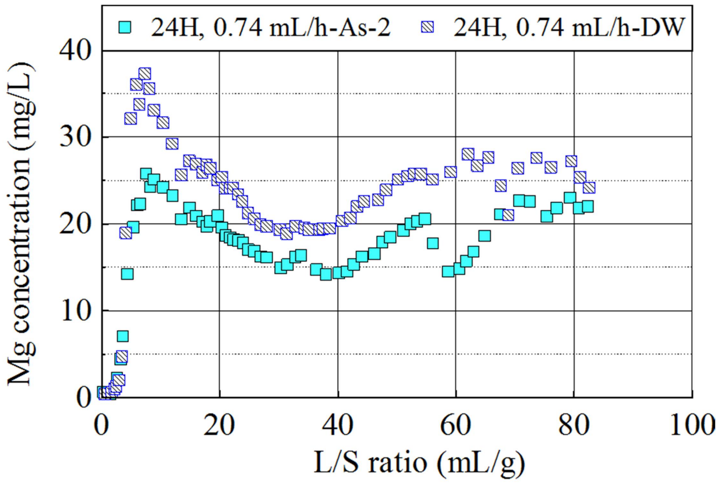


Fig. 5.26 Effluent Mg concentration for 5%, 24-hour contact with and without sorption

Concentration of Ca is similar until L/S ratio over 70, when arsenic concentrations in the leachate were already over 0.4 mg/L. Thus, precipitation of Ca and As might happen from this stage. Concentration of Mg with sorption was obviously lower than the case with permeation of distilled water. Thus, Mg in the leachate might directly precipitate with arsenic. Variation of pH and EC shown in Fig 5.27 and Fig 5.28 suggested that leaching of Mg is the major affecting factor on EC and pH is less affected by Ca and Mg.

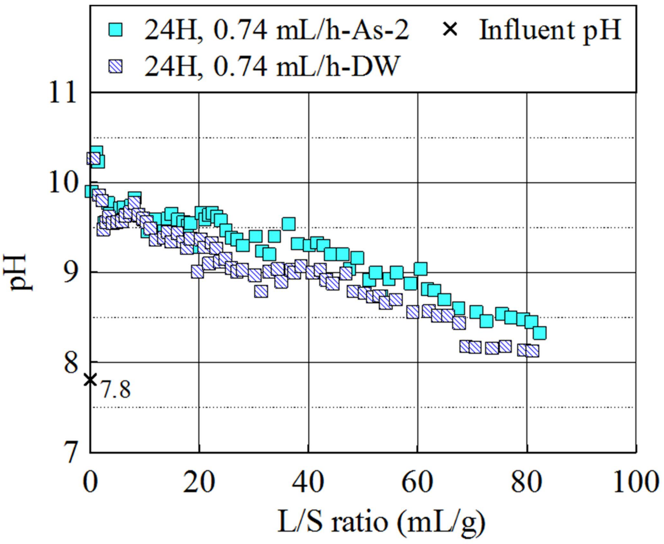


Fig. 5.27 Variation of pH for 5% cases under 24-hour contact with and without sorption

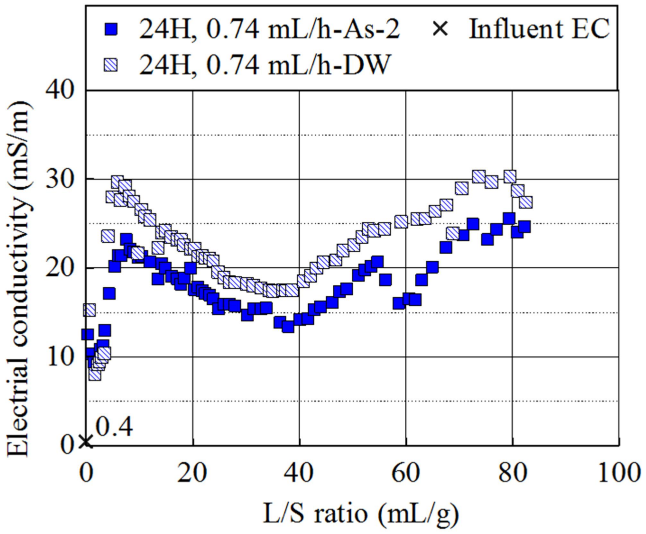


Fig. 5.28 Variation of EC for 5% cases under 24-hour contact with and without

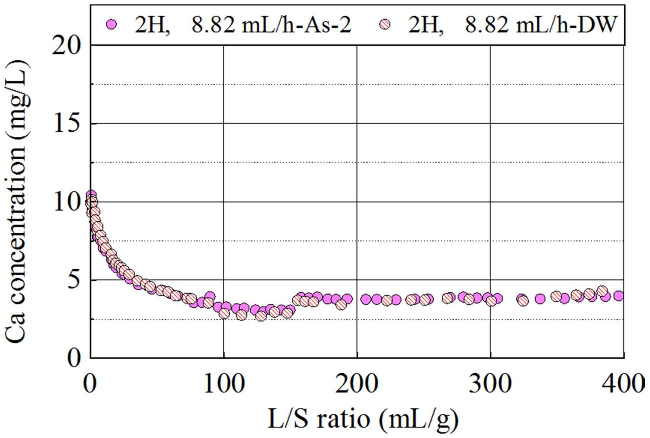


Fig. 5.29 Effluent Ca concentration for 5%, 2-hour contact with and without sorption

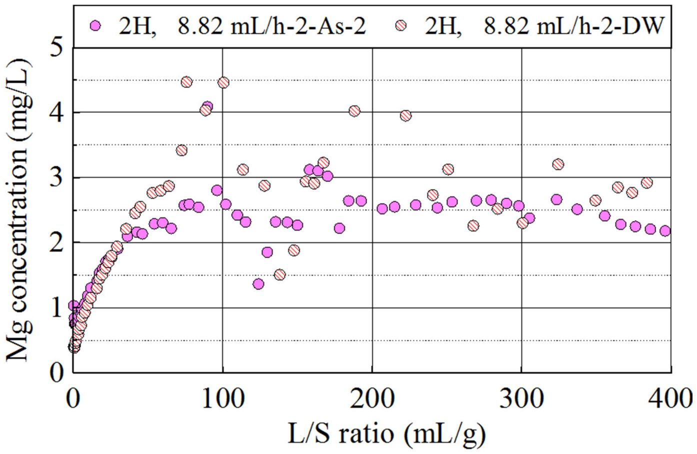


Fig. 5.30 Effluent Mg concentration for 5%, 2-hour contact with and without sorption

For the cases of T_c = 2 hours, variation of Ca and Mg concentration in effluent for mix proportion of 5% with and without sorption was shown in Fig. 5.29 and Fig. 5.30.

Variation trends of Ca and Mg concentrations were similar with and without arsenic sorption, suggesting that sorption of arsenic has no obvious impact on their leaching behavior when contact time is short. Thus, Precipitation of arsenic with Ca and Mg in the leachate might not be the major sorption mechanism. Surface attraction on the soil-agent mixture might be the major mechanism instead.

Variation of pH and EC for the cases of T_c = 2 hours were shown in Fig 5.31 and Fig 5.32. The variation trend is similar with and without sorption of arsenic, which is probably due to the similar concentration of Ca and Mg in the leachate.

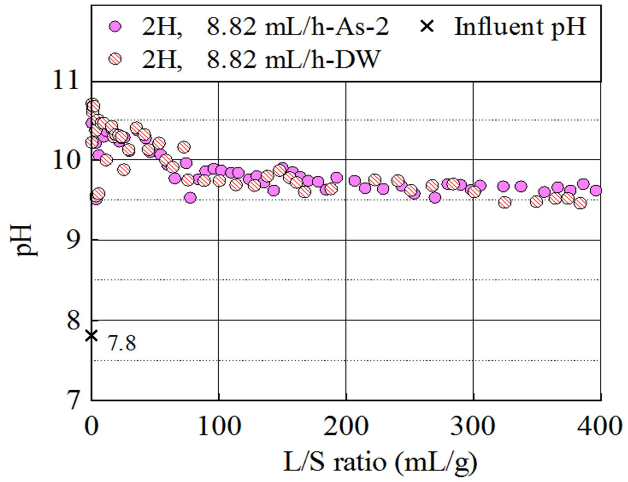


Fig. 5.31 Effluent Ca concentration for 5%, 2-hour contact with and without sorption

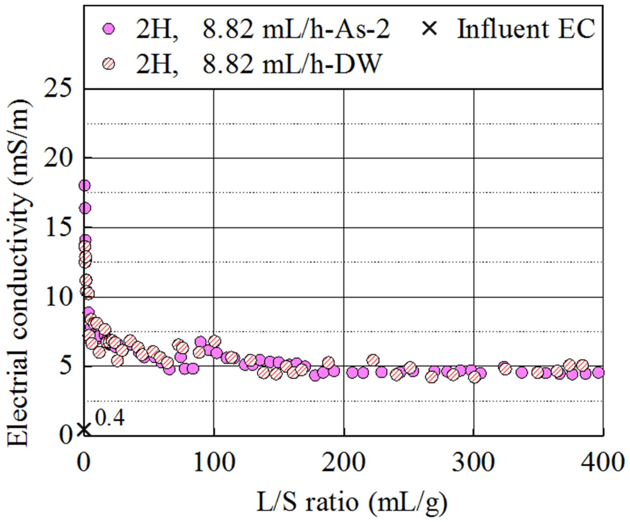


Fig. 5.32 Effluent Mg concentration for 5%, 2-hour contact with and without sorption

5.4 Conclusions for this chapter

In this chapter, time-dependent sorption behavior of decomposed granite soil amended with Ca-Mg composite powder was studied based on the results of both batch sorption test for different shaking times and up-flow column percolation tests applying different flow rate. Variation trend of effluent concentration of arsenic, calcium and magnesium along with change of pH and EC value was studied. The main results obtained in this chapter can be summarized as follows:

(1) For batch sorption test, sorption performance increases with longer shaking time. When the equilibrium arsenic concentration was 0.01 mg/L, which corresponds to initial arsenic concentration around 1 mg/L for contact time T_c = 12 and 24 hours, sorption amount was almost same. With relatively lower initial concentration, the effect of longer contact time on sorption performance became much less obvious.

(2) For up-flow column percolation test, sorption performance also increased with longer contact time up to 12 hours in early permeation stage which is consistent with batch sorption test.

(3) A reversed sorption performance was observed after long-term permeation. Higher sorption capacity was obtained in shorter contact time. For T_c = 24 hours, effluent arsenic concentration almost reached to 1 mg/L around L/S of 120. For T_c = 12 hours, effluent arsenic concentration reached to 1 mg/L at L/S of 150. The breakthrough point was L/S of 200 for T_c = 4 hours and L/S of 300 for T_c = 2 hours.

(4) For T_c = 24 hours, even though breakthrough point was reached earlier in dimensionless time scale, it did show stronger sorption performance in the initial stage and took much longer realistic time than shorter contact case before leaching of arsenic happened.

(5) For different curing periods, variation of arsenic concentration in effluent was almost same. Effect of curing periods was not obvious even under different contact time.

(6) Decrease trend of pH value was much quicker under longer contact time, suggesting the acid buffering capacity lost efficacy soon and alkaline environment which favors the sorption of arsenic was unable to be maintained in long term.

(7) Leaching of magnesium from soil-agent mixture into solution was obviously affected by different contact time and leaching of calcium was also affected. Leaching of Ca was also affected by contact time with less obvious impaction compared to the variation trend of Mg.

(8) Higher leaching concentrations of Mg^{2+} and Ca^{2+} in the effluent under longer contact time probably resulted in lower acid buffering capacity and lower sorption performance of the specimen. Decreasing pH and dissolution of $Mg(OH)_2$ after long term permeation might lead to total lower sorption capacity in the column test under longer contact time.

CHAPTER 6

Practical implications

6.1 General remarks

Sorption layer method is a newly developed countermeasure against huge amount of excavated soil with low-level natural contamination and its design method has not been completely established yet. Unlike hydraulic conductivity or thickness of a liner system, there are no specific criteria to be referred when evaluating its performance. The concept of sorption layer method is that concentration of contaminants in the leachate should not exceed certain requirement, which is close to a performance-based evaluation approach. Thus, the hydraulic and sorption properties of soil-agent mixture obtained in previous chapters were applied under some assumed simplified practical conditions to evaluate whether the hydraulic and sorption performance is appropriate for the application of sorption layer.

6.2 Long-term hydraulic performance

Based on previous discussion in Chapter 3, hydraulic conductivity of soil-agent mixture would decrease after PVFs are over 100. Thus, number of years was calculated to evaluate the duration that a sorption layer applying this material can maintain a relatively stable hydraulic conductivity. PVF obtained in the experiment was converted to total infiltration volumes of leachate at first, with considering the annual percolation, number of years can be calculated. Assuming that thickness of layer (L) is 45 cm, porosity (n) is 0.31 and annual percolation (AP) is 500 mm, number of years (Y) was calculated using the following relationship and the result is shown in Fig. 6.1.

$$Y = (PVF \times L \times n) / AP \tag{6.1}$$

It was found that a relatively stable hydraulic conductivity can be maintained for at least 20 years. This result suggested that even though hydraulic conductivity might decrease in the long term, soil-agent mixture can still maintain a stable hydraulic performance for a certain long period of time.

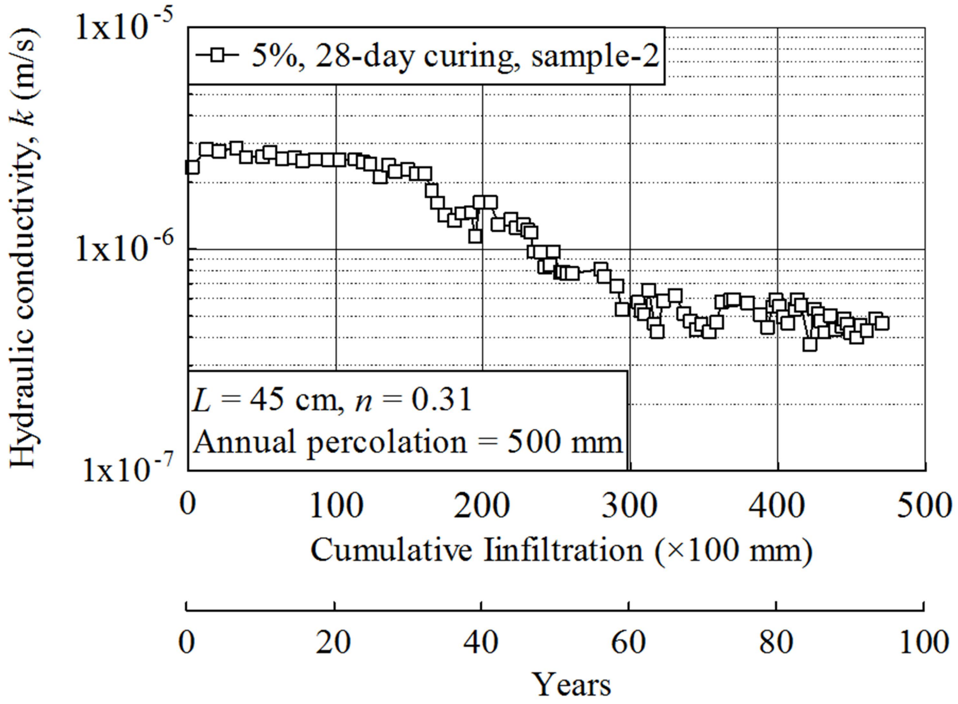


Fig. 6.1 Analysis of long-term hydraulic performance

6.3 Solute transport analysis

A simplified field condition was assumed under a constant water head (h_w) of 30 cm over a saturated sorption layer as shown in Fig. 6.2. In actual site, water head decreases and sorption layer is considered unsaturated. Soil-water retention capacity is expected to help sorption by retaining leachate inside layer. However, these effects were not considered in this study and thus a relative more conservative assumption is applied.

Performance of sorption layer can be evaluated using the solute transport parameters obtained in Chapter 4. The transport of arsenic with cumulative infiltration of the leachate was

Fig. 6.2 Conceptual model of a simplified field condition

Table 6.1 Condition and parameters applied in solute transport analysis

Layer thickness L (cm)	R_d	P_e	T_c	h_w (cm)	k (m/s)	n
45	580.80	37.38	23.3	30	1×10^{-6}	0.31
15	822.59	33.02	4.3			

calculated considering two kinds of layer design which correspond to contact times (T_c) approximately 24 and 4 hours.

Since Eq. 4.6 applied in Chapter 4 for the regression analysis to determine the solute transport analysis meets the measured data, it is used here to calculate the transport of arsenic, assuming that seepage is steady-state and sorption layer is homogenous. The solute transport parameter applied is summarized in Table 6.1.

It should be noticed that the parameters determined in this study were based on the initial arsenic concentration of 1 mg/L, which is higher than the common leaching contamination of naturally derived heavy metal(loid)s. The effect of initial concentration was not evaluated in the study and the parameters may vary if the initial condition changes.

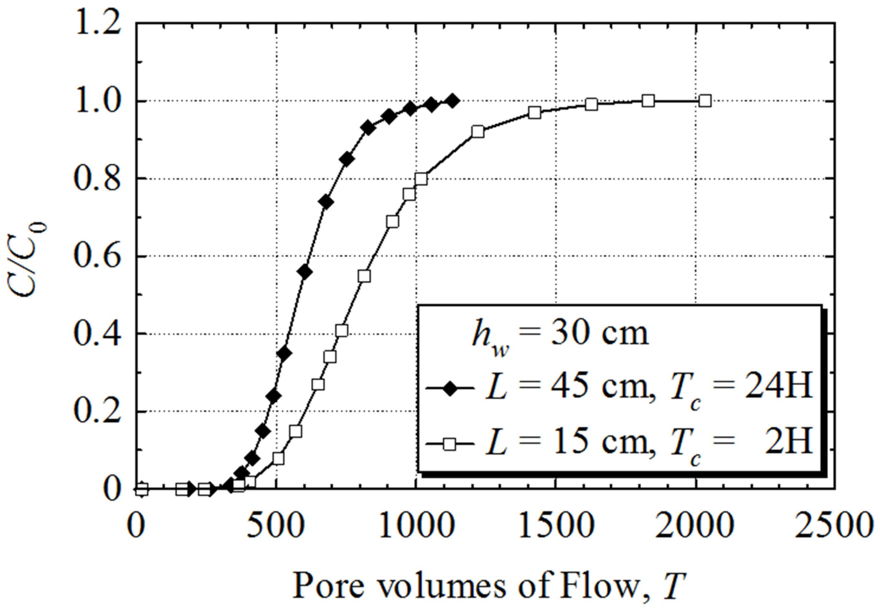


Fig. 6.3 Results of solute transport analysis considering contact time

The calculation results with pore volumes of flow considering the effect of different contact time is shown in Fig. 6.3 and variation of effluent concentration is consistent with the experimental results. The case of T_c = 4 hours, which correspond to the layer thickness of 15 cm, exhibited higher sorption capacity in the long term permeation and takes more pore volumes of flow for the concentration of effluent flow to become same with the initial concentration. However, the layer thickness and the volume of voids of these two cases are different thus the cumulative infiltration (*CI*) of the two layer design is actually different. Pore volumes of flow can be converted into cumulative infiltration (*CI*) using the following relationship and variation of effluent concentration with cumulative infiltration is shown in Fig. 6.4.

$$CI = T \times L \times n \tag{6.2}$$

Results of solute transport analysis considering cumulative infiltration suggests that the layer thickness design of 45 cm can be effective much longer than the case with layer thickness of 15 cm since the cumulative infiltration to reach the breakthrough point is larger. Even though the longer contact time shows relatively lower sorption capacity compared to shorted contact time in the long term permeation, it is still possible to achieve a stronger performance through the design of other parameters such as layer thickness.

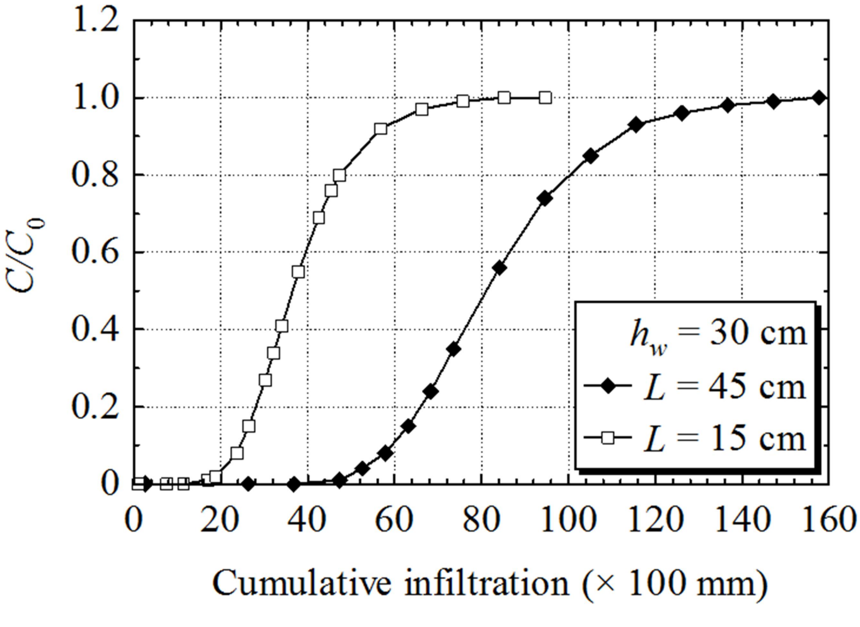


Fig. 6.4 Results of solute transport analysis considering cumulative infiltration

Table 6.2 Years needed to reach environmental standard

Layer thickness L (cm)	C_0 (mg/L)	C (mg/L)	Annual percolation (mm)	Cumulative infiltration (mm)	Year
45	1	0.01	500	462500	92
15				17000	35

As previously described in section 6.2, number of years can be calculated using cumulative infiltration based on Eq. 6.1. Assuming an initial concentration of 1 mg/L and annual rain infiltration of 500 mm, the years to reach the environmental standard of 0.01 mg/L, which is a common condition in Japan, is calculated and summarized in Table 6.2.

Even for the layer design of 15 cm, which correspond to contact time of 4 hours, it takes at least 35 years for concentration of arsenic to reach the environmental standard. The analysis results suggest that soil-agent mixture is a very promising material for the application of sorption layer.

CHAPTER 7

Conclusions and future research

7.1 Major conclusions

This study was conducted to evaluate the feasibility of the decomposed granite soil amended with Ca-Mg composite powder mixing as a constituent material for the sorption layer method. Hydraulic and sorption performance, as well as the time-dependent sorption behavior of the soil-agent mixture was evaluated. The main results are summarized as follows:

In Chapter 1, the overall study background was clarified. The objectives and the contents of the thesis were presented.

In Chapter 2, the origins of natural contamination of heavy metal and metalloids were presented, as well as leaching characteristics of natural arsenic contamination. Countermeasures applied to treat excavated soils and rocks with natural contamination were reviewed. Previous research on the sorption layer method were summarized.

In Chapter 3, hydraulic performance of decomposed granite soil amended with Ca-Mg composite powder was studied based on the results of hydraulic conductivity test. Effects of mix proportion, curing period and hydraulic gradient were evaluated and long-term hydraulic performance was discussed.

Hydraulic conductivity of the soil-agent mixture was maintained at around 1×10^{-6} m/s. Initial addition of Ca-Mg composite slightly increases the hydraulic conductivity of decomposed granite soil. There is no obvious difference between the mix proportion of 3% and 5%. Further addition of Ca-Mg agent after 3% has little influence on the structure of soil-agent mixture. Fine soil particles were observed in the effluent of 0% cases in initial permeation phase but not in 3% and 5% cases during application of a same hydraulic gradient. This observation indicates that amendment of the Ca-Mg composite powder in 3% and 5% cases might interlock the fine particles and mitigate the erosion. Hydraulic conductivity remained almost same at hydraulic gradient of 1 and hydraulic gradient of 5. Hydraulic gradient under 5 has no obvious effect. Specimens cured for 7 and 28 days exhibited similar hydraulic conductivity values, which are relatively higher than that of 0-day curing specimen. Higher hydraulic conductivity of cured soil-agent mixture might be attributed to the fast hydration process of MgO. There is no obvious effect of longer curing period confirmed in this study due to two potential reasons. First is the lower range around 9 to 10 which is not favoured by the pozzolanic reaction. Second, hydration products probably covered the surface of soil particles and hindered the leaching of calcium and silicate, and accordingly pozzolanic reactions were limited.

For long-term hydraulic performance, hydraulic conductivity was kept almost constant until the PVFs reached around 40 and started decreasing after the PVFs reached 100, which corresponded to a liquid/solid ratio (L/S) (mL/g) of approximately 20. Decreasing trend became less obvious after the PVFs = 200. Dissolution of $Mg(OH)_2$ might happen during that period and some agglomerated particles might be flushed and obstructed the flow path.

In Chapter 4, primary sorption performance of decomposed granite soil amended with Ca-Mg composite powder was studied based on the results of both batch sorption test and up-flow column percolation test. Effects of mix proportion and curing period were evaluated and differences between batch tests and column tests were discussed.

Pure decomposed granite soil showed certain sorption capacity when initial arsenic concentration (C_0) was relatively low. The arsenic removal rate was 77% at C_0 of 0.1 mg/L, close to the performance of soil-agent mixture (99%). However, At C_0 of 10 mg/L, removal rate dropped to 30%, which is only 1/3 of the removal rate of soil-agent mixture. Addition of Ca-Mg composite powder increases the sorption performance and effect is more obvious when C_0 is high. For mix proportion of 3% and 5%, the removal rate remained over 90% for C_0 from 0.1 mg/L to 10 mg/L. The remove rates were over 99% at C_0 of 0.1 mg/L and over 97% at 1 mg/L. For 5% case, removal rate was still over 95% at C_0 of 10 mg/L. The residue concentration of 5% case was around 0.01 mg/L at C_0 of 1 mg/L and 0.3 mg/L at C_0 of 10 mg/L, suggesting strong sorption performance. The Freundlich model fitted the sorption isotherms best. If the initial concentration range was narrowed to 0.1 to 1 mg/L, the Freundlich model based sorption isotherms can be simplified to linear shape.

Sorption performance increases with mix proportion in batch sorption test. Under a hypothetic equilibrium concentration of 0.01 mg/L, 3% addition of Ca-Mg composite powder increase the sorption amount of arsenic on soil for 10 times and 5% addition is at least 1.5 times higher than that of 3%, which is almost in consistent with the increment of agent mount.

Ca-Mg composite powder used in this study achieved much stronger sorption performance than original raw dolomite material. The production process for including calcination, grinding to powder and adding special additives provided larger specific surface and more sorptive ingredient.

Fitted curve using advection-dispersion equation recommended by van Genuchten and Parker (1984) for a finite column basically accorded with the measured data for soil-agent mixture of 5% in column tests. The Peclet number obtained for all specimens are over 20, thus advection dominates the transport process. Effect of curing periods was not obvious in both batch and column tests. Quickly completed hydration process in the early curing phase and no-obvious pozzolanic reaction in the long term might be responsible. Sorption amount on soil is consistent between batch test and column test for 5% cases, suggesting that result of column test can be reflected by easily conducted batch test under relatively lower L/S ratio range. For pure decomposed granite soil, column test exhibited higher sorption performance than batch test, probably due to the higher concentration of Ca^{2+} in the solution.

In Chapter 5, time-dependent sorption behavior of decomposed granite soil amended with Ca-Mg composite powder was studied based on the results of both batch sorption test for different shaking time and up-flow column percolation test applying different flow rate. Variation trend of effluent concentration of arsenic, calcium and magnesium along with change of pH and EC value was studied.

For batch sorption test, sorption performance increased with longer shaking time. When the equilibrium arsenic concentration is 0.01 mg/L, which corresponds to initial arsenic concentration around 1 mg/L for contact time T_c = 12 and 24 hours, sorption amount was almost same. With relatively lower initial concentration, the effect of longer contact time on sorption performance became much less obvious. For up-flow column percolation test, sorption performance also increased with longer contact time up to 12 hours in early permeation stage which is consistent with batch sorption test. A reversed sorption performance was observed after long-term permeation. Higher sorption capacity was obtained in shorter contact time. For T_c = 24 hours, effluent arsenic concentration almost reached to 1 mg/L around L/S of 120. For T_c = 12 hours, effluent arsenic concentration reached to 1 mg/L at L/S of 150. The breakthrough point was L/S of 200 for T_c = 4 hours and L/S of 300 for T_c = 2 hours. For T_c = 24 hours, even though breakthrough point was reached earlier in dimensionless time scale, it did show stronger sorption performance in the initial stage and took much longer realistic time than shorter contact case before leaching of arsenic happened. For different curing periods, variation of arsenic concentration in effluent was almost same. Effect of curing periods was not obvious even under different contact time.

Decrease trend of pH value was much quicker under longer contact time, suggesting the acid buffering capacity lost efficacy soon and alkaline environment which favors the sorption of arsenic was unable to be maintained in long term. Leaching of magnesium from soil-agent mixture into solution was obviously affected by different contact times and leaching of calcium was also affected. Leaching of Ca was also affected by contact time with less obvious impact compared to the variation trend of Mg.

Higher leaching concentrations of Mg^{2+} and Ca^{2+} in the effluent under longer contact time probably resulted in lower acid buffering capacity and lower sorption performance of the specimen. Decreasing pH and dissolution of $Mg(OH)_2$ after long term permeation might lead to total lower sorption capacity in the column test under longer contact time.

In Chapter 6, by assuming a simplified site conditions for application of the sorption layer method, hydraulic and sorption performance were evaluated using the results obtained in this study. Analysis results suggested that stable hydraulic conductivity can be maintain for at least 20 years and leaching concentration of arsenic might reach to the environment standard after 30 years, suggesting that decomposed granite soil mixing with Ca-Mg composite powder is a promising material for the application of sorption layer method.

7.2 Future research

There are three aspects worth considering for the future research of sorption layer method. First is the materials applied for sorption layer, second is the evaluation of performance under more complex conditions, third is a practical design method for the embankment using sorption layer.

In this study, only one type of base material and immobilizing agent, which was decomposed granite soil amended with Ca-Mg composite powder, was applied as sorption layer material. As a matter of fact, base soils should be chosen depending on the location of the sites and different local soils might be used in sorption layer method. Although Ca-Mg composite has strong performance and is effective for a wide range of natural contaminants, there are other agents which may also be promising. Thus, more combination of soils and agents should be evaluated to verify the idea that base soils amended with special additives to strength the performance is feasible for the application of sorption layer method.

Except for the different combination, the interaction between base materials and agents should be studied in the future. It is important to find out the impact on physical and chemical properties such as change of microstructure, potential reaction, etc. for evaluating the performances and understanding the mechanisms involved. Analysis method using X-ray fluorescence (XRF), X-ray diffraction (XRD) and Scanning Electron Microscope (SEM) should be considered in future.

Test conditions applied in this study is rather simple and ideal. Distilled water and pure arsenic solution was used in most cases to evaluate the hydraulic and sorption performance. In actual conditions, leachate from excavated soils and rocks might contain several contaminants and other ions and the pH condition might also be different. Thus, it is necessary to evaluate the performance under more complex conditions involving different pH, coexisting ions and contaminants. Simulated leachate should be used instead of distilled water or pure solution in the future research.

In addition, optimization and modification of the experiments in the current study should also be considered to better evaluate the hydraulic and sorption performance. Variation of water head can be measured in the up-flow percolation test to investigate the hydraulic conductivity and sorption performance at same time. Redox conditions can be monitored and detailed chemical analysis can be conducted to identify As(III), As(V) and other ions in the solution. Size effect on the test should also be considered (Tang et al. 2015).

Additional experiments can be considered to figure out the working condition of sorption layer on site. With understanding the actual condition of sorption layer, it might be easier to decide whether and how to handle the site conditions such as heterogeneity, unsaturated condition and preferential flow. Experimental studies for properties such as distribution of saturation degree and soil-water retention capacity is also useful in the numerical simulation of solution transport.

For long term future research, it is necessary to establish a reliable evaluation and design system for sorption layer method. Since it is hard for in door experiments to fully reproduce site conditions, a reliable numerical method for solute transport analysis should be developed for the design of sorption layer. A reliable evaluation system is also important to obtain the parameters necessary for the numerical analysis. A general instruction on the evaluation and design method for sorption layer method is critical to popularize this promising method to treat excavated soils and rocks containing natural contamination.

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