Doctoral Dissertation

Accelerated pH neutralization of alkaline construction sludge by paper sludge ash-based stabilizer and carbon dioxide

ペーパースラッジ灰系改質材と二酸化炭素を用いたアルカリ建設汚泥の中性化促進

by

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ABSTRACT

Construction sludge frequently exhibits fluidity which cannot be piled up on dump truck. Thus, cement or lime are commonly used to harden construction sludge at site in Japan. This process increases the pH of construction sludge to around 11 that does not satisfy the Japanese environmental regulation which regulates $5.8 \leq pH \leq 8.6$. When alkaline construction sludge is reused as a construction material in earth works, it is necessary to adopt measures to reduce its impact on the environment.

The aim of this study is to experimentally investigate the potential of combining accelerated carbonation and a paper sludge ash-based stabilizer (PSAS) to neutralize the pH of alkaline construction sludge in a short period and to improve its strength for using as a recycled material. Moreover, due to the high alkalinity, the construction sludge is expected as a potential material for capturing CO_2. Hence, parallel with considering alkaline treatment by accelerating the carbonation, the amount of CO_2 captured in alkaline construction sludge treated by PSAS associated with pH neutralization is also investigated in this study.

The experimental results indicate that the addition of a PSAS significantly granulated the alkaline sludge, and once granulated, the PSAS successfully accelerated the pH neutralization of the alkaline sludge. It was also found that the decrease in dry density, ρ_d and the degree of saturation, S_r of the PSAS-treated sludge was able to reduce the period required for the pH neutralization, t_N. The decrease in ρ_d is thought to allow fresh CO_2 gas to penetrate the specimen more easily. However, if S_r is below a certain limit, it does not strongly facilitate the reduction of t_N. This implies that pH neutralization cannot be accelerated when the amount of water in the sludge is below a certain level.

In addition, it was found that mean particle diameter D_{50} also affected t_N. Thus, the effects of sample crumbling prior to accelerated carbonation on the pH neutralization period were analyzed from the test results. It is discovered that crumbling sludges prior to CO_2 gas exposure accelerate the pH neutralization of the sludge. This suggests that a short pH neutralization period is realizable by reducing the particle size. Therefore, the effect of the particle size of PSAS-treated sludges on the pH neutralization period was investigated. The results showed that the pH neutralization period decreased with the particle size which could be attributed to the following: the CO_2 gas carbonated the particle surface, and the pH neutralization progressed gradually from the surface to the particle interior.

By conducting SEM analysis, the porosity of micro-structure of PSAS as well as PSAS treated sludge was considered as the factor facilitating the pH neutralization. SEM photos showed that the intra open voids produced by PSAS probably facilitate the penetration of CO_2 gas deeply and widely into the particles. Hence, the surface area of chemical reaction was increased. However, the carbonation was active with an appropriate water content that issues the necessary aqueous condition required for carbonation reaction.

Based on the experiment results, the production flow of the pH neutralized recycled sludge is suggested. The flow suggested introduces, in addition to the conventional processes of PSAS addition and mixing, two processes, those are curing and crumbling of the treated sludge before the treated sludges are exposed to a concentrated CO_2 gas. The granulation via crumbling differs from granulation generated immediately after the addition of PSAS. The granulation via crumbling takes the effects of change in properties of the sludge over time as a result of the hydration reaction of stabilizers into the granulation.

The strength development of the PSAS treated sludge was evaluated using a series of cone index tests. It was found that strength of alkaline construction sludge was significantly improved by adding PSAS. For the Ao clay sludge, the strength of the alkaline sludge without the PSAS was decreased by accelerated carbonation but was significantly increased even after accelerated carbonation when the PSAS was present. Due to the porosities of the remaining PSAS particles, most of the contribution of the water absorption and retention performance of the PSAS to the strength development of the PSAS treated sludge was secured after accelerated carbonation. In addition, the granulated particles of the PSAS treated sludge retained their granular shape to some extent. Therefore, it is presumed that the friction of the particles did not decrease significantly. It was also found that, after carbonation, the q_c of the PSAS treated sludge increased more rapidly than that of the alkaline sludge without the PSAS. The same experimental procedure was also applied for Kasaoka clay but with a higher amount of PSAS. In this case, a small decrease in strength of PSAS treated sludge was seen for samples undergone accelerated carbonation. This is probably because of the higher amount of PSAS caused a significant degradation of hydrated production which contribute to the strength development. A further detailed examination of the test results showed that under air-curing conditions, the q_c of the sludge with accelerated carbonation increased relatively gradually compared to that of the sludge without accelerated carbonation.

To utilize the application of alkaline construction sludge treated with PSAS and CO_2, it is necessary to investigate CO_2 capture and storage by using PSAS treated sludge as a feedstock. The experimental results pointed out that high CO_2 concentration, low dry density, and small particle size of sludge sample could influence the CO_2 captured content at the early stage of accelerated carbonation.

Keywords: pH neutralization, Accelerated carbonation, Alkaline construction sludge, Paper sludge ash-based stabilizer, Alkaline treatment, Cone index, Strength development, Particle size, Crumbling effect, CO_2 capture and storage, CO_2 emission, Cement treated soil, Water absorption

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LIST OF PUBLICATIONS

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Trung, N. D., Ogasawara, T., Hayano, K., & Yamauchi, H. (2021). Accelerated carbonation of alkaline construction sludge by paper sludge ash-based stabilizer and carbon dioxide. *Soils and Foundations 61*(5), 1273-1286.

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CHAPTER 1

INTRODUCTION

1.1 Recycle of construction and demolition waste, construction sludge in Japan

In developed countries such as Japan, the lack of land space in large cities promotes the construction of underground works. This construction activities generated a huge amount of excavated surplus soil or construction sludge that need to be treated and recycled in large quantities. Moreover, not only the development of infrastructure in new areas or re-development urbanized areas, but the need of common construction such as removing soils to install foundation to build houses, buildings and superstructure are unavoidable and is generating surplus construction soil that needs to be removed from site. The development of infrastructure requires a large work of soil excavation and reclamation. Various construction activities such as cut and fill of inclined ground to prepare usable land, removing surplus soil for installing foundation are generating a huge amount of construction sludge. In particular, the re-innovation and development at metropolis where the population density is high, and lack of land space induces the development of underground construction. Moreover, very few construction projects of both civil engineering and architecture engineering can be completed without generating construction and demolition waste. This causes the demand of treating a huge amount of excavated surplus soils which was estimated to be about 140 million m^3 in 2012, according to the Japanese Ministry of Land, Infrastructure, Transport and Tourism (MLIT 2014).

Therefore, it is necessary to manage the excavated soil generated from construction work. With the limitation of area for landfill as well as natural resources in Japan, the recycled management of construction and demolition waste has become very important. Reused and recycled excavated soils significantly reduce the unusable soil that was often disposed of previously. Moreover, recycled materials as well as the generation of by-products including excavated soils have a large potential of application.

The Soil Contamination Countermeasures Law in 2002 pays a strong concern on contamination including excavated soils and construction sludge. Environmental criteria that regulate the pH of discharged water exist. For example, in Japan, the Water Pollution Prevention Act stipulates that the pH of the discharged water should be between 5.8 and 8.6. Consequently, the demand for recycling construction sludge as a resource for alternative construction materials is low, owing to concerns regarding alkali leaching.

To achieve the sustainable development, the construction and demolition waste (CDW) should be recycled to mitigate disposing amount of waste which may harm the environment as well as to reduce the exploitation of resources. Like many developed countries, this activity has been strongly promoted in Japan for the last 25 years as shown in Fig 1.1. Compared to other developed countries, Japan is one of leading countries in recycling construction and demolition waste with recycling ratio is around 96% in 2012 as shown in Table 1.1.

Table 1.1. Construction and Demolition Waste (CDW) recycling ratio of Japan and major EU countries (PCRCMW.2019)

Country		Data annual	Amount of excavated soil generated (million tons)	CDW excluding excavated soil		Remarks
				Generation amount (million tons) *2	Recycling ratio (%) *2	
EU *1	Belgium	2012		14.8	97.6	
	Germany	2012	113.7	82.2	96.0	The recycling ratio not including backfill is 68%
	Netherlands	2012		24.2	93.0	
	United Kingdom	2012	54.4	44.8	86.5	
	Italy	2012		38.8	76.0	
	Spain	2012		27.6	68.0	
	France	2012		64.2	63.0	
Japan *3		FY 2012	180.1	66.1 (72.7)	97.0 (96.0)	Values in ( ) include construction sludge

*1: EU country data are organized by the Promotion Council for Recycling Construction
*2: excluding construction sludge
The recycling ratio of EU includes backfill
*3: The data of Japan is MLIT "Survey Results of CDW 2012"

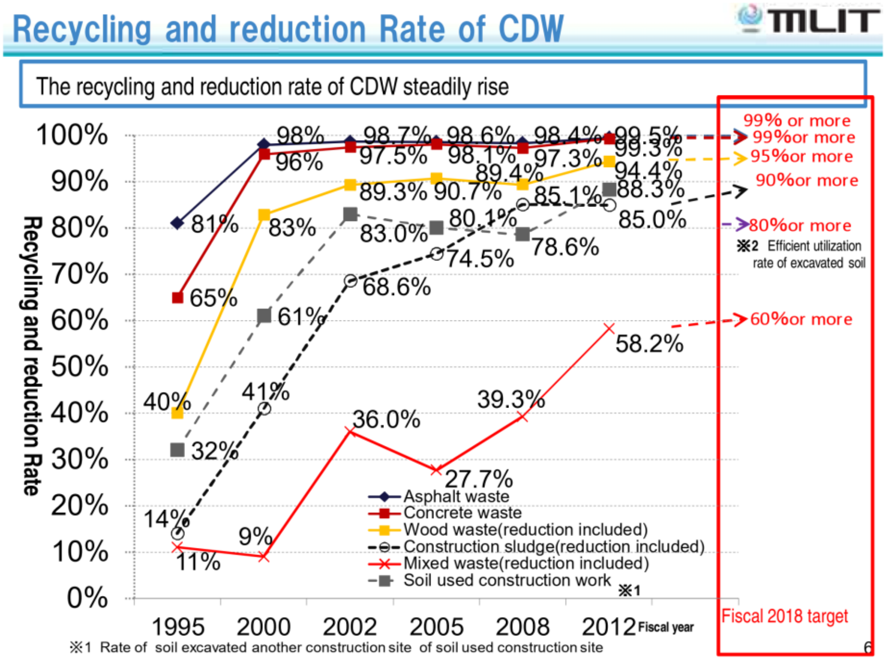


Figure 1.1. Recycling and reduction rate of construction and demolition waste (PCRCMW. 2019)

Even the recycled ratio of construction sludge in Japan is relatively high (more than 90%) but compared to other kinds of construction waste, especially asphalt or concrete waste as shown in Fig 1.2, recycling construction sludge still need to be improved because the mass of construction sludge generated from excavation is extremely high.

In 2020, the Japanese Ministry of Land, Infrastructure, Transport and Tourism issued the 5th plan of recycled building materials which promote the recycled action of building material. After four times of establishment in 1997, 2002, 2008 and 2014, this 5th time of plan focused on improving the quality of recycled building materials. With the objective aims of sustainable development, the treatment and recycling of construction sludge are expected to be further promoted in the future.

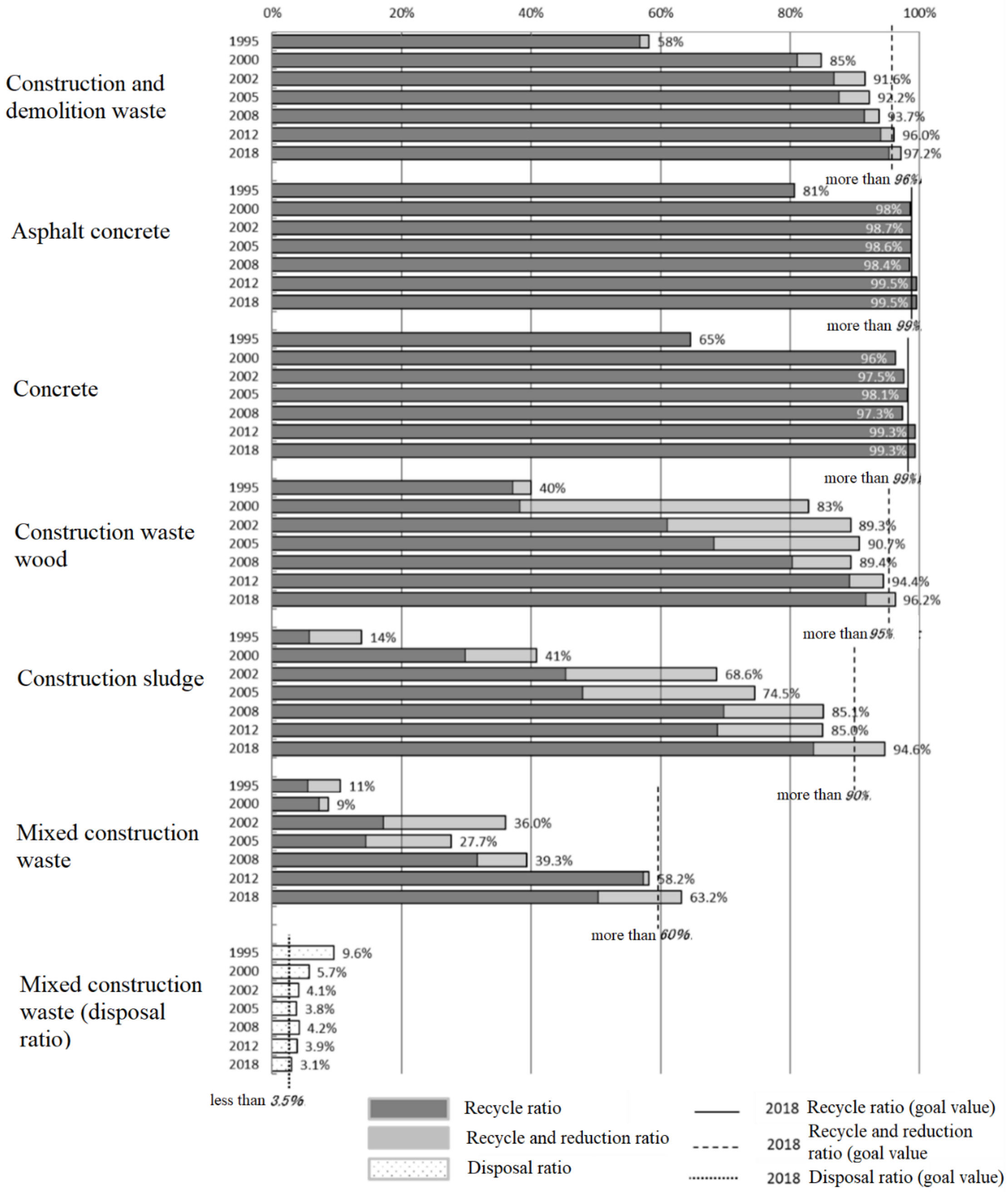


Figure 1.2. Recycle ratio of different types of construction and demolition waste in Japan (MLIT 2020)

1.2 Alkaline treatment of construction sludge by accelerated carbonation

Construction sludge generated from the excavation frequently exist as liquid state that need to be hardened to form solid or semi solid state as present in Fig 1.4. This requires the intermediate treatment in which additives such as quick lime or cement is frequently used. However, this process induces the high alkalinity of treated construction sludge due to the hydration reaction of the additives (Kamon et al., 2005) increases the pH around 11 as shown in Fig 1.5 that does not satisfy the current regulation in Japan stipulating the pH of discharged water should be $5.8 \leq \mathrm{pH} \leq 8.6$.

There are several solutions to overcome this, the alkaline filtration cover layer with clayey soil was created to have a function as an alkaline buffer that can mitigate the leachate from stabilized soil as shown in Fig 1.3. In this method, the thickness of the cover layer is designed depending on the pH of stabilized soil. Parameters such as buffer ability and permeability of the cover layer are very important to control alkali migration (Kamon et al., 2003). The other ways are to use additives with low alkalinity or new mixing/curing method for decreasing the pH of stabilized sludge (Kamon et al., 2005). These reduced the impact of high alkaline stabilized soil on the environment but cannot treat the alkalinity thoroughly because stabilized soil is itself still high alkalinity.

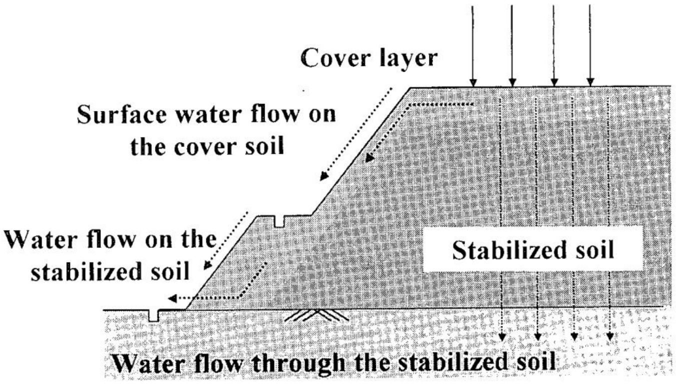


Figure 1.3. Alkaline filtration cover (Kamon et al., 1996)

Another common method which has been applied widely for capturing CO_2 is to accelerate carbonation of waste materials. However, the use of CO_2 to treat the alkalinity of alkaline construction sludge has not been studied broadly and has a large potential for application. The alkaline construction sludge could be cured under a high concentration of carbon dioxide to shorten its pH neutralization period. Hence, pH quickly falls, and the desired pH could be rapidly obtained. This method is expected not only to solve the environmental impact caused by the high level pH of alkaline construction sludge but also to capture and store CO_2 that mitigates the CO_2 emission. Referring to the wide application of industrial alkaline waste that has been doing to capture CO_2, alkaline construction sludge is expected to be a potential material for capturing and storing CO_2 which can contribute to sustainable development.

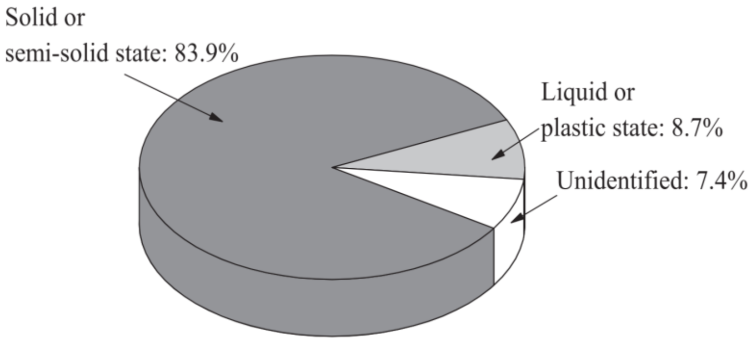


Figure 1.4. Variation in the soil state of actual construction sludge samples collected after intermediate treatment (Imai et al. 2020)

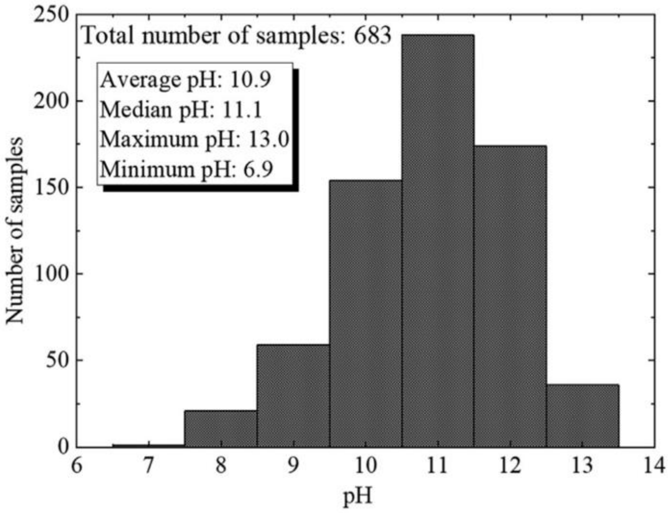


Figure 1.5. Variation in pH of actual construction sludge samples collected after intermediate treatment (Imai et al. 2020)

1.3 Potential application of PSAS

Paper sludge ash (PS ash) is the by-product of paper mills, a cinder generated from the incineration of paper sludge, has been widely an alternative sustainable material in construction industry. The production of paper has stably developed for many years producing a stable amount of paper sludge ash as presented in Fig 1.6 and hence, paper sludge ash has a wide potential for the application. Currently, most PS ash has been disposed of in landfills or used as concrete materials so far (Kumar et al., 2016; Mochizuki, 2019). Because PS ash particles have a porous microstructure with many complex irregularities and voids, PS ash can absorb and retain excess water in soft soil. Therefore, the application of PS ash to stabilize muds in construction work such as dredging in harbors, rivers, and lakes or excavating tunnels and underground pits has been increasing in practice (Kawasaki & Ishimito, 1992; Mochizuki et al., 2003).

Like other materials, the application of PS ash in the construction industry needs to satisfy environmental regulations in Japan. Because of the heavy metals in original PS ash may cause harmful impacts on the environment, PSAS was produced as an eco-friendly material by insolubilizing the heavy metals from PS ash. The advantaged characteristics of PS ash in soil treatment such as water absorption and retention performance are remained in PSAS.

Although the application of PSAS has been studied previously especially in improving the strength of surplus soil, the research on the accelerated carbonation of alkaline construction sludge has not been widely considered. Since the PSAS has the water absorption and retention performance (Kato et al., 2005; Mochizuki., 2016; Kawai et al., 2018), it could granulate as well as adjust the water content of sludge. This facilitates the accelerated carbonation of alkaline construction sludge as discussed later. Therefore, it is important to investigate the ability of using PSAS as additive to further accelerate the pH neutralization of alkaline construction sludge.

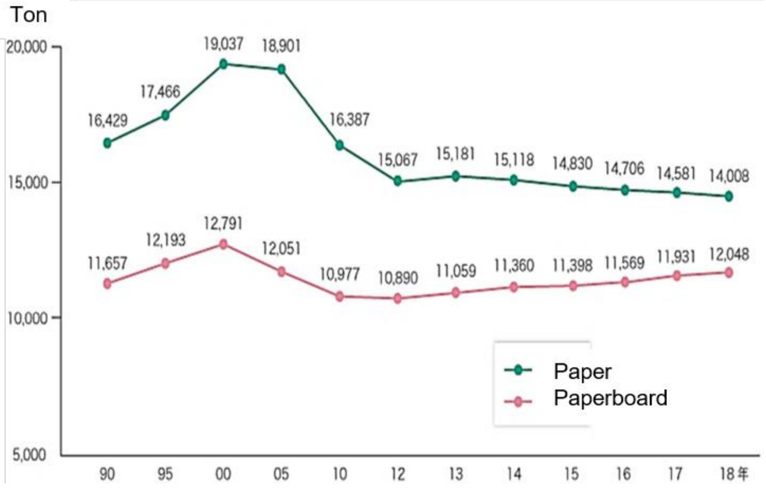


Figure 1.6. Production of paper and paperboard in Japan (Japan Paper Association homepage)

1.4 Objectives, methods, and scope of research

This research mainly aims to develop a new pH neutralization method for alkaline construction sludge by the combination of paper sludge ash-based stabilizer (PSAS) and carbon dioxide (CO_2). To contribute to sustainable development, waste materials such as alkaline construction sludge, paper sludge ash-based stabilizer and carbon dioxide were considered in this study. The pH of alkaline construction sludge which is commonly around 11 was expected to be rapidly neutralized to 8.6 by curing under high concentration of carbon dioxide.

To further investigate the applications, CO_2 capture capability and strength development of alkaline construction sludge treated by PSAS and CO_2 was also considered. PSAS treated alkaline construction sludge is expected as a potential material that can be used to capture and store CO_2 effectively. Moreover, PSAS is also expected to strengthen alkaline sludge to be a useful recycled construction material such as backfill.

In this study, two types of clay which are CH (clay (high liquid limit)) and CL (clay (low liquid limit)) were considered to prepare alkaline construction sludge. By mixing alkaline construction sludge with PSAS followed by CO_2 curing, the alkalinity of construction sludge is expected to decrease to less than 8.6 which satisfies the Japanese environmental criterion ($5.8 \leq pH \leq 8.6$). The of objectives of this research together with their methodology are presented in Table 1.2.

Table 1.2. Objective of research and methodololy

Objective	Methodology
Effect of PSAS on pH neutralization period and pH rebound	Accelerated carbonation using CO_2 incubator, pH measurement
Introduction of crumbling process	Accelerated carbonation using CO_2 incubator, pH measurement, Sieve analysis
Mechanism for contribution of PSAS and crumbling	SEM analysis
Strength development of accelerated carbonate construction sludge	Accelerated carbonation using CO_2 incubator, cone index test
CO_2 capture ability of the accelerated carbonate sludge	Accelerated carbonation using CO_2 incubator, $CaCO_3$ evaluation test

1.5 Dissertation organization

This dissertation is organized into 8 chapters.

The first chapter introduces the information about the generation of construction and demolition waste, construction sludge with the encouraged plan and policies from the governments to recycle waste materials, the potential of PSAS and the application of accelerated carbonation to treating alkalinity of alkaline construction sludge. Then the application of accelerated carbonation for alkaline construction sludge is also summarized. Technologies to accelerate carbonation of construction sludge with their advantage and disadvantage also pointed out as well as the method of using accelerated carbonation to treat alkalinity of construction sludge was presented in this research. The shortcomings of alkaline treatment of construction sludge will be discussed. The overall objective and the scope of this study are also presented. Beyond that this study follows the objects and is arranged as following chapters:

Chapter 2 briefly reviews relevant literature on accelerated carbonation with the introduction of technologies to carry out. A summary on the methodology and performance of current alkaline treatment, previous studies on characteristic of PSAS and strength improvement of carbonate alkaline construction sludge are also presented.

Chapter 3 introduces the effect of PSAS on pH neutralization of alkaline construction sludge and pH rebound. PSAS having porous microstructure and hence, is expected to produce the porosity of PSAS treated sludge by mixing PSAS with alkaline construction sludge. The porosity of PSAS treated sludge is expected to facilitate the penetration of CO_2 gas and accelerate the pH neutralization. PSAS also has the water absorption and retention performance which implies that it could reduce the free water content of the construction sludge to an appropriate value that facilitate the accelerated carbonation. In addition, due to the water reduction, PSAS treated sludge change its state from liquid to solid or semi-solid. Thus, the PSAS treated sludge was easily granulated under the mixing process by using a top-bench mixer. The granulation decreases the particle size of PSAS treated sludge which means increases the surface area that facilitate the accelerated carbonation.

Chapter 4 introduces the crumbling process and the effects of crumbling on accelerated carbonation. The granulation caused by PSAS is considered as one of factors that accelerate the carbonation. However, even being likely granulated by crumbling, pH of alkaline construction sludge without PSAS could not be neutralized to reach 8.6. In addition, PSAS itself is high alkaline material which implies that a large amount of PSAS could induce a negative impact on pH neutralization. From this point of view, non-granulated sludge with less amount of PSAS was intentionally crumbled prior to accelerated carbonation to decrease the particle size, increase the surface area while remain the effectiveness of PSAS in producing the porosity of treated sludge. This is expected to further shorten the pH neuralization period.

Chapter 5 provides some discussion about the mechanism related to effects of PSAS and crumbling on the accelerated carbonation with explanation based on the SEM analysis. Photos taken by SEM machine showed the porosity on the surface of particles as well as the intra open voids of PSAS treated sludge caused by the addition of PSAS that allows CO_2 gas to penetrate more easily and deeply inside the particle and hence, facilitate the chemical reaction.

Chapter 6 presents the strength development of accelerated carbonate construction sludge treated with PSAS. A series of cone index test was conducted to investigate the strength improvement of alkaline construction sludge treated with PSAS undergone the accelerated carbonation. It was found that the water absorption caused by PSAS strengthened the construction sludge before and after the accelerated carbonation.

Chapter 7 investigates the potential of CO_2 captured ability by PSAS treated alkaline construction sludge. The X-ray diffraction analysis reveals that PSAS has a large amount of Calcium oxide, CaO which is necessary to capture CO_2. The investigation of CO_2 capture by PSAS-treated sludge is introduced. Amount of CO_2 can be captured as well as factors affecting the CO_2 captured contents are also discussed.

Chapter 8, the last chapter summaries the contents and results obtained from this research. The conclusions are issued, the limitation and recommendations are given for further study.

CHAPTER 2

BACKGROUND (LITERATURE REVIEW)

2.1 Accelerated carbonation:

Fossil fuels is considered to produce 80-85% the total of global energy. However, this energy production is generating the vast amount of CO_2 due to the combustion and calcination in heavy industry, transportation, or power generation (Goldberg et al., 2001; Metz et al., 2005). The other sources of CO_2 emissions come from land use changes or deforestation, and decomposition of carbonates (Goyal & Sharma, 2020). The largest contribution to decomposition of carbonate is from cement industry (Andrew, 2018). CO_2 is emitted in two forms, the burning of fuel to heat raw materials up to more than 1000°C, and the releasing of CO_2 gas during the decomposition of carbonates into oxides and carbon dioxide caused by the production of clinker. Hence, to mitigate the impacts of CO_2 on climate change, efforts to reduce as well as to capture and store CO_2 has been strongly promoted by many countries.

The accelerated carbonation is commonly known as an effective method to capture and store CO_2. Most of research on accelerated carbonation aims to maximize the CO_2 content that captured by alkaline materials wherein CO_2 is captured and stored in solid form instead of being released into the atmosphere. In fact, the carbonation can take place in atmospheric conditions with very low rate because the concentration of CO_2 in natural conditions is very low, around 0.03% (Nakarai & Yoshida, 2015) making the natural storage of CO_2 insignificantly. One of the natural carbonation or weathering occur by the reaction of natural CO_2 with alkaline silicates are as follows (Pan et al., 2012):

$$CaSiO_{3(s)} + 2CO_{2(aq)} + H_2O_{(l)} \rightarrow Ca^{2+}_{(aq)} + 2HCO_3^- + SiO_{2(s)} \qquad [2.1]$$

$$Mg_2SiO_{4(s)} + 4CO_{2(aq)} + 2H_2O_{(l)} \rightarrow 2Mg^{2+}_{(aq)} + 4HCO^-_{3(aq)} + SiO_{2(s)} \qquad [2.2]$$

The atmospheric CO_2 dissolve in natural water from the rain and become weak carbonic acid. This kind of acid react with calcium and magnesium silicates from the mineral and then flow to the river or ocean, end with the precipitation of carbonates as solid state. The natural carbonation take long time because the extremely low kinetics of natural carbonation as well as the complicated conditions of nature.

The development of industries and agriculture nowaday are generating a huge amount of CO_2 that the natural carbonation cannot solve itseft. Consequenty, CO_2 or the greenhouse gas causes the global warming and other extreme weather events. Therefore, it is necessary to positively capture CO_2 by accelerating carbonation of alkaline minerals, especially alkaline wastes as adsorbents.

The process of accelerated carbonation allows alkaline materials react with high-purity CO_2 gas under high concentration degree in the presence of moisture. It was first proposed by Seifritz. (1990), the accelerated carbonation could reduce the reaction to a timescale of a few minutes or hours (Lim et al., 2010). According to Pan et al. (2012), accelerated carbonation can be classified into two types which are mineral carbonation and alkaline solid waste carbonation.

The mineral carbonation is defined as the reaction between minerals and CO_2 to form the production of carbonate. The result of carbonation produces a low pH of carbonated production which inhibit the leaching metal and solubility which are mobilized at high pH (Costa et al., 2007). The alkaline solid waste carbonation is the reaction of an alkaline waste with CO_2 as presented in Table 1.3.

Table 2. 1. Alkaline solid waste (Pan et al., 2012)

Types of alkaline solid waste	Examples	References
Slag	Steelmaking slag Coal slag Blast furnace slag	Huijgen et al., (2005); Bonenfant et al., (2008); Eloneva et al., (2008); Kodama et al., (2008); Baciocchi et al., (2009); Doucet (2010); Chang et al., (2011)
Air pollution control (APC) residue	Municipal solid waste incinerator (MSWI) APC residue Cyclone dust	Costa et al., (2007); Baciocchi (2009); Montes-Hernandez et al., (2009); Nyambura et al., (2011); Cappai et al., (2012)
Fly ash	MSWI fly ash Coal fly ash Oil shale ash	Li et al., (2007)
Bottom ash	MSWI fly ash	Arickx et al., (2006)
Cement wastes	Cement kiln dust Cement bypass dust Construction and demolition waste Cement/concrete waste Blended hydraulic slag cement	Haselbach., (2009)
Mining and mineral processing waste	Asbestos tailings Nickel tailings Red mud (Bauxite)	Khaitan et al., (2009)
Sludge ash	Sewage sludge incinerator ash Steel wastewater sludge Paper sludge ash	Gunning et al., (2010)
Paper pulping and mill waste	Paper mill waste Green sludge dreg Lime mud Lime slaker grits	Bird and Talberth., (2008)

The most common objective of accelerated carbonation so far is to maximize the storage of CO_2. Most researchers focus on optimizing the conditions that facilitate accelerated carbonation such as pressure, temperature, liquid to solid ratio (or water content), gas humidity, gas flow rate, liquid flow rate, particle size of feedstock (Chang, Chen, et al., 2011; Chang, Pan, et al., 2011; Costa et al., 2007; Haug et al., 2010; Huntzinger et al., 2009).

Method for accelerating carbonation can be separated into 2 types: direct carbonation and indirect carbonation (Pan et al., 2012). The direct carbonation is the process when minerals or alkaline waste directly react with CO_2 under 2 types of condition which are dry and wet depending on the liquid to solid ratio less than 0.2 or more than 5, respectively. The indirect carbonation requires an extracted process of alkaline metals from solid matrix by acid followed by carbonation. Mineral carbonates theoretically can store CO_2 permanently under ambient conditions. However, there is a risk that mineral carbonates may react with strong acid and CO_2 is released back into the natural environment.

To capture CO_2 by accelerated carbonation, natural silicate minerals such as vollastonite ($CaSiO_3$), serpentine ($Mg_3SiO_5(OH)_4$), talcum ($Mg_3Si_4O_{10}(OH)_2$), olivine (Mg_2SiO_4), pyroxene, and amphibole, etc. could be used due to their high calcium or magnesium conent. However, technological carbonation of these mineral consumes energy and resouces. Another way to overcome this is to use alkaline waste as presented in Table 2.3.

Other application of accelerated carbonation is the curing of precast concrete components. Insteatd of steam curing, accelerated carbonation has been gradually applied as an alternative curing due to it advantages. In the 1970s, accelerated carbonation curing was not attractive because of backward technology at that time cause the high costs of CO_2 capture.(Berger, 1979; Berger & Klemm, 1972a, 1972b; Bukowski & Berger, 1979; Good Brake et al., 1979a, 1979b; Shi et al., 2012). However, the development of CO_2 capture technology in the recent few decades allows the feasibility of accelerated carbonation curing. It was reported that the general energy requirement of steam curing is 2300KJ to cure one standard concrete block while that of accelerated carbonation curing is only 500KJ (Shi et al., 2012). The accelerated carbonation curing is expected to reduce the curing time as well as increase the strengh of concrete. The natural carbonation takes place for many years called weathering carbonation is considered as the factor deteriorates the strength of concrete due to the decalcification of CSH gel when reacting with atmospheric CO_2. However, the acceleated carbonation allows CO_2 intentionally injected to concrete at early ages of curing. Thus, CO_2 could react with unhydrated cement phases and hydration products to produces $CaCO_3$. The dense microstructure of CSH is produced and intermingled with $CaCO_3$, resulting the improvement of strength (Goyal & Sharma, 2020).

2.2 Technology of accelerated carbonation

Two laboratory test methods can be used to accelerate the carbonation of soil samples. One is to inject CO_2 gas at a predetermined concentration into a container or an incubator and then cure the soil specimens (Cai et al., 2015; Imai et al., 2020; Nabeshima, 2002; Nakarai & Yoshida, 2015; Nishi et al., 2004; Shoji et al., 2014; Trung et al., 2021). In this case, carbonation proceeds from the surface of the soil specimens. Moreover, because the test method is relatively simple, multiple specimens can be carbonated simultaneously. The other method is to inject CO2 gas from one end of a soil cylindrical specimen using a column test device or a triaxial test device, allowing CO_2 gas to permeate through the specimen, thereby causing CO_2 gas to flow out from the other end (Nishi et al., 2004; Umino et al., 2014; Yi et al., 2013a, 2013b). In this case, the carbonation of the entire specimen is accelerated. However, the second test method is more complicated than the first method, and the number of specimens that can be tested at one time is limited. In this study, the first method was adopted because pH measurements had to be performed based on the JGS standard on many specimens to determine the relationship between the amount of CO_2 captured in sludge and pH change.

2.3 Factors effect accelerated carbonation

The factors that accelerate carbonation can be inferred from the principle of accelerated carbonation reaction. A review by Pan et al. (2020) pointed out that the mechanism of accelerated carbonation occurred in four routes: (a) transportation-controlled mechanisms such as CO_2 and Ca^{2+}-ions diffusion to/from reaction sites; (b) boundary layer effects (diffusion across precipitate coatings on particles); (c) dissolution of $Ca(OH)_2$ at the particle surface; (d) pore blockage; and (e) precipitate coating. The mechanism of carbonation reaction is illustrated in Fig 1.6.

The particle size, surface area

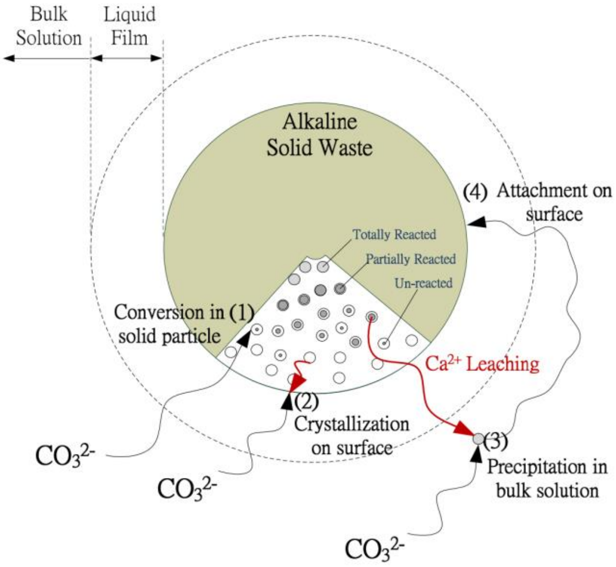


Figure 2.1. Illustration of mechanism of accelerated carbonation reaction of alkaline solid waste (Pan et al., 2012)

To start the reaction, Ca^{2+} ion must leach from the inside to the surface of particle to react with CO_3^{2-} as presented in Fig. 1.6. According to previous studies, the rate of calcium leaching is inversely proportional to particle size and pH or increase with the increasing pressure and surface area (Chang, Chen, et al., 2011; Chang, Pan, et al., 2011; Costa et al., 2007; de Windt et al., 2011; Gerdemann et al., 2007; Iizuka et al., 2004; Lekakh et al., 2008; Tai et al., 2006). The same conclusion was also found from other studies. The average grain particle sizes around 100~150mm is the optimum range for efficient carbonation of slag grinding (Costa, 2009). In addition, Eloneva et al. (2012) found the size 100 to 500mm was the optimal for kinetic of calcium leaching. In other words, the smaller particle size of the feedstock facilitates the accelerated carbonation. Iizuka et al. 2004 proposed a method to capture CO_2 by using cementitious waste and pointed out that the calcium extraction was increased with pressure.

Maroto-Valer et al. (2005) reported that reducing the particle size, which corresponds to an increase in surface area, is effective for carbonating magnesium-rich minerals such as olivine and serpentine. These previous reports suggested that appropriately preparing the L/S ratio or the particle size of the alkaline construction sludge prior to accelerated carbonation can be important for the promotion of pH neutralization. The finer particle sizes of supplementary cementing materials provide higher specific surface area for reaction and accelerate the rate of carbonation (Monkman & Shao, 2010).

The water content or liquid to solid ratio (L/S ratio)

The influence of liquid to solid ratio on accelerated carbonation of municipal solid waste incineration fly ashes was studied by Li et al. (2007). It was found that the optimum L/S ratio was 0.3 by weight of ash at ambient temperature. Similarly, the L/S ratio of 0.2-0.3 for air pollution control residues (APC) and 0.3-0.4 for bottom ash (BA) residues was found by Fernández Bertos et al. (2004). As presented in Fig 1.7. The optimum L/S ratio for the carbonation of steelmaking slag is suggested from 10:1-20:1 (mL/g) by Chang, Chen, et al. (2011); Chang, Pan, et al. (2011).

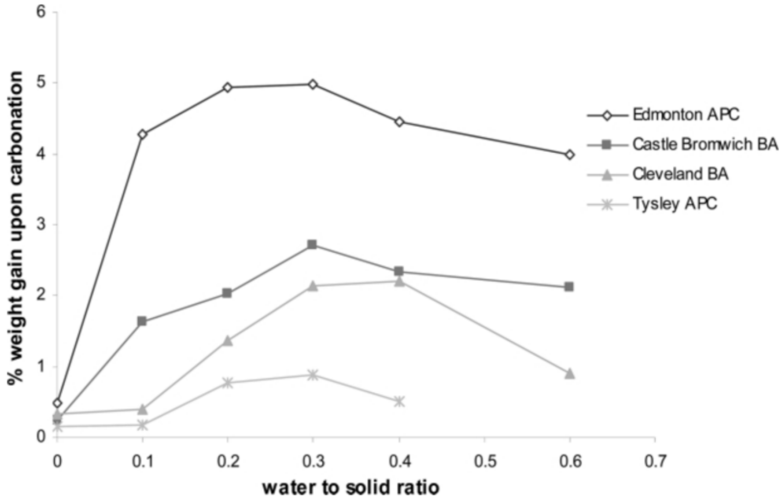


Figure 2.2. Relationship between water to solid ratio and the gain in weight upon carbonation (Fernández Bertos et al., 2004)

Also, Goyal & Sharma. (2020) reported that water to binder ratio has a significant impact on CO_2 sequestration capability of concrete, and because the carbonation requires an aqueous ambient to proceed the hydration reaction, a sufficient water is necessary. However, too much water in the pores can block the passage of CO_2 gas.

CO_2 concentration

Imai et al. (2020) conducted a series of experiment to investigate the effect of CO_2 concentration in the incubator on accelerating the carbonation of alkaline construction sludge and found that the pH neutralization rate increased with the increase in CO_2 concentration but up to 10%. The authors found that there was no significant improvement of pH neutralization rate by increasing the CO_2 concentration from 10% to 20%.

Eloneva et al. (2008) conducted a series of experimental test to investigate the effect of carbon dioxide concentration on the pH stabilization. Flue gas (i.e., a mix of CO_2 and N_2) and pure carbon dioxide were used to neutralize pH to a stabilization. The authors found that the CO_2 concentration affect the pH neutralization time with the curing period of the pure CO_2 gas and the mixed gas contained 10% of CO_2 are 24 min and 71 min, respectively.

2.4 Accelerated carbonation of alkaline construction sludge

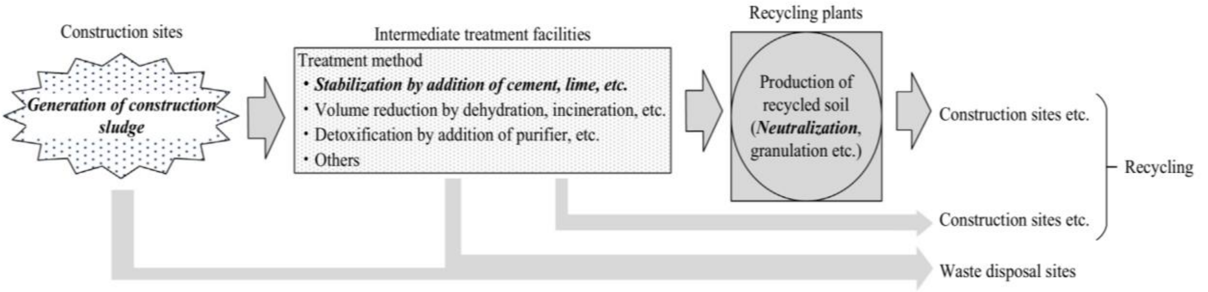


Figure 2.3. Schematic illustration of treatment and recycle of construction sludge (Imai et al., 2020)

Even though research on accelerated carbonation has been widely implemented and promoted, especially to capture CO_2 by using mineral feedstock, the application of treating the pH of alkaline construction sludge has not been paid attention to enough so far. Construction sludge frequently has high alkalinity after its generation or during the intermediate treatment process. When alkaline sludge is reused as a construction material in earth works, it is necessary to adopt measures to reduce its impact on the environment (Kamon et al., 2003). To solve the alkalinity problem, the authors proposed a method to accelerate the neutralization of the pH of alkaline sludge by curing it under a high carbon dioxide concentration in an underground pit, as shown in Fig. 2.4. By exposing alkaline sludge to concentrated CO_2 gas, the cement hydrates comprising the sludge, such as calcium hydroxide ($Ca(OH)_2$) and calcium–silicate–hydrate (C–S–H), form calcium carbonate ($CaCO_3$). The generation of $CaCO_3$ is expected to reduce the pH of the sludge. The chemical reactions are expressed as follows:

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \qquad [2.3]$$

$$(CaO)_x(SiO_2)(H_2O)_y + xCO_2 \rightarrow xCaCO_3 + (SiO_2)(H_2O)_t + (y-t)\, H_2O \qquad [2.4]$$

Previous laboratory experiments have shown that accelerating the pH neutralization of alkaline sludge can be successfully achieved by exposure to CO_2 gas (Imai et al., 2020). The author conducted a series of experiment and found that pH almost constant under sealed curing conditions and could be slowly neutralized under air curing conditions as shown in Fig 2.5. To investigate effect of accelerated carbonation on pH neutralization, the authors attempted to simulate alkaline construction sludge having pH≈11 by mixing Ao clay with blast furnace cement type B. After the material preparation, sludges with different water contents was placed in cup with the height of 20 mm and placed into a CO_2 incubator for curing. Indeed, the accelerated carbonation significantly shortened the pH neutralization period of alkaline construction sludge. The results indicated the initial water content of the sludge and CO_2 concentration degree are the factors that could accelerate carbonation of alkaline construction sludge as shown in Fig 2.6.

It could be seen that a higher CO_2 concentration yields a higher neutralization rate. However, there is a limit beyond which increases in the CO_2 concentration will not accelerate the neutralization rate any further as mentioned previously, suggesting that the excessive use of CO_2 concentrations to produce neutralized sludge could be uneconomical. The results also indicated that the use of higher CO_2 concentrations to further promote the neutralization of alkaline waste is limited.

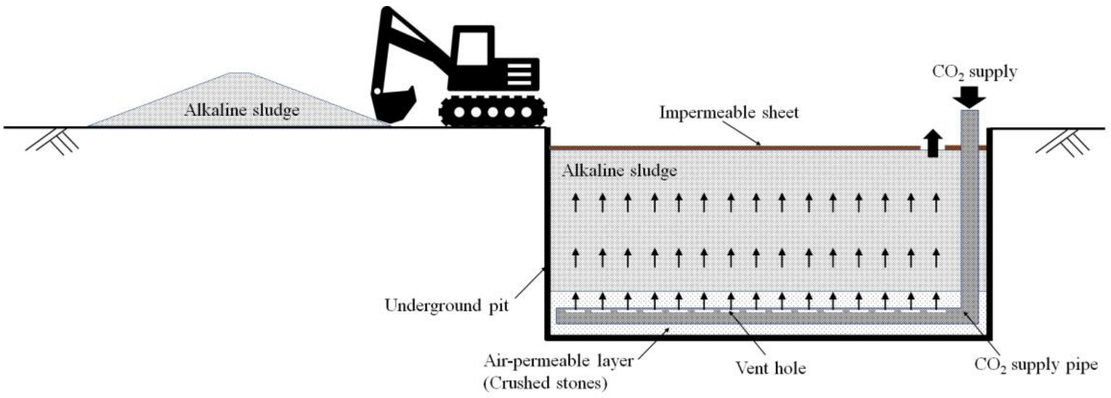


Figure 2.4. Schematic of accelerated carbonation scheme to neutralize construction alkaline sludge

Therefore, these findings suggest that other effective methods, in addition to CO_2 concentration control, should be explored to enhance the pH neutralization of construction sludge under accelerated carbonation.

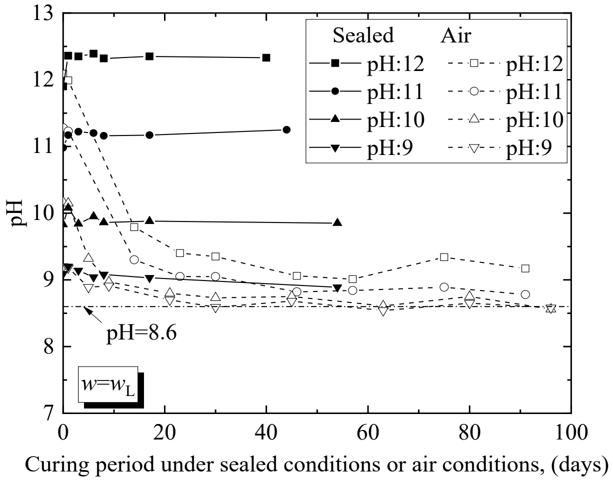


Figure 2.5. pH neutralization of alkaline construction sludge under sealed curing and air curing conditions (Imai et al., 2020)

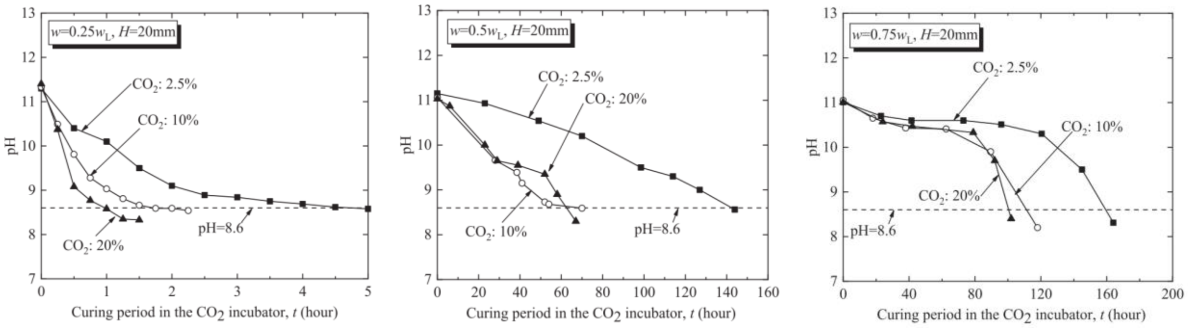
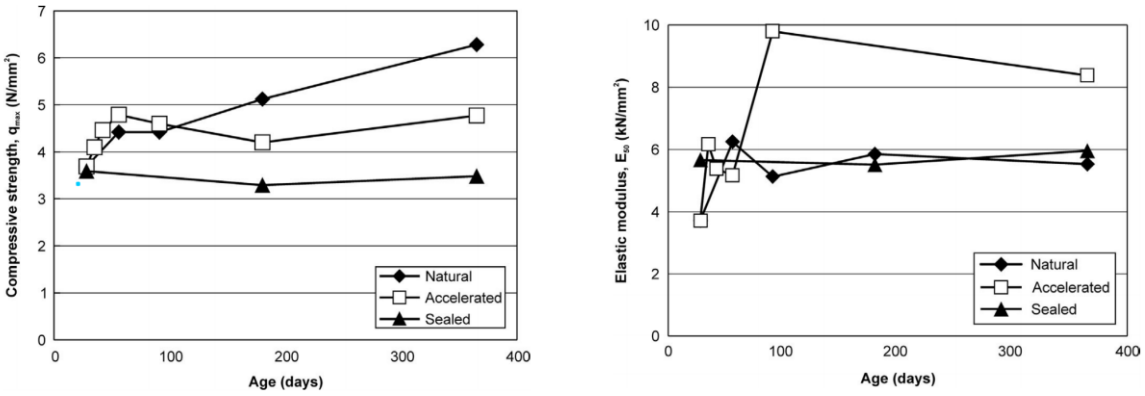


Figure 2.6. pH neutralization of alkaline construction sludge by accelerated carbonation (Imai et al., 2020)

2.5 Previous research on strength development of carbonate alkaline construction sludge

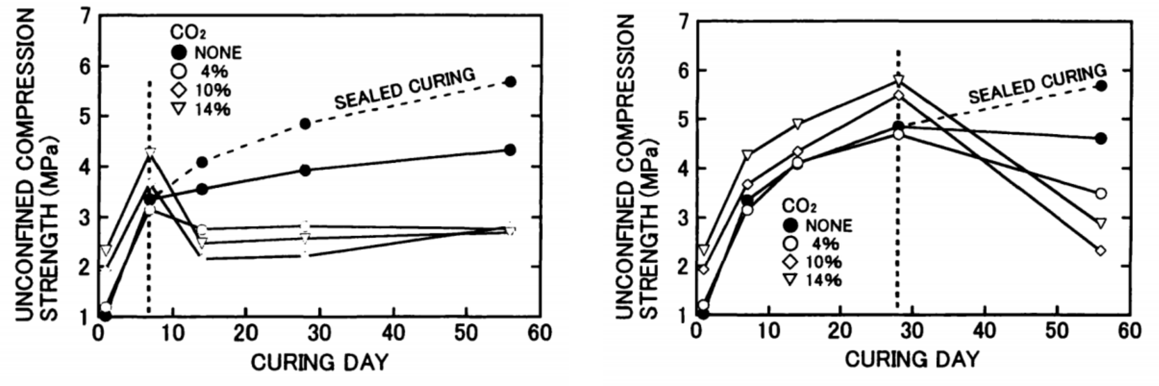
The application of accelerated carbonation on strengthen the precast concreate at early ages of curing has been widely studied. However, very few studies focus on the strength development of carbonate cement-treated soil. Most of the previous studies in the field of geotechnical engineering have used accelerated carbonation technology to improve the strength of stabilized soil (Cai et al., 2015; Nakarai & Yoshida, 2015; Yi et al., 2013a). Nakarai et al. (2015) investigated the effect of carbonation of cement-treated Toyoura silica sand on the strength development under sealed curing, ambient curing and accelerated carbonation. The authors found the strength development was affected by the carbonation. Strength of specimens undergone the sealed curing for 28 days was almost constant whereas an increase of strength under natural curing ($CO_2 \approx 0.03\%$) and accelerated carbonation ($CO_2 = 5\%$) was observed. Note that the specimens were sealed for 6 days before curing under natural conditions or accelerated carbonation. The increase in strength of CO_2 curing specimens was more significant compared to that of natural curing at the early ages of curing whereas natural curing specimens showed a higher strength after long period of curing. Not only strength, the elastic modulus of sealed curing specimens was also constant even after more than 1 year. The elastic modulus of natural curing specimens was also constant but that of CO_2 treated samples were significantly increased.



(a) (b)

Figure 2.7. Change in (a) strength, and (b) elastic modulus of cement-treated Toyoura silica under natural, accelerated carbonation, and sealed curing conditions (Nakarai & Yoshida, 2015)

Another research related to strength development of cement-stabilized soils was carried out by Nishi et al. (2004). In this research, the authors investigated the effect of accelerated carbonation on strength development by conducting unconfined compression test, and pH of construction waste sludges treated by cement. After the preparation, cement treated sludge was cured under sealed curing for 7 days or 28 days prior to accelerated carbonation. The results showed that the unconfined compressive strength of CO_2 treated sludge undergone 7 days of sealed curing was significantly decreased to a certain value then gradually increased whereas that of 28 days sealed curing specimens decreased without a rebound.



(a) CO_2–TREATED AFTER SEALED CURING FOR 7d (b) CO_2–TREATED AFTER SEALED CURING FOR 28d

Figure 2.8. Strength development of cement stabilized soils under CO_2 curing conditions (Nishi et al., 2004)

2.6 The water absorption and retention performance, porosity, and micro-structure of PSAS

As mentioned above, PS ash-based stabilizer (PSAS) is the by-product generated from the production of paper after insolubilizing heavy metals in the original PS ash. Phan. (2021) reported that the water absorption performance of PSAS is not different from original PS ash. As shown in Fig. 2.9, owning the surface morphology of porous structures with many complex irregularities and voids, PSAS can absorb and retain excess water in soft soil.

(a) Scanning electron microscope image of PSAS

(b) Water absorption by a PSAS particle

Figure 2.9. Ability to absorb water of PSAS: (a) Scanning electron microscope image of PSAS, and (b) Schematic image of water absorption by PSAS treated sludge (Dong et al., 2011).

It has been found that PSAS can instantly improve the stability of mud and sludge when PSAS is mixed with them. Fig. 2.10(a) shows the appearance of the treated clay just after the PSAS was mixed to the Ao clay (initial water content $w_i = w_L$) with the different A_{PS} and the corresponding total water content of the mixture, w'. Compare with the appearance of Ao clay mixtures at the same w' shown in Fig. 2.16(b), the treated clay showed much lower fluidity than that of Ao clay. This indicates that the PSAS instantly absorbed clay-water after being mixed and thus reduced the amount of water in voids, resulting in low fluidity of the treated clay.

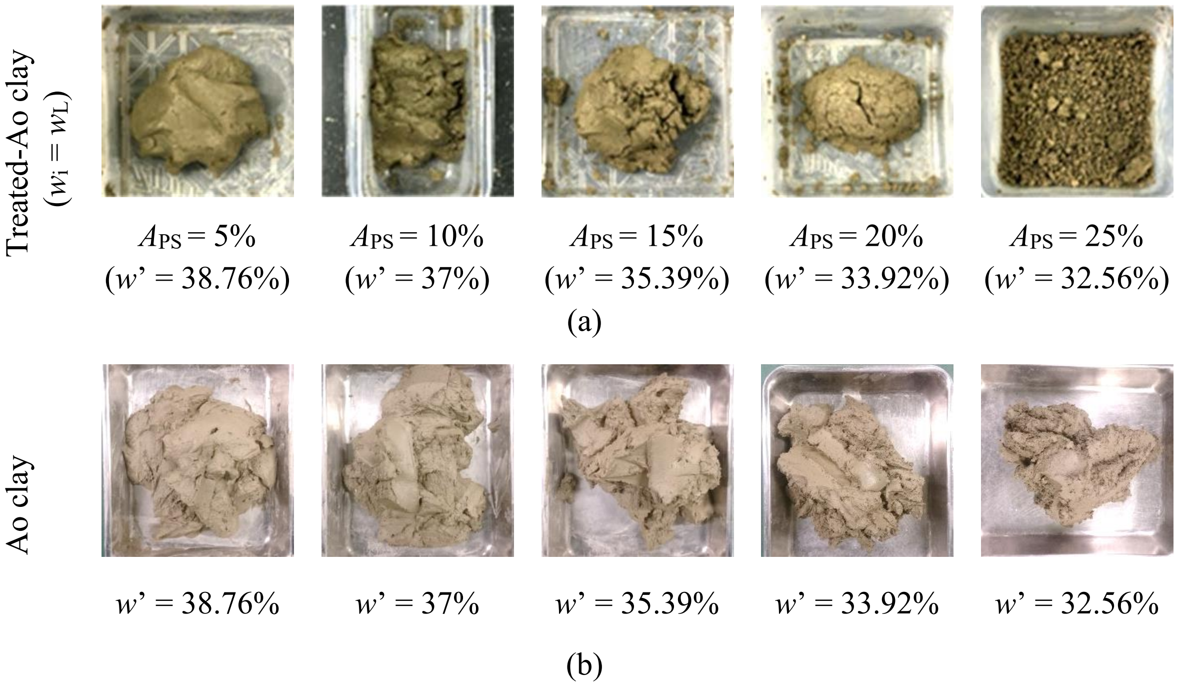


Figure 2.10. Appearance of (a) treated clay just after mixing Ao clay with PSAS (Kawai et al., 2018), and (b) Ao clay at corresponding total water content, w'.

CHAPTER 3

EFFECT OF PSAS ON PH NEUTRALIZATION AND PH REBOUND

PSAS having porous microstructure (Phan et al., 2021) and hence, is expected to produce porosity of PSAS treated sludge by mixing with construction sludge. The porosity of treated sludge is expected to facilitate the penetration of CO_2 gas and accelerate the pH neutralization. PSAS also has water absorption and retention performance which implies that it could adjust the water content of the construction sludge to an appropriate value that facilitate the accelerated carbonation. In addition, due to the water reduction, PSAS treated sludge change its state from liquid to solid or semi-solid. Thus, the PSAS treated sludge was easily granulated under the mixing process by using a top-bench mixer. The granulation decreases the particle size of treated-PSAS sludge which means increases the surface area that also facilitate the accelerated carbonation.

3.1 Material introduction, sludge preparation

a. Material

To prepare the construction sludge, Ao clay and Kasaoka clay was used. Ao clay (w_L = 40.7%, w_p = 23.7%, ρ_s = 2.716 g/cm^3, and pH = 7.0) is categorized as CL (clay (low liquid limit)) whereas Kasaoka clay (liquid limit: w_L = 60.4%, w_P = 26.0%, ρ_s = 2.680 g/cm3, pH = 9.1) was categorized as CH (clay (high liquid limit)) based on the Unified Soil Classification System.

The alkaline construction sludge was simulated by mixing Ao clay or Kasaoka clay with blast furnace cement type B (BFCB), which are commercially available in Japan. BFCB satisfies the current Japanese industrial standards. BFCB (ρ_s = 3.04 g/cm^3 and pH = 12.3) is a mixture of ground granulated blast furnace slag (BFS) and Portland cement with the amount of BFS ranging from 30% to 60%, as specified in JIS R 5211. BFCB was selected because the pH of this sludge changes more slowly with changes in the amount than quicklime or ordinary Portland cement, making it easier to adjust the pH of the sludge specimens to a target value as shown in Fig 3.1. As a previous study demonstrated that the dominant pH value of actual construction sludge at treatment facilities is approximately 11 (Imai et al., 2020), sludge having a pH of approximately 11 was targeted in this experiment.

A paper sludge ash based-stabilzer (PSAS) commercially available in Japan was used to treat a portion of the alkaline sludge specimens. The ρ_s of the PSAS was 2.603 g/cm^3, the pH was 11.7, and the PSAS was classified as non-plastic (NP). Immediately after each alkaline sludge specimen was prepared, the PSAS was added to it, followed by mixing to obtain a PSAS treated sample. In this study, the addition ratio A_{PS} of the PSAS to the Ao clay was defined as the dry weight ratio. The chemical compositions and the particle size distribution of Ao clay, Kasaoka clay, BFCB, and PSAS are shown in Table 3.1 and Figure 3.2.

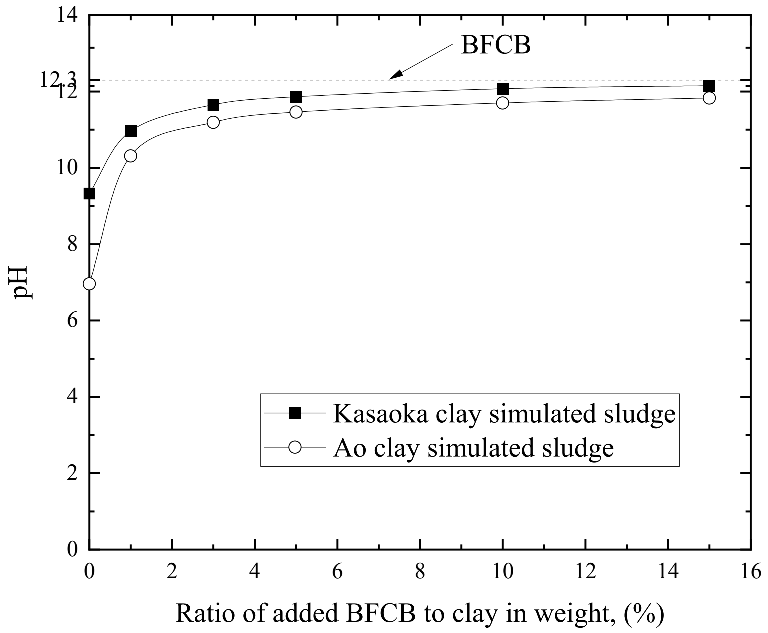


Figure 3.1. Relationship between ratio of added BFCB to clay and pH of sludge

Table 3.1. Chemical components of materials

a) Ao clay:

SiO_2	Fe_2O_4	Al_2O_3	K_2O	CaO	TiO_2	MgO	P_2O_5	MnO	others
56.96	15.41	15.27	4.41	2.83	1.54	2.36	0.54	0.31	0.55

b) Kasaoka clay

SiO_2	Fe_2O_3	Al_2O_3	K_2O	CaO	TiO_2	MgO	MnO	others
69.07	5.46	20.22	2.75	0.91	0.63	0.81	0.03	0.12

c) BFCB

CaO	SiO_2	Al_2O_3	SO_3	Fe_2O_4	MgO	TiO_2	MnO	P_2O_5	others
65.57	19.07	5.26	3.98	2.91	1.98	0.60	0.17	0.23	0.23

d) PSAS

CaO	SiO_2	Al_2O_3	SO_3	Fe_2O_4	MgO	TiO_2	ZnO	P_2O_5	others
63.89	13.55	6.89	6.06	3.27	1.31	3	0.23	0.95	0.85

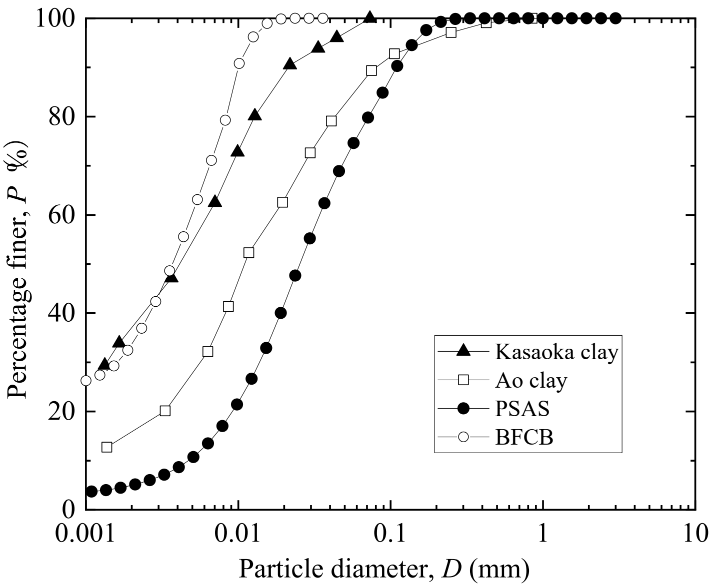


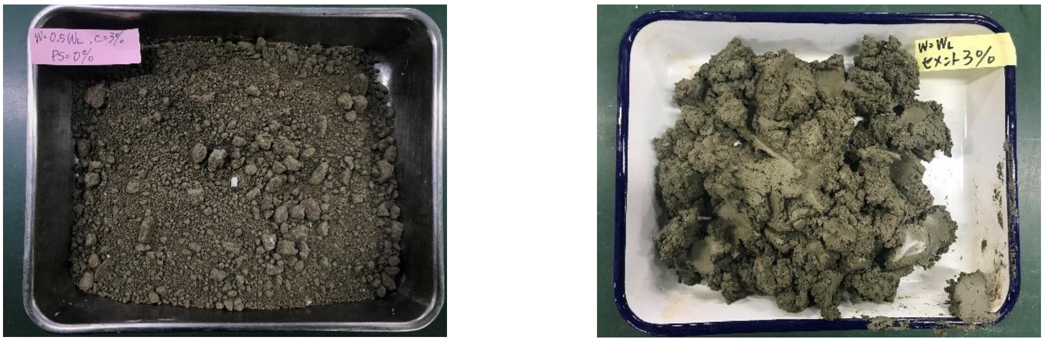
Figure 3.2. Particle size distribution of Ao clay, Kasaoka clay, PSAS, and BFCB

b. The preparation of alkaline construction sludge

To investigate the effect of PSAS on accelerating carbonation of alkaline construction sludge, different amounts of A_{PS} were tested on different alkaline sludge specimens, as summarized in Table 3.2. Thus, 11 types of each PSAS-treated Ao clay sludge and PSAS - treated Kasaoka clay sludge ($A_{PS} > 0\%$), having a pH of 11.2 to 12.0, were obtained. Figure 3.3 shows the appearance of some of the sludge samples: alkaline sludge ($A_{PS} = 0\%$) and PSAS-treated sludge ($A_{PS} = 15$, 50% under the $w = 0.5w_L$ condition, and $A_{PS} = 20$, 50% under the $w = 1.0w_L$ condition) prepared by Ao clay.

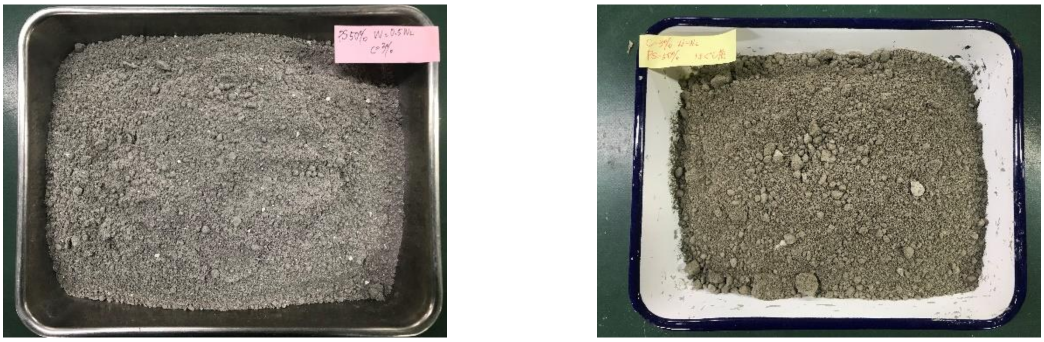
First, the initial water content, w_i of Ao clay or Kasaoka clay was adjusted to $0.5w_L$ or $1.0w_L$ by adding an appropriate amount of distilled water and stirring for 3 mins by using a bench-top mixer. Subsequently, BFCB was added to clay at a 3% dry mass ratio and mixed thoroughly to obtain alkaline sludges with pH values of 11.2 to 12.0. The prescribed amounts of PSASs were added to the sludge and mixed thoroughly. PSAS exists as dry form and is stored under dry conditions due to its hydration when exposed to water or even atmospheric conditions. The PSAS addition ratio A_{PS} was defined as the dry mass ratio of the PSAS to clay. Various A_{PS} values ranging from 0% to 70% were attained. It is noteworthy that at this point, the sludges except those with $w_i = 1.0w_L$ and $A_{PS} = 0\%$, 10%, or 20% for Kaosaoka clay sludge, or with $w_i = 1.0w_L$ and $A_{PS} = 0\%$, 5% for Ao clay sludge were granular. This because small amount of PSAS produces the low ability of water absorption and retention performance. Consequently, the water reduction is not enough to cause the solid or semi-solid state of PSAS treated sludge, and hence sludge could not be granulated.

Finally, sludge samples were cured under sealed conditions for 7 days. Figure 3.4 shows the particle size distributions (PSDs) of the alkaline sludge and PSAS-treated sludge prepared from Ao clay, except for those with $w = 1.0w_L$ and $A_{PS} = 0\%$ and 5%. The PSDs were obtained using sieve analyses, in which each sludge specimen was air dried for 24 h and then sieved for 10 min using an electromagnetic sieve shaker machine with sieves ranging from 19 mm to 75 μm and a sieving amplitude of 1.5 mm. In the $w_i = 1.0w_L$ and $A_{PS} = 0\%$ and 5% samples, the sludge did not granulate after mixing; therefore, the PSDs could not be obtained. The PSDs of the Ao clay and the PSAS are also shown in Fig. 3.2. It was found that in the $w_i = 1.0w_L$ cases, the particle size tended to decrease as the A_{PS} increased for both types of clay. The PSDs of Kasaoka clay sludge are expressed in Figure 3.5. Similarly to Ao clay, Kasaoka clay sludge with low A_{PS} (i.e., 0, 10, 20%) were not granulated so that their PSDs are not shown. Note that the liquid limit of Ao clay and Kasaoka clay, w_L are 40.7% and 60.4%, respectively so that the needed A_{PS} for the granulation of sludges are also different.



Alkaline sludge (A_{PS} = 0%) Alkaline sludge (A_{PS} = 0%)

PSAS treated sludge (A_{PS} = 15%) PSAS treated sludge (A_{PS} = 20%)



PSAS treated sludge (A_{PS} = 50%) PSAS treated sludge (A_{PS} = 50%)

a) Ao clay under $w_i = 0.5w_L$ condition b) Ao clay under $w_i = 1.0w_L$ condition

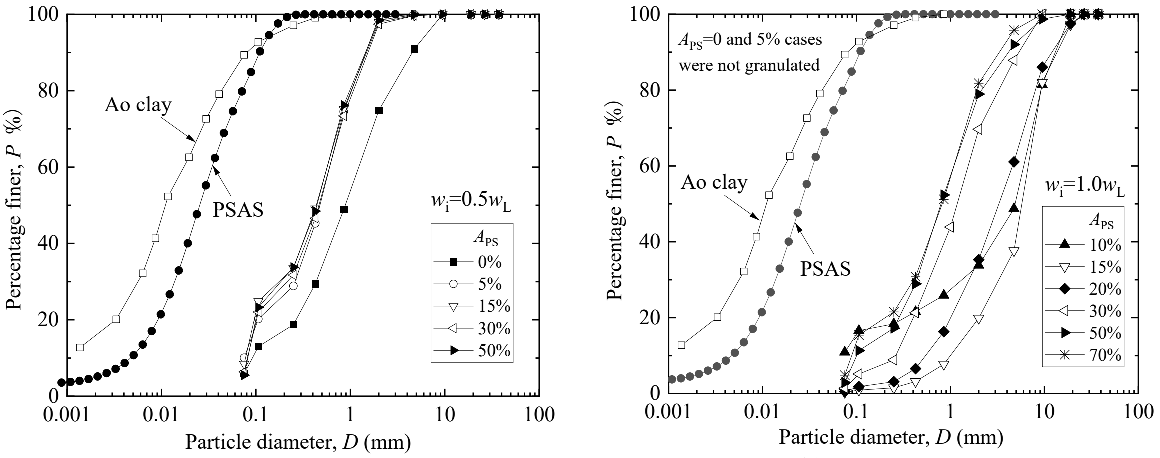
Figure 3.3. Examples of alkaline sludge and PSAS treated sludge prepared using Ao clay

The change in particle size was primarily attributed to the water absorption and retention performance of the PSAS. By absorbing and retaining water, the PSAS induced a semi-solid or solid sludge with an increase in the A_{PS}. Then, under mixing conditions, the sludge was granulated, and the particle size decreased with increases in the A_{PS}. However, when the A_{PS} increased above a certain level, the sludge could not absorb or retain additional water, and further changes in the particle size were minimal. In contrast, little change was observed in the

PSDs with increases in the A_{PS} for sludge with a low initial water content (w_i=0.5 w_L). This is because the sludge was already initially in a semi-solid state, the amount of free water that the PSAS could absorb and retain was limited even if the A_{PS} increased.

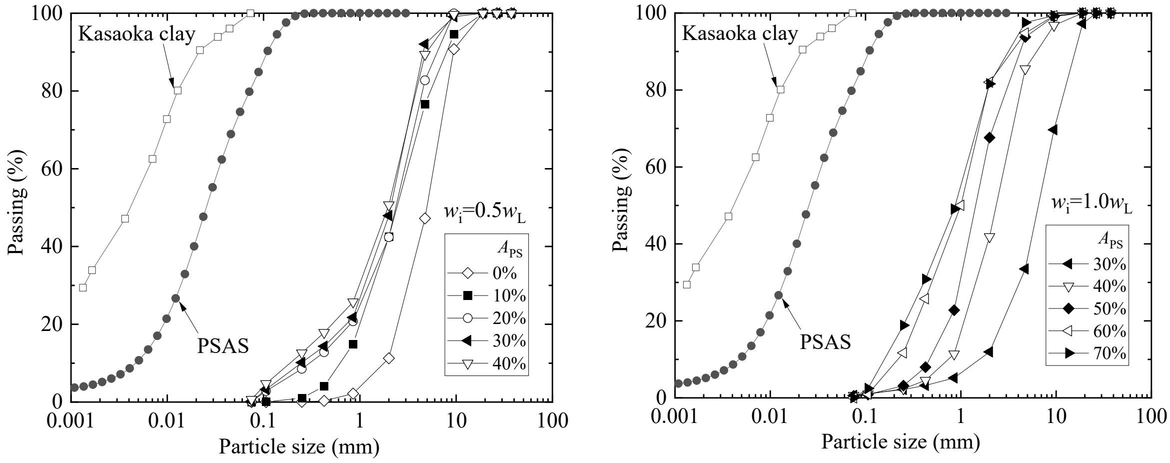
Table 3.2. Mixture conditions for preparation of alkaline sludge and addition ratios of PSAS used in treatment experiments

Clayey type	Initial water content of clay, w_i (%)	Addition ratio of BFCB, A_{cement} (%)	Addition ratio of PSAS, A_{PS} (%)
Ao clay	$0.5w_L$	3.0	0, 5, 15, 30, 50
	$1.0w_L$		0, 5, 10, 15, 20, 30, 50, 70
Kasaoka clay	$0.5w_L$		0, 10, 20, 30, 40
	$1.0w_L$		0, 10, 20, 30, 40, 50, 60, 70



(a) $w_i = 0.5w_L$ (b) $w_i = 1.0w_L$

Figure 3.4. Particle size distributions of alkaline sludge (A_{PS} = 0%) and PSAS-treated sludge (A_{PS} > 0%) prepared from Ao clay



(a) $w_i = 0.5w_L$ (b) $w_i = 1.0w_L$

Figure 3.5. Particle size distributions of alkaline sludge (A_{PS} = 0%) and PSAS-treated sludge (A_{PS} > 0%) prepared from Kasaoka clay

3.2 Experimental procedure, accelerated carbonation of alkaline sludge and PSAS treated sludge

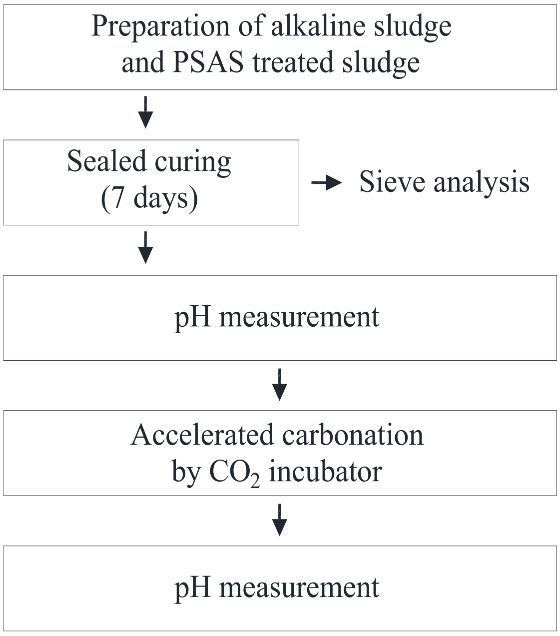
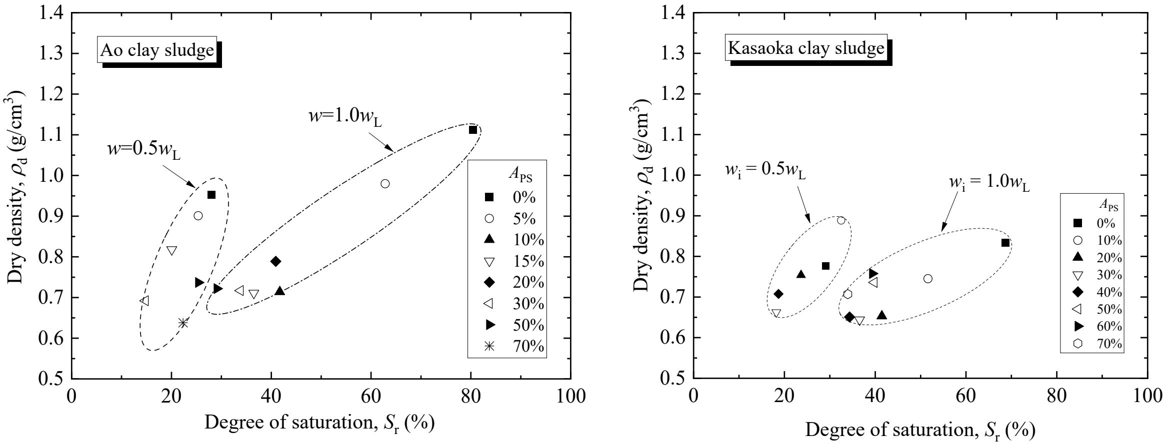


Figure 3.6. Test procedure flow chart

The effect of PSAS on pH treatment of alkaline construction sludge was investigated by conducting accelerated carbonation using CO_2 incubator. As presented in Fig 3.6, after the preparation, alkaline sludge and PSAS treated sludge were stored in plastic bags for curing under sealed curing conditions. The purpose of curing samples in sealed conditions is to attain the stable pH of sludge. The particle size distribution as shown in Fig 3.4 and 3.5 was determined by the sieve analysis conducted after sealed curing for granulated sludge.

In parallel with that, another part of sludge samples was carefully placed into plastic cups from a zero height until a 30-mm-thick layer was formed. Each type of sludge that did not granulate was first added until it filled a cup and was subsequently statically compressed into a 30-mm-thick flat layer. The purpose of this procedure in the experiment was to simulate the in-situ treatment of actual alkaline construction sludge. As shown in Fig 2.4, in-situ alkaline construction sludge is poured into an underground pit without compaction. The alkaline sludge falls freely into the pit, and then CO_2 gas is injected from the bottom and flows to the top of the pit. Strictly speaking, the density of the sludge varies from the top to the bottom, depending on the height. However, this experiment attempted to simulate the actual sludge in its loose state, laid on upper layers that are closed to the surface. To reflect this, sludge samples were prepared in cups, paying attention to the preparation procedure in order to mimic their authentic in-situ state. Figure 3.7 shows the relationship between degree of saturation, S_r and dry density, ρ_d for each sludge sample prepared in a cup. The dry density was measured by determining the volume under wet condition and the mass of soil particles of sludges in the plastic cups prior to the accelerated carbonation. S_r and ρ_d tend to decrease with increasing A_{PS}. This is related to the water absorption and retention performance of the PSAS and the light-weight characteristics of the porous PSAS particles.

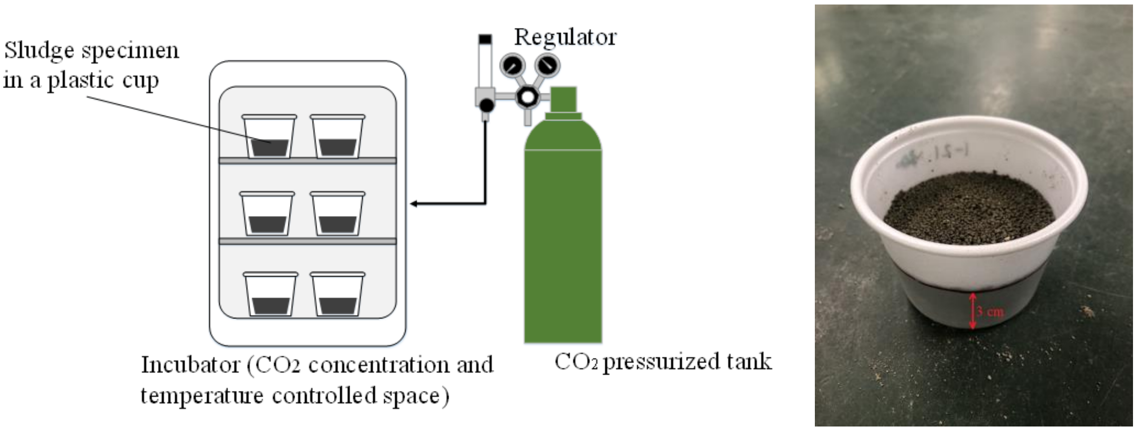
To accelerate the neutralization of the pH, accelerated carbonation of the untreated and the treated alkaline sludge specimens was conducted using a CO_2 incubator, in which the CO_2 concentration and temperature were controlled at 10% and 25C, respectively as present in Fig 3.8. In practice, alkaline construction sludge having high water content is placed in an underground pit for injecting CO_2 gas as presented in Fig 2.4. Hence, the particles located deeply inside the soil mass are under high humidity conditions. Therefore, the humidity inside the incubator was setup around or higher than 90% to simulate the real conditions of the in-situ sludges placed in the underground pit where the humidity is high. After an arbitrary CO_2 curing periods, samples were taken out of the incubator for pH measurement. Note that the pH measurement was conducted before and after accelerated carbonation process to evaluate the decrease in pH as well as the pH neutralization rate.



(a) Sludge samples prepared from Ao clay

(b) Sludge samples prepared from Kasaoka clay

Figure 3.7. Relationship between degree of saturation and dry density of each sludge specimen prepared in a cup



(a) (b)

Figure 3.8. Schematic of accelerated carbonation by CO_2 incubator: a) CO_2 incubator supplied by CO_2 storage tank, b) sludge in plastic cup with the thickness of 3 cm

Table 3.3. Accelerated carbonation conditions

CO_2 concentration (%)	Temperature (°C)	Humidity (%)
10	25	90 or higher

3.3 Effect of PSAS on pH neutralization rate

Figures 3.9 and 3.10 show the change in the pH of each sludge specimen with respect to the curing time for the $w = 0.5w_L$ and $w = 1.0w_L$ cases, respectively. It was found that the pH values of all the sludge types decreased as the curing time increased. However, a longer curing time was required to neutralize the PSAS untreated sludge than the treated sludge. In this study, neutralization was considered complete when the pH reached 8.6 as shown in Fig 3.11, which is the standard value stipulated by the Prevention of Water Pollution Act in Japan. It should be noted that, as shown in Fig 3.9a and 3.9b, the accelerated carbonation tests for Ao clay sludge were performed twice on the alkaline sludge for the $w = 0.5w_L$ case when $A_{PS} = 0\%$. This was because in the first trial, the pH did not drop below 8.6, and all specimens were consumed before the maximum time limit was reached. Therefore, in the second trial, the accelerated carbonation test was conducted using a larger number of specimens. As shown in the figure, the behaviors observed in the first and second trials were similar, which confirmed the reproducibility of the experiment, indicating that the t_N value could be evaluated from the results of the second trial. It could be seen that the pH of most of granulated sludge fell quickly under CO_2 curing whereas that of the ungranulated cases could only rapidly decrease at the initial stage of pH neutralization. After falling closely to 8.6, pH of ungranulated sludge samples became stable and decreased very slowly.

Table 3.4 summarizes the t_N values of all the sludge specimens along with their physical properties, such as the mean particle density (D_{50}), ρ_d, and S_r. The soil particle density of each sludge specimen and ρ_s were calculated from the particle densities of the Ao clay or Kasaoka clay, BFCB, and PSAS using the mixture ratio, and ρ_s was used to calculate the void ratio e of each sludge type. In Table 3.4, the t_N of the $0.5w_L$, $A_{PS} = 0\%$ Ao clay alkaline sludge is considerably longer than the others. As mentioned above, this is because, as shown in Fig. 6(a), the pH became almost constant above a pH of 8.6 after having dropped sharply in the early stages. Similarly, t_N of the Kasaoka clay sludge with $A_{PS}=0\%$ for both $w_i=1.0w_L$ and $0.5w_L$ could not be obtained after nearly 400 h cured under CO_2 curing. It can be seen the difference in the ultimate pH of the alkaline sludge and PSAS treated sludge after accelerated carbonation. This probably because the chemical composition of PSAS has Sulfur Trioxide, SO_3. Therefore, the reaction of SO_3 with water to form Sulfuric acid (H_2SO_4) as presented in Eq (3.1) is considered the reason to further decrease the pH of PSAS treated sludge.

$$SO_3 + H_2O \rightarrow H_2SO_4 \quad [3.1]$$

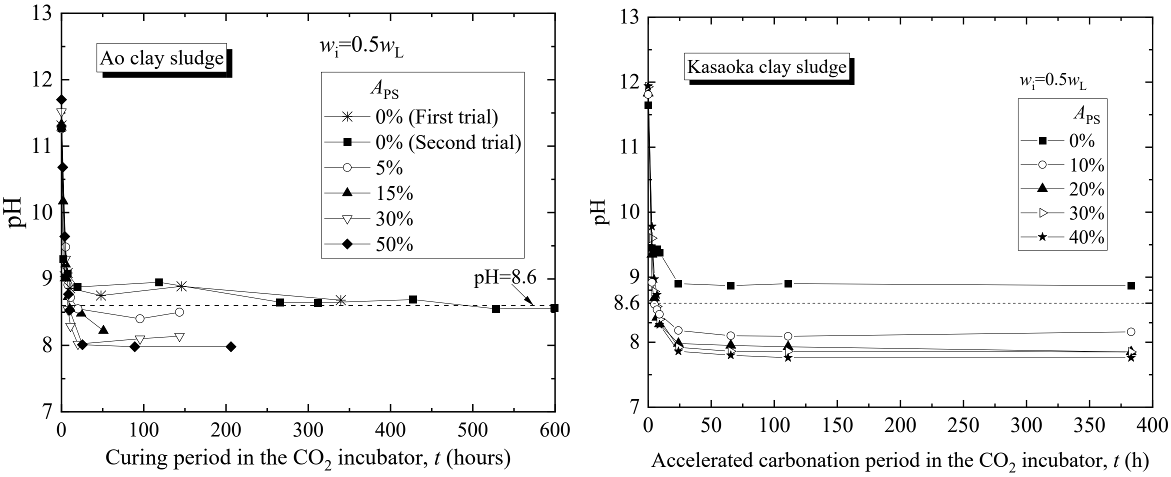
Figure 3.12 shows a plot of the t_N for each sludge specimen versus A_{PS}. In both the $w = 0.5w_L$ and $1.0w_L$ cases, the addition of the PSAS significantly reduced the t_N. Note that for the Kasaoka clay sludge, t_N of the $A_{PS}=0\%$ sludge could not be obtained. However, when A_{PS} was extremely high (for example, 50% or 70% in the $w_i = 1.0w_L$ cases), the t_N tended to be slightly longer. It could be clearly seen for the case of Ao clay sludge when t_N of the $A_{PS}= 50\%$ or 70%

in the $w_i = 1.0w_L$ samples were higher than that of the low A_{PS} (i.e., 20% or 30%). Sludge samples prepared from Kasaoka clay having a higher liquid limit, w_L=60.4% (higher than that of Ao clay, w_L=40.7%) also demonstrated the same behavior when t_N of the high A_{PS} sludge samples slightly increase but not as significant as Ao clay sludge. Furthermore, the figure indicates that the t_N values were different between the $1.0w_L$ and $0.5w_L$ cases having the same A_{PS}. This implies that t_N is affected by water content, A_{PS} as well as clayey types. For Ao clay sludge, the $1.0w_L$ cases required less time for the pH neutralization than the $0.5w_L$ cases, except when A_{PS}=5% which is the ungranulated sludge. However, for the Kasaoka clay, t_N of the $1.0w_L$ sludges with A_{PS} = 10, 20, and 30% are more than that of $0.5w_L$ sludge because these sludges were not granulated due to the higher w_L of Kasaoka clay. To investigate the factors that caused the differences, the t_N was assessed from the physical properties of sludge, ρ_d, S_r, and D_{50}. Note that beyond a certain value of A_{PS}, the effect of increasing A_{PS} on reducing t_N becomes insignificant. This is because beyond a certain value of A_{PS}, the addition of PSAS did not significantly reduce the particle size further. In addition, parallel with the reduction in the size of particles, the PSAS also produces a porous microstructure of the particles (which is mentioned in chapter 5) that influences accelerated carbonation. CO_2 gas can react with the alkali not only at the surface of the particles but also inside the particles after penetrating through intra open voids. Therefore, effect of increase in PSAS on accelerated carbonation becomes equal. In fact, the increase in PSAS causes a slight increase in pH because PSAS is an alkaline material.

For the CL clay (Ao clay), t_N tends to decrease with the decrease of ρ_d and S_r. Figure 3.13 shows the relationship between ρ_d and t_N, while Figure 3.14 shows the relationship between S_r and t_N for each sludge type. Note that the dry density prior to accelerated carbonation was measured by determining the volume and the mass of sludges in the plastic cups prior to the accelerated carbonation. Because sample was poured into plastic cup with a thickness of 3 cm therefore, the volume here was evaluated by the volume of water in the cup rising up to 3 cm. As shown in Fig 3.13(a), t_N tended to decrease with a decreasing ρ_d for Ao clay sludge. This occurred because, with a decrease in ρ_d, fresh CO_2 penetrates the specimens more easily. Thus, even as CO_2 is consumed by the carbonation process, a predetermined CO_2 concentration can be easily achieved in the sludge and can promote pH neutralization. However, from Fig 3.13, for the same ρ_d, the $w_i = 0.5w_L$ specimens tend to require longer t_N than the $w_i = 1.0w_L$ specimens. The effect of ρ_d on t_N of Kasaoka clay sludge was not siginificant because ρ_d did not change with change in A_{PS} as shown in Fig 3.13(b). Therefore, factors other than ρ_d appear to influence t_N. As shown in Fig 3.14, t_N decreased with the decrease in S_r for both the $0.5w_L$ and $1.0w_L$ cases. Specifically, t_N decreased significantly from 95 h to less than 7 h, when S_r decreased from 80.4% to 41.7% for w_i=$1.0w_L$. For w_i=$0.5w_L$, t_N rapidly decreased, while S_r decreased from 28.0% to approximately 20%. However, further decreases in S_r did not strongly facilitate a reduction in t_N. This implies that neutralization cannot be accelerated when the amount of water in the sludge falls below a certain level. For the experimental conditions, reducing the S_r of treated sludge to approximately 20% and 40% is suggested to optimally accelerate the pH neutralization for the $0.5w_L$ and $1.0w_L$ cases, respectively.

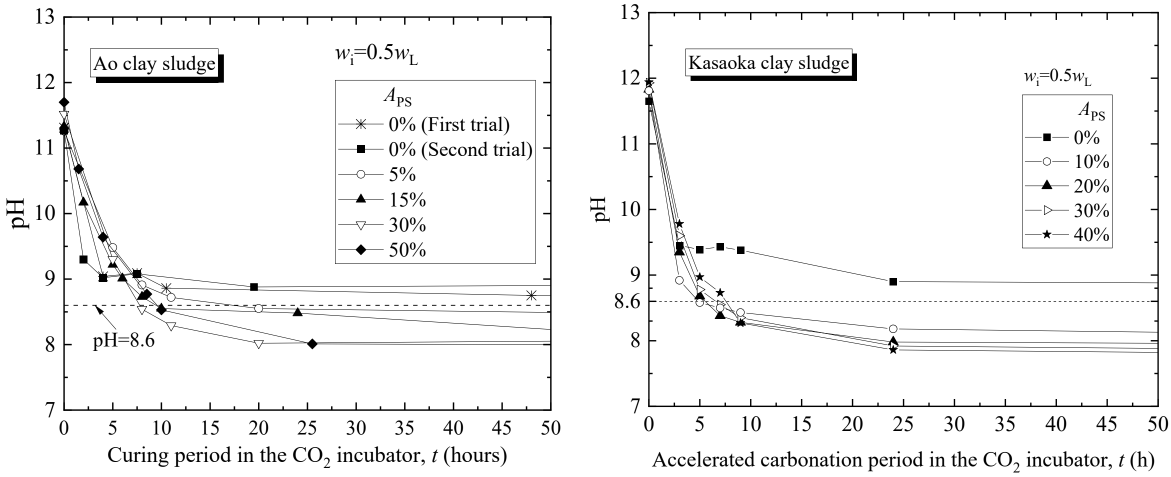
Figure 3.15 shows the relationship between D_{50} and t_N for each sludge specimen. Note that t_N of ungranulated sludges (lumpy sludges) are presented by arrows because their D_{50} could not be obtained. As mentioned, the addition of the PSAS significantly granulated the alkaline sludge. Once granulated, the D_{50} of the PSAS treated sludge varied from approximately 0.5

mm to 6 mm, causing t_N to rapidly decrease to less than 18 h. However, in evaluating the figure in detail, it is found that, when the D_{50} of the treated sludge is less than 0.5 mm, t_N tends to increase with a decrease in D_{50}. This occurs because, as the particle size decreases, the gas permeability coefficient also decreases, making it more difficult for CO_2 to penetrate the specimen. As the D_{50} of the treated $w_i = 0.5w_L$ specimens is less than that of the treated $w_i = 1.0w_L$ specimens, t_N can be longer even if both ρ_d and S_r of the former are lower than those of the latter. On the other hand, it is noted in the figures that the t_N of the sludge having D_{50} of 5.0–6.0 mm was longer than that of the sludge with D_{50} of 1.0–3.5 mm, and t_N tends to increase with the increase in D_{50}. The same trend was also seen for Kasaoka clay sludge. This probably occurred because, when the particle size is large, a relatively long time is needed for the carbonation to progress from the surface of the particle to the inside of the particle.



(a) Accelerated carbonation period t: 0–600 h of Ao clay sludge

(c) Accelereated carbonation period, t: 0–400h of Kasaoka clay sludge

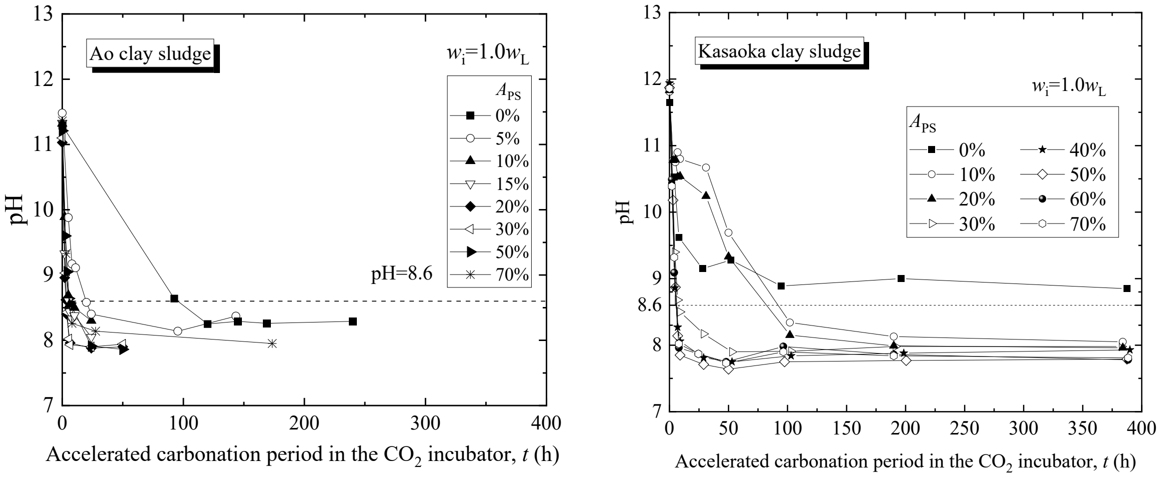


(b) Accelerated carbonation period, t: 0–50 h of Ao clay sludge

(d) Accelerated carbonation period, t: 0–50 h of Kasaoka clay sludge

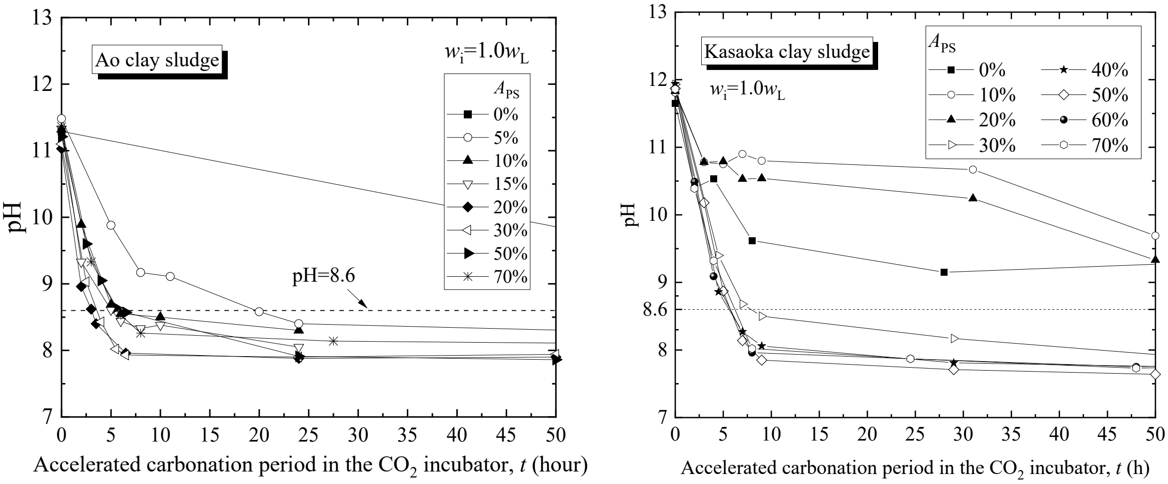
Figure 3.9. Relationship between accelerated carbonation period in CO_2 incubator and pH of each sludge specimen ($w_i = 0.5w_L$)

The needed amount of PSAS in Ao clay sludge and Kasaoka clay sludge to attain the optimum t_N are different. This is because the liquid limit, w_L of Kasaoka clay is higher than that of Ao clay ($w_{L,\text{Kasoka clay}}$=60.4% compared with $w_{L,\text{Ao clay}}$=40.7%), Kasaoka clay is categorized CH clay (clay of high plasticity) and therefore the needed amount of PSAS, A_{PS} to granulate the sludge prepared from Kasaoka clay at liquid limit state is higher. For instance, as shown in Figure 3.4(b) and 3.5(b), the Ao clay sludge was granulated with 10% amount of PSAS (A_{PS}=10%) to clay whereas, the A_{PS}=20% of Kasaoka clay sludge was not granulated. Therefore, to obtain the same mean of particle, D_{50}, a larger amount of PSAS is required for Kasaoka clay. In addition, the pH neutralization rate is significantly affected by the particle size as shown in Figure 3.15. The low t_N is obtained when D_{50} is around 1~6mm. Thus, the A_{PS} of Kasaoka clay sludge corresponding to the optimum t_N is higher than that of the Ao clay sludge.



(a) Accelerated carbonation period, *t*: 0–600 h of Ao clay sludge

(c) Accelerated carbonation period, t: 0-400 h of Kasaoka clay sludge



(b) Accelerated carbonation period, *t*: 0–50 h of Ao clay sludge

(d) Accelerated carbonation period, t: 0-50 h of Kasaoka clay sludge

Figure 3.10. Relationship between accelerated carbonation period in CO_2 incubator and pH of each sludge specimen ($w_i = 1.0w_L$)

Table 3.4. Physical properties of sludge specimens and accelerated carbonation periods required for pH to reach 8.6

Clay type	w_i (%)	A_{PS} (%)	D_{50} (mm)	ρ_s (g/cm^3)	ρ_d (g/cm^3)	e	S_r (%)	t_N (h)
Ao clay sludge	$0.5w_L$	0	0.90	2.72	0.95	1.86	28.0	489.6
		5	0.48	2.72	0.90	2.02	25.4	17.3
		15	0.44	2.71	0.82	2.31	20.1	9.4
		30	0.47	2.70	0.69	2.90	14.8	7.8
		50	0.45	2.68	0.74	2.64	17.6	9.3
	$1.0w_L$	0	---	2.72	1.11	1.45	80.4	95.2
		5	---	2.72	0.98	1.77	62.8	19.7
		10	5.0	2.71	0.76	2.55	41.7	5.6
		15	5.9	2.71	0.71	2.81	36.5	5.1
		20	3.3	2.70	0.79	2.43	40.9	3.0
		30	1.2	2.70	0.72	2.76	33.8	3.6
		50	0.80	2.68	0.72	2.72	29.1	6.1
		70	0.81	2.67	0.64	3.19	22.3	5.7
Kasaoka clay sludge	$0.5w_L$	0	5.05	2.69	0.78	2.45	29.1	---
		10	2.60	2.68	0.89	2.01	32.5	4.9
		20	2.52	2.68	0.75	2.57	23.7	5.5
		30	2.13	2.67	0.66	3.05	18.2	6.6
		40	1.97	2.67	0.71	2.76	18.7	7.6
	$1.0w_L$	0	---	2.69	0.83	2.24	68.7	---
		10	---	2.68	0.75	2.57	51.6	92.0
		20	---	2.68	0.65	3.12	41.5	82.2
		30	6.91	2.67	0.64	3.17	36.6	19.2
		40	2.51	2.67	0.65	3.11	34.4	5.6
		50	1.55	2.66	0.74	2.59	39.8	5.7
		60	0.88	2.66	0.76	2.50	39.4	5.7
		70	0.85	2.65	0.71	2.73	34.0	6.2

w_i: Initial water content of Ao clay

A_{PS}: Addition ratio of PSAS

D_{50}: Mean particle diameter

ρ_s: Particle density

ρ_d: Dry density

e: Void ratio

S_r: Degree of saturation

t_N: Accelerated carbonation period required for pH to reach 8.6

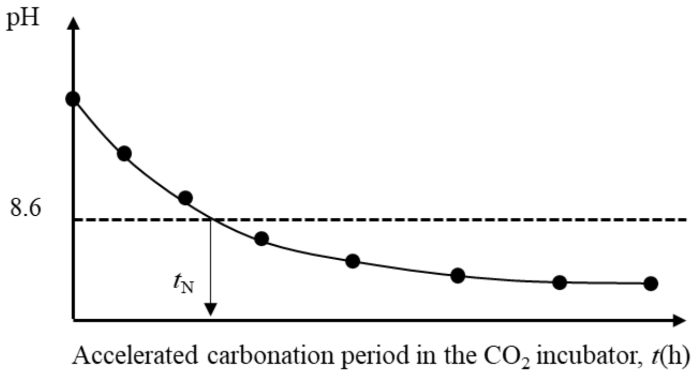
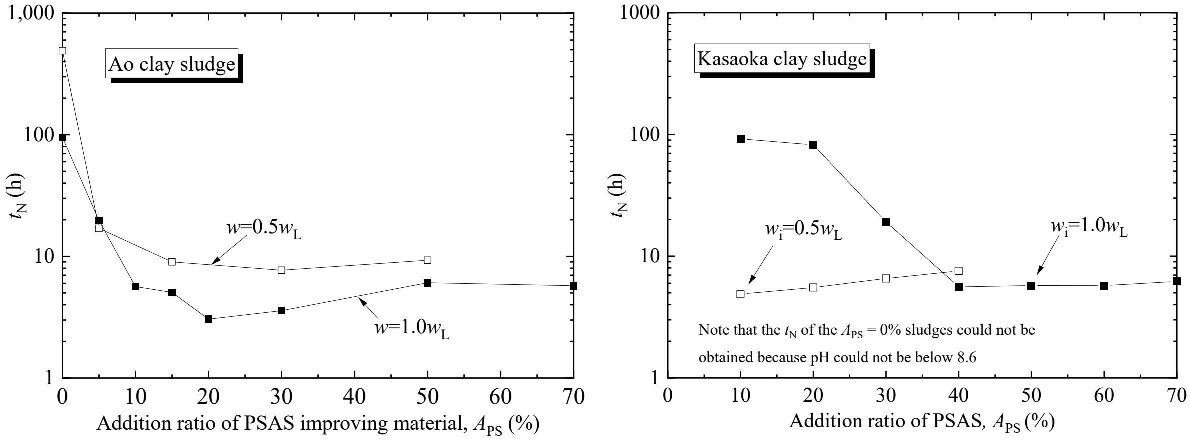
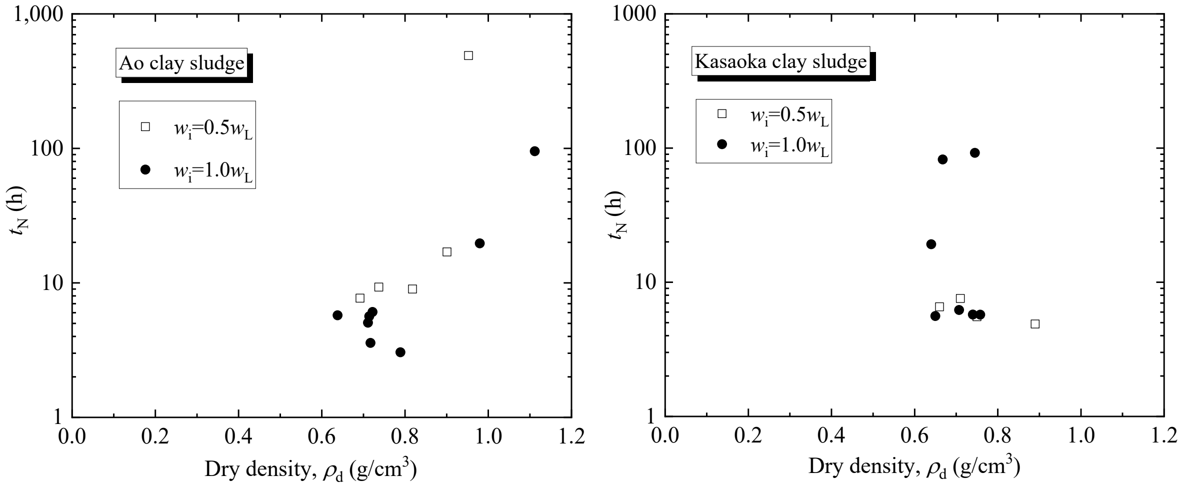


Figure 3.11. Definition of neutralization completion time t_N



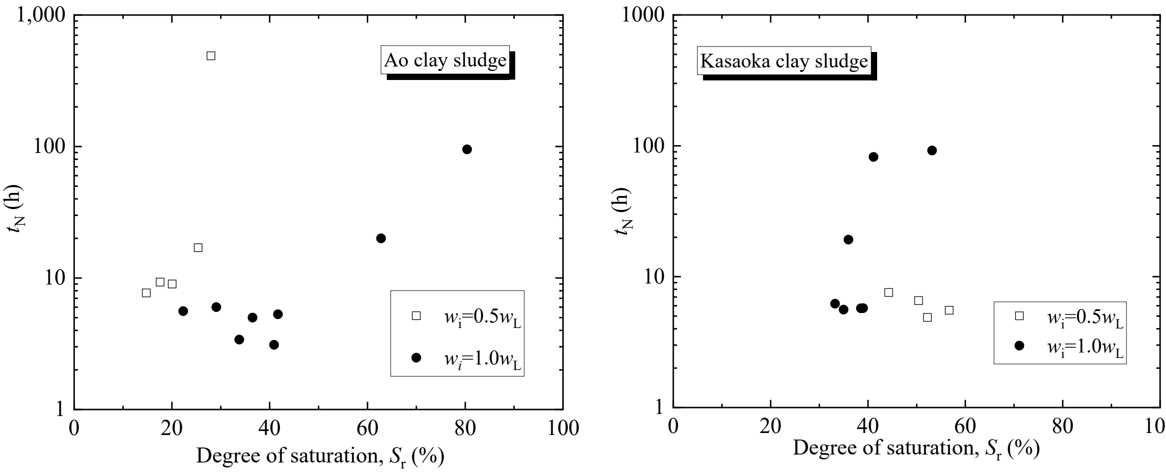
(a) Ao clay sludge (b) Kasaoka clay sludge

Figure 3.12. Relationship between A_{PS} and t_N



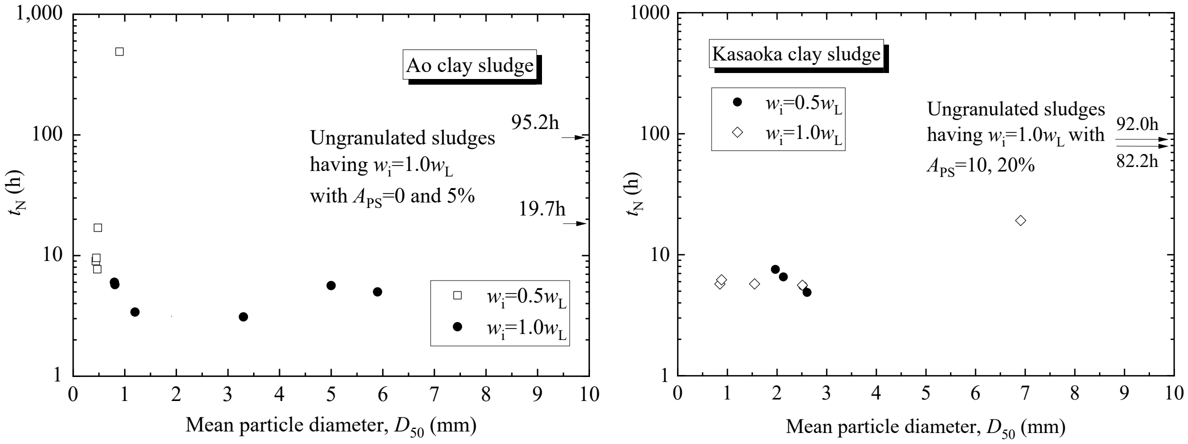
(a) Ao clay sludge (b) Kasaoka clay sludge

Figure 3.13. Relationship between dry density and t_N



(a) Ao clay sludge (b) Kasaoka clay sludge

Figure 3.14. Relationship between degree of saturation and t_N



(a) Ao clay sludge (b) Kasaoka clay sludge

Figure 3.15. Relationship between mean particle diameter and t_N

3.4 pH rebound

Accelerated carbonation shortened the pH neutralization period of alkaline constructions sludge. However, the stabilization of pH of treated sludge has not been investigated. To fully assess the effectiveness of accelerated carbonation in pH treatment, pH of sludge undergone CO_2 curing was monitored for 28 days. The results showed that after accelerated carbonation, pH rebounded to a certain value and then gradually decreased. The stable pH values thereafter seem higher than the pH obtained right after the accelerated carbonation. The experimental procedure for the investigation of pH rebound is shown in Fig 3.16.

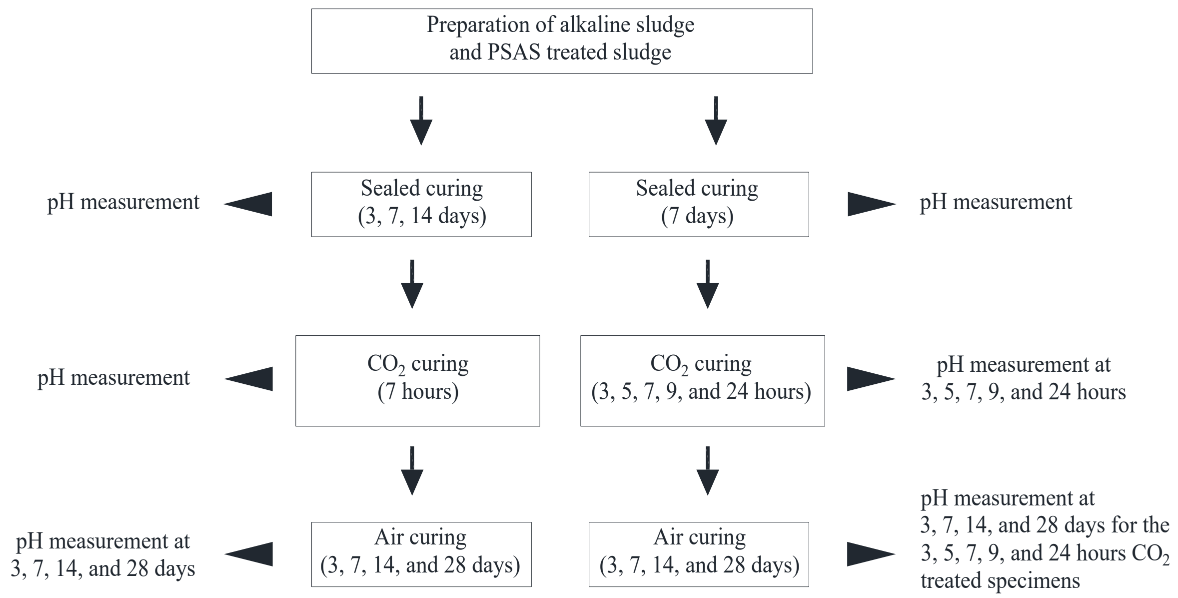
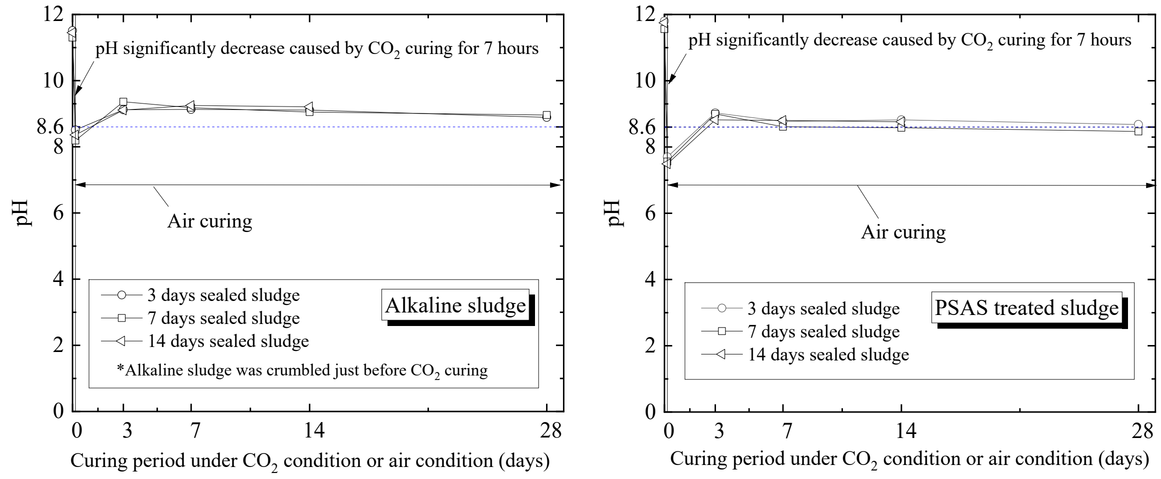


Figure 3.16. Experimental flow chart of pH rebound investigation

Fig 3.17 shows the pH level of sludge prepared from Ao clay under CO_2 curing and air curing conditions. The pH level was dramatically decreased from more than 11.5 to around 8.6 after 7 hours of CO_2 curing. It could be explained that the OH^--ions causing high alkalinity were dissolved by CO_2 gas. With the same CO_2 curing conditions and curing time, the pH of PSAS treated sludge was seen to be decreased more significantly than that of the alkaline sludge. This can be explained by the porous microstructure of PSAS treated sludge arising from its size particles that allows the penetration of CO_2 gas. In contrast, the alkaline sludge which was not granulated prevents the approach of CO_2 deeper into the particles. However, the results showed that the pH level of all samples rebounded but did not return to the original value. It reached a maximum value after being cured for almost 3 days under air conditions and then gradually decreased. This phenomenon probably arose from the residual hydration after CO_2 curing. The results also revealed that pH neutralization and pH rebound of alkaline sludge as well as PSAS treated sludge were not strongly affected by the period of sealed curing.



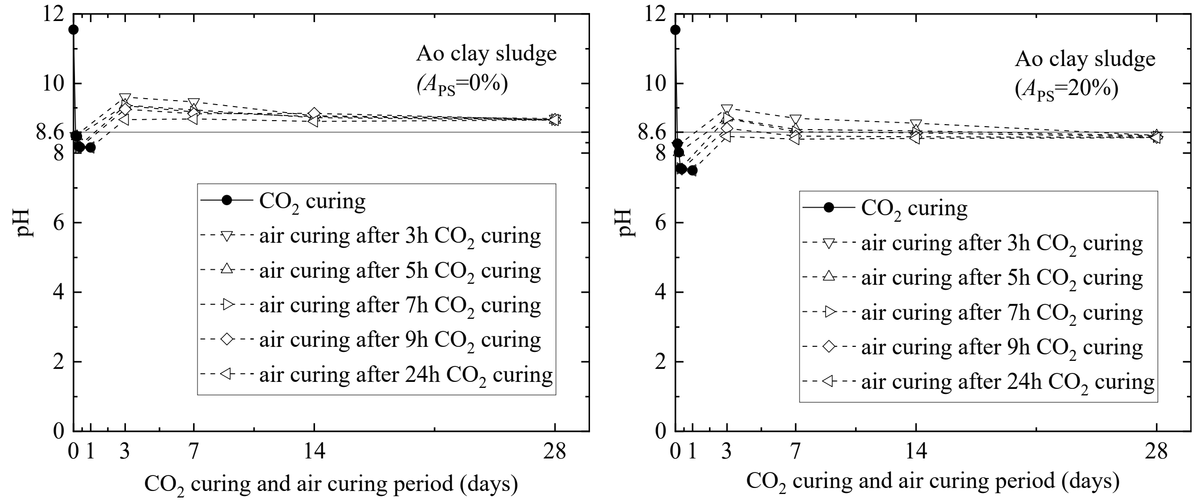
(a) (b)

Figure 3.17. pH rebound of simulated sludge after CO_2 curing: (a) alkaline sludge, (b) PSAStreated sludge.

Figure 3.18 expresses the pH rebound of the 7 days sealed alkaline sludge and PSAS treated sludges prepared from Ao clay and Kasaoka clay, cured under different period of CO_2 curing time. The pH fell dramatically (from 11.54 to 7.56 and 11.55 to 8.19 in the case of PSAS treated sludge and alkaline sludge respectively) after 7 hours of CO_2 curing but then continued slightly decrease (from 7.56 to 7.5 and 8.19 to 8.16 in the case of PSAS treated sludge and alkaline sludge respectively) during the rest of curing time up to 24 hours.

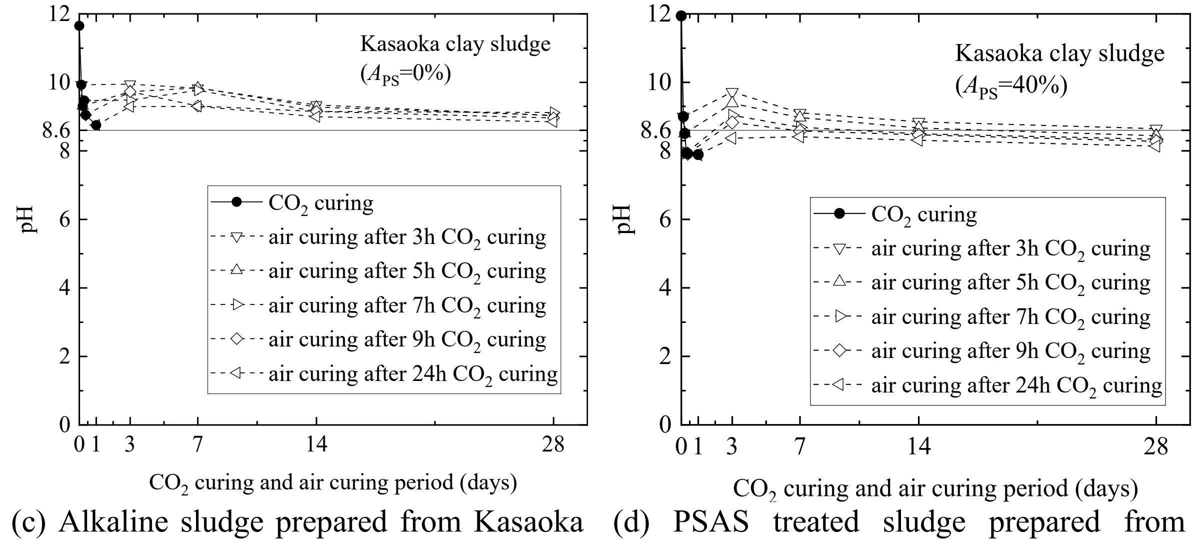
At the end of 24 hours CO_2 curing, pH of alkaline sludge could not be decreased to less than about 8 whereas that of PSAS treated sludge fell to 7.5. It can be seen that the pH at the end of the CO_2 curing is the crucial factor influencing the following pH in long-term durability. Although affected by the pH rebound phenomenon, the upcoming pH of specimens having the pH less than about 8 at the end of the CO_2 curing was maintained at the values less than 8.6 several days after air curing to satisfy the requirement of Japanese Law.

Although the effectiveness in reducing pH after 7 hours to 24 hours of CO_2 curing was negligible, the results showed that a longer curing time shows a better effect in suppressing the pH rebound, and hence contributes to a low maintenance of pH thereafter.



(a) Alkaline sludge prepared from Ao clay

(b) PSAS treated sludge prepared from Ao clay



(c) Alkaline sludge prepared from Kasaoka clay

(d) PSAS treated sludge prepared from Kasaoka clay

Figure 3.18. pH rebound of sludges after such periods of CO_2 curing time

CHAPTER 4

INTRODUCTION OF CRUMBLING PROCESS

4.1 Effect of crumbling on pH neutralization rate

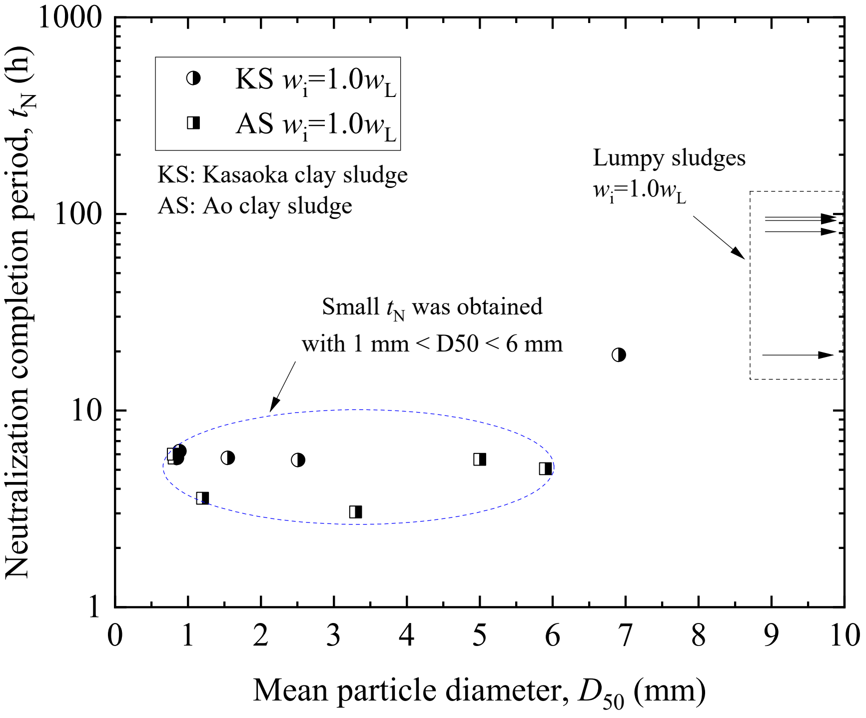


Figure 4.1. The Relationship between tN and D50 of PSAS treated sludge prepared from Ao clay and Kasaoka clay

From the preceding discussion, the pH neutralization period, t_N tend to decrease with the decrease in D_{50} and the increase in A_{PS} under the same accelerated carbonation conditions, the duration required to complete the pH neutralization (t_N) of PSAS treated sludge was significantly less than that of alkaline sludge. It was discovered that the addition of PSAS granulated the alkaline sludge, and once the Ao clay sludge and Kasaoka clay sludge were granulated with the D_{50} ranges from 1mm to 6 mm, t_N of PSAS treated sludge was successfully shortented to less than 10 hours as shown in Fig 4.1. It should be noted that granulation of the treated sludge means that the sludge produced sand and gravel-like granules. Granulation was induced by the water absorption and retention performance of the PSAS, which reduced the plasticity of fines in the soil samples, according to Watanabe et al. (2021).

However, it should minimize the additional ratio of PSAS because (1) in order to treat sludge economically, and (2) PSAS itself is an alkaline material so that the addition of PSAS may cause a negative impact on pH neutralization even D_{50} is reduced. As previous mentioned, samples with significant addition amounts of PSAS in relation to Ao clay (i.e., 50% or 70% dry weight ratio) required a longer duration to achieve pH neutralization than those with lower amounts of PSAS (for example, 20% or 30%). This trend was also obserbed for Kasaoka clay sludge when t_N slightly increase with the increase in A_{PS}. In fact, various types of alkaline sludge exist, and it is expected that significant amounts of PSAS must be added to the sludge to granulate it in certain cases. Hence, the crumbling of alkaline sludge treated with small amount of PSAS was proposed. Once granulated, the water evaporation was facilitated, and the stiffness of particles was enhanced due to the reduction of water content. Even there is possibility that the contribution of bonding strength was decreased by the crumbling, the experimental results revealed that strength of sludge was significantly improved. The crumbling followed by air curing decreases the particle size of treated sludge, produces a porosity and reduces the water content of treated sludge and is expected to treat alkaline sludge more effectively and economically. The proposed procedure of alkaline treatment of sludge with crumbling process is shown in Fig 4.2. Note that the granulation via crumbling differs from granulation generated immediately after the addition of PSAS. The granulation via crumbling takes the effects of change in properties of the sludge over time as a result of the hydration reaction of stabilizers into the granulation.

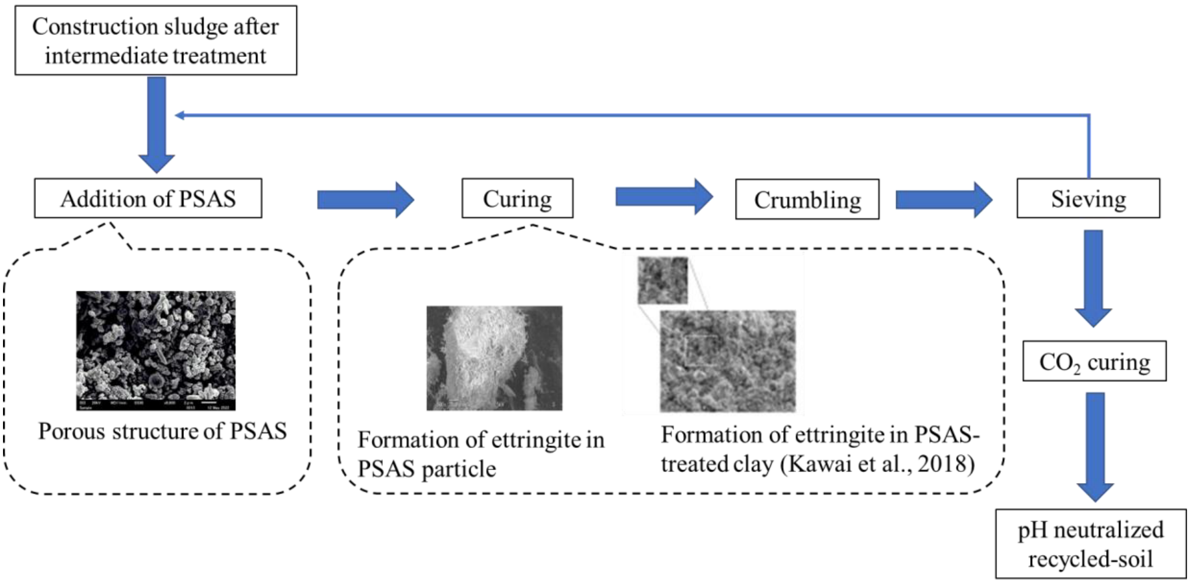


Figure 4.2. Proposal of production flow for pH neutralized recycled-soil

To comprehensively investigate the effectiveness of crumbling on pH neutralization rate, crumbling was applied for the sludge samples treated with and without PSAS. Alkaline sludges treated with low amounts of PSAS were cured for a certain time and then crumbled into sand and gravel-like granules to facilitate accelerated carbonation. Granulation via crumbling utilizes the change in the consistency of the sludge over time as a result of the hydration reactions of the stabilizers.

4.1.1 Sample preparation with or without crumbing

As presented in Fig 4.3, ungranulated sludges were prepared for both Ao clay and Kasaoka clay to investigate the effect of crumbling on accelerated carbonation. Similar to the preparation of sludge sample as mentioned previously, liquid limit of clay, w_L was firstly achieved by thoroughly mixing distilled water with clay by using a bench-top mixer for 3 min. Then blast furnace cement type B was added and homogeneously stirred for 7 more minutes to form alkaline sludge. Finally, PSAS treated sludge was formed by adding paper sludge ash based-stabilizer to the alkaline sludge with a different proportions as presented in Table 4.1. To keep the pH steady, sludge was cured under sealed curing for 7 days.

After the sealed curing, ungranulated sludges were segregated into two portions, one of which was maintained in the ungranulated state, as shown in Fig 4.4(a), whereas the other was crumbled into sand and gravel-like granules using a bench-top mixer, as shown in Fig 4.4(b), and cured in air for 1 day. Granulation via crumbling is based on the change in the consistency of the sludge over time as a result of the hydration reaction of stabilizers (Hayano et al., 2016). The alkaline sludge transformed from liquid to plastic, and then to a semi-solid during the sealed curing. Based on this transformation, crumbling, which refers to re-stirring of the processed alkaline sludge, was performed to yield granules, as shown in Fig 4.4(b).

The particle size distributions (PSDs) of the crumbled sludges, were examined via sieve analysis, followed by the measurement of water content. Sieve analyses are generally conducted on dry samples washed with water and oven-dried. However, the process of washing with water and oven drying might cause the granules, that is, the particles clustered by stabilizers, to become finer. Such a process does not occur when pH neutralization is performed by CO_2 curing, as shown in Fig 2.4. Therefore, to maintain the particle size as close as possible to what is actually expected, sieve analyses were performed on the wet samples in their original states of water content. Particle size distribution of crumbled sludge is shown in Fig 4.5.

Figure 4.6 shows the relationship between the degree of saturation S_r and the dry density ρ_d for each type of sludge prepared in a cup. In general, S_r and ρ_d decreased as the A_{PS} increased or the particle size decrease. This is associated with the lightweight characteristics of PSAS porous particles or with the crumbling effect.

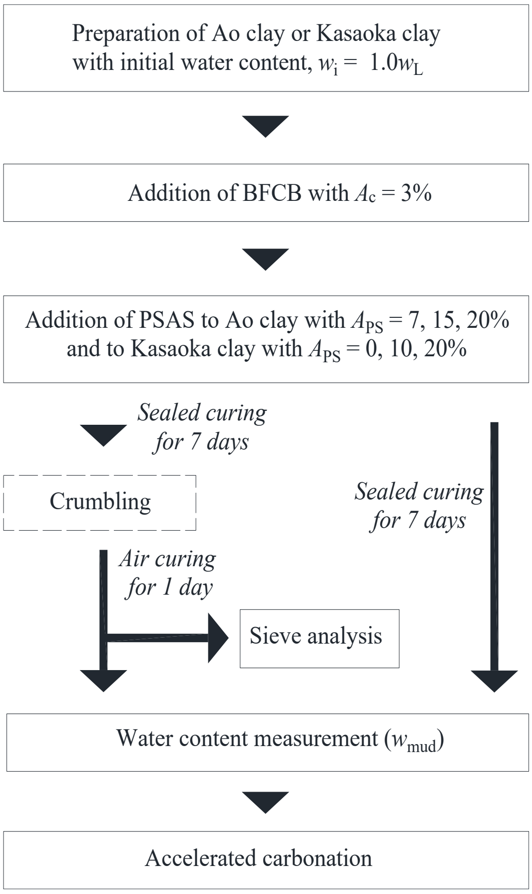


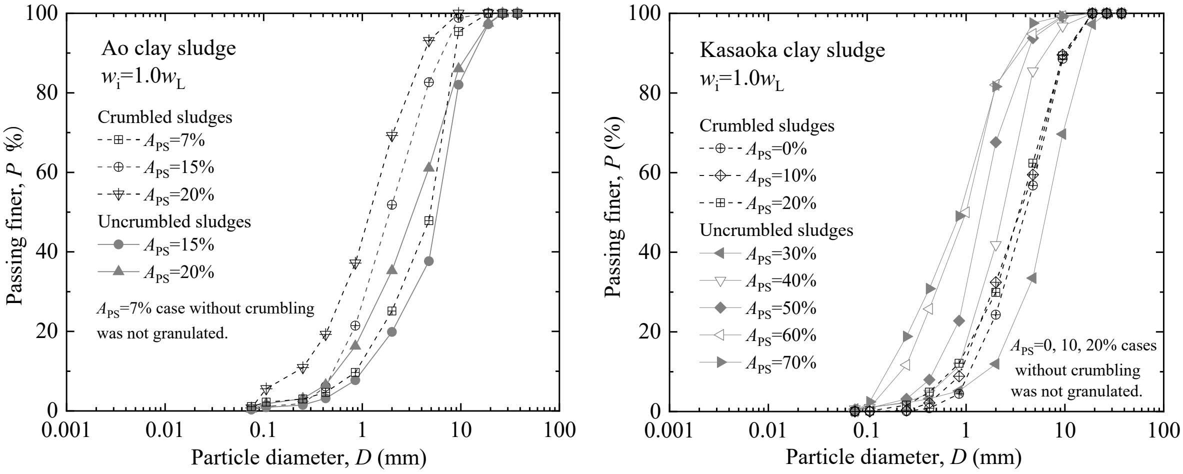
Figure 4.3. Experimental flow chart

Table 4.1. Mixture conditions for preparation of crumbling sludge

Clay type	Initial water content of clay, w_i (%)	Addition ratio of blast furnace cement type B (BFCB), A_c (%)	Addition ratio of paper sludge ash-based stabilizer (PSAS), A_{PS} (%)
Kasaoka clay	$1.0w_L$	3	0, 10, 20
Ao clay			7, 15, 20


(a) (b)

Figure 4.4. Sludges with or without crumbling ($w_i = 1.0w_L$ and $A_{PS} = 0\%$): (a) Uncrumbled sludge; (b) crumbled sludge



(a) Ao clay sludge (b) Kasaoka clay sludge

Figure 4.5. Particle size distribution of crumbled and uncrumbled sludges

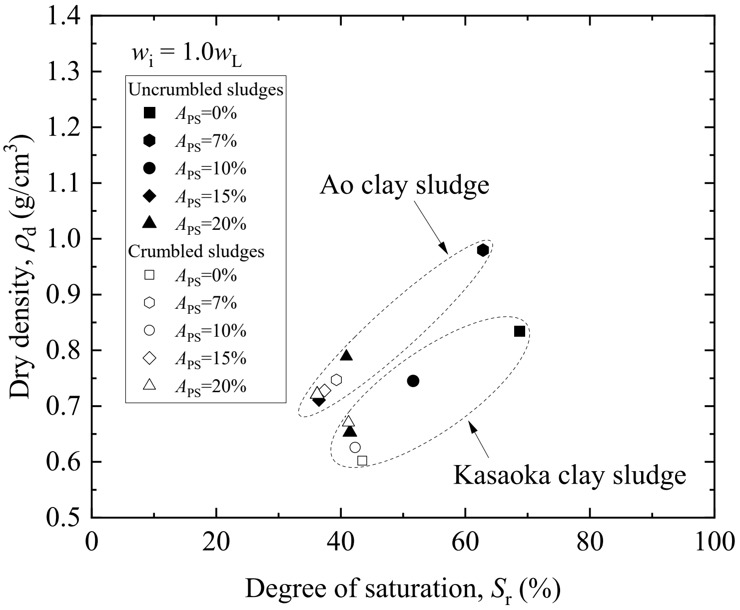


Figure 4.6. Relationship between dry density, ρ_d and degree of saturation, S_r

4.1.2 Change in pH neutralization period associated with crumbling

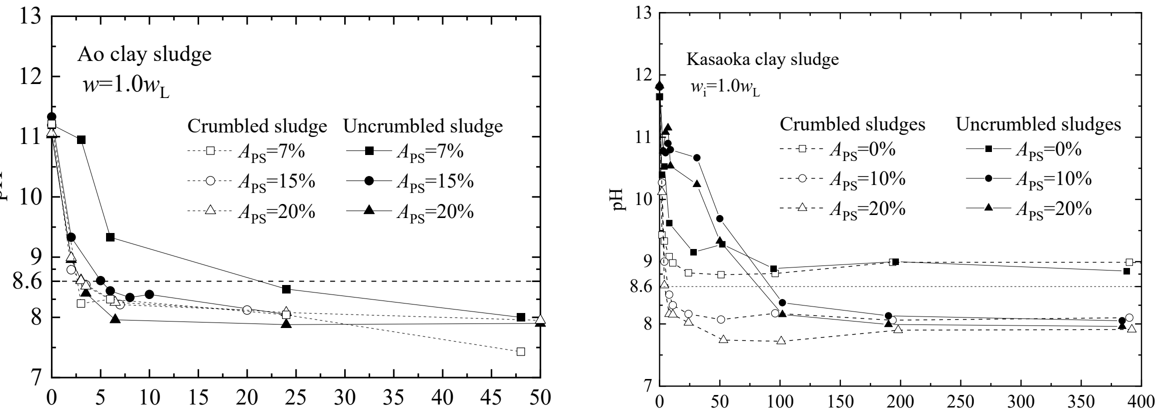
Accelerated carbonation

After preparation, accelerated carbonation was conducted for all types of sludge. Granulated sludges were softly placed to plastic cups with a diameter of 82 mm and filled up to the height of 3 cm from the bottom of the cup. The uncrumbled sludges were placed in cups and statically compressed manually to form a 30 mm-thick flat layer. These preparation procedures were performed to simulate the in situ treatment of actual alkaline construction sludge. As shown in Fig 2.4, the in situ alkaline construction sludge was poured into an underground pit without compaction. The alkaline sludge dropped unrestrictedly into the pit. Subsequently, CO_2 gas was injected from the bottom and flowed to the top of the pit. To reflect this, the sludges were prepared in cups, and the adopted preparation procedures mimicked the authentic in situ states.

The sludges prepared in the cups were used as the specimens for accelerated carbonation. Approximately 5 to 10 specimens of each sludge type were placed in a CO_2 incubator. Subsequently, accelerated carbonation was conducted while maintaining the CO_2 concentration and temperature at 10% and 25 °C, respectively. A CO_2 concentration of 10% was adopted in accordance with the results of Imai et al. (2020).

Consequently, the pH of the specimens removed from the incubator sequentially during an arbitrary elapsed curing period was measured based on the Japanese Geotechnical Society Standards (JGS 0211). After placing each specimen in a beaker, water was added at an amount equivalent to five times the dry mass of the specimen. The solution was then suspended using a stirring rod and left for 30 min before the pH was measured by a portable pH meter.

Change in pH neutralization



(a) Ao clay sludge (b) Kasaoka clay sludge

Figure 4.7. pH neutralization of crumbled and uncrumbled sludges

Figure 4.7 shows the pH of the sludge specimens with respect to the accelerated carbonation period in a CO_2 incubator. The pH of all types of sludge decreased with time. However, the pH of the A_{PS}=0% sludge (ungranulated sludge) remained high, even after a certain curing time for the Kasaoka clay sludge samples. In addition, the crumbling effectively influenced pH neutralization rate but for the PSAS treated sludge (A_{PS}=10, 20%). It is noteworthy that the ultimate pH of A_{PS}=0% sludge samples after being treated by CO_2 curing could not be fallen to 8.6 even after being crumbled and t_N could not be obtained. Crumbling only accelerated the carbonation at early stage of curing and did not affect the ultimately treated pH of PSAS treated sludge.

Similar to Kasaoka clay sludge, ungranulated Ao clay sludge samples (i.e., the A_{PS}=7% sludge) undergone the crumbling process significantly accelerate the pH neutralization rate. However, the same procedures applied for the granulated sludge samples (i.e., the A_{PS}=15 and 20%) did not effectively enhance the rate of pH neutralization. This is probably because crumbling did not remarkably adjust the particle size of the granulated sludge as presented in Fig 4.5b.

It could be seen that both A_{PS} and particle size affect the pH neutrazliation rate. As previously discussed in Fig 3.12, it was discovered that the t_N of the PSAS treated sludges with $w_i = 0.5w_L$ (the uncrumbled sludge) was less than 10 h for Kasaoka clay sludge or from 10 h to 20 h for Ao clay sludge, and that the t_N among the sludges did not differ significantly compared to that of alkaline sludge. A slight increase of t_N along with the increase of PSAS can be seen. This is because the sludges with w_i=0.5w_L are granulated and have no significant difference in particle size. When the effect of particle size on pH neutralization is the same, the amount of PSAS contributes the difference in pH neutralization due to the alkalinity of PSAS. Meanwhile, for the uncrumbled sludges with $w_i = 1.0w_L$, t_N decreased significantly as A_{PS} increased as shown in Fig 4.8. For the uncrumbled sludges with A_{PS} = 10% and 20%, their t_N was approximately 100 h, whereas those with $A_{PS} \geq 40\%$ was only a few hours This is due to the granulation and the increase in surface area caused by a certain amount of PSAS. However, it was discovered that crumbling significantly accelerated the carbonation of sludges with low A_{PS} values. As shown in the figure, for the same A_{PS}, the t_N of the crumbled sludges was considerably less than that of the uncrumbled sludges.

Table 4.2 and 4.3 summarizes the t_N obtained after accelerated carbonation. The soil particle density ρ_s of each sludge was calculated based on the particle densities of the clay, BFCB, and PSAS using the mixture ratio. It is noteworthy that the t_N of the Kasaoka sludges untreated by PSAS could not be obtained because the pH did not reach 8.6, as shown in Fig. 4.7.

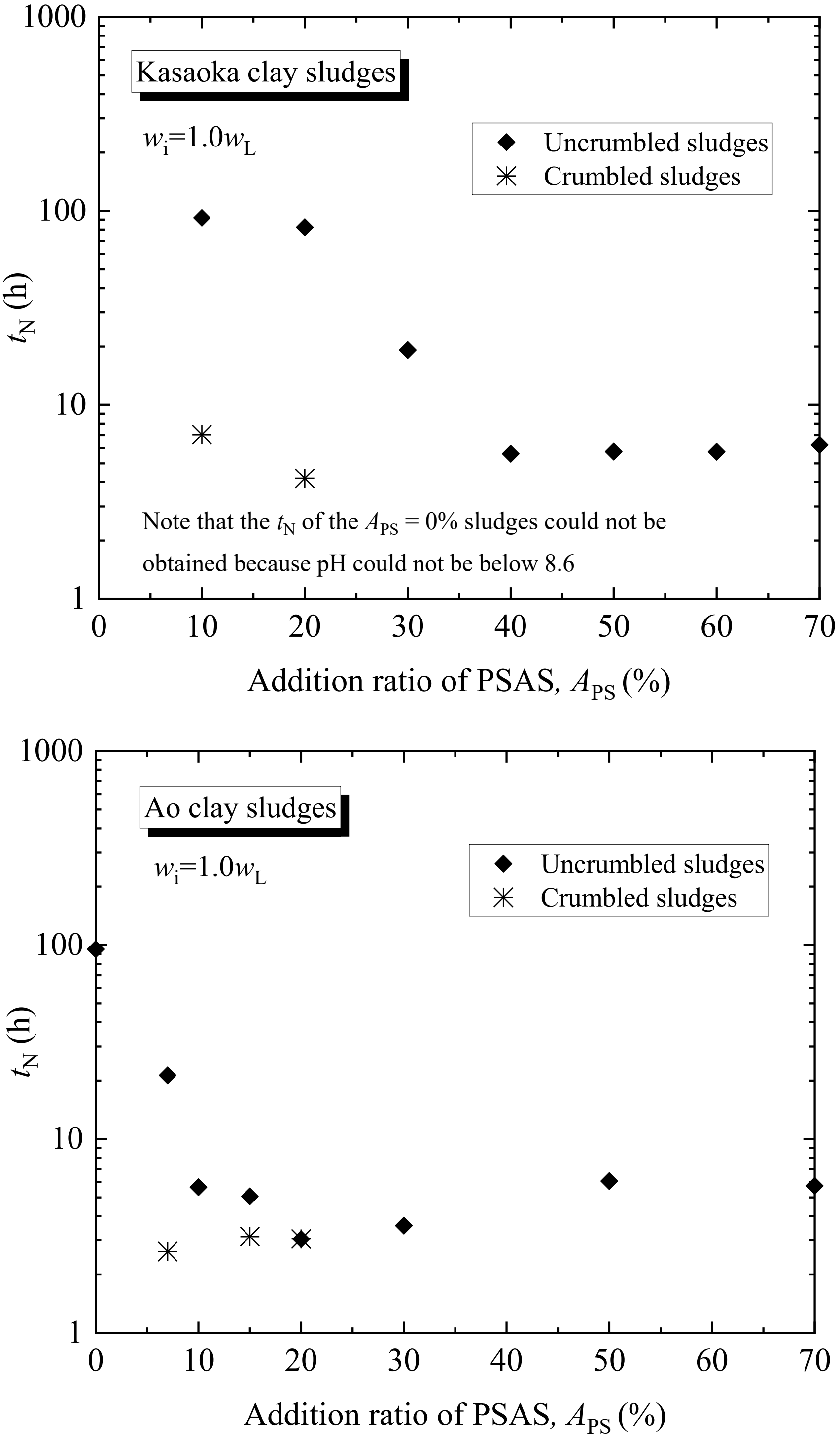


Figure 4.8. Relationship between A_{PS} and t_N

Table 4.2. Physical properties of Kasaoka clay sludges and accelerated carbonation periods required to attain pH 8.6

Samples with or without crumbling	w_i (%)	A_{PS} (%)	ρ_s (g/cm^3)	D_{50} (mm)	w_{mud} (%)	ρ_d (g/cm^3)	S_r (%)	t_N (h)
Uncrumbled sludges	1.0w_L	0	2.69	n/a	56.8	0.83	68.7	n/a
		10	2.68	n/a	49.8	0.75	51.6	92.0
		20	2.68	n/a	46.1	0.65	41.5	82.2
		30	2.67	6.91	43.1	0.64	36.6	19.2
		40	2.67	2.51	39.7	0.65	34.4	5.6
		50	2.66	1.55	39.1	0.74	39.8	5.7
		60	2.66	0.88	37.1	0.76	39.4	5.7
		70	2.65	0.85	35.2	0.71	34.0	6.2
Crumbled sludges		0	2.69	4.18	53.3	0.60	43.5	n/a
		10	2.68	3.79	45.5	0.63	42.3	7.0
		20	2.68	3.70	41.7	0.67	41.2	4.2

Table 4.3. Physical properties of Ao clay sludges and accelerated carbonation periods required to attain pH 8.6

Samples with or without crumbling	w_i (%)	A_{PS} (%)	ρ_s (g/cm^3)	D_{50} (mm)	w_{mud} (%)	ρ_d (g/cm^3)	S_r (%)	t_N (h)
Uncrumbled sludges	1.0w_L	7	2.72	n/a	38.3	1.08	68.5	21.3
		15	2.71	6.07	37.9	0.71	36.5	5.6
		20	2.70	3.57	36.7	0.79	40.9	5.1
Crumbled sludges		7	2.72	4.96	38.1	0.75	39.3	2.63
		15	2.71	1.94	37.5	0.73	37.4	3.14
		20	2.70	1.31	36.8	0.72	36.2	3.06

4.2 Effect of particle size on t_N

As mentioned in the previous section, crumbling sludge prior to exposing them to CO_2 gas could shorten t_N of the sludges that had not been granulated by adding PSAS. The characteristic feature of crumbling was the reduction in the particle size of the sludges. Therefore, the particle size may affect the t_N. The relationships between t_N and the mean particle diameter D_{50} of each type of sludge are summarized in Fig 4.9 based on Table 4.2 and 4.3. It could be seen that t_N is relatively small and approximately constant with D_{50} of granulated sludges, which implies that that the pH neutralization rate is mainly affected by particle size. A certain value of D_{50} (i.e., around or less than 4 mm) is necessary to facilitate the accelerated carbonation. For the uncrumbled sludge prepared from Kasaoka clay with w_i = 1.0w_L and A_{PS} = 10% and 20%, and from Ao clay sludge with A_{PS}=7%, the D_{50} was set to > 10 mm because the particle size could not be obtained via sieve analysis owing to the lumpiness of the sludge (see Fig. 4.4 a)). As shown in the Fig 4.9, a short t_N is realizable when the particle size is reduced to a certain extent. However, particle sizes other than D_{50}, as well as the water content and density of the sludge may affect t_N. Therefore, the effect of particle size on t_N was investigated by conducting accelerated carbonation on sludges with narrow particle size ranges.

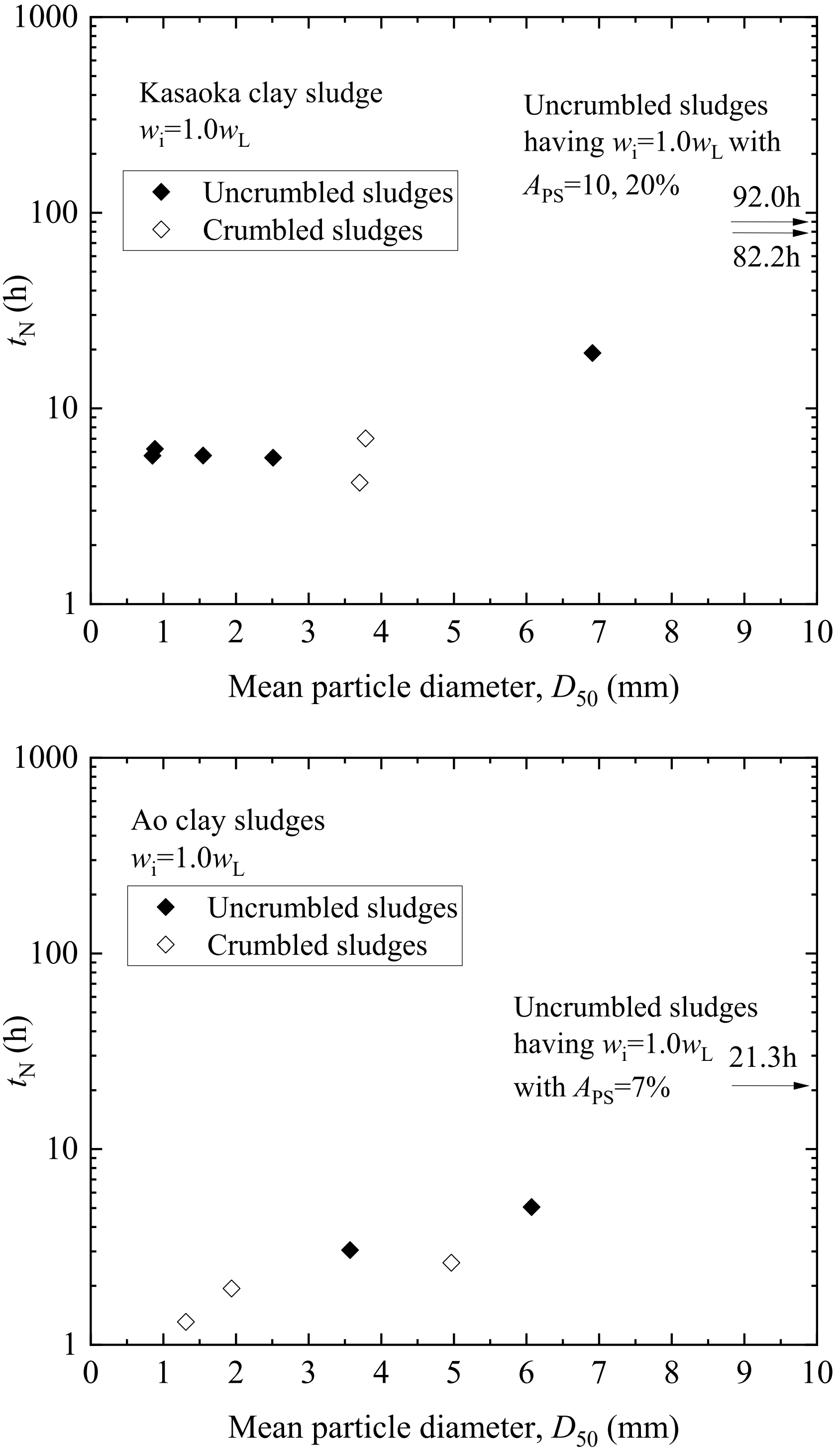


Figure 4.9. Relationship between t_N and D_{50}

4.2.1 Preparation of particle size adjusted sludges

To investigate the effect of particle size on t_N, Kasaoka sludge was preferentially selected to study because Kasaoka clay is high plasticity clay that is hard to be granulated by mixing with PSAS compared to Ao clay. First, sludges were prepared by adding BFCB with A_c = 3% to the Kasaoka clay with different water contents, followed by PSAS treatment with A_{PS}=10% and 40% as shown in Table 4.3. The A_{PS}=40% sludge was choosen because this is the proportion of PSAS that granulate alkaline sludge and produce the optimum t_N. Moreover, the A_{PS}=10% sludge having low amount of PSAS is not granulated and difficult to neutralize its pH. However, after crumbling its pH neutralization rate was effectively enhanced making its t_N nearly equal to that of A_{PS}=40% sludge. After several trials, Kasaoka clays with w_i = 0.78, 1.0, and 1.26w_L were prepared for PSAS addition with A_{PS} = 40%, whereas Kasaoka clays with w_i = 0.62, 0.8, and 1.0w_L were prepared for that with A_{PS} = 10%. The abovementioned w_i values were selected such that the water content of the treated sludges was approximately 30%, 40%, and 50% for each A_{PS}. After mixing, all sludges were cured under sealed conditions for 7 days.

After curing, the water content and w_{mud} of each PSAS-treated sludge were measured, as shown in Fig 4.10. Subsequently, each type of sludge with A_{PS} = 40% and 10% (w_i = 0.62w_L) was sieved to be separated into three different particle size ranges, i.e., 0.85 mm ≤ D < 2.0 mm, 2.0 mm ≤ D < 4.75 mm, and 4.75 mm ≤ D < 9.5 mm. Sludges with a particle size D < 0.85 mm or D > 9.5 mm were removed. Sludges with A_{PS} = 10% (w_i = 0.8 and 1.0w_L) were crumbled before they were sieved to separate the particles in the same manner as that for the A_{PS} = 40% sludge.

Table 4.4. Preparation condition for particle-size-adjusted sludges and physical properties obtained from accelerated carbonation

Sludges with or without crumbling	w_i (%)	A_c (%)	A_{PS} (%)	D (mm)	w_{mud} (%)	ρ_d (g/cm^3)	S_r (%)	t_N (h)
Uncrumbled sludges	0.78w_L	3	40	0.85 ≤ D < 2.0	30.8	0.69	28.9	4.6
				2.0 ≤ D < 4.75				4.6
				4.75 ≤ D < 9.5				4.6
	1.0w_L			0.85 ≤ D < 2.0	39.7	0.65	34.1	3.2
				2.0 ≤ D < 4.75				4.7
				4.75 ≤ D < 9.5				9.1
	1.26w_L			0.85 ≤ D < 2.0	49.9	0.60	39.1	2.4
				2.0 ≤ D < 4.75				4.7
				4.75 ≤ D < 9.5				9.0
	0.62w_L		10	0.85 ≤ D < 2.0	31.3	0.69	29.1	4.8
				2.0 ≤ D < 4.75				4.9
				4.75 ≤ D < 9.5				4.9
Crumbled sludges	0.8w_L			0.85 ≤ D < 2.0	40.6	0.65	34.5	5.9
				2.0 ≤ D < 4.75				6.3
				4.75 ≤ D < 9.5				6.7
	1.0w_L			0.85 ≤ D < 2.0	49.8	0.60	39.0	4.2
				2.0 ≤ D < 4.75				4.8
				4.75 ≤ D < 9.5				9.2

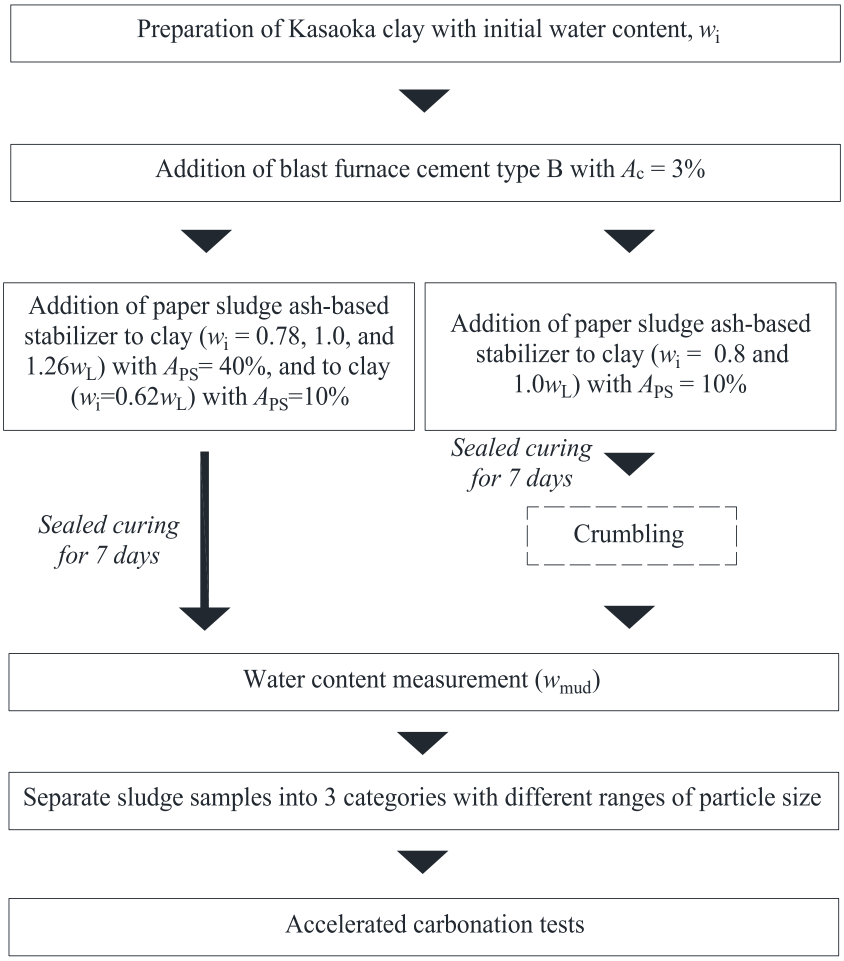
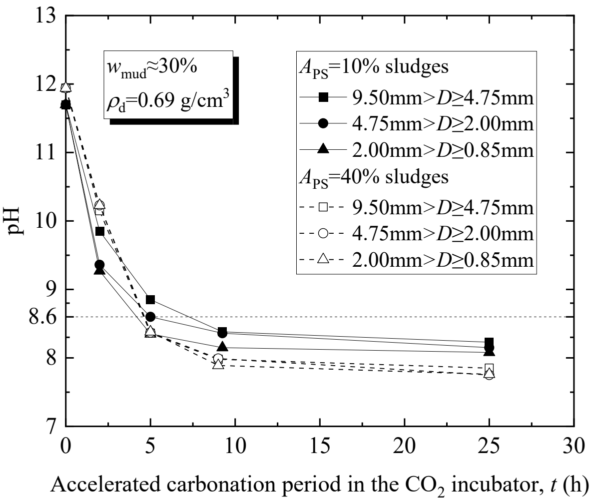


Figure 4.10. Experimental flow chart of preparation of particle size range-controlled sludges for accelerated carbonation

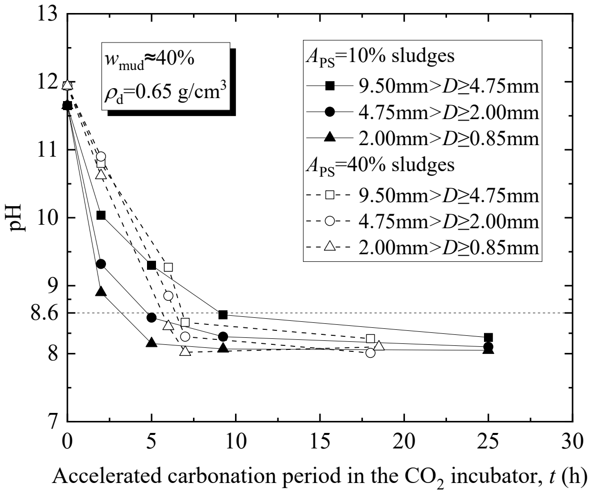
4.2.2 Accelerated carbonation

Accelerated carbonation was performed by placing the sludge in cups in a CO_2 incubator. To accelerate carbonation, a CO_2 concentration of 10% and a temperature of 25 °C were adopted, similar to those described in Section 3.2. As presented in Table 4.4, the sludges were prepared in cups such that the dry densities ρ_d of the sludges with different particle size D ranges (i.e., 0.85 mm $\leq D <$ 2.0 mm, 2.0 mm $\leq D <$ 4.75 mm, and 4.75 mm $\leq D <$ 9.5 mm) would be the same under the same mixture conditions. The densities were adjusted by depositing the sludge in the cups at zero height and then lightly compacting them to avoid fracturing the particles. The thickness of the sludge in each cup was 30 mm.

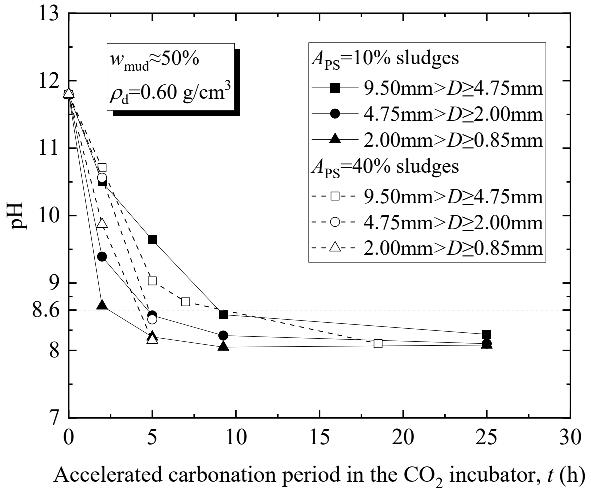
Subsequently, the sludge in the cups was removed from the incubator at an arbitrary elapsed curing period of up to approximately 25 h to measure the pH. Figure 4.11 shows the pH of the sludge with respect to the accelerated carbonation period in the CO_2 incubator. The pH values of all the types of sludge decreased significantly in the first 5 h; subsequently, the pH neutralization rate decreased, particularly when the pH decreased to less than 8.6. Based on the definition of the neutralization completion period presented in Fig 3.11, the t_N of each particle-size-range-controlled sludge was obtained, as listed in Table 4.4.



(a) Particle size range-controlled sludges with w_{mud} ≈ 30%



(b) Particle size range-controlled sludge with w_{mud} ≈ 40%.



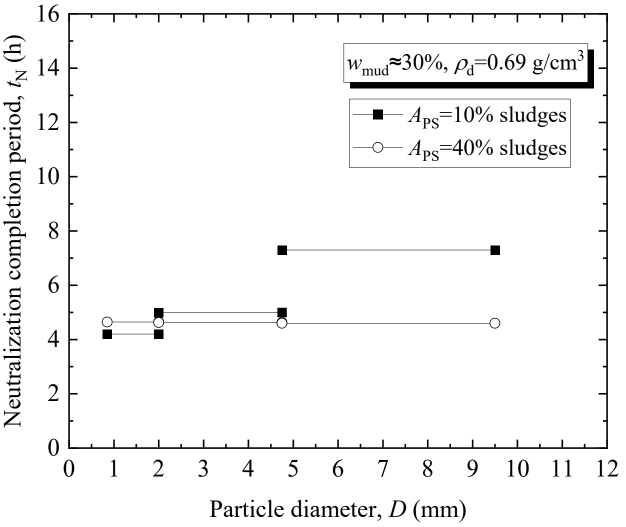
(c) Particle size range-controlled sludge with w_{mud} ≈ 50%.

Figure 4.11. Relationship between accelerated carbonation period and pH of particle size range-controlled sludges

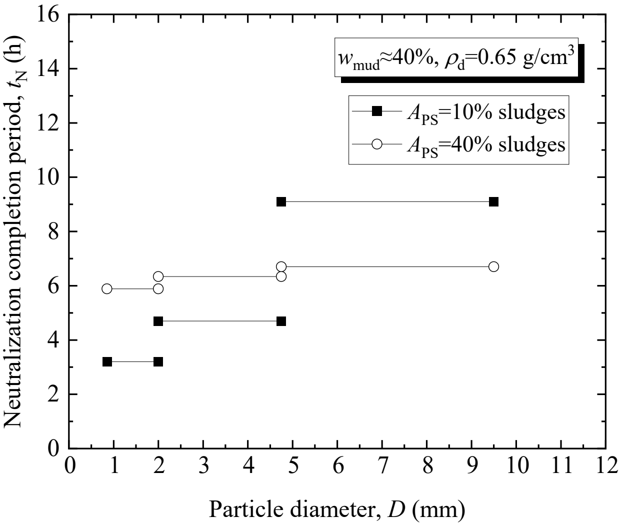
4.2.3 Change in t_N with the change in particle size

Figure 4.12 (a), (b), and (c) show the t_N obtained from the results shown in Fig 4.11 for the *D* range of each sludge with $w_{mud} \approx 30\%$, 40%, and 50%, respectively. As shown in the figures, t_N decreased as *D* decreased in most cases, which could be attributed to the following: CO_2 gas carbonated the particle surface, and pH neutralization progressed gradually from the surface to the particle interior. Therefore, a smaller particle size facilitated pH neutralization of the entire particle.

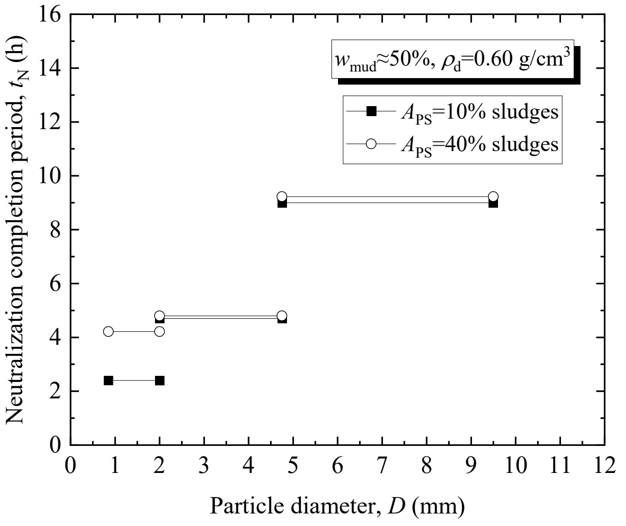
Looking at the results in Fig 4.12 in detail, it is found that the effect of *D* on the change in t_N varies with A_{PS}. The higher the A_{PS} is, the smaller the change in t_N caused by the difference in *D*. The reason for this is not fully understood, but it is probably due to differences in the structure of the particles which is described in the next chapter. As mentioned earlier, BFCB and PSAS caused the clay particles to bind together to form sand and gravel-like granules. In this process, the particles can open intra-open voids, as reported by Dong et al. (2011). Thus, it is expected that particles containing more porous PSAS particles might develop more intra-open voids. In this case, CO_2 gas could penetrate the particles through the open voids, and the change in t_N caused by the difference in *D* could be small.



(a) Particle size range-controlled sludge with w_{mud} ≈ 30%.



(b) Particle size range-controlled sludge with w_{mud} ≈ 40%.



(c) Particle size range-controlled sludge with w_{mud} ≈ 50%.

Figure 4.12. Effects of particle size on t_N

CHAPTER 5

MECHANISM FOR THE CONTRIBUTION OF PSAS AND CRUMBLING

5.1 Microstructure of PSAS and PSAS-treated sludge by SEM analysis

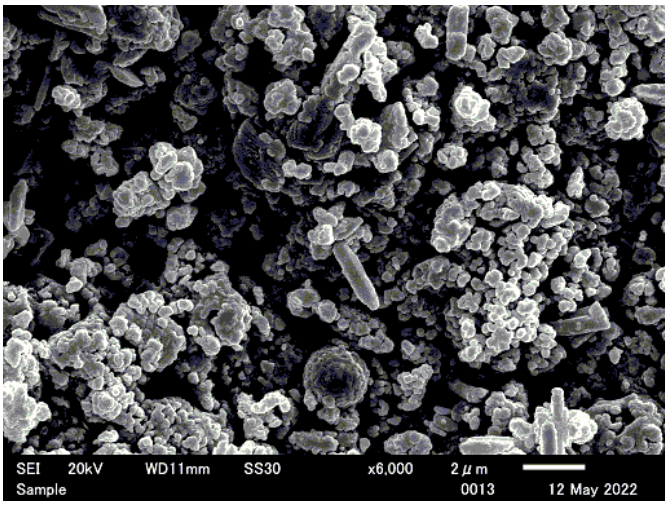
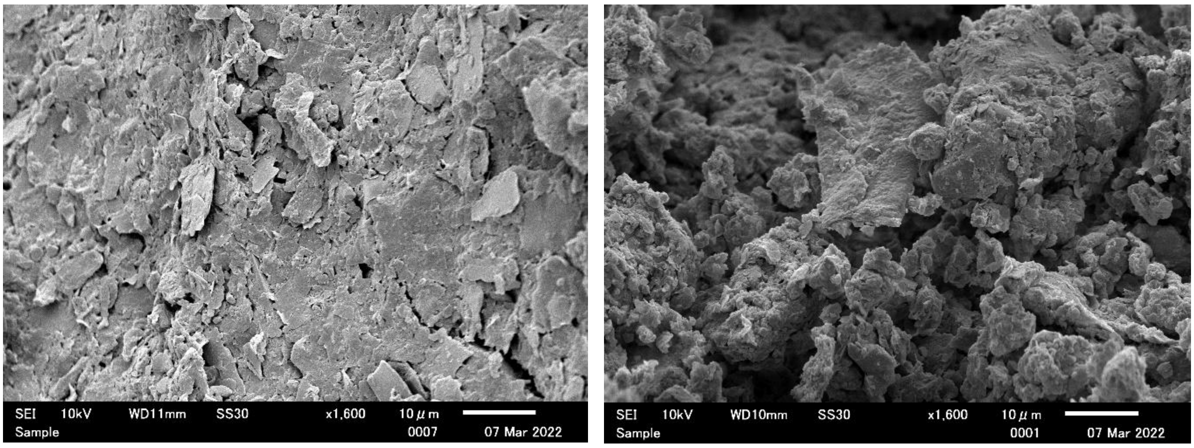


Figure 5.1. Scanning electron microscope image of PSAS

Figure 5.1 shows the scanning electron microscope image of PSAS. It easily can be seen that PSAS has porous microstructure. The porous microstructure of PSAS accords with its low particle density, ρ_s = 2.603 g/cm^3 making it is the lightest material compared to Ao clay with ρ_s = 2.716 g/cm^3, Kasaoka clay with ρ_s = 2.680 g/cm^3 or BFCB with ρ_s = 3.04 g/cm^3. In addition, Binh et al. (2021) investigated the water absorption performance of PSAS due to its microstructure. Dong et al. (2011) proposed the intra-open void and intra closed void concept. Referring to previous research, it could be inferred that the free water can be absorbed and stored in these intra-open voids and intra closed voids.

On the other hand, according to Pan et al. (2012), the precipitation of $CaCO_3$ resulted from the reaction between Ca^{2+} ions and CO_3^{2-} ions of the carbonation is taken place in the bulk solution. Hence, the addition of PSAS is expected not only granulate the sludge to increase the surface area, the porosity of PSAS can also facilitate the penetration of CO_2 gas into the particles but the absorbed water also contributes to accelerate carbonation of PSAS treated sludge.

To investigate the effect of PSAS on creating the porous microstructure as well as to clarify the appearance of intra open void, SEM was conducted for the A_{PS}=0% and A_{PS}=10% sludge. Figure 5.2 shows the scanning electron microscope image of the particle surface of alkaline construction sludge treated with and without PSAS under the same scale. As presented, the A_{PS}=0% sludge has very few intra open voids at the surface of particle. In contrast, it can be clearly seen that the A_{PS}=10% sludge has a porous microstructure with many intra open voids appearing on the surface of particle which can facilitate the penetration of CO_2 gas as well as the chemical reaction of carbonation.



a) A_{PS}=0%, w=1.0w_L b) A_{PS}=10%, w=0.41w_L

Figure 5.2. SEM images of Kasaoka clay sludge with (a) A_{PS}=0% and (b) A_{PS}=10%

5.2 Mechanism for the contribution of crumbling and PSAS for accelerating carbonation

The previous study on mechanism of accelerated carbonation is reviewed in section 2.3. Accordingly, the principle of carbonation reaction of alkaline material occurs in 4 routes: (a) transportation-controlled mechanisms such as CO_2 and Ca^{2+}-ions diffusion to/from reaction sites; (b) boundary layer effects (diffusion across precipitate coatings on particles); (c) dissolution of $Ca(OH)_2$ at the particle surface; (d) pore blockage; and (e) precipitate coating.

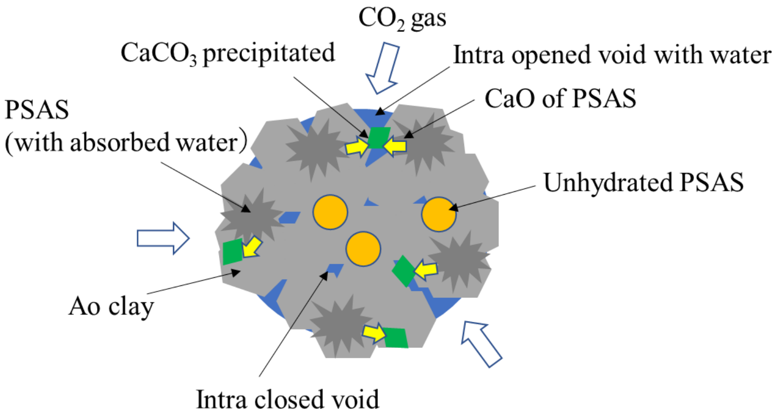


Figure 5.3. Illustrated mechanism of carbonation of PSAS treated sludge

Figure 5.3 presents the proposed mechanism of accelerated carbonation of PSAS treated sludge. As shown in the figure, the addition of PSAS produced the intra open voids and intra closed voids (Dong et al., 2011). These kinds of void allow the water absorption performance of PSAS. Free water is absorbed and stored in intra open voids and intra closed voids. With an appropriate water kept in these voids, the CO_2 gas could penetrate into deep inside the particle. In addition, water is also an essential environment that facilitate the carbonation because the precipitation of $CaCO_3$ from carbonation reaction takes place in the water surrounding the particle as mentioned previously in Fig 2.1. However, it can be inferred that too much water could block the penetration of CO_2 gas through intra open voids and decrease the effectiveness of porous microstructure in accelerated carbonation.

As shown in Figure 4.10, the neutralization completion period, t_N is affected by the amount of PSAS, A_{PS} and particle size of samples. Generally, the difference of t_N of different ranges of particle size cases became larger as the water content increased. For the same water content, this difference of the A_{PS} = 40% samples was seen unsignificant compared to that of the lower A_{PS} =10% cases. Moreover, the A_{PS} = 10% samples with small particle size (0.85 mm $< D \leq$ 2.0 mm) gave a smaller t_N compared to that of A_{PS} = 40% regardless of the water content. In contrast, when the particle size becomes larger, the A_{PS} = 40% samples performed the smaller t_N except for the high-water content sample cases (i.e., w_{mud}=50%).

This is because at low water content (w_{mud} = 30% and 40%), the high A_{PS} sample having porous microstructure allows the penetration of CO_2 gas regardless the particle size of samples. The intra open voids induced by the addition of PSAS facilitate the penetration of CO_2 gas deeply and widely inside the particle. Hence, the penetration of CO_2 gas was not strongly affected by the size of particles. In contrast, the alkaline sludge (without PSAS) showed dense-liked at the surface of particles without intra open void. Thus, CO_2 gas could not penetrate into the core of particles and hence, CO_2 could only dissolve to a part which is near the surface of particle. This strongly affected the carbonation of large particle whereas the pH neutralization of the small particle was not affected since the surface is closer to the core. Therefore, t_N was the same for the A_{PS}=40% sludge but increased with the increase in particle size for the A_{PS}=0% sludge.

However, in this study the water content of sludge was intentionally increased up to a certain level (w_{mud} = 50%) which is enough to fill the intra opend voids of the A_{PS}=40% sludge. In this case, the porosity produced by PSAS could not facilitate the penetration of CO_2 gas due to the occupation of water. Consequently, the effect of porosity on shortening t_N became negligible and the sludges with large particles showed a higher t_N which is similar to the alkaline sludge.

The main purpose of crumbling is to intentionally reduce the particle size, especially for the sludge with small amount PSAS which cannot be granulated. Obviously, the small particle size samples take less time to neutralize the pH compared to the bigger ones because (1) CO_2 gas can penetrate more easily to the core of particle due to the small distance from the surface to the core of particles, and (2) the smaller particle size induces the larger surface area that can be approached by CO_2. Moreover, for all cases of sludge (w_{mud}=30, 40, and 50%) having particle sizes ranging from 0.85 mm to 2 mm, the A_{PS} =10% samples showed smaller t_N compared to that of the A_{PS} = 40% because PSAS itself is a high alkaline material. In addition, the porous microstructure of the A_{PS}=40% sludge induced by PSAS seems not significantly improve the pH neutralization for the small particle size because the distance from the surface to the core of particle is short enough to facilitate the carbonation that makes the effectiveness of porous microstructure on accelerated carbonation becomes less significant. Hence, crumbling is expected to effectively accelerate the carbonation of alkaline construction sludge treated with small amount of PSAS. Note that, the presence of PSAS even with a small amount is necessary to accelerate carbonation of alkaline construction sludge because t_N of the A_{PS}=0% sludge could not be obtained although being crumbled as shown in Fig 4.5(a).

However, t_N of the A_{PS}=10% sludge generally increase with the increase in particle size which implies that CO_2 gas probably could not penetrate easily to the inside of the large particle size samples. To overcome this, a higher amount of PSAS is expected to produce more intra-open voids inside the high A_{PS} samples. For the large particle size sludge, CO_2 gas could penetrate to the core of particle via the intra open voids as shown in Fig 5.2b and Fig. 5.3. Under the appropriate water content, these intra open voids have enough empty space that allow the penetration of CO_2 gas deeply and widely into the inside of particles. As shown in Fig 4.10a, the A_{PS}=40% samples with w_{mud}=30% having different particle sizes produced the same t_N. This is probably because the number of intra open voids generated by PSAS is sufficient to allow the penetration of CO_2 gas that facilitate the accelerated carbonation even for large particle size. Thus, the effect of particle size reduction on accelerated carbonation was not significant.

In contrast, under high water content conditions, these open intra voids are occupied by water that inhibit the penetration of CO_2 gas. Consequently, impact of water content on accelerated carbonation becomes more significant when particle size becomes larger as shown in Fig 5.4. In this case, the effect of porosity on accelerated carbonation caused by PSAS becomes negligible. The results also shows that the small particle samples with the highest water content produced the smallest t_N, and vice versa for both A_{PS}=10% and 40% cases. When CO_2 approach the surface of particles, a liquid firm and bulk water solution covering the particle is needed as the catalyst for the carbonation reaction. This liquid environment allows the diffusion of CO_2 and Ca^{2+} -ions to/from the reaction sites and the precipitation of $CaCO_3$ (Pan et al., 2012). For the small particle, once CO_2 gas approach the surface of particles, it is very closed to the core which means it could react with a higher percentage of Ca^{2+} -ion in the particle compared to the larger one, even under high water content conditions (i.e., w_{mud}=50%). In contrast, under high water content conditions, the intra voids are occupied by water that hinder the penetration of CO_2 gas into deep inside and CO_3^{2-} -ions can only react with a small part of Ca^{2+} -ions near the surface of particle. Consequently, accelerated carbonation is just partly taken place.

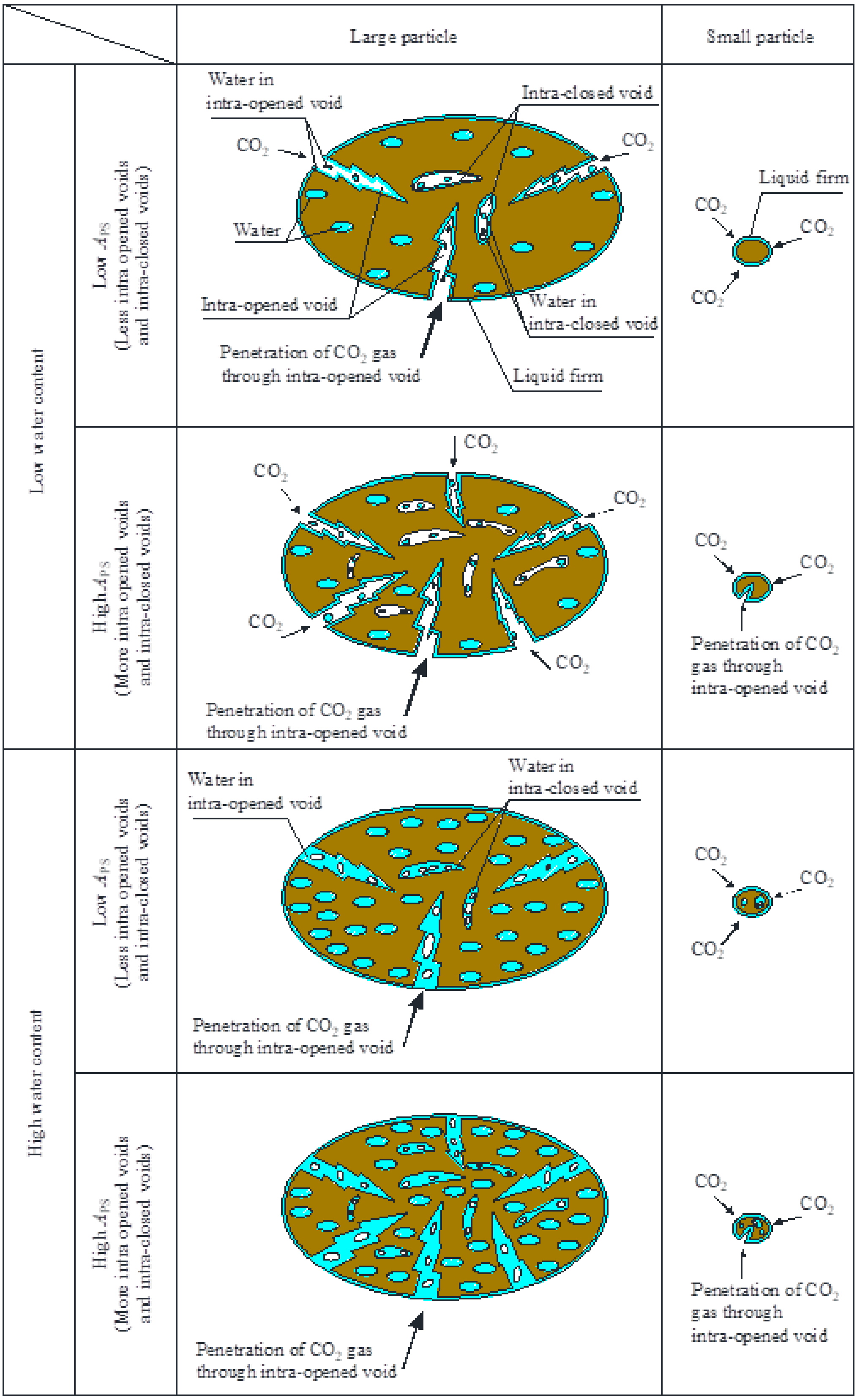


Figure 5.4. Proposed illustration for the explanation of effect of intra open void, water content, and particle size on the penetration of CO_2 gas into particles

CHAPTER 6

STRENGTH DEVELOPMENT OF ACCELERATED CARBONATE CONSTRUCTION SLUDGE

As mentioned previously, the addition of the PSAS to alkaline sludge significantly shortened the pH neutralization period under accelerated carbonation. However, the effects of the PSAS on the strength development of the sludge under accelerated carbonation have not been investigated in detail. Therefore, a series of cone index tests was conducted in this study on alkaline and treated sludge specimens subjected to accelerated carbonation as shown in Fig 6.1. For comparison, cone index tests were also conducted on sludge specimens that did not undergo accelerated carbonation. The test procedures and test results are discussed in this chapter. Discussions on the strength development mechanism are also presented.

To establish an accelerated carbonation method for neutralizing alkaline construction sludge, another important aspect is to ensure that the strength of the alkaline sludge remains after carbonation. It is known that the C–S–H produced during cement hydration plays an important role in the strength development of cement-treated soils. Therefore, the degradation of C–S–H in alkaline sludge caused by accelerated carbonation is considered to be a factor in the decreased strength of alkaline sludge (Nishi et al., 2004). However, the change in the strength of compacted neutralized sludge after carbonation was not fully clarified because Nishi et al. (2004) evaluated the strength of alkaline sludge using unconfined compression tests. In contrast, the sludge after pH neutralization was compacted to evaluate its practical application as a construction geomaterial in the present study to examine the impact of accelerated carbonation on the strength properties of compacted sludge.

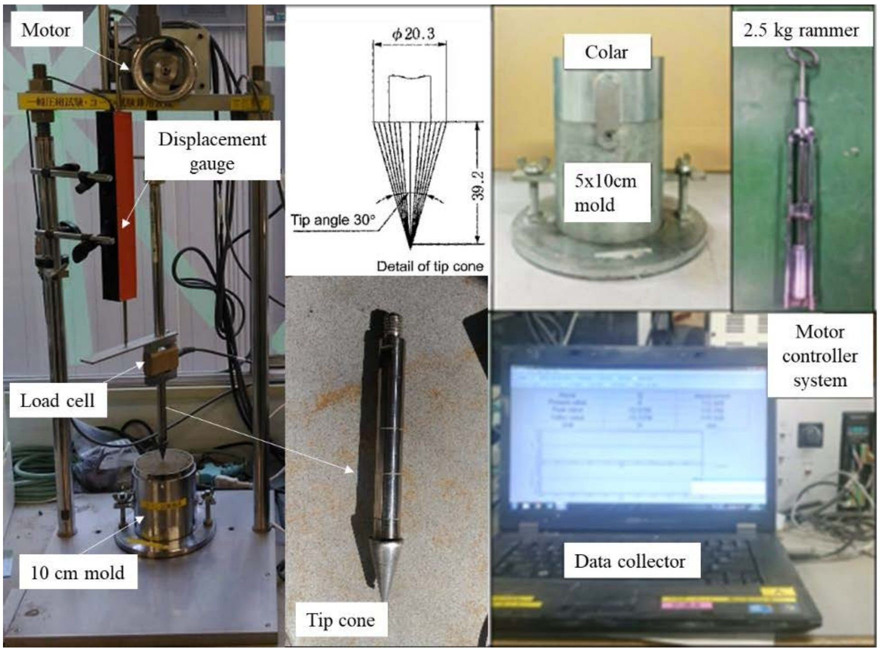


Figure 6.1. Cone index test equipment

6.1 Material preparation

To investigate the impact of the PSAS on the strength development of the sludge under accelerated carbonation, four types of sludge prepared from Ao clay and Kasaoka clay with different proportions of the addition ratio, A_{PS}, were prepared, as shown in Table 6.1. They were alkaline sludge (A_{PS} = 0%) and PSAS treated sludge with an A_{PS} of 20% and 40% for the Ao clay sludge and Kasaoka clay sludge, respectively. For each clay, six specimens for each type of sludge were prepared to examine the strength development under the following conditions: 1) three periods of sealed curing time (3 days, 7 days, and 14 days), and 2) with and without accelerated carbonation, as shown in Table 6.2.

To prepare the alkaline sludge specimens for both the untreated and treated cases, dry Ao clay was stirred with distilled water to achieve the desired liquid limit state, w_L. Subsequently, BFCB was added to the clay, and the mixture was stirred thoroughly. To prepare the treated sludge specimens, PSAS with an A_{PS} of 20% or 40% was sequentially added to the alkaline sludge immediately after their preparation, and the mixture was stirred thoroughly. Using the above-described methods, 24 specimens weighing 3 kg each were produced. Each specimen was subsequently poured into a plastic bag and cured under sealed conditions at a room temperature of 25°C.

Table 6.1. Mixing conditions for preparation of sludge specimens

Clayey type	Type of sludge	Initial water content of clay, w_i (%)	Addition ratio of blast furnace cement B (BFCB), A_{cement} (%)	Addition ratio of paper sludge ash-based stabilizer (PSAS), A_{PS} (%)
Ao clay sludge	Alkaline sludge	$1.0w_L$	3.0	0
	PSAS treated sludge			20
Kasaoka clay sluge	Alkaline sludge			0
	PSAS treated sludge			40

Table 6.2. Sealed curing and accelerated carbonation periods

Type of sludge	Sealed curing period	Accelerated carbonation period
Alkaline sludge	3, 7, and 14 days	0 and 7 h
PSAS-treated sludge		

6.2 Cone index tests on specimens with and without accelerated carbonation

As shown in Table 6.2 and Fig. 6.1, each specimen was cured under sealed conditions at 25°C. Subsequently, after a predetermined number of curing days (3, 7, and 14 days), half of the specimens were subjected to 7 h of accelerated carbonation followed by cone index tests. For comparison, the other half of them were subjected to cone index tests without undergoing accelerated carbonation.

1) Test procedure for specimens subjected to accelerated carbonation

For the accelerated carbonation tests, the specimens were poured into trays and placed in a CO_2 incubator for 3, 7, and 14 days under sealed curing. Before being placed in the CO_2 incubator, the height of each specimen in the trays was adjusted to approximately 25 mm. It should be noted that the alkaline sludge specimens were deliberately and manually crumbled before being poured into trays to accelerate the pH neutralization tests. The particle size of the crumbled alkaline sludge was 10 mm or less. However, this crumbling process requires considerable time and effort. Therefore, the addition of the PSAS is proposed in this study to achieve granulation without manual or mechanical intervention.

Similar to the investigation of the effect of PSAS on accelerating carbonation, the CO_2 concentration, temperature, and humidity in the CO_2 incubator were set to 10%, 25°C, and 90% or higher, respectively (the same values as in Table 3.3). The curing period was set to 7 h, and once the pH levels of the specimens decreased to approximately 8.6 or lower, the specimens were immediately removed from the CO_2 incubator, and the cone index tests were conducted on the specimens based on the Japanese Geotechnical Society Standards (JGS 0716). The cone index tests require compacted specimens per the Japanese Geotechnical Society Standards (JGS 0711). Therefore, each specimen was placed in a 10-cm mold by first dividing the sludge into three equal layers. Each layer was sequentially added to the mold and compacted 25 times by dropping a 2.5-kg hammer from a height of 30 cm. After full compaction, a cone index test was conducted by penetrating the tip cone at a speed of 1 cm/s into each compacted specimen held in a 10-cm mold. The force acting on the cone when the tip cone penetrated 5 cm, 7.5 cm, and 10 cm from the top surface of the specimen was used to calculate the cone index value, q_c.

Following the cone index test conducted immediately after accelerated carbonation, each specimen was manually crushed to obtain particle sizes of approximately 10 mm or less and each specimen was then homogeneously mixed after its removal from the compaction mold. All the specimens were then placed in plastic bags and air-cured at a temperature of 25°C. As shown in Fig 6.2, after 3 days of air curing, the cone index test was repeated for each specimen. Subsequently, the specimen was removed from the compaction mold and curing continued under ambient conditions. This procedure was repeated to conduct the cone index test on each specimen after 7 days, 14 days, and 28 days of air curing.

2) Test procedure for specimens without accelerated carbonation

Cone index tests and air curing were also conducted on specimens that did not undergo accelerated carbonation. The procedures were similar to those for the specimens subjected to accelerated carbonation, except that the accelerated carbonation process was omitted (Fig 6.2).

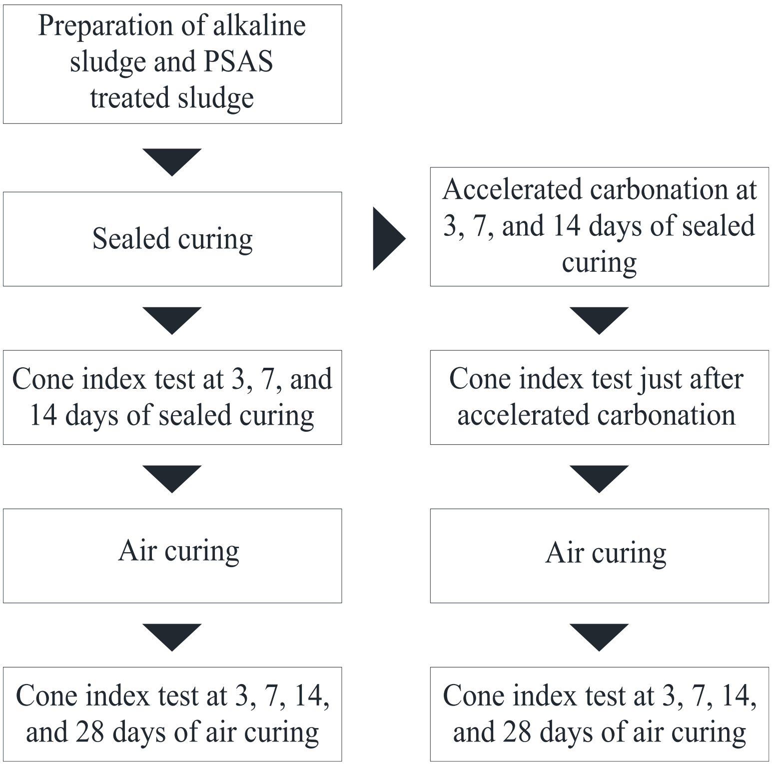


Figure 6.2. Test procedure flow chart

6.3 Cone index test results and discussion

1) Strength development during sealed curing before accelerated carbonation

Accelerated carbonation is abbreviated as AC in Figs 6.3, 6.4, 6.5, and 6.6. Figures 6.3(a)–(c) show the changes in q_c after 3 days, 7 days, and 14 days of sealed curing, respectively. In the figures, q_c is plotted against the number of days after the preparation of the sludge specimens. The figures indicate that the cone index q_c of the PSAS treated sludge under sealed curing was much higher than that of the alkaline sludge, irrespective of the number of curing days. The reasons for this can be explained as follows:

When clay alone was at liquid limit w_L, the cone index was almost zero. Therefore, the strength of the alkaline sludge that developed after compaction was considered to be mainly the result of the bonding strength generated by the hydration of the cement. On the other hand, in addition to the effect of the cement hydration, the effects of water absorption and retention introduced by the PSAS are thought to have further contributed to the strength development of the PSAS-treated sludge. Kawai et al. (2018) conducted cone index tests on Ao clay treated only with a PSAS and demonstrated that q_c increased with increases in A_{PS} and the sealed curing period. They also reported that a nonlinear correlation between liquidity index I_L and q_c was observed, and that the addition of the PSAS decreased I_L and increased q_c. In this study, the addition of both the PSAS and BFCB further strengthened this tendency in the PSAS treated sludge. Moreover, the PSAS treated sludge remained granular to some extent even after compaction, whereas the alkaline sludge became lumpy (agglomerated) when compacted. Hence, friction and interlocking among particles also contributed to the strength development of the PSAS treated sludge. Consequently, the strength of the PSAS treated sludge was much higher than that of the alkaline sludge.

2) *Change in strength after accelerated carbonation*

As shown in Fig 6.3, accelerated carbonation significantly reduced the q_c of the alkaline sludge. The reduction became more apparent as the sealed curing period increased. However, in the case of the PSAS treated sludge, there was almost no decrease in q_c after carbonation. The reason for this difference is considered to be as follows.

When cement and cement-based stabilizers are added to soil, the cement reacts with the water to produce calcium hydroxide crystals, $Ca(OH)_2$ and calcium silicate hydrate (C-S-H) (Japan Cement Association, 2012; Kitazume & Terashi, 2013). The production of $Ca(OH)_2$ and C-S-H improves the strength of the soil. A previous study showed that the interlocking mechanism between $Ca(OH)_2$ and C-S-H generated from the hydration of cement is responsible for the bonding strength of cement-treated sludge (Duggal, 2009). Similarly, some strength development was observed in the alkaline sludge in this experiments, and the production of $Ca(OH)_2$ and C-S-H is thought to have contributed to this result. Therefore, the decrease in the q_c of the alkaline sludge observed after accelerated carbonation was considered to be due to the partial degradation of $Ca(OH)_2$ and C-S-H induced by the carbonation. By applying accelerated carbonation, the reaction of $Ca(OH)_2$ and C-S-H with CO_2, as expressed by Eqs. (2.1) and (2.2), broke the interlocking mechanism between the former two, and consequently, weakened the bonding strength.

Furthermore, a longer sealed curing period implies that more cement hydrates were formed. However, these hydrates became larger with carbonation, such that their q_c decreased more significantly, as shown in Fig 6.3. Similar to the alkaline sludge, the cement hydrates of the PSAS treated sludge will be partially degraded by accelerated carbonation. However, because the porosity of the PSAS particles remained, most of the contribution of the water absorption and retention performance of the PSAS to the strength development of the PSAS treated sludge was preserved even after accelerated carbonation. In addition, the granulated particles of the PSAS treated sludge did not become lumpy; they retained their granular shape to some extent. Therefore, it is presumed that the friction and interlocking among particles did not decrease significantly.

3) *Strength development during air curing after accelerated carbonation*

In Fig 6.3, the q_c of most of the specimens increased with an increase in the air-curing period. The increase in q_c of the PSAS-treated sludge was remarkable compared to that of the untreated alkaline sludge. The reason for this could be the significant decrease in the saturation degree, S_r, of the PSAS-treated sludge as follows.

Figures 6.4, 6.5, and 6.6 present the changes in water content w, dry density ρ_d, and degree of saturation, S_r, obtained from the cone index tests, respectively. As shown in Fig 6.4, w gradually decreased with an increase in the air-curing period for both the alkaline sludge and the PSAS-treated sludge. It is also observed in Fig 6.5 that the ρ_d of the alkaline sludge gradually increased as the air-curing period increased, whereas the change in the ρ_d of the PSAS-treated sludge was less significant. In the case of the PSAS-treated sludge, the compaction curve was relatively flat because of the PSD. Therefore, the change in ρ_d with changes in w is small. Thus, as shown in Fig 6.6, the S_r of the PSAS-treated sludge significantly decreased with air curing, whereas that of the alkaline sludge was less significant. The decrease in S_r can increase the suction, resulting in an increase in the q_c of the treated sludge.

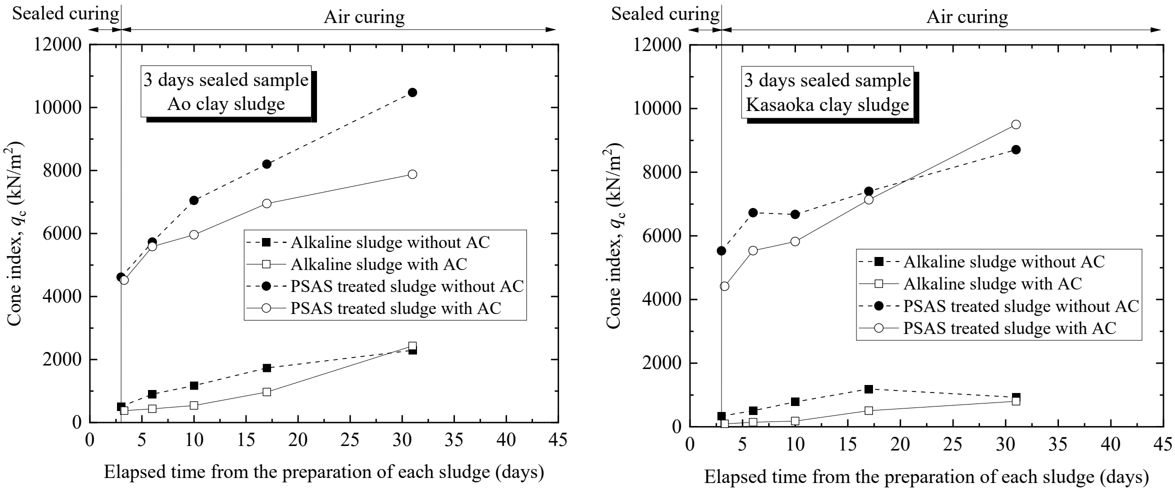
It is also observed in Fig 6.3 that under the air-curing conditions used in the experiments, the q_c of the PSAS treated sludge specimens under accelerated carbonation developed relatively slowly compared to the specimens that did not undergo accelerated carbonation. Nishi et al. (2004) and Nakarai et al. (2015) argued that not only the cement hydrates, as presented in Eqs. (2.1) and (2.2), but also the unhydrated cement components of C_3S and C_2S, react with CO_2, as follows:

$$3CaO.SiO_2 + (3\text{-}x)CO_2 + yH_2O \rightarrow (CaO)_x.(SiO_2)(H_2O)_y + (3\text{-}x)CO_2.CaO \quad [6.1]$$

$$2CaO.SiO_2 + (2\text{-}x)CO_2 + yH_2O \rightarrow (CaO)_x.(SiO_2)(H_2O)_y + (2\text{-}x)CO_2.CaO \quad [6.2]$$

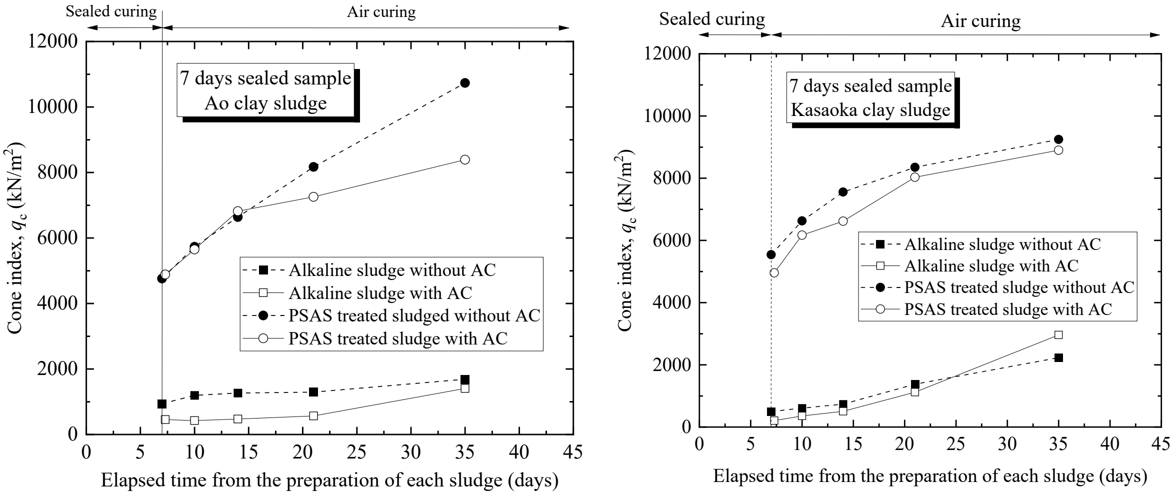
The chemical compositions of PSAS are relatively similar to that of cement as shown in Table 3.1 with a large proportion of CaO. Therefore, the contribution to strength development from the liked-cement hydration of PSAS is expected similar to cement. Indeed, a formation of needle-like crystals (ettringite) was found in hydrated PSAS as shown in Fig 6.7. Nishi et al. (2004) demonstrated that the generated C-S-H gel has a lower Ca/Si molar ratio compared to that of a normal C-S-H gel. The decrease in the Ca/Si molar ratio in the C-S-H gel generated by accelerated carbonation could preserve the increase in strength of the sludge after accelerated carbonation. In particular, the contribution of C_2S to the strength development is significant after a certain curing time as presented in Fig 6.8. However, the decomposition of C_2S caused by accelerated carbonation, as presented in Eq. (6.2), inhibits further strength improvement thereafter. Hence, after accelerated carbonation under the air-curing conditions, the q_c of the PSAS-treated sludge experiencing accelerated carbonation developed more slowly compared to the PSAS-treated sludge that did not experience accelerated carbonation.

Figure 6.9 presents the ratios between the cone index, q_c of sludge treated with and without CO_2 curing for alkaline sludge and PSAS treated sludge. PSAS can preserved the strength even after accelerated carbonation. Meanwhile, the strength of alkaline sludge without PSAS was reduced significantly by accelerated carbonation, but it may recover for longer curing period. This might be induced by the delayed hydration because free water for the hydration could exist sufficiently in the sludge without PSAS, while free water could exist little in the sludge with PSAS. In general, a values were around 1 after 28 days of air curing which implies the difference between q_c of sludge with and without AC was insignificant.



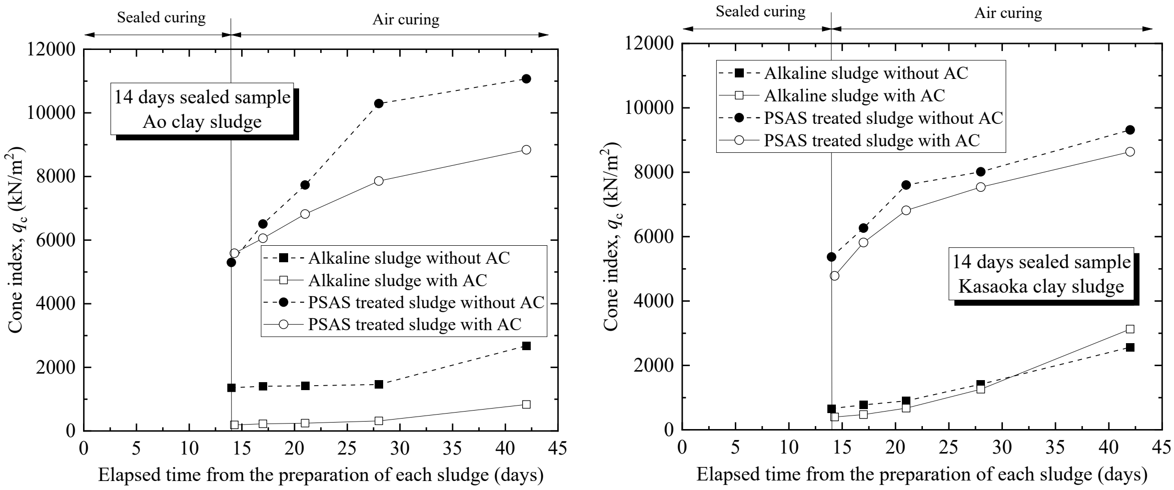
a) 3 days of sealed curing

d) 3 days of sealed curing



b) 7 days of sealed curing

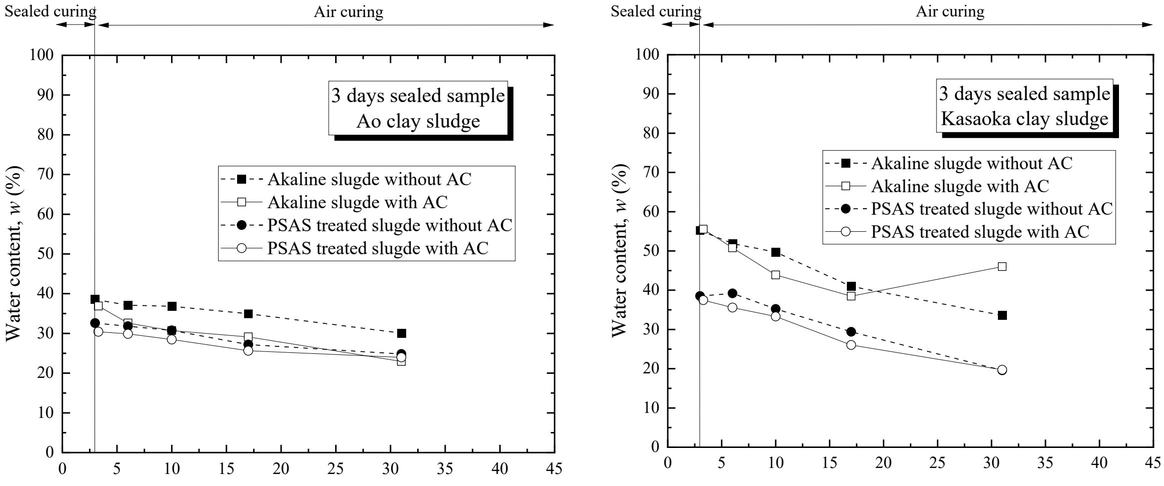
e) 7 days of sealed curing



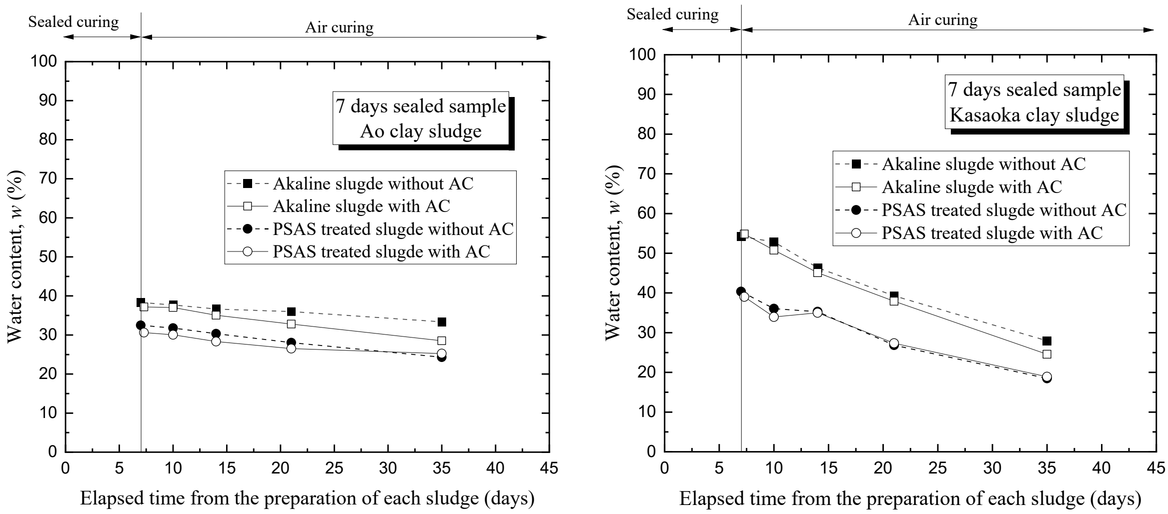
c) 14 days of sealed curing

f) 14 days of sealed curing

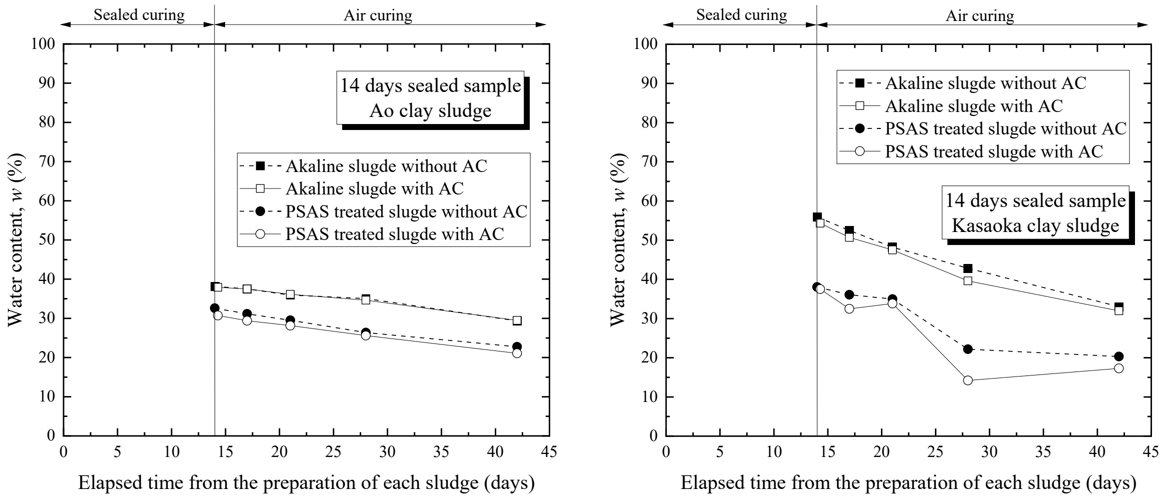
Figure 6.3. Cone index of specimens based on time elapsed after their preparation



a) 3 days of sealed curing d) 3 days of sealed curing

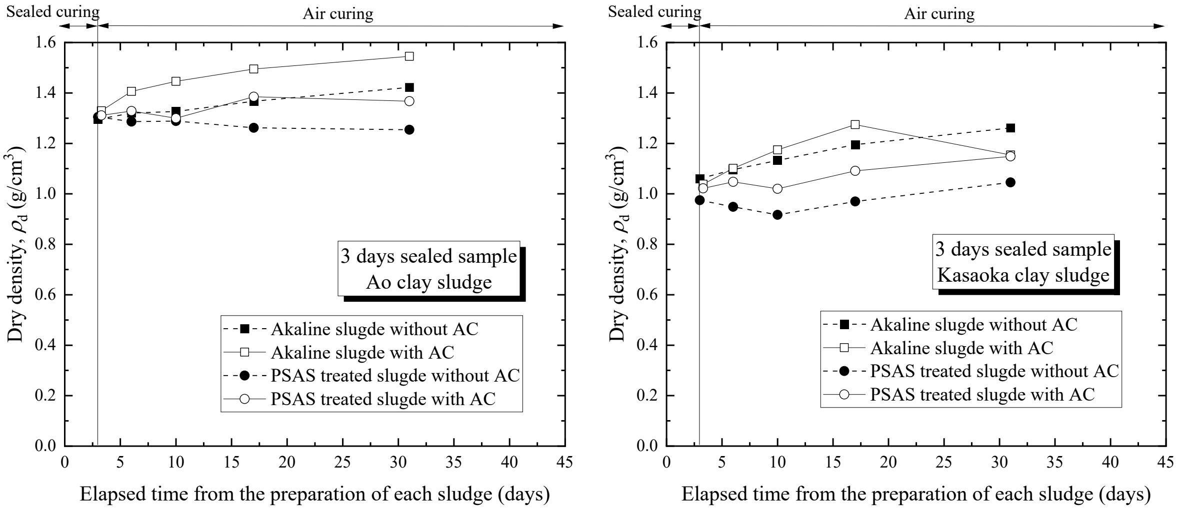


b) 7 days of sealed curing e) 7 days of sealed curing



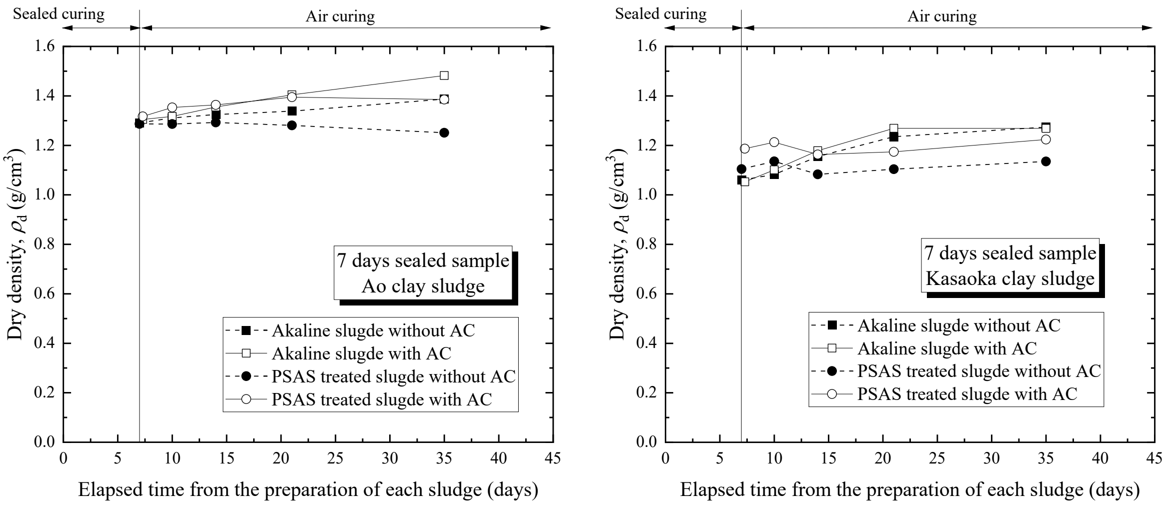
c) 14 days of sealed curing f) 14 days of sealed curing

Figure 6.4. Water content of cone index test specimens based on time elapsed after their preparation



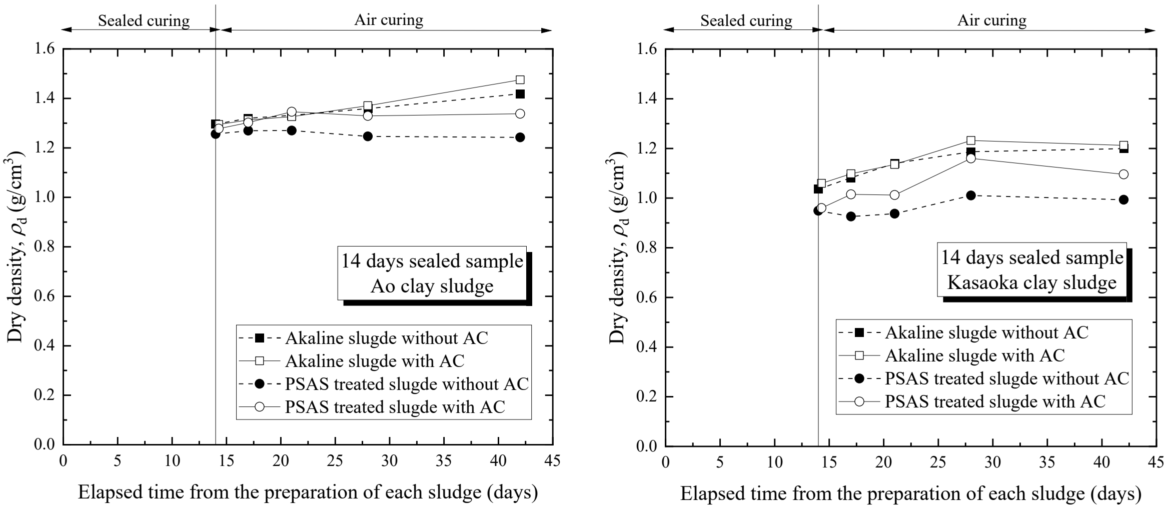
a) 3 days of sealed curing

d) 3 days of sealed curing



b) 7 days of sealed curing

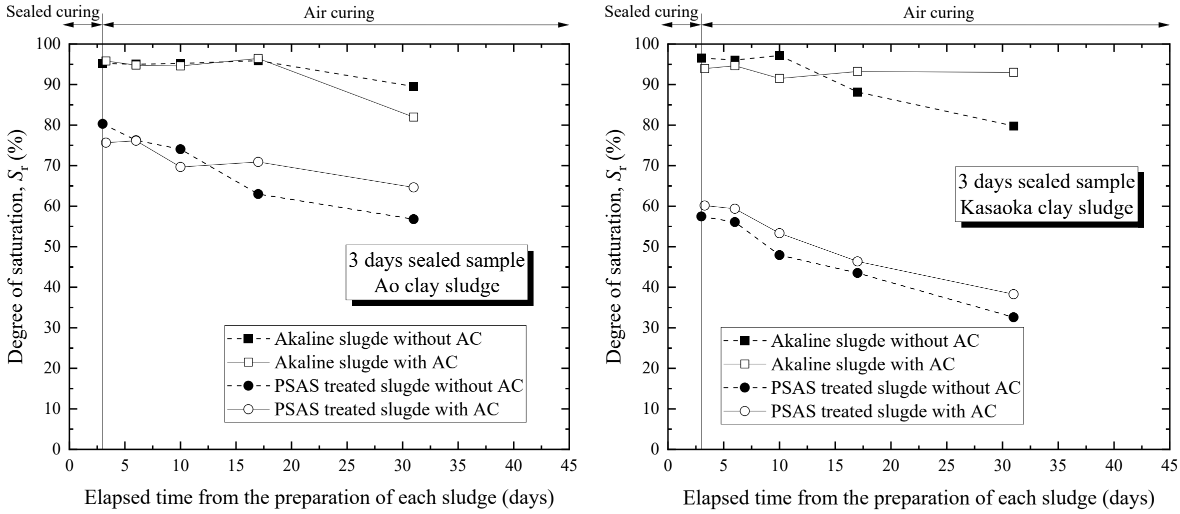
e) 7 days of sealed curing



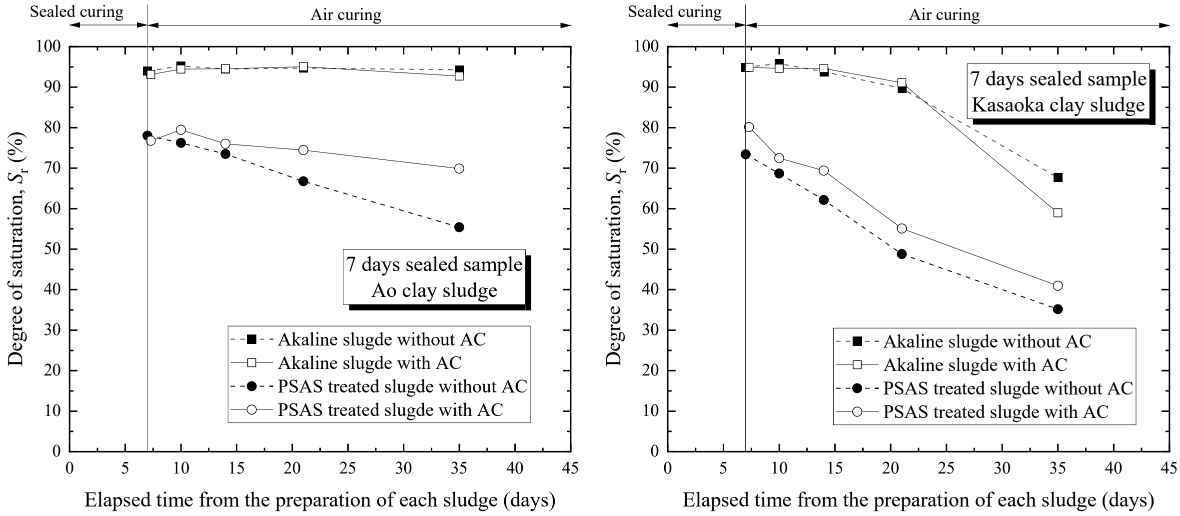
c) 14 days of sealed curing of ACS

f) 14 days of sealed curing of KCS

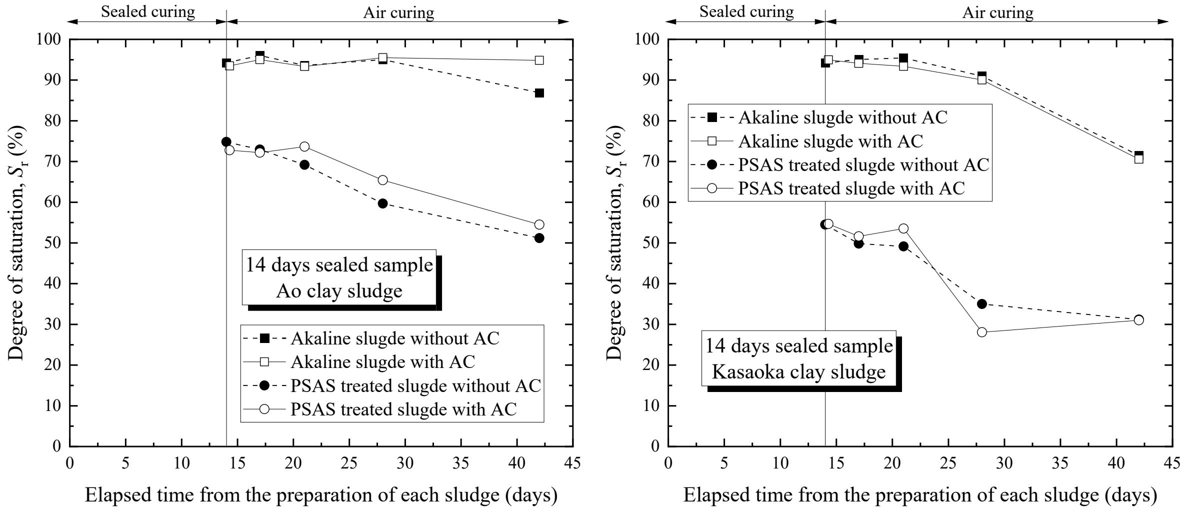
Figure 6.5. Dry density of cone index test specimens based on time elapsed after their preparation



a) 3 days of sealed curing d) 3 days of sealed curing



b) 7 days of sealed curing e) 7 days of sealed curing



c) 14 days of sealed curing f) 14 days of sealed curing

Figure 6.6. Saturation degree of cone index test specimens based on time elapsed after their preparation

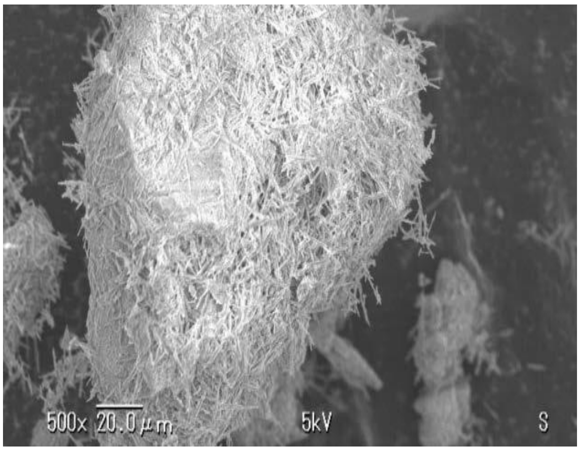


Figure 6.7. Formation of needle-like crystals in PSAS

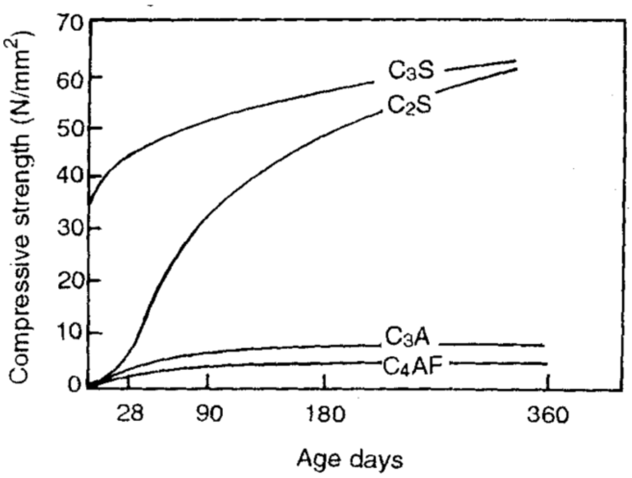
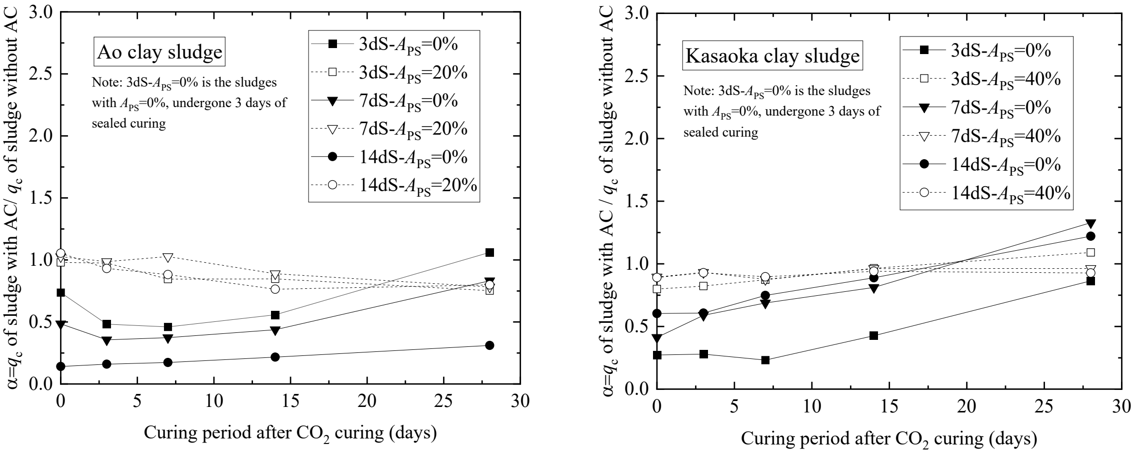


Figure 6.8. Contribution of cement compounds on strength of cement (Duggal et al., 2009)



(a) Ao clay sludge (b) Kasaoka clay sludge

Figure 6.9. The strength development ratios of sludge treated with and without CO_2 curing

6.4 Effect of crumbling and pre-air curing on strength development

Material preparation and test procedures

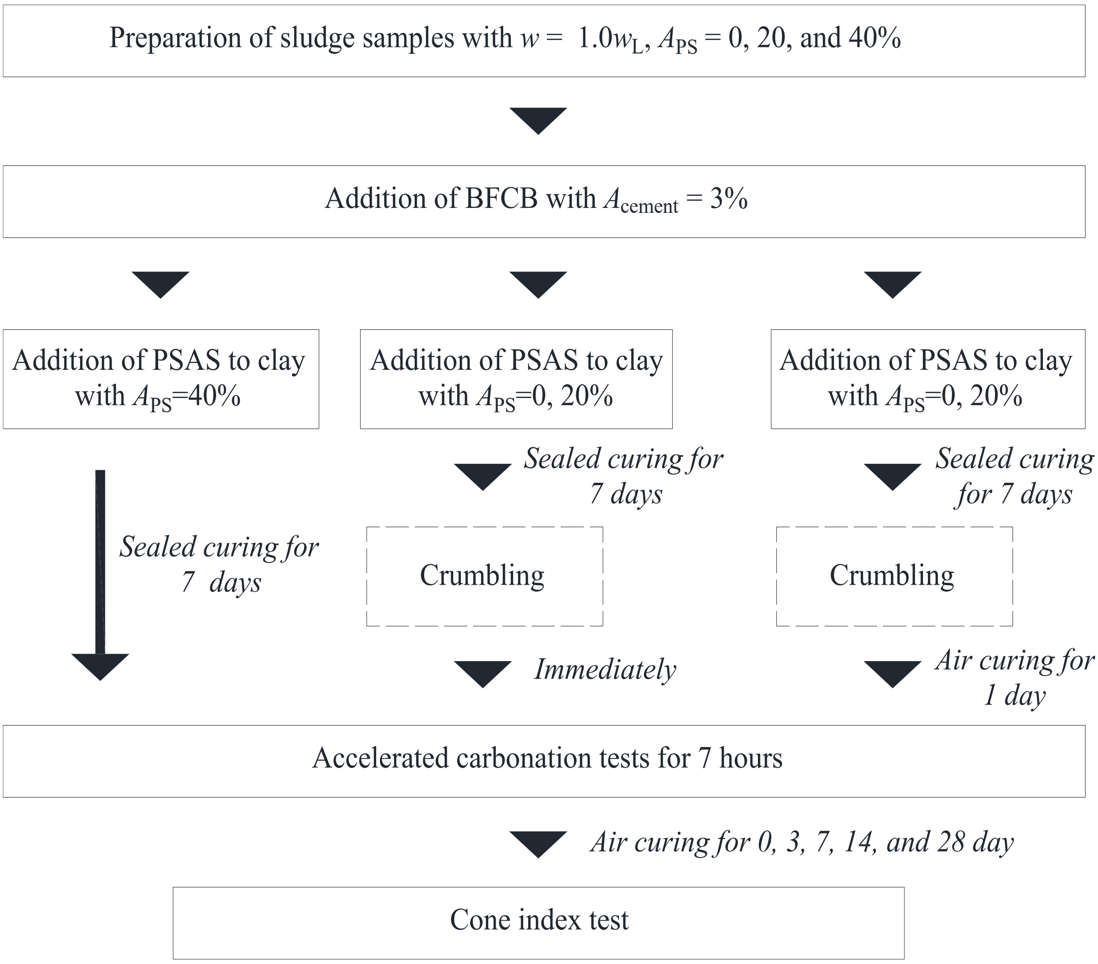


Figure 6.10. Experimental flow chart of crumbling and pre-air curing prior to accelerated carbonation and cone index test

As mentioned previously, the crumbling process significantly shortened the pH neutralization curing period. It means that alkaline construction sludge treated with a smaller amount of PSAS undergoing the crumbling prior to accelerated carbonation can produce a t_N which is similar to that of a higher amount of PSAS-treated sludge. However, for the applications, the strength development of crumbled samples must be considered by comparing with that of non-crumbled samples having a higher A_{PS}.

From the viewpoint that the strength development of PSAS treated sludge came from the granulation and the reduction of free water induced by the water absorption and retention of PSAS, an attempt to reduce the amount of PSAS while keeping its effects on accelerated carbonation as well as strength development was carried out. To do so, the ungranulated alkaline construction sludge treated with and without PSAS were selected with the A_{PS} = 0%, 20%, and 40% to accelerate carbonation and conduct cone index test. As presented previously, PSAS shows its effectiveness in accelerating carbonation for the Kasaoka sludge having A_{PS}=40% when a smallest t_N was obtained. By crumbling, t_N of A_{PS}=20% sludge was remarkably decreased from 82 hours to 4.2 hours which is slightly less than that of A_{PS}=40% sludge (i.e., 5.6 hours). Therefore, to comprehensively investigate the effectiveness of crumbling effect, this research focused on investigating strength development of A_{PS}=40% sludge and that of A_{PS}=20% undergone crumbling and pre-air curing.

Sludges were prepared by mixing Kasaoka clay at liquid limit state, w_L with 3% blast furnace cement type B to form alkaline sludge. Then PSAS was added with 2 different proportions to attain PSAS treated sludge with A_{PS}=20 and 40%. Before the accelerated carbonation, ungranulated sludges (i.e., the A_{PS}=0% and A_{PS}=20% sludge) were separated to 2 categories. The first part was intentionally crumbled and then cured under atmospheric curing conditions for 24 hours which is called pre-air curing (PAC) to obtain granulated sludge having PSDs shown in Fig 4.3(b) prior to accelerated carbonation. Another part was also crumbled and immediately cured under CO_2 curing. After accelerated carbonation, cone index test was conducted for all specimens. The detail of test procedure for investigating effect of crumbling and pre air curing of carbonated sludge on strength development is demonstrated in Fig 6.10.

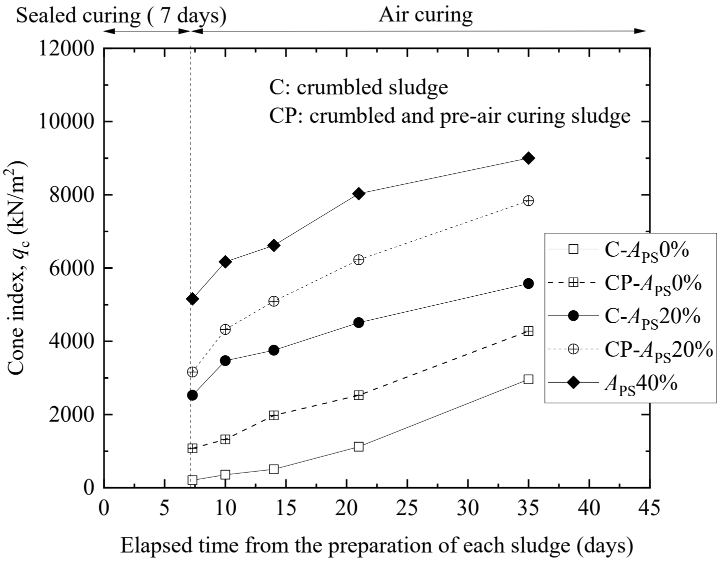


Figure 6.11. Cone index of crumbled and uncrumbled sludge sample

Effect of crumbling and pre-air curing on strength development of carbonated sludge

Figure 6.11 shows the cone index test of sludges undergone accelerated carbonation. It can be seen that crumbling and PAC significantly increased the strength of both A_{PS}=0% and A_{PS}=20% sludge. The initial q_c of PAC sludge was remarkably higher than that of non-PAC sludge. This probably due to the water reduction caused by the evaporation during the pre-air curing. After the accelerated carbonation, the A_{PS}=0% sludge with PAC performed a higher strength development q_c compared to that of without PAC. However, after accelerated carbonation, the strength development rate of crumbled and uncrumbled sludge was almost the same. The crumbling and pre-air curing raised the initial q_c of the A_{PS} 0% sludge and hence induced the higher values of q_c thereafter. This is because the granulation effect itself increase the friction and interlocking of particles. Nevertheless, the granulation facilitates the evaporation accelerating the water reduction and hence, the particle with less of water content became stiffer. Therefore, the friction and interlocking together with the harder the particles became raised the improvement of strength.

Similarly, the ungranulated A_{PS}=20% samples undergone crumbling and pre-air curing conditions improved its q_c. Moreover, q_c of A_{PS}=20% sludge with PAC developed rapidly after CO_2 curing and tended to be equal to that of the A_{PS} 40% samples along with the air curing after accelerated carbonation. Thus, the crumbling and pre-air curing effects could reduce amount of PSAS while maintain the q_c of CO_2 treated sludge as well as the strength development after accelerated carbonation.

Consequently, by crumbling and then pre-air curing, not only the amount of PSAS and t_N were remarkably reduced, but q_c was also enhanced significantly. The q_c of the crumbled A_{PS} =20% could be induced from the pre-air curing process. This implies that less amount of PSAS together with crumbling effect and pre-air curing conditions could accelerate water reduction as shown in Fig 6.12, increase the stiffness of particles by water absorption and retention of PSAS as well as water evaporation under air curing conditions. That, in brief, the crumbling effect coming with the pre-air curing conditions could strengthen the stiffness of particles effectively which is the alternative method for increasing amount of PSAS.

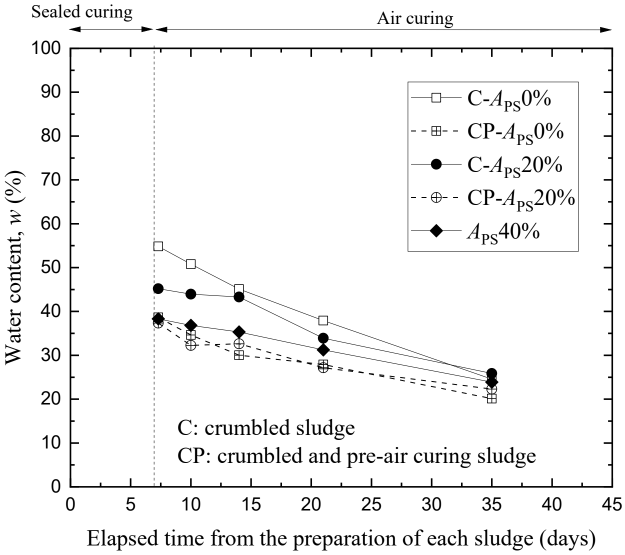


Figure 6.12. Water content of crumbled and uncrumbled sludge sample based on time elapsed after their preparation

CHAPTER 7

CO_2 CAPTURE BY ACCELERATED CARBONATION OF ALKALINE CONSTRUCTION SLUDGE TREATED WITH PSAS

7.1 Experimental methodology to measure the CO_2 captured content

Obviously, accelerated carbonation of alkaline construction sludge not only treat the pH of sludge but also consumes CO_2. Hence, to comprehensively investigate the application of alkaline construction sludge treated with PSAS and accelerated carbonation, it is necessary to investigate CO_2 capture and storage by using PSAS treated sludge as a feedstock.

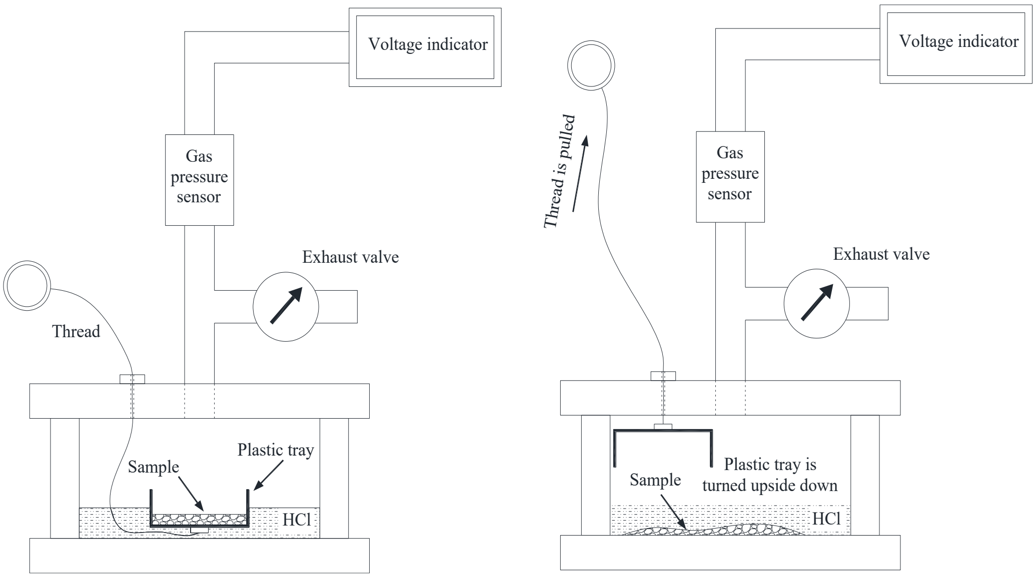


Figure 7.1. Schematic illustration of experimental device to evaluate $CaCO_3$ content

There are several methods to evaluate the CO_2 captured content in material such as ignition loss method, X-ray diffraction, CO_2 capture columns, etc. In this study, the carbonate content evaluation based on a gas pressure method (Fukue et al., 1999) was chosen to conduct because it is relatively simple and quick that can be applied widely in field sites for estimating the CO_2 captured ability of actual sludge.

As described in Chapter 2, the accelerated carbonation of PSAS treated sludge is expected to form calcium carbonate, $CaCO_3$ by the reaction of hydrated cement components with CO_2 as presented in Eq (2.3) and Eq (2.4). Moreover, the un-hydrated cement components of C_3S and C_2S also can react with CO_2 to form $CaCO_3$ as presented in Eq (6.1) and Eq (6.2).

Hence, the CO_2 captured content by accelerating carbonation of PSAS treated sludge can be evaluated indirectly by estimating the amount of $CaCO_3$ of the carbonated sludge. To do so, the gas pressure method was carried out as follows. First, 3g PSAS treated sludge undergone accelerated carbonation is poured to a small plastic tray having the diameter around 35 mm. Subsequently, the tray was carefully placed into a vessel containing 20 ml HCl and then tightly covered by a lid to make an enclosed chamber. Note that there is a small hole with a rubber seal on the lid just enough to pass a thread. This thread connects to the bottom of the plastic tray as shown in Fig 7.1 to turn the tray upside down by pulling the thread outside of the chamber.

Figure 7.2. Experimental device to evaluate $CaCO_3$ content

After pulling the thread, the overturned plastic tray poured the sample fall to and react with HCl solution in an enclosed chamber where the reaction of calcium carbonate ($CaCO_3$) with hydrochloric acid (HCl) could be taken place to generate CO_2 as follows:

$$CaCO_3 + 2HCL \rightarrow CaCl_2 + H_2O + CO_2 \uparrow \quad [7.1]$$

The gas pressure caused by the generation of CO_2 in Eq (7.1) was measured by a sensor connected to a voltage indicator where the pressure value is indicated as shown in Fig 7.2. After the measurement, CO_2 gas was release by open the exhaust valve. To determine the amount of $CaCO_3$ of PSAS treated sludge based on the pressure measurement of CO_2 gas, a calibration was previously conducted. Instead of PSAS treated sludge, different amounts of pure $CaCO_3$ were used to react with HCl. The CO_2 gas pressure generated from the chemical reaction presented in Eq (7.1) were measured to make a calibration curve as shown in Fig 7.3. Using this calibration curve, the amount of $CaCO_3$ of PSAS treated sludge can be determined based on the gas pressure of CO_2 generated from the chemical reaction when soaring sludge into HCl solution.

The amount of CO_2 captured was estimated based on the amount of $CaCO_3$. Because the molecular masses of CO_2 and $CaCO_3$ are 44 and 100, respectively, the amount of CO_2 captured per 1 g of dry mass of each sludge specimen, denoted by m_{CO2} ($1/g_{dry\text{-}sludge}$) can be estimated as follows:

$$m_{CO2}(1/g_{dry\text{-}sludge}) = m_{CaCO3}(1/g_{dry\text{-}sludge}) \times 44/100 \quad [7.2]$$

It has a possibility that the pressure in the chamber is not induced by only the generation of CO_2 gas from the chemical reaction as presented in Eq. (7.1) but other gases or sludge had already a certain amount of $CaCO_3$ before the accelerated carbonation. It means that the gas pressure measured as mentioned above does not indicate accurately the amount of CO_2 captured by accelerated carbonation. To evaluate the amount of CO2 captured by accelerating the carbonation of sludge, the test was conducted before and after accelerated carbonation. The difference of pressure measured before and after accelerated carbonation is considered as the pressure induced by CO_2 gas captured. The contribution of PSAS to capture and storage CO_2, the carbonate captured test was conducted for both alkaline sludges treated with and without PSAS followed by the CO_2 captured measurement. The difference between the two measurement is considered the CO_2 captured content induced by PSAS.

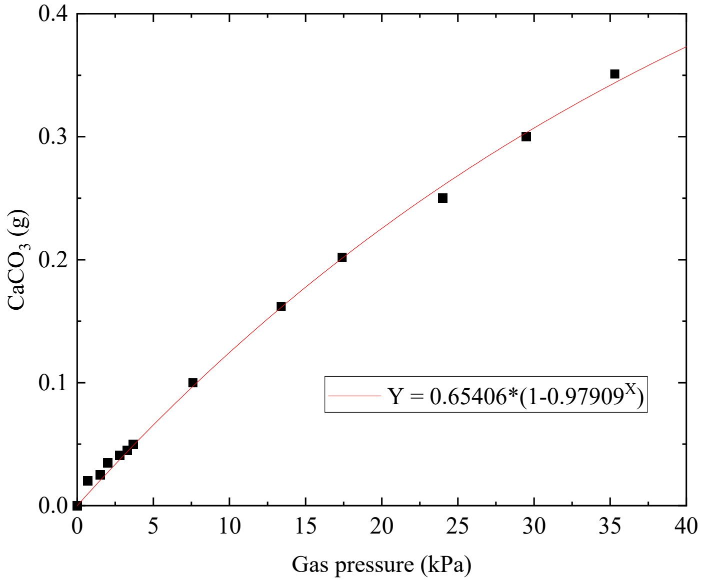


Figure 7.3. $CaCO_3$ evaluated calibration curve

7.2 Investigation of factors influencing CO_2 captured content

Material preparation

To investigate the application of using PSAS treated sludge as a feedstock to capture and storage CO_2, alkaline sludge was produced by mixing Ao clay with an amount of 3% in weight of blast furnace cement type B. Next, PSAS treated sludge was simulated by adding PSAS to the alkaline sludge with a ratio of 20% in weight of dry Ao clay followed by sealed curing. Note that the proportion of PSAS to Ao clay, A_{PS}=20% was chosen because the A_{PS}=20% case performed the minimum of t_N for Ao clay sludge as shown in Fig 3.11(a). In this study, three factors influencing CO_2 capture of PSAS treated sludge were aimed to investigate which are CO_2 concentration in the chamber, dry density, and particle size of sludge samples.

In the preparation, all sludge samples were intentionally adjusted their water to attain the water content of sludge after sealed curing, w_{mud}≈30% prior to accelerated carbonation. This is because 1) the liquid to solid (L/S) ratio around 0.3 was reported as the optimum ratio influencing accelerated carbonation, and 2) as shown in Fig 4.10, min of t_N was generally obtained for all of particle sizes ranging from 0.85 mm to 9.5 mm at w_{mud}≈30%. In addition, t_N of all sludges having particle sizes ranging from 0.85 mm to 9.5 mm are almost equal which implies that it could be more easily controlled the quality of pH neutralization when w_{mud} is around 30%. Depending on the investigation purposes of factors influencing the CO_2 capture, the material preparation as well as experimental conditions were separately set up as shown in Table 7.1. Sludge samples were poured gently into plastic cups and then placed into incubator for accelerated carbonation. The temperature and humidity inside the incubator were set up at 25ºC and more than 90%, respectively.

Table 7.1. Mixture conditions to investigate factors affecting CO_2 captured test

Factors affect CO_2 capture	w_i	A_c (%)	A_{PS} (%)	w_{mud} (%)	ρ_d (g/cm^3)	Particle size D (mm)	Concentration (%)
CO_2 concentration	$1.0w_L$	3	0, 20	30.1~32.0	0.73~0.76	$D<9.5$	1.3, 2.5, 5, and 10
Dry density			20	31.6	0.74		10
				30.9	0.93		
				30.7	1.16		
Particle size	$0.9w_L$			30	0.82	$0.85\leq D<2.0$, $2.0\leq D<4.75$, $4.75\leq D<9.5$	
	$0.76w_L$		0	30	0.84		

Effect of CO_2 concentration degree on CO_2 capture

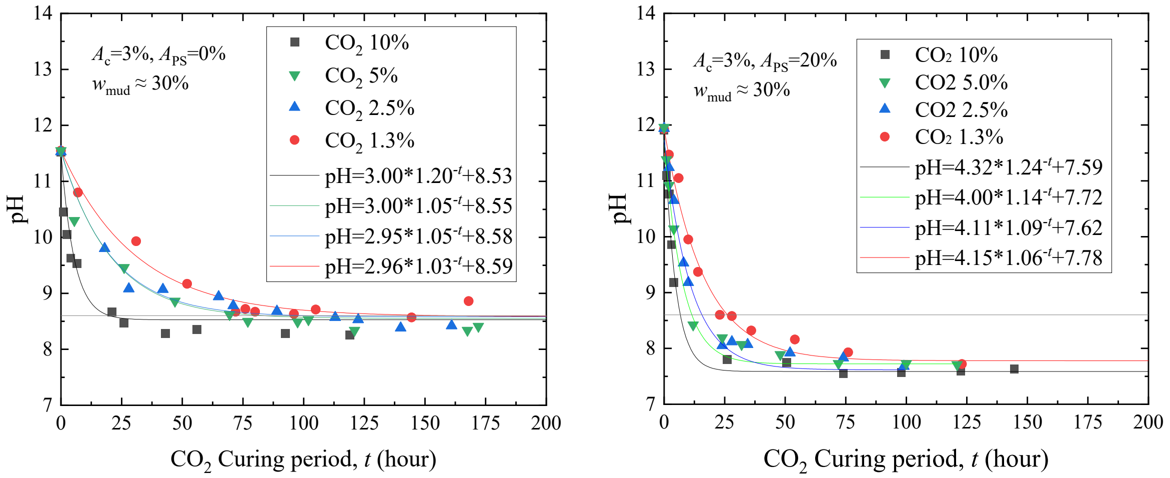


Figure 7.4. Effect of CO_2 concentration on pH neutralization

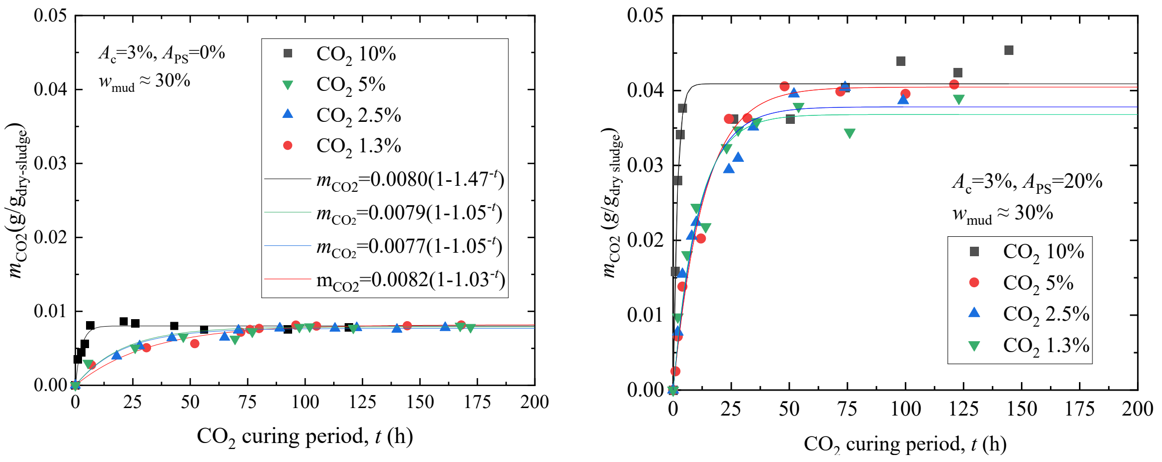


Figure 7.5. Effect of CO_2 concentration on CO_2 capture

The carbon dioxide concentration was found to affect the time that it took for the solution pH to stabilize. Effect of CO_2 concentration on CO_2 captured content of PSAS treated sludge was investigated by a conducting accelerated carbonation under four different CO_2 concentration (i.e., CO_2 concentration of 10, 5, 2.5, and 1.3%). After the preparation, sludges were cured under sealed curing conditions for 5 days, then particle sizes of sludge larger than 9.5 mm were removed. The A_{PS}=20% sludge samples were then cured under CO_2 curing and taken out after arbitrary curing periods up to nearly 150 hours.

Figure 7.4 and 7.5 shows the effects of CO_2 concentration on pH neutralization and CO_2 captured content, respectively. For the CO_2 concentration equal or less than 10%, the results shows that CO_2 concentration significantly affect the pH neutralization, especially at the initial stage of curing periods (the first 24 hours). The higher CO_2 concentration produces the smaller $t_{N,}$ and vice versa. It can be said that the CO_2 concentration is proportional to the pH neutralization rate of A_{PS}=20% sludge. After a long CO_2 curing period, the pHs tended to be gathering and fell to a certain value regardless the CO_2 concentration.

Logically, the pH neutralization rate has the relationship with the CO_2 capture. Indeed, the sludge undergone the highest CO_2 concentration, $C_{CO2=}$10% captured a largest amount of CO_2 as shown in Fig 7.5. The amount of CO_2 captured contents of lower CO_2 concentration degrees were much less than that of the C_{CO2}=10% case. In addition, the difference of CO_2 captured content was negligible for sludge undergone other lower CO_2 concentration degrees (i.e., CO_2 concentration of 5, 2.5, 1.3%). However, even the difference of CO_2 captured content was quite large at the initial stage of CO_2 curing, the final CO_2 captured content after a long CO_2 curing period seems to be gathering regardless CO_2 concentration degrees.

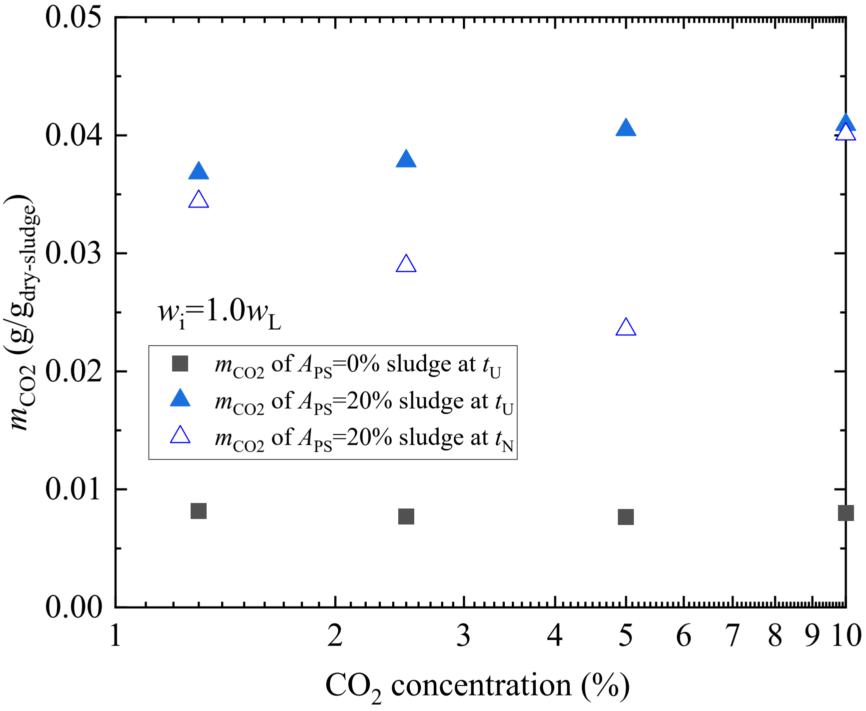


Figure 7.6. Relationship between CO_2 concentration and maximum CO_2 capture

Hence, the CO_2 concentration of 10% remarkably showed the enhancement in capturing CO_2 and pH neutralization, especially in shorten the CO_2 curing period. Fig 7.6 presented the relationship between CO_2 captured after an ultimate curing period, t_U or after t_N and CO_2 concentration. The maximum of CO_2 captured by alkaline sludge was constant with the CO_2

concentration whereas that of PSAS treated sludge was slightly increased. Fig 7.7 shows the relationship between t_N and CO_2 concentration. Obviously, CO_2 captured at t_N is less than at t_U but an interesting point here is the difference in CO_2 captured at t_N and t_U was negligible when the CO_2 concentration is 10% for PSAS treated sludge. This means that the A_{PS}=20% and CO_2 concentration of 10% is not only the optimum conditions for accelerating the carbonation by producing a minimum t_N as mentioned in chapter 3 but also for capturing CO_2. Because PSAS is alkaline material so that A_{PS}=20% is probably just an enough proportion that does not strongly raise the pH while producing an appropriate porous microstructure that facilitate the carbonation reaction of PSAS treated sludge.

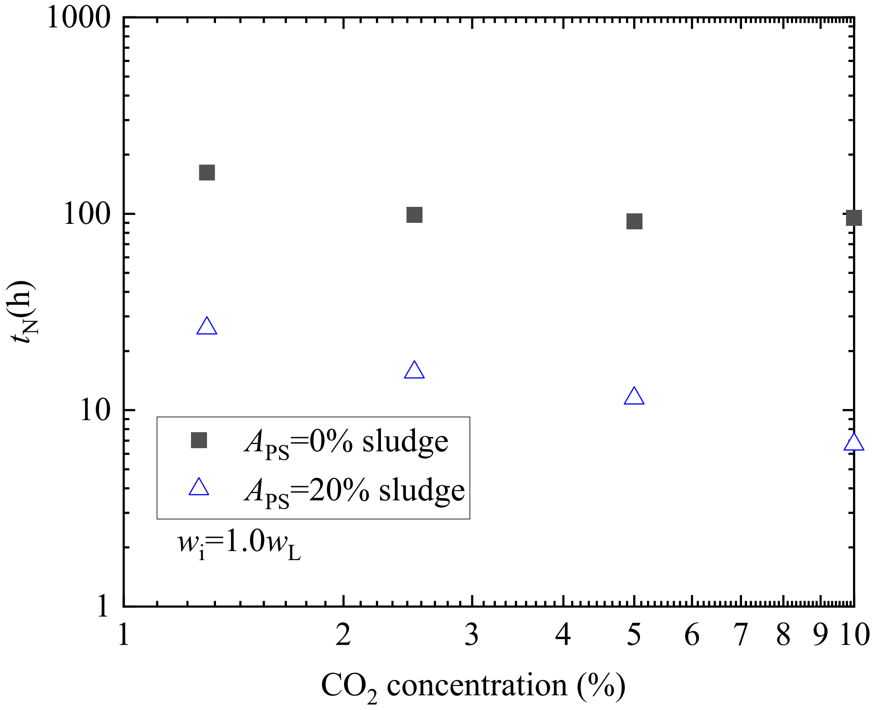


Figure 7.7. Effect of CO_2 concentration on t_N

Effect of dry density on CO_2 capture

To investigate effect of dry density on CO_2 capture, PSAS treated sludge with A_{PS}=20% were prepared. To achieve the different dry density values (i.e., ρ_d = 0.74, 0.93, and 1.16 g/cm^3), sludge samples were gently poured into plastic cups from a zero height then intentionally and statically compressed to achieve a calculated weight prior to the accelerated carbonation. Similar to the investigation of effect of CO_2 concentration on CO_2 capture, the particle size here was also adjust to D<9.5 mm. Sludge samples were cured under CO_2 concentration and temperature of 10% and more than 90%, respectively, then taken out after arbitrary curing periods. Figure 7.8 shows the relationship between dry density and CO_2 captured content of sludge cured under CO_2 curing condition for t_U, and t_N. Again, t_U is the CO_2 curing period to attain the constant CO_2 captured content, and t_N is the needed curing time to neutralize the pH of sludge to 8.6. The results in Fig 7.8 and 7.9 showed that the dry density strongly affected both pH neutralization and CO_2 captured content of the A_{PS}=20% sludge samples.

It can be seen from Fig 7.10 that the CO_2 captured content at t_U is higher than that at t_N but the difference was not significant. CO_2 captured content obtained by CO_2 curing was not significantly increased after t_N. And because t_N of low dry density sludge is much shorter than that of the high dry density sludge as shown in Fig 7.11, the reduction of dry density is expected to neutralize pH to 8.6 as well as to obtain an amount of CO_2 capture which is nearly equal to the maximum CO_2 could be captured within a short curing period.

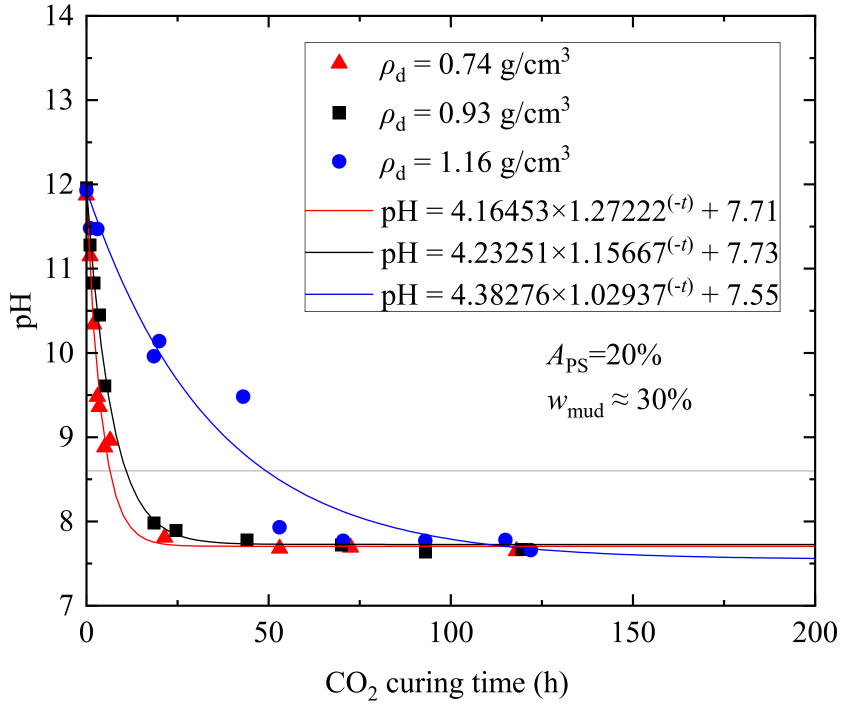


Figure 7.8. Effect of dry density on pH neutralization

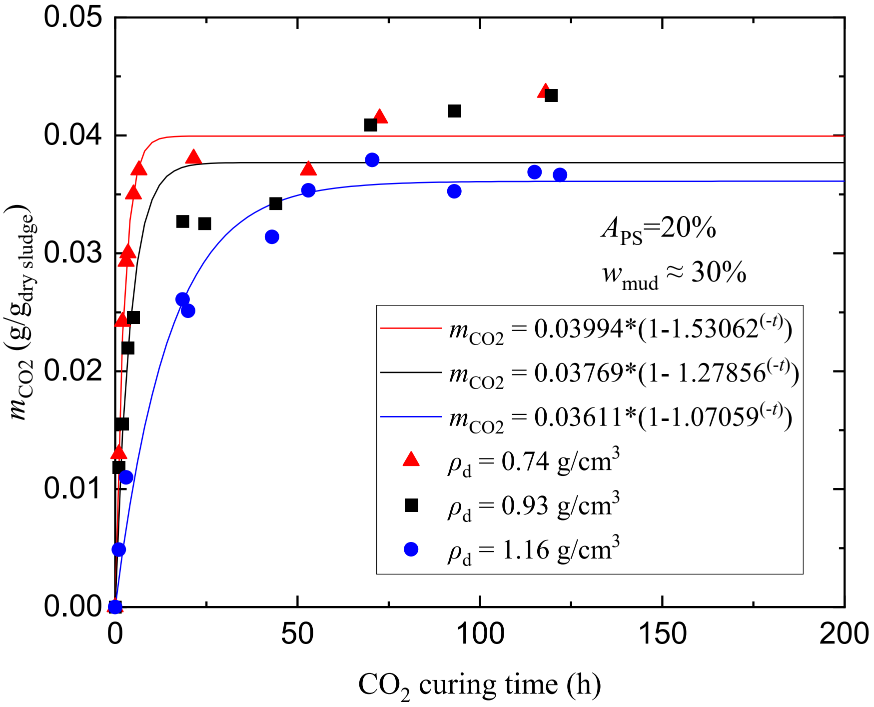


Figure 7.9. Effect of density on CO_2 capture

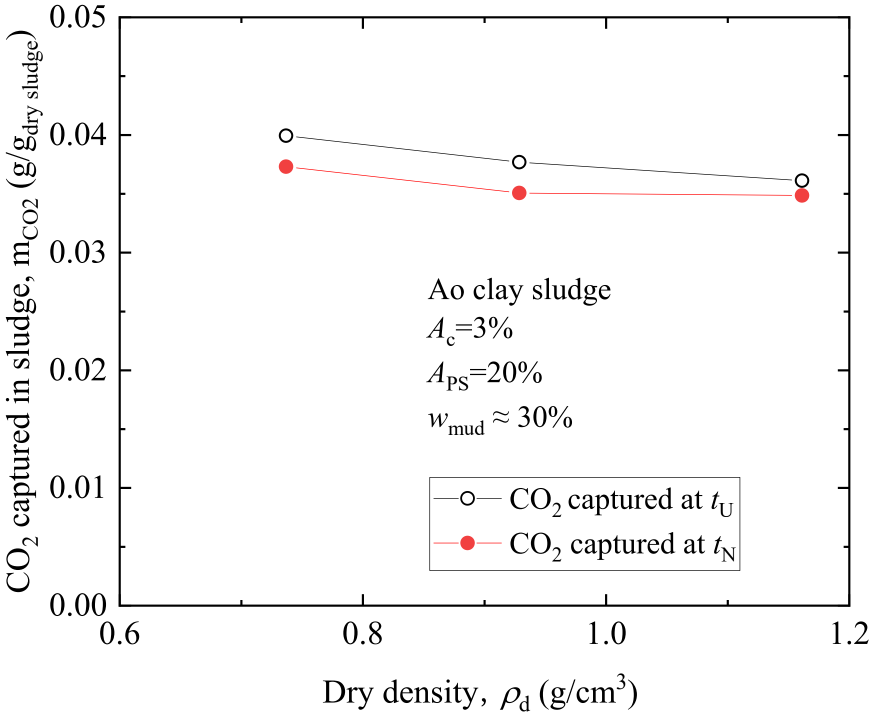


Figure 7.10. Relationship between dry density and CO2 captured content

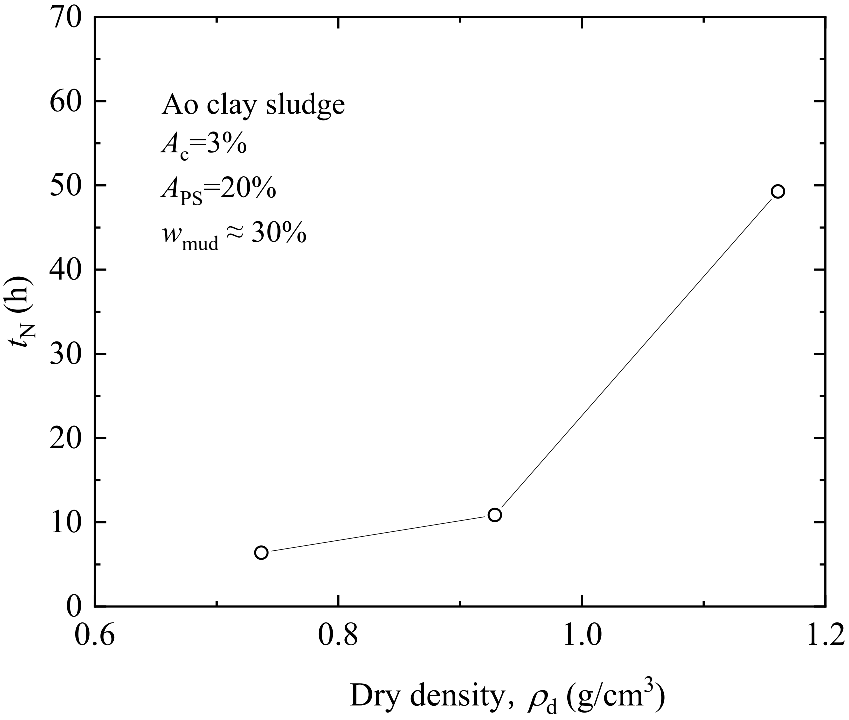


Figure 7.11. Relationship between dry density and tN

CO_2 captured content and pH neutralization rate increase with the decrease in dry density at the initial stage of accelerated carbonation. The ultimate pH and CO_2 capture tends to be gathering for all sludge samples regardless the dry density. However, the value closed to maximum CO_2 captured content and the low and stable pH was rapidly obtained for the low dry density of sludge samples.

Effect of particle size and A_{PS} on CO_2 capture

To investigate effect of particle size and A_{PS} on CO_2 capture, alkaline sludge (A_{PS}=0%) and PSAS treated sludge (A_{PS}=20%) were prepared. The water content of Ao clay was firstly adjusted to w_i=0.76w_L and 0.9w_L to obtain alkaline sludge and PSAS treated sludge having water content, w_{mud} around 30% thereafter, respectively. Sludge samples were then cured under sealed curing conditions for 7 days. After sealed curing, alkaline sludge was crumbled because it was not granulated. Then, the particle size of all sludges was separated into 3 ranges, 0.85 mm $\leq D <$ 2 mm, 2 mm $\leq D <$ 4.75 mm, 4.75 mm $\leq D <$ 9.5 mm and placed in plastic cup for accelerating carbonation by a CO_2 incubator. After accelerated carbonation, pH and CO_2 captured content of sludges were measured. The test procedures of CO_2 captured test was presented in Fig 7.12.

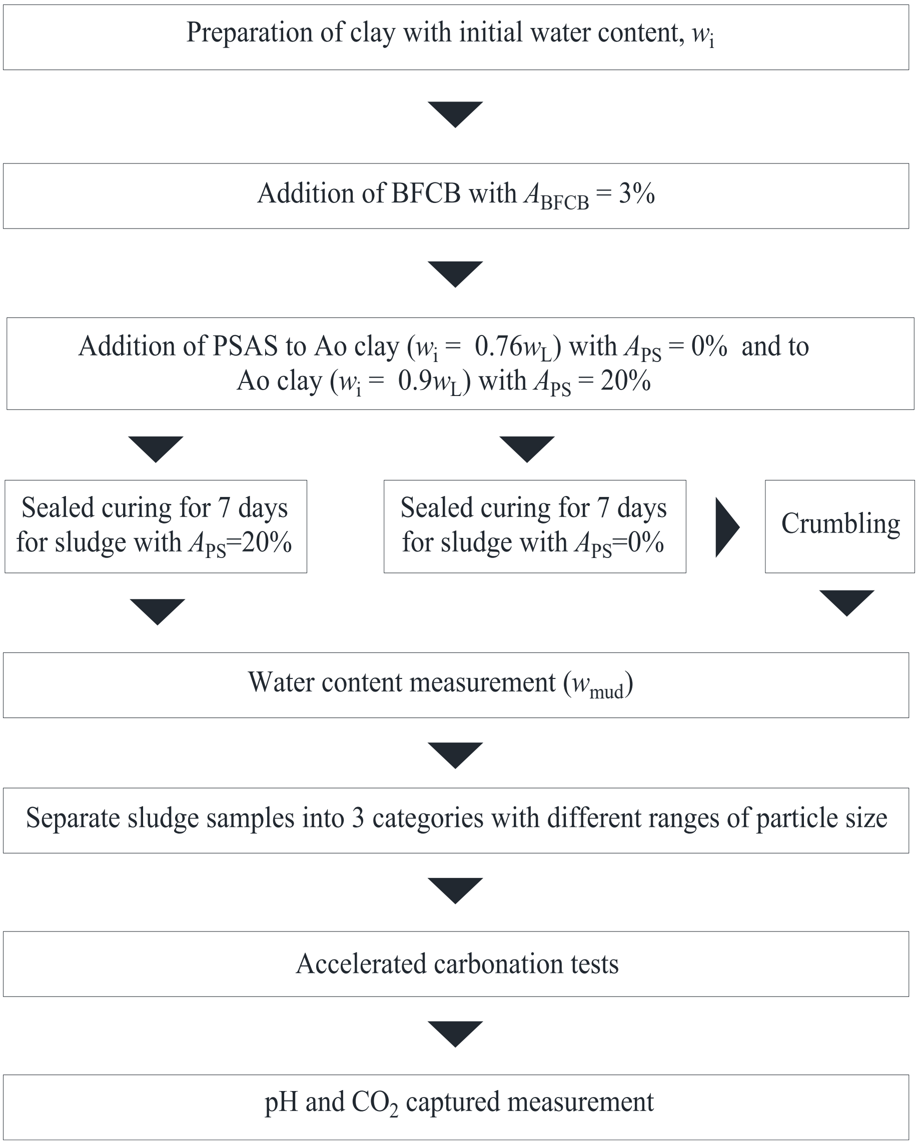


Figure 7.12. Experimental flow to investigate effect of particle size on CO_2 capture

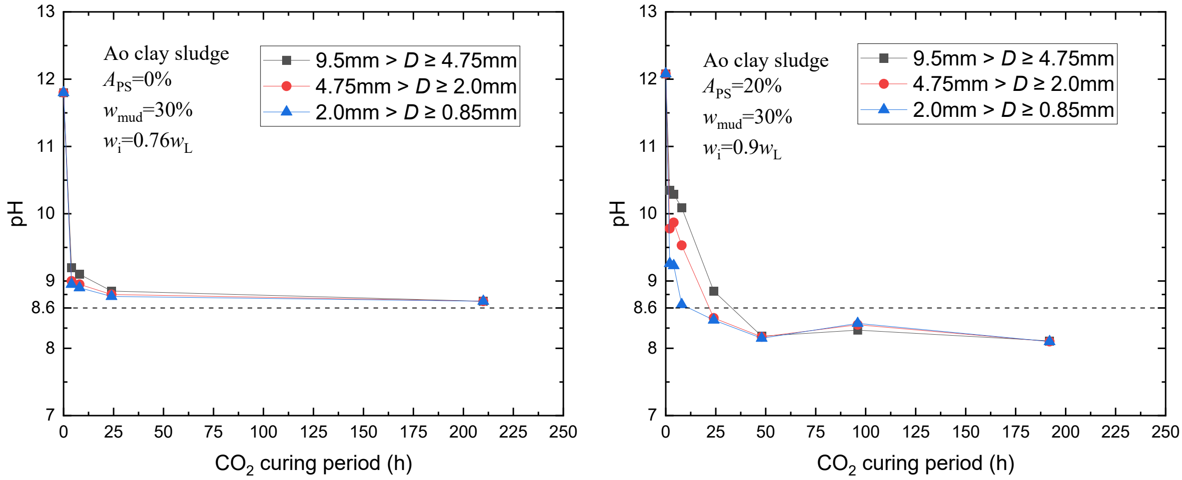


Figure 7.13. Effect of A_{PS} and particle size on pH neutralization

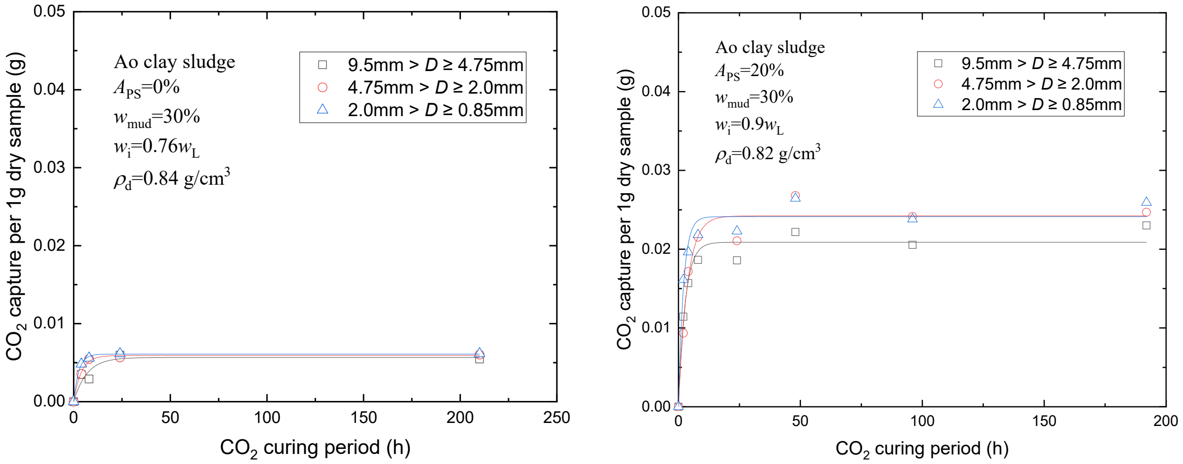


Figure 7.14. Effect of A_{PS} and particle size on CO_2 capture

Before the accelerated carbonation, pH of alkaline sludge and PSAS treated sludge were measured at 11.8 and 12.1, respectively. As presented in Fig 7.13, both pH of alkaline sludge and PSAS treated sludge decrease along the CO_2 curing period. However, only pH of PSAS treated sludge could be fallen to 8.6 whereas that of alkaline sludge maintain stably more than 8.6 even after more than 200 hours of CO_2 curing. This accords with the behavior of accelerated carbonation of alkaline sludge with w_i=w_L as mentioned previously in chapter 3. Even being granulated, results showed that pH of alkaline sludge without PSAS could not be neutralized to 8.6.

It is obvious that the higher A_{PS} causes the higher amount of CO_2 captured content. By adding 20% PSAS by weight of Ao clay to alkaline sludge, the CO_2 captured content was raised generally from 5 g to 25 g CO_2 per 1 kg dry sample. This is because of the high proportion of CaO in the chemical compositions of PSAS (i.e., 63.89%) as presented in Table 3.1. It can be seen that the increase in CO_2 captured content is proportional to the decrease in pH of both alkaline sludge and PSAS treated sludge. Similar to the quick falling of pH at initial accelerated carbonation, most of CO_2 content is captured at the first 24 hours of accelerated carbonation. After that, although CO_2 captured content still increased but with a negligible amount.

Similar to CO2 concentration and dry density, particle size also affected both pH neutralization and CO2 captured content of sludges undergone accelerated carbonation, especially at the initial CO_2 curing period. Basically, the smaller particle size influenced the pH neutralization rate and CO_2 capture, and vice versa for both alkaline sludge and PSAS treated sludge as shown in Fig 7.14.

For summary, the first 24h of accelerated carbonation strongly affect the pH neutralization and CO_2 capture whereas accelerated carbonation thereafter did not produce a significant difference. This was observed for all experimental cases when conducting experiment to investigate factors (i.e., CO_2 concentration, dry density, and particle size and A_{PS}) influencing CO_2 capture.

CHAPTER 8

CONCLUSIONS, LIMITATIONS AND RECOMMENDATIONS

8.1 Conclusions

Construction sludge is frequently existing as liquid state after excavation that makes inconvenient to pile up on a standard dump truck. Thus, in Japan, the construction sludge is commonly treated immediately by mixing cement or other additives to harden the sludge prior to be disposed or recycled. This process raises the pH of construction sludge to around 11 that does not satisfy the environmental requirements in Japan which regulates $5.8 \leq pH \leq 8.6$. The pH of alkaline sludge could be naturally neutralized in atmospheric conditions but very slowly because of the low CO_2 concentration (0.03%). Therefore, this experimental study mainly aims to develop a method to accelerate the pH neutralization of alkaline construction sludge by curing the sludge under high concentration of CO_2. The pH neutralization of alkaline sludge was accelerated by using an CO_2 incubator. To improve the pH neutralization rate of alkaline construction sludge, paper sludge ash-based stabilizer (PSAS) was added to granulate and decrease the particle size of alkaline sludge. Then the crumbling process was produced to treat the alkaline sludge more effectively. Not only that, PSAS showed its effects on improving the strength as well as increasing the capability of CO_2 capture and storage of alkaline construction sludge. The following conclusions are drawn from the research.

a. Effect of PSAS on pH neutralization of alkaline construction sludge and pH rebound

- PSAS showed its effectiveness in shortening the need curing time to neutralize the pH to 8.6 which is called t_N, especially for sludge having high water content. For instance, t_N of alkaline construction sludge prepared from Ao clay (w_i=1.0w_L) was reduced from 95.2 hours to 3 hours by adding 20% of PSAS to clay by weight. For alkaline sludge prepared from Kasaoka clay (w_i=1.0w_L), t_N could not be obtained because after almost 400h of CO_2 curing, pH could not fall to 8.6. However, the addition of a weighted 40% PSAS to Kasaoka clay reduced the t_N to 5.6 h. The A_{PS}=20% and 40% are also the PSAS proportion that produce the optimum t_N for Ao clay sludge and Kasaoka clay sludge, respectively.

- Alkaline sludge prepared from clay (w_i=1.0w_L) appears in lumpy sludge for both Ao clay and Kasaoka clay and t_N was very high or could not be obtained for the ungranulated sludge. The addition of PSAS, A_{PS} significantly granulate the sludge and decrease the particle size. The higher A_{PS} is, the smaller particle size could be achieved that increase the surface area. However, there is a threshold of value that the particle size cannot be decreased by adding PSAS. The increase in A_{PS} just decreases the particle size to a certain value. Consequently, the change in the pH neutralization rate with the change in the particle size become less significant for the sludge with higher addition of PSAS. This is also probably due to the increase in the number of opened voids of the particles with the increase in the number of PSAS particles.

- The optimum t_N was obtained with a certain $A_{PS.}$ Beyond this A_{PS} value, t_N seems increase with the increase in A_{PS} because 1) PSAS itself is high alkaline material so that too much PSAS cannot further decrease the particle size but significantly increase the alkalinity, and

2) because the carbonation requires a certain amount of water surrounding particles, but the high A_{PS} strongly decreases the water of sludge that inhibit the carbonation.

- After the accelerated carbonation, pH rebounded with an increase of around 1.0 then gradually decreased to a certain value. The ultimate pH values were higher than the initially treated ones. The magnitude of pH rebound is inversely proportional to the CO_2 curing period. Hence, it is necessary to neutralize pH to a certain level lower than 8.6 to make sure pH rebounds to a value less than 8.6.

b. Effect of crumbling and pre-air curing

- To decrease the particle size while avoiding the increase in pH caused by a large amount of PSAS, crumbling was considered. Crumbling was applied to PSAS treated sludge with small A_{PS} to investigate the effects of crumbling on accelerated carbonation. The crumbling followed by pre-air curing prior to accelerated carbonation significantly reduced t_N of the alkaline sludge treated with small amount of PSAS because of the reduction of particle size and water content.
- Even being crumbled, t_N of the alkaline sludge (A_{PS}=0%) prepared from Kasaoka clay could not be obtained. This is probably due to the imporous surface and the lack of porosity of the particle of alkaline sludge.
- Based on the experiment results, the production flow of the pH neutralized recycled sludge is suggested. The flow suggested introduces, in addition to the conventional processes of PSAS addition and mixing, two processes, those are curing and crumbling of the treated sludge before the treated sludges are exposed to a concentrated CO2 gas. The granulation via crumbling differs from granulation generated immediately after the addition of PSAS. The granulation via crumbling takes the effects of change in properties of the sludge over time as a result of the hydration reaction of stabilizers into the granulation.

c. Mechanism for contribution of PSAS and crumbling

- The crumbling and the granulation by PSAS decreased the particle size, increased the surface area that influence the accelerated carbonation of PSAS treated sludge.
- The SEM images revealed that PSAS has the surface morphology of porous microstructure with many complex irregularities and voids. By mixing with PSAS, the surface of the A_{PS}=10% sludge particles became more porous with the increase in intra open voids. The addition of PSAS not only effectively absorbs the water and adjusts the water content of sludge to an appropriate content that facilitates the carbonation but also produces the intra open voids that are expected to influence the penetration of CO_2 gas more deeply and widely into the particles.
- PSAS showed its effectiveness in accelerating the carbonation of sludge by producing intra open voids that allows the penetration of CO_2 gas. For the small particle size sludge, the effect of intra open voids induced by PSAS was not significant because of the short distance from the surface to the core of particle. In this case, the low A_{PS} could also produce a short t_N. But for large particle size, the low A_{PS} sludge spent long curing periods to neutralize pH to 8.6 and produced long t_N. Therefore, crumbling is expected to decrease the particle size of low the A_{PS} sludge that influences the pH neutralization.

d. Strength development of accelerated carbonate construction sludge

- Strength of sludge was evaluated by conducting a series of cone index test. PSAS could significantly increase the strength of the sludge and preserve it even after accelerated carbonation. These were attributed to the followings; 1) most of the strength is contributed by the water absorption and retention performance of PSAS, and 2) the granulation by PSAS produces friction among particles. Meanwhile, the strength of alkaline sludge without PSAS was reduced by accelerated carbonation. This was because cement hydrates which alone can contribute the development of the strength, degraded by the carbonation, resulting in the reduction of the bonding strength of the alkaline sludge.
- The crumbling followed by the pre-air curing could further enhance the strength of low A_{PS} sludges because this induces the water reduction due to the evaporation. The granulation by crumbling increased the friction between particles, the water reduction by pre-air curing increased the stiffness of particles and hence improved the strength of sludges.

e. CO_2 capture by accelerated carbonation of alkaline construction sludge treated with PSAS

- CO_2 was successfully captured by using PSAS treated sludge as a feedstock under CO_2 curing.
- The high CO_2 concentration, low dry density, and small particle size of PSAS treated sludge are the factors influencing the CO_2 captured content at the early stage of accelerated carbonation process.
- The CO_2 captured content significantly increased with the curing periods at the early stage of CO_2 curing but then became negligible after t_{N}. This implies that t_{N} could be considered an economical curing period to capture CO_2.

8.2 Recommendations for further study

To comprehensively investigate the application of alkaline construction sludge treated by PSAS and CO_2 curing, together with monitoring the development of strength (q_c), investigation on sludge bearing cyclic loading under the changing of wet and dry curing conditions should be considered.

In practice, CO_2 gas is injected from the bottom to the top of the underground pit storing the sludge. Thus, it should be conducted the experiments of pH neutralization by CO_2 column test to simulate accurately the real conditions of pH treatment.

CO_2 captured content of PSAS treated sludge was evaluated by the gas pressure method. The advantage of this method is simple and can be applied widely anywhere regardless of the conditions of equipment in laboratory. However, it should be compared the results of CO_2 capture obtained by the gas pressure method with other methods such as loss on ignition method or CO_2 column test to have an accurate verification.

Further investigation by mercury intrusion porosimetry should be considered to fulfill the understanding of effect of porosity and specific surface area on pH neutralization of PSAS treated sludge.

REFERENCES

Andrew, R. M. (2018). Global CO_2 emissions from cement production. *Earth System Science Data*, *10*(1), 195–217. https://doi.org/10.5194/essd-10-195-2018

Association, J. C. (2012). *Ground improvement manual using cement-based solidification material* (Vol. 3). Japan Cement Association.

Berger, R. L. (1979). Stabilization of silicate structures by carbonation. *Cement and Concrete Research*, *9*(5), 649–651. https://doi.org/https://doi.org/10.1016/0008-8846(79)90150-9

Berger, R. L., & Klemm, W. A. (1972a). Accelerated curing of cementitious systems by carbon dioxide: Part II. Hydraulic calcium silicates and aluminates. *Cement and Concrete Research*, *2*(6), 647–652. https://doi.org/https://doi.org/10.1016/0008-8846(72)90002-6

Berger, R. L., & Klemm, W. A. (1972b). Accelerated curing of cementitious systems by carbon dioxide: Part II. Hydraulic calcium silicates and aluminates. *Cement and Concrete Research*, *2*(6), 647–652. https://doi.org/https://doi.org/10.1016/0008-8846(72)90002-6

Bukowski, J. M., & Berger, R. L. (1979). Reactivity and strength development of CO2 activated non-hydraulic calcium silicates. *Cement and Concrete Research*, *9*(1), 57–68. https://doi.org/https://doi.org/10.1016/0008-8846(79)90095-4

Cai, G., Du, Y., Liu, S. Y., & Singh, D. (2015). Physical Properties, Electrical Resistivity and Strength Characteristics of Carbonated Silty Soil Admixed with Reactive Magnesia. *Canadian Geotechnical Journal*. https://doi.org/10.1139/cgj-2015-0053

Chang, E.-E., Chen, C.-H., Chen, Y.-H., Pan, S.-Y., & Chiang, P.-C. (2011). Performance evaluation for carbonation of steel-making slags in a slurry reactor. *Journal of Hazardous Materials*, *186*(1), 558–564. https://doi.org/10.1016/j.jhazmat.2010.11.038

Chang, E.-E., Pan, S.-Y., Chen, Y.-H., Chu, H.-W., Wang, C.-F., & Chiang, P.-C. (2011). CO2 sequestration by carbonation of steelmaking slags in an autoclave reactor. *Journal of Hazardous Materials*, *195*, 107–114. https://doi.org/https://doi.org/10.1016/j.jhazmat.2011.08.006

Costa, G. (2009). *Accelerated carbonation of minerals and industrial residues for carbon dioxide storage*.

Costa, G., Baciocchi, R., Polettini, A., Pomi, R., Hills, C. D., & Carey, P. J. (2007). Current status and perspectives of accelerated carbonation processes on municipal waste combustion residues. *Environmental Monitoring and Assessment*, *135*(1), 55–75. https://doi.org/10.1007/s10661-007-9704-4

de Windt, L., Chaurand, P., & Rose, J. (2011). Kinetics of steel slag leaching: Batch tests and modeling. *Waste Management*, *31*(2), 225–235. https://doi.org/https://doi.org/10.1016/j.wasman.2010.05.018

Dong, P. H., Hayano, K., Kikuchi, Y., Takahashi, H., & Morikawa, Y. (2011). Deformation and Crushing of Particles of Cement Treat Granulate Soil. *Soils and Foundations*, *51*(4), 611–624. https://doi.org/https://doi.org/10.3208/sandf.51.611

Duggal, S. K. (2009). *Building Materials*. New Age International (P) Limited. https://books.google.co.jp/books?id=7AaBev3DjZAC

Eloneva, S., Said, A., Fogelholm, C.-J., & Zevenhoven, R. (2012). Preliminary assessment of a method utilizing carbon dioxide and steelmaking slags to produce precipitated calcium carbonate. *Applied Energy*, *90*(1), 329–334. https://doi.org/https://doi.org/10.1016/j.apenergy.2011.05.045

Eloneva, S., Teir, S., Salminen, J., Fogelholm, C.-J., & Zevenhoven, R. (2008). Steel Converter Slag as a Raw Material for Precipitation of Pure Calcium Carbonate. *Industrial & Engineering Chemistry Research*, *47*(18), 7104–7111. https://doi.org/10.1021/ie8004034

Fernández Bertos, M., Li, X., Simons, S. J. R., Hills, C. D., & Carey, P. J. (2004). Investigation of accelerated carbonation for the stabilisation of MSW incinerator ashes and the sequestration of CO2. *Green Chem.*, *6*(8), 428–436. https://doi.org/10.1039/B401872A

Fukue, M., Nakamura, T., & Kato, Y. (1999). Cementation of Soils Due to Calcium Carbonate. *Soils and Foundations*, *39*(6), 55–64. https://doi.org/https://doi.org/10.3208/sandf.39.6_55

Gerdemann, S. J., O’Connor, W. K., Dahlin, D. C., Penner, L. R., & Rush, H. (2007). Ex Situ Aqueous Mineral Carbonation. *Environmental Science & Technology*, *41*(7), 2587–2593. https://doi.org/10.1021/es0619253

Goldberg, P., Chen, Z.-Y., O’Connor, W., Walters, R., & Ziock, H. (2001). CO2 Mineral Sequestration Studies in the U.S. *Conference: National Conference on Carbon Sequestration, Washington DC, (United States), 15-17 May 2001.*

Goodbrake, C. J., Young, J. F., & Berger, R. L. (1979a). Reaction of Beta-Dicalcium Silicate and Tricalcium Silicate with Carbon Dioxide and Water Vapor. *Journal of the American Ceramic Society*, *62*(3–4), 168–171. https://doi.org/https://doi.org/10.1111/j.1151-2916.1979.tb19046.x

Goodbrake, C. J., Young, J. F., & Berger, R. L. (1979b). Reaction of Hydraulic Calcium Silicates with Carbon Dioxide and Water. *Journal of the American Ceramic Society*, *62*(9–10), 488–491. https://doi.org/https://doi.org/10.1111/j.1151-2916.1979.tb19112.x

Goyal, S., & Sharma, D. (2020). CO2 sequestration on cement. In F. Pacheco-Torgal, E. Rasmussen, C.-G. Granqvist, V. Ivanov, A. Kaklauskas, & S. B. T.-S.-U. C. (Second E. Makonin (Eds.), *Start-Up Creation* (pp. 109–142). Woodhead Publishing. https://doi.org/10.1016/b978-0-12-819946-6.00006-0

Haug, T., Kleiv, R., & Munz, I. (2010). Investigating dissolution of mechanically activated olivine for carbonation purposes. *Applied Geochemistry - APPL GEOCHEM*, *25*, 1547–1563. https://doi.org/10.1016/j.apgeochem.2010.08.005

Hayano, K., Yamauchi, H., Wakuri, N., & Tomiyoshi, S. (2016). A New Granulation Method with the Process of Crumbling Partially-cemented Liquid Muds and its Application to a Motocross Track. *Procedia Engineering*, *143*, 98–103. https://doi.org/https://doi.org/10.1016/j.proeng.2016.06.013

Huntzinger, D. N., Gierke, J. S., Sutter, L. L., Kawatra, S. K., & Eisele, T. C. (2009). Mineral carbonation for carbon sequestration in cement kiln dust from waste piles. *Journal of Hazardous Materials*, *168*(1), 31–37. https://doi.org/10.1016/j.jhazmat.2009.01.122

Iizuka, A., Fujii, M., Yamasaki, A., & Yanagisawa, Y. (2004). Development of a New CO2 Sequestration Process Utilizing the Carbonation of Waste Cement. *Industrial & Engineering Chemistry Research*, *43*(24), 7880–7887. https://doi.org/10.1021/ie0496176

Imai, K., Hayano, K., & Yamauchi, H. (2020). Fundamental study on the acceleration of the neutralization of alkaline construction sludge using a CO2 incubator. *Soils and Foundations*, *60*(4), 800–810. https://doi.org/https://doi.org/10.1016/j.sandf.2020.05.008

Kamon, M., Boutouil, M., Jeoung, J., & Inui, T. (2003). Microstructure and Leaching Characteristics of Sludge Treated with Low Alkalinity Additives. *Soils and Foundations*, *43*(2), 105–114. https://doi.org/https://doi.org/10.1016/S0038-0806(20)30805-2

Kamon, M., Jeoung, J. H., & Inui, T. (2005). Alkalinity control properties of the solidified/stabilized sludge by a low alkalinity additive. *Soils and Foundations*, *45*, 87–98.

Kamon, M., Katsumi, T., & Oyama. (1996). Environmental impact and control of alkaline migration by cement stabilized soil. *Environmental Geotechnics*, *2*, 751–756.

Kato, Y., Imagi, G., Ohmukai, N., Mochizuki, Y., Saito, E., & Yoshino, H. (2005). Studieson improvement of liquid mud by use of paper sludge ash. *40th Japan National Conference on Geotechnical Engineering*, 677–678.

Kawai, S., Hayano, K., & Yamauchi, H. (2018). Fundamental study on curing effect and its mechanism on the strength characteristics of PS ash-based improved soil. *Journal of Japan Society of Civil Engineers, Ser. C (Geosphere Engineering)*, *74*, 306–317. https://doi.org/10.2208/jscejge.74.306

Kawasaki, K., & Ishimito, K. (1992). Technology of treatment and utilization of surplus soils in construction work-Improvement technology for sludge produced in shield tunneling work: PMF super additive for sludge produced using industrial waste effectively. *Mon. J. Sewerage*, *15*, 81–84.

Kitazume, M., & Terashi, M. (2013). *The Deep Mixing Method*. Taylor & Francis. https://books.google.com.vn/books?id=15A4WRNqkuEC

Kumar, S., Amit, S. K., & Islam, M. (2016). *Application of paper sludge ash in construction industry – a review*.

Lekakh, S. N., Rawlins, C. H., Robertson, D. G. C., Richards, V. L., & Peaslee, K. D. (2008). Kinetics of Aqueous Leaching and Carbonization of Steelmaking Slag. *Metallurgical and Materials Transactions B*, *39*, 125–134.

Li, X., Bertos, M. F., Hills, C. D., Carey, P. J., & Simon, S. (2007). Accelerated carbonation of municipal solid waste incineration fly ashes. *Waste Management*, *27*(9), 1200–1206. https://doi.org/https://doi.org/10.1016/j.wasman.2006.06.011

Lim, M., Han, G.-C., Ahn, J.-W., & Yoo, K. (2010). Environmental Remediation and Conversion of Carbon Dioxide (CO2) into Useful Green Products by Accelerated Carbonation Technology. *International Journal of Environmental Research and Public Health*, *7*, 203–228. https://doi.org/10.3390/ijerph7010203

Maroto-Valer, M. M., Fauth, D. J., Kuchta, M. E., Zhang, Y., & Andrésen, J. M. (2005). Activation of magnesium rich minerals as carbonation feedstock materials for CO2 sequestration. *Fuel Processing Technology*, *86*(14), 1627–1645. https://doi.org/https://doi.org/10.1016/j.fuproc.2005.01.017

Metz, B., Ogunlade, D., Coninck, H. de, Manuela, L., & Meyer, L. (2005). *Carbon dioxide capture and storage*. https://doi.org/https://www.ipcc.ch/report/carbon-dioxide-capture-and-storage/

Mochizuki, Y. (2016). Study on subjects and applicability for mud improvement due to mixing with paper sludge ash. *Japanese Geotechnical Society Special Publication*, *4*, 105–108. https://doi.org/10.3208/jgssp.v04.j19

Mochizuki, Y. (2019). Evaluation of water absorption performance of various PS ashes produced with different incineration methods and its applicability for mud improvement 焼却方法が異なる各種PS灰の吸水性評価と泥土改質への適用性. *Journal of Japan Society of Civil Engineers, Ser. C (Geosphere Engineering)*, *75*, 155–166. https://doi.org/10.2208/jscejge.75.155

Mochizuki, Y., Saito, E., Yoshino, H., & Takaaki Ogata. (2003). *Effects of soil improvement due to mixing with paper sludge ash*.

Monkman, S., & Shao, Y. (2010). Carbonation Curing of Slag-Cement Concrete for Binding CO2 and Improving Performance. *Journal of Materials in Civil Engineering - J MATER CIVIL ENG*, *22*. https://doi.org/10.1061/(ASCE)MT.1943-5533.0000018

Nabeshima, Y. (2002). Neutralization of crushed cement-stabilized sludge by carbon dioxide. *Proceedings of 4th International Congress on Environmental Geotechnics, 2002*, *1*, 475–479.

Nakarai, K., & Yoshida, T. (2015). Effect of carbonation on strength development of cement-treated Toyoura silica sand. *Soils and Foundations*, *55*(4), 857–865. https://doi.org/https://doi.org/10.1016/j.sandf.2015.06.016

Nishi, Yamada, M., Suzuki, M., & Takeo. (2004). Neutralization of Cement-Stabilized with Carbon Dioxide. *Mem. Fac. Eng. Osaka City Univ.*, *45*.

Pan, S.-Y., Chang, E. E., & Chiang, P.-C. (2012). CO2 Capture by Accelerated Carbonation of Alkaline Wastes: A Review on Its Principles and Applications. *Aerosol and Air Quality Research*, *12*(5), 770–791. https://doi.org/10.4209/aaqr.2012.06.0149

Phan, N. B. (2021). Development of new water absorption and retention evaluation method for PS ash-based stabilizers and its geotechnical applications. *Doctoral dissertation* [Yokohama National University]. https://doi.org/doi/10.18880/00014114

Phan, N. B., Hayano, K., Mochizuki, Y., & Yamauchi, H. (2021). Mixture design concept and mechanical characteristics of PS ash–cement-treated clay based on the water absorption and retention performance of PS ash. *Soils and Foundations*, *61*(3), 692–707. https://doi.org/https://doi.org/10.1016/j.sandf.2021.02.006

Seifritz, W. (1990). CO2 disposal by means of silicates. *Nature*, *345*(6275), 486. https://doi.org/10.1038/345486b0

Shi, C., Wang, D., He, F., & Liu, M. (2012). Weathering properties of CO2-cured concrete blocks. *Resources, Conservation and Recycling*, *65*, 11–17. https://doi.org/https://doi.org/10.1016/j.resconrec.2012.04.005

Shoji, M., Morioka, M., Yoshida, T., & Nakarai, K. (2014). Investigation on mechanism of long-term strength development of carbonated cement-treated sand. *Cement Science and Concrete Technology*, *68*(1).

Tai, C. Y., Chen, W.-R., & Shih, S.-M. (2006). Factors affecting wollastonite carbonation under CO_2 supercritical conditions. *Aiche Journal*, *52*(1), 292–299. https://doi.org/https://doi.org/10.1002/aic.10572

Trung, N. D., Ogasawara, T., Hayano, K., & Yamauchi, H. (2021). Accelerated carbonation of alkaline construction sludge by paper sludge ash-based stabilizer and carbon dioxide. *Soils and Foundations*. https://doi.org/https://doi.org/10.1016/j.sandf.2021.06.012

Umino, M., Komine, H., Murakami, S., & Setoi, K. (2014). Carbon Dioxide Fixation Properties and Mechanism of Steel Slag in the Use for Formation of Low-carbon Society. *Japanese Geotechnical Journal*, *9*, 469–478. https://doi.org/10.3208/jgs.9.469

Watanabe, Y., Nguyen Binh, P., Hayano, K., & Yamauchi, H. (2021). New mixture design approach to paper sludge ash-based stabilizers for treatment of potential irrigation earth dam materials with high water contents. *Soils and Foundations*, *61*(5), 1370–1385. https://doi.org/https://doi.org/10.1016/j.sandf.2021.08.004

Yi, Y., Liska, M., Unluer, C., & Al-Tabbaa, A. (2013a). Carbonating magnesia for soil stabilization. *Canadian Geotechnical Journal*, *50*(8), 899–905. https://doi.org/10.1139/cgj-2012-0364

Yi, Y., Liska, M., Unluer, C., & Al-Tabbaa, A. (2013b). *Initial investigation into the carbonation of MgO for soil stabilisation* (Vol. 5).