Evaluation on Long Term Durability of Cement Stabilized Soils under Sea Water Environment

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ABSTRACT

Cement stabilization techniques have been developed and applied widely in practice for on land and marine constructions. It can be used in stabilizing foundation, reducing settlement, preventing liquefaction of ground and so on. The application of cement stabilization techniques has achieved great social and economic benefits. However, the long-term durability of cement stabilized soils in corrosive environment is concerned nowadays. Durability can be defined as the ability of cement stabilized soils to retain stability and integrity over years of exposure to corrosive environment. The corrosive environment refers to sea water intrusion, acid rain, industrial pollution, landfill leachate, irrigation sewage and groundwater flow area. The durability of cement stabilized soils is often threatened in these areas. The dike foundation located in Kyushu Island, Japan encounters leaking and forms swamps after 20 years construction. The seawall foundation at Daikoku Pier after 20 years construction reached a deterioration degree of 30 ~ 50 mm. The decomposition of hydration products in acid rain area over a long period of time weakens the durability of cement stabilized soils and causes economic losses of society. The sulfate-rich environment can affect the mechanical properties of cement stabilized soils which may cause serious damage to structures. The application of cement stabilized soils in coastal areas of China exhibited lower strength and poor integrity after several years of construction. It is obvious that the surrounding environment has critical influence on long-term durability of cement stabilized soils. This research focuses on the sea water environment influence on long-term durability of cement stabilized soils.

In Japan, the total volume of stabilized soil by the deep mixing method from 1977 to 2010 reached more than 100 million m^3 which was initiated to improve the stability of port facilities such as breakwaters and revetments. The repair and maintenance of existing cement stabilized structures cost a lot each year. The Chinese government will be confronted with the same problem in the near future. Therefore, it is significant to evaluate the long-term durability of cement stabilized soils in sea water environment.

Field investigations have confirmed the phenomenon of reduction in strength after several years of exposure to sea water environment. It is believed that calcium leaching phenomenon and magnesium reaction with hydration products induced the strength

reduction of cement stabilized soils. Numerous prediction models have been developed on the basis of the calcium leaching phenomenon.

The research in this thesis mainly investigates the static and dynamic sea water pressure influence on long-term durability of cement stabilized Ariake clay soils. It is found that the static sea water pressure has no influence on long-term durability. However, the dynamic sea water pressure has obvious influence on long-term durability. The research results provide data basis for the application of cement stabilization techniques in tidal zone. The predictive methodology on long-term deterioration depth is proposed. The prediction results have been verified by experimental data. The proposed predictive methodology is time saving and feasible. The mechanism of deterioration is explained from calcium leaching, magnesium reaction, microstructures and Ca/Si ratio aspects. The understanding of deterioration mechanism provides theoretical basis for proposing countermeasures to prevent deterioration in sea water environment.

This dissertation consists of seven chapters. This dissertation consists of seven chapters. Chapter 1 outlines the issues in application of cement stabilization soils. The targets research on long-term durability of cement stabilized soils in sea water environment is clarified. The framework and original contributions of the thesis are included. Chapter 2 introduces the cement stabilization method from its definition, clarification and application patterns. A brief literature review of previous researches on deterioration of cement stabilized soils is summarized. The deterioration mechanism is introduced from aspects of calcium leaching phenomenon and corrosive ions reaction with hydration products. The applications of empirical formula in predicting long term deterioration depth is listed in this chapter. The numerical method of prediction based on calcium leaching phenomenon is introduced also. A method of evaluating long-term durability of cement stabilized soils in sea water environment is proposed in this chapter.

Chapter 3 introduces the details of research methodology. The mould is designed for one dimension deterioration and the curing chambers are designed for supplying water pressures. The procedures of preparing and testing specimen are described in details. The materials and apparatus used in this study is included in this chapter. In Chapter 4 the experimental results of engineering behaviors include cone penetration test, unconfined compressive strength, water content and density are listed. The static and dynamic water pressures influence on deterioration process is discussed. The static sea water pressure has no influence on long-term durability of cement stabilized soils. However, the dynamic sea water pressure has obvious influence on long-term durability. The higher sea water concentration induces greater deterioration degree. Higher initial strength can effectively prohibit the deterioration process in sea water environment. Chapter 5 explains the deterioration mechanism of cement stabilized soils in sea water environment from chemical and microstructure aspects. The mechanism is clarified from: 1) Ca^{2+} and Mg^{2+} ions concentration distribution with depth of specimen; 2) Ca/Si ratio changes as curing time becoming long; 3) Comparison between porosity at different depths of specimen; 4) The scanning electron images at deteriorated area and non-deteriorated area of cement stabilized soils. 5) The compound constitute of specimen analyzed through Powder X-ray diffractometer.

In Chapter 6 proposes methodology of predicting long term deterioration depth of cement stabilized soils under sea water environment based on experimental data under higher sea water concentration. There are two parameters a, b in the prediction equation. The parameter a is a constant because the initial experiment condition is same. The parameter b is a variable and depends on the salt concentration of sea water which is known as sea water concentration hereafter. The parametric study indicates that the parameter a influences the whole deterioration rate and parameter b influences the deterioration rate at early stage. The deterioration rate under different sea water concentrations will be eventually equal to each other. Based on parametric study, it is assumed that the sea water concentration will mainly influence the deterioration rate at early stage and this effect is proportion to the ratio of sea water concentration. Therefore, the predictive methodology can be described as following steps. Firstly, fit the experimental data of higher sea water concentration by using prediction equation. Then, keep the parameter a as a constant and calculate the parameter b by using the relationship, $b_H/b_L=C_L/C_H$. Finally, the predictive curve can be described using prediction equation by substituting the parameters a and b_L into it. The end Chapter 7 gives out the conclusions of this thesis and descriptions of future works on evaluation on long term durability of cement stabilized soils.

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NOTATION

ρ_s	gravity of soil
ω_L	liquid limit
ω_p	plastic limit
I_p	plastic index
D	deterioration depth
t	elapsed time
α ,β	constants
A	deterioration coefficient
C_{Mg}	concentration of magnesium ions
W/C	water to cement ratio
k_{Mg}	proportionality constant related to magnesium ions concentration
k_T	proportionality constant related to temperature
k_{ST}	proportionality constant related to binder type
k_S	proportionality constant related to soil type
$k_{W/C}$	proportionality constant related to water to cement ratio
S_e	standard error
J_i	flux of ions
k	Boltzmann constant
T	temperature
B	absolute mobility
γ	activity coefficient
C	ion concentration
x	distance from exposure surface
e	elementary charge
$Z_\pm$	valence of cationic and anionic ion
μ	constant
υ	constant
a_i	ion size parameter
I	ionic strength

ε	void ratio
τ	tortuosity
B_0	absolute mobility in liquid
C_{soil}	clay particle
C_{solu}	concentration of calcium in fine pore water
K_d	adsorption coefficient
b	constituents of clay particle and soil condition
K_W	product constant of water
$K_{Ca(OH)2}$	solubility product of $Ca(OH)_2$
ε_0	void ratio at early stage
M_{CH}	molecular weight of $Ca(OH)_2$
d_{CH}	density of $Ca(OH)_2$
C_{p0}	calcium concentration of hydration products at early stage
C_p	calcium concentration of hydration products
K_{CaCO3}	solubility of $CaCO_3$
M_{CC}	molecular weight of $CaCO_3$
d_{CC}	density of $CaCO_3$
F	penetration resistance
γ	surface tension of mercury
θ	cosine of the contact angle
P	pressure
A	area
Pw	water pressure
Csw	concentration of sea water
b_L	value of parameter b under lower sea water concentration
b_H	value of parameter b under higher sea water concentration
C_L	lower sea water concentration
C_H	higher sea water concentration
d_{Csw}	deterioration depth under corresponding sea water concentration
a	a constant of prediction equation
b	a variable of prediction equation

Chapter 1 INTRODUCTION

1.1 Backgrounds

Cement stabilization techniques have been developed and applied widely in practice for on land and marine constructions in the world because of its economic and efficiency, such as stabilizing foundation ground or embankments, reducing settlement, preventing liquefaction of ground and so on.

There are numerous studies on the physical and mechanical properties of stabilized soil, the interaction between stabilized soil and original soil, design and execution methods, and quality control and assurance. In recent years, the study on durability of stabilized soil in corrosive environment becomes an international highly attention objects (Han 2009).

Durability can be defined as the ability of a material to retain stability and integrity over years of exposure to the destructive forces of weathering, is one of the most important properties. The unconfined compressive strength of soil cement mixtures has been extensively used to characterize their mechanical properties, which are the basic materials properties used in the analysis and design of foundation. Two ASTM standard test methods are available to evaluate durability of soil-cement mixtures: wetting and drying, freezing and thawing. To assure the mixture has the potential to perform satisfactorily in the field it should satisfy criteria based on both durability and strength (Shihata and Baghdadi 2001).

The research in this thesis is focusing on long-term durability of cement stabilized soils in sea water environment.

Filed investigations and laboratory tests found that deterioration process can weaken the durability of cement stabilized soils.

Stabilized Ariake clay used for the dike foundation located in Kyushu Island, Japan plays a very important role in surroundings of drainage basin to protect the resident area from flooding due to heavy rain. 20 years of construction, a leaking from the stabilized layer is found at the toe of dike and form swamps in the surrounding area. This leakage will gradually damage the durability dike foundation and further threatening the human activities and life safety (Hara et al. 2008).

Degradation of nowadays environment due to industrialization, for instance, the acidification of rain is one of the environmental factors affect engineering properties of cement stabilized soils, the cement stabilized soils in general a high alkalinity which can be neutralized by acid rain over a long period of time, the neutralization causes decomposition of hydration products which weakens the durability of cement stabilized soils and causes economic losses of society (Kamon et al. 1996). The Na^+ and SO_4^{2-} in the surrounding environment of cement-soil piles may affect the mechanical properties of cemented soil, which may cause some serious damage to structures (Han and Bai 2010).

There are failure cases of cement deep mixing method application in coastal cities of China due to the deterioration caused by aggressive ions in sea water.

Cement mixing method once applied for stabilization of soft clay in Jiaozhou Bay, Qingdao, China. The stabilized soil-cement exhibited a failure of low strength. This issue has been one of my research targets during master degree. The soft clay in Jiaozhou Bay is a type of chlorine saline soil with a pH value of 8.40. In previous study fly ash was introduced as a countermeasure for this issue. However, explore the applicability of cement mixing method in such alkaline soil and overcome the strength growth and integrity defects in such kind of soil are necessary in future research.

Deep mixing technology was used to treat the soft clay ground distributed widely in the Lianyungang District of Jiangsu Province, China. Several test sections were constructed at the Lianyungang-Yancheng Expressway in which cement was used to treat the soft clay. However, the bearing capacity of the cement-treated foundation was founded to be lower than the expected (Xing et al. 2009). A mineral analysis for the cement-treated soft clays indicated that these soils contain much higher content of Mg^{2+}, Cl^- and SO_4^{2-} than common soft clay soils. It was postulated that the lower bearing capacity was caused by the high salt content. It is urgent to clarify the mechanism of deterioration on cement stabilized soils exposed to salt-rich environment. The achievement can be the theoretical basis for future application of cement deep mixing method.

Durability issue of cement-based materials in others scopes:

Durability-performance evaluation for concrete is urgently demanded in connection to its application to radio-active waste repository which needs ultra long-term durability.

Common concrete structures also require an advanced method for minimizing the life-cycle cost.

Long term durability of marine concrete, unexpected early deterioration of concrete structures is becoming a serious social problem (Fukute and Hamada 1993).

Cement stabilization method has developed much from the beginning of its application, however, the design process with no consideration of long term durability so far. Nowadays, there is a tendency of economic in design which requires lower cement content and smaller pile diameter or bulk of soil-cement block in future (Hayashi et al. 2004a).The seawall foundation in Daikoku Pier at 20 years later strength is much higher than that of expected requirement. It is proved to be some waste of cement resource. The deterioration depth reaches 30 ~ 50 mm at the boundary exposed to original clay soil for 20 years (Ikegami et al. 2002), the deterioration effect on durability of foundation can be ignored in this case. So, it is necessary to consider the durability factor in design process for reducing the unnecessary economic losses of society.

In order to achieve the above targets, two aspects needed to be considered:

1) Explanation on the mechanism of deterioration process is a critical task currently.
2) It is necessary to propose a methodology for evaluating long-term durability of cement stabilized soils in sea water environment.

1.2 Framework and Outlines of the Thesis

The goal of this thesis is derived from the background. Cement stabilization methods often used for improving the performance of soft ground in coastal areas. So the cement stabilized soils always exposed to the original soft ground which is saturated with sea water. Except of the deterioration caused by sea water effect, the different pressure along the depth and the initial strength effects on durability of cement stabilized soils should be considered in practice.

The stabilization depth especially for deep mixing method always exceeds 10 meters in ground. The cement stabilized body will suffer different pressure at different depth in the ground which is saturated with sea water. According to previous researches the deterioration process is closely related to the diffusion of aggressive ions from outer to inwards. When the aggressive ions concentration in seawater is determined, the increased pressure can accelerate the diffusion of ions, which has been verified in study on behavior of concrete affected by sea-water under high pressure (Van Der Wegen et al. 1993), it indicated that high hydrostatic sea-water pressure increased the depth of sea-water penetration and the rate of swelling of the concrete, especially for ordinary Portland cement. It may be assumed that higher pressure leads to greater deterioration.

In addition, cement mixing in-suit with soft soils, there is no standard curing of the stabilized soils, the cement stabilized body exposed to the corrosive environment from the very beginning. So the strength increment and deterioration at boundary occurs simultaneously. In this thesis, most specimens are submerged into sea water environment directly after manufacture. Initial strength without standard curing nearly equals to zero, and the permeability decreased to very low values with increase of time. However, at the beginning which the initial strength is almost zero, the permeability may be lower than original soils but very high compared with 10^{-9} cm/s of completely hydrated cement stabilized soils, there is several orders of magnitude compare with 10^{-5} cm/s of original clay soils. This issue further amplifies the sea water pressure effect on deterioration of cement stabilized soils, especially at the short term of stabilization. It cannot be ignored during the application of cement mixing method in field.

Thus, the objectives of the thesis are:

1) First of all, the dissertation conducts targeted experiments to study the sea water pressure influence on deterioration process of cement stabilized soils. Based on the mechanical data the dissertation gives out an overview of pressure influence on deterioration under sea water environment.
2) Secondly, the dissertation tries to explain the mechanism of sea water pressure influence on deterioration process from microstructure, porosity and chemical constituent consideration.
3) Thirdly, the dissertation tries to predict the long term tendency of deterioration of cement stabilized soils under sea water environment in limited time. The method of increasing the salinity concentration of sea water is adopted to accelerate the deterioration process.

This dissertation consists of seven chapters. Chapter 1 outlines the issue of cement stabilization method in practical application especially in coastal area, where the ground is saturated with sea water. The cement stabilized soils corroded by aggressive ions in sea water. Moreover, it suffers different sea water pressure at different depth in the ground. In order to develop the application scale of cement stabilization methods and achieve the economic effectiveness, it is necessary to evaluate the sea water pressure influence on deterioration process of cement stabilized soils. In Chapter 2 a brief review about previous studies on deterioration of cement stabilized soils in various corrosive environments. It introduces evaluation methods on long term durability of cement stabilized soils. Empirical formula and numerical prediction methods have attempted to predict the long term tendency of deterioration of cement stabilized soils in previous studies, some prediction instances are listed in this chapter.

In Chapter 3, the methodology of research is described. This chapter introduces the test items and corresponding apparatus. The items involves mechanical properties of penetration resistance and unconfined compressive strength, chemical properties of calcium and magnesium ions concentration, and microstructure properties of scanning electronic image and porosity distribution. The procedure of preparing, analyzing specimen and the materials used in this dissertation are explained in this chapter.

Chapter 4 is the results and discussions of experiments. The sea water pressure influence on long term strength of cement stabilized soils is showed. A comparison between static sea water pressure less than 30 kPa and 100 kPa is conducted. The dynamic sea water pressure influence is considered which attempt to study the tide effect on underground water in coastal area. In addition, the properties of specimen with standard curing for 14 days then submerge into sea water are investigated which tries to compare with the specimen directly submerge into sea water condition.

Accelerating experiment results is list in this chapter, the salinity of curing sea water is 36 g/L in this dissertation which is approximate to natural sea water, the accelerating method increases the salinity of sea water in 2 time (72 g/L) and 3 times (108 g/L). The increasing concentration of aggressive ions in sea water can accelerate the diffusion rate and chemical reaction rate so that accelerate deterioration process.

In Chapter 5, mechanism of deterioration under various sea water pressure and salinity conditions is explained from point of chemical constituents and microstructure views. The atomic absorption test for calcium and magnesium variation with depth of specimen under various conditions explains the major cause of deterioration; the scanning electronic image observes the microstructures of deteriorated area and non-deteriorated area; the X-ray analyses the detailed chemical compounds included in each layer of the specimen which can verify the causes of deterioration.

In Chapter 6 gives out the prediction equations on long term deterioration tendency based on experiment data, and compares it with other prediction methods and verified by the investigation data in previous researches. In Chapter 7, the obtained results together with the conclusions are summarized. On the basis of the dissertation, future development of research work has been delineated in this chapter.

1.3 Original Contributions

Targeted study has been conducted in the research on evaluating the long term durability of cement stabilized soils under sea water environment. Therefore, the majority of the present works include following original contributions:

1) In Chapter 3 the mould is designed for one dimension deterioration which ensures the accuracy of relationship between deterioration depth and elapsed time. The specimen is submerged under sea water environment without any standard curing which simulates the in-situ cement stabilization of sea water saturated ground.
2) In Chapter 4 there is a preliminary understanding of water pressure influence on deterioration process of cement stabilized soils. The static and dynamic water pressures are considered in this dissertation. It is found that static water pressure obviously influences the deterioration process at short term. The dynamic water pressure influences the deterioration process both at short term and long term. The dynamic water pressure shows a greater degree of influence on deterioration than that of static water pressure. However, the impact degree is not proportional to the increasing of water pressure. Higher water pressure increases the depth of water penetrating into specimen. The results provide data basis for application of cement stabilization method in tidal zone. In addition, the water content distribution with depth of specimen in sea/pure water environment is investigated. It is found that the water content distribution with depth is in good consistency with strength distribution.
3) In Chapter 5 the deterioration mechanism of cement stabilized soils in sea water environment is explained from chemical and microstructure aspects. The results verified the calcium leaching phenomenon and formation of magnesium compounds. The magnesium ions influence on pozzolanic reaction is proved through analyzing the montmorillonite constitute. The further understanding of deterioration mechanism provides theoretical basis for proposing countermeasures to prevent deterioration of cement stabilized soils in sea water environment.

4) In Chapter 6 a predictive methodology on long term deterioration depth of cement stabilized soils in sea water environment is proposed based on experimental data under higher sea water concentration. The predicted results are verified through laboratory experiments. The proposed predictive methodology is time saving and laboratory feasible.

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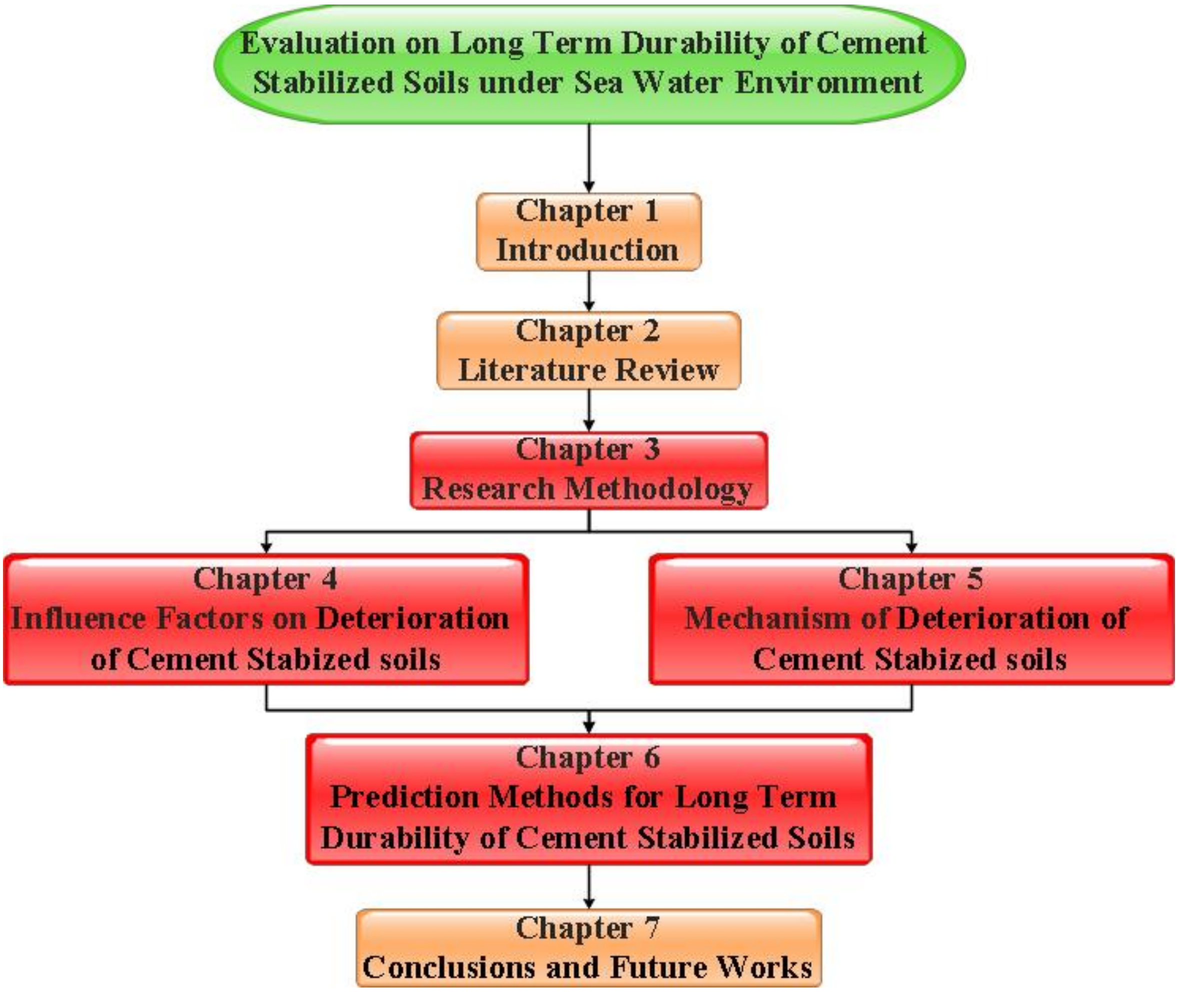

Figure 1.1 Flowchart of research

Chapter 2 LITERATURE REVIEW

2.1 Introduction

Cement stabilization methods has widely applied worldwide and its development has spread a long history. Until now, it is also an effective way to improve the performance of ground. From the beginning of its application, there are numerous and continuous studies on its mechanical properties, chemical reactions, structure development, long-term strength and so on.

This chapter reviews the previous literatures and summarizes the mechanism of deterioration process and the methodology of evaluation on deterioration of cement stabilized soils as much as possible.

First, the chapter introduces the classification of cement stabilized soil and clarified into two types: shallow mixing method and deep mixing method. Based on the “binder” or “additive” injected in a slurry or wet (W) form, or in a dry (D) state the mixing method can be classified into slurry type and powdery type. Based on the “binder” mixed with the soil via rotary energy only (R) or is the mixing enhanced by high pressure jet (J) grout type, the deep mixing method also refers to the jet grouting method.

The application of cement stabilized soils is introduced, for instance, applied for improving foundation ground for many types of structures (breakwater, quay wall, revetment, pier, man-made islands, tank, retaining wall, road, dike or embankment, liquefaction prevention and so on), it can also be used for temporary structures (cut-off wall, self retaining wall, underground brace and so on). Especially the patterns of application are listed: block-type improvement, wall-type improvement, lattice-type improvement, group column-type improvement and columns in contact-type improvement.

Second, the mechanism of deterioration is introduced from three aspects: 1) mechanism of strength increasing; 2) mechanism of deterioration; 3) evaluation methods on deterioration.

The deterioration process is a long-term phenomenon occurring in cement stabilized soils exposed to various corrosive environments. There exists two aspects of the strength development of cement stabilized soils simultaneously, one is that the strength increases inside as time becomes long; another is that the strength decreases at the periphery exposed to corrosive environment due to deterioration.

This chapter introduces the mechanism of strength increasing of cement stabilized soils, and summarizes the mechanism of deterioration process, mainly from calcium leaching phenomenon and aggressive ions reactions with stabilized soils aspects. Also, based on mechanism analysis, a number of evaluation methods of deterioration are proposed by previous researchers. This chapter clarified these methods into two types one is simplified method of prediction. The empirical formula proposed that the deterioration depth is proportional to the square root of elapsed time. It determines the proportional coefficient based on experiment data or investigation data in field to predict the deterioration depth of hundred or thousand years later. Another is numerical method of predicting deterioration, it consists of 4 models, namely, 1) ion migration model considering with the effect of other ions; 2) Ca adsorption model in surrounding soils; 3) dissolution model from hydrates and 4) carbonation model in stabilized soil. In this method, there is a need to input initial data like cement type, content, mixing proportion, properties of original ground, properties of improved ground and co-existed ions concentration, then conduct corresponding calculation of each model. Finally verify the accuracy of prediction method through comparing the calculated results with laboratory or field investigation data, further to achieve the prediction of deterioration on long term.

2.2 Cement Stabilized Soil Methods

2.2.1 Classification of cement stabilized soil methods

Cement stabilized soil method is a technique of mixing chemical binder with soil to improve the consistency, strength, deformation characteristics, and permeability of the soil. The improvement becomes possible by the ion exchange at the surface of clay minerals, bonding of soil particles and/or filling of void spaces by chemical reaction products. Although a variety of chemical binders has been developed and used, most frequently used binders nowadays are lime and cement due to their availability and cost. Lime/cement mixing method has been used to improve the properties of soils since old times. Deep stabilization of soft soils with lime and/or cement stabilized columns has been the subject of research in Sweden, Japan, and other countries for a very long period.

Ground improvement principle: densification of the ground by physical force; consolidation/dewatering through dewater the water in pore solution; admixture stabilization bonding of soil particles by chemical reaction. The last method is type of chemical stabilization technique. The detailed classification of cement stabilized soils methods is showed as Figure 2.1.

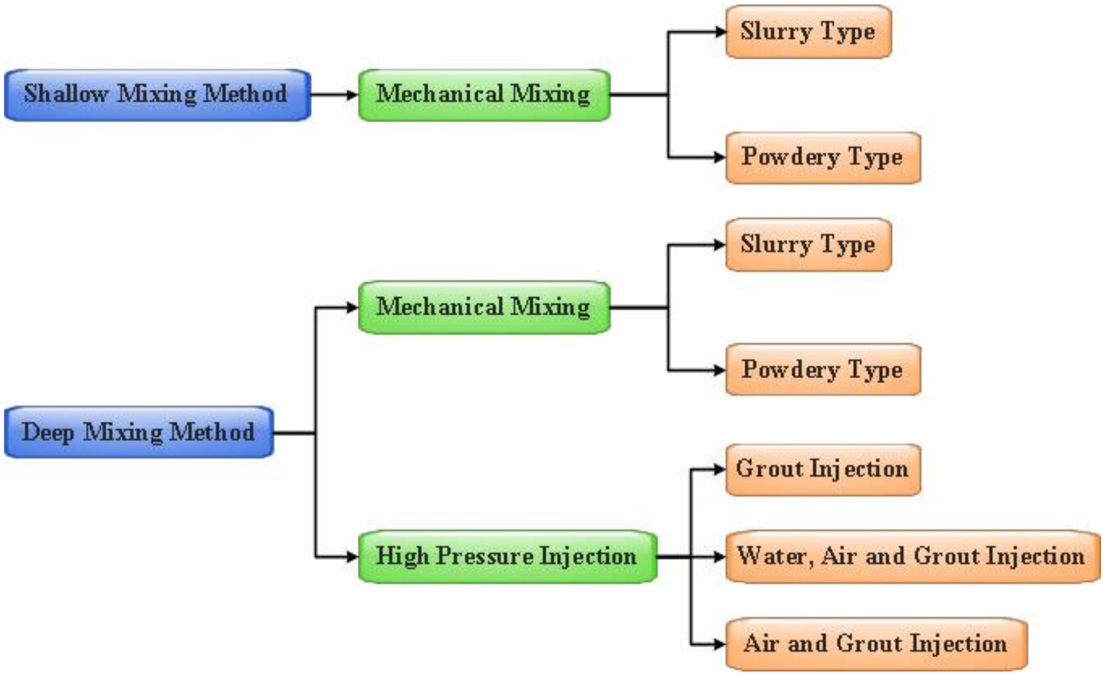

Figure 2.1 Classification of cement stabilized soil methods

2.2.2 Shallow mixing method

The purposes of improvement and applications of shallow mixing and hence the expected function of stabilized soil do not differ from those of deep mixing. However, when the depth of improvement is smaller than around 3 m, it is not efficient to use an ordinary deep mixing machine. For improvement of shallow depth, a simpler mixing tool such as bucket mixing, blade mixing and trencher mixing are preferred. These simpler machines originally developed for shallow mixing are sometimes used up to a depth around 10 to 13 m.

In the bucket mixing, a hydraulic excavator consisting of a boom, a bucket with mixing blades and a cab on a rotating platform is used. Several mixing blades are installed in the bucket, which rotate vertically to mix soil and binder thoroughly. The binder is usually spread on the ground surface at first and then mixed with the soil by the machine. The soil binder mixture can pass through the slatted plates on the rear of bucket, so that the machine can mix soil and binder thoroughly during excavation work.

In the blade mixing, a beam equipped with mixing blades is attached to the arm of a backhoe instead of the bucket. Two set of mixing blades are installed on the both sides of the beam. The beam is penetrated into the ground up to a depth of about 10 to 13 m while rotating the mixing blades vertically. During the penetration, binder slurry is injected from the outlets close to the mixing is blades and is mixed with the soil. A stabilized soil with rectangular parallelepiped shape is constructed by the procedure. Any shape of improved ground can be constructed by successive installations.

In the trencher mixing, a sort of chainsaw is used for mixing the soil and binder. The chainsaw cuts and disturbs the soil, so that the soils along the whole depth are mixed uniformly. The binder slurry is injected from the bottom end of the chainsaw together with compressed air to mix the soil and binder. The chainsaw can move vertically and horizontally, which can construct continuous stabilized soil wall and slab. The machine can stabilize the ground up to a depth of about 13 m for various purposes such as improving stability, constructing an impermeable wall and preventing liquefaction.

Shallow mixing was developed to improve soft and compressible soft, but also dredged sediment and waste deposits. The treatment depth is limited to a few meters. Shallow mixing is also a suitable method for in situ remediation of contaminated soils and sludge. In such application, the soils have to be thoroughly mixed in situ with an appropriate amount of wet or dry binders to ensure stabilization of the entire volume of treated material.

Dry shallow mixing is known as “mass stabilization”. It can be carried out with conventional lime-cement column equipment or by purpose-built machines. Laterally overlapping columns are created with upward and downward movements of one or several rotating mixing tools. This method is most cost-effective when using large-diameter mixing augers or multiple shaft arrangements, as practiced for example in the USA.

More recently, another method of mass stabilization has been developed in Finland. The Finish Road Administration initiated in 1992 a research project with the objective to develop a suitable and economical method to peat stabilization. The base machine is a conventional excavator, equipped with a mass stabilization mixer. The binder is fed to the mixing head while the mixer rotates and simultaneously moves vertically and horizontally within the stabilized soil block.

The mixing tools can have different shapes, for instance mixing/cutting heads equipped with blades rotating about a vertical or a horizontal axis. The diameter of the mixing tool is normally 600 to 800 mm, and the rotation speed lies between 80 and 100 rpm. The mixing pattern of mass stabilization is planned taking into account site specific conditions and capabilities of the mixing machine and the mixing tool. Usual practice is to stabilize in one sequence a block of soil within the operating range of the machine, typically corresponding to 8 to 10 m^2 in plan and 1.5 to 3 m in depth.

Common to the shallow mixing is that the operator controls the vertical and horizontal movement of the mixing tool. Hence both the degree of mixing and uniform binder delivery depends upon the skill of the operator to a larger extent in comparison with the deep mixing.

2.2.3 ***Deep mixing method***

Deep mixing refers to the blending of cement, lime, slag, and/or other binders in powder or slurry form to stabilize soil in-situ. Deep mixing methods may be classified into two categories in terms of binder injected state, namely: a) dry jet mixing methods and b) wet mixing methods.

1) Dry deep mixing method

Chida (1982) proposed a method that uses cement powder or quicklime instead of slurry called the ‘Dry Jet Mixing Method (DJM method).’ In this method, the cement or quicklime powder is injected into the deep ground through a nozzle pipe with the aid of compressed air and then the powder is mixed mechanically by rotating wings. In the DJM method, no water is added to the ground, and hence, a much higher improvement is expected than using slurry (Bergado 1994).

The dry jet mixing method (DJM) is a dry method of deep mixing, which was put into practice in 1980 and has been frequently applied to on-land works in Japan. The system of the method consists of a DM machine and the binder plant. The binder plant consists of a generator, air compressor(s), an air tank, a binder silo, binder feeder(s), and a control room. The DJM machine consists of a mixing tool and a crawler crane with a leader as a base carrier.

By the dry deep mixing, columns with a diameter of 0.5 to 1.2 meter can be manufactured to a depth of normally 15 to 25 meters. The mixing and monitoring process has been improved gradually and is today executed using electronic process control systems. The installation is carried out according to the procedure: 1) the mixing tool is correctly positioned; 2) the mixing shaft penetrates to the desired depth of treatment with simultaneous disaggregation of the soil by the mixing tool; 3) after reaching the desired depth, the shaft is withdrawn and at the same time, the binder in granular or powder form is injected into the soil; 4) the mixing tool rotates in the horizontal plane and mixes the soil and the binder; 5) completion of the treated column.

In Sweden, dry deep mixing, initially also known as the "lime column method" (because initially, lime only was used as binder), has been applied commercially since the mid 70-ies, mainly for the support of highway and railway embankments on soft, compressible clays, but also in organic clays and clayey silts.

2) Wet mixing method

Wet mixing method is a ground improvement technique that improves the characteristics of weak soils by mechanically mixing them with cementitious binder slurry. To construct columns, a powerful drill advances drill steel with radial mixing paddles located near the bottom of the drill string. The binder slurry is pumped through the drill steel to the tool as it advances and additional soil mixing is achieved as the tool is withdrawn. To perform mass wet soil mixing, or mass stabilization, a horizontal axis rotary mixing tool is located at the end of a track hoe arm.

The binder slurry is injected through a feed pipe attached to the arm. The process constructs individual soil-crete columns, rows of overlapping columns or 100% mass stabilization, all with a designed strength and stiffness. The technique has been used to increase bearing capacity, decrease settlement, increase global stability, and mitigate liquefaction potential for planned structures, tanks, embankments and levees. Wet soil mixing has also been used to construct in situ gravity retaining structures, and to facilitate tunnel construction or remediate the impact tunneling may have on nearby structures. Soil stabilization by wet soil mixing can provide structural support and/or it can greatly reduce lateral loads on bulkhead walls.

Wet soil mixing is best suited for soils with moisture contents up to 60 percent. Soft cohesive soils are usually targeted as other soil types can often be treated more economically with other techniques. If the moisture content is greater than 60 percent, dry soil mixing may be more economical. Soils vary widely in their ability to be mixed, depending on the soil type, strength, water content, plasticity, stratigraphy, and texture. Almost any soil type, including organics, can be treated with wet soil mixing although some soils may require significant binder and/or pretreatment. With wet soil mixing, treatment is possible to depths up to 100 feet. Depending on the soil type, excess soil-crete generated may range from 10 to 40 percent of the treated volume. Stiff soils and obstructions are sometimes predrilled ahead of the soil mixing process.

Mixing shaft speed, penetration rate, batching, and pumping operations are typically adjusted after constructing one or more test columns in a convenient area on site. Pre-production laboratory testing is used to prescribe mix methodology, energy, and the grout slurry system. Hayward Baker has developed proprietary special equipment and software for the real-time monitoring of all mixing parameters during the wet soil mixing process. Wet sampling in fresh columns and coring of cured columns can be used to verify strength. Test columns can be excavated for visual inspection of the soil-crete. Visual inspection is possible with a camera lowered into a core hole.

2.2.4 Jet grouting method

The jet grouting technique was developed in circa 1965 in Japan, inspired by the large-scale water jet used in coal mine excavation. In the method, a high-pressure pump is used to convey the binder through an injection pipe to a set of nozzles located just above the drill bit. The high-pressure fluids or binders are injected into the soil at high velocities. They break up the soil structure completely and replace/mix the soil particles in situ to create a homogeneous mass. This ground modification/ground improvement of the soil plays an important role in the field of foundation stability, particularly in the treatment of foundation ground under new and existing buildings; excavation support; seepage control in tunnel construction; and to solidification of contaminated soils and groundwater.

The jet grouting technique can be used regardless of soil type, permeability, or grain size distribution. It is possible to improve most soils, from soft clays and silts to sands and gravels by the jet grouting technique.

Jet grouting method consists in drilling a small diameter hole in the soil and injecting a pure cement grout at very high pressure (up to 600 bars), which breaks up and mixes with the soil matrix to form a column (or block) of "soil-crete". This method complements the other soil improvement techniques. Jet grouting can also be used to penetrate deep into the soil (up to 50 m) and make deep inclusions at the required depth of the compressible layer.

There are three jet grouting methods: single fluid jet grouting, double fluid jet grouting and triple fluid jet grouting. In the double fluid method, soil is excavated and filled by an air-coated grout jet. The triple-fluid method excavates soil with an air-coated water jet then mix/replace the soil with a separate binder slurry jet. The latter two methods rapidly spread nationwide in the 1970s. The jet grouting method was then exported to Europe and USA and was accepted worldwide by the 1980s.

2.2.5 Application of cement stabilized soil methods

Since above introduction, deep and shallow mixing methods have diversified, equipment performance has improved and processes become more complex. Electronic control and monitoring of the mixing process are today standard requirements. New binder combinations have been introduced.

Shallow mixing method is used extensively for infrastructure projects, which require the treatment of superficial layers of peat, mud or soft clay.

Deep mixing methods is extensively applied for improving foundation ground for many types of structures (breakwater, quay wall, revetment, pier, man-made islands, tank, retaining wall, road, dike or embankment, liquefaction prevention and so on), it can also be used for temporary structures (cut-off wall, self retaining wall, underground brace and so on). With advantages of improving the bearing capacity of foundation, shortening the construction period, preventing of uneven settlement, improving earthquake resistance, no pollute or contaminate the environment, lowering construction costs and enabling the reliable quality control. Patterns of applications include (Kitazume 2002):

1) Block-type improvement

In the block-type improvement, a huge improved soil mass is formed in the ground by overlapping every stabilized column. This improvement can achieve the most stable improvement, but the cost is rather higher than the other improvements. This type of improvement is normally applied to heavy permanent structures such as the port and harbor structures.

2) Wall-type improvement

In the wall-type improvement, the improved ground consists of long and short soil walls, where each wall is formed by overlapping every stabilized column. The long wall has the function to bear the weight of superstructures and other external forces and transfers them to the deeper rigid ground layer. The short wall has the function to combine the long walls in order to increase the rigidity of the total improved soil mass. In recent time this improvement has been commonly applied in port and harbor constructions because of its reasonable cost.

3) Lattice-type improvement

The lattice-type improvement is recognized as an intermediate type between the block-type improvement and the wall-type improvement. The stabilized columns are constructed so that a lattice-shaped improved mass is formed in the ground. This improvement has usually been applied to soil improvement under sea revetment, but recently it is also applied as a counter measure against ground liquefaction.

4) Group column-type improvement

In the group column-type improvement, many stabilized columns are constructed in rows with rectangular or triangular arrangements in the ground, where each column consists of several units of single soil columns linked together. In Japan, this improvement has been widely applied to relatively low embankments, foundations of light weight structures and temporary structures, in order to reduce settlement and/or to increase the stability.

5) Columns in contact type improvement

This is a modified method of the group column improvement, where stabilized columns are in contact with the adjacent columns without overlapping. This improvement has larger bearing capacity against horizontal forces than the group column-type improvement.

2.3 Deterioration of Cement Stabilized Soil

2.3.1 Mechanism of Strength Increasing

The increase in strength and decrease in compressibility of the soft ground based on the reaction of the clay with lime and/or cement through the processes of ion exchange and flocculation as well as pozzolanic reactions. The divalent calcium ions replace the monovalent sodium and hydrogen ions in the double layer surrounding each clay mineral. Thus, fewer divalent calcium ions are needed to neutralize the net negative surface charge of each clay mineral reducing the size of the double layer, and thus increasing the attraction of the clay particles leading to flocculated clay structure. Furthermore, the silica and alumina in the clay mineral react with the calcium silicates and calcium aluminate hydrates in process called pozzolanic reaction.

1) Hydration reaction

Cement is often used as an additive to improve the strength and stiffness of soft clayey soils. The fundamental mechanism of soil cement stabilization has been clarified by S. H. Chew et al. (2002), amongst others. The main ingredients of common Portland cement are tricalcium silicate ($3CaO \cdot SiO_2$), dicalcium silicate ($2CaO \cdot SiO_2$), tricalcium aluminate ($3CaO \cdot Al_2O_3$), and calcium ferrite aluminate ($4CaO \cdot Al_2O_3 \cdot Fe_2O_3$). The sum of $3CaO \cdot SiO_2$ and $2CaO \cdot SiO_2$ in the common Portland cement is approximately 65 to 85%. These four main constituents are major strength producing components. When the pore water of soil comes into contact with cement, hydration reaction of the cement occurs rapidly and primary cementitious products, namely hydrated calcium silicates (C-S-H), hydrated calcium aluminates (C-A-H) and hydrated lime $Ca(OH)_2$ are formed. The first two cementitious products are the primary cementitious products.

A secondary pozzolanic reaction between the hydrated lime and the silica and alumina from the clay minerals leads to the formation of additional calcium silicate hydrates and calcium aluminate hydrates (Kamruzzaman 2003; Nakarai et al. 2006).

When the Portland cement is mixed with soft soil, hydrolysis and hydration reaction take place at first, which can be expressed as follows:

$$2(3CaO\cdot SiO_2) + 6H_2O \rightarrow 3CaO\cdot 2SiO_2\cdot 3H_2O + 3Ca(OH)_2$$

$$2(2CaO\cdot SiO_2) + 4H_2O \rightarrow 3CaO\cdot 2SiO_2\cdot 3H_2O + Ca(OH)_2$$

$$3CaO\cdot Al_2O_3 + 6H_2O \rightarrow 3CaO\cdot Al_2O_3\cdot 6H_2O$$

$$4CaO\cdot Al_2O_3\cdot Fe_2O_3 + 2Ca(OH)_2 + 10H_2O \rightarrow 3CaO\cdot Al_2O_3\cdot 6H_2O + 3CaO\cdot Fe_2O_3\cdot 6H_2O$$

$$3CaSO_4 + 3CaO\cdot Al_2O_3 + 32H_2O \rightarrow 3CaO\cdot Al_2O_3\cdot 3CaSO_4\cdot 32H_2O$$

$$3CaO\cdot Al_2O_3 + Ca(OH)_2 + 12H_2O \rightarrow 3CaO\cdot Al_2O_3\ Ca(OH)_2\cdot 12H_2O$$

Hydrates production of $3CaO\cdot 2SiO_2\cdot 3H_2O$ (C-S-H) and $3CaO\cdot Al_2O_3\ Ca(OH)_2\cdot 12H_2O$ (C-A-H) forms a gridding framework enwrapping soil particles. As a result, the strength of soil-cement is enhanced.

2) Cation exchange and flocculation-agglomeration

The clay particles carry a net negative charge on their surface. Large negative charges are derived from larger specific surfaces. In the cation exchange and flocculation-agglomeration reactions, the monovalent cations generally associated with clays are replaced by the divalent calcium ions. The cations can be arranged in a series based on their affinity for exchange:

$$Al^{3+} > Ca^{2+} > Mg^{2+} > NH_4^+ > K^+ > Na^+ > Li^+$$

Any cation can replace the ions to its right. For example, calcium ions can replace potassium and sodium ions from clay. Flocculation-agglomeration produces a change in the texture of clay soils. The clay particles tend to clump together to form larger particles, thereby (a) decreasing the liquid limit, (b) increasing the plastic limit, (c) decreasing the plasticity index, (d) increasing the shrinkage limit, (e) increasing the workability, and (f) improving the strength and deformation properties of a soil.

The ionized Ca^{2+} exchanges with Na^+ and K^+ adsorbed in soil particles to reduce the thickness of electric layers so that soil particles become closer. This process leads to an increase in the pH value.

3) Pozzolanic reaction

The strong bases react with the soil silica and alumina (which are inherently acidic) both from the clay minerals and amorphous materials on the clay particle surfaces, in a manner similar to the reaction between a weak acid and a strong base. The hydrous silica and alumina will then gradually react with the calcium ions liberated from the hydrolysis of cement to form insoluble compounds (secondary cementitious products), which hardens the stabilized soil. This secondary reaction is known as the pozzolanic reaction.

The active Al_2O_3 and SiO_2 are dissolved to react with the residual Ca^{2+}. This reaction produces C-S-H and C-A-H as follows:

$$SiO_2\ (Al_2O_3) + Ca(OH)_2 + nH_2O \rightarrow CaO \cdot SiO_2 \cdot (n+1)H_2O\ (CaO \cdot Al_2O_3 \cdot (n+1)H_2O)$$

4) Carbonation

Carbon dioxide from air can react with the calcium hydroxide in cement stabilized soil. This process is called carbonation which is essentially the reversal of the chemical process of calcinations of lime taking place in a cement kiln. Carbonation is a slow and continuous process progressing from the outer surface inward, but slows down with increasing diffusion depth. The reaction products $CaCO_3$ is insoluble in water which increasing the strength of cement stabilized soils:

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3\downarrow + H_2O$$

Carbon dioxide continues to react with other hydration products and increases the amount of $CaCO_3$ as followings:

$$3CaO \cdot 2SiO_2 \cdot 3H_2O + CO_2 \rightarrow CaCO_3\downarrow + 2(CaO \cdot SiO_2 \cdot H_2O) + H_2O$$

$$(CaO \cdot SiO_2 \cdot H_2O) + CO_2 \rightarrow CaCO_3\downarrow + SiO_2 + H_2O$$

Carbonation has two effects, namely, it increases mechanical strength and impermeable ability of cement stabilized soil, but it also decreases alkalinity, which is essential for hydration reaction and pozzolanic reaction.

However, because of its low content in surrounding original soils and slow reaction rate, it can be ignored in practical engineering.

2.3.2 Mechanism of Deterioration

It is significant to clarify the mechanism of deterioration in point of geotechnical and environmental engineering view. Deterioration is an interaction between cement or/and lime stabilized soils and surrounding environment. The property of the contacted environment media is an external factor to influence the deterioration progress. Various investigations on deterioration of stabilized soils have been conducted on laboratory scale and field scale.

1) Calcium leaching phenomenon

Field investigation on deterioration of bridge abutment foundation 17 years after construction at Hokkaido (Hayashi et al. 2004b) confirmed that calcium liquates out from cement stabilized column to surrounding original soil which may lead to strength reduction at the periphery of column.

The bridge abutment foundation stabilized by Dry Jet Mixing method of plover arrangement piles with a diameter of 1 meter a length of 8 meters. Stabilization binder is blast-furnace slag Portland cement B type, the details of ground improvement is listed in Table 2.1.

Table 2.1 Ground improvement construction record

Construction	DJM method	Binder factor	Upper 3 m	290 kg/m^3
Year	1984		Lower 5 m	130 kg/m^3
Diameter	1.0 m	Injection type	Inject at retrieval process	
Deep	8.0 m	Penetration rate	1.3 m/min	
Designed strength	265 kPa	Retrieval rate	Upper 3 m	0.5 m/min
Improvement ratio	50 %		Lower 5 m	0.9 m/min
Cement type	Blast-furnace slag Portland cement	Rotation round	Penetration	24 rpm
			Retrieval	48 rpm

Investigation samples boring from centre, inter space between adjacent columns and untreated soils separately, conduct for needle penetration test, unconfined compressive test and atomic absorption spectrometry measurement. The results indicate that the calcium oxide distribution consistent with unconfined compressive strength distribution. Calcium oxide concentration in untreated soils near periphery of column is 5 times of that far away from column. It verifies that calcium ions leach from cement stabilized soil to surrounding original soils, which may be one cause of strength reduction at periphery of column.

Laboratory investigation on mechanism of deterioration from point of porosity distribution view was conducted by Hayashi et al. (2004). Test samples in laboratory adopt same soils (Table 2.2) in field site at Hokkaido and Blast-furnace slag Portland cement B type, two binder factors: 50, 290 kg/m^3, where 290 kg/m^3 samples can satisfy the designed strength (265 kPa). Samples are exposed to tap water environment directly after preparation, until designed age conduct needle penetration test and atomic absorption measurement. Porosity distribution of 0~10 mm part from exposure surface and 100 mm from exposure surface part were measured through mercury intrusion porosimetry. Test results show that calcium oxide (CaO %) content near exposure surface is lower and there is an increase of large pores volume. The porous phenomenon can lead to an increment of permeability coefficient which will speed up the deterioration process. The study also verified that low strength cement stabilized matrix (50 kg/m^3) tends to be deteriorated under tap water environment.

Table 2.2 Physical properties of in-situ disturbed original soil

Gravity ρ_s (g/cm^3)	Liquid limit w_L (%)	Plastic limit w_P (%)	Granularity		
			Sand (%)	Silt (%)	Clay (%)
2.679	44.5	28.6	31.7	45.3	23.0

Field and laboratory investigations indicated that the leaching of calcium caused by diffusion, the calcium ions transport from high concentration (cement stabilized soils) to low concentration (tap water environment), which leads to dissolution of calcium hydroxide and C-S-H gel, so a coarse pore structure in cement stabilized soils, finally leads to strength reduction.

Field investigations on long-term strength of cement stabilized soils were conducted at Daikoku Pier of Yokohama in Tokyo bay (Ikegami et al. 2002), it is a seawall construction surrounding new reclaimed land, which construction was started in 1971 and reclamation was completed in 1990. There are 25 berths in this pier. The foundation ground for 9 berths, called T1 ~T9 berth, were improved by CDM method as seawall foundation. This is the site where the wet method of deep mixing was first applied in large scale by Port and Harbor Bureau, Japanese Ministry of Transport (currently, Ministry of Land, Infrastructure and Transport). The test site is located at the end of T2 berth. The original ground at T2 berth was thick clay layer from elevation -12 to -70 m overlying bedrock of mudstone. The layer from sea bottom to around El. -50 m is soft alluvial clay. The ground improvement was applied to increase shear strength of soft alluvial clay for stability of seawall. The binder used was the ordinary Portland cement with binder factor of 160 kg/m^3. The deep mixing machine used had eight shafts. The clay ground was improved to depth of El -49 m as massive block with 57 m in length and 35.9 m in thickness. The improved ground is a floating-type structure, which bottom remains in the soft ground. Boring are conducted to obtain undisturbed core samples for investigation after 20 years of construction, needle penetration test and atomic absorption measurement results verified that strength reduced at the boundary surface of stabilized soil, the progress of deterioration in past 20 years is around 30 to 50 mm in depth from the boundary. It is evident that Ca leaching phenomenon from stabilized soil to original soil. The strength reduction is closely related to calcium leaching.

(Kitazume et al. 2002) conducted a serious of laboratory test to investigate deterioration process of stabilized soils. Samples in experiment exposed to different environments up to two years to determine the possibility of deterioration.

The soil used is Kawasaki marine clay, its properties is listed in Table 2.3. Ordinary Portland cement was used as binder with a binder factor of 30 % (dry weight ratio). The water content of the clay was adjusted to 160 % and mixing with binder, after 2 weeks standard curing the samples are placed in three different environments (artificial sea water, original clay soils and fresh water). Until designed age, the samples were taken to conduct unconfined compressive test, needle penetration test and atomic absorption spectrometry measurement.

Table 2.3 Major characteristics of Kawasaki marine clay

Gravity ρ_s (g/cm^3)	Liquid limit w_L (%)	Plastic limit w_P (%)	Granularity		
			Sand (%)	Silt (%)	Clay (%)
2.688	83.4	38.6	2.8	44.9	52.3

The study found that the strength reduction is associated with the leaching of Ca from the stabilized soils, which is same as above investigations in field and laboratory.

Until now, the possible one reason of strength reduction of stabilized soils at long-term is the deterioration caused by calcium leaching phenomenon. However, it is still necessary to conduct further research on mechanism of deterioration, calcium leaching explanation is just an initial recognize about deterioration progress. Previous investigations (Terashi et al. 2006, Ikegami et al. 2004) indicated that the depth of deterioration is in an order of sea water > clay soils > fresh water. If the calcium leaching process is controlled only by diffusion, the diffusion rate is in an order of fresh water > sea water considering the ions concentration gradient, but the test results showed the fact that sea water environment influence more seriously on deterioration of stabilized soils than fresh water environment, this indicates that only explain deterioration progress from calcium leaching phenomenon is not comprehensive. The associated aggressive ions in sea water must influence the deterioration process simultaneously. Clay soils is a complicated media itself, the minerals composition, water content and so on will influence the interaction between stabilized soils and surrounding original soils. So researchers gain different results on deterioration of stabilized soils exposed to various clay soils environment (Terashi et al. 1983, Kitazume et al. 2003). It is a challenge to clarify the mechanism of deterioration of stabilized soils exposed to various original soils.

Investigations on long-term deterioration of cement-based improved soil were conducted by (Saito et al. 2005). The investigated site is composed of complex soil layers with groundwater level of -1 m, porous Cl^- concentration is 16000 mg/l of in-situ ground, the details of in-situ soils is listed in Table 2.4, ground improvement columns were arranged in lattice patterns for countermeasure of liquefaction. Binder usage is blast-furnace slag Portland cement with a binder factor of 200 kg/m^3, water to cement ratio is 100%, improved depth reached GL -20 m. The construction was finished in 1995 year, 7 years later conducted boring for investigation. The samples were tested for pH, needle penetration resistance distributions, EPMA (Electron Probe Micro Analyzer) for elements distributions and X-ray, SEM, thermal analysis for hydrate products in both deteriorated and sound parts. The test results indicated that the deterioration depth of cement stabilized clayey soils reached 10~15 mm from the exposed surface, pH value decrease to 8.1~10.5 compared with sound part 10.5~11.0.

Table 2.4 Characteristics of in-situ soils

Soil classification		Clayey soil	Gravel soil
Gravity	ρ_s (g/cm^3)	2.702	2.643
Moisture content	(%)	66.2	18.7
Granularity (%)	Gravel 2~75mm	1.3	37.7
	Sand 75μm~2mm	5.0	58.8
	Silt 5~75μm	35.6	2.3
	Clay <5μm	58.1	1.2
Liquid limit (%)	w_L	89.5	NP
Plastic limit (%)	w_p	31.4	NP
Plastic index	I_p	58.1	NP

Calcium oxide (CaO) and chloride (Cl) reduced at deteriorated part, but magnesium oxide (MgO) increased, and sulfur oxide (SO_3) showed no change. The deterioration depth of cement stabilized sandy soils was 8~10 mm, with a reduction of pH, CaO and Cl, an increment of SO_3, no change of MgO. It verified the hydrated products of monocarbonate (AFm $3CaO \cdot Al_2O_3 \cdot CaCO_3 \cdot 12H_2O$) existed at deteriorated part of stabilized clayed soils, ettringite (AFt $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$) at deteriorated part of stabilized sandy soils. The investigation verified pH, CaO, strength reduction due to deterioration, which may be caused by calcium leaching and sulfate reaction with existed hydration products.

Hara et al. (2010) conducted a series of laboratory investigations on the property changes of lime/cement treated soil under sea water environment. The cement (lime) stabilized soil was Ariake clay soil, its characteristics is listed in Table 2.5. Ordinary Portland cement (lime) was adopted as binder with a binder factor of 70 kg/m^3 (35 kg/m^3), the initial water content of clay was adjusted to 1.5 times liquid limit (270.5%) before mixing with cement binder, the mixture was poured into plastic mould with a diameter of 50 mm and a height of 100 mm, then sealed and cured under air condition, 28 days later cured under sea water environment with NaCl concentration of 0, 5, 10, 20, 40 g/L separately. Until designed age conduct cone (φ= 6mm; tip angle = 60°) penetration test, pH test and element analysis.

Table 2.5 Characteristics of Ariake clay soil

	Cement stabilization	Lime stabilization
Moisture content (%)	217.3	195.2
Gravity ρ_s (g/cm^3)	2.69	2.69
Liquid limit w_L (%)	180.3	163.1
Plastic limit w_p (%)	51.4	47.1
Gravel	0.0	0.0
Sand	0.3	0.2
Silt	25.7	24.7
Clay	74.0	75.1

The laboratory studies indicated the same tendency as above field investigation on deterioration phenomenon of cement stabilized soils, namely, the reduction of pH and Ca content, the higher NaCl concentration the larger degree deterioration. The deterioration depth of lime stabilized soil in 168 days is 2.9, 10.7, 15.0, 21.1 and 28.9 mm corresponding to the curing sea water of NaCl concentration 0, 5, 10, 20, 40 g/L. In addition, reduction of Ca content is consistent with the increment of Mg content at deteriorated part of lime stabilized soil. Forgoing descriptions of laboratory and field investigations on deterioration of cement stabilized soils on long-term indicate that calcium leaching phenomenon may be one significant cause of deterioration, however, the surrounding media contacted with stabilized soil usually complicated, various aggressive ions such as Mg^{2+}, SO_4^{2-}, Cl^- and so on can also induce or accelerate the deterioration process, their influence on deterioration of stabilized soils can be ignored, the previous studies on aggressive ions influence on deterioration are given followings.

2) Reactions between aggressive ions and cement stabilized soils

Cement stabilized soils is formed by mixing through of cement with in-situ soils, it generally have high water-to-cement ratios and contain large voids, aggressive soils (organic soils) or aggressive ions such as Mg^{2+}, SO_4^{2-}, Cl^-, H^+ in pore water of surrounding environment (sea water intrusion, acid rain, industry pollutions and so on) corrode the cement stabilized soils easier.

a) Sulfate reaction with stabilized soils

Sulfate can react with calcium hydroxide $Ca(OH)_2$ to produce gypsum ($CaSO_4 \cdot 2H_2O$):

$$Ca(OH)_2 + H_2SO_4 = CaSO_4 \cdot 2H_2O$$

The gypsum crystals in pores of cement stabilized soils to generate expansion stress. Meanwhile the gypsum takes chemical reaction with hydrated calcium aluminates (C-A-H) to generate ettringite crystallizing resultants (Liu et al. 2006):

$$3CaO \cdot Al_2O_3 \cdot 6H_2O + 3(CaSO_4 \cdot 2H_2O) + 19H_2O = 3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 31H_2O$$

When such crystallizing resultants are large enough, the inflating force would be greater than the sticking force within the cement stabilized soils, so cracks may bring about in the cement stabilized soils and the strength would be reduced. Therefore, the SO_4^{2-} corrosion to cement stabilized soils is a sort of crystallizing corrosion.

Ettringite is known as one of the main substances responsible for severe cracking of cement paste and resultant deterioration of concrete (Ouhadi and Yong 2008). Chemical interactions involved in ettringite formation during lime (CaO or $Ca(OH)_2$) stabilization of soil are given in summary, using information from Hunter (1988) and Ouhadi (1997) as follows:

$CaO + H_2O \rightarrow Ca(OH)_2$ (Hydration of quicklime)

$Ca(OH)_2 \rightarrow Ca^{2+} + 2(OH)^-$ (Ionization of calcium hydroxide; pH rises > 12.3)

$Al_2Si_4O_{10}(OH)_2 \cdot nH_2O + 2(OH)^- + 10H_2O \rightarrow$ 2(Nakarai et al.) + nH_2O (dissolution of clay mineral, at pH > 10.5)

$M_xSO_4 \cdot nH_2O \rightarrow XM^{Y+} + SO_4^{2-} + nH_2O$ (dissolution of sulfate minerals; $x=1$, $y=2$ or $x=2$, $y=1$)

Sulfate (from soil or groundwater)

+ Aluminum compounds (released from the clay)

+ Calcium (from hydrated lime or quicklime)

→ calcium-aluminum sulfate (ettringite)

$6Ca^{2+} + 2Al(OH)_4^- + 4OH^- + 3(SO_4)^{2-} + 26H_2O \rightarrow Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O$ (formation of ettringite)

b) Magnesium reaction with stabilized soils

High concentration of magnesium salts in ancient sea water or pore water solution in foundation mainly compounds are magnesium sulfate ($MgSO_4$) and magnesium chloride ($MgCl_2$). The reactions between magnesium salts and cement stabilized soils are as following:

$$Ca(OH)_2 + MgSO_4 + 2H_2O = CaSO_4 \cdot 2H_2O + Mg(OH)_2$$

$$Ca(OH)_2 + MgCl_2 = CaCl_2 + Mg(OH)_2$$

The solubility of $CaCl_2$ is greater than $CaSO_4$ and $Ca(OH)_2$, which explains the calcium leaching phenomenon. The solubility of $Mg(OH)_2$ (brucite) is lower, so it accumulates in pores and interspacing of cement stabilized soils and plays a role of filling. However, brucite has lower strength it disperses among hydrated calcium silicate (C-S-H) and reduces the gelatification of C-S-H, which reduces the strength of cement stabilized soils. In addition, $Mg(OH)_2$ has lower solubility than $Ca(OH)_2$. So Mg^{2+} firstly combines with OH^- to produce $Mg(OH)_2$ and then it replaces $Ca(OH)_2$ to carry out chemical reaction with active SiO_2, which can be expressed as following:

$$Mg(OH)_2 + SiO_2 \rightarrow MgO \cdot SiO_2 \cdot H_2O$$

Therefore, the Mg^{2+} replaces Ca^{2+} to produce low strength M-S-H ($MgO \cdot SiO_2 \cdot H_2O$) and restrains the formation of C-S-H, which can enhance the strength of cement stabilized soils.

c) Chloride reaction with stabilized soils

Sodium chloride (NaCl) is the major ingredient of sea water and highly exists in sea water intrusion ground, it can reduce the production of C-S-H since Cl^- combines with $3CaO \cdot Al_2O_3$ to produce $3CaO \cdot Al_2O_3 \cdot 3CaCl_2 \cdot 32H_2O$ without gelatinization. The process consumes Ca^{2+} and $Al(OH)_3$, and then restrain from the formation of C-S-H and

$Ca_6Al_2(SO_4)_3(OH)_{12}26H_2O$.

$$Ca(OH)_2 + 2NaCl \Leftrightarrow CaCl_2 + 2Na^+ + 2OH^-$$

$$3CaO \cdot Al_2O_3 + 3CaCl_2 + 32H_2O \rightarrow 3CaO \cdot Al_2O_3 \cdot 3CaCl_2 \cdot 32H_2O$$

The chemical reaction consumes much $Ca(OH)_2$ and then blocks the production of C-S-H and C-A-H. Therefore, Cl^- not only affects the strength of stabilized soils but also is a main factor influencing long-term strength of cement stabilized soils (Xing et al. 2009).

2.3.3 Evaluation Methods of Deterioration

1) Empirical formula prediction method

Ikegami et al. (2004) predicted long term deterioration depth of cement stabilized soils through following equations:

$$\log(D) = \log(D_0) + 1/2 \times (\log(t) - \log(t_0)) \tag{2.1}$$

$$D = D_0 \times (t/t_0)^{0.5} = A \times (t/1)^{0.5} = A \times (t^*)^{0.5} \tag{2.2}$$

Where, D_0 is deterioration depth at t_0 time, A is deterioration depth at t_0 =1 year, t^* is ratio of t to 1 year.

Hayashi et al. (2004) predict long term deterioration depth through following equation:

$$D = \alpha * t^{\beta} \tag{2.3}$$

Where, t is elapsed time (year), D is deterioration depth at time t (mm), α and β are constants.

Table 2.6 Investigations and prediction method on deterioration

Case	Exposure	Soil type	Binder	q_{u28} (MPa)	$D = \alpha * t^{\beta}$	
					α	β
This study	Tap water	Hokkaido clay	Blast-furnace B type	0.28	23.6	0.45
Terashi et al. (1983)	Sea water	Kawasaki clay	Ordinary Portland Cement	1.5	14.8	0.49
	Soils				8.0	0.38
Saito (1988)	Sea water	Yokohama port clay	Ordinary Portland Cement	4.8	8.0	0.55
	Soils				7.0	0.55
Kitazume et al. (2003)	Pure water	Kawasaki clay	Ordinary Portland Cement	0.5	13.1	0.51

Note: D is deterioration depth (mm), t is time (year).

The α equals to deterioration depth at elapsed time of 1 year, and β is about 0.5 in average according to previous investigation data. So, the deterioration depth is proportional to the square root of elapsed time. It is possible to predict long term deterioration depth through equation (2.3).

Hara et al. (2012) also adopted above empirical formula to predict long term deterioration:

$$d_n = A\sqrt{t} \tag{2.4}$$

Where, d_n is deterioration depth, A is deterioration coefficient, t is curing time.

In addition, the research assumed that Mg^{2+} ion diffusion is one cause of deterioration:

$$dd_n / dt = k \cdot C_{Mg} / d_n \tag{2.5}$$

Where, C_{Mg} is concentration of Mg^{2+}, the deterioration depth d_n = 0 at curing time t_0 = 0, k is proportional coefficient.

$$d_n = k\sqrt{C_{Mg} \cdot t} \tag{2.6}$$

$$k = A / \sqrt{C_{Mg}} \tag{2.7}$$

Table 2.7 The deterioration coefficient A

Concentration of Mg^{2+} (%)	Water to cement ratio W/C (%)		
	17.3	12.36	8.65
0.024	1.084	0.840	0.650
0.048	1.566	1.237	0.873
0.072	1.770	1.400	0.985

Here, the proportionality constant k is external and internal factor of deterioration of cement stabilized soils under sea water. Mg^{2+} ion concentration in sea water (k_{Mg}), water to cement ratio ($k_{W/C}$), temperature (k_T), soil type (k_S), binder type (k_{st}) are assumed.

$$k = k_{Mg} \cdot k_{W/C} \cdot k_T \cdot k_S \cdot k_{st} \tag{2.8}$$

Coefficient $k_{W/C} \cdot k_T \cdot k_S \cdot k_{st}$ is fixed, the coefficient k_{Mg} can be determined through C_{Mg} based on experimental data:

$$k_{Mg} = 1.075 - 1.552 C_{Mg} \tag{2.9}$$

$$d_n = (1.075 - 1.552 C_{Mg}) B \sqrt{C_{Mg} / 0.048 \cdot t} = (4.904 - 7.085 C_{Mg}) B \sqrt{C_{Mg} \cdot t} \tag{2.10}$$

The temperature in this study is 20 degree centigrade, soil type is Ariake clay and stabilized agent is ordinary Portland cement, so the value of $k_T \cdot k_S \cdot k_{st}$ is not studied here and equals to 1 and B is $k_{W/C}$ can be expressed by variable W/C. Two variables were introduced into the equation, namely, concentration of magnesium and water to cement ratio. The coefficient k can be represented through these two variables as equation (2.12).

$$k_{W/C} = 0.075W/C + 0.237 \tag{2.11}$$

$$d_n = (4.904 - 7.085C_{Mg}) \times (0.075W/C + 0.237) \times \sqrt{C_{Mg} \cdot t} \tag{2.12}$$

However, the scope of this prediction method, the magnesium ion concentration ranges from 0.024% ~ 0.072% (NaCl concentration: 10 ~ 30 g/L), W/C: 8.65 ~ 17.30 % (binder factor: 50 ~ 100 kg/m^3).

The simplified prediction method on deterioration originated from reinforced concrete structure exposed to sea water environment and concrete/cement paste for radioactive waste disposal. The leaching of calcium can be a matter of concern for the durability of concrete structures. It increases the porosity of the surface layer, and detrimentally affects the resistance of the material to mechanical loads. The leaching of calcium may have a negative influence on the long-term durability of various concrete structures. For instance, the phenomenon is critical in regards with the durability of nuclear waste containments for which the required service life ranges from a few hundred years to several thousand years. Several studies have clearly demonstrated that the leaching of calcium from cement-based materials is essentially a diffusion-controlled phenomenon.

(Adenot and Buil 1992; Buil et al. 1992) proposed a simplified numerical model governed by the laws of diffusion based on the assumption of local equilibrium between composition of the pore solution and hydrates. The transport of ions in the interstitial solution of cement hydrates has been considered as resulting from a diffusion process. No convection transport has been taken into account. It is found that in the case of a semi-infinite medium and uniform initial and constant surface conditions, the evolution of calcium loss follows a $\sqrt{t}$ law.

$$\eta = \frac{x}{\sqrt{t}} \tag{2.13}$$

The simplified model can fairly accurately describe the phenomenon of cement attack by an under saturated lime solution. It only needs a few parameters which are measurable by simple experiments. The model can be easily applied to different types of cements where the major hydrated constitutes is C-S-H, such as Portland, pozzolanic, or fly ash cements. A major drawback is that the model is limited to pure water or lime solution attacks.

Investigations on the durability of concrete exposed in marine environment (Fukute and Hamada 1993) introduce this simple model to predict the carbonation/deterioration depth

(Yamaji 2010). The carbonation depth can be easily monitored in field site, so it is chosen to be one important indicator for determining the deterioration degree.

The study gave out the regression lines between carbonation depth (Y) and deterioration depth (X) of other factors (Mg^{2+}, S, Ca, Si and Cl^-), then assumed $Y = X$ to calculated standard error S_e

$$S_e = \sqrt{\frac{\sum_{i=1}^{n}(X - Y)^2}{n - 2}} \tag{2.14}$$

Where, X is various factors (mm), Y is carbonation depth (mm), n is number of data. Through calculation the S_e value was the lowest one between magnesium erosion depth and carbonation depth. So it is determined the magnesium erosion depth as the indicator to predict the deterioration. The prediction based on the general theory that the erosion depth is a proportional to the square root of time, namely,

$$y = A\sqrt{t} \tag{2.15}$$

Where, y is objects erosion depth (mm), A is proportional coefficient (mm/year$^{0.5}$), t is time (year).

The coefficient A is dependent on cement type, water to cement ratio (W / C), service environment (tidal zone) and so on. The dissertation predicted the deterioration depth of 50 years later based on this model. However, accumulation of investigation data in field and laboratory scale is needed in future research.

2) Numerical prediction method

(Nishida and Ohishi 2004) propose a numerical prediction method on deterioration of cement stabilized soil in point of Ca leaching from cement stabilized soils to surrounding original soils view. The method consists of 4 models, namely, a) ion migration model considering with the effect of other ions; b) Ca adsorption model in surrounding soils; c) dissolution model from hydrates and d) carbonation model in stabilized soil, and the validity of this method was confirmed by comparing with the available field data.

a) Ion migration model

Ions of Ca^{2+}, Na^+, K^+, Mg^{2+}, Cl^-, OH^-, SO_4^{2-}, H^+, CO_3^{2-} in cement stabilized soils and surrounding original soils are considered in this model.

Nernst-Plank equation:

$$J_i = -k \cdot T \cdot \frac{B_i}{e \cdot Z_i} \cdot \left(1 + \frac{\partial \ln \gamma_i}{\partial \ln C_i}\right) \cdot \frac{\partial C_i}{\partial x} - B_i \cdot C_i \cdot \frac{\partial \phi}{\partial x} \tag{2.16}$$

Where i is ion specie, J is the flux of ions [mol/cm^2/sec], k is Boltzman constant [J/K], T is temperature, B is absolute mobility [cm^2/sec/V], γ is activity coefficient, C is ion concentration [mol/cm^3], x is distance from exposure surface [cm], e is elementary charge (=1.60×10^{-19}) [C], Z is the valence of ionic species, ϕ is electric potential [V]. The first item at right of equation is diffusion forced by ionic concentration gradient, and the second item is diffusing particles moved with respect to the fluid by electrostatic forces.

Activity coefficient γ is expressed based on Debye-Hückel equation:

$$\log \gamma_{i\pm} = -\frac{u \cdot |Z_+ \cdot Z_-| \cdot \sqrt{I}}{1 + v \cdot a_i \sqrt{I}} \tag{2.17}$$

Where $|Z_+ \cdot Z_-|$ is absolute value of the multiplied valence between anionic and cationic ion, u is constant (=0.5115) [mol$^{-1/2}\cdot$ $l^{1/2}$], v is constant (=0.3291) [mol$^{-1/2}\cdot$ $l^{1/2}$], a_i is ion size parameter [nm], I is ionic strength [mol/l].

$$I = \frac{1}{2} \sum_i \left(Z_i^2 \cdot C_i\right) \tag{2.18}$$

Now it needs to determine the value of a_i in Debye-Hückel equation, usually is 0.3 [nm], the simplified equation:

$$\log \gamma_i = -\frac{u \cdot Z_i^2 \cdot \sqrt{I}}{1 + \sqrt{I}} \tag{2.19}$$

Then partial differential by concentration can get following equation:

$$\frac{\partial \ln \gamma_i}{\partial \ln C_i} = \ln 10 \times C_i \times \frac{-u \cdot Z_i^4}{4 \cdot \sqrt{I} \cdot \left(1 + \sqrt{I}\right)^2} \tag{2.20}$$

Electrical Neutrality principle:

In any macroscopic sample of any aqueous solution, the sum of all the positively charged ion concentrations always equals the sum of all the negatively charged ion concentrations. An aqueous solution is always electrically neutral.

$$\sum_i \left(Z_i \cdot J_i\right) = 0 \tag{2.21}$$

So,

$$\frac{\partial \phi}{\partial x} = -\frac{\sum_i \left(\left(1 + \frac{\partial \ln \gamma_i}{\partial \ln C_i} \right) \cdot B_i \cdot \frac{\partial C_i}{\partial x} \right)}{\sum_i \left(Z_i \cdot B_i \cdot C_i \right)} \cdot \frac{k \cdot T}{e} \tag{2.22}$$

The flux of arbitrary ion specie is expressed as:

$$\frac{\partial \phi}{\partial x} = -\frac{\sum_i \left(\left(1 + \frac{\partial \ln \gamma_i}{\partial \ln C_i} \right) \cdot B_i \cdot \frac{\partial C_i}{\partial x} \right)}{\sum_i \left(Z_i \cdot B_i \cdot C_i \right)} \cdot \frac{k \cdot T}{e} \tag{2.23}$$

$$\begin{aligned} J_i = -k \cdot T \cdot \frac{B_i}{e \cdot Z_i} \cdot \left(1 + \ln 10 \times C_i \times \frac{-u \cdot Z_i^4}{4 \cdot \sqrt{I} \cdot \left(1 + \sqrt{I} \right)^2} \right) \cdot \frac{\partial C_i}{\partial x} \\ + \frac{k \cdot T \cdot B_i \cdot C_i}{e} \cdot \frac{\sum_j \left(\left(1 + \frac{\partial \ln \gamma_j}{\partial \ln C_j} \right) \cdot B_i \cdot \frac{\partial C_j}{\partial x} \right)}{\sum_i \left(Z_j \cdot B_j \cdot C_j \right)} \end{aligned} \tag{2.24}$$

Absolute mobility in engineering:

Evaluation for void ratio and tortuosity based on cylinder model and B_i is the absolute mobility in engineering:

$$B_i = \frac{\varepsilon}{\tau^2} \cdot B_{0,t} \tag{2.25}$$

Where ε is void ratio, τ is tortuosity (= $\sqrt{2}$), B_0 is absolute mobility in liquid [cm^2/sec/V].

b) Adsorption model

The calcium adsorption model is based on Freundlich adsorption equation:

$$C_{soil} = K_d \cdot C_{solu}^b \tag{2.26}$$

Here, C_{soil} (mg/kg) is adsorption Ca of unit clay particles, C_{solu} (mg/l) is concentration of Ca^{2+} in fine pore water, K_d is adsorption coefficient and b is constituents of clay particle and soil condition.

c) Calcium leaching model

There are two stages of calcium leaching from cement stabilized soils. One is the calcium leaching from $Ca(OH)_2$, the other is the calcium leaching from hydration products C-S-H. The second stage is beginning at the end of the first stage of calcium leaching. The balancing model of calcium ions in solid and liquid phases is showed in Figure 2.2.

When calcium leaching from Ca(OH)2, the concentration of calcium ions in liquid phase can be calculated as following equations:

$$C_{H^+} \cdot C_{OH^-} = K_W \tag{2.27}$$

$$C_{Ca^{2+}} \cdot C_{OH^-}^2 = K_{Ca(OH)_2} \tag{2.28}$$

$$\sum_i Z_i \cdot C_i = 0 \tag{2.29}$$

Where K_W is ion product constant of water 1×10^{-14}, $K_{Ca(OH)_2}$ is solubility product of Ca(OH)2 which equals to 5.5×10^{-6}. Equation 2.27 and 2.28 express the ion balance of H_2O and Ca(OH)2, when equation 2.29 represents the electrical neutrality condition.

The second stage which is calcium leaching from hydration products C-S-H, the calcium ion concentration can be calculated by balance model of calcium in solid and liquid phases which is based on the Ca/Si ratio of hydration products. Point A, represents the Ca/Si ratio at completed hydration condition with a value of 1.7 where the calcium ions leaching from Ca(OH)2 completely consumed (Figure 2.2). In addition, the Ca/Si ratio and calcium ion concentration at point B is determined by previous research data.

So, the leaching of calcium phenomenon induces the porosity of cement stabilized soil. It is said that 1 mol calcium leaching corresponds to 1 mol decreasing of Ca(OH)2 in form of unit volume. The equation in following can evaluate the void ratio of cement stabilized soils in consideration of unit volume.

$$\varepsilon = \varepsilon_0 + \frac{M_{CH}}{d_{CH}} \cdot (1 - V_c) \cdot (C_{p0} - C_p) \tag{2.30}$$

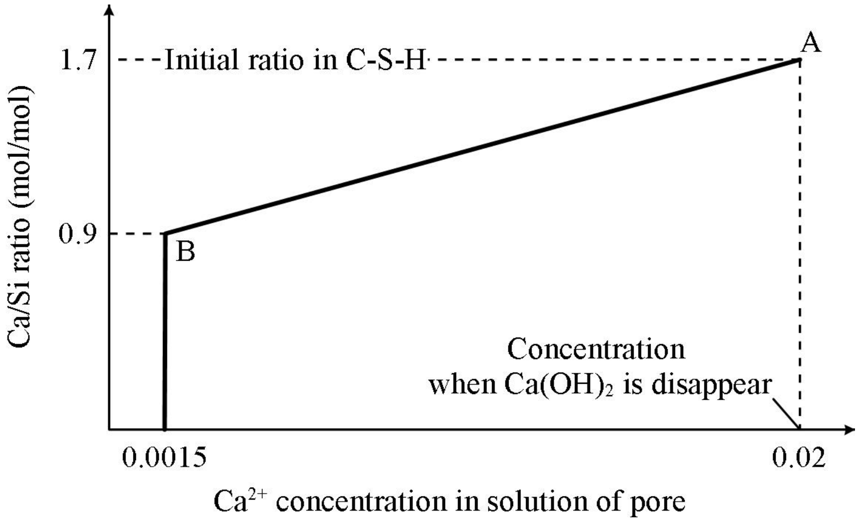

Figure 2.2 The local equilibrium between C-S-H and pore solution

Where ε_0 is early stage void ratios, M_{CH} is molecular weight of Ca(OH)$_2$ which equals to 74 g/mol, d_{CH} is density of Ca(OH)$_2$ which equals to 2230 g/l, V_c is volume ratio $V_c = 1/\left(d_c \times W/C + 1\right)$, d_c is density of cement with unit of g/l, W/C is water to cement ratio, C_{p0} is Ca^{2+} concentration of hydration products at early stage, C_p is Ca^{2+} concentration of hydration products.

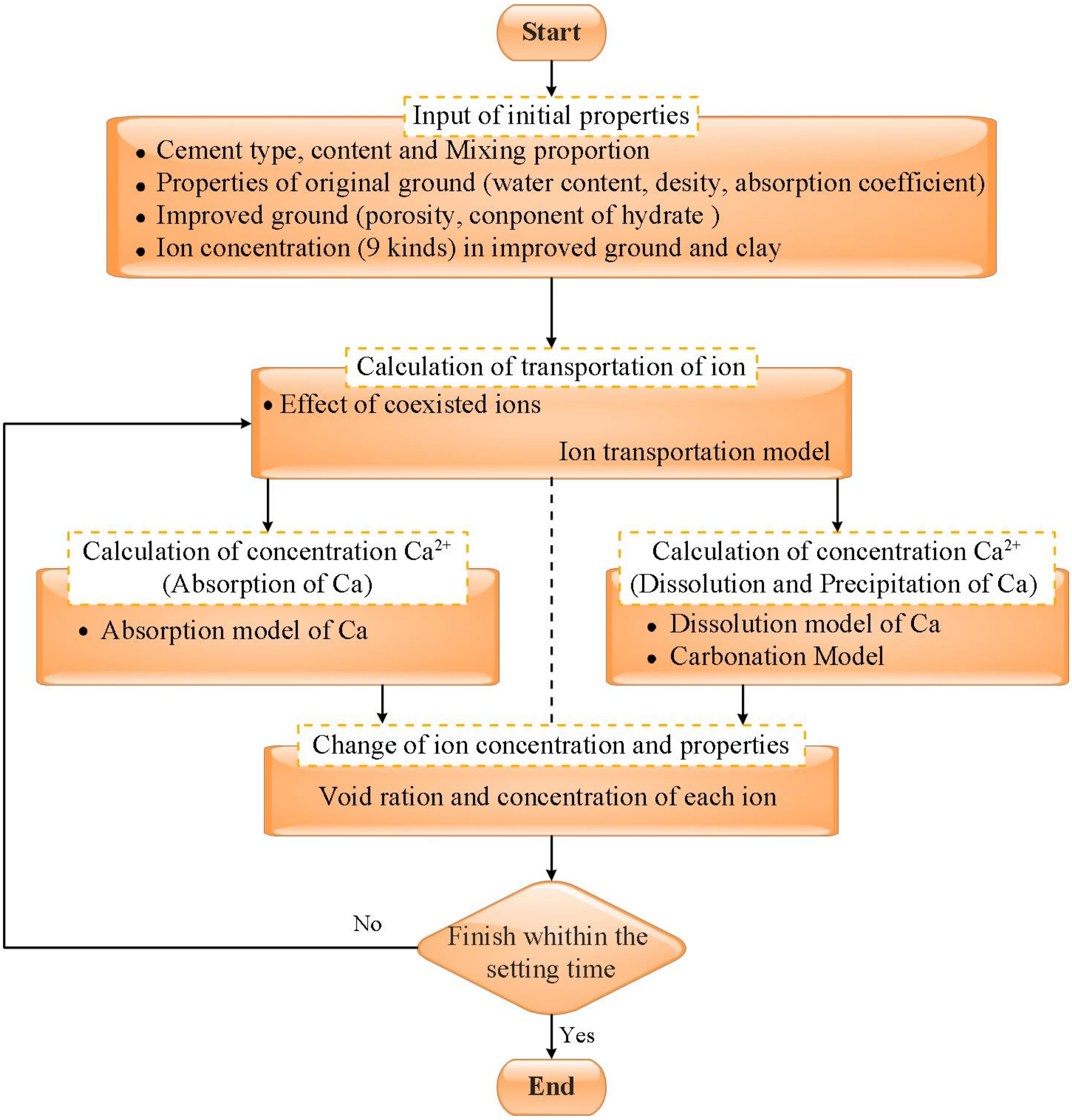

Figure 2.3 Procedure of numerical prediction method of calcium leaching

d) Carbonation model

The solubility of $C_{Ca} \cdot C_{CO_3} \geq K_{CaCO_3}$ condition, the precipitation of CaCO$_3$ is calculated by equation:

$$C_{Ca} \cdot C_{CO_3} = K_{CaCO_3} \tag{2.31}$$

Here, K_{CaCO_3} is solubility which equals to $1.0\times10^{-8.35}$ and 1 mol Ca^{2+} reacts with CO_3^{2-} precipitated 1 mol $CaCO_3$ which reduces the void ratio of stabilized foundation.

The void ratio per unit can be evaluated by following equation:

$$\varepsilon = \varepsilon_0 - \frac{M_{CC}}{d_{CC}} \cdot (1 - V_c) \cdot (C_p - C_{p0}) \tag{2.32}$$

Here, M_{CC} is molecular weight of $CaCO_3$ (=100) [g/mol], d_{CC} is density of $CaCO_3$ which equals to 2720 g/l. The Structure of numerical prediction method of calcium leaching is showed as Figure 2.3.

2.4 Summary

This chapter firstly introduces the clarification of cement stabilization methods and its application in engineering. Second, the previous researches on mechanism of deterioration of cement stabilized soils are summarized. Third, the developed prediction methods on long term deterioration under corrosive environment are clarified.

Based on the review of literatures it is necessary to propose a convenient and accurate methodology for evaluating the long term deterioration of cement stabilized soils. The originality of evaluation on deterioration is listed as following:

1) The convection transport of ions is considered through static and dynamic water pressure exposure experiments. In the diffusion-controlled kinetics model ($\sqrt{t}$ law), convection transport of ions has not been taken into account because the fact that the pores of hydrated cement are small enough to prevent thermal convection and the hydraulic pressure gradient is very low under the clay cover at the waste disposal site. However, the cement stabilized soils formed in ground saturated with sea water suffers different water pressures at different depths. The influence cannot be ignored especially at the beginning of stabilization which the permeability is high and the pores are not small enough to prevent thermal convection. The cement stabilized soils in tidal zone also suffers the cycling pressures time to time, namely, dynamic pressures. The investigation on deterioration of cement stabilized soil in this dissertation is close to the actual situation.
2) The deterioration process is time consuming and it is difficult to accurately access the experiment results at a long term. This dissertation proposes an acceleration method to achieve the prediction of long term deterioration in limited laboratory time.

Considering that the concentration gradient is an important factor on diffusion process, the study attempts to accelerate the deterioration process through increasing the ions concentration in sea water environment. The relationship between deterioration rate and sea water concentration helps to predict long term deterioration under natural sea water environment based on experiment data under higher sea water concentration in limited time.

The evaluation methodology in this dissertation is a good simulation of actual situation and laboratory feasible.

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Chapter 3 METHODOLOGY OF RESEARCH ON DETERIORATION OF CEMENT STABILIZED SOILS

3.1 Introduction

This chapter introduces the apparatus and materials used in this dissertation.

The apparatus involved can be clarified into three groups in term of its testing items. 1) Apparatus for physical behavior testing, include micro cone penetration, unconfined compression which test the penetration resistance distribution with depth and unconfined compressive strength of specimens; 2) Apparatus for chemical behavior testing, include atomic absorption spectrometry (AAS), energy dispersive X-ray (EDX) and X-ray powder diffractometer (XRD) which test the calcium and magnesium ions distributions with depth, Ca/Si ratio in solid phase and compound constitutes of specimens. 3) Apparatus for microstructure analyze, include scanning electron microstructure (SEM) and mercury intrusion porosimetry (MIP) which can analyze the microstructures and porosity of specimens. In addition, the procedures of apparatus operation and specimen preparation are introduced in this chapter.

The materials used in this dissertation include Ariake clay soils, Portland blast furnace slag cement B type, artificial sea water, in-situ sea water, moulds and curing chambers. The physical and chemical properties of Ariake clay soils are tested, the components of aggressive ions in pore water of Ariake clay soil and in-situ sea water are tested also.

The Portland blast furnace slag cement is selected as the major stabilizing agent during the study, and the advantage of this cement type is explained through the chemical reactions between clay, cement, slag and water. The specification of cement types are listed also.

The artificial sea water is prepared by mixing a certain amount (36g) ocean powder with one liter pure water thoroughly. The components of it are approximate to the natural sea water condition which can simulate the in-situ sea water environment.

The moulds and curing chambers are manufactured with perspex material which is corrosion resistant. The mould is designed specially which can allow the deterioration progress at one dimension. The procedure of making test specimen and curing methodology is clarified in details.

The procedure of analyzing prepared specimens is listed in as following:

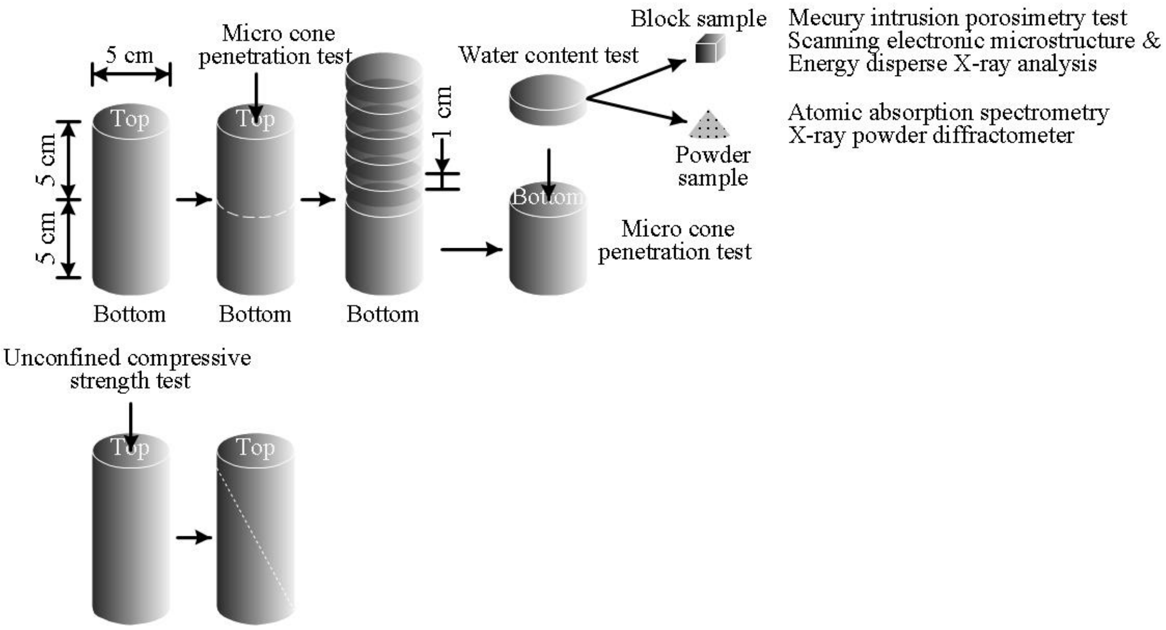


Figure 3.1 Procedure of analyzing prepared specimens

3.2 Apparatus

3.2.1 Equipment for Mechanical Behaviors Test

The apparatus for mechanical behaviors test consists of motor, load cell, micro cone penetrator/disk, displacement meter, data logger and personal computer (Figure 3.2).

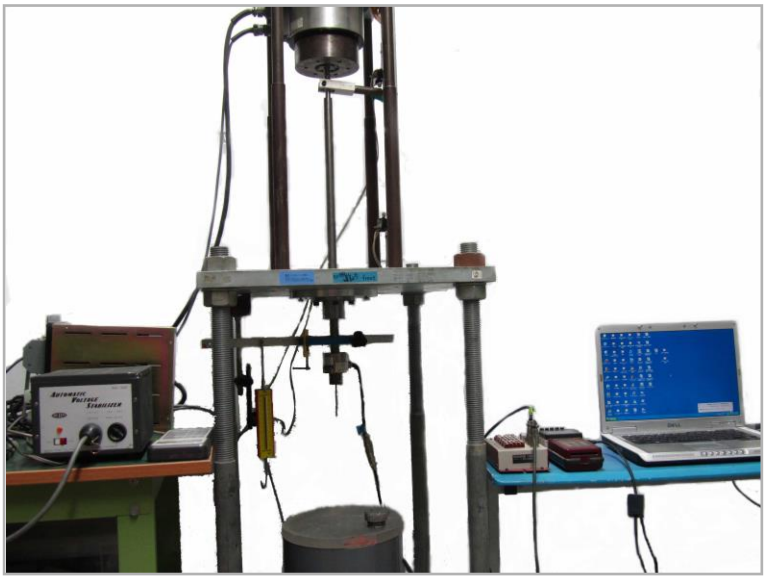


Figure 3.2 Micro cone penetration and unconfined compressive strength test apparatus

1) *Micro cone penetration test*

A micro cone penetrator with a diameter of 3 mm and tip angle of 60 degree penetrates into the specimen at a constant speed of 3 mm/min (Figure 3.3).

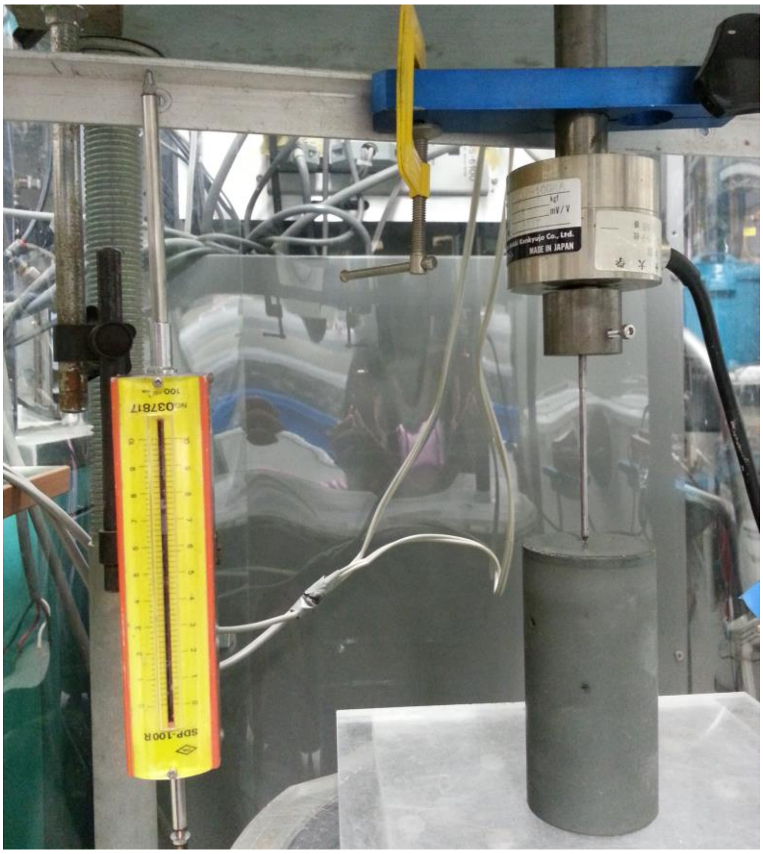


Figure 3.3 Micro cone penetration tests

Figure 3.4 Unconfined compressive strength tests

During the penetration, the penetration resistance F / (N) is measured continuously and the penetration depth can reach 50 mm degree.

2) Unconfined compressive strength test

Replace the micro cone penetrator with the disk in a diameter of 50 mm for unconfined compressive strength test of cement stabilized soils (Figure 3.4). The force and displacement are recorded at a step of 3 seconds.

3.2.2 Atomic Absorption Spectrometry

Atomic Absorption Spectrophotometer (ANA-182 type) manufactured by Tokyo photo electric co., LTD (Figure 3.5) can analyze the concentration of elements in a liquid sample based on energy absorbed from certain wavelengths of light (190 to 900 nm).

Atomic absorption spectrophotometers typically include a flame burner to atomize the sample (most commonly a hollow cathode lamp), a mono chromato, and a photon detector.

Figure 3.5 Atomic absorption spectrophotometer (ANA-182) apparatus

The procedure of preparing samples for atomic absorption analyzing (Figure 3.6) is listed. The samples first dried at 110 degree centigrade in oven, then weigh accurately for 5.0 to 10.0 g mixing with de-ionized water with ratio of 1:5. Vibrate for 1 hour at rate of 200 rounds per minute. Stand for separation and extract upper layer liquid for 9 ml, adding 1 ml prepared $SrCl_2\ 6H_2O$ chemical reagents with concentration of 10^{-5} ppm (mg/l). Finally, test the ions concentration with atomic absorption spectrophotometer apparatus.

Two types of ions in this dissertation are tested which are calcium and magnesium ions, the wavelength of calcium analysis is 421 nm, and current is 10 mA. The wavelength of magnesium is 284 nm, and current is 10 mA. The fire condition keeps at C_2H_2 1.8 L/min and air at 7.5 L/min.

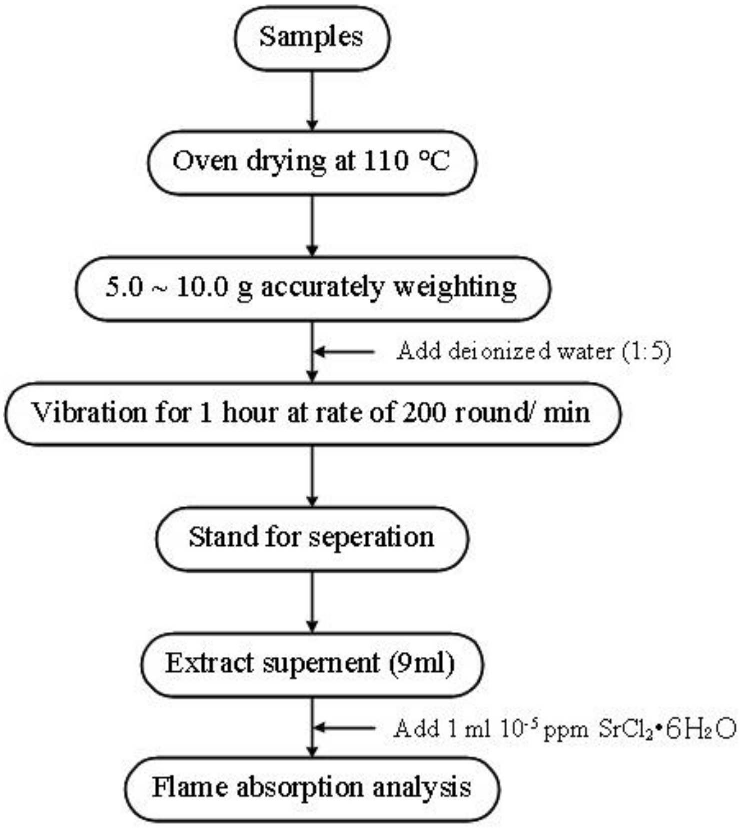


Figure 3.6 Flowchart of preparing atomic absorption samples

3.2.3 Mercury Intrusion Porosimetry

1) Porosimetry defined

The term "porosimetry" is often used to include the measurements of pore size, volume, distribution, density, and other porosity-related characteristics of a material. Porosity is especially important in understanding the formation, structure, and potential use of many substances. The porosity of a material affects its physical properties and, subsequently, its behavior in its surrounding environment. The adsorption and permeability, strength, density, and other factors influenced by substance porosity determine the manner in which it can be appropriately used.

2) Analysis defined

Since mercury is not wet most substances and will not spontaneously penetrate pores by capillary action, it must be forced into the pores by the application of external pressure. The required equilibrated pressure is inversely proportional to the size of pores, only slight pressure being required to intrude mercury into large macro pore, whereas much greater pressures are required to force mercury into small pores. Mercury porosimetry analysis is the progressive intrusion of mercury into a porous structure under stringently controlled pressures. From the pressure versus intrusion data, the instrument generates volume and size distributions using the Washburn equation. Clearly, the more accurate the pressure measurements, the more accurate the resulting pore size data.

3) Theory

It is the non-wetting property of mercury combined with its high surface tension that almost uniquely qualifies it for use in probing pore space. At each surface interface with a liquid, there is tension that acts tangentially to the interface. This is termed ‘surface tension’ and acts like an elastic membrane contacting the surface until the surface forces are in equilibrium with the forces tending to increase the surface area of the interface.

Surface tension, then, can be defined as the force per unit length acting along the surface of a liquid at right angles to a line that separates two phases. If mercury is placed in contact with a pore opening, the surface tension of the mercury acts along the line of contact with the opening equal in length to the perimeter of the opening and creating a force-resisting entry.

The magnitude of resisting force is proportional to the length of the line of contact, the surface tension (γ) of mercury, and the cosine of the contact angle (θ). For a pore with a circular opening at the surface, the resisting force is expressed as

$$f_R = \pi D \gamma \cos\theta \tag{3.1}$$

An externally applied pressure tending to force mercury into the opening acts over the surface of the interface bridging the opening. The externally applied force, therefore, is the product of the pressure (P) and area (A) over which the pressure is applied. For a pore of circular cross-section,

$$f_{Ext} = PA = P\pi D^2 / 4 \tag{3.2}$$

At equilibrium, just before the resistive force is overcome, the equation is,

$$-\pi D \gamma \cos\theta = \pi D^2 P / 4 \tag{3.3}$$

Therefore, at any pressure, the pores into which mercury has intruded have diameters greater than

$$D = -4\gamma \cos\theta / P \tag{3.4}$$

By measuring the volume of mercury that intrudes into the sample material with each pressure change, the volume of pores in the corresponding size class is known. The volume of mercury that enters pores is measured by a mercury penetrometer (an electrical capacitance dilatometer). These devices are very sensitive and can detect a change in mercury volume of under 0.1 μl.

4) AutoPore III Mercury Porosimeter

The AutoPore III Mercury Porosimeter used in this thesis (Figure 3.7) is high-pressure mercury porosimeter performs high-pressure mercury intrusion up to 400 MPa. This corresponds to the pore radii of 1.5 nm.

The penetrometer (Figure 3.8) is constructed of glass (an insulator) and filled with mercury (a conductor). The stem of the penetrometer is a capillary that acts as a reservoir for the analytical volume of mercury. The stem is plated with metal (a conductor). The two conductors, mercury, and the metal plating, are separated by glass, thus forming a coaxial capacitor. As pressure forces mercury out of the capillary and into the sample, the mercury inside the capillary decreases and so is the capacitance. The decrease in capacitance, therefore, is proportional to the volume of mercury leaving the capillary with each change in pressure.

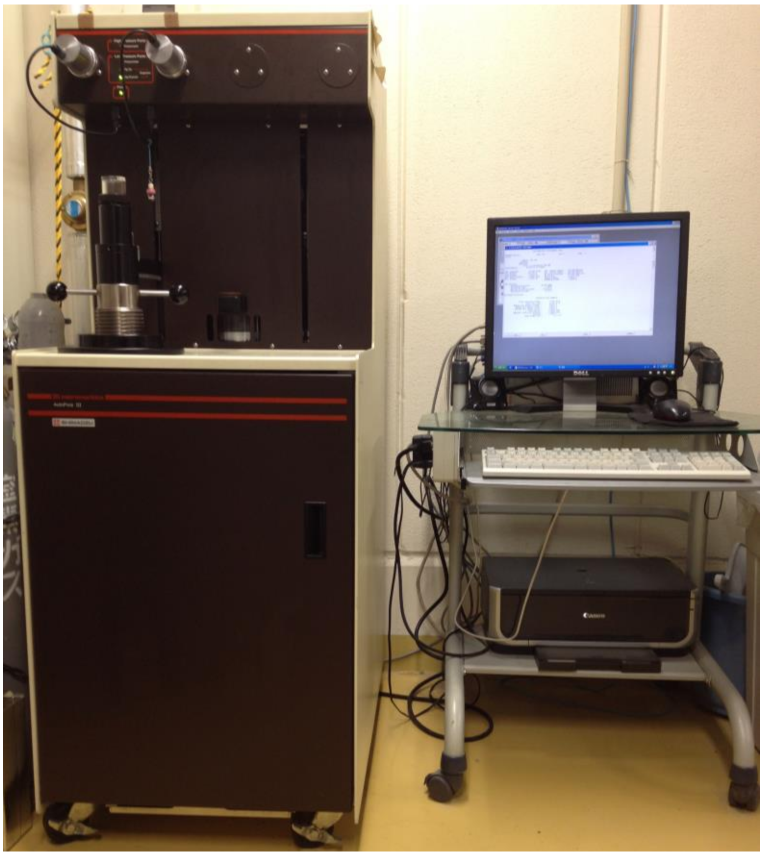


Figure 3.7 AutoPore III Mercury Porosimeter apparatus

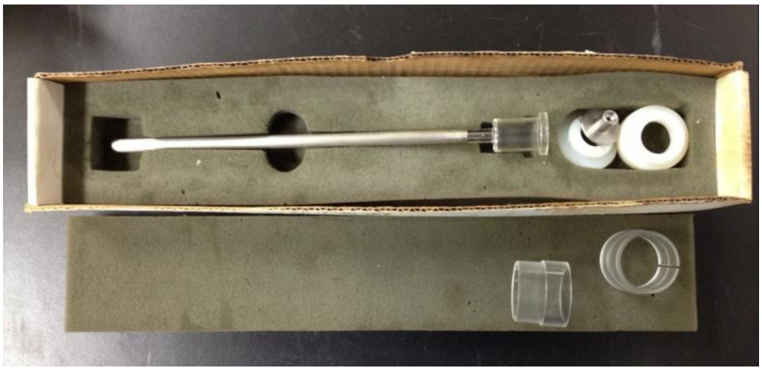


Figure 3.8 Mercury penetrometer

3.2.4 Scanning Electronic Microstructure and Energy Disperse X-Ray Analysis

The instrument of scanning electronic microstructure (SEM) SS-550 produced by Shimadzu corporate of Japan (Figure 3.9) is a type of electron microscope that produces images of a sample by scanning it with a focused beam of electrons. The electrons interact with electrons in the sample, producing various signals that can be detected and that contain information about the sample's surface topography and composition. The electron beam is generally scanned in a raster scan pattern, and the beam's position is combined with the detected signal to produce an image. SEM can achieve resolution better than 1 nanometer. Specimens can be observed in high vacuum and low vacuum. Furthermore, energy dispersive X-ray (EDX) systems (Genesis2000) are attachments to SEM, the data generated by EDX analysis consist of spectra showing peaks corresponding to the elements making up the true composition of the sample being analyzed.

Energy Dispersive X-Ray Analysis (EDX), referred to as EDS or EDAX, is an x-ray technique used to identify the elemental composition of materials. Applications include materials and product research, troubleshooting, de-formulation and more.

The dry sample is broken to several blocks, and each block is placed on an aluminum stub by a double-sided conducting tape, with the flat broken face facing upwards (Figure 3.10).

The pretreatment of samples involves Pt coating. The coating apparatus JFC-1600 produced by JEOL corporation (Figure 3.11). After numbering of test samples, set it into Pt coating apparatus with a current of 40 mA condition.

Figure 3.9 Scanning Electron Microscope (Super scan SS-550)

Figure 3.10 Preparation of scanning samples

Figure 3.11 Pt coating apparatus JFC-1600

3.2.5 X-Ray Powder Diffractometer (MultiFlex)

1) Introduction of MultiFlex

X-ray diffractometers find wide application from quality assurance to materials research, covering new materials, ceramics, metals, minerals, semiconductors, polymers, and more with a variety of sample types.

The MultiFlex (Figure 3.12) is newly designed to meet such diverse measurement requirements. Its compact theta-theta goniometer holds a sample in a horizontal and stationary position, eliminating the possibility of sample spillage during a measurement. It also allows simple handling of samples regardless of the sample shape, size, or type.

The MultiFlex measurement software allows users to define multiple scan procedures for repeated use. Comprehensive analysis software enables phase identification, profile fitting, and other varied applications.

2) Features

a) Sample stays horizontal

The sample is mounted horizontally, which is an ideal configuration when dealing with large of irregular samples, loose powders, or a high-temperature stage.

b) Compact, space-saving design

Because lab space is often at a premium, the system’s footprint is now reduced by 40% compared with other models of Rigaku stand-alone X-ray diffractometers. Casters are provided for ease of moving the system.

c) Safety design

Safety interlocks and automatic alignment ensure safe and convenient operation.

d) Rigaku measurement software (optional)

Powerful, flexible software handles system alignment, X-ray generator control, routine measurements, and control of the optional high-temperature attachment. Real-time data display allows you to see the results as each data point is collected. Predefined measurement conditions and an intuitive interface make the system accessible even to beginners. With an optional sample changer, multiple samples can be loaded and measured with individual procedures to increase throughput.

e) A variety of attachments (optional)

Six-sample automatic sample changer enables up to six samples to be measured in succession. With its integrated sample spinning mechanism, this device effectively measures samples having large grains or preferred orientation.

Figure 3.12 Automated Powder X-ray Diffractometer (MultiFlex)

High-temperature attachment enables programmed heating and cooling studies from ambient to 1300 ℃ under software control. Study the effects of thermal processing conditions on material properties.

Diffracted-beam monochromator ensures high resolution and signal to noise by removing K*β*, continuous X-rays, and sample fluorescence from the diffracted beam.

3) Specifications

The specifications of X-ray powder diffractometers (MultiFlex) is listed in Table 3.1

Table 3.1 Specifications of X-ray diffractometers

X-ray generator	Rated voltage	40 kV
	Rated current	30 mA
	Wavelength	CuKa / 1.541862 Å
Goniometer (Smartlab)	Scan mode	Continuous
	Scan speed/counting time	1.000 deg/min
	Scan axis	2θ / θ
	Scan range	5.0000 – 60.0000 deg
	2θ	3.6108 deg

3.3 Testing Procedures

3.3.1 Preparing of Soil Specimen

The Ariake Sea, with a maximum tidal range of 6 m is a shallow sea whose bottom is made of sandy mud and its water is a mixture of seawater flowing from the outer sea and fresh river water. Sandy mud and rich nutrients flow into the sea from the rivers and the bay is shallow for a long distance from the shore. Therefore, on full or new moon nights, a vast flat land can be seen (Figure 3.13).

Figure 3.13 Low tide period

Figure 3.14 High tide period

The soil used in experiments is taken from the in-suit site at low tide period. Ariake Sea is a body of salt water surrounded by Fukuoka, Saga, Nagasaki, and Kumamoto Prefectures, all of which lie on the island of Kyushu in Japan. It is the largest bay in Kyushu. Its deepest point is only about 50 m deep, and extreme tides exceed 4 m. The site for taking soil and water samples is located at Saga Prefecture. The mixing water used in experiments is taken from the same in-suit site at high tide period (Figure 3.14).

The procedures of preparing tested specimens: First, adjust the initial water content of Ariake clay soil to 200.0% (about 1.5 times of liquid limit). Second, introduce the stabilizing agent and mix thoroughly to manufacture homogeneous soil cement matrix. In this text, Portland blast-furnace slag cement B type is selected as the stabilizing agent, with a stabilizing factor α_w of 30% (amount of stabilizing agent, defined as a ratio of the dry weight of stabilizing agent to the dry weight of original soil). The whole mixing process is done within 10 minutes to avoid hardening of the soil cement matrix. Third, pour the matrix into special designed perspex mould with a diameter of 50 mm and a height of 100 mm (Figure 3.15). The mould is easily demolded and consisting of three parts: upper part with a diameter of 50 mm and a height of 25 mm; lower part with a diameter of 50 mm and a height of 75 mm, and bottom with a diameter of 50 mm and a height of 10 mm which is sealed with rubber ring. A special manufactured membrane with a diameter of 45 mm is adopted as a substitution for the upper part of the mould 24 hours later (Figure 3.15 (c)). During the preparation process, care is taken to remove the entrapped air bubbles.

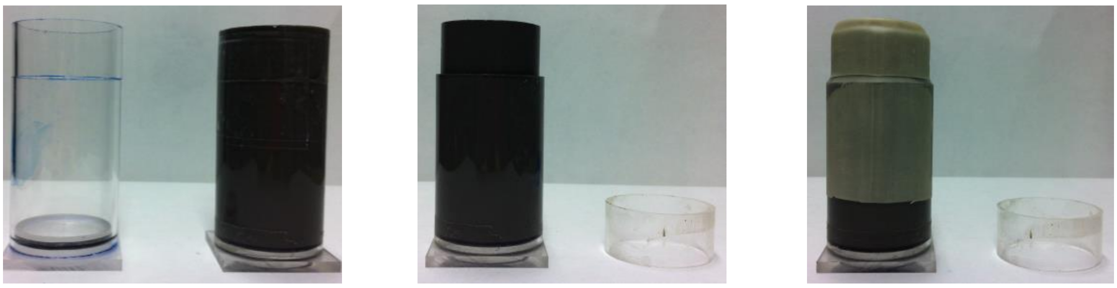

(a) (b) (c)

Figure 3.15 Special designed perspex mould for specimen

3.3.2 Test Conditions

The manufactured specimens were exposed to one of 15 exposure conditions. Details of the exposure conditions are listed in Table 3.2.

Table 3.2 Test case and exposure conditions

No.	Exposed to	Exposure conditions
1	Sea water	Submerged in sea water with 0.1 kPa
2		Submerged in sea water with 15 kPa
3		Submerged in sea water with 30 kPa
4		Submerged in sea water with 100 kPa
5		Submerged in sea water with salinity of 36 g/L
6		Submerged in sea water with salinity of 72 g/L
7		Submerged in sea water with salinity of 108 g/L
8		Submerged in sea water with pressure cycling of 0.1 to 15 kPa
9		Submerged in sea water with pressure cycling of 0.1 to 30 kPa
10	Pure water	Submerged in pure water with 0.1 kPa
11		Submerged in pure water with 30 kPa
12		Submerged in pure water with 100 kPa
13		Submerged in pure water with pressure cycling of 0.1 to 15 kPa
14		Submerged in pure water with pressure cycling of 0.1 to 30 kPa
15	Air	Cured in humidity container with 20℃ and RH > 98%

The chambers for curing specimens are showed from Figure 3.16 to Figure 3.18.

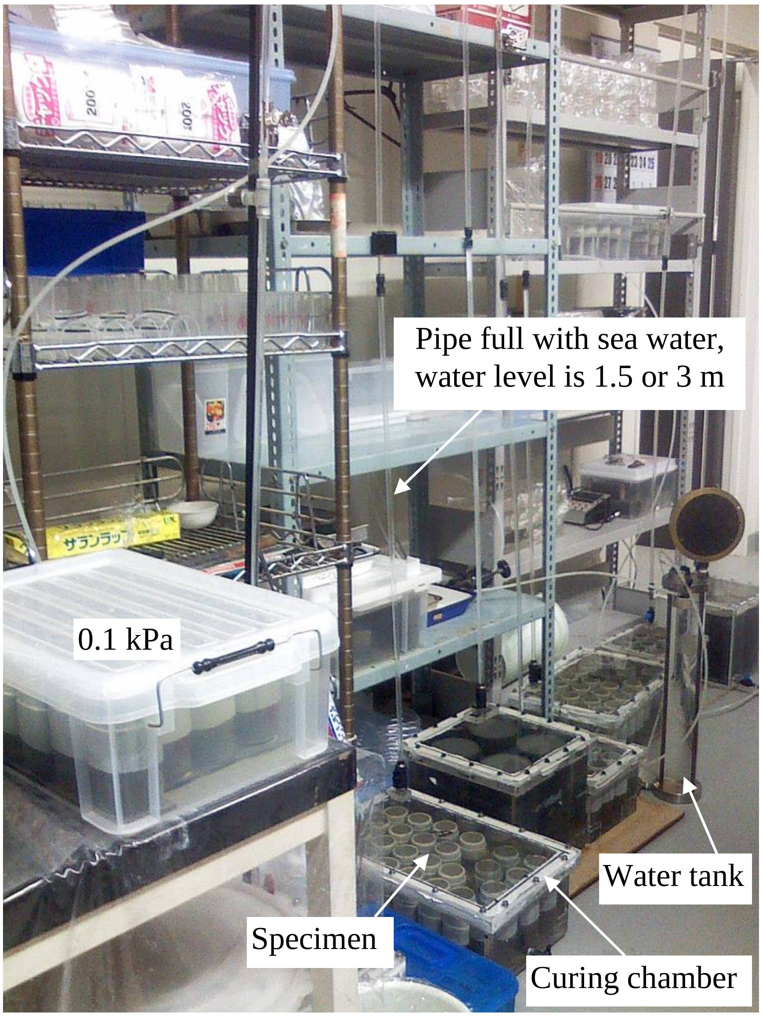


Figure 3.16 Curing chamber of static pressure lower than 30 kPa

Figure 3.17 Curing chamber of static pressure up to 100 kPa

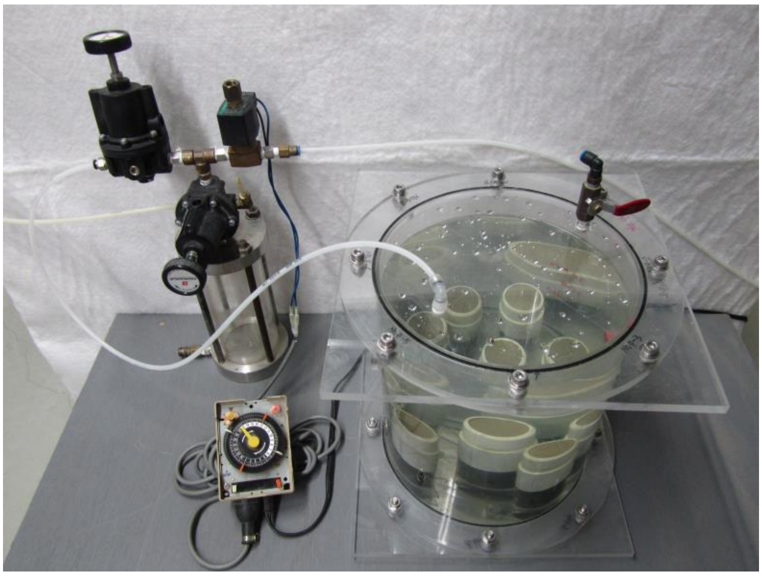


Figure 3.18 Curing chamber of dynamic pressure lower than 30 kPa

3.4 Properties of Ariake Clay and Cement

3.4.1 Ariake clay soil

Ariake clay is a sedimentation product from the Ariake Bay area, western Kyushu, Japan with surface now above sea level (altitude < 5 m), covers several hundred square km around the bay. The depths of Ariake clay generally vary from 15 to 20 m, with the maximum being about 40 m. The predominance of smectite characterizes the geotechnical index properties of the clay deposits: the liquid limit and activity of Ariake clay, which is a typical recent marine deposit of Japan, are in the range of 50 ~ 140% and 0.7 ~ 2.3, respectively. The natural water content ranges from 160 ~ 200%.

Ohtsubo et al. (2000) investigated the chemistry of the Ariake clay profile. The Cl^- concentration at 2 m depth was almost equal to that of sea water. The profile showed lowest concentration at the base of the sediment and highest near the surface, although the salinity decreases slightly at a depth of 1.5. This is common profile for the deposits in the Ariake Bay area. The variation of Na^+ concentration with depth was similar to that of Cl^-. The K^+ concentration was lower than 0.01 mol/ L throughout profile. The concentration of Mg^{2+} and Ca^{2+}, ranging from 0.005 to 0.05 mol/ L was greater in the deeper zone. The pH value varied from 4.2 to 9.3, the organic matter content was in the range of 1.5-3.3%.

The XRD analysis on Ariake clays indicated the presence of smectite which is low-swelling which is believed to be an in-suit formation product from pyroclastic material in recent marine deposits. The physical properties and chemical properties of Ariake clay is listed in Table 3.3 and Table 3.4.

Table 3.3 Physical properties of Ariake clay

Gravity ρ_s (g/cm^3)	Liquid limit w_L (%)	Plastic limit w_P (%)	Plastic index I_P	Granularity (%)		
				Sand	Silt	Clay
2.60	128.5	52.0	76.5	6.72	23.28	70

Table 3.4 Chemical properties of Ariake clay

Water quality analysis				2011/4/12 Reception
Items	Unit	Samples		Lower limit value
		1	2	
		Pore water	Sea water	
Ca^{2+}	mg/l	24	284	1
Mg^{2+}	mg/l	53	1070	1
K^+	mg/l	49	328	1
Cl^-	mg/l	1200	11600	1
HCO_3^-	mg/l	63.0	98.3	0.1
SO_4^{2-}	mg/l	210	1700	10
Soluble silica	mg/l	18	4	1

3.4.2 Cement type

The stabilizing agents used in practice are, in majority of cases, Portland cement and lime, but dozens of stabilizing agents is now available on the market. Some of these newly developed special stabilizing agents are designed for the improvement of clay soils with high water content or organic soils, for which ordinary cement or lime is not very effective. Some other stabilizing agents are designed for cases where the rate of strength increase has to be controlled for the convenience of the construction.

1) *Cement-type stabilizing agents*

The cement types used as stabilizing agents are “Portland cement” or “Portland blast furnace slag cement”. Portland cement is made by adding gypsum to cement clinker and grinding it to powder. Cement clinker is formed by minerals; $3CaO \cdot SiO_2$, $2CaO \cdot SiO_2$, $3CaO \cdot Al_2O_3$ and $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$. A cement mineral, $3CaO \cdot SiO_2$, for example, reacts with water in the following way to produce cement hydration products.

$$2(3CaO \cdot SiO_2) + 6H_2O = 3CaO \cdot 2SiO_2 \cdot 3H_2O + 3Ca(OH)_2$$

During the hydration of cement, calcium hydroxide is released. The cement hydration product has high strength, which increases as it ages, while calcium hydroxide contributes to the pozzolanic reaction as in the case of lime stabilization. Portland blast furnace slag cement is a mixture of Portland cement and blast furnace slag. Finely powdered blast furnace slag does not react with water but has the potential to produce pozzolanic reaction products under high alkaline conditions. In Portland blast furnace slag cement, the SiO_2 and Al_2O_3 contained in the slag are actively released by the stimulus of the large quantities of Ca^{2+} and SO_4^{2-} released from the cement, so that a fine hydration product abounding in silicates is formed rather than a cement hydration product, and the long-term strength is enhanced.

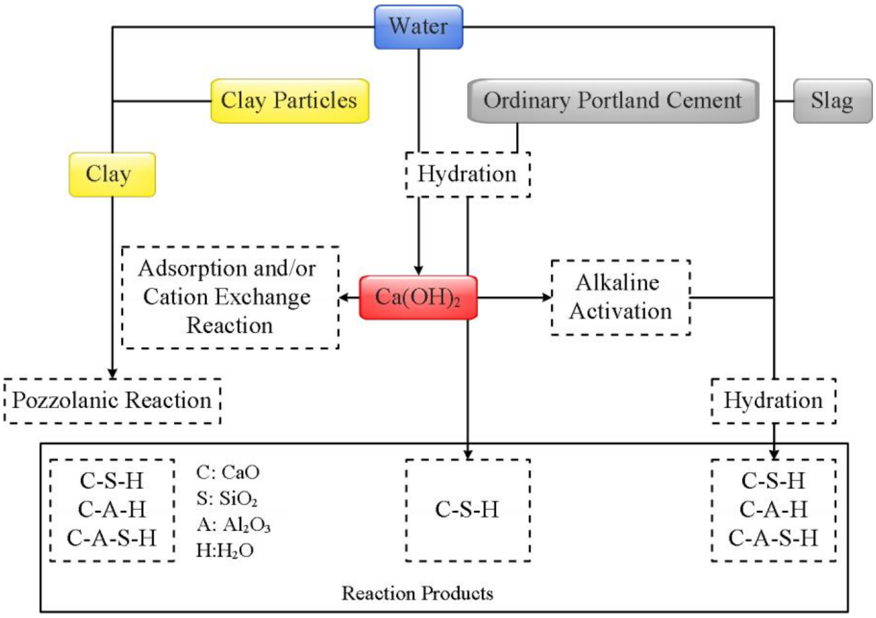


Figure 3.19 Chemical reactions between clay, cement, slag and water (Saitoh et al., 1985)

The complicated mechanism of cement stabilization is simplified and schematically shown in Figure 3.19 for the chemical reactions between clay, pores water, cement and slag (Saitoh et al. 1985).

2) *Special cement-type stabilizing agents*

Special cement-type stabilizing agents are cements that are specially prepared for the purpose of stabilizing soil or similar material by reinforcing certain constituents of the ordinary cement, by adjusting the grain size or by adding ingredients effective for particular soil types. The improvement effect in organic soils is said to be affected by the ratio ((SiO_2 + Al_2O_3)/CaO) of the constituent elements in cement-type stabilizing agents. “Delayed stabilizing” or “long term strength control” type stabilizing agents by which the rate of strength increase can be controlled, are obtained by adjusting the quantities of ingredients such as gypsum of lime.

The characteristics of Portland blast furnace slag cement B type are listed in Table 3.5.

Table 3.5 Specification of cement types in this study

Type of Cement / Cement Quality		Portland blast furnace slag cement B JIS R 5211			
		JIS	Testing		
			Ave.	Standard error	Max. (Min.)
Specific Gravity g/cm^3		-	3.04	-	-
Specific surface Area cm^2/g		>3000	3770	78	-
Setting time	W/C (%)	-	29.2	-	-
	Initial (h-min)	>60 min	3-02	-	(2-35)
	Final (h-min)	<10 h	4-38	-	5-02
Stability		Good	Good	-	-
Compressive Strength N/mm^2	1 d	-	-	-	-
	3 d	>10.0	21.9	1.36	-
	7 d	>17.5	37.4	1.79	-
	28 d	>42.5	65.0	2.04	-
Hydration heat J/g	7 d	-	-	-	-
	28 d	-	-	-	-
Chemical component (%)	MgO	<6.0	3.28	-	3.64
	SO_3	<4.0	2.14	-	2.50
	Igloss	<5.0	1.86	-	2.18
	Alkali	-	-	-	-
	Chloride	-	0.011	-	-
	SiO_2	34.1	-	-	-
	Al_2O_3	12.8	-	-	-
	Fe_2O_3	0.3	-	-	-
	CaO	41.8	-	-	-

3.5 Summary

This chapter introduces the materials and apparatus used in this dissertation. The procedures of preparing and analyzing specimen are clarified clearly. It gives an overview of experiments groups under various exposure conditions.

The evaluation of micro and macro mechanics behaviors of cement stabilized soils is achieved through micro cone penetration test and unconfined compressive strength.

The atomic absorption spectrometry (AAS), energy dispersive X-ray (EDX), X-ray powder diffractometer (XRD) and mercury intrusion porosimetry (MIP) are used for analyzing chemical, microstructures and compound constitute of specimen.

The originality of this chapter is the design of mould for specimen. It is ideal for resisting sea water corrosion and achieving the deterioration at one dimension.

Chapter 4 RESULTS AND DISCUSSIONS OF INFLUENCE FACTORS ON DETERIORATION

4.1 Introduction

This chapter introduces water pressure, sea water concentration and initial strength influence on deterioration process of cement stabilized soils.

The study of water pressure influence on deterioration involves static water pressure (0.1, 15, 30, 100 kPa) and dynamic water pressure (cycling 0.1 - 15 kPa and 0.1 - 30 kPa at intervals of 6 hours) conditions.

The study of sea water concentration influence on deterioration involves 36 g/L, 72 g/L and 108 g/L conditions. The sea water concentration of 36 g/L is approximate to natural sea water.

The study of initial strength influence on deterioration is achieved through curing the specimen in air (20 degree centigrade and relative humidity 98%) for 14 days to gain enough strength and then submerge it into sea water environment with different static water pressures (0.1, 15, 30 kPa).

One group of specimen is cured in air (20 degree centigrade and relative humidity 98%) for 1, 7, 14, 28, 90 and 180 days as a blank test.

The penetration resistance, water content, density and unconfined compressive strength are tested.

This chapter introduces the definition of deterioration depth based on penetration results. This index can conveniently evaluate the deterioration degree under various exposure conditions.

The penetration resistance distribution with depth indicates two aspects of strength development at non-deteriorated area and deteriorated area. The factors exhibit different influence on deterioration degree. The water content distribution shows different tendency under various exposure conditions. The density changes little before and after exposure and distributes at a range of 1.32 ~ 1.36 g/cm^3. The sea water environment influences serious on the unconfined compressive strength.

The detailed results of cone penetration test, deterioration depth, water content distribution, density and unconfined compressive strength under various exposure conditions are listed in this chapter.

4.2 Sea water Pressure Influence

4.2.1 Static water pressure

The research on behavior of concrete under sea water with high pressure indicated that high hydrostatic sea water pressure had no detrimental effect on strength, but increased the depth of sea water penetration and the rate of swelling of the concrete, especially for ordinary Portland cement (G. Vander et al., 1993). However, the cemented soils generally have high water-to-cement ratios and contain large voids, and so are thought to deteriorate more quickly than ordinary concrete due to calcium leaching from cement hydrates(Nakarai et al. 2006). The research of sea water pressure influence on behaviors of cement stabilized soils is limited until now. The experiments on static water pressure influence are listed in Table 4.1.

Table 4.1 Experiments of static water pressure influence on deterioration

Binder type	Blast-furnace slag Portland cement B
Binder factor (%)	30
Initial water content (%)	200.0
Curing age (days)	7, 14, 28, 90, 180, 360, 450
Exposure conditions	
Case 1	Submerged in sea water environment with 0.1 kPa
Case 2	Submerged in sea water environment with 15 kPa
Case 3	Submerged in sea water environment with 30 kPa

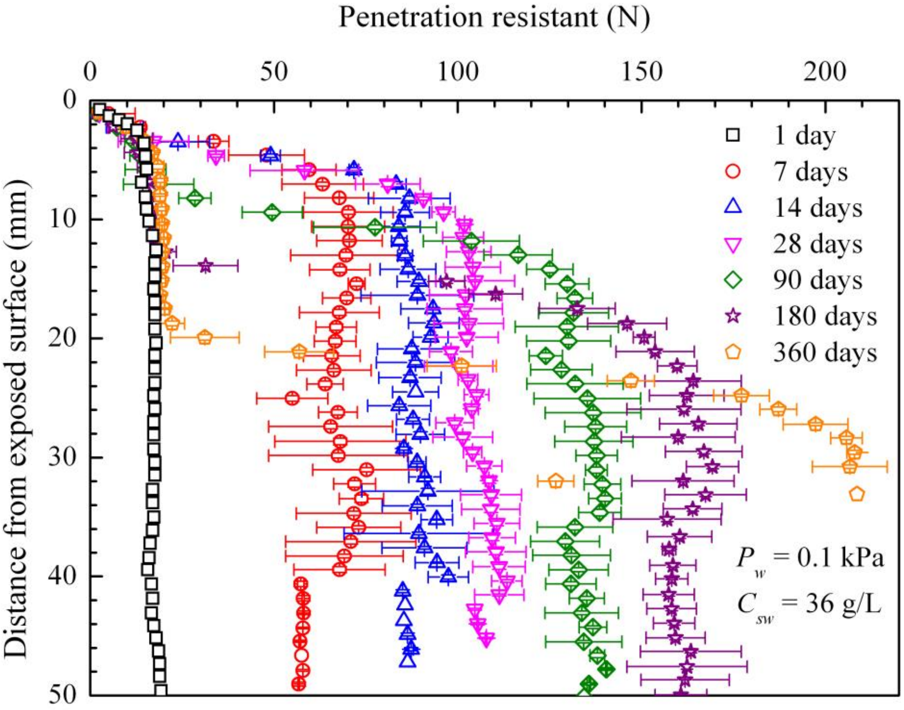
The curing artificial sea water is refreshed at an interval period of 2 weeks and one specimen corresponds to one liter sea water.

1) Cone penetration test results

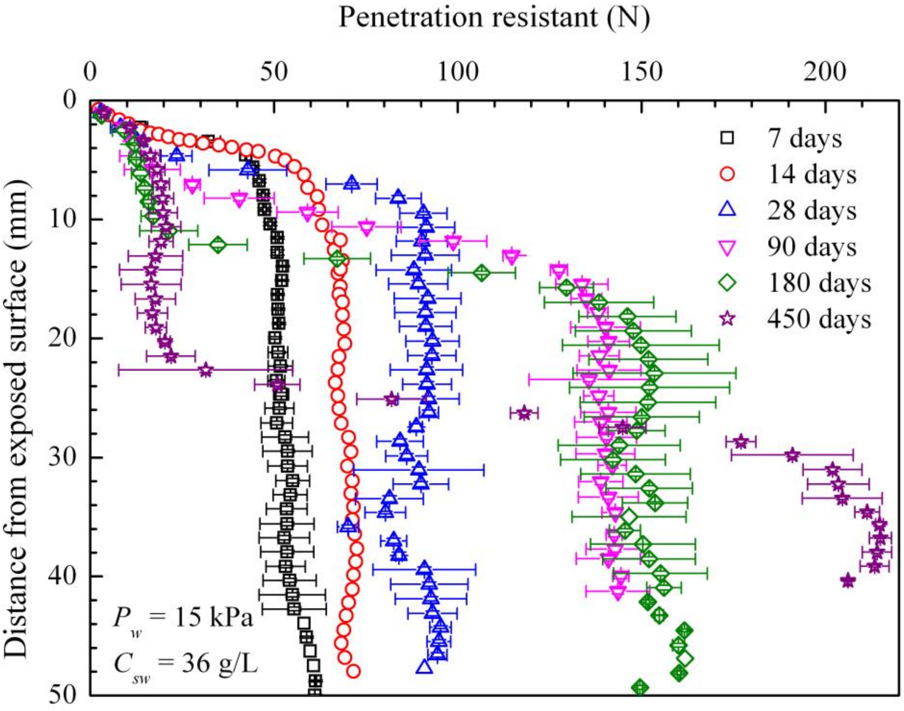
The penetration resistance distributions with depth of specimens cured under 0.1 kPa, 15 kPa and 30 kPa at each designed age is showed in Figure 4.1. The horizontal axis represents penetration resistance, and the vertical axis represents distance from the exposed surface.

The results show two aspects of strength development. One aspect is that the strength decreases as elapsed time becomes long near exposure surface; another aspect is that the strength increases as elapsed time becomes long at inner part of specimen. This phenomenon has already been verified in laboratory and field investigations (Hayashi et al. 2004a; Hayashi et al. 2004b; Ikegami et al. 2004; Kitazume et al. 2002). Deterioration of cement stabilized soils under sea water environment leads to the strength decreasing.

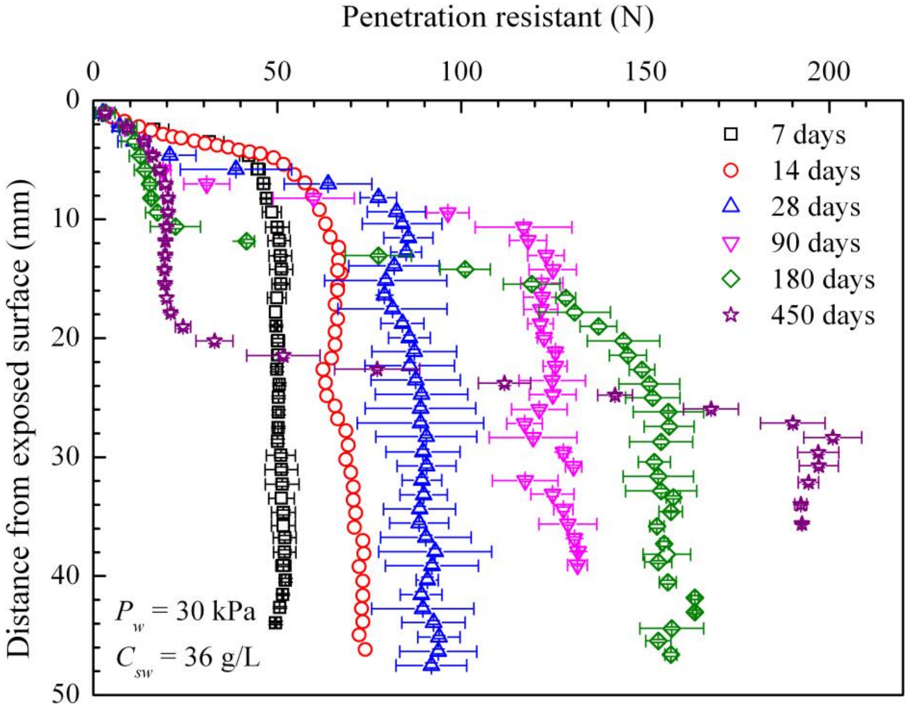
The deterioration becomes more serious as exposure time grows. The strength at 450 days decreases to 20 N from exposure surface to around 20 mm depth. However, it develops to about 200 N at inner part of specimen.



a) 0.1 kPa



(a) 15 kPa



(b) 30 kPa

Figure 4.1 The penetration resistance distribution with depth under static water pressure

It is also obvious that the strength under 0.1 kPa at short term (7, 14 and 28 days) develops greater than 15 kPa and 30 kPa. As exposure time becomes long, this difference is disappearing.

It indicates that the static water pressure only has influence on the strength development at short term.

2) *Definition of deterioration depth*

In order to quantitatively analyze the factors influence on deterioration of cement stabilized soils, it is necessary to propose a method for accessing the deterioration depth accurately.

The method of accessing the deterioration depth in this dissertation based on cone penetration test results. The specimen is penetrated both from exposure surface (deteriorated area) and bottom surface (non-deteriorated area). Then calculate the slopes of penetration curves and plot the data k_1, k_2, k_3 … k_n (Figure 4.2). Fit the plotted data to know the corresponding depth of each peak point D_N (mm) and D_D (mm). D_N is the deterioration depth penetrated from bottom surface. D_D is the deterioration depth penetrated from exposure surface. The deterioration depth of the specimen is equal to (D_D-D_N) mm.

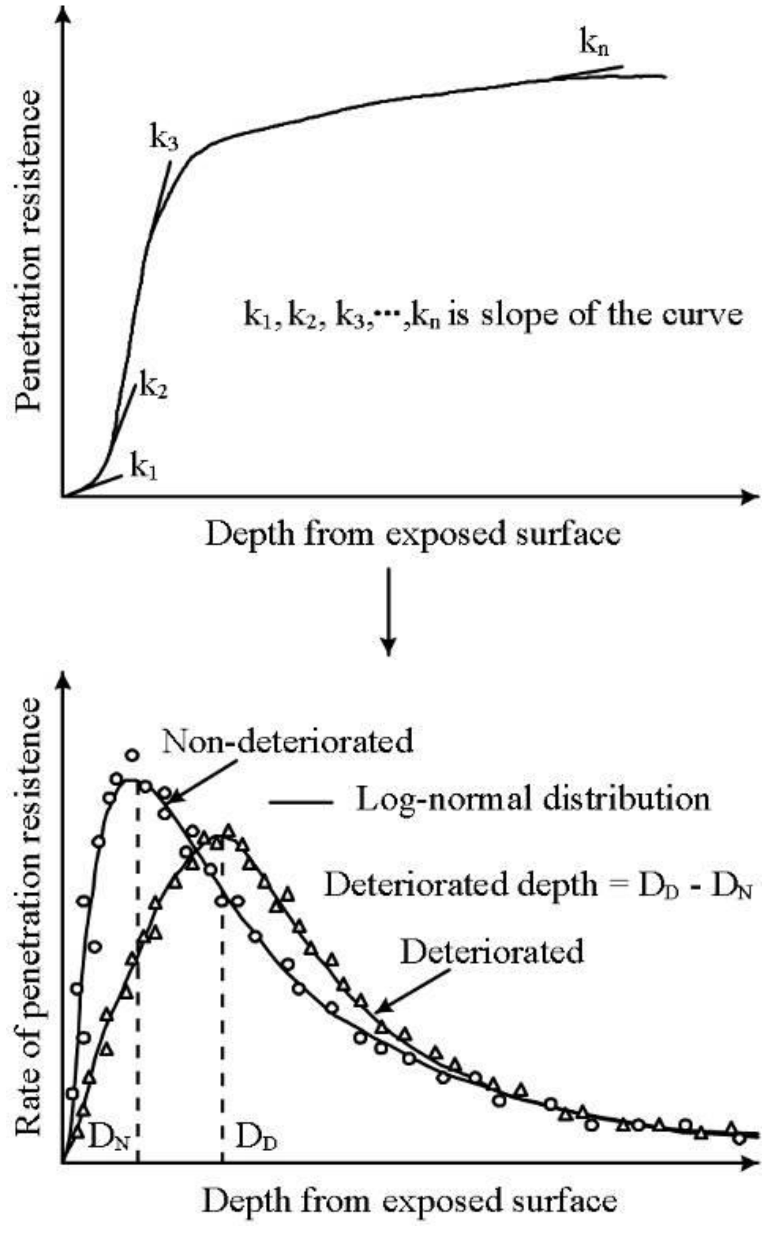


Figure 4.2 The schematic of definition of deteriorated depth

3) Deterioration depth

The deterioration depths of specimen under static water pressures are showed in Figure 4.3. The horizontal axis represents elapsed time and the vertical axis represents deterioration depth.

It is clear that the deterioration depths under 0.1 kPa are larger than that under 15 kPa and 30 kPa at short term (< 28 days). The three curves overlap at around 90 days. As elapsed time grows, there is no apparent order of deterioration depths under different static water pressures.

The deterioration depth becomes larger as elapsed time increases and reaches 20 mm at 450 days which is in good consistency with the strength development.

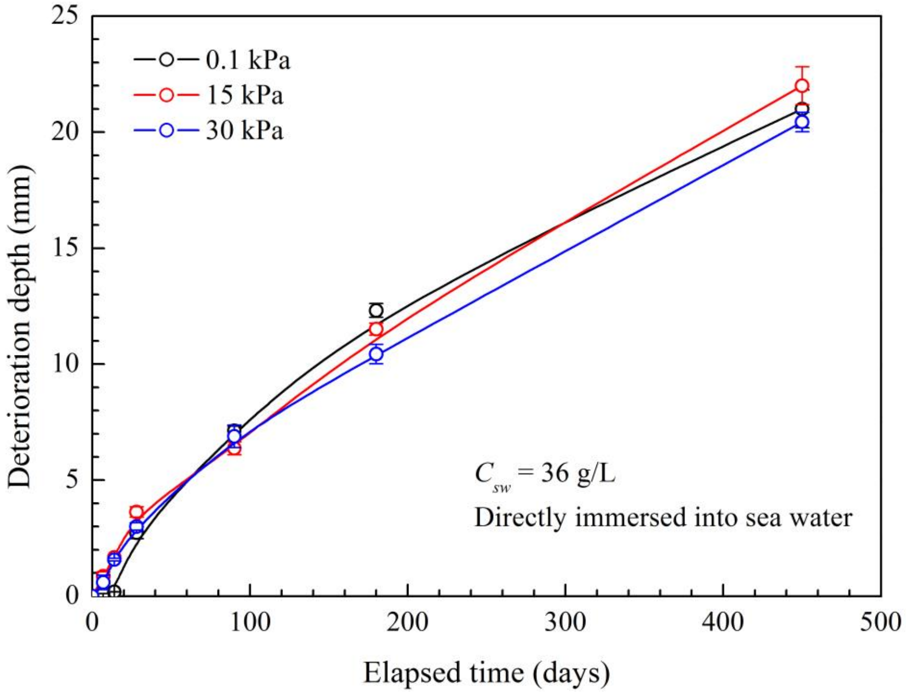


Figure 4.3 The deterioration depth of specimen under static water pressures

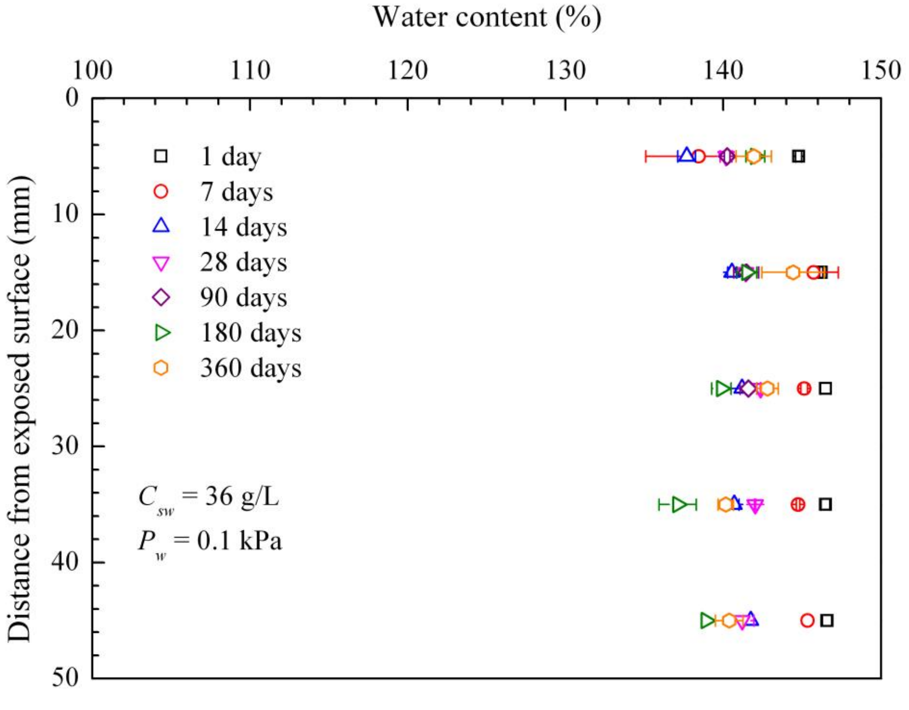
4) Water content distribution

There is a need to investigate the water distribution inside specimen because water plays an important role both in ions transportation and chemical reaction. The initial water content is adjusted to 200.0% (about 1.5 times liquid limit) for homogeneity of the specimen.

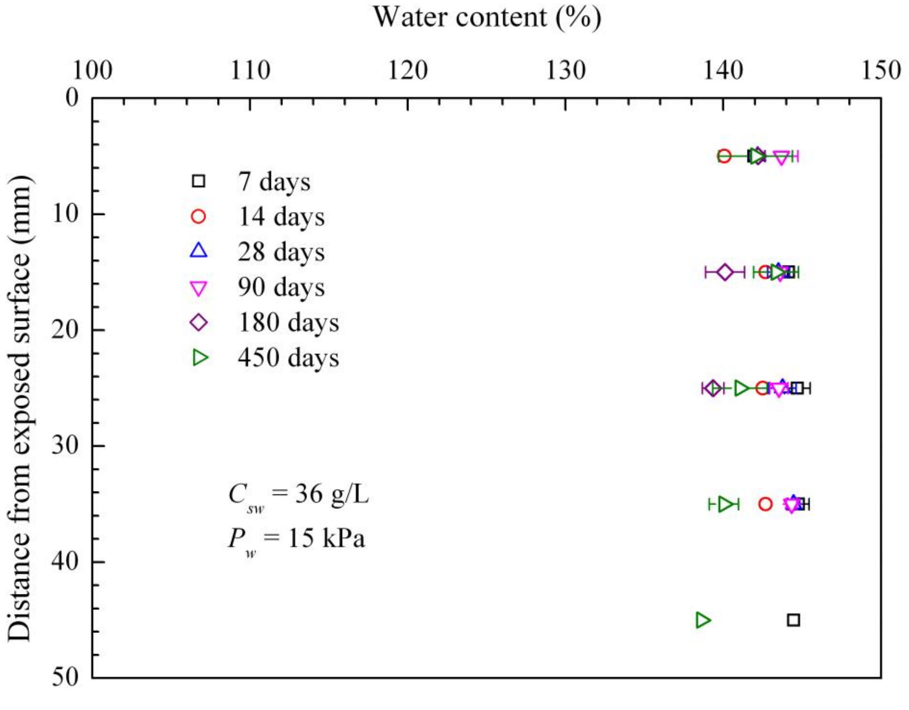
Figure 4.4 shows the water content distribution with depth of specimen under static water pressures. The water content ranges from 140 ~ 146% under 0.1, 15 and 30 kPa sea water.

The water content changes with elapsed time showing different tendency at deteriorated area and non-deteriorated area. At deteriorated area the water content at 180 and 360 days is higher than 7, 14 and 28 days, when at non-deteriorated area the water content at 180 and 360 days is lower than 7, 14 and 28 days.

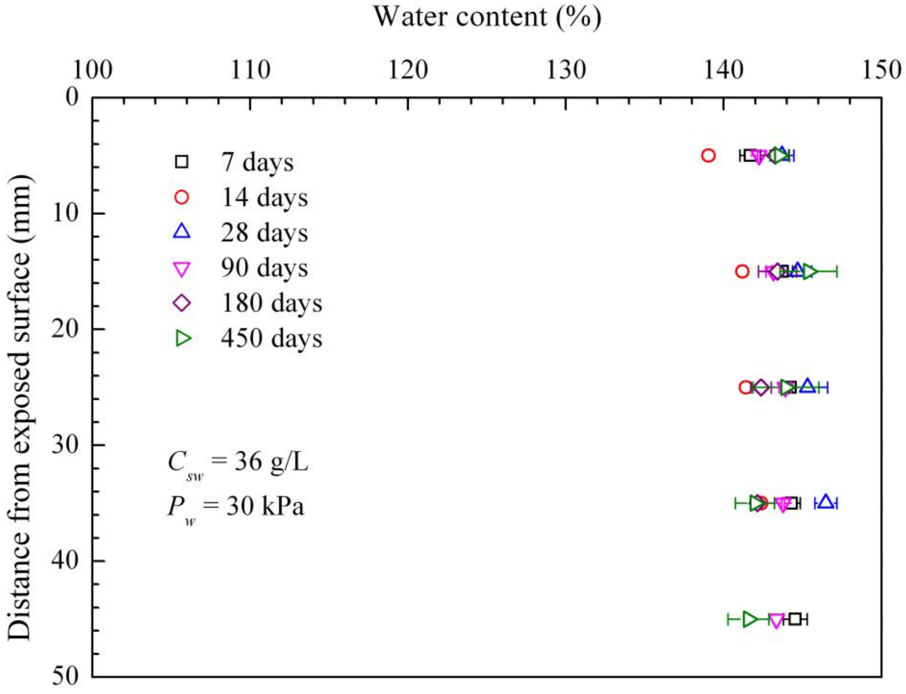
The water content variation with depth of specimen also shows different tendency at short term and long term. At short term of 7, 14 and 28 days the water content increases from exposure surface to inner part of specimen, when at long term of 180 and 360 days the water content decreases from exposure surface to inner part of specimen. In addition, the water content at 90 days from exposure surface to inner part of specimen is very similar.



a) 0.1 kPa



b) 15 kPa



c) 30 kPa

Figure 4.4 The water content distribution with depth under static water pressures

4.2.2 Higher static water pressure

There is no clear distinction between surface stabilization and deep mixing. However, CENTC (European Committee for Stabilization/Technical Committee) 288 specifies deep mixing as treatment of the soil to a minimum depth of 3 m. The static water pressure referred above is 30 kPa in maximum. In practical engineering projects, the stabilization depth usually extends to a length deeper than 10 m.

Table 4.2 Experiments of higher static water pressure influence on deterioration

Binder type	Blast-furnace slag Portland cement B type	
Binder factor (%)	30	
Initial water content (%)	200.0	
Curing age (days)	7, 14, 28	
Exposure conditions		
Case 1	Sea water environment	0.1 kPa
Case 2	Pure water environment	
Case 3	Sea water environment	30 kPa
Case 4	Pure water environment	
Case 5	Sea water environment	100 kPa
Case 6	Pure water environment	

According to forgoing results, the static water pressure has influence on the strength development of stabilized soils at short term. The following experiments are designed to investigate the higher static water pressure influence on strength development at short term. In addition, pure water environment is also considered. The details of experiments are listed in Table 4.2.

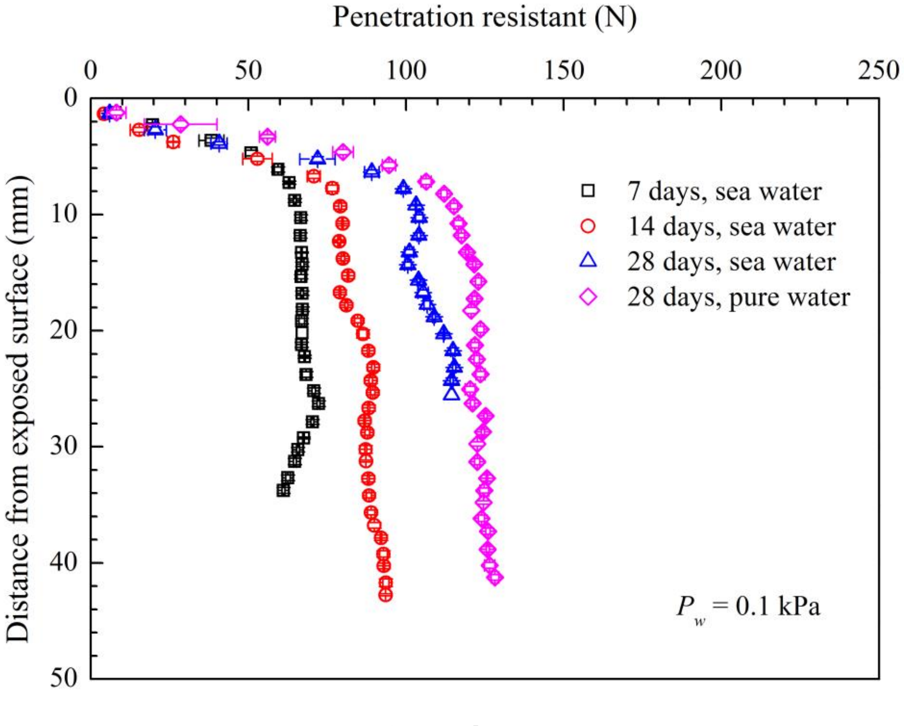
1) Cone penetration test results

The penetration resistance distributions with depth of specimens cured under 0.1 kPa, 30 kPa and 100 kPa at each designed age is showed in Figure 4.5. The horizontal axis represents penetration resistance, and the vertical axis represents distance from the exposed surface.

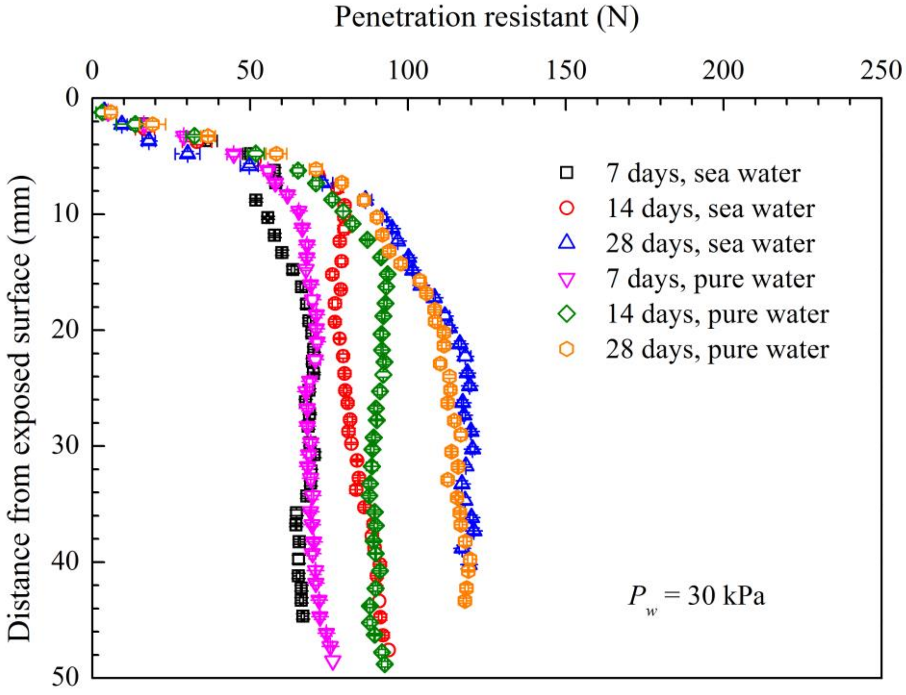
It is obvious that the strength near exposure surface under 0.1 kPa is greater than 30 kPa and 100 kPa both in sea water and pure water environment. For instance, the strength at depth 5 mm reaches 60, 70 and 100 N at 7, 14 and 28 days separately under 0.1 kPa, but only 50 N under 30, 100 kPa. The higher static water pressure can delay the strength development to a certain extent.

The strength continuously increases at inner part of specimen as elapsed time grows in sea water environment, although a little lower than in pure water environment.

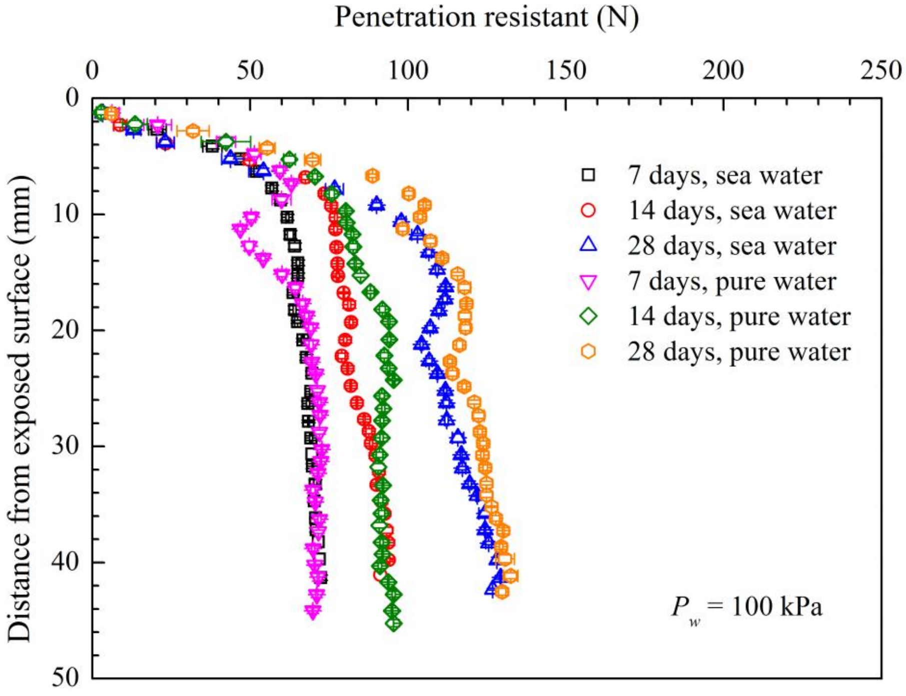
The strength development under 30 kPa and 100 kPa is very similar. It indicates that the effect degree is not proportional to the increasing of pressure.



a) 0.1 kPa



b) 30 kPa



c) 100 kPa

Figure 4.5 The penetration resistance distribution with depth under higher static water pressure

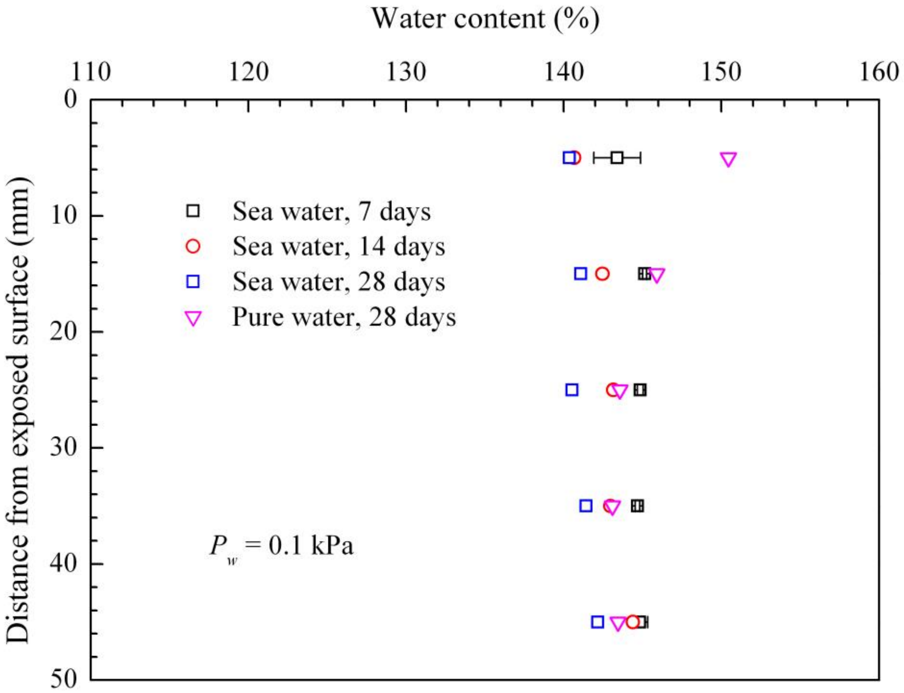
2) Water content distribution

Figure 4.6 shows the water content distribution with depth of specimen under higher static water pressures. The water content ranges from 140 ~ 144% under 0.1, 30, 100 kPa sea water and ranges from 144 ~ 154% under 0.1, 30, 100 kPa pure water.

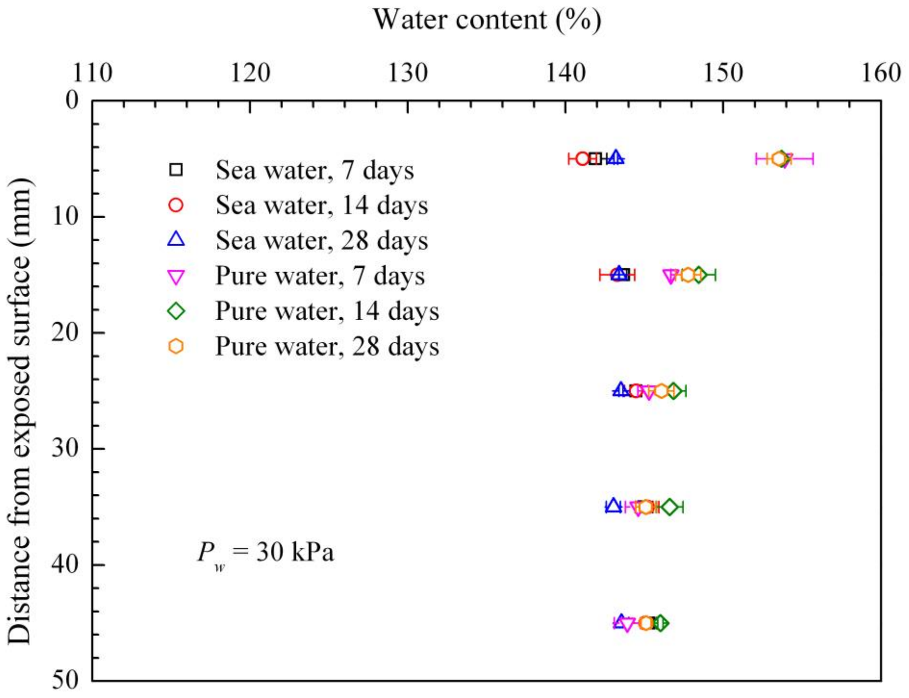
The water content increases from exposure surface to inner part of specimen under sea water environment. On the contrary, the water content decreases from exposure surface to inner part of specimen under pure water environment.

The impact on water content distribution of 100 kPa pure water environment is the greatest, then 30 kPa, the least is 0.1 kPa. But it is not so obvious in sea water environment. It is said that at the beginning of stabilization, the permeability of cement stabilized soils is high. So the higher static water pressure accelerates the water diffusion from outer environment into inner part of specimen. However, this acceleration doesn't work under sea water environment. The only difference between sea water and pure water is the ions concentration.

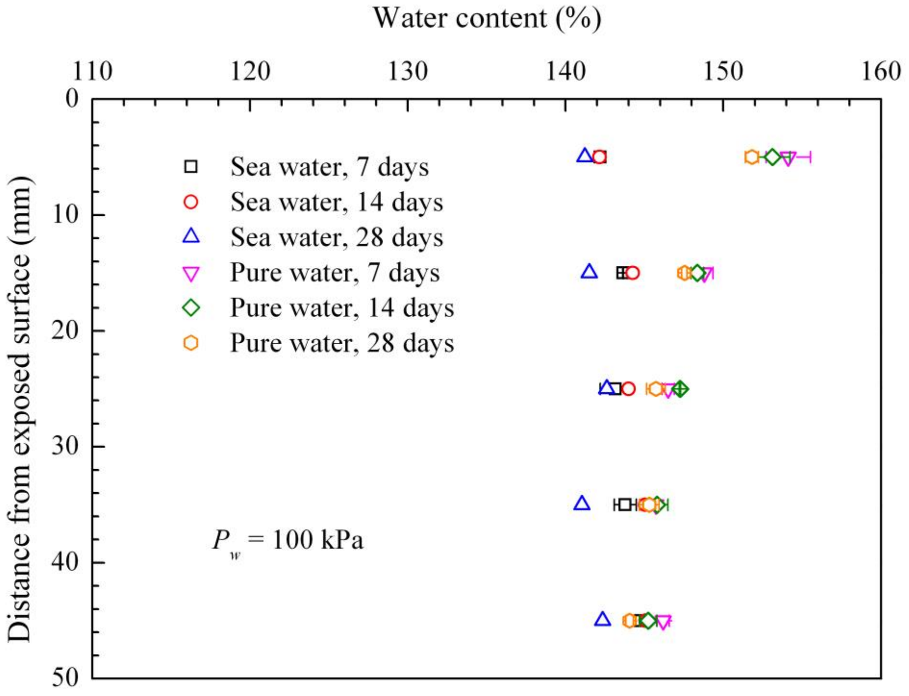
The ion migration direction is different in sea water and pure water when the water diffusion direction is same. These two processes are carrying on simultaneously. The Ca^{2+}, Mg^{2+} and SO_4^{2-} ions are the reactive substances which can transform free water to bound water through ion-exchange action and chemical reaction. In sea water environment, one little part of free water diffuses to the inner part of specimen, the left part is consuming during the chemical reaction process.



a) 0.1 kPa



b) 30 kPa



c) 100 kPa

Figure 4.6 The water content distribution with depth under higher static water pressure

In pure water environment, the diffusion of ions from specimen to outer space due to ion concentration gradient leads to decreasing of water consuming. And higher static water pressure can accelerate this process especially at 7 and 14 days.

4.2.3 Dynamic water pressure

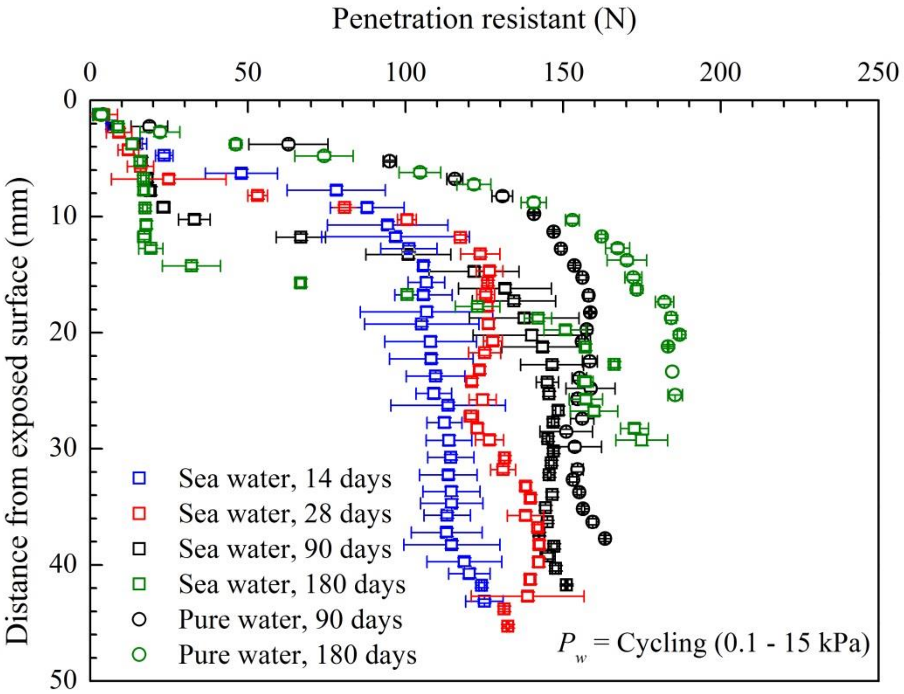
The cement stabilization method often used at tidal zone, the water level will change time to time daily. The body of cement stabilized soils will suffer pressure cycling in field site. The cycling of pressure influence on deterioration of cement stabilized soils is studied. The experimental details are listed in Table 4.3.

Table 4.3 Experiments of dynamic water pressure influence on deterioration

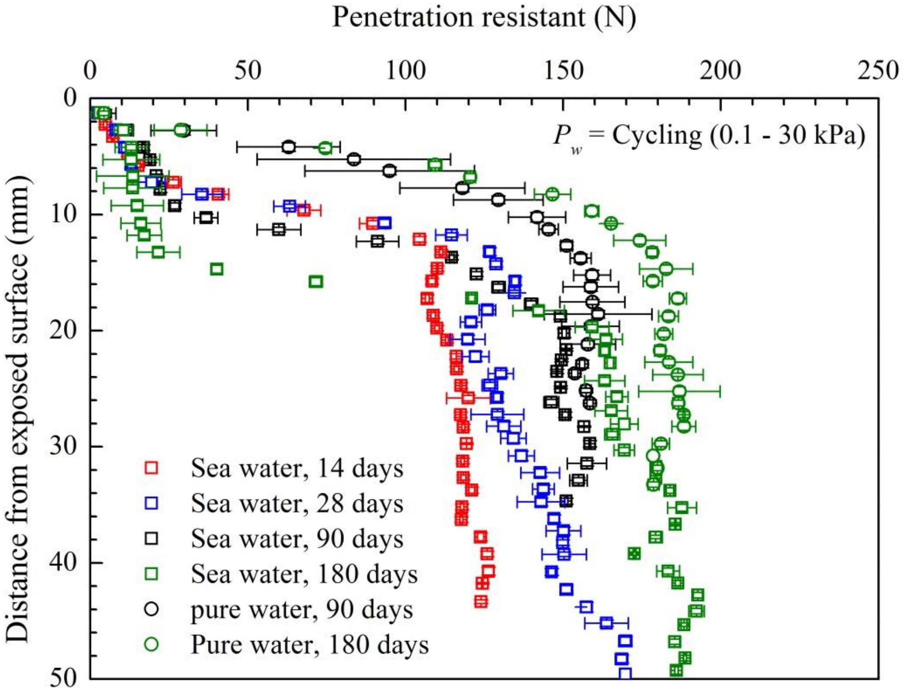
Binder type		Blast-furnace slag Portland cement
Binder factor (%)		30
Initial water content (%)		200.0
Curing age (days)		14, 28, 90, 180
Exposure conditions		
Case 1	Sea water environment	Cycling (0.1 - 15 kPa), interval time 6 hours
Case 2	Pure water environment	
Case 3	Sea water environment	Cycling (0.1 - 30 kPa), interval time 6 hours
Case 4	Pure water environment	

1) Cone penetration test results

The penetration resistance distributions with depth of specimens cured under dynamic water pressures at each designed age is showed in Figure 4.7. The horizontal axis represents penetration resistance, and the vertical axis represents distance from the exposed surface.



a) Cycling (0.1 - 15 kPa)



b) Cycling (0.1 - 30 kPa)

Figure 4.7 The penetration resistance distribution with depth under dynamic water pressure

It can be seen that the strength at deteriorated area decreases as elapsed time grows under sea water environment. But increases as elapsed time grows at non-deteriorated area.

The strength under pure water environment is greater than that under sea water environment. It is not so obvious difference between two cycling conditions.

2) *Deterioration depths*

The deterioration depths of specimen under higher static water pressure and dynamic water pressure are showed in Figure 4.8. The horizontal axis represents elapsed time and the vertical axis represents deterioration depth.

The results show that higher static water pressure induces greater degree of deterioration at less than 28 days. The deterioration depth under cycling (0.1 - 30 kPa) is larger than that under cycling (0.1 - 15 kPa) at less than 28 days. When elapsed time reaches 90, 180 days, the deterioration depth under cycling (0.1 - 30 kPa) equals to that under cycling (0.1 - 15 kPa) condition.

It is clear that the deterioration depth is greater under dynamic pressures that that under 0.1 kPa static sea water pressure at 180 days. It indicates that dynamic pressure influences the deterioration process both at short term and long term and the dynamic pressures influences more seriously than static water pressure. But the impact degree is not proportional to the increasing of cycling pressure.

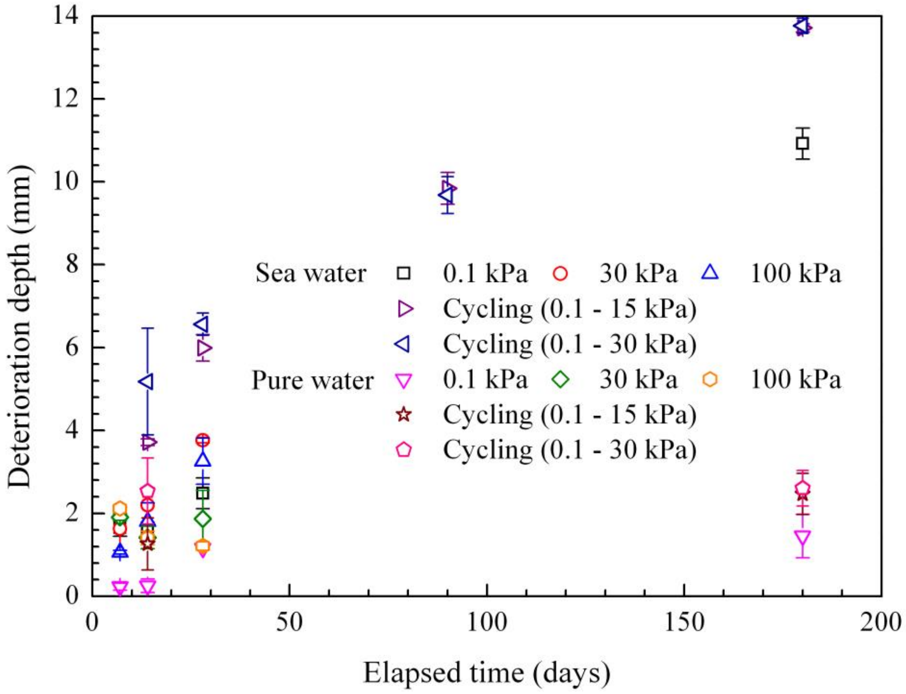
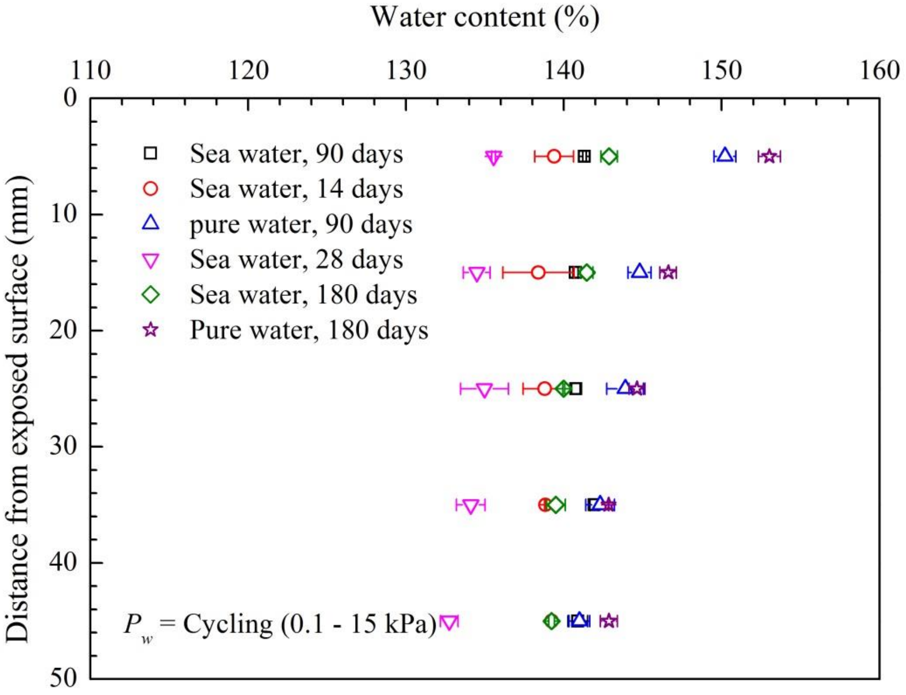


Figure 4.8 The deterioration depth of specimen under different water pressures

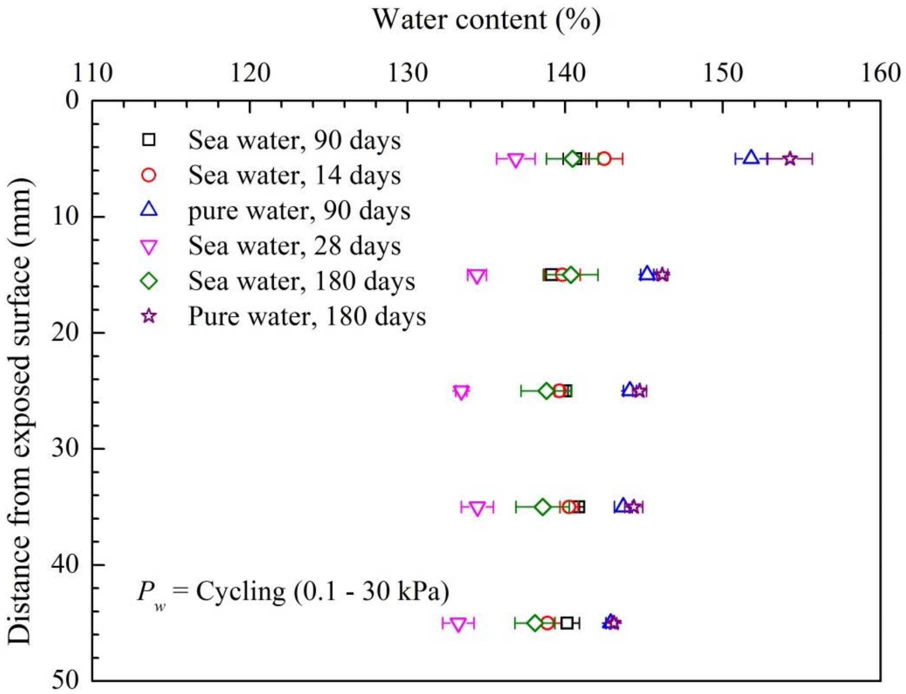
3) *Water content distribution*

Figure 4.9 shows the water content distribution with depth of specimen under dynamic water pressure.

The water content distribution under sea water varies little from exposure surface to inside of specimen. The water content decreases at non-deteriorated area as time grows.



a) Cycling (0.1 - 15 kPa)



b) Cycling (0.1 - 30 kPa)

Figure 4.9 The water content distribution with depth under dynamic water pressure

The water content distribution under pure water environment shows similar tendency as that under higher static pure water pressure condition.

The water content decreases from exposure surface to inner part of specimen and the value is a little higher under cycling (0.1 - 30 kPa) than that under cycling (0.1 - 15 kPa) condition. Higher cycling pressure leads to greater depth of water penetration.

4.3 Sea water concentration Influence

The deterioration process is a very slow process, laboratory investigation on deterioration is time consuming and it is difficult to control the curing environment at a long term.

Table 4.4 Experiments of sea water concentration influence on deterioration

Binder type	Blast-furnace slag Portland cement
Binder factor	30 %
Initial water content	200.0 %
Curing age (days)	7, 14, 28, 90, 180, 360
Exposure conditions	
Case 1	Directly submerged into 0.1 kPa sea water environment (36 g/L)
Case 2	Directly submerged into 0.1 kPa sea water environment (72 g/L)
Case 3	Directly submerged into 0.1 kPa sea water environment (108 g/L)

The accuracy decreases due to long term span. To achieve the purpose of accelerating deterioration process and improving accuracy of experimental results, the study increases the concentration of sea water. The details are listed in Table 4.4.

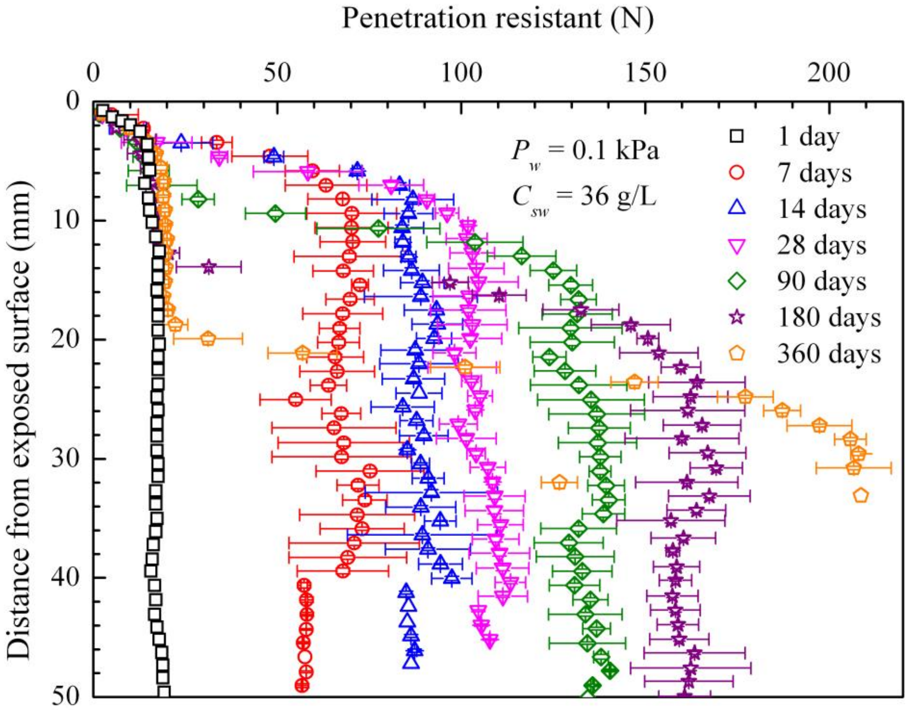
1) Cone penetration test results

The penetration resistance distributions with depth of specimens cured under 0.1 kPa with 36 g/L, 72 g/L and 108 g/L at each designed age is showed in Figure 4.10. The horizontal axis represents penetration resistance, and the vertical axis represents distance from the exposed surface.

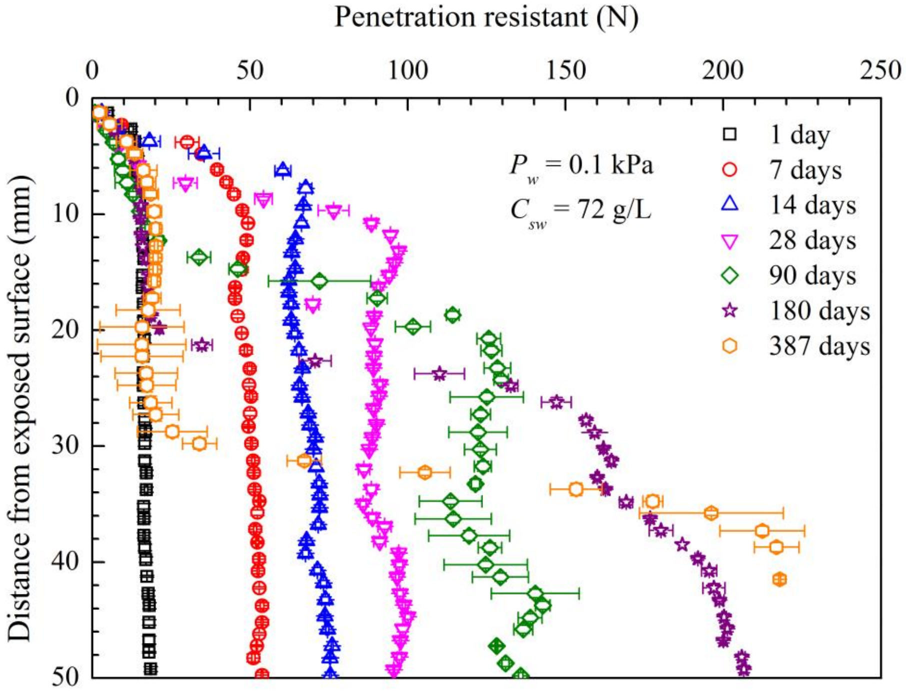
The results show obviously the deterioration induced by higher sea water concentration. The strength of specimen from exposure surface 0 mm to 50 mm is obviously lower under 72 g/L and 108 g/L conditions than that under 36 g/L at elapsed time less than 90 days.

The results show two aspects of strength development. One aspect is that the strength decreases as elapsed time becomes long near exposure surface; another aspect is that the strength increases as elapsed time becomes long at inner part of specimen.

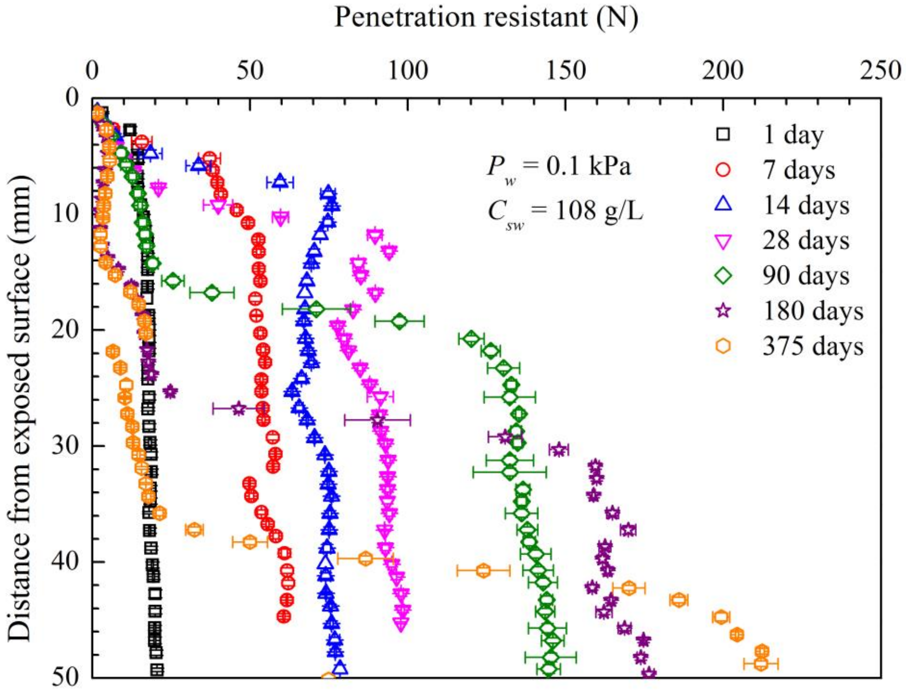
The strength around 360 days decreases to 20 N at deteriorated area. However, it develops to about 200 N at non-deteriorated area of specimen.



a) 36 g/L



b) 72 g/L



c) 108 g/L

Figure 4.10 The penetration resistance distribution with depth under different sea water concentrations

2) *Deterioration depth*

The deterioration depths of specimen under 0.1 kPa with different sea water concentrations are showed in Figure 4.11. The horizontal axis represents elapsed time and the vertical axis represents deterioration depth.

The deterioration depth at corresponding elapsed time under 0.1 kPa with sea water concentration of 36 g/L equals to 3 mm, 7 mm, 12 mm and 21 mm at corresponding elapsed time of 28 days, 90 days, 180 days and 360 days separately.

The results of deterioration depth under 72 g/L equals to 6 mm, 13 mm, 22 mm and 28 mm at corresponding elapsed time of 28 days, 90 days, 180 days and 387 days. And it equals to 8 mm, 15 mm, 26 mm and 36 mm at corresponding elapsed time of 28 days, 90 days, 180 days and 375 days under salinity concentration of 108 g/L condition.

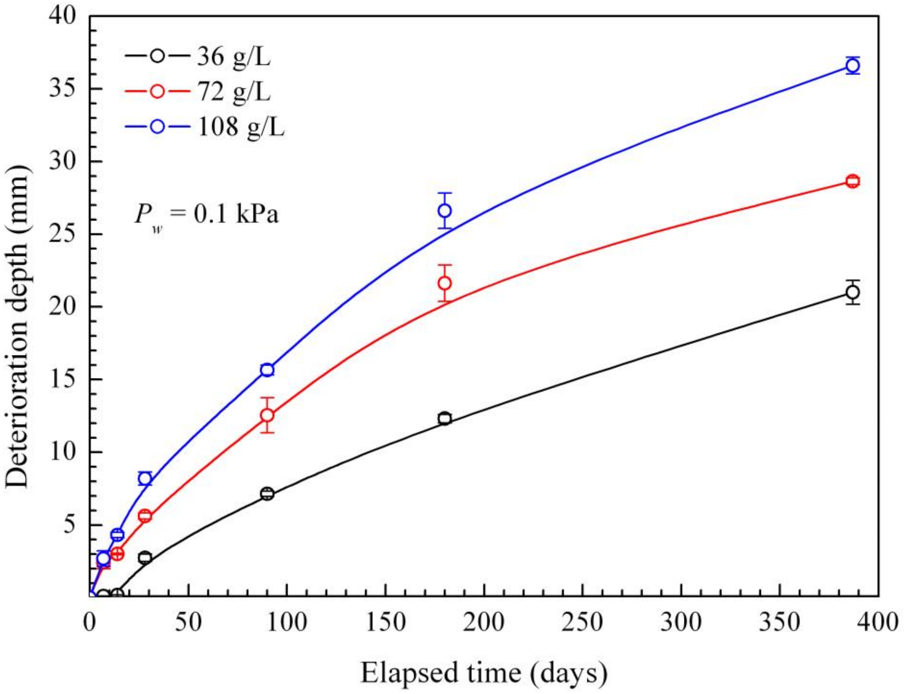


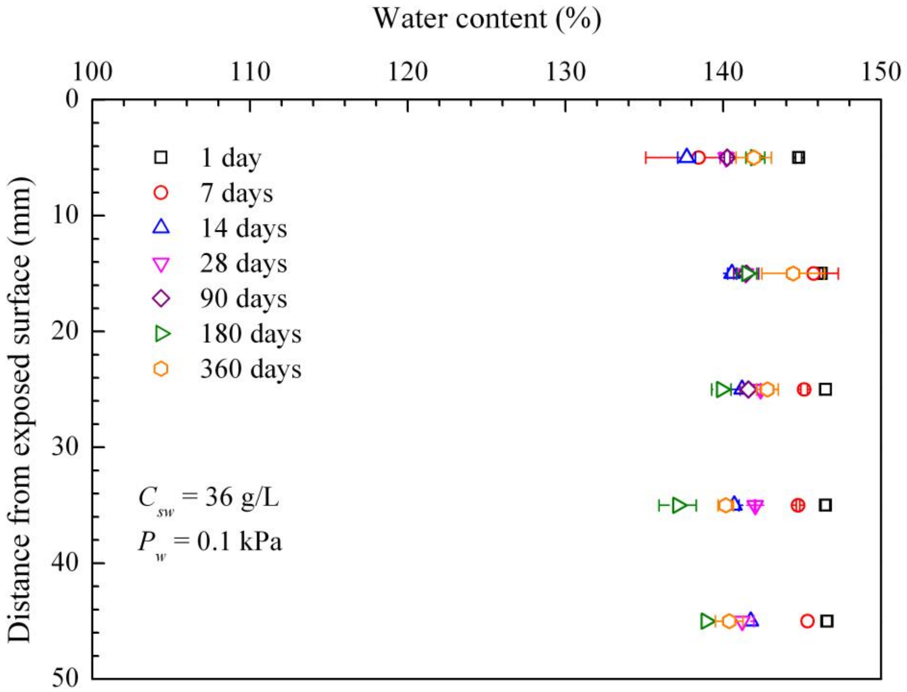
Figure 4.11 The deterioration depth of specimen under different sea water concentrations

The deterioration degree is in an order of 108 g/L > 72 g/L > 36 g/L at corresponding elapsed time. It indicates that increasing of sea water concentration is an effective method to accelerate the deterioration process. It can predict deterioration situation on relative longer time in laboratory scale under higher sea water concentration in limited time.

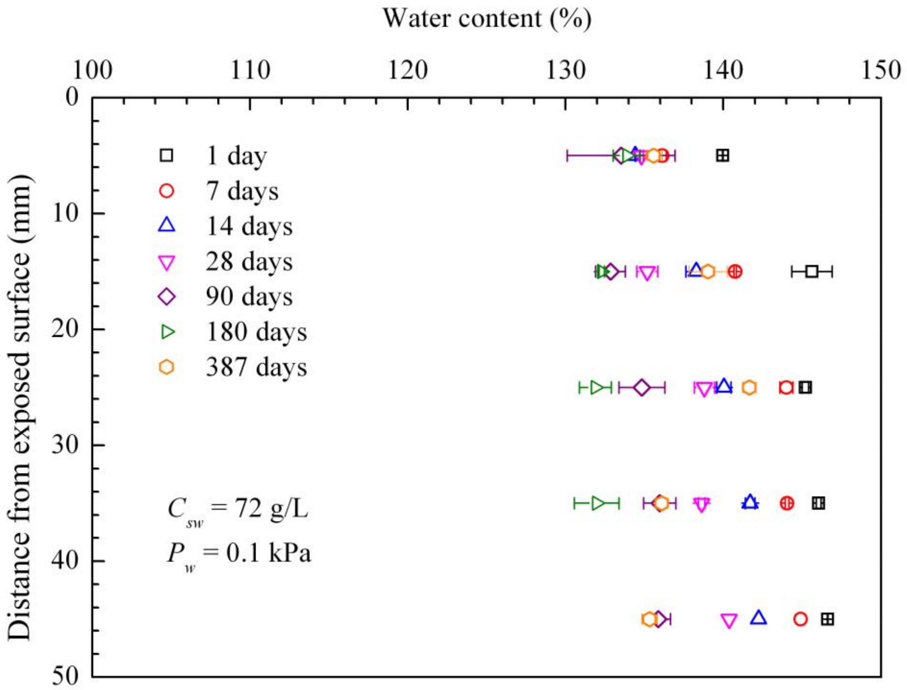
3) *Water content distribution*

Figure 4.12 shows the water content distribution with depth of specimen under higher sea water concentrations. The water content ranges from 138 ~ 148% under 0.1 kPa with 36 g/L sea water concentration and ranges from 128 ~ 148% under 0.1 kPa with 72, 108 g/L conditions.

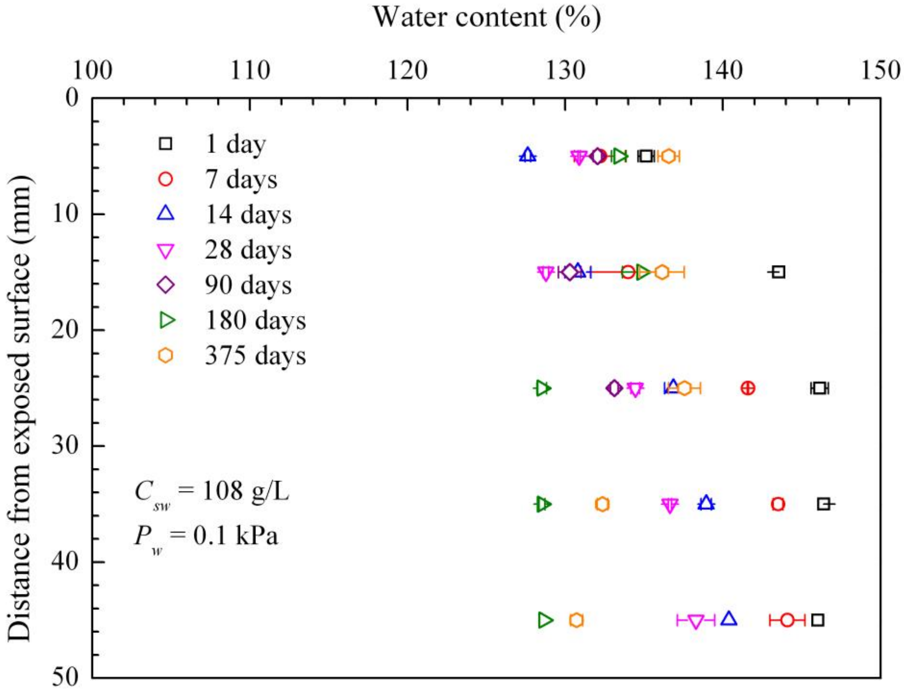
The water content variation with depth of specimen shows different tendency at short term and long term. At short term of 7, 14 and 28 days the water content increases from exposure surface to inner part of specimen, when at long term of 180 and 360 days the water content decreases from exposure surface to inner part of specimen. And this tendency is becoming more obvious under 72 g/L and 108 g/L conditions.



a) 36 g/L



b) 72 g/L



c) 108 g/L

Figure 4.12 The water content distribution with depth under different sea water concentrations

The higher sea water concentration leads to more quickly reduction of water content in specimen both at deteriorated area and non-deteriorated area.

The water content at non-deteriorated area distributes in an order of 180 days < 360 days < 28 days < 14 days < 7 days and it is more obvious under higher sea water concentration. The water content distribution with depth is in good consistency with strength distribution.

It indicates that ion concentration in sea water environment has great impact on water content distribution with depth of specimen.

4.4 Initial strength influence

The specimen in above experiment groups is submerged directly into sea water from the beginning of stabilization, which attempts to simulate the process in field site. According to previous researches, the specimen is usually exposed to corrosive environment after it gains enough strength cured under air condition with temperature of 20 degree centigrade and relative humidity of 98%. The initial strength is very different of these two conditions. The compared experiments are conducted meanwhile to investigate the impact of standard curing of specimen before exposing on deterioration (Table 4.5).

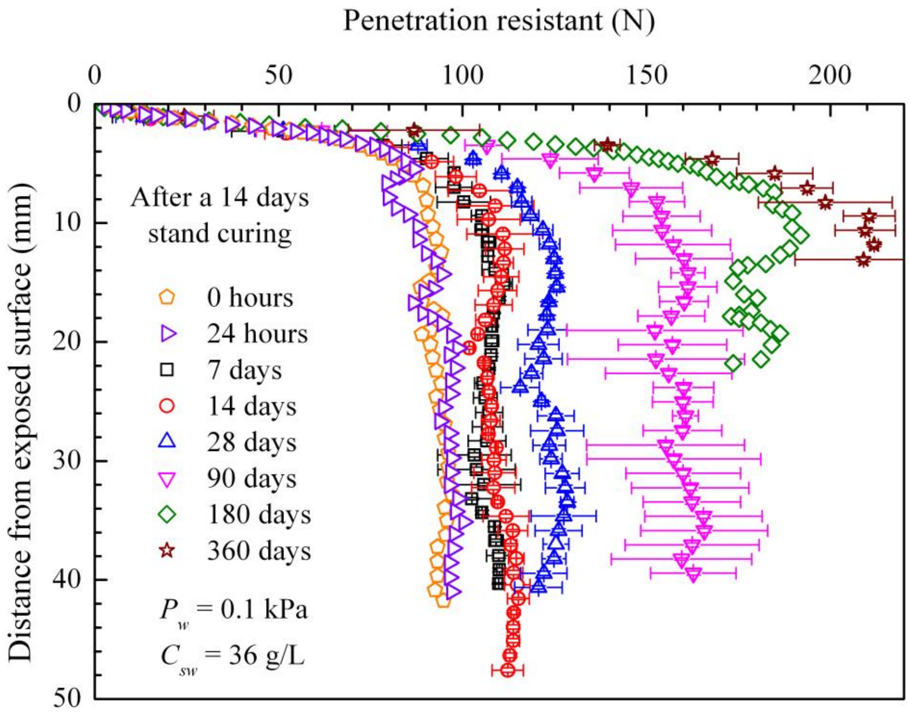
Table 4.5 Experiments of standard curing influence on deterioration

Binder type	Blast-furnace slag Portland cement
Binder factor (%)	30
Initial water content (%)	200.0
Curing age (days)	7, 14, 28, 90, 180, 360
Exposure conditions	
Case 1	Standard curing 14 days later submerge into 0.1 kPa sea water environment
Case 2	Standard curing 14 days later submerge into 15 kPa sea water environment
Case 3	Standard curing 14 days later submerge into 30 kPa sea water environment

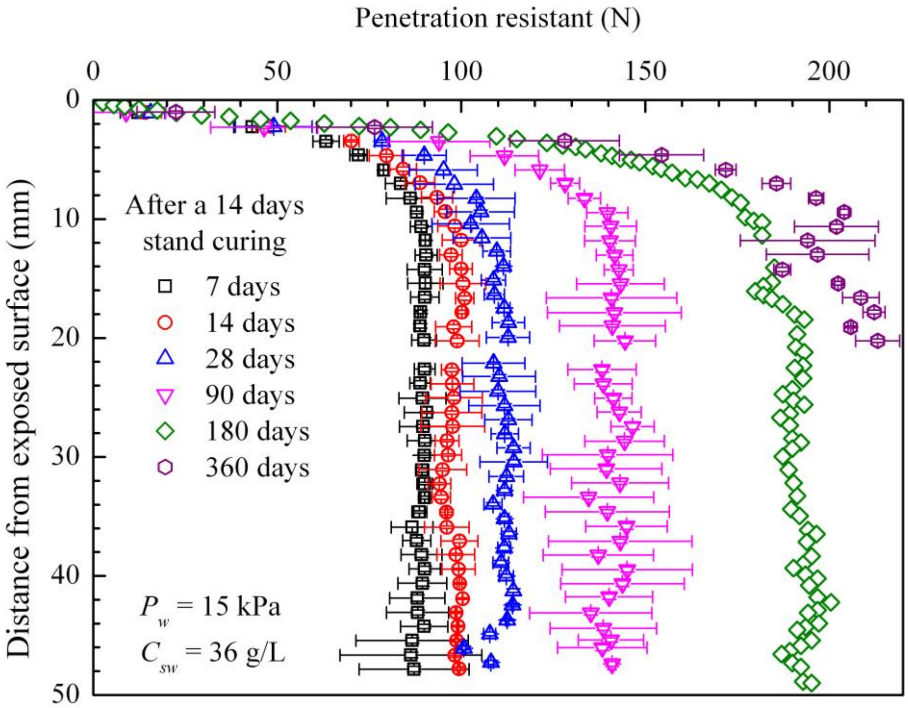
1) Cone penetration test results

The penetration resistance distributions with depth of specimens cured under 0.1, 15 and 30 kPa static water pressures with standard curing for 14 days before exposure is showed in Figure 4.13. The horizontal axis represents penetration resistance, and the vertical axis represents distance from the exposed surface.

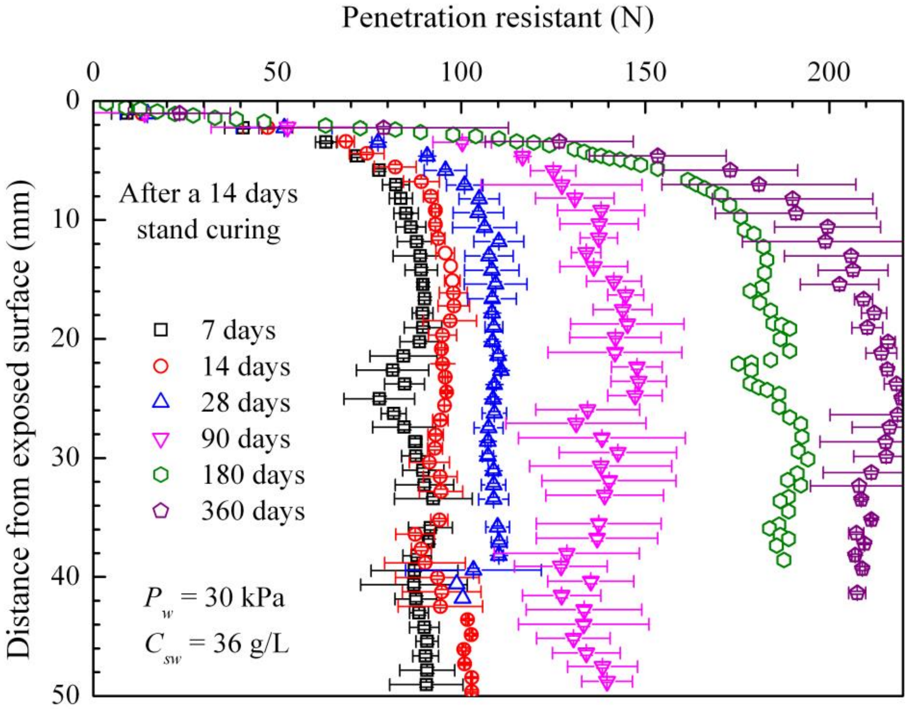
The results indicate that the standard curing before exposure can effectively prohibit the deterioration of stabilized soils. The strength continuously increases as elapsed time becomes longer. Only the exposure surface shows lower strength than inner part of specimen. The strength under 15 kPa and 30 kPa conditions is a little lower than that under 0.1 kPa at short term (< 90 days). As elapsed time grows to 180 days and 360 days, the strength under three static water pressures develops to a similar value.



a) 0.1 kPa



b) 15 kPa



c) 30 kPa

Figure 4.13 The penetration resistance distribution under different static water pressures with standard curing

2) Deterioration depths

The deterioration depths of specimen under 0.1, 15 and 30 kPa static water pressures with standard curing before exposure are showed in Figure 4.14. The horizontal axis represents elapsed time and the vertical axis represents deterioration depth.

It can be seen that the deterioration depths range from 2 ~ 3 mm under different static water pressures. It indicates that the standard curing can release the deterioration process of cement stabilized soils. The deterioration depths variation is consistent with the strength development.

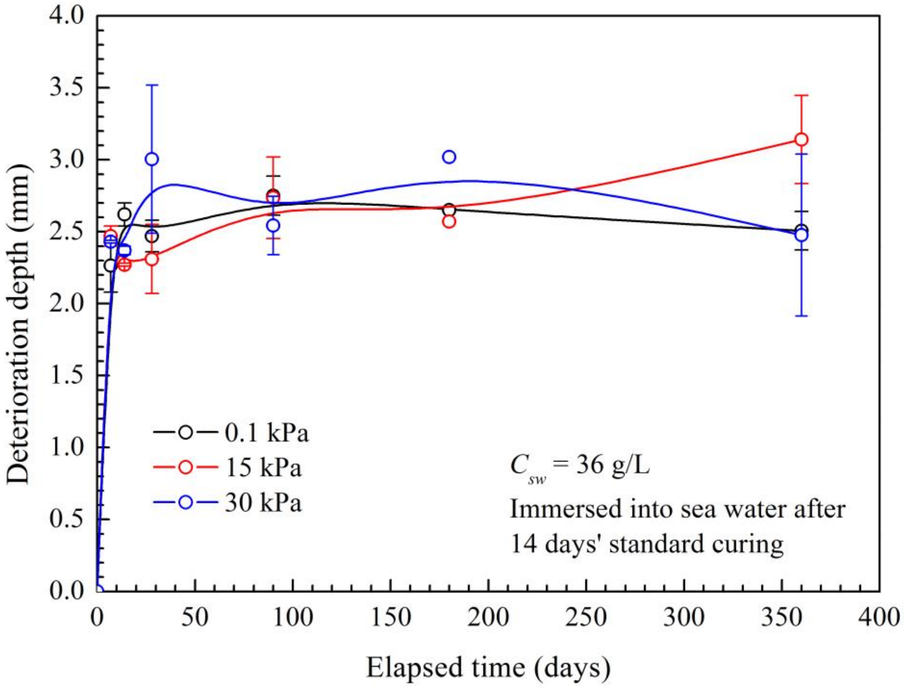


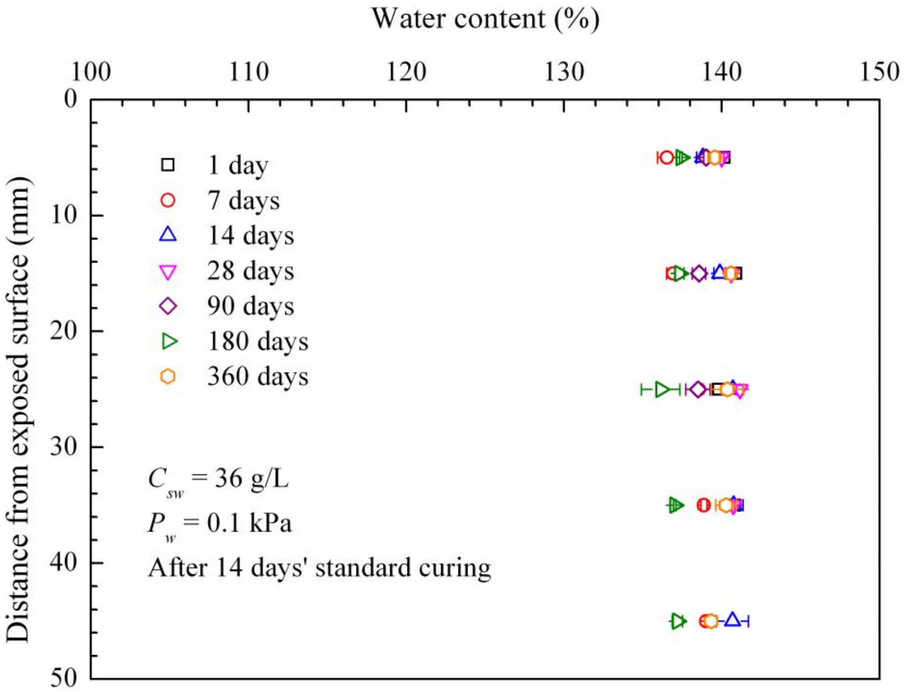
Figure 4.14 The deterioration depth of specimen under different static water pressures with standard curing

3) *Water content distribution*

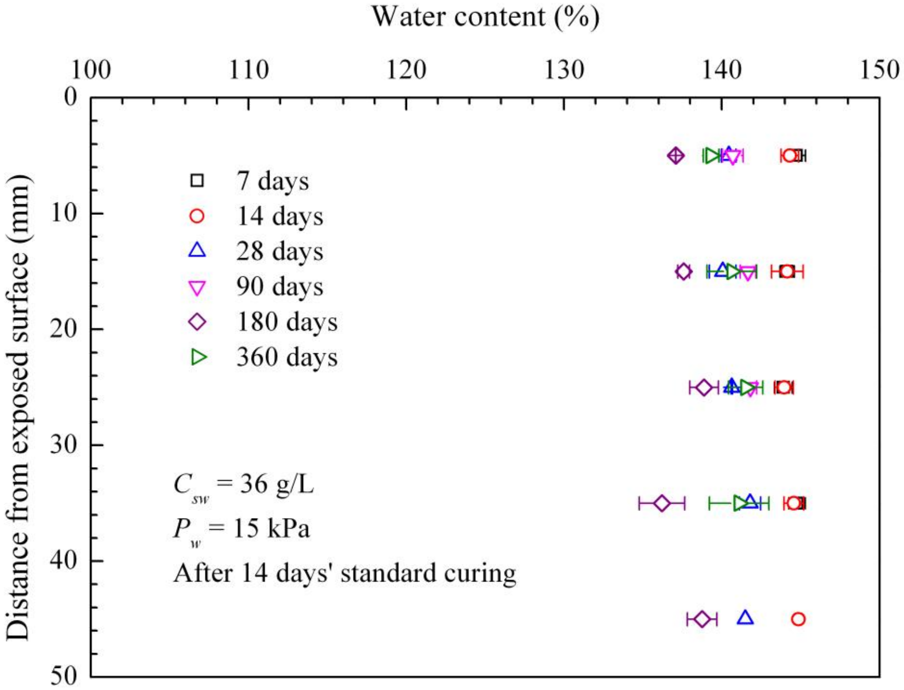
Figure 4.15 shows the water content distribution with depth of specimen under 0.1, 15 and 30 kPa static water pressures with standard curing before exposure.

The water content under 0.1 kPa is a little lower than that under 15 and 30 kPa conditions. The water content at 7 and 14 days increases clearly under higher static water pressure. The water content distribution is in good consistency with strength distribution when compare the results under three static water pressures. However, the water content at inner part of specimen shows an order of 180 days > 360 days which has been observed in forgoing experiment results. This is not so consistent with the strength distribution order of 360 days > 180 days.

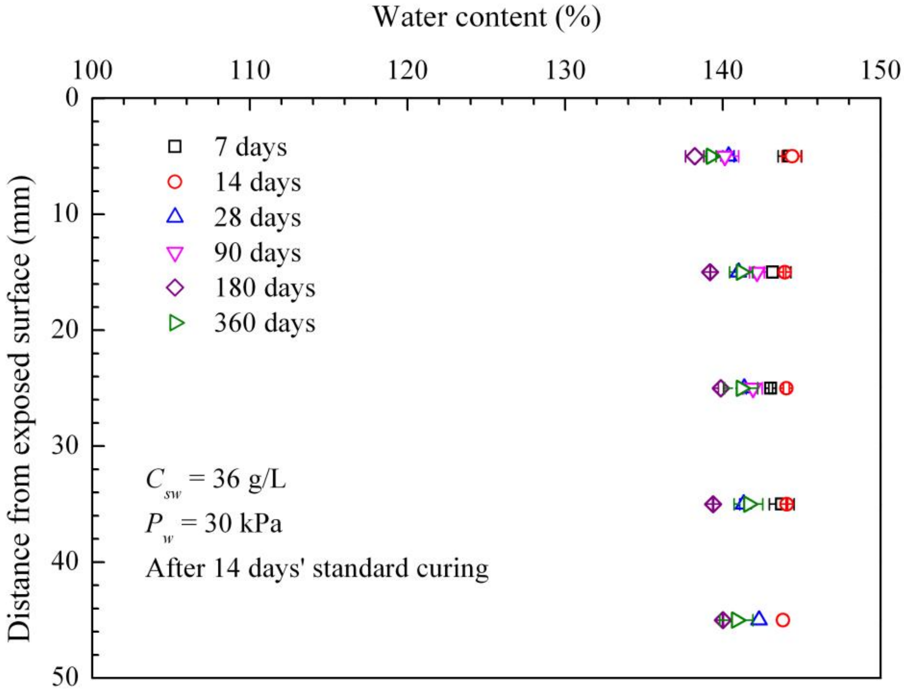
So, it is assumed that the specimen prepared in this dissertation has largest degree of reaction at 180 days. The water consuming reaches a maximum at this age.



a) 0.1 kPa



b) 15 kPa



c) 30 kPa

Figure 4.15 The water content distribution with depth under different static pressures with standard curing

4.5 Density

The density of specimen under various exposure conditions are plotted in Figure 4.16.

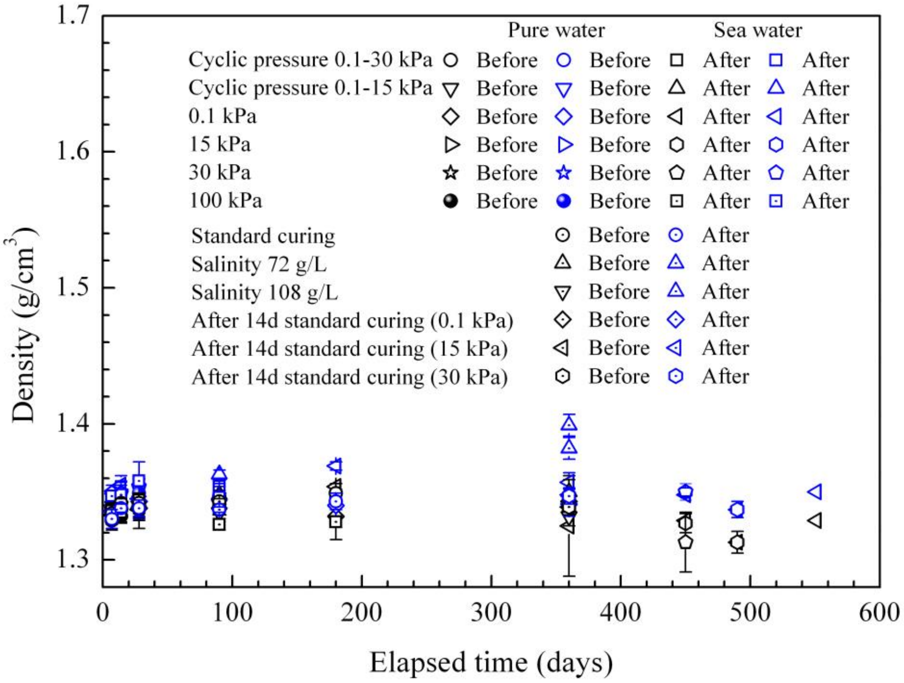


Figure 4.16 The density of specimens under different exposure conditions

It is clear that the density of specimen changes little before and after exposure and distributes at a range of 1.32 ~ 1.36 g/cm^3.

4.6 Unconfined compressive strengths

The unconfined compressive strength of specimen under various exposure conditions are also tested in this dissertation.

Figure 4.17 illustrates the relationship between unconfined compressive strength and strain under three exposure conditions.

It is obvious that deterioration induces the reduction of unconfined strength delays the appearance of strength peak value.

The strength increases continuously as time grows under standard curing (20 degree centigrade and relative humidity of 98%). The specimen with 14 days standard curing then submerged into sea water environment also develops well as time grows and even higher than that under standard curing condition. The strength of specimen cured under pure water environment although keeps increasing as time grows, but the value is some lower than that under standard curing condition. The specimen directly submerged into sea water shows the lowest strength amongst all the exposure conditions.

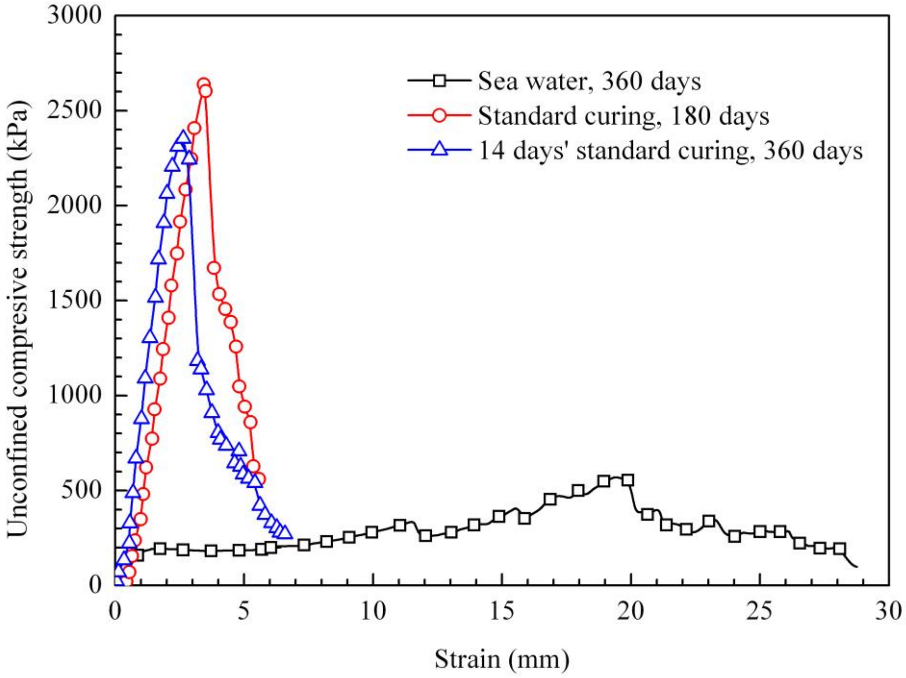


Figure 4.17 The relationship between unconfined compressive strength and strain

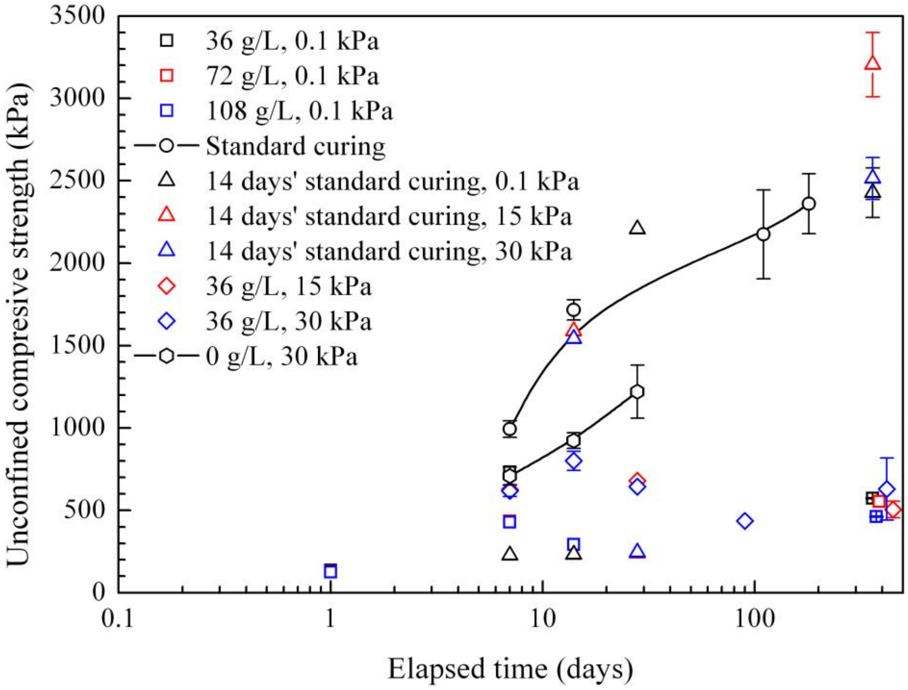


Figure 4.18 The unconfined compressive strength under different exposure conditions

It indicates that sea water environment has serious impact on unconfined compressive strength at long term which weakens the durability of cement stabilized soils as a foundation.

4.7 Summary

The originality of this chapter is summarized as following:

1) The specimen is directly exposed to corrosive environment after manufacture which attempts to simulate the actual situation in field site.
2) The static and dynamic water pressures influence on deterioration process are considered.
3) It proposes a methodology to predict long term deterioration situation in limited time.
4) The definition of deterioration depth based on cone penetration test is given out and it accurately accesses the deterioration degree under various exposure conditions.

The experimental results of this chapter are summarized as following:

1) The cone penetration results indicate two aspects of strength development. One aspect is that the strength decreases as elapsed time becomes long near exposure surface; another aspect is that the strength increases as elapsed time becomes long at inner part of specimen.

2) The deterioration depth results indicate that static water pressure influence obviously on deterioration process at short term. The dynamic pressure influences the deterioration process both at short term and long term. The dynamic water pressure shows a greater degree of influence on deterioration than static condition. The deterioration degree is not proportional to the pressure increasing.
3) The increasing of sea water concentration successfully accelerate the deterioration process, it can predict long term deterioration situation under natural sea water environment based on experimental data under higher concentration in limited time.
4) The standard curing in air (20 degree centigrade and relative humidity 98%) of specimen before exposed to sea water environment can effectively prohibit the deterioration process.
5) The water content distribution with depth shows good consistency with strength distribution. There is a different tendency of water content distribution in sea water environment and pure water. The water content distribution with depth in sea water environment shows an increasing tendency from exposure surface to inside at short term but on a contrary at long term. The water content distribution with depth in pure water environment shows a decreasing tendency from exposure surface to inside. The higher water pressure leads to a greater degree of water penetration depth in specimen.
6) The density of specimen changes little before and after exposure and distributes at a range of 1.32 ~ 1.36 g/cm^3.
7) The unconfined compressive strength of specimen is in an order of air curing > pure water > sea water.

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Chapter 5 MECHANISM OF DETERIORATION OF CEMENT STABILIZED SOILS

5.1 Introduction

This chapter explains the mechanism of deterioration of cement stabilized soils exposed to different environments from chemical and microstructure aspects.

The calcium ions and magnesium ions distributions along the depth of specimens are analyzed through atomic absorption apparatus. The microstructures of deteriorated area and non-deteriorated area of specimen is observed through scanning electronic microstructure (SEM) apparatus and the ratio of Ca/Si is analyzed through energy dispersive X-ray (EDX) attached on SEM apparatus. The porosity changing of specimen is measured through mercury intrusion porosimetry (MIP) equipment. The compounds constitute of specimen is analyzed through automated powder X-ray diffractometer (XRD) apparatus.

The calcium, magnesium ions distribution with depth under static water pressure and different sea water concentrations are introduced in this chapter. The possible existing reactions and inducing consequences are clarified.

Typical samples are selected to conduct SEM, EDX, MIP and XRD analysis.

The detailed results of microstructures, Ca/Si ratio, porosity and compound constitute are introduced in this chapter.

5.2 Influences of Calcium Iron

5.2.1 Calcium concentration distribution

1) Static sea water pressure conditions

Pore fluid chemistry analysis is performed in order to focus attention on the chemical aspects of soil samples. Atomic Absorption Spectrophotometer is used to analyze soil pore fluid of samples. The concentration of calcium and magnesium ions distribution with depth is tested through Atomic Absorption Spectrophotometer (ANA-182 type) apparatus.

Figure 5.1 shows Ca^{2+} concentration distribution with depth and corresponding strength development of specimen under 0.1 kPa, 15 kPa and 30 kPa conditions.

The top horizontal axis represents penetration resistance and the bottom horizontal axis represents Ca^{2+} concentration, the vertical horizontal axis represents distance from exposure surface of specimen.

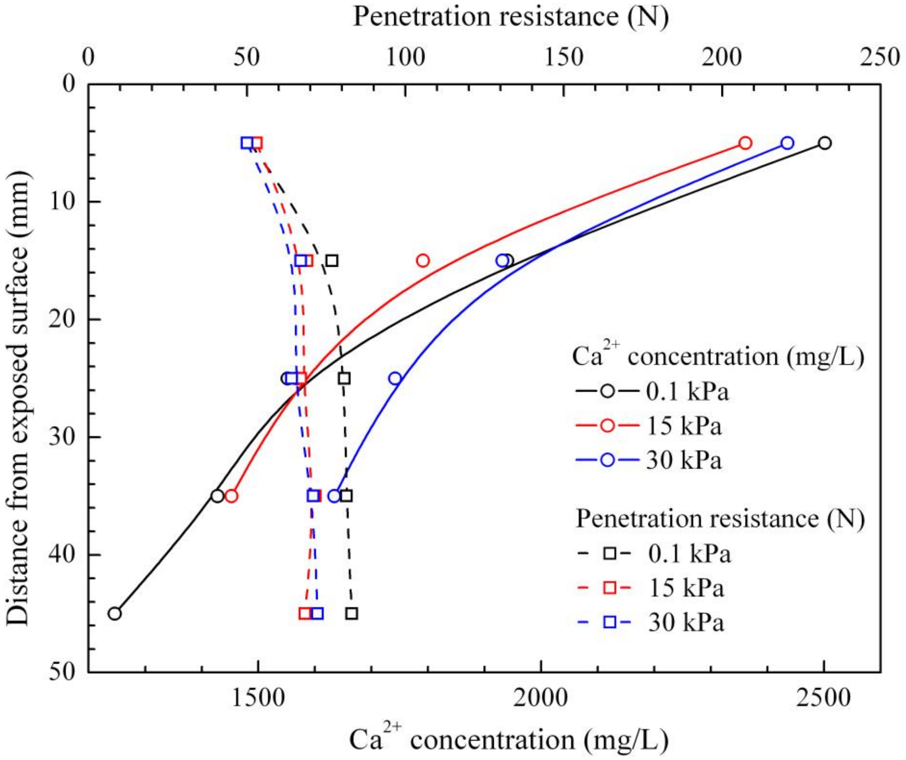
It is clear that Ca^{2+} concentration at 14 and 28 days is higher at area near exposure surface. However, it is lower at area near exposure surface at 180 and 450 days.

The Ca^{2+} concentration distribution with depth is in good consistency with strength distribution at long term. It indicates that the lowering of Ca^{2+} concentration may be one cause of decreased strength. This phenomenon has been reported in previous studies (Kitazume et al. 2002).

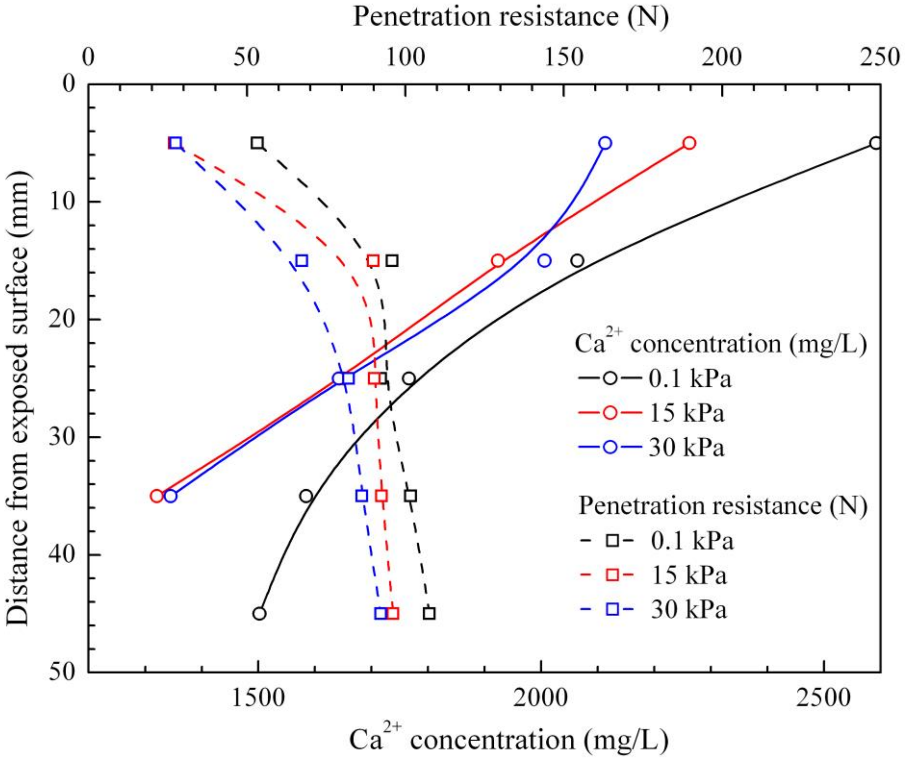
The existing form of Ca^{2+} in cement stabilized soils includes the calcium ion in liquid phase; the calcium ion in solid phase which is present mainly in the cement hydrates of C-S-H gel and calcium hydroxide; the physic chemically bound calcium ion. For ordinary soil materials, the amount of bound calcium is assumed to be zero. When the target soil material has the capacity to absorb ions such as mineral clays, the absorbed ions are treated as bound calcium (Nakarai et al. 2006). For Ariake clay, the binding of calcium ions, caused by the ion exchange of sodium ions in montmorillonite, is considered as bound calcium.

At the beginning of stabilization, when the pore water of soil comes into contact with cement, hydration reaction of the cement occurs rapidly and produces cementitious hydrated calcium silicates (C-S-H), hydrated calcium aluminates (C-A-H) and hydrated lime $Ca(OH)_2$. This process is water consuming and producing excessive $Ca(OH)_2$.

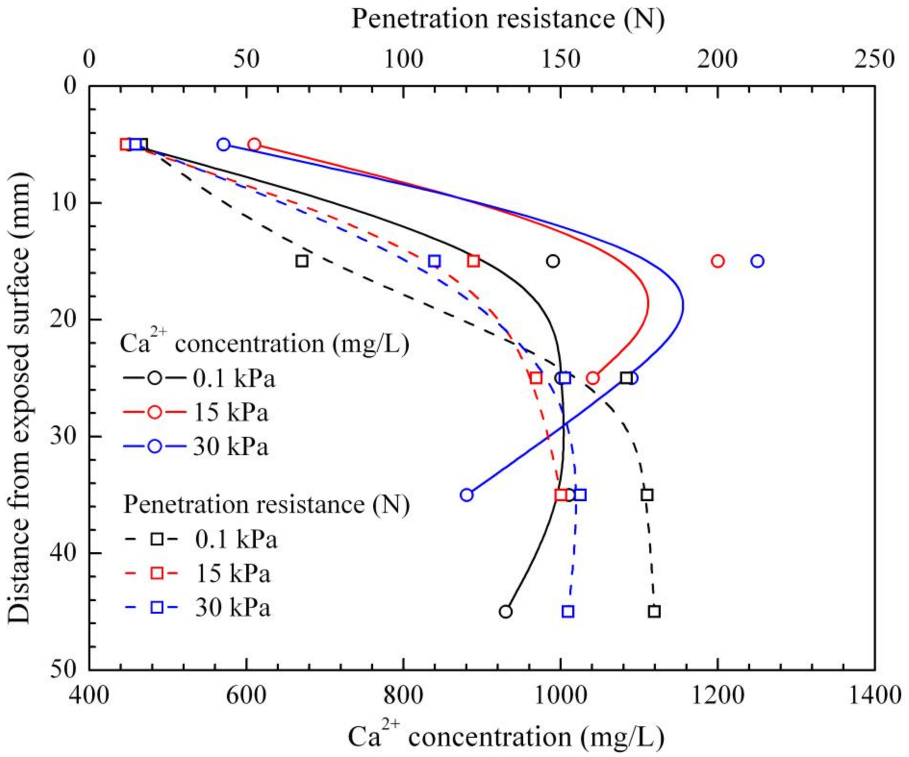
The calcium in solid phase $Ca(OH)_2$ can be transformed to bound calcium through the ion exchange of sodium ions in montmorillonite of Ariake clay. The calcium concentration gradient between solid phase and liquid phase leads to the leaching of calcium from $Ca(OH)_2$ to pore water.



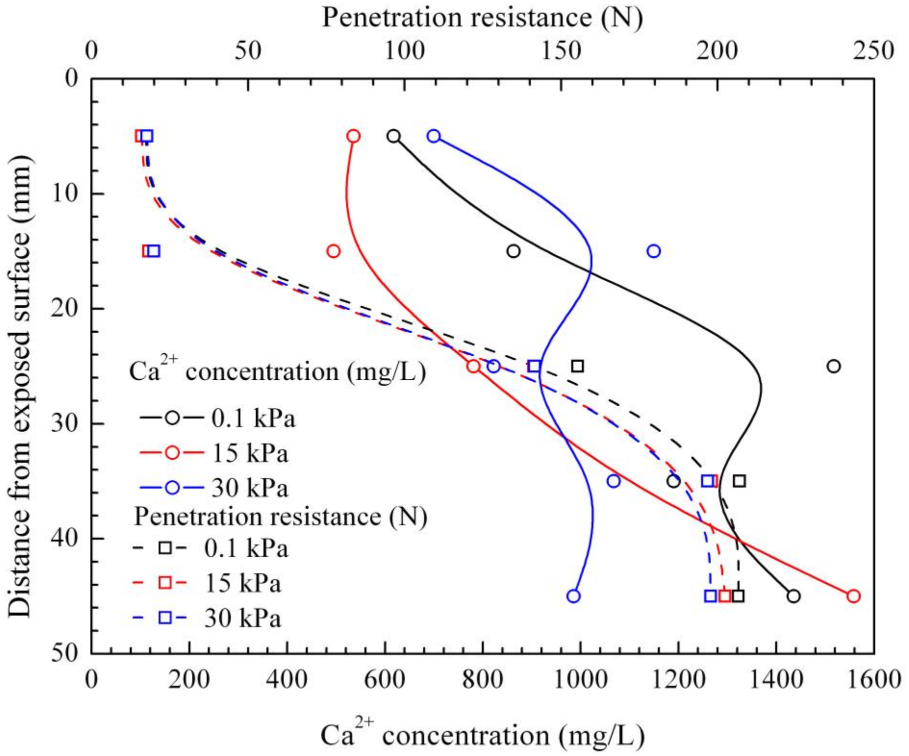
a) 14 days



b) 28 days



c) 180 days



d) 450 days

Figure 5.1 Calcium ions concentration distribution with depth under static water pressure

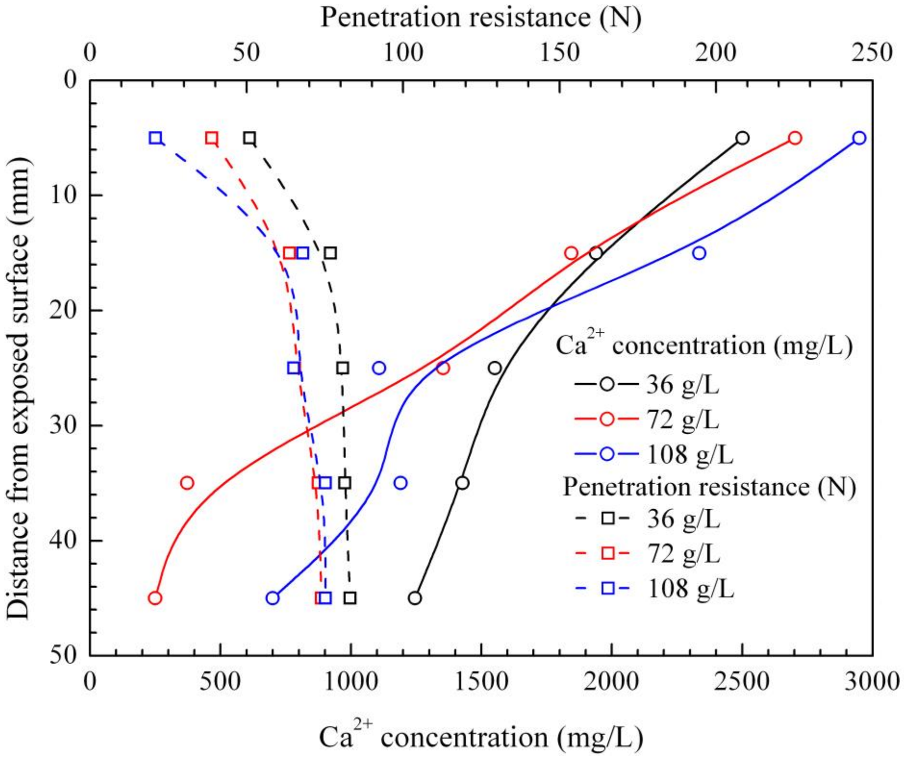
The calcium ions concentration is higher near exposure surface area at 14 and 28 days because the permeability is higher at the initial stage of stabilization so that water diffuses from outer environment into specimen and react with cement to produce more $Ca(OH)_2$. The calcium distribution with depth is not consistent with strength development at short term but at long term. It indicates that calcium leaching is a long term effects. At short term $Ca(OH)_2$ is the major source of Ca^{2+} in pore water, higher Ca^{2+} in pore water represents a much more production of C-S-H. As time grows, the reaction between cement, water and soil is fully completed and the $Ca(OH)_2$ is completely consumed. The calcium leaching from C-S-H occurs to equilibrium the calcium in solid phase and liquid phase. So, at long term the lower Ca^{2+} represents less amount of hydration product C-S-H which induces the reduction of strength finally.

There is no obvious discipline of static water pressure influence on calcium distribution with depth.

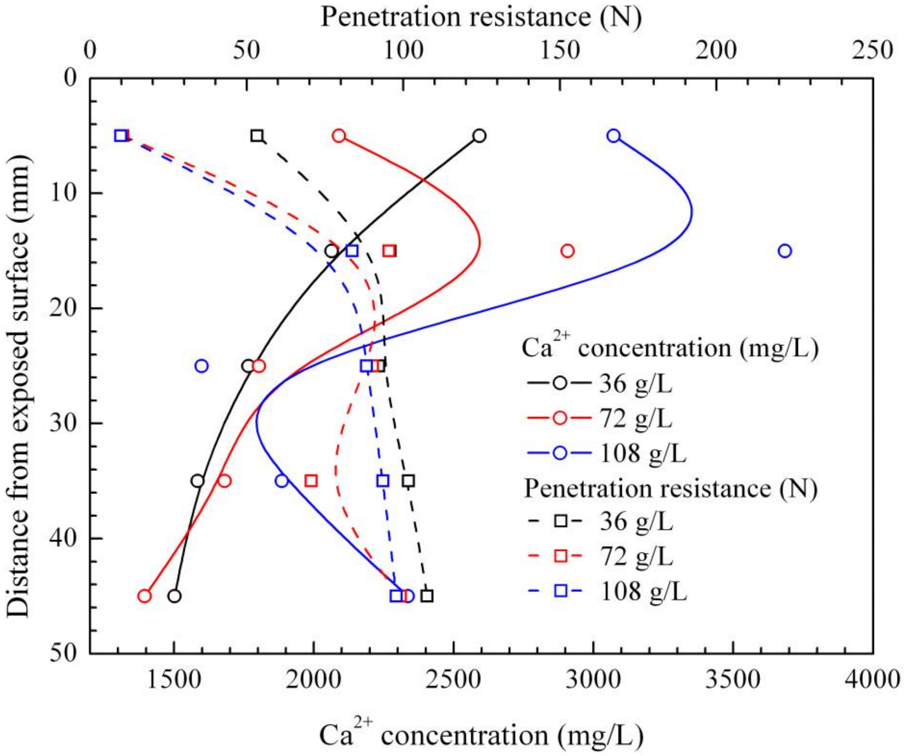
2) Sea water concentration conditions

Figure 5.2 shows Ca^{2+} concentration distribution with depth and corresponding strength development of specimen under 0.1 kPa with 36, 72, 108 g/L conditions.

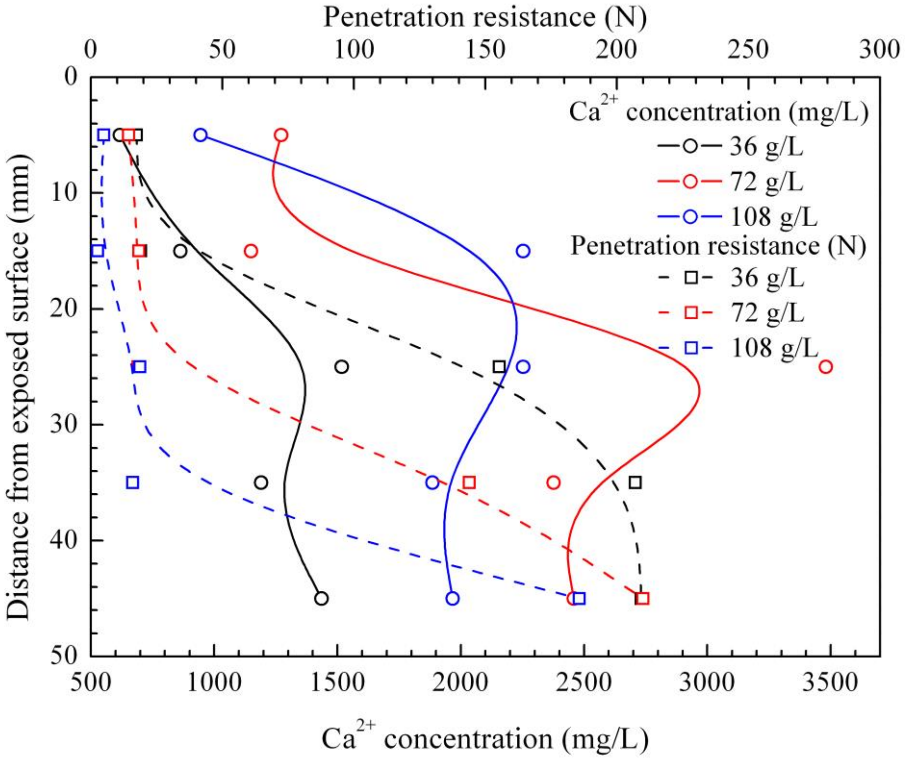
The calcium distribution with depth at 14 days shows same tendency as above mentioned. However, the calcium ion concentration is a little lower near exposure surface. it indicates that higher sea water concentration can accelerate the progress of deterioration.



a) 14 days



b) 28 days



c) 387 days

Figure 5.2 Calcium ions distribution with depth under different concentrations

One year later, the calcium distribution with depth is very different under three concentrations, just like the water content distribution with depth introduced in chapter 4. The concentration of sea water also impacts serious on the calcium ion distribution.

5.2.2 Possible Existing Reactions and Consequences

The first three reactions produce major hydration products to achieve the strength continuous increasing. The other two processes cause the porous structure of stabilized soils and decomposition hydration products, further the strength reduction.

1) Hydration reaction:

$$2(3CaO\cdot SiO_2) + 6H_2O \rightarrow 3CaO\cdot 2SiO_2\cdot 3H_2O + 3Ca(OH)_2$$

$$2(2CaO\cdot SiO_2) + 4H_2O \rightarrow 3CaO\cdot 2SiO_2\cdot 3H_2O + Ca(OH)_2$$

2) Pozzolanic reaction:

$$SiO_2\ (Al_2O_3) + Ca(OH)_2 + nH_2O \rightarrow CaO\cdot SiO_2\cdot (n+1)H_2O\ (CaO\cdot Al_2O_3\cdot (n+1)H_2O)$$

3) Carbonation reaction:

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3\downarrow + H_2O$$

$$3CaO\cdot 2SiO_2\cdot 3H_2O + CO_2 \rightarrow CaCO_3\downarrow + 2(CaO\cdot SiO_2\cdot H_2O) + H_2O$$

$$(CaO\cdot SiO_2\cdot H_2O) + CO_2 \rightarrow CaCO_3\downarrow + SiO_2 + H_2O$$

4) Dissolution of calcium from $Ca(OH)_2$:

$$Ca(OH)_2 \rightarrow Ca^{2+} + 2OH^-$$

5) Dissolution of calcium form hydration products C-S-H:

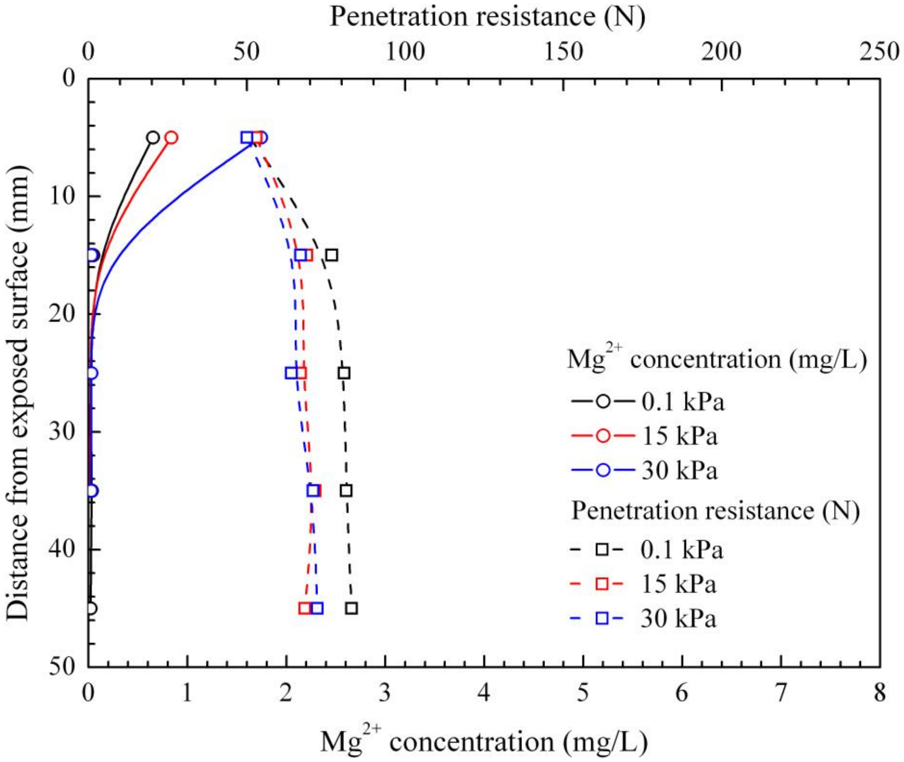
$$3CaO\cdot 2SiO_2\cdot 3H_2O \rightarrow 2SiO_2 + 3Ca(OH)_2$$

5.3 Influences of Magnesium Iron

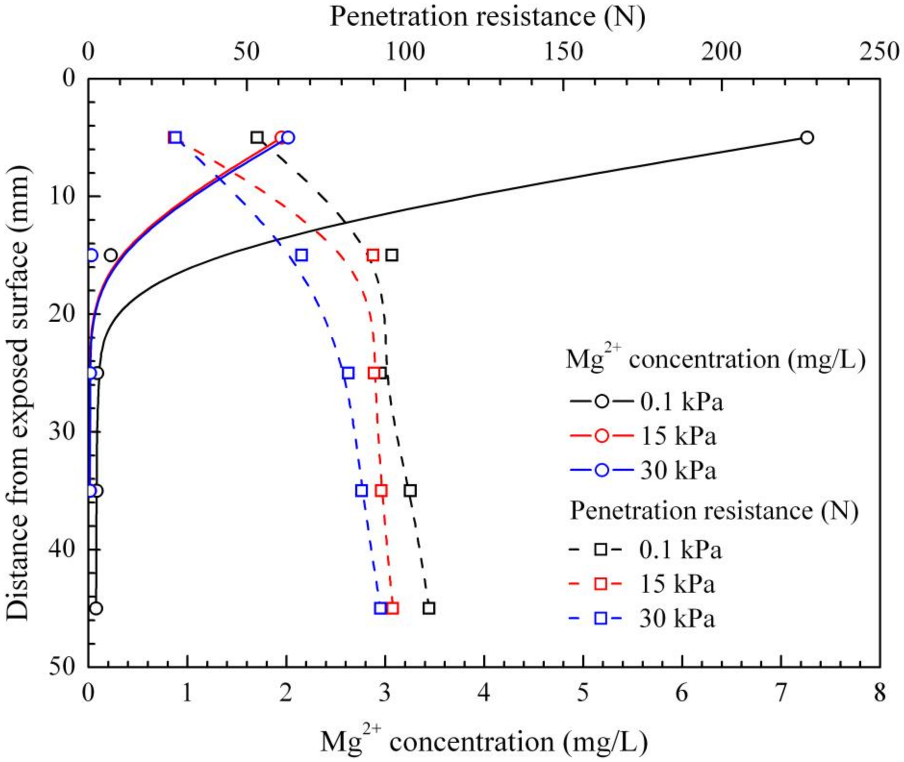
5.3.1 Magnesium concentration distribution

1) Static sea water pressure conditions

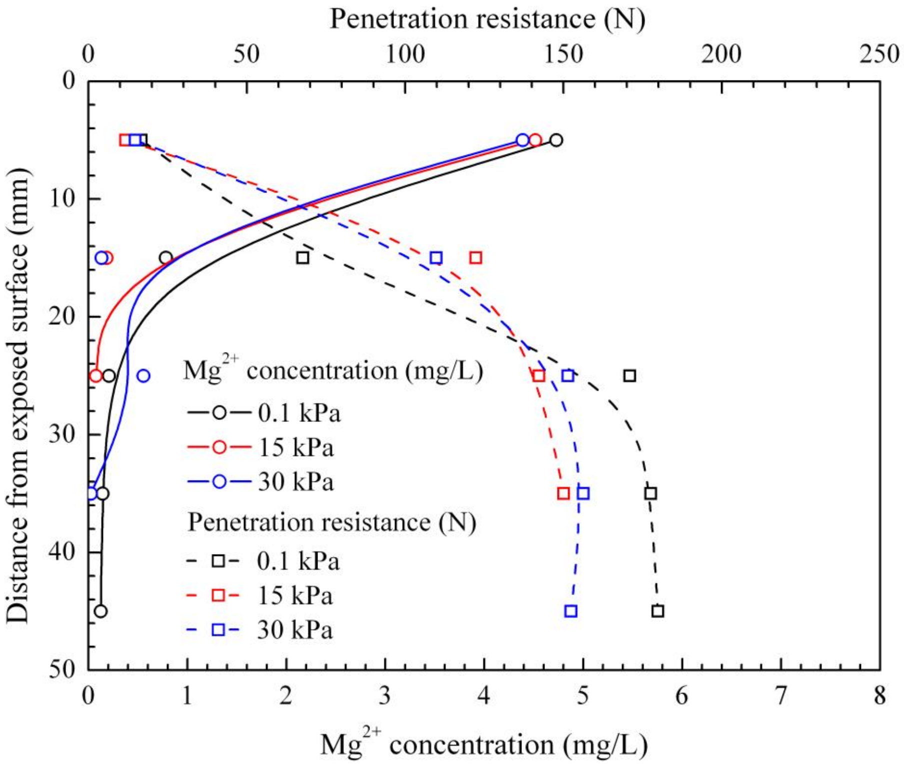
Figure 4.9 shows magnesium concentration distribution with depth and corresponding strength development of specimen under 0.1, 15 and 30 kPa conditions. The top horizontal axis represents penetration resistance and the bottom horizontal axis represents magnesium concentration. Where the vertical horizontal axis represents distance from exposed surface of specimen. The magnesium concentration is gradually decreases from the exposed surface to inside of specimen.



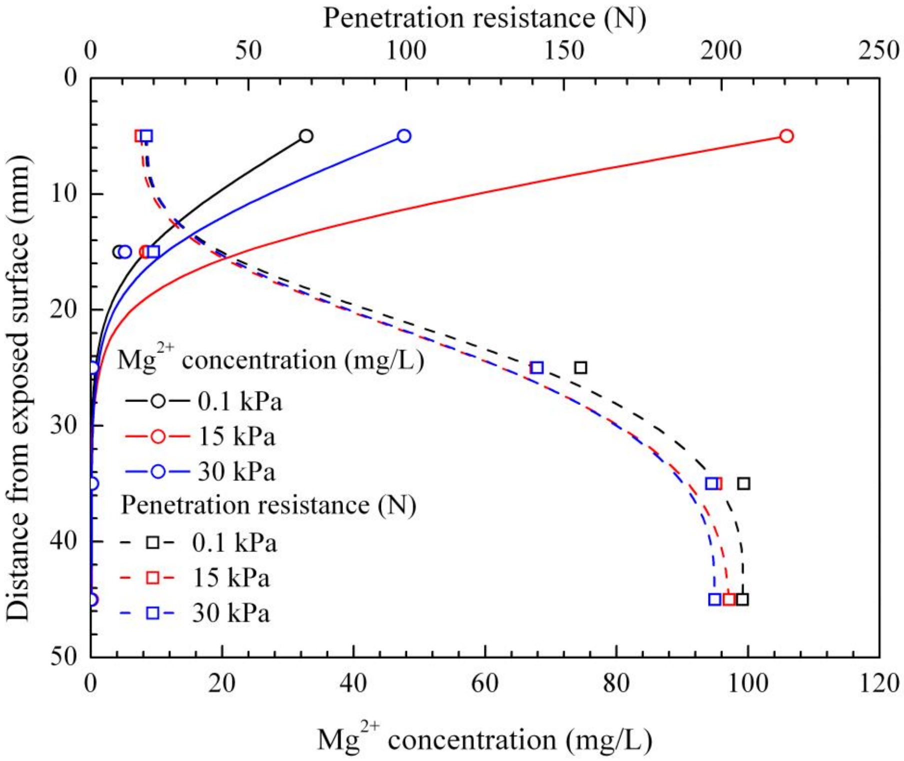
a) 14 days



b) 28 days



c) 180 days



d) 450 days

Figure 5.3 Magnesium ions distribution with depth under different pressures

The results show that the magnesium ion concentration distribution with depth is consistent with strength development. It indicates that deterioration caused by magnesium ions occurs at the very beginning of stabilization. The Mg^{2+} can replace Ca^{2+} to produce brucite $Mg(OH)_2$ or $MgO \cdot SiO_2 \cdot H_2O$ with lower strength and poor cementitious. Finally reduce the strength of cement stabilized soils.

There is no obvious discipline of different static water pressure influence on magnesium ion concentration distribution with depth.

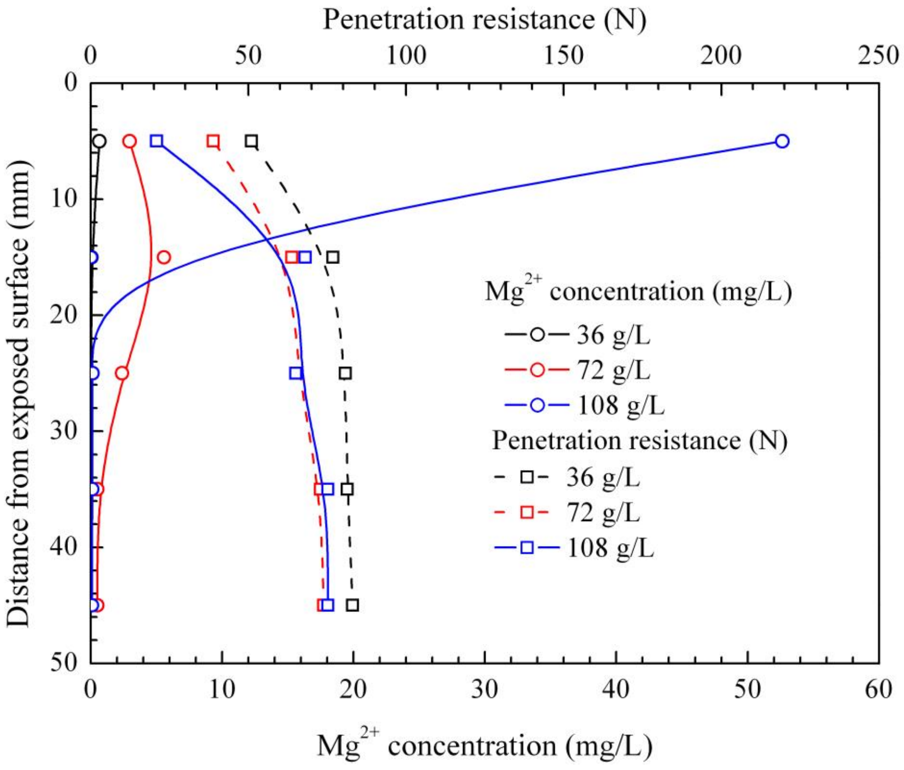
2) Sea water concentration conditions

Figure 4.9 shows magnesium concentration distribution with depth and corresponding strength development of specimen under 0.1 kPa with 36, 72 and 108 g/L conditions.

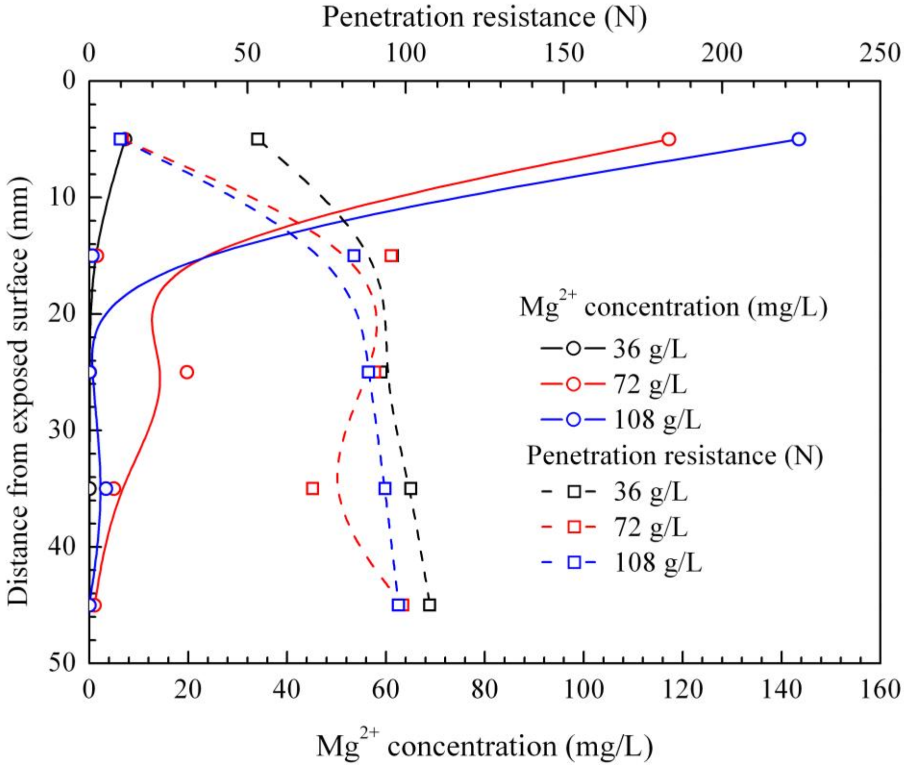
The magnesium distribution with depth is very consistent with strength distribution. The sea water concentration impacts obviously on the magnesium distribution with depth. The effect degree is in an order of 108 g/L > 72 g/L > 36 g/L.

The greater magnesium ion concentration gradient accelerates the deterioration process effectively. The magnesium effect on deterioration of stabilized soils from the very beginning of stabilization and last a long period.

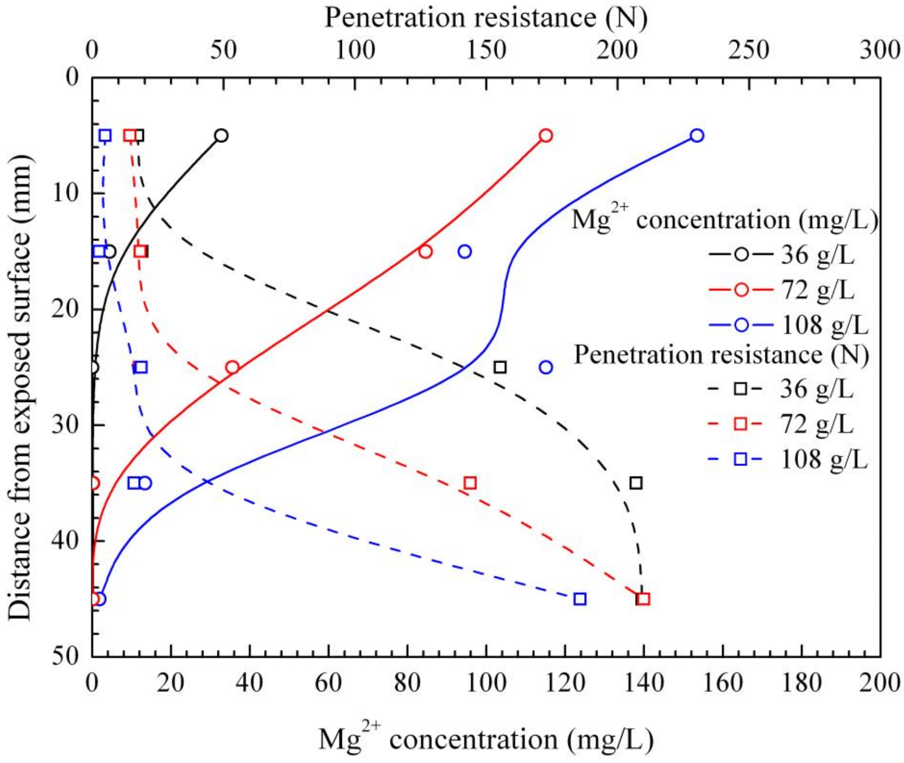
It indicates that magnesium reaction with stabilized soils is another major cause of strength reduction.



a) 14 days



b) 28 days



c) 387 days

Figure 5.4 Magnesium ions distribution with depth under different sea water concentration

5.3.2 Possible Existing Reactions and Consequences

The magnesium ion reactions with hydration products are listed as followings:

$$Ca(OH)_2 + MgSO_4 + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O + Mg(OH)_2$$

$$Ca(OH)_2 + MgCl_2 \rightarrow CaCl_2 + Mg(OH)_2$$

$$Mg(OH)_2 + SiO_2 \rightarrow MgO \cdot SiO_2 \cdot H_2O$$

$$Mg(OH)_2 + CaO \cdot SiO_2 \cdot H_2O \rightarrow Mg(SiO_2)(OH)_2 + Ca(OH)_2$$

$$Mg(OH)_2 + CO_2 \rightarrow MgCO_3 + H_2O$$

The magnesium ions replace Ca^{2+} to produce $Mg(OH)_2$ with lower cementation behavior. It reacts with hydration products C-S-H or SiO_2 dissolved from clay particles to form magnesium silicate hydration products with lower strength. The consuming of Ca^{2+} during these processes delays the pozzolanic reaction and prohibits the continuous hydration reaction. The strength development is slowed down and the final strength is lower under magnesium intrusion environment.

The effect of magnesium ions on deterioration acts from the very beginning stabilization and last for a long time. However, the leaching of calcium process is a long term effect. At early stage, the hydration reaction is the dominant factor.

5.4 Verification

5.4.1 Microstructures and Elements analysis

1) Microstructure

Scanning electronic microstructure (SEM) SS-550 is used for analyzing the microstructure of cement stabilized soils.

Figure 5.5 shows the microstructure of deteriorated area of specimen cured under 0.1 kPa with 72 g/L condition for 387 days. Three levels of image magnification: × 500, × 2000, × 5000.

The image shows that the structure is very loosely and there are a large amount of holes. The porosity is obviously increasing due to deterioration.

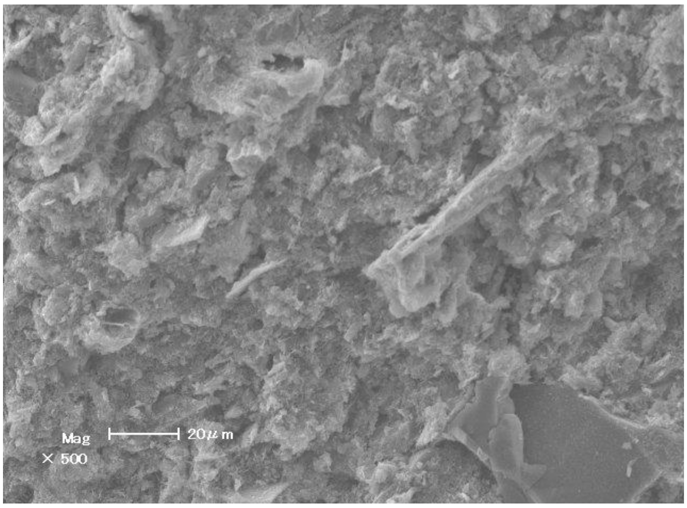
Figure 5.6 shows the microstructure of non-deteriorated area of specimen cured under 0.1 kPa with 72 g/L condition for 387 days. Two levels of image magnification: × 500, × 1000.

The microstructure of non-deteriorated area is very dense, the hydration products binding together tightly. At deteriorated area this binding structure is broken by aggressive ions intrusion. The calcium leaching and magnesium reaction with hydrated products lead to dissolution of C-S-H and lower cementation in cement stabilized soils.

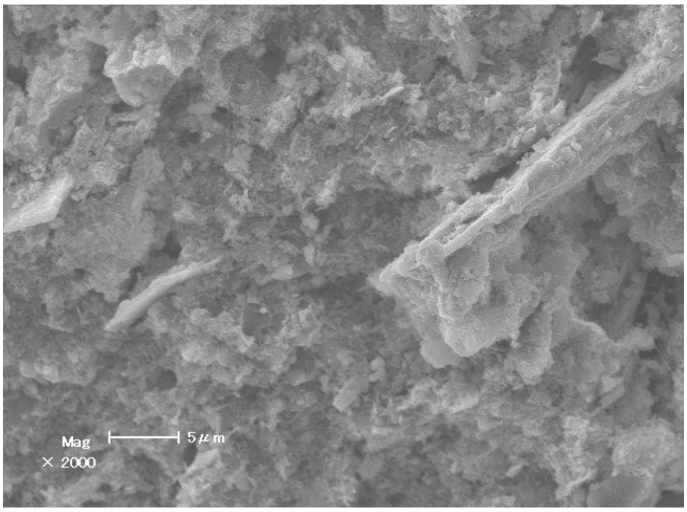
Figure 5.7 shows the microstructure of specimen cured under air (20 degree centigrade and relative humidity 98%) condition for 28 days. Two levels of magnification: ×1000, × 2000.

It is obvious that the flocculent products are gradually entrapping the clay particles and binding together, then the little clay particles flocculated to a larger one. On the other hand, the produced hydration products fill the pores in stabilized soils. So, the strength of stabilized soils is enhanced.

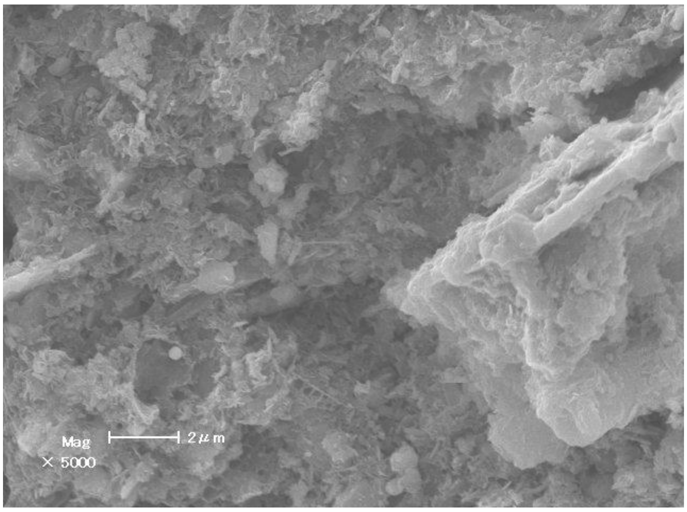
The clay particle can be observed at 28 days, but it is difficult to distinguish clay particle and hydration products at age of 387 days. At non-deteriorated area of 387 days the clay particles are entrapped completely and integrated to a dense structure.



a) ×500

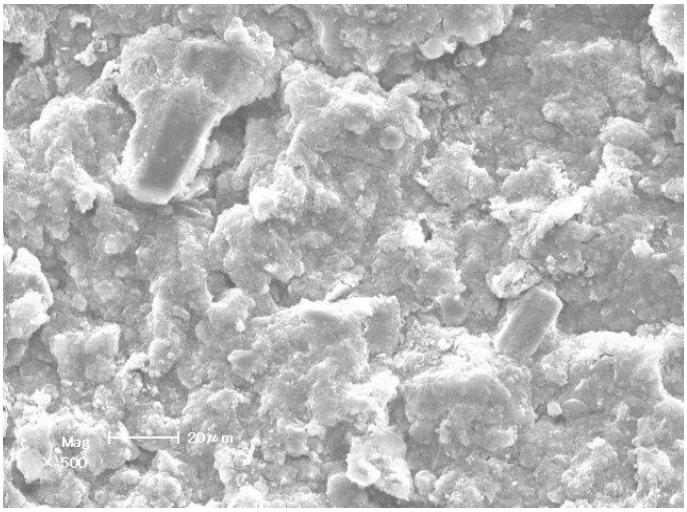


b) ×2000

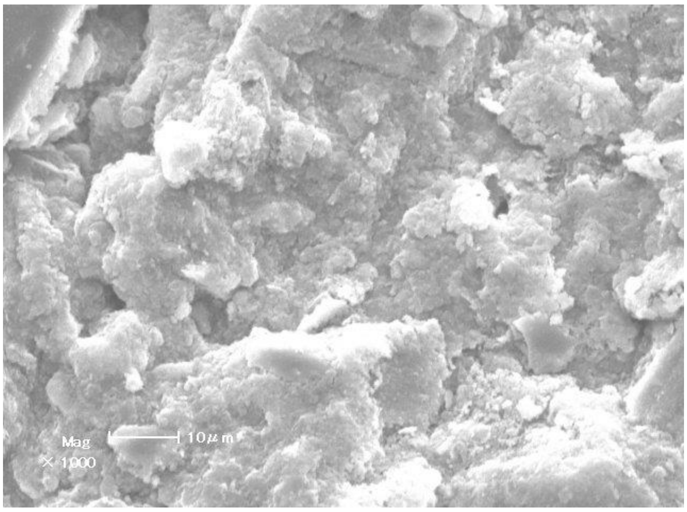


c) ×5000

Figure 5.5 SEM image of deteriorated area

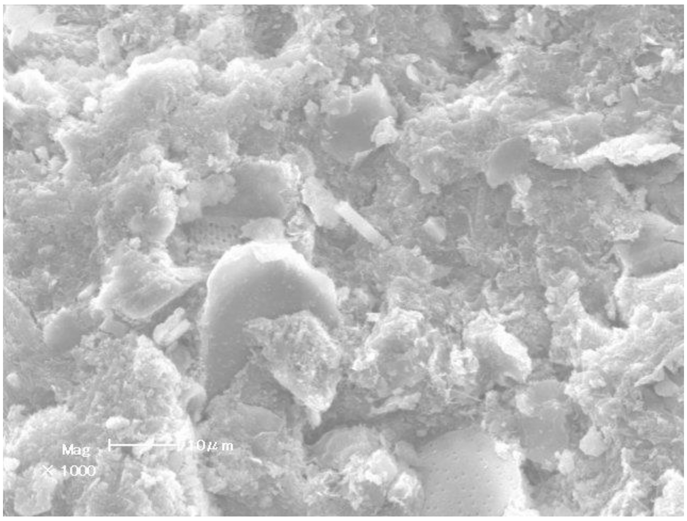


a) ×500

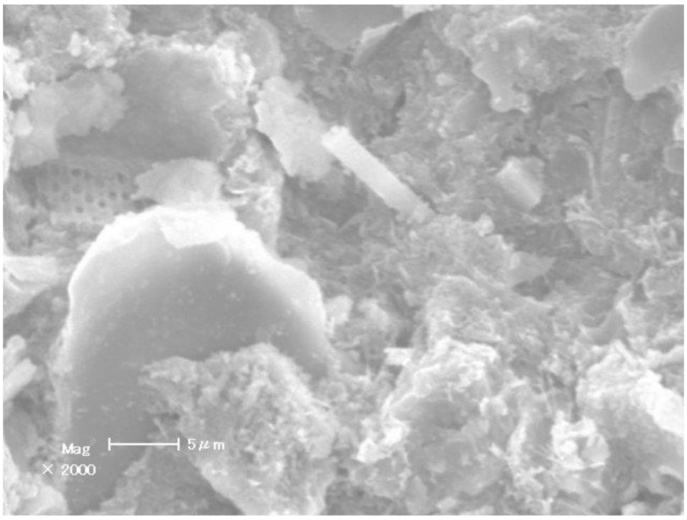


b) ×1000

Figure 5.6 SEM image of non-deteriorated area



a) ×1000



b) ×2000

Figure 5.7 SEM image of specimen cured in air for 28 days

2) *Ca/Si ratio*

The scanning electronic microstructure apparatus has an attachment of energy dispersive X-ray (EDX) system (Genesis 2000) and the data generated by EDX analysis consist of spectra showing peaks corresponding to the elements making up the true composition of the sample being analyzed. The CaO to SiO_2 (Ca/Si) ratio can be analyzed.

Figure 5.8 shows the Ca/Si ratio with depth under sea water environment with 0.1 kPa pressure at 28 and 180 days.

It can be seen that the Ca/Si ratio at 28 days keeps a constant value of 0.68 from exposure surface to inner part of specimen. The Ca/Si ratio at 180 days is lower near exposure surface and gradually increasing to a value of 1.0 at depth of 20 ~ 30 mm.

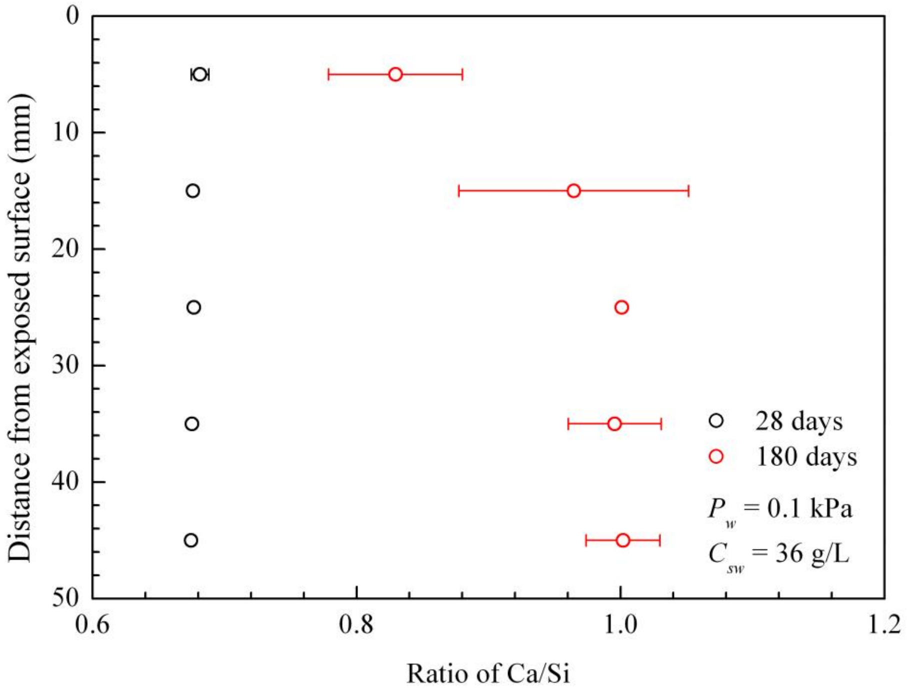


Figure 5.8 The Ca/Si ratio with depth under sea water environment with 0.1 kPa

The CaO and SiO_2 are major constitutes of hydration products C-S-H, reduction of Ca/Si ratio near exposure surface further verified the leaching fact of calcium from C-S-H at long term.

5.4.2 Mercury intrusion test results

The porosity of stabilized soils collected from the different depths of the specimens made with blast-furnace slag Portland cement B type is shown in Figures 5.9 ~ 5.14.

Generally, pore size from 0.01 – 1μm is defined as the capillary pore. The volume of the capillary pores determines the permeability of ions in concrete (Mohammed et al. 2003).

The cemented soils generally have high water-to-cement ratios and contain large voids, and so are thought to have voids much larger than the pores in cement paste. Volume of capillary pore decreases as hydration takes place. It is found that after 180 days curing in air, the pore volume reduces.

Figure 5.11 shows porosity at different depths of specimen cured under 0.1 kPa, 36 g/L condition for 180 days. It is obvious that after a long-term of exposure, pore size shifts to larger pores near exposure surface of the specimens. The curves of cumulative pore volume indicate a relative denser microstructure is formed at inner part of specimen.

The finer pores reduces near exposure surface (0 - 10 mm) compared with inner part (40 - 50 mm) which induces coarser and porous structure.

Figure 5.12 shows the comparison of porosity at different depths of specimen cured under 0.1 kPa, 36 g/L condition for 360 days. It is found that the finer pore volume reduces gradually from the inner layer (40 - 50 mm) of specimen to outer layer (0 - 10 mm).

The deterioration induces porous microstructure of specimen which accelerates ions transport and water diffusion.

Figure 5.13 shows the comparison of porosity at different depths of specimen cured under 0.1 kPa, 72 g/L condition for 387 days.

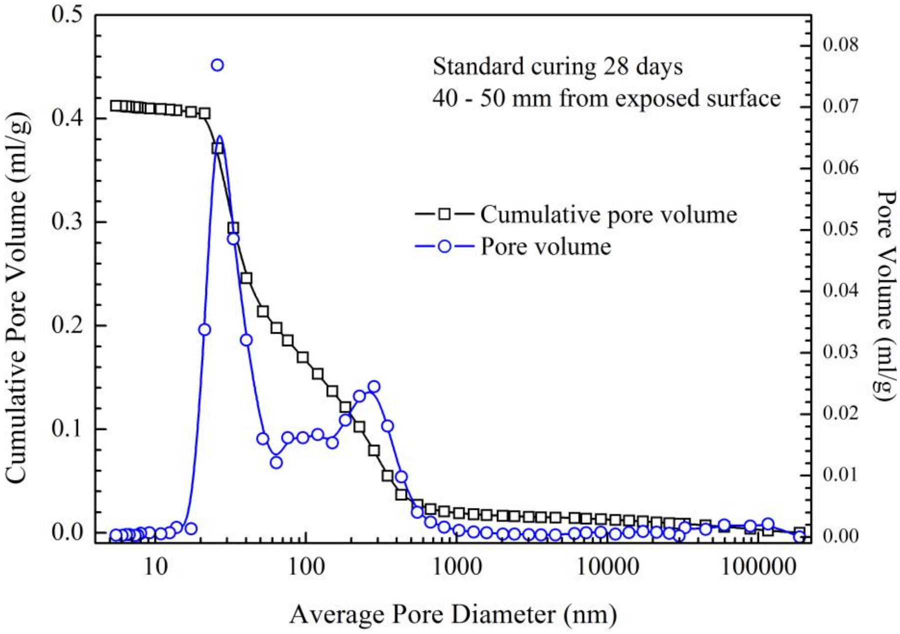


Figure 5.9 Porosity of the specimen cured in air for 28 days

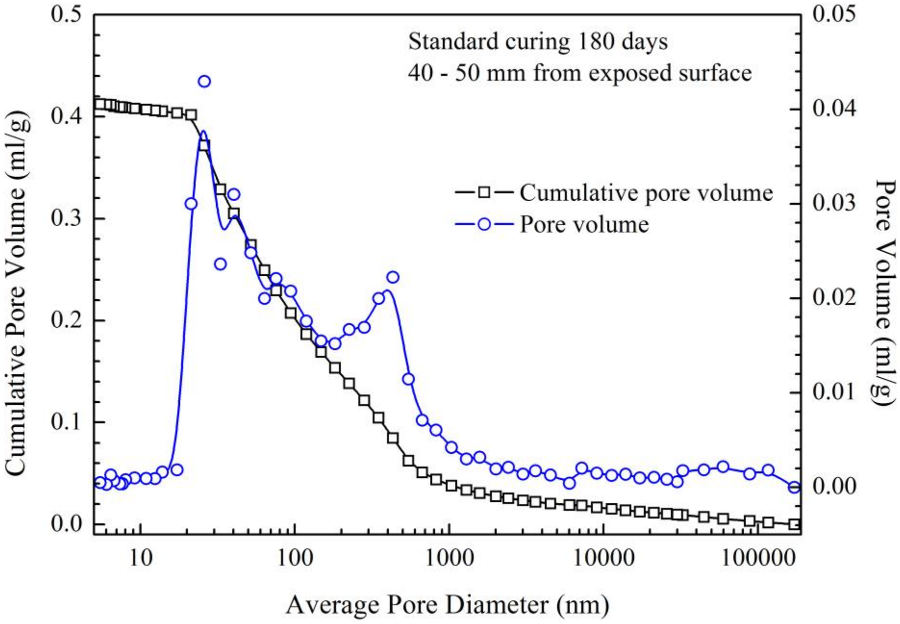


Figure 5.10 Porosity of the specimen cured in air for 180 days

It is shows that finer pore volume reduces at all layers of specimen. The sea water concentration influences seriously on porosity distribution. Higher ions concentration in outer environment accelerates the shifting of finer pores to coarser pores.

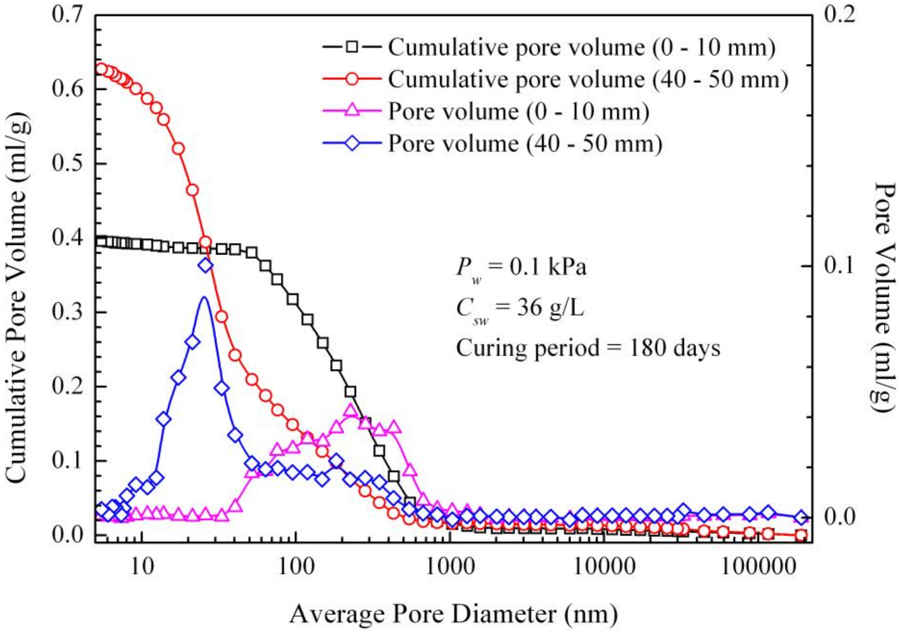
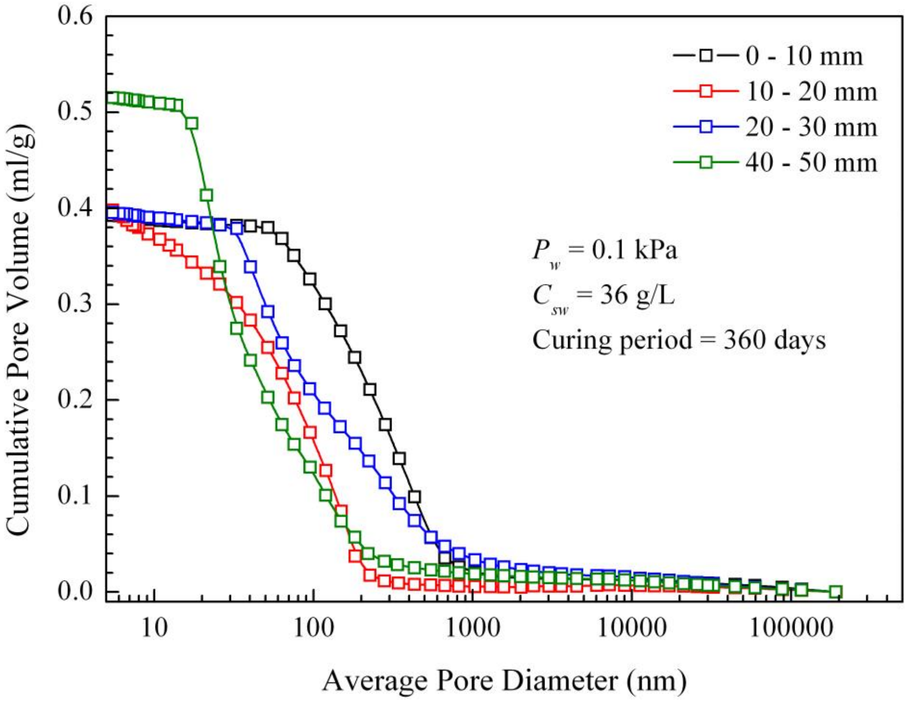
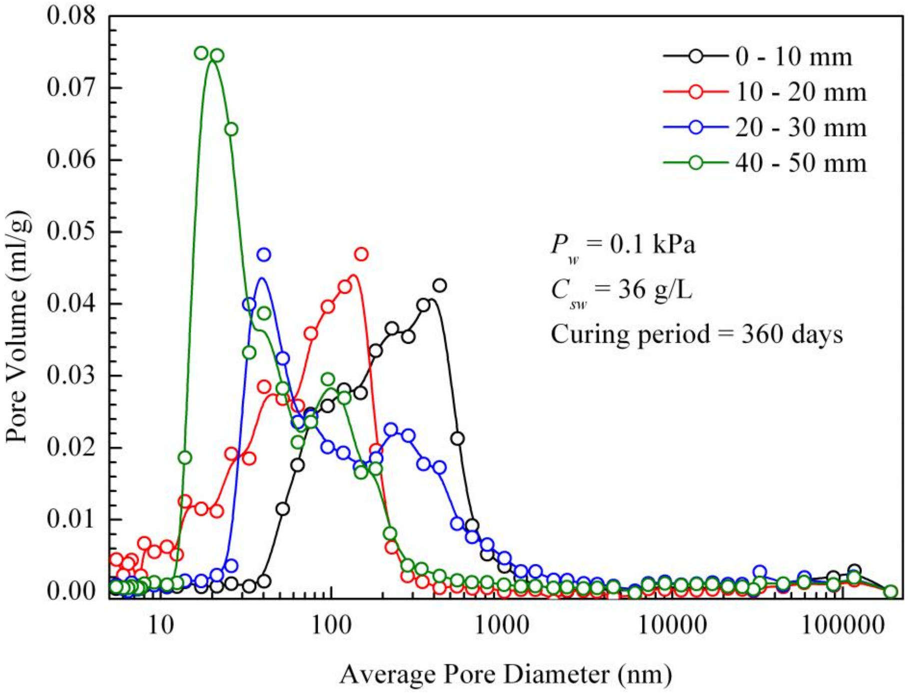


Figure 5.11 Comparison of Porosity at different depths of specimen cured under 0.1 kPa, 36 g/L for 200 days

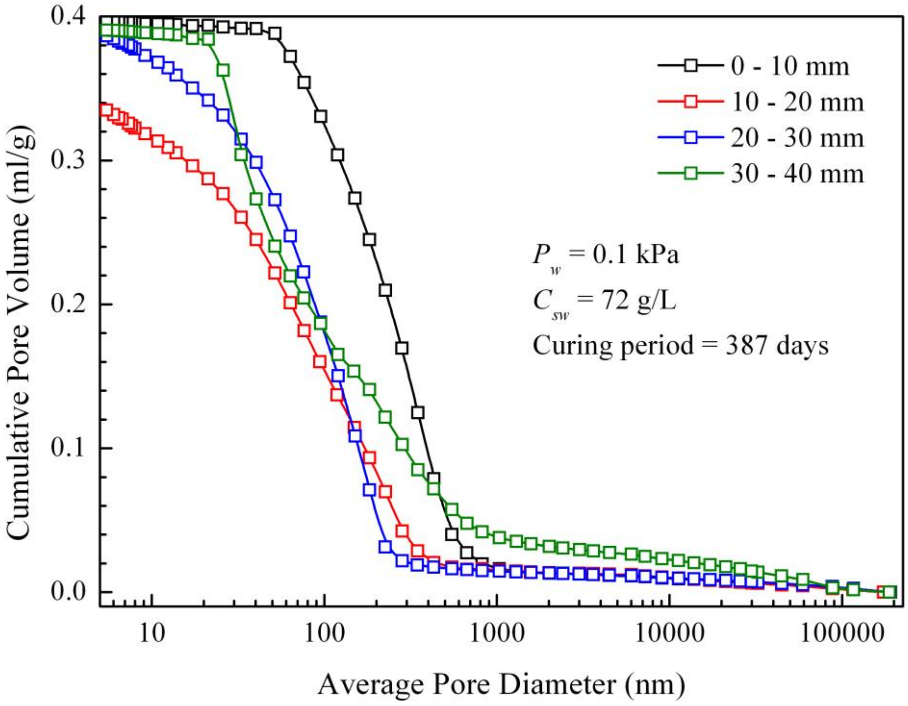


a) Cumulative pore volume

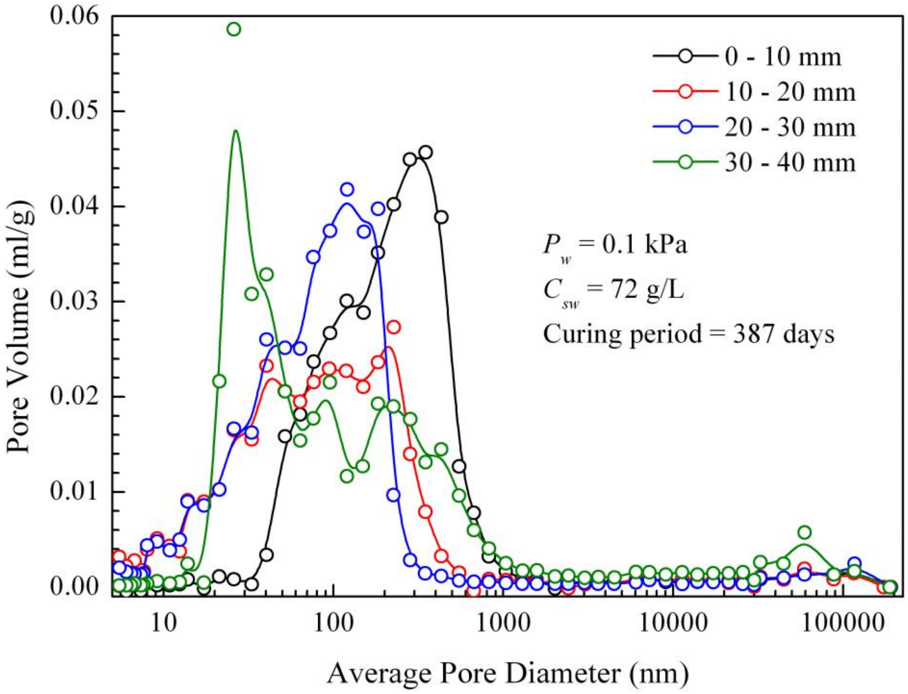


b) Pore volume

Figure 5.12 Comparison of Porosity at different depths of specimen cured under 0.1 kPa, 36 g/L for 360 days

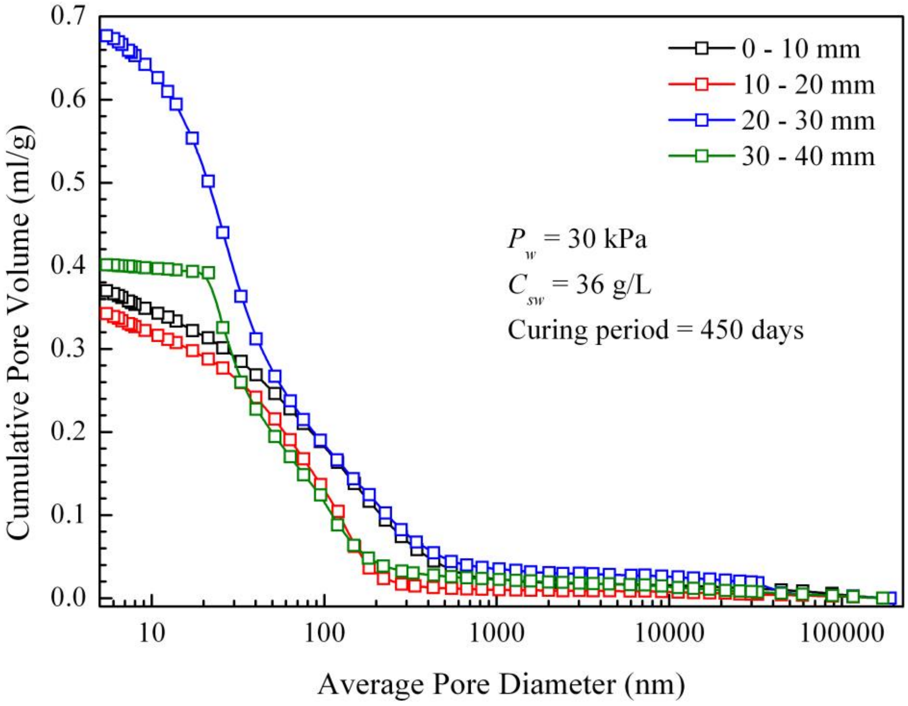


a) Cumulative pore volume

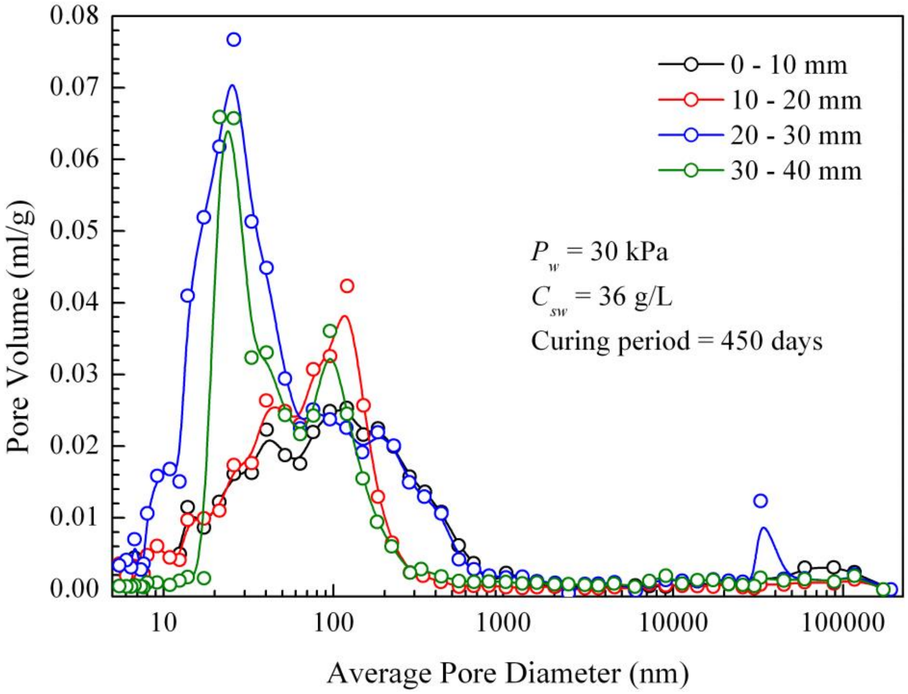


b) Pore volume

Figure 5.13 Comparison of Porosity at different depths of specimen cured under 0.1 kPa, 72 g/L for 387 days



a) Cumulative pore volume



b) Pore volume

Figure 5.14 Comparison of Porosity at different depths of specimen cured under 30 kPa, 36 g/L for 450 days

5.4.3 X-ray analysis

X-ray diffraction (XRD) analysis of cement treated Ariake clay is carried out using Automated Powder X-ray Diffractometer (MultiFlex). XRD patterns are obtained using a Cu-Kα (λ = 1.54178 Å) X-ray tube with input voltage of 40 kV and current of 30 mA. A continuous scan mode and a scan rate of 1-degree per minute are selected. The air-dried powdered samples of soil samples are used. A θ-2θ scan is taken from 5 to 60 degree to get the possible fundamental peaks of the minerals present in the sample with a sampling pitch of 0.02 degree. The X-ray diffraction mineral patterns were identified by comparison with file standard X-ray powder diffraction patterns (International Centre for Diffraction Data (ICDD), Mineral Powder diffraction file Search Manual, 1988) of the most commonly found minerals.

The minerals constituents of Ariake clay are identified as montmorillonite, quartz, kaolinite and halloysite.

Montmorillonite is a member of the smectite family, it has 2 tetrahedral sheets sandwiching a central octahedral sheet. It is the main constituent of the volcanic ash weathering product, bentonite.

Kaolinite consists of repeating layers of elemental silica-gibbsite sheets in a 1:1 lattice. It is layered silicate mineral, with one tetrahedral sheet linked through oxygen atoms to one octahedral sheet of alumina octahedral.

Halloysite is a 1:1 aluminosilicate clay mineral with the empirical formula $Al_2Si_2O_5(OH)_4$. It can occur intermixed with kaolinite, montmorillonite and other clay minerals.

The silt fraction is found to contain mainly quartz.

Figure 5.15 ~ 5.27 show the XRD analyzed results of compounds constitutes at different depths under various exposure environments and elapsed times.

Through Comparing the XRD results at different depths of specimen cured under 0 .1 kPa, 72 g/L for 387 days (Figure 5.15 and Figure 5.16), it is found that several types of magnesium compounds are formed $Mg(OH)_2$, $Mg_2(Al_4Si_5O_{18})$, $Mg_2(SiO_4)$, $Ca_2Mg_5(Si_8O_{22})(OH)_2$. It indicates that the intrusion magnesium ions replace Ca^{2+} to produce lower strength compounds. And also there is peak intensity of $CaCO_3$ which is formed by the reaction of leaching Ca^{2+} from hydration products with CO_2 in air. In addition, the figure shows an intensity of NaCl compounds. The intensity of compounds at 0 - 10 mm depth is stronger than that at 40 - 50 mm.

Figure 5.17 shows the compounds at depth (40 - 50 mm) of specimen cured in air for 28 days. The mineral of calcium montmorillonite exist in a huge amount. However, it disappears in the specimen cured under 72 g/L for 387 days, only sodium montmorillonite is observed. Large percent of calcium montmorillonite is consumed during the pozzolanic reaction. It cannot be observed $Mg(OH)_2$ compound. The intensity of NaCl compound is much lower than that under 72 g/L condition.

Figure 5.18 shows the compounds at different depths of specimen cured under 0.1 kPa, 36 g/L for 180 days. The magnesium compounds are formed at depth 0 - 10 mm, and $CaCO_3$, NaCl. The intensity of $Mg(OH)_2$, $CaCO_3$ and NaCl is stronger at depth 0 - 10 mm than that at depth 40 - 50 mm (Figure 5.19). The montmorillonite intensity is different from that under 72 g/L at depth 0 - 10 mm. The calcium and sodium montmorillonite exist simultaneously. It indicates that the ions in sea water environment can delay the pozzolanic reaction. The Mg^{2+} replaces the Ca^{2+} to produce $Mg(OH)_2$, the leaching Ca^{2+} combine with Cl^- or CO_2 to form $CaCl_2$. The consuming of $Ca(OH)_2$ delays the pozzolanic reaction. That is why calcium montmorillonite disappears at depth 40 - 50 mm.

Figure 5.20 shows the compounds at different depths of specimen cured in air for 180 days. The magnesium compounds decreases obviously and no montmorillonite minerals are observed. It indicates that the reactions between slag cement, water and clay minerals are completely carried out.

The compounds constitutes show little difference at different depths of specimen cured under 0.1 kPa, 36 g/L for 180 days with 14 days cuing in air before submerging (Figure 5.21 and Figure 5.22). The intensity of $CaCO_3$ compound is obviously stronger at depth 0 - 10 mm than that at depth 40 - 50 mm. The curing in air before submerging can prohibit the deterioration process effectively.

Figure 5.23 ~ 5.27 shows the XRD results at different depths of specimen cured under 0.1 kPa, 36 g/L for 360 days. The intensity of $Mg(OH)_2$, $CaCO_3$, NaCl decreases gradually from depth 0 - 10 mm to 40 - 50 mm. It is found that compound $Mg_3(OH)_2(Si_4O_{10})$ is formed at depth 20 - 30 mm. The calcium and sodium montmorillonite exist simultaneously. It indicates the layer is the transition zone of deterioration.

The XRD analysis results explain the mechanism of deterioration process. The magnesium ions intrusion consumes large amount of $Ca(OH)_2$ which delays the pozzolanic reaction and produces lower strength magnesium compounds simultaneously. The reducing of Ca^{2+} in pore water further accelerates the leaching of Ca^{2+} from C-S-H.

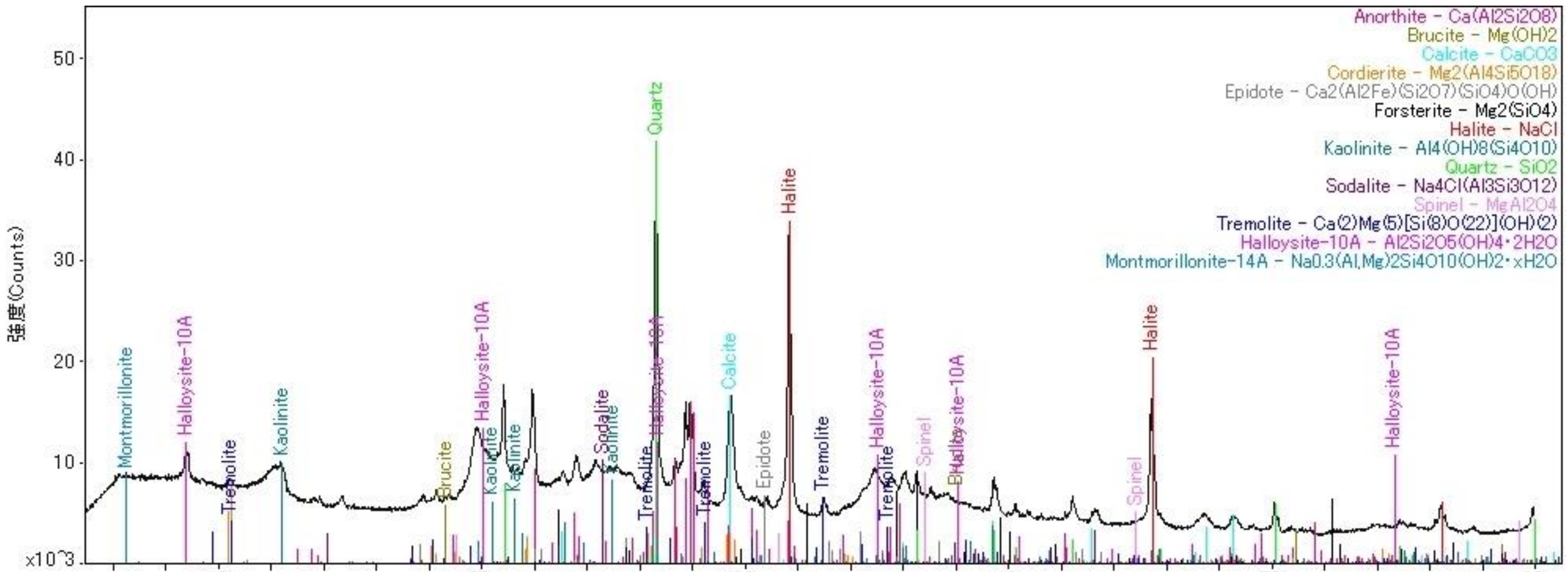


Figure 5.15 X-ray results of specimen cured under 0 .1 kPa 72 g/L for 387 days (0 - 10 mm)

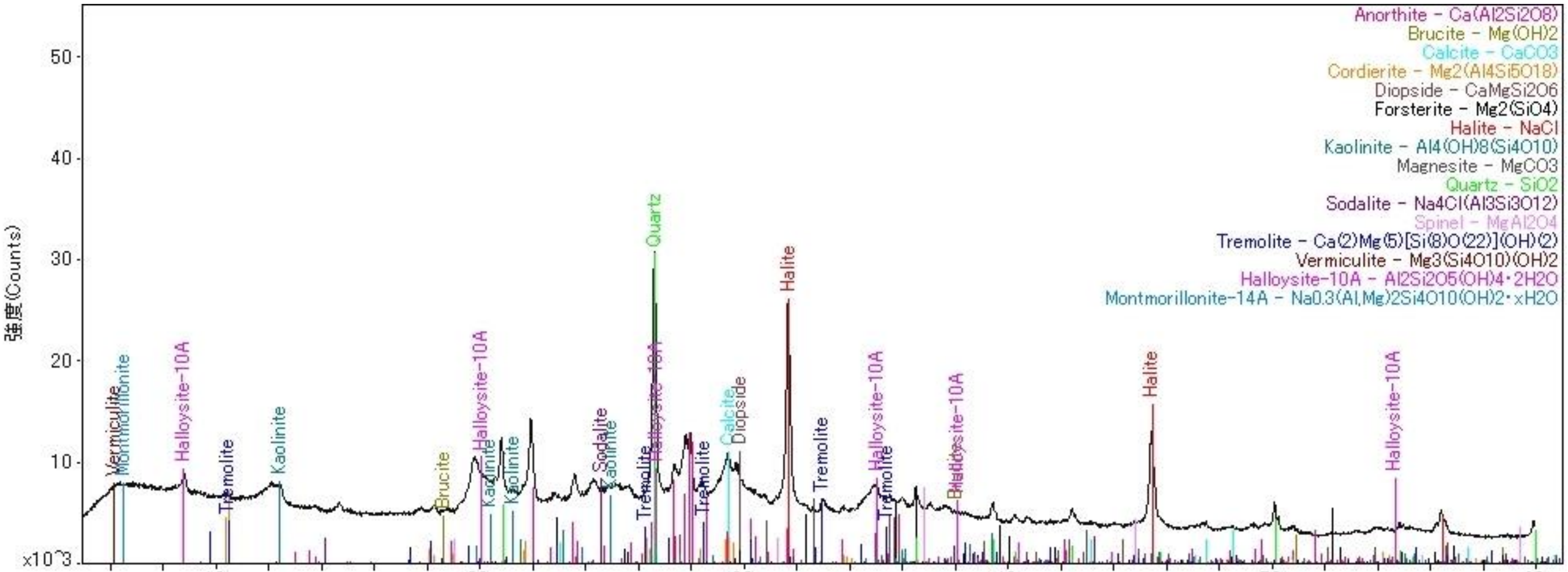


Figure 5.16 X-ray results of specimen cured under 0 .1 kPa 72 g/L for 387 days (40 - 50 mm)

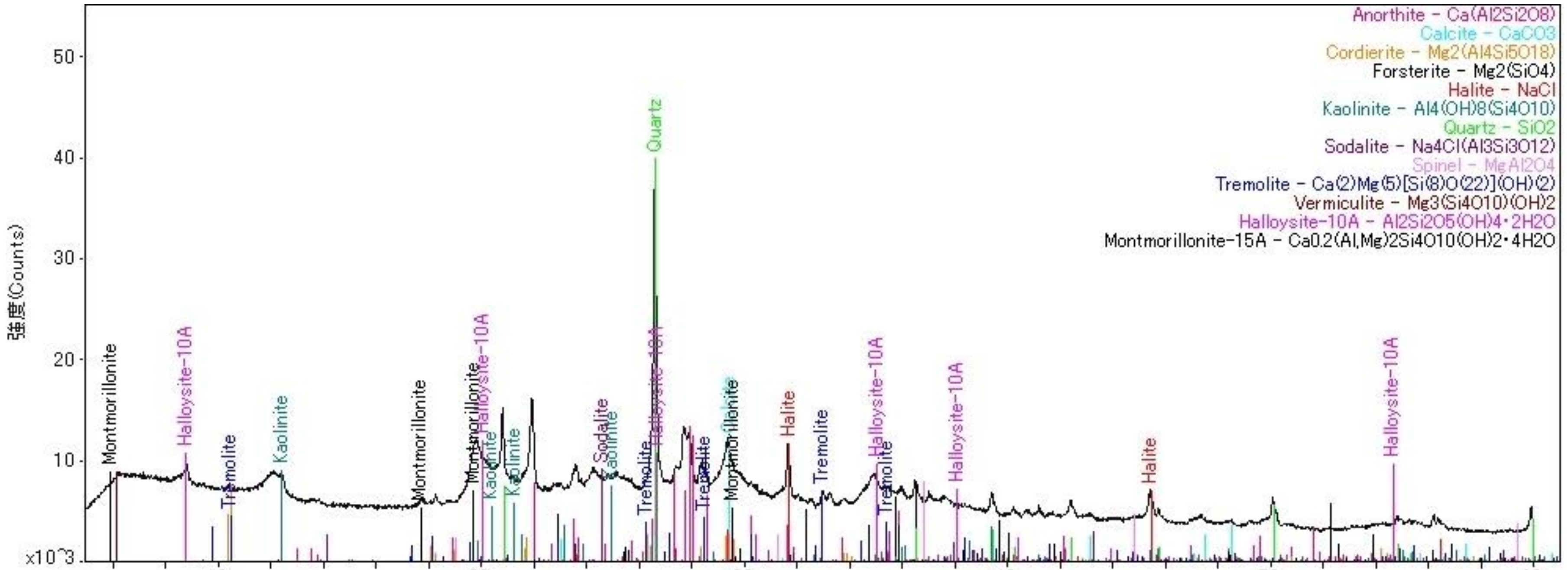


Figure 5.17 X-ray results of specimen cured in air for 28 days (40 - 50 mm)

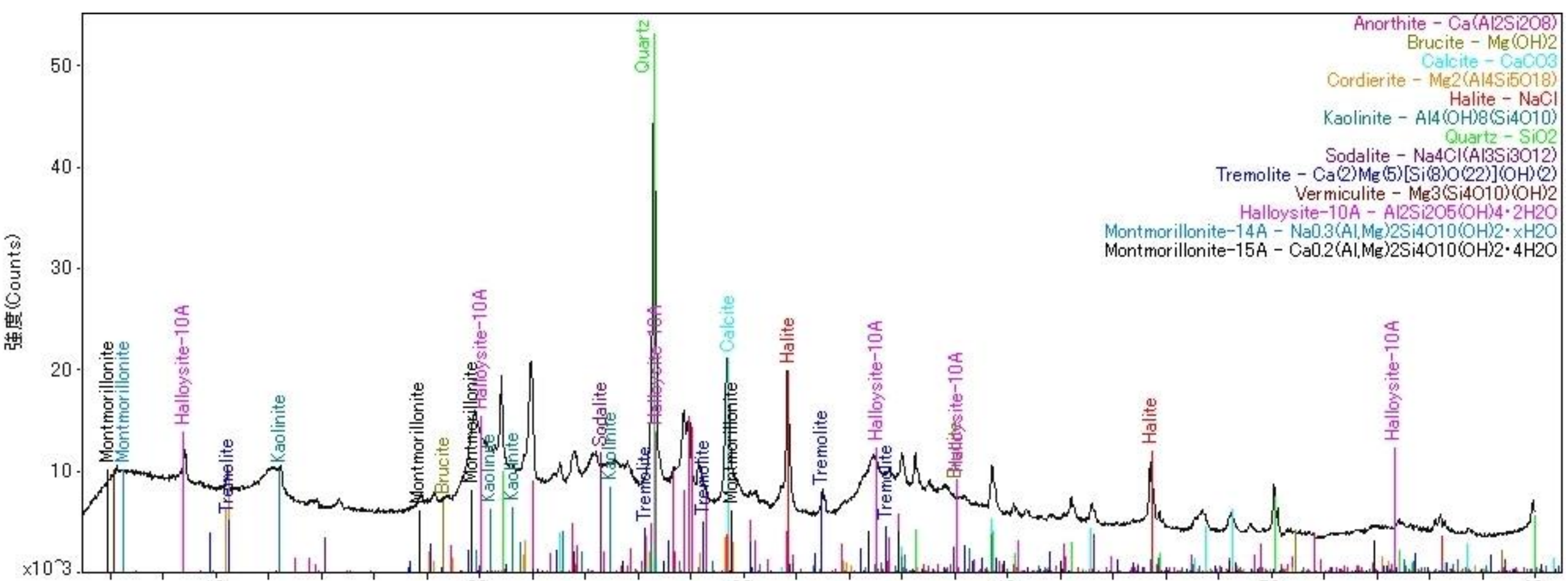


Figure 5.18 X-ray results of specimen cured under 0.1 kPa 36 g/L for 180 days (0 - 10 mm)

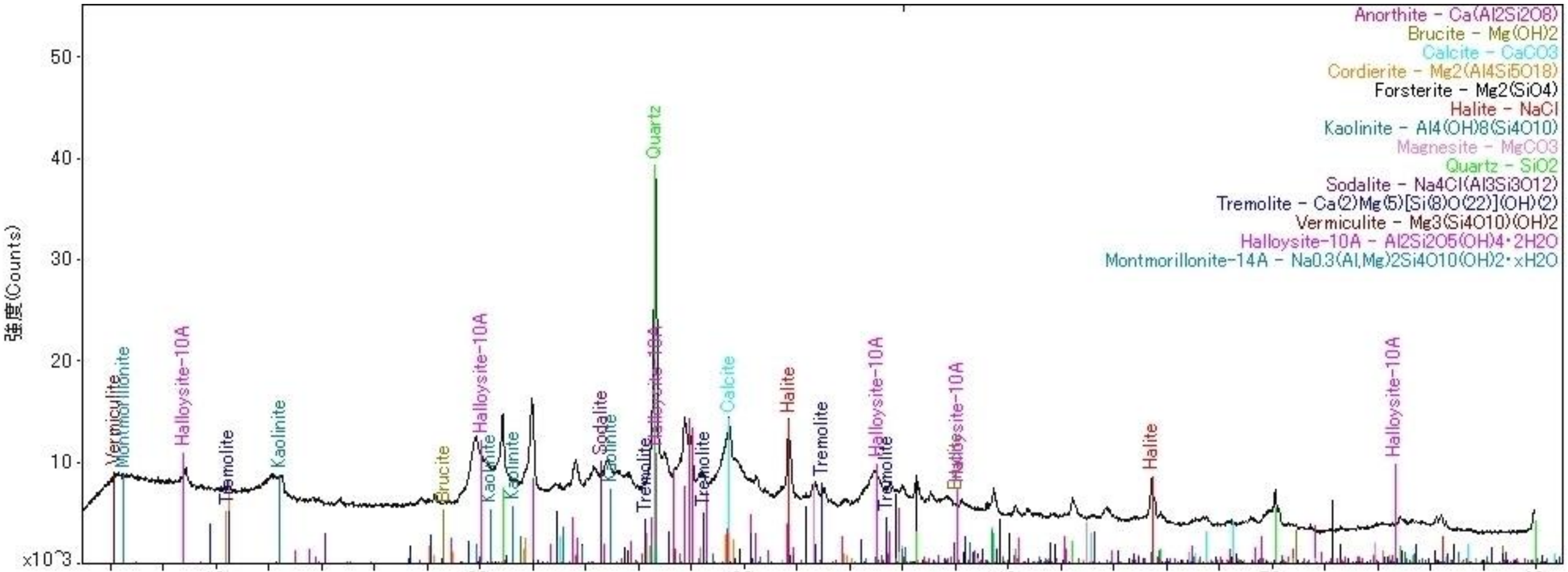


Figure 5.19 X-ray results of specimen cured under 0.1 kPa 36 g/L for 180 days (40 - 50 mm)

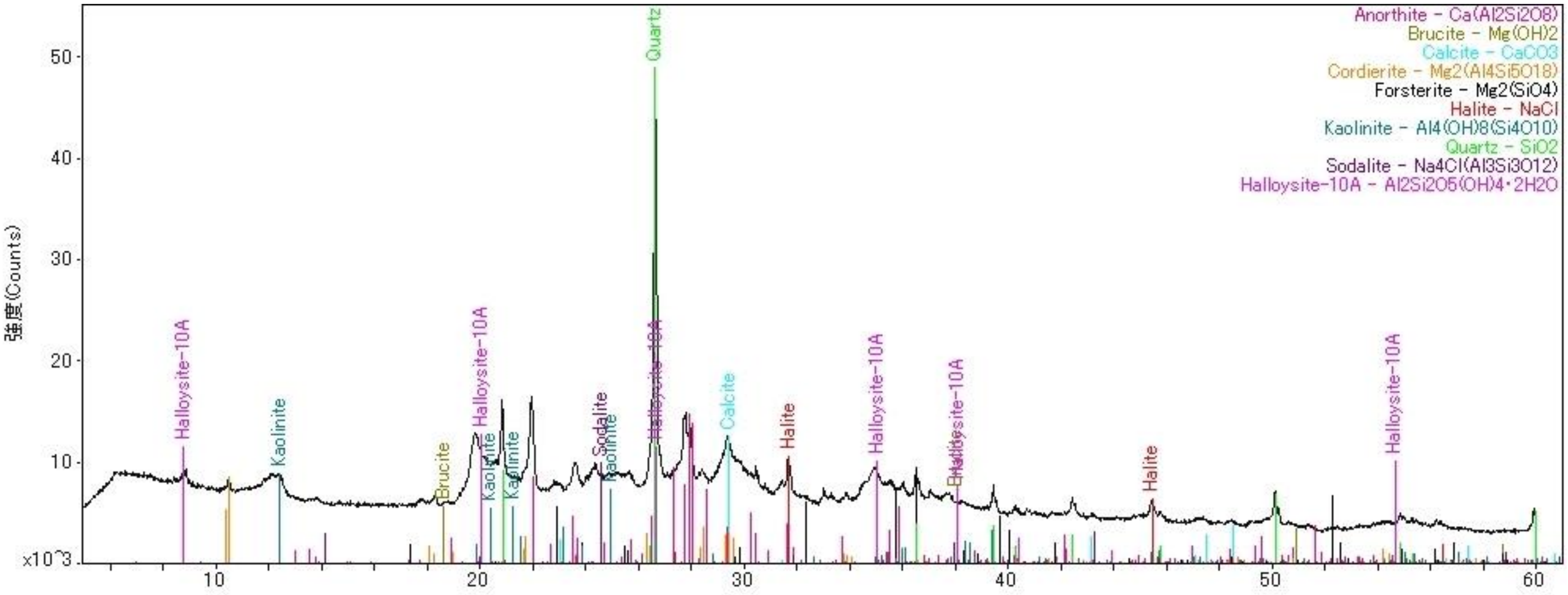


Figure 5.20 X-ray results of specimen cured in air for 180 days (40 - 50 mm)

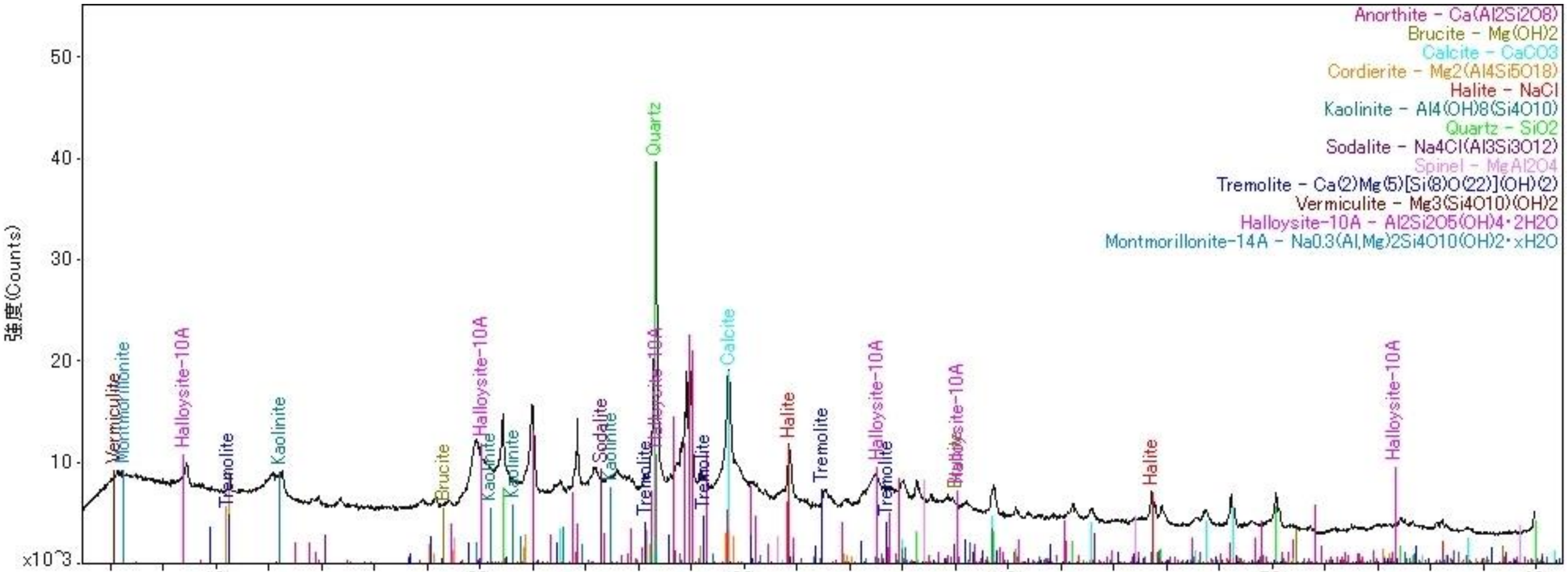


Figure 5.21 X-ray results of specimen with 14 days air curing then submerged into 0.1 kPa 36 g/L for 180 days (0 - 10 mm)

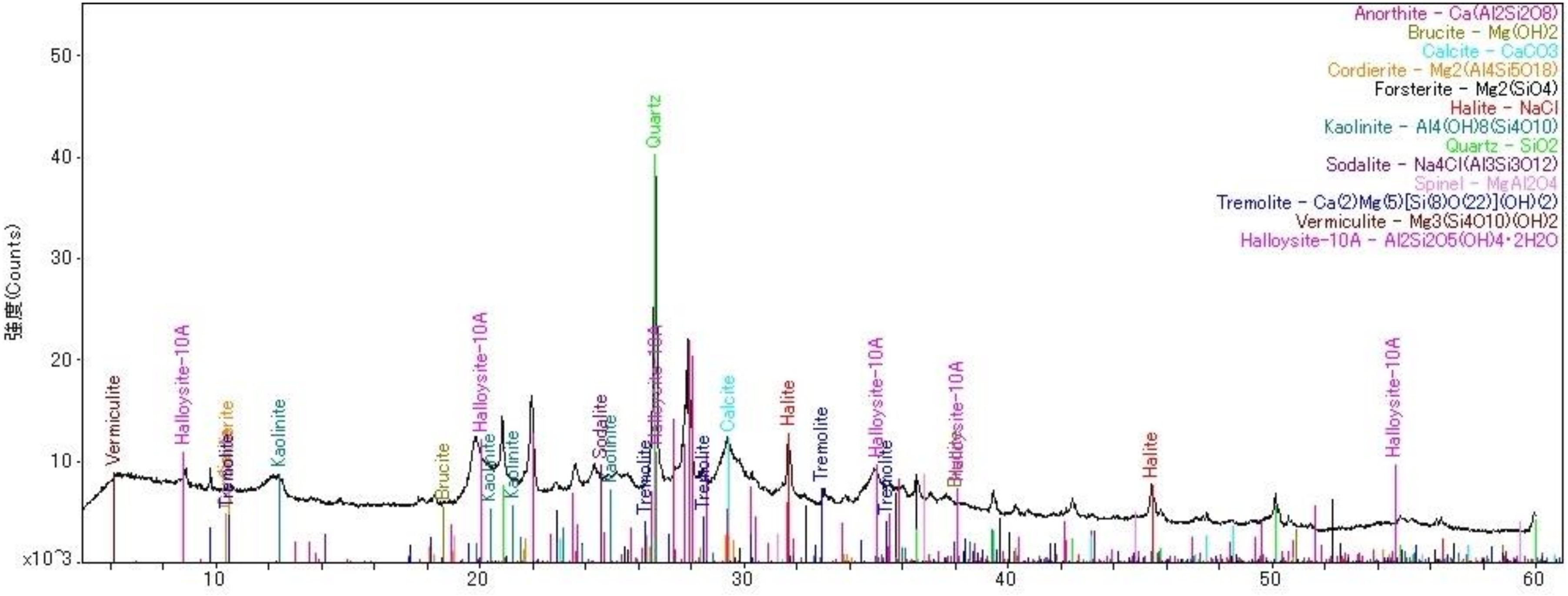


Figure 5.22 X-ray results of specimen with 14 days standard curing then submerged into 0.1 kPa 36 g/L for 180 days (40 - 50 mm)

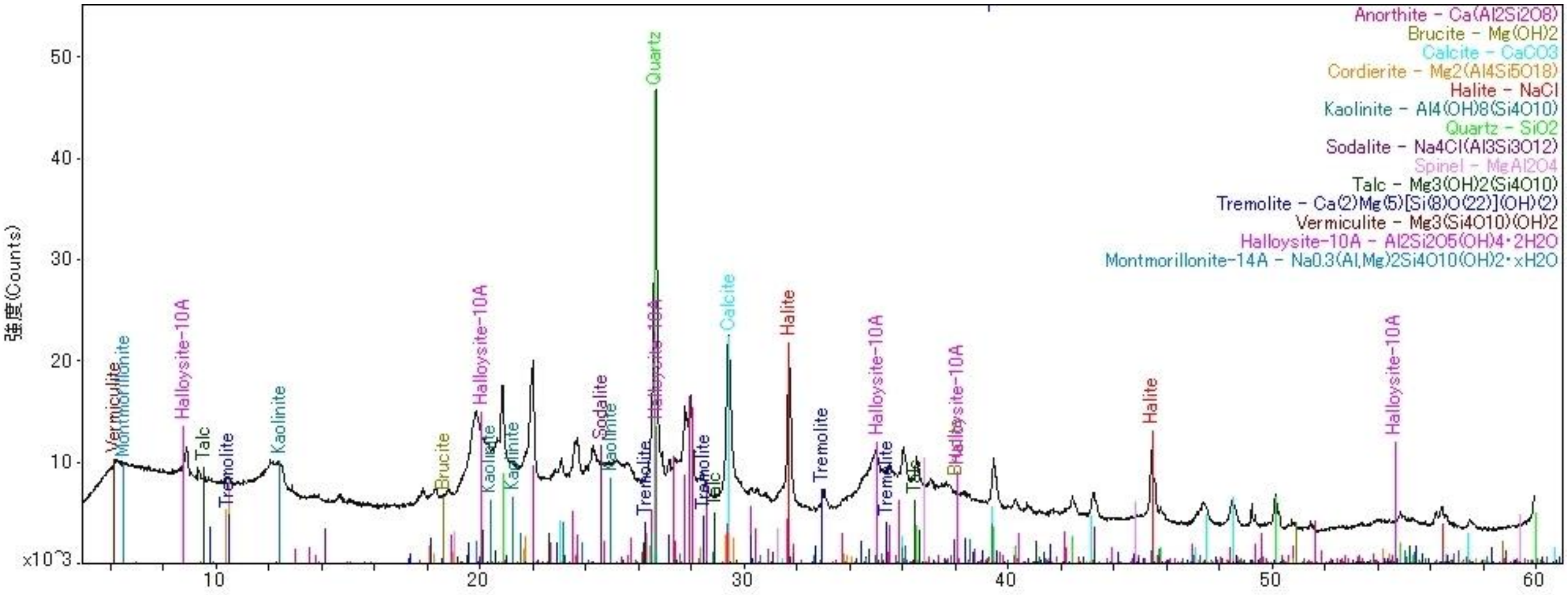


Figure 5.23 X-ray results of specimen cured under 0.1 kPa 36 g/L for 360 days (0 - 10 mm)

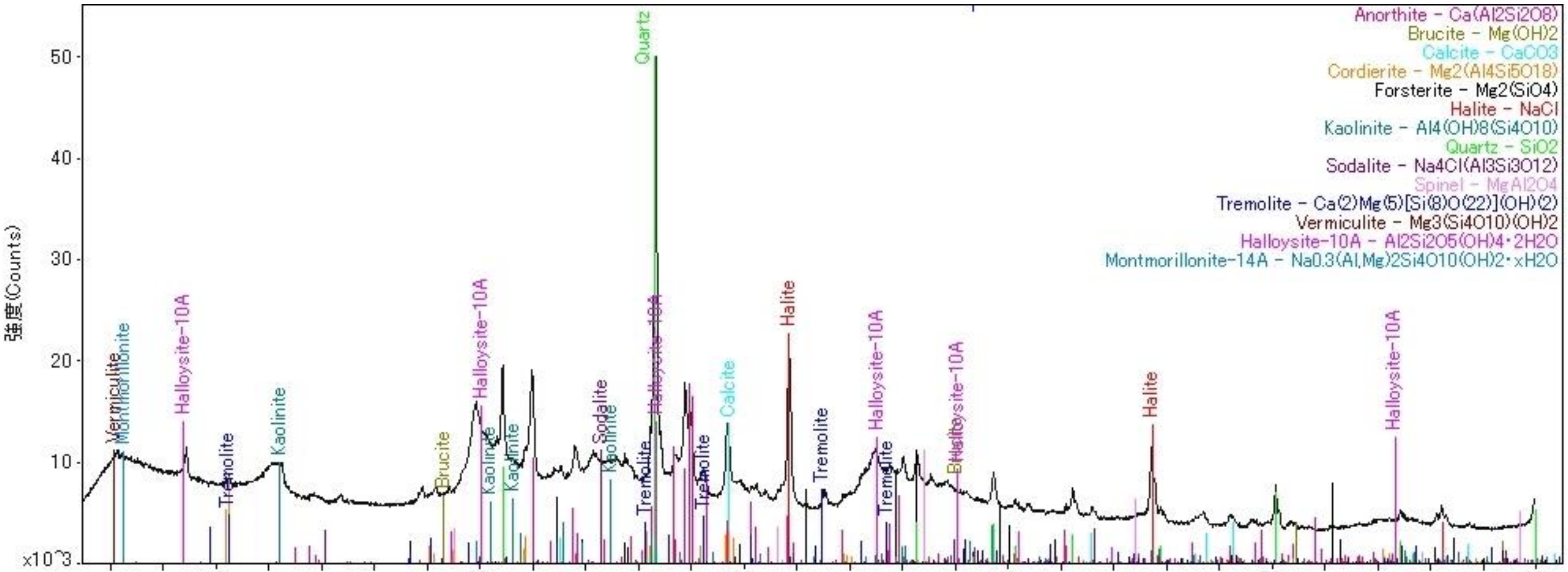


Figure 5.24 X-ray results of specimen cured under 0.1 kPa 36 g/L for 360 days (10 - 20 mm)

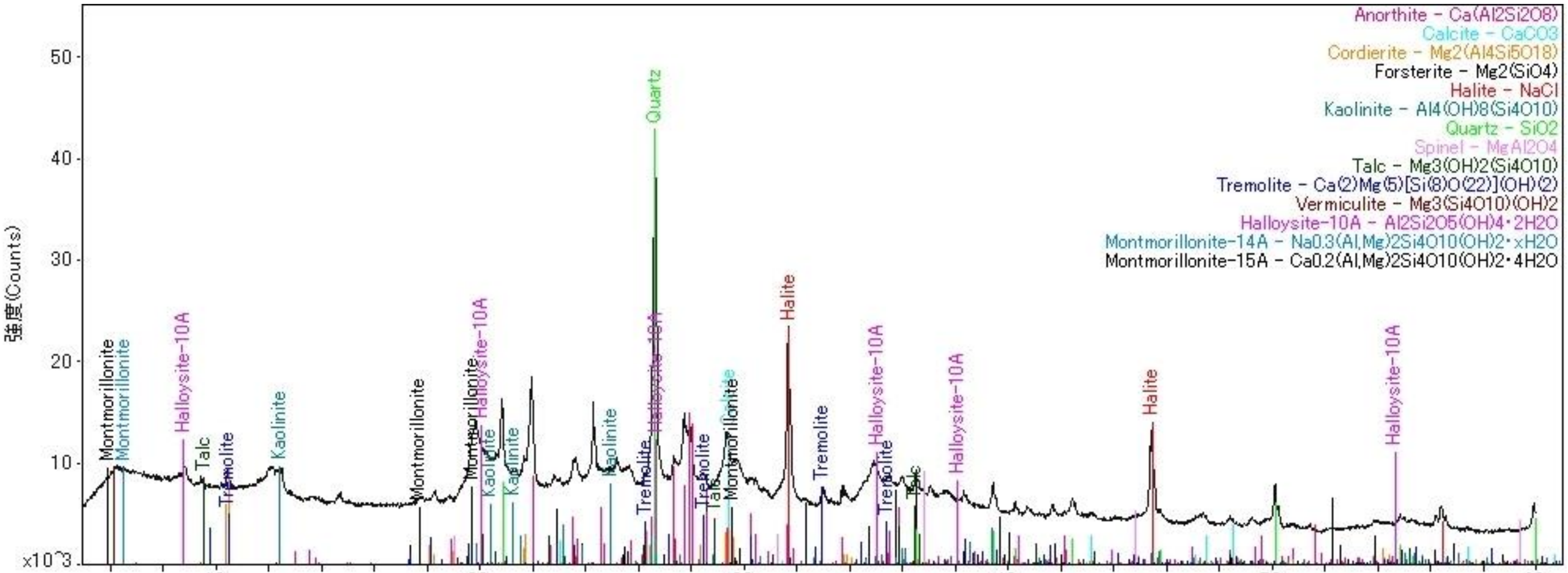


Figure 5.25 X-ray results of specimen cured under 0.1 kPa 36 g/L for 360 days (20 - 30 mm)

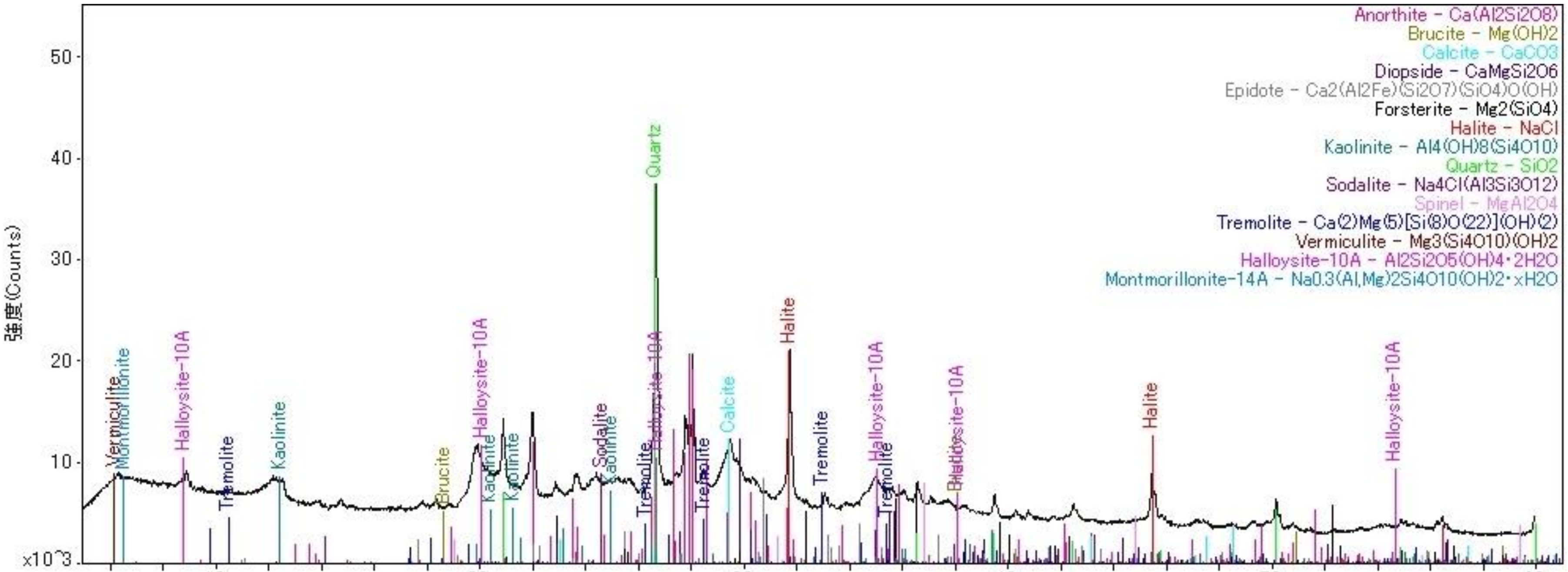


Figure 5.26 X-ray results of specimen cured under 0.1 kPa 36 g/L for 360 days (30 - 40 mm)

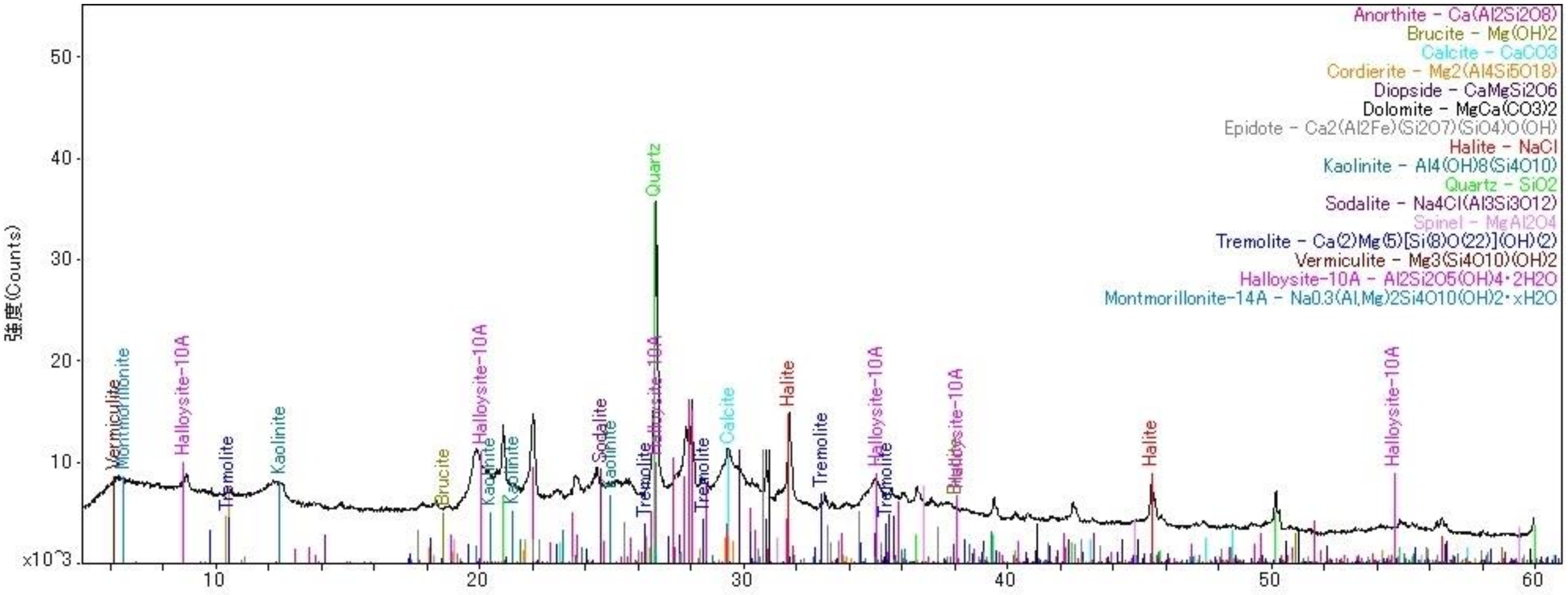


Figure 5.27 X-ray results of specimen cured under 0 .1 kPa 36 g/L for 360 days (40 - 50 mm)

5.5 Summary

This chapter explains the mechanism of deterioration of cement stabilized soils under sea water environment from chemical, element composition and microstructure aspects.

The analyzed results of this chapter can be summarized as following:

1) The calcium ions concentration distribution with depth indicates that the calcium leaching is a long term effect. At early stage of stabilization, the hydration reaction plays a dominant role of strength development. That is why the calcium ions concentration distribution with depth is consistent with strength distribution at long term but on a contrary at short term.
2) The magnesium ions concentration distribution with depth indicates that the magnesium impacts on strength development at the very beginning of stabilization and last for a long period. That is why the magnesium ions concentration distribution with depth is in good consistent with strength distribution during the curing time.
3) The image of SEM at deteriorated area shows that the structure is very loosely and there are a large amount of holes. The image at non-deteriorated area shows a dense microstructure and the hydration products binding together tightly.
4) The reduction of Ca/Si ratio near exposure surface further verified the leaching fact of calcium from C-S-H at long term.
5) The comparison of porosity at different depths of specimen indicates that the finer pores reduces near exposure surface (0 - 10 mm) compared with inner part (40 - 50 mm) which induces coarser and porous structure. The deterioration induces porous microstructure of specimen which accelerates ions transport and water diffusion.
6) The minerals constituents of Ariake clay are identified as montmorillonite, quartz, kaolinite and halloysite through XRD analysis. The magnesium ions intrusion consumes large amount of $Ca(OH)_2$ which delays the pozzolanic reaction and produces lower strength magnesium compounds simultaneously. The reducing of Ca^{2+} in pore water further accelerates the leaching of Ca^{2+} from C-S-H.

References

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Kitazume, M., Nakamura, T., Terashi, M., and Ohishi, K. 2002. Laboratory tests on long-term strength of cement treated soil. Geotechnical Special Publication, 1: 586-597.

Chapter 6 PREDICTION METHODS FOR LONG TERM DURABILITY OF CEMENT STABILIZED SOILS

6.1 Introduction of prediction equation

The targeted soil used in this dissertation is Ariake clays. The stabilizing agent is blast-furnace slag Portland B type with a binder factor of 30% (dry weight of cement to dry weight of clay soil). The initial water content is adjusted to 200.0% (about 1.5 time liquid limit). The artificial sea water is prepared through mixing 36 g sea ocean power with 1 L pure water together which is approximate to natural sea water. The sea water pressure is keeping at 0.1 kPa. The specimen is submerged into sea water environment without any standard curing. The initial condition of specimen is keeping the same, only changing the sea water concentration in curing environment.

The prediction equation is expressed as following:

$$d_{(C_{sw})} = a \ln b - a \times \ln(t + b) \tag{6.1}$$

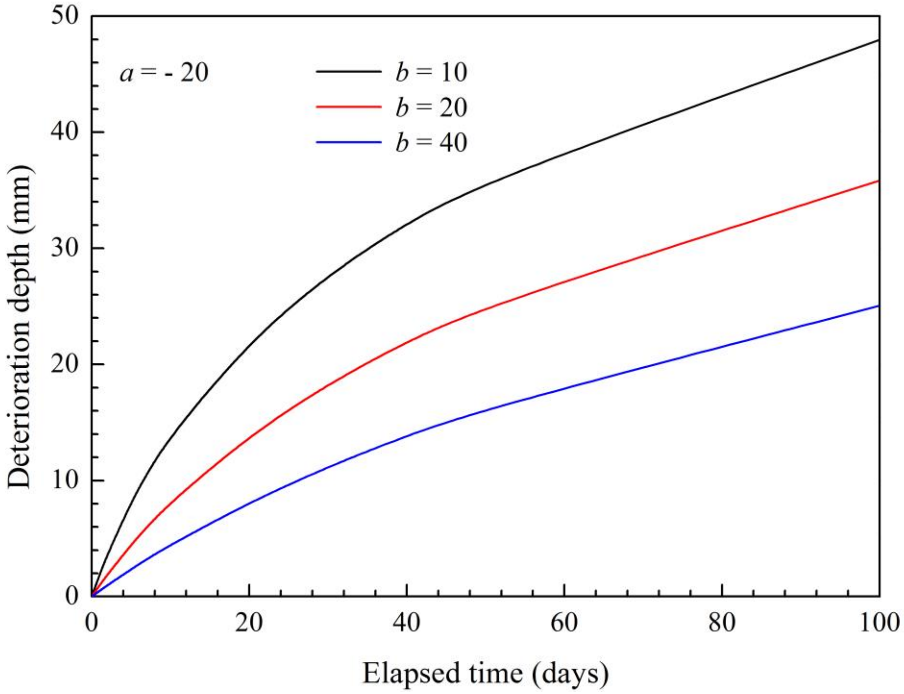
Where, $d_{(Csw)}$ is the deterioration depth under corresponding sea water concentration, the parameter *a* is a constant determined by the initial condition, *b* is a variable determined by the sea water concentration, *t* is elapsed time.

6.2 Parametric study

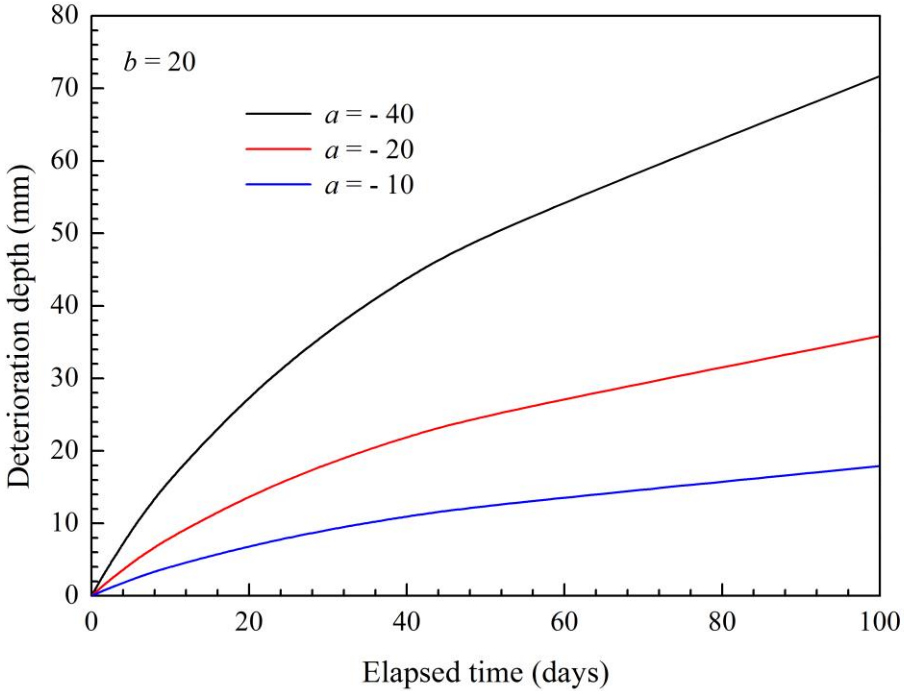
The figure shows the parametric study of equation 6.1 in Figure 6(a), the parameter *a* is constant, the parameter *b* varies from 10 to 40. It can be seen that the parameter *b* mainly influence the slope of the curve at the first stage. On the other hand the parameter *a* influence the slope of the whole curve as shown in Figure 6(b). The slope of the curve represents the deterioration rate of specimen in sea water environment.

The initial deterioration rate (t = 0) equals to ($-a$)/b, and the deterioration depth $d_{(Csw)}$ = 0 mm. The half-rate ($-a/2b$) of deterioration is reached at t = b. Therefore, *b* is closely related to half-rate time of deterioration of specimen in sea water environment.

When t = 9b, the deterioration rate equals to one tenth of the initial deterioration rate. It is considered that the deterioration rate at this time is same under different sea water concentrations. Because the *b* is determined by the concentration so the time reaches one tenth of the initial deterioration rate is different under various sea water concentrations.



(a) Parametric study of *b*



(b) Parametric study of *a*

Figure 6.1 Parametric study of prediction equation

6.3 Prediction on long term deterioration

Based on the discussion above, one assumption is adopted here. The sea water concentration will mainly influence the deterioration rate at the beginning and this effect is proportion to the ratio of sea water concentration. Therefore, the predictive methodology can be described as following steps. Firstly, fit the test data of higher concentration by using equation 6.1. Then keep the parameter *a* as a constant and calculate the parameter *b* using the relationship, $b_H/b_L = C_L/C_H$. Finally, the predictive curve can be described using equation 6.1 by substituting the parameters *a* and b_L into it.

Figure 6.2 shows the predictive curves on long-term deterioration depth of cement stabilized soils. The blue one is the fitting curve of experimental data under sea water concentration of 108 g/L. The red and black curves are the calculating results based on relationship of $b_H/b_L = C_L/C_H$. The predicting deterioration depths of 72 g/L and 36 g/L are fitting very well with the experimental results.

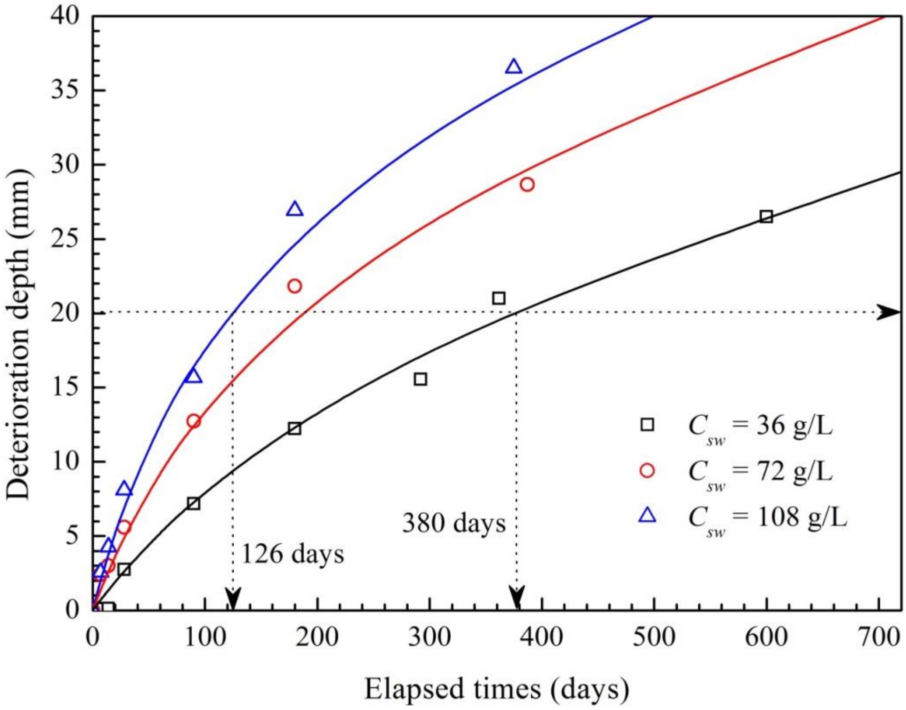


Figure 6.2 Predictive curves on long-term deterioration depth of cement stabilized soils

6.4 Limitation of prediction equation

The predictive methodology is only considering the sea water concentration factor. In Chapter 4 the experimental results indicate that the dynamic sea water pressure obviously influence the deterioration depth of cement stabilized soils. However, the related experimental data is limited in this study, so the dynamic sea water pressure factor is not included in the prediction equation. The cement type, binder factor, initial water content is fixed in this study, there are many factors can influence the value of parameter *a*. Therefore, it is necessary to study the parameter *a* variation with influence factors.

Chapter 7 CONCLUSIONS AND FUTURE WORKS

7.1 Introduction

In the present study, the long term durability of cement stabilized soils under sea water environment from the beginning of stabilization is evaluated. Physic-chemical as well as micro structural behaviors of cement stabilized Ariake clays are investigated. The physic-chemical as well as micro structural properties are investigated using cone penetration test, unconfined compressive test, atomic absorption spectrometry (AAS), scanning electron microscopy (SEM), energy dispersive X-ray (EDX), mercury intrusion porosimetry (MIP) and powder diffractometer (XRD). The water content distribution with depth and density of cement stabilized soils are measured also.

The influences of static water pressure, dynamic water pressure, sea water concentration and initial strength on deterioration process are investigated. Several conclusions on physic-chemical and micro structural behavior of cement stabilized Ariake clays are drawn. The findings aid in prediction of long term deterioration depth and explanation of practical engineering problems.

7.2 Factors influence on deterioration of cement stabilized soils

1. The strength development of specimen which is directly exposed to sea water environment shows two aspects. One aspect is that the strength decreases as elapsed time becomes long at deteriorated area; another aspect is that the strength increases as elapsed time becomes long at non-deteriorated area. The strength development of specimen with the initial strength of 14 days curing in air before exposing to sea water environment shows continuously increasing as elapsed time becomes long from exposure surface to inside. Although the strength is lower near exposure surface than inside. The higher sea water pressure or concentration can delay the strength development of specimen and this phenomenon disappears as elapsed time becomes long.
2. The deterioration depth is an important index to evaluate the factors influence on deterioration degree. It is found that static water pressure influence obviously on deterioration process at short term. The dynamic pressure influences the deterioration process both at short term and long term. The dynamic water pressure shows a greater degree of influence on deterioration than static condition. The deterioration depth

under different sea water concentration is in an order of 108 g/L > 72 g/L > 36 g/L at same curing time. The increasing of ions concentration in sea water effectively accelerates the deterioration process. The deterioration depth of specimen with 14 days standard curing in air (20 degree centigrade and relative humidity of 98%) before exposure ranges from 2 ~ 3 mm. It verified that the stronger initial strength can prohibit the deterioration under sea water environment.

3. The water content distribution with depth of specimen is investigated in this dissertation because water plays an important role both in ions transportation and chemical reaction. The initial water content is adjusted to 200.0% (about 1.5 time liquid limit). The water content distribution with depth shows good consistency with strength distribution. There is a different tendency of water content distribution in sea water environment and pure water. The water content distribution with depth in sea water environment shows an increasing tendency from exposure surface to inside at short term but on a contrary at long term. The water content distribution with depth in pure water environment shows a decreasing tendency from exposure surface to inside. The higher water pressure leads to a greater degree of water penetration depth in specimen. Ion concentration in sea water environment has great impact on water content distribution with depth of specimen. The higher sea water concentration leads to more quickly reduction of water content in specimen both at deteriorated area and non-deteriorated areas.
4. The density of specimen changes little before and after exposure and distributes at a range of 1.32 ~ 1.36 g/cm^3.
5. The unconfined compressive strength of specimen which is directly exposed to sea water environment is much lower than that cured in air or pure water environment.

7.3 Mechanism of deterioration process

The mechanism of deterioration process is explained and verified through atomic absorption spectrometry (AAS), scanning electron microscopy (SEM), Energy dispersive X-ray (EDX), mercury intrusion porosimetry (MIP) and powder X-ray diffractometer (XRD) analysis.

1. The calcium ions concentration is lower at deteriorated area than non-deteriorated area. It increases gradually from exposure surface to inside of specimen at long term. The calcium ions concentration distribution with depth is consistent with strength

distribution at long term. However, at elapsed time less than 28 days, the calcium ions concentration is higher near exposure surface and gradually decreases to inside of specimen. The leaching of calcium process is a long term effect. At the very beginning of stabilization, the hydration reaction produces extra $Ca(OH)_2$ and plays a dominant role on strength development. There is no obvious discipline of sea water pressure influence on calcium distribution with depth. It indicates that calcium leaching is one cause of strength reduction.

2. The magnesium ions concentration is higher at deteriorated area than non-deteriorated area. It decreases gradually from exposure surface to inside of specimen both at short term and long term. The magnesium ions concentration distribution with depth is consistent with strength distribution. The intrusion of magnesium ions from sea water to cement stabilized soils is the major cause of strength reduction at short term. The magnesium ions impact the deterioration at the very beginning of stabilization and last for a long time.
3. The images of scanning electron microscopy (SEM) at deteriorated area and non-deteriorated area show the microstructures of specimen. The microstructure at deteriorated area is loose and porous. The leaching of calcium ions from Ca(OH)2 and hydration products (C-S-H) induces the porosity of structure. The magnesium ions reaction with $Ca(OH)_2$ and hydration products (C-S-H) produces $Mg(OH)_2$ and magnesium silicate hydration (M-S-H) with lower strength and cementation which induces loose structure of specimen.
4. The Ca/Si ratio at 28 days keeps a constant value of 0.68 from exposure surface to inside of specimen. The Ca/Si ratio at 180 days is lower near exposure surface and gradually increasing to a value of 1.0 at depth of 20 ~ 30 mm. The reduction of Ca/Si ratio near exposure surface further verified the fact of calcium leaching from C-S-H at long term.
5. The mercury intrusion porosimetry (MIP) analysis verified that a shifting of finer pores to coarser pores occurs at deteriorated area. The deterioration induces porous microstructure of specimen which accelerates ions transport and water diffusion in turn.
6. The compound constitutes analysis through powder X-ray diffractometer (XRD) verified that several magnesium compounds are formed, such as $Mg(OH)_2$, $Mg_2(Al_4Si_5O_{18})$, $Mg_2(SiO_4)$, $Ca_2Mg_5(Si_8O_{22})(OH)_2$. And the intensity of magnesium

compound is obviously stronger at deteriorated area than that at non-deteriorated area. The intensity of $CaCO_3$ decreases from deteriorated area to non-deteriorated verified the calcium leaching is more serious at deteriorated area. The minerals constituents of Ariake clay are identified as montmorillonite, quartz, kaolinite and halloysite. It is found that montmorillonite is the first to be consumed during pozzolanic reaction between clay soils and hydration products. And the magnesium ions intrusion delays the pozzolanic reaction because magnesium can replace the calcium to form magnesium compounds, this process consumes large amount of $Ca(OH)_2$ which is the major reaction mass of pozzolanic reaction.

7.4 Predictive methodology

A predictive methodology on long term deterioration depth of cement stabilized soils under sea water environment is proposed. Based on the experimental data under higher sea water concentration in limited laboratory time, the prediction equation of sea water condition can be derived.

Two parameters a, b are introduced in the prediction equation. The parameter a is constant and related to initial conditions. The parameter b varies as sea water concentration. Fit the test data of higher concentration by using proposed equation 6.1. Then keep the parameter a as constant and calculating the parameter b using the relationship of $b_H/b_L = C_L/C_H$. Finally, the predictive curve can be described using equation 6.1 by substituting the parameters a and b_L into it.

7.5 Future works

1. In the present study, static water pressure, dynamic water pressure, sea water concentration and initial strength influence on long term deterioration is evaluated. The water pressure influence on strength development at short term is needed to be considered. It is important to gain enough initial strength of cement stabilized soils before exposing to corrosive environment. The data of higher sea water concentration can be applied to predict long term deterioration depth of natural sea water environment. This dissertation explains the mechanism of deterioration process which supplies the theory basis for application and improvement of cement stabilization method.

2. Only one type of stabilizing agent and binder factor used in this dissertation. The long term durability of cement stabilized soils is influenced by a number of factor, because the basic mechanism of chemical reactions between soil and the stabilizing agents. The factors can be roughly divided into four categories: I characteristics of stabilizing agent (type of stabilizing agent, quality, mixing water and additives); II characteristics and conditions of soil (physical chemical and mineralogical properties of soil, organic content, pH of pore water, water content); III mixing conditions (degree of mixing, time of mixing/re-mixing); IV curing conditions (temperature, humidity, wetting and drying, freezing and thawing. The collection of experiment data in future is necessary.
3. It is necessary to compare prediction results between empirical method and numerical method. The future research will focus on numerical method considering the relationship between diffusion rate and chemical reaction rate. The results will be used in evaluating the performance of cement stabilized soils as bearing pile or friction pile.