

Master's Programme in Geoengineering

Carbon Dioxide Sequestration Capacity of Stabilized Malmi Clay

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Abstract

For decades, various deep mixing methods have been implemented for improving the engineering properties of poor ground condition. The huge amount of material and energy involved in deep mixing opens opportunity for significant reduction in environmental impact. The search for ways to developing environmentally friendly deep mixing practice is getting popular by day.

This thesis aimed at examining on CO₂ sequestration capacity of Malmi clay stabilized with different binder types in laboratory conditions. Variety of binders produced from recycled material and low CO₂ emission were used in the study.

Carbonation of stabilized samples were performed in autoclave and carbonation chamber where the effect of carbonation environments on CO₂ absorption assessed. Thermogravimeter analysis (TGA) were used to measure the amount of CO₂ absorbed by carbonated-stabilized samples. The strength development was studied using unconfined compression test while microstructures analysis was investigated using Scanning Electron Microscope (SEM).

Carbonation of stabilized soil samples has shown to be a soil stabilization technique which can generate zero carbon dioxide emission. For the four binder types studied, the sequestration capacity of carbonated-stabilized soil was found to range between 2.8% to 4.1% of dry mass or 25 to 37 kg per cubic meter of mixture. The binder type that has the biggest potential to be carbon negative was Nordkalk Terra GTC3. While the use of plant fly ash (UPM Jämsänkoski) with Cement type II as an activator has shown to bring an emission value closer to zero. Despite its relatively high sequestration capacity of Cement type III the relatively bigger emission at production of binder holds the effort to reach zero emission value. Carbonation has shown to reduce 70% of the emission factor during production of cement type III. Carbonation was found to have effect on compressive strength (UCS) of stabilized clay. For samples under normal CO_2 environment the strength was lower (by 17% to 80%) than the reference samples strength. Whereas, for samples under elevated temperature and pressure environment the compressive strength found to vary by binder type.

Keywords CO₂ sequestration, sustainable deep mixing, Stabilized clay, Recycled binder, Thermogravimeter

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Preface

The work presented in this thesis deals with the sequestration capacity of clay soil with different binders. The study was carried out within CARBMIX2LIFE prestudy research project at Aalto university. My supervisor was Prof. Kork-iala-Tanttu Leena. The laboratory tests were done in Aalto university and VTT laboratories.

Financial support of the project was provided by Helsinki city, Espoo City, Vantaa City, Finnish transport infrastructure agency (FTA) and Tiina and Antti Herlin Foundation. The steering group consisted of Veli-Matti Uotinen (FTA), Mirva Koskinen (city of Helsinki), Heikki Kangas (city of Vantaa), and Silke Savikurki (city of Espoo).

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Abbreviations

CEMI	Cement type I/52.5 R
CEMIII	Cement type III/A 52.2L
CEMI_SC	Cement type I stabilized clay
CEMIII_SC	Cement type III stabilized clay
CFA	Coal fly ash
CASH	Calcium aluminate silicate hydroxide
CSH	Calcium silicate hydroxide
DTG	Derivative of thermogravimeter plot
GGBS	Ground granulated blast furnace slag
GTC3	Nordkalk Terra GTC binder with CEMIII
GTC3_SC	GTC3 stabilised clay
kg CO ₂ eq. e.	Kilo gram carbon dioxide equivalent emission
SEM	Scanning Electron Microscopy
SCO2	Supercrtitical carbon dioxide (CO ₂ held above its critical
	temperature and critical pressure)
TG	Thermogravimeter
TGA	Themogravimeter analysis
UPM	Fly ash from UPM-Kymmene Oyj, a Finnish forest industry
	company
UCS	Unconfined compressive strength
UCEMI_SC	Fly ash from UPM Jämsänkoski factory + cement type I sta-
	bilized clay
UCEMII_SC	Fly ash from UPM Jämsänkoski factory UPM + cement
	type II stabilized clay

1 Introduction

The increasing global population raised the demand for expanding civil infrastructure construction in areas which are undeveloped and/or previously bypassed due to weak soil condition. Construction of civil infrastructure on clay soil is often difficult due to its insufficient strength, excessive compressibility, or shrinkage and swelling property with time. Thus far, various method of deep mixing has been implemented on poor soil condition; however, implementing sustainable ground improvement techniques that ensures suitable ground for infrastructure needs with low environmental impact is still an existential challenge for engineers. This thesis study CO_2 sequestration capacity of stabilised soil towards promoting the use of ground improvement in CO_2 sequestration technology.

The thesis focuses on experimental investigation of CO₂ sequestration capacity of stabilised Malmi clay. The thesis aims to answer the following research questions: how much CO₂ can be absorbed through carbonation of stabilized clay? What is the effect of binder type on CO₂ absorption capacity of stabilized clay? What is the effect of carbonation on strength of stabilized clay?

The absorption capacity of stabilised clay was studied by mixing four binder types. The four binder mixtures were selected from Nordkalk Oy, UPM-Kymmene Oyj, and two more from Finnsementti Oy.

Clay and binder mixture was made using dry mixing method in laboratory scale. For each sample six specimen were prepared where three of them served as a reference while the remaining three were placed in carbonation environment. Two carbonation vessels where used - carbonation chamber and auto clave. Three different carbonation environments were investigated in two carbonation equipment. The carbonation environment differs in CO₂ content, CO₂ pressure, temperature and duration of carbonation.

Thermogravimeter analysis were used to obtain the amount of weight loss from decarbonation, from which the amount of bound CO₂ was estimated. The strength of stabilised clay was assessed using unconfined compression test at 28 and 90 days of curing. To assess the effect of carbonation on microstructure of carbonated samples, a Scanning Electron Microscope (SEM) analysis was performed on natural clay, stabilized reference sample and stabilized carbonated sample.

The experiment was done at laboratory scale which might produce the maximum potential of CO₂ sequestration than investigation performed on site stabilisation. The study is delimited to one clay type (Malmi clay), which is a natural clay with low organic content. Further, the experiments are done for single binder content per binder type and three parallel samples were considered per one experiment.

The thesis presents the result and discussion from experimental study of CO₂ sequestration capacity of different binder types exposed in different carbonation environment and duration. Net CO₂ emission factor (kg CO₂ eq./m³) of carbonated stabilized clay was used as an indicator to identify binder mixture with the lowest CO₂ equivalent emission. The CO₂ sequestration capacity of 1 cubic meter mixture was deducted from the manufacturer emission factor (kg CO₂ eq./binder content) of the binder to obtain net emission factor.

2 Literature review

2.1 Background

Ground improvement is an expanding sector of geotechnical engineering driven by high demand for civil infrastructure on previously bypassed areas due to poor ground condition or/and new areas with challenging ground condition. The huge quantity of material and energy involved in geotechnical work gives an opportunity for significant reduction in environmental impact.

To minimize energy consumption and carbon dioxide emissions; geotechnical engineering sector could play leading role by improving geotechnical construction material and practices therefore enhancing sustainability of the natural system. The consideration of both the economic cost and environmental impact when deciding the design alternatives of geotechnical ground improvement projects can lead to more sustainable projects (Shillaber et al., 2015).

One of the widely used ground improvement method is deep soil stabilization. Deep soil stabilization (or deep mixing) is a method of soil stabilization by mixing binder with soft soil in order to improve the engineering properties of the soil. Soil stabilization has main interest to increase the strength of soft soil, improve deformation properties and increase dynamics stiffness of the soft soils. The binder can be mixed with the soil in dry method or wet method. In dry method the binder power will be mixed with soil where the binder reacts chemically with the pore water during curing. While in wet mixing, a slurry of binder and water is used. Dry method is widely used in Nordic countries (Design Guide Soft Soil Stabilization, 2010).

The soil stabilization can be made either by forming a column of stabilized soil (column stabilization) or by stabilizing the entire soil mass (mass stabilization) (Design Guide Soft Soil Stabilization, 2010). Column stabilization is used to stabilize soil in deep depth (up to 25 meters in Nordic countries) while mass stabilization can achieve up to 5 meters in normal soil condition and up to 8 meters in favourable soil conditions. The efficiency of mixing process will mainly determine the soil improvement attained (Hansbo, 1994).

The common type of binder used in soil stabilization has been a mixture of lime and cement (two component). Whereas the use of three component binder could also be most suitable. Other binder blends used in soil stabilization are gypsum, blast furnace slag and/or fly ash. The mechanical and chemical properties of clay or peat will determine the appropriate binder type

used for stabilization. After mixing of the binder with clay will change the chemical and physical significantly, where the strength development depends on the type of binder. In most stabilized soil using cement only as binder, the strength development takes place in the first month. Whereas if other binder types used in combination (i.e. lime, gypsum, blast furnace slag or fly ash) the chemical reaction and curing could go more than a month (EuroSoilStab, 2010).





Clay-binder chemical reaction

The various chemical reaction processes occurring in soil stabilization with varieties of binder have been presented by several literatures. However, the widely studied binder types for stabilization are cement and lime (Åhnberg, 2006). Stabilization of clay caused by cement and lime occurs by ion exchange. The ion exchange has effect on undrained shear strength of soil. As such the type of ion involved influence undrained shear strength, biggest effect is achieved by aluminum ion whereas calcium ion has limited effect (Hansbo, 1994).

The choice of binder depends on varies factors including soil properties and soil type. A mixture of cement and lime has greater strength and low compressibility than a stabilized soil with only lime. Cement can stabilize any type of inorganic soils, where it will best stabilize well graded soil with less than 50% fine and plasticity index less than 20%. Fly ash and gypsum are also used in a condition such as in silt with clay content below 20% and as to improve organic soil, respectively (Hansbo, 1994).



Figure 2-2 rough outline of the principal chemical reaction and reaction products formed by different types of binders in soil (Åhnberg, 2006)

Chemical composition of binders determines the rate of reaction and reaction type in the mixture. It can be possible to characterize various binders based on the content of CaO, AI_2O_3 , and SiO_2 . An increased reactivity of binder is related to the higher content of total CaO + AI_2O_3 + SiO_2 (Taylor, 1997 as cited in Åhnberg, 2006).

Generally higher amount of CaO is attributed to high potential forming large reaction product in the soil. Whereas, in slag the ratio of CaO to is small, thus the initial reactions are slower in binder containing slag than cement. Pozzolanic reactions are characterized by slow rate due to the limit availability of alumina and silica in the soil. In cement reaction forming Calcium silicate hydroxide (CSH) is already available in the binder thus the reactions are faster than pozzolanic reactions with the soil(Åhnberg, 2006).

2.2 Emission from production of binders

The process manufacturing binder from raw material and delivering it to construction site involves emission of CO₂ to the environment. The emission is from the production of the binder, the raw material transportation to the production factory and the transportation of binder to construction site. The major portion of the emission related to binder occur during the production process of the binder (Betoniteollisuus ry, 2022). A data on the equivalent emission factor CO₂ in tonne per production of a tonne of binder was obtained from manufacturers. The data is presented in the table below. the reported emission amount does not include the emission from transportation of binder to the construction site.

Supplier	Binder type	tonne CO ₂	kg CO ₂ eq.	kg CO2 eq.	
	& Designa-	emis-	emis-	emission	
	tion	sion/tonne	sion/ton	/100kg	
				Binder	
Finnsementti*	CEMIII/A	0.47	470	47	
	52.2L				
	CEMII/B-	0.626	626	62.6	
	M(s-LL)				
	42.5N				
	CEMI 52.5 R	0.776	776	77.6	
UPM-Kym-	UPM Jäm	0.0	0.0	0.0	
mene					
Оуј					
	UPM+CE-	0 * 0,7 + 0,626	187.8	**28.2	
	MII (7:3)	* 0,3 = 0,178			
Nordkalk	Nordkalk	0.186	186	18.6	
Oy***	GTC3				
*Courses DV love	Loorbon aloogifi	antion nort 1 (Dat	apitaellieuue	m ()())	

Table 2-1 Equivalent CO2 emission value of binder production reported bysuppliers

*Source: BY- low carbon classification part 1 (Betoniteollisuus ry, 2022) **CO₂ eq. emission per 150kg of binder (70% UPM and 30% CEMII) ***Source: (Nordkalk, 2022a) also presented under Annex 4.

As presented in table 2-1, cement type CEMI has the highest equivalent CO₂ emission, while GTC3 has the least emission value. More environmentally friendly alternative is substitution of cement with recycled material (i.e., blast furnace slag, fly ash) as such cement type CEMIII has lower emission value than ordinary cement (cement type CEMI).

2.3 Carbon dioxide sequestration

Carbonation is a natural chemical reaction where atmospheric CO2 dissolved in water react with hydration products of binder (e.g., calcium hydroxide, magnesium hydroxide, calcium hydrate, and calcium aluminum hydrate) to form carbonates (e.g., calcium carbonate, magnesium carbonate (Kaliyavaradhan and ling 2017 as cited by Tiwari et al., 2020). The chemical reactions are shown in equation 1 to 3.

$$Ca (OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$
(1)

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

 $3CaO \cdot Al_2O_3 \cdot 13H_2O + 4CO_2 → 4 CaCO_3 + 2 AI (OH)_3 + 10 H_2O$ (3)

2.3.1 Effect of pressure and temperature on carbon dioxide sequestration

The recent development in creating sustainable ground improvement method, studies in assessing CO₂ the sequestration capacity of stabilized soil are getting popular. In this subsection, the effect of carbon dioxide test environment varying in pressure and temperature is reviewed.

Previous studied done on carbonation of soil and/or concrete materials found the pressure of carbon dioxide environment, the duration of carbonation and the moisture content of the mixture affects the CO₂ sequestration of different materials. Carbonation of engineering materials were investigated by several studies including carbonation of cement stabilized clay (Cai and Liu, 2017), olivine treated clay (Fasihnikoutalab *et al.*, 2017), reactive MgO treated silt (Cai and Liu, 2017), reactive MgO treated silty clay (Yi *et al.*, 2013), coal fly ash (Ukwattage et al., 2013); Revathy *et al.*, 2015) and GGBS stabilized clay (Mohammed *et al.*, 2017). Some studies has also explored the effect of exposing stabilized clay to different CO₂ pressure, duration of exposure (Fasihnikoutalab *et al.*, 2017) and availability of water in the mix (Mohammed *et al.*, 2021; Yu *et al.*, 2021).

On studies performed on coal fly ash (CFA) response to carbonation, high CO₂ pressure was found to increase the diffusion of CO₂ in coal fly ash slurry and faster rate of carbonation (Ukwattage, Ranjith and Wang, 2013; Revathy *et al.*, 2015). Direct carbonation of fly ash indicated that the rate of carbonation is affected by CO₂ pressure and duration. On the other hand, the availability of alkaline oxide in the fly ash slurry is the controlling factor (Fernandez Bertos et al., 2009 as cited by Revathy *et al.*, 2015).

Emmanuel *et al.*, (2021), indicated that for olivine-activated clay the formation of MgCO₃ is affected by olivine content, CO₂ pressure and CO₂ exposure duration. The study investigated the effect of olivine concentration, carbonation duration and carbonation pressure on hydraulic conductivity of olivine-treated clay which was planned for hydraulic barrier material in land-fills. The study identified the optimum olivine content, CO₂ pressure and CO₂ exposure duration to be 24.7%, and 161 kPa and 20.1 hours, respectively. With the prementioned optimum values the hydraulic conductivity of the clay was reduced by 98%.



Figure 2-3 Sequestration capacity of CFA at room temperature with (a) varying Co2 initial pressure (b) varying reaction time at constant CO₂ Pressure of 1000 kPa (1 bar=100 kPa) (Revathy *et al.*, 2015)

Revathy *et al.*, (2015) investigated the CO₂ sequestration capacity of CFA. Samples were exposed to a CO₂ pressure of 200, 400, 600 and 1000 kPa for constant duration (1 hour) at room temperature. The CO₂ absorption capacity show increase with increase in pressure. In figure 2-3, the effect of duration of carbonation was investigated at a constant pressure of 1000 kPa, sequestration capacity of CFA reached its maximum capacity in 1 hour which then showed slight decrease at slow rate and stable. In the study it was also suggested from the result that the presence of water was observed to influence the carbonation process, as the water has a vital role in dissolution of both CO₂ and metal species.

2.3.2 Effect of pressure and duration on strength of stabilized clay

Fasihnikoutalab *et al.*, (2017), investigated effect of alkali concentration and CO_2 pressure on stabilization of soil by applying CO_2 pressure of 100 kPa and 200 kPa for a duration 12, 24, 48 and 168 hours. UCS test of 90 days cured sample indicated that the higher CO_2 pressure and duration samples (200 kPa, 168 hour) were found to have higher UCS than samples at lower pressure and smaller CO_2 duration, see figure 2-4.



Figure 2-4 UCS of carbonated alkaline-activated olivine-treated soil exposed to carbonation for 12, 24, 48 and 168 hours with CO₂ pressure of 100 and 200 kPa (Fasihnikoutalab *et al.*, 2017).

Mohammed *et al.*, (2021) studied the effect of carbonation on GGBS stabilized brown kaolin clay. Strength gain of 20 and 25% GGBS mixed kaolin was examined in terms of CO₂ pressure (100 kPa and 200 kPa), carbonation period (1,3, 6, and 24 hour) and curing duration of 24 hour and 7 days. The result suggested that the strength gain in GBBS stabilized kaolin clay was highly related to the CO₂ pressure (100 kPa and 200 kPa). While the strength development increment observed to reach peak during first one hour of carbonation then show slow rate of increase afterwards.

Whereas, a study by Yu *et al.*, (2021) found the drastic increase CO₂ absorption for the early 4 hours carbonation and followed by gradual increase for 72 hrs. Carbonation of MgO treated silty soil seen to attain 28 day strength equivalent in 1hr, 1.5hr and 3hr for CO₂ pressure of 200 kPa, 100 kPa and 50 kPa (Yi *et al.*, 2013).

Yi *et al.*, (2013) indicated that, for carbonation of the same mix, increase in CO₂ pressure will result in shorter carbonation period and the strength gain will be attained faster. The study also investigated the relation of binder content and carbonation period under same CO₂ pressure, with increase in binder content the carbonation period required to achieve the 28-day equivalent strength get longer. Thus, the result suggest that the use of higher CO₂ pressure will insure faster carbonation and strength gain.

Yu *et al.*, (2021), performed laboratory scale investigation of strength performance of carbonated steel slag stabilized experimental soil. The raw materials for laboratory prepared soils where from powder of quartz (AS-Q), kaolinite (AS-K), and montmorillonite (AS-M). Samples were prepared by mixing the soil with 30% steel slag (by total dry mass of soil) at moisture content from 12% to 24%.

The samples were carbonated with 200 kPa CO₂ pressure for a duration of 4 and 24 hour. The study aimed to get the optimum moisture content and carbonation time for the highest strength gain and CO₂ uptake of steel slag stabilized soil. In figure 2-5, the result on the effect of moisture content on CO₂ absorption capacity and strength of steel slag stabilized clay showed that the CO₂ capacity increase with an increase in moisture content of the mix to a certain optimum content (18%, 20% & 22% for slag mixed with quartz, kaolinite, and montmorillonite clay, respectively). Which then declined in both the strength and the CO₂ absorption of the carbonate-stabilized clay (Yu *et al.*, 2021).



Figure 2-5 (a.) Effect of moisture content on CO₂ absorption capacity and UCS of steel slag stabilized quartz (AS-Q-S-C2) (b.) CO₂ absorption of three types of carbonated steel slag stabilized soils with moisture content (Yu *et al.*, 2021)

In conclusion, the CO₂ pressure has significant effect on the total amount of CO₂ sequestration by clay. In the beginning carbonation was seen to happen fast during the early hours of carbonation, which could be affected by binder, organic clay, and silt type, and continue to gradually increase with slow rate afterwards. The highest CO₂ absorption capacity was found to be related to certain optimum moisture content of stabilized clay and the optimum moisture content varies with the type of clay mineral. However, there is a need to study the CO₂ absorption capacity of stabilized clay in its natural moisture content and clay mineral characteristics.

2.4 Thermogravimeter analysis

One of the methods used for studying CO₂ sequestration capacity of materials is thermogravimetry analysis. Several studies have used TGA instrument for determining carbonation content (Revathy *et al.*, 2015; Unluer and Al-Tabbaa, 2013; Cai and Liu, 2017; A. M.A. Mohammed *et al.*, 2021; Yu *et al.*, 2021).

This subsection describes thermogravimeter (TG) and derivative of thermogravimeter (DTG) curve interpretation. In the figure 2-6, the Thermogravimeter test result of CEMIII stabilized clay presented. This plot will be used for illustration while reviewing previous studies about thermogravimeter plot. Thermogravimeter result of test performed at end of carbonation (5-days) and after 28-days of curing are presented (figure 2-6). Thermogravimeter instrument measures the weight loss of specimen in the furnace along with the temperature in the furnace. The plot of TGA graph is for the phase 2 of the analysis, which is temperature starting 105 °C to 950 °C.

A point on the weight percent curve indicates how much of the percentage of sample weight remained on the pan as a given temperature (figure 2-6). For example, at a point k (figure 2-6), the sample has lost 6% of its weight by the time the furnace has reached 680 °C.

Only observing the weight-temperature graph it is difficult to accurately determine the temperature at the start, center, or end of decomposition step or if it is centered around multiple decomposition steps. Whereas, from derivative of weight-temperature graph, the peak temperature at which a specific decomposition occur can be observed. Thus, by using weight-temperature graph and derivative of weight-temperature graph one can determine the temperature range related to the specific decomposition. When calculating the weight loss for a decomposition, two points should be selected. One before and another after the peak temperature, the difference in weight between two points is weight change for the decomposition step.



Figure 2-6 TGA result for CEMIII carbonated specimen using autoclave (autoclave I) -presented for illustration purpose

In figure 2-6, three clear peaks can be seen at temperature ranges of <250 °C, 300 °C to 580 °C and 600 °C to 800 °C. These large peaks originate around 600°C and drop back to straighter after reaching around 800 °C. According to previous studies the first peak may be associated to removal of bound water or crystallization water with in carbonated sample (Yu *et al.*, 2021; Cai and Liu, 2017). The peaks are centered around 728 °C and 740 °C for specimen tested at 5 days and 28 days respectively. These peaks are close to calcite peak (720°C) found on Thermogravimeter plot of steel slag stabilized clay by Yu et al. (2021).

Unluer and Al-Tabbaa (2013) indicated that mass loss in temperature range 250 °C to 475 °C (second peak) may be attributed to the dehydroxylation of brucite (Mg (OH)₂) and calcium hydroxide (Ca (OH)₂) that has not yet carbonated. In the thermogravimeter analysis (TGA) of steel slag stabilized clay carbonation the peak temperature for brucite (Mg (OH)₂) and calcium hydroxide (Ca (OH)₂) was identified to be around 380 °C and 430 °C, respectively. In the study these peaks were seen do disappear on TGA plots of carbonated sample. Similarly, here reference specimen has peaks at 300 °C to 580 °C (figure 4-1) which is seen to be very low peak on TGA plot of carbonated specimen (figure 2-6).

Regarding the third large peak previous studies obtained various temperature range all referring to decomposition of carbonate (Cai and Liu, 2017). These peaks can also clearly be seen on thermogravimeter test result presented on figure 2-6. Thus, in figure 2-6, the weight loss between 475 °C and 800 °C could be due to decarbonation of calcium and magnesium. Yu et al (2021) attributed, in a study of steel slag stabilized kaolinite and montmorillonite clay, the decomposition of calcite to be in a temperature range of 550 °C to 750 °C.

In figure 2-6, the thermogravimeter curve of reference sample the decomposition in a temperature range of 350 °C to 600 °C could be attributed to decomposition of clay mineral. As Yu et al (2021) found the decomposition of kaolinite and montmorillonite clay to be in a temperature range of 400 °C to 650 °C and 500 °C to 720 °C, respectively. This may indicate the possibility of overlap in temperature range of decomposition of carbonates and clay minerals. In the study, the TGA result was found consistent with XRD results of same samples.

Furthermore, the content of calcite computed from thermogravimeter analysis (TGA) plot in a temperature range of 550 °C to 750 °C, was obtained to be 4.8% to 4.93% for steel slag stabilized kaolinite and montmorillonite clay, respectively (Yu *et al.*, 2021).



Figure 2-7 Thermogravimeter and derivative of thermogravimeter result of concrete samples at different curing duration (Dung et al., 2018)

Figure 2.7 shows the thermogravimeter analysis and derivative of thermogravimeter result of reactive magnesium oxide cement (RMC) based concreter samples from a study by Dung et al (2019). For MgO stabilized cement. The study has found that weight loss from decarbonation was found to be 5.0%, 5.2%, 6.1%, 6.4% and 6.6% at curing duration of 1 day, 3 days, 7 days, 14 days, and 28 days, respectively.

2.5 Microstructure analysis of stabilized clay

Scanning electron microscopy (SEM) analysis is one of analysis methods used to investigate the microstructure change in treated/stabilized and untreated soil. The method is used in several studies to investigate the formation, development and growth of cementitious products, strength development, effect of carbonation and the effect of curing period of stabilized soil (Nontananandh *et al.*, 2005; Horpibulsuk *et al.*, 2010; Yi *et al.*, 2013; Fasihnikoutalab *et al.*, 2017; Chen *et al.*, 2020; Yu et al. 2021).

SEM image investigation of natural clay soil displayed sheet-like structure which are flaky in shape and plate like particles (Nontananandh *et al.*, 2005). Carbonate formation in soils (mainly clay and silt), as revealed using SEM, exhibit compact morphology without major discontinuity (Yi *et al.*, 2013; Fasihnikoutalab *et al.*, 2017) and agglomeration around clay particles (Chen *et al.*, 2020).

A qualitative morphological SEM analysis on red clay mixed with precipitated calcium carbonate, Chen *et al.*, (2020) revealed calcium carbonate spindles are embedded in the lamellar soil layers in random distribution with no specified shape. Calcium carbonate particles are bigger particle size than clay particles (Chen *et al.*, 2020).

Yi *et al.*, (2013), SEM images of MgO stabilized soil, carbonated samples display dense microstructure and show formation of nesquehonite and dypingite-hydromagnesite. At early stage of curing (0.5hr) the formation brucite was displayed which disappear in at longer duration (6hr).

Fasihnikoutalab *et al.*, (2017) investigated SEM on stabilized soil which undergo carbonation at CO₂ pressure of 200 kPa for 12, 24, 48 and 168h duration. In the study, olivine (Mg₂SiO₄) from 0 to 20% propotion was used to treat soil (silt-60%, clay-30% and sand-10%). Morphonologal anlaysis of SEM image 20% olivine treated samples at 90 days of curing shows compact and more homogenous microstructure with longer carbonation duration.

Horpibulsuk *et al.*, (2010) investigated the strength development of cementstabilized silty clay by using SEM and UCS. Based on SEM images from 3-, 7-, 28- and 90-day stabilized samples, the formation of calcium silicate hydrate (CSH) and ettringite were determined. With longer curing period growth of reaction products and hardened ettringites lead to largening of soil-cement cluster. These states were seen, by the researchers, as the reaon for denser and stronger stabilized soil structure as time progresses.

Ettringite has significant effect in strength of stabilized soil (Ahmed, 2014). In the study by Ahmed (2014), the volume and size of ettringite increased with the longer curing duration. The amount of ettringite is much influenced by the availability of silica and alumina in the stabilized soil. When the amount of silica and alumina is not sufficient to form ettringite other minerals will react with calcium to form calcite, gypsum and pozzolanic compounds (Ahmed, 2014).

Figure 2.8 and 2.9 shows SEM images of steel slag stabilized quartz (AS-Q-S-C2), steel slag stabilized kaolinite (AS-K-S-C2) and steel slag stabilized montmorillonite (AS-M-C2). As shown in the figure 2.8 and 2.9, the SEM analysis result of carbonated steel slag stabilized clay, Yu et al., (2021) found spindle like cluster. According to Nielsen et al., (2020) cited by (Yu et al, 2019) calcite could be observed from SEM images as a spindles like structure formation on morphology of carbonated product. The study by Yu et al. (2021) had considered four hours and 18 hours carbonation duration. The author has indicated that the SEM images results showed larger calcite formation for carbonated steel slag carbonated for 18hr than the ones carbonated for four hours.



Figure 2-8 SEM images of AS-Q-S-C1 (a) steel slag stabilized quartz (AS-Q-S-C1) (b) local magnification-10k for (a)

The study had performed wetting and drying cycle on carbonated sample. The SEM analysis of carbonated samples after six drying and wetting cycle showed consistent calcite without sign of decomposition. This indicates generated calcite is table over the time of drying and curing cycle and after the end of drying and wetting cycle (Yu *et al.*, 2021).



Figure 2-9 AS-K-S-C2 and AS-M-C2 (c) steel slag stabilized kaolinite (AS-K-S-C2) (d) local magnification-10k for (c) (e) steel slag stabilized montmorillonite (AS-M-C2) (f) local magnification 10k for (e) (Yu *et al.*, 2021)

3 Research material and methods

3.1 Raw materials

3.1.1 Malmi Clay

Soil samples were obtained from Malmi old airfield, Helsinki, Finland (figure 3-1 & 3-2). The ground surface elevation at the site is around +15.2 m above sea level. Hard stratum elevation on the site varies between +8.1m to +4.2m above sea level while the estimated depth of dry crust is 1 meter.



Figure 3-1 Satellite map showing the sampling area (former Malmi airport and location of sampling points, Malmi, Helsinki, Finland (Geological Survey of Finland)



Figure 3-2 Geological map of Malmi former airfield, Malmi, Helsinki, Finland (Geological Survey of Finland)

Figure 3-3 below shows index properties of selected samples from point 43 and 45. The index properties presented include water content, undrained shear strength of undisturbed samples (S_u), sensitivity (S_t), density and unit **weight of samples unit weight (\gamma) and density. Visua**l assessment of sample showed that, the soil exhibits grey-clay and some black dots at depth between 1.17 m and 2.21 m. Some silt indicative points were observed on specimens at depth 3.69 m and 4.69 m. Several samplings were performed on the test site for other studies in the laboratory and the sampling points are located very close to one another (less than 2 meter), table 3-1 shows a nearby sampling point index and chemical properties of Malmi clay on the northern side. In addition, representative index properties were performed on selected sampling points (43, 45 and 49) and results are presented in the figure (3-3).





The clay moisture content is recorded high from 2 meter to 4 meter which is 100% to 125%. Whereas the water content in deeper depth (4m to 5 m) is below 80%. Thin silty layer formation was observed on sample between 4 to 5 m depth. Based on the index property tests, it was recommended to use clay soil found at a depth 2.5 m to 5 m. A total of eight sampling points used for the study. The sampling points were 34, 36, 43, 44, 45, 47,48 and 49.

Malmi old-airfied northern site

DEPTH (M)	W (%)	ρ (g/cm ³)	C _{u-100} (kPa)	C _{u-10} (kPa)	St	Estima- ted o' vo (kPa)	Organic content LOI (%)	рН
1.19-1.25	95.3	19.0	12.3	0.7	17.1	19.0	1.1	5.2
1.69-1.75	54.9	22.4	10.9	0.6	19.1	22.4	0.9	6.2
2.19-2.25	104.5	24.8	12.7	0.3	39.6	24.8	1.6	6.8
2.69-2.75	124.3	26.9	9.9	0.3	37.9	26.9	1.6	7.0
3.19-3.25	134.3	28.9	9.7	0.3	34.5	28.9	2.0	7.2
3.69-3.75	95.6	31.4	11.8	0.3	45.4	31.4	0.9	7.6
4.19-4.25	104.4	33.7	10.2	0.3	40.8	33.7	0.9	7.8
4.69-4.75	55.1	37.1	16.9	-	-	37.1	1.3	8.1
5.19-5.25	95.1	39.5	16.8	0.3	56.0	39.5	1.4	8.4
5.69-5.75	60.3	42.8	32.4	0.4	73.6	42.8	0.6	8.4
6.19-6.25	52.9	46.5	20.0	0.5	41.6	46.5	1.3	8.3
6.69-6.75	40.9	50.7	35.1	0.3	113.2	50.7	0.9	8.4

Table 3-1 Index properties of the Malmi clay

Figure 3-4 below shows the pH values of clay samples at different depths, which were determined in the laboratory. From the figure it shows that the clay has acidity at the top layers (top 1.5 meter) and getting more alkaline with increase in depth. For the selected clay (2.5 m to 5 m) for stabilization the pH range between 5.8 and 7.8. pH test on sampling point 49 at depth 1.7 m and 2.21 m was tested to be 5.96 and 7.29, respectively. Which is a typical soil pH profile for most Finnish clay layer.



Figure 3-4 Natural pH values of Malmi clay at different depths (north site)

3.1.2 Binders

A total of four binder types were used and investigated to strength and CO₂ sequestration capacity of stabilized clay. These were ordinary Portland cement (Cement type I), and the remaining three binders are produced partly from recycled materials from industries. The binders were obtained from three binder suppliers Finnsementti Oy, Nordkalk oy and UPM-Kymmene Oyj.

<u>Nordkalk Oy</u>

Nordkalk oy manufactures several binders that are manufactured for soil stabilization. Nordkalk GTC3 is one of the new blends supplied by the manufactured with lowest CO₂ equivalent emission per tonne. Nordkalk GTC3 contains gypsum (33%), slaked lime (33%) and cement type III (33%) (Nordkalk, 2022a).

<u>Finnsementti Oy</u>

Cement type I (CEMI 52.5 R), Cement type II (CEMII / B-M (S-LL) 42.5 N) and Cement type (CEMIII/A 52.2L) were obtained from Finnsementti. Cement type III has replaced about 40% to 45% of cement by a blast furnace slag. Whereas in Cement type II 21% to 35% of cement is replaced with lime-stone and blast furnace slag. The detail information and constitute the products are presented in the Annex 4.

<u>UPM-Kymmene Oyj</u>

The binder designated as UPM Jämsänkoski is produced from plant fly ash. The manufacturer produces the fly ash from forest residues and wood by-products sawdust, bark, and sludges (UPM-Kymmene Oyj 2020 as cited by Nguyen T. 2021). In the study cement was used as an activator for the fly ash. Thus, UPM was mixed with CEMII at proportion of 70% (UPM) and 30% (CE-MII).

Table 3-2 Binder type and	proportion u	used for stabilization	of Malmi clay
---------------------------	--------------	------------------------	---------------

Binder Designa-	Binder
tion	amount
	kg/m³
CEMIII/A 52.2L	100
CEMI 52.5 R	100
UPM Jäm+CEMI (7/3)	100
UPM Jäm+CEMII (7/3)	150
GTC3	100

3.2 Sample preparation methods

A. Binder content

As presented in Table 3-2, 100 kg/m³ binder content was used for three of the binders, Nordkalk-GTC3, CEMIII and CEMI. For the fourth binder, UPM, the activator amount used was 30% of the total weight of design binder. At the beginning, for experiments performed in carbonation chamber, CEMI was used as activator for UPM fly ash (UPM+CEMI (7/3)) with 100kg/m³ binder content. Then what was noted from the 14th days strength test result was that the sample has significantly low hardening, which was indicated by the low UCS (<50 kPa). Thus, for the samples prepared for the next experiments, experiments in autoclave, it was proposed to change the activator and increase binder content for UPM fly ash. Hence, for all samples experimented using autoclave CEMII were used as activator and binder content of (UPM+CEMII (7/3)) 150 kg/m³.

B. <u>Clay -binder mixing, mould size, number of specimen and compaction</u> A batch of mix was prepared which equal the amount of six specimens, out of which three specimens were carbonated and the remaining three were reference specimen. The size of mould for the test specimens had diameter of 50 mm and height of 100mm. Compaction was done in five layers with 10 blows for each layer. The moisture content of a batch was recorded.

The average density clay was computed which then was used to compute the weight of binder required for preparing six specimens. The mixing of clay and binder was performed at room temperature. As shown in figure 3-5a mixing was done using a hook-like mixer tool fixed in a mechanical mixing equipment. The mixing time was five minutes.





Figure 3-5 (a)tools used for clay-binder mix sample preparation (b) Claybinder mixer. The first plan was to extrude specimen from the mould just after preparation of specimen. However, from visual observation it was noticed that the specimen loosens and deforms from its original vertical form. To avoid such problem specimens were allowed to cure in the mould for 24hr at room temperature. Specimen for carbonation was extruded and placed in carbonation chamber or autoclave for carbonation, see figure 3-4b. Whereas the reference specimens were placed in storage room. Samples are tightly covered by plastic bags to avoid moisture loss during storage, see figure 3-6b. The storage room had a controlled temperature replicating the temperature in deep ground where clay material was sampled. The storage room had a temperature of $6\pm 2^{\circ}C$.



b.
Figure 3-6 (a) 3 samples extruded from plastic tube and prepared for carbonation (b) Samples in plastic tube covered with plastic bags and stored in

at temperature of 6±2°C

C. <u>Experiment matrix, binders, carbonation method, curing dates, speci-</u><u>mens</u>

Four binder types were used to stabilize the clay. The curing dates considered are 14 days, 28 days, and 90 days. The experiment matrix is shown in the figure below.



Figure 3-7 plot indicating the experimental test matrix

3.3 Carbonation experiments

Carbonation of samples were done in two different carbonation instruments. First, in carbonation chamber, the carbonation environment had CO₂ content of 0% to 15% at atmospheric pressure. The second carbonation environment is in autoclave. Autoclave is a pressure vessel which enable placing sample in a vessel with 100% CO₂ environment and possibility of raising temperature to required level.



Figure 3-8 carbonation instruments (a) carbonation chamber (b) autoclave

The sequestration capacity of sample was tested at three curing durations after carbonation of samples. The samples carbon dioxide sequestration capacity was evaluated by placing samples in different temperature and pressure amount. The carbonation environments considered in this study varies in carbonation method (the carbonation instrument), carbon dioxide concentration in chambers, duration of carbonation and curing duration. Table 3-2 shows detail information about the carbonation environments considered in this study.

Table 3-2 experimental work detail for carbonation using autoclave with CO₂ content 99%.

Carbonation	Autoclave							
equipment								
Co2 concen-		99%						
tration (%)								
Carbonation		5				5		
_period (days)								
Curing pe- riod (days)		28				28		
Binder type	GTC3	UPM+CEMII	CEM	CEMI	GTC3	UPM+CEMII	CEM	CEMI
		(7/3))	111			(7/3))	111	
Cell tempera-	95 to	98 degree Celsiu	s & 6.6 to 7	.4 MPa	22.5°C	to 24°C & 4.8 to 4	4.97MPa	
ture & CO ₂								
Pressure								
Binder Con-	100	150	100	100	100	150	100	100
tent (kg/m³)								
No of sample	4	4	4	4	4	4	4	4
(per method)								
Carbonation	Autoclave I_SCO ₂				Autoclave II_CO ₂			
environment								
namo					1			

Table 3-3 experimental work detail for carbonation using carbonation chamber

Carbonation	Carbonation chamber								
equipment									
Co ₂ concen-	10-15%								
tration (%)					1070				
		10			1		01		
Carbonation		13					21		
period (days)									
Curing period		14				28	& 90		
(days)									
Rinder type	CTC		CEM	CEM	CTC			CEM	
Binder type	GIC		CLIVI	CLIVI	GIC			CLIVI	
	3	(//3))			3	(//3))	111		
Cell tempera-		11 degree Celsius	& 0.1013 k	Pa	22.5-24 degree Celsius & 0.1013 kPa				
ture & CO ₂		0				0			
Prossure									
Ne efermale	/	/	/	/	/	/	/		
No or sample	0	0	0	0	0	D	0	0	
(per method)									
Binder Con-	100								
tent (ka/m³)									
Carbonation	- Carbo	nation chamber I	II (14 day)	T-110C	Carb	onation chamb	or IV (28 d	(00) V (00)	
	Carbonation chamber in (14-day) _1=n-c Carbonation chamber in (22-day) V (90-								
environments	day)_1=11°C								

3.3.1 Carbonation using autoclave

Autoclave consists of a high-pressure steam vessel with thermometer and pressure gauge. In addition, it has a vent valve to allow the escape of air, at the time of degassing the vessel, and to release of steam pressure at the end of the cooling pressure. It is possible to heat up recording temperature and pressure data simultaneously. Enough water should be added to the autoclave so that saturated steam will be maintained (AASHTO, 2007). Thus, at initial temperature of (+24 to +27 °C) 100 ml water was added to the autoclave.

The specimens were placed on circular steel racks so that all sides of specimen exposed to the gas in the autoclave. The first step was to place rack with specimen in the vessel and tighten up the vessel cover. Connect the inflow valve to CO₂ gas container and release the outflow valve to take out air present inside the cell. After 15 minutes, the outflow valve will be closed, and the inflow will be kept open until it equals the maximum pressure of CO₂ gas container. Two carbonation environments were tested using autoclave, see table 3-1.

In autoclave two environments were created. The first is normal temperature and carbona dioxide pressure, which is named as autoclave II. The second carbonation environment in autoclave is created by raising the pressure and temperature to 7400 kPa and 95 °C, respectively. The method in autoclave where the pressure and temperature are raised from the normal is named as autoclave I. This naming, autoclave I and autoclave II are used to refer carbonation performed in autoclave at raised pressure and temperature and at normal pressure and temperature, respectively.

In autoclave I, a supercritical CO₂ environment was created in the autoclave. The CO₂ is set to be in pressure and temperature above its critical point above 7200 kPa (72 bar) and temperature above +31.1 °C (Sihvonen *et al.*, 1999). After attaining the maximum pressure from the gas container, the heat supply of the vessel was turned on and the inflow valve was closed. It is heating up stopped as the pressure reach 7400 kPa (74 bar) at a temperature of +98°C. Specimen has stayed in vessel for 5 days with a slight temperature fluctuation of +97±2 °C. During the first day, the pressure drops from 7400 to 6800 kPa. For the remaining 4 days the pressure drop was only 200 kPa.

Autoclave II, sample placed pressure and temperature a below critical point of CO₂. The specimens were placed in vessel at room temperature (+22.5 to +24 °C) and at pressure (4800 to 4970 kPa). Then the specimens were exposed to CO₂ gas for 5 days. The temperature and pressure drop, during the 5 days test, was from +24 to +22.5 °C and 4970 to 4800 kPa, respectively.



Figure 3-9 (a) Autoclave instrument (top view): containing samples for carbonation (b) Samples placed on steel rack to be placed in autoclave

3.3.2 Carbonation using carbonation chamber

The carbonation chamber was set at a temperature of $+11^{\circ}$ C and relative humidity of 90%. The concentration in the carbonation chamber is measured by external concentration detector tool – Vaisala MI70. Based on data from CO₂ concentration sensor, the concentration of carbon dioxide in the carbonation chamber was observed to range between 10% and 15%.

Samples from four binder types were tested at three curing dates - 14 days, 28 days, and 90 days. The samples for 13 days curing date were carbonated in the chamber for 13 days, as the first 24 hour was in the mould at room temperature. Whereas the samples for 28 days and 90 days curing date where in the carbonated for 21 days. The notion for fixing the curing carbonation at 21 days being the observation from the trial experiment. From the trial experiment done in the carbonation chamber, the placement of specimen for longer period than 14 days observed to result in no significant improvement in carbonation rather caused weathering of specimens-small crack lines on the surface of specimens. Thus, the samples in chamber which were planned for 28 days, and 90 days curing were moved to storage room after 21 days of carbonation in the chamber.



Figure 3-10 (a) carbonation instruments (b) samples in carbonation chamber before carbonation (C) Samples in carbonation chamber after 14 days of carbonation
3.4 Methods of analysis

In this section the methods used for analysis of specimen is discussed. To determine the carbon dioxide content in specimen thermogravimetry analysis tool was used. For assessing the effect of carbonation on strength of stabilized samples unconfined compressive strength test was performed.

3.4.1 Thermogravimeter analysis (TGA)

A thermogravimeter instrument TGA 951 was used. The temperature range was $+50-950^{\circ}$ C with a heating rate of $+20^{\circ}$ C/min. To provide time for water loss at $+100^{\circ}$ C the heating phase was divided in to two phases. The first run from $+50^{\circ}$ C to $+100^{\circ}$ C and stay constant at 100° C for 10 min. The second phase continues to increase from +100 to $+950^{\circ}$ C. As flow medium, helium gas was used with a flow rate of 110 mL/min.

As discussed previously in section 2.4, several studies have used thermogravimetry instrument for determining carbonation content (Revathy *et al.*, 2015; Unluer and AI-Tabbaa, 2013; Cai and Liu, 2017; A. M.A. Mohammed *et al.*, 2021; Yu *et al.*, 2021). The analysis was done for both reference and carbonated specimen.

Based on the thermogravimeter curve and review of previous studies the weight loss between $+475^{\circ}$ C and $+800^{\circ}$ C could be due to decarbonation of calcium and magnesium. Thus, this temperature range was used to compute the carbonate content of samples (Unluer and AI-Tabbaa, 2013; Cai and Liu, 2017; Yu et al, 2021). The weight loss in the range was be computed for both reference and carbonated specimen. Then, the bound CO₂ amount was the difference in weigh loss of sample from decomposition of carbonates in temperature range $+475^{\circ}$ C to $+800^{\circ}$ C.



Figure 3-11 (a)Thermogravimeter instrument (b) Helium gas container (c) Data recording computer (d) Part of thermogravimetry instrument where specimen burning takes place.

3.4.2 Unconfined compression test

Unconfined compression test is used by several studies to develop relation between the strength and curing time for binder-stabilized clay (Mohammed *et al.*, 2021; Fasihnikoutalab *et al.*, 2017). Unconfined compression test was performed in accordance with ASTM D2166-06.

The axial load rate for the test was performed at rate of 1mm per min. All specimen prepared for test were checked for the requirement of height to diameter ratio greater than two. The criterion for selecting maximum load is when the load reach peak value before reaching 20% strain. Whereas, when the strain passes 20% the test was halted and the maximum load at 20% strain was taken (ASTM D2166, 2006).

To ensure proper strength comparison between reference and carbonated samples. The curing of reference sample followed the same procedure as applied for carbonated samples. Which is reference samples were also extruded from plastic tube after one day of curing in the plastic tube. Thus, both reference and carbonated samples were not confined by the plastic tube used during compaction.

3.4.3 Microstructure analysis: scanning electron microscope (SEM)

Samples were examined after carbonation by FEI ESEM Quanta 450 FEG. **"Low vacuum model" was used without imaged without the need of a con**ductive layer.

The SEM images were analyzed to identify the difference in morphology between carbonated and uncarbonated samples. Samples were examined by FEI ESEM Quanta 450 FEG. Pieces of soil samples taken from central region of the post-test UCS test specimen and were oven dried. The dried carbonated and uncarbonated samples were mounted in phenolic resin base. This preparation method was previously used by Mahesh Bhat and Nayak, (2021). "Low vacuum model" was used without the need of conductive layer.

4 Results and analysis

In this chapter discusses the thermogravimeter test result, compressive strength test result and SEM analysis result. A comparison of CO₂ sequestration capacity of Malmi clay was made with the finding of previous studies. In addition, an estimation of CO₂ equivalent emission was made to understand the reduction in production emission factor of binders.

4.1 Thermogravimetric analysis

4.1.1 Thermogravimetry test result for experiment in autoclave

This subsection presents the response, regarding CO₂ absorption capacity, of stabilized clay when exposed to normal CO₂ and supercritical CO₂ environment. These CO₂ environments are established in autoclave. The TG test were performed on 5 days (at the end of carbonation) and 28 days cured sample.

As presented in table 3-1, Autoclave I and II involves surrounding sample with supercritical CO₂ and normal CO₂ environment, respectively. Overall result of Thermogravimeter analysis for samples under both methos found the weight loss (%) due to decomposition of carbonates range to be between 4.6 to 6.4% (for UCEMII_SC¹); 5.5 to 6.6% (for CEMIII_SC²); 5.1 to 6.4% (for CEMII_SC³) and 4.4 to 4.9% (for GTC3_SC⁴).

To obtain the CO₂ absorption capacity of stabilized sample due to carbonation, it is necessary to compute the amount of bound CO₂. Amount of bound CO₂ refers to difference in the weight loss, from carbonate decomposition, of samples carbonated and sample which is noncarbonated. Accordingly, the bound CO₂ amount was found to range between 2.4 to 4.2% (for UPM+CE-MII); 3.5 to 4.5% (for CEMIII); 2.8 to 4.1% (for CEMI) and 2.6 to 3% (for GTC3).

Figure 4-2, DTA of reference sample shows three peaks for both reference and carbonated samples. The peaks temperature ranges 100 °C to 250 °C, 300 °C to 580 °C (reference sample), 450 °C to 600 °C (carbonated sample), and 600 °C to 800 °C. in a temperature prior to 450 °C the peaks related to uncarbonated samples are higher than the carbonated samples. This could be the amount of the dehydroxylation of brucite (Mg(OH)₂) and calcium hydroxide (Ca(OH)₂) found in reference specimen (Unluer and Al-Tabbaa, 2013).

¹ UPM+Cement type II (7/3) stabilized clay

² Cement type III stabilized clay

³ Cement type I stabilized clay

⁴ GTC 3 stabilized clay



Figure 4-1 Autoclave I & II: comparing TG derivative (%/°C) results of reference and carbonated specimen of CEMIII

It may also be another indication that dehydroxylation of brucite $(Mg(OH)_2)$ and calcium hydroxide $(Ca(OH)_2)$ has reacted to external CO₂ diffused to form carbonates. Cai and Liu (2017) indicated that part of CO₂ that diffused into the voids of stabilized soil will partly produce carbonic ions (CO_3^{2-}) . The produced carbonic ions (CO_3^{2-}) will then react with brucite or Mg to form hydrated magnesium carbonates, as depicted in Equations (1) & (2) (Cai and Liu, 2017).

$$Mg(OH)_2(s) + CO_2(g) + H_2O(aq) \rightarrow MgCO_3 \bullet 3H_2O(s)$$
 (1)

Or

$$\begin{array}{l} Mg(0H)_2(s) + CO_2(g) + H_20 \ (aq) \\ \rightarrow \ Mg_5(CO_3)(0H)_2 \bullet (3 \ or \ 4 \ or \ 5 \)H_2O(s) \end{array}$$
(2)

After a temperature of 450°C, the peaks related to carbonated samples are significantly higher than the uncarbonated peaks. In figure 4-1, two decomposition peaks (the 2nd and 3rd peak) were observed risen above uncarbonated samples. As discussed previously, these peaks could indicate higher decomposition of calcium and magnesium carbonates. Which mean these peaks are indicator of higher carbonate content of the samples after carbonation.

It is possible to quantify this difference in amount of decomposition by computing the weight loss from TGA plot. Taking the carbonate decomposition range 475 °C to 800 °C. In this range, the reference specimen has carbonate decomposition with weight loss of 2.1% by weight. For carbonated sample, a sample placed in supercritical CO₂ environment and cured for 28 days has weight loss of 6.6% (figure 4-2). Whereas CO₂ environment and cured for 28 days has weight loss of 5.9%.



Figure 4-2 Autoclave I & II: TGA result of reference and carbonated specimen of CEMIII binder at different curing time

To quantify the outcome of exposing samples to CO_2 , computation for the bound CO_2 (net weight loss) was made (figure 4-2). The net bound CO_2 can be obtained deducting weight loss of carbonate decomposition in uncarbonated sample from the carbonated one. As illustrated in figure 4-2, weight loss from decomposition of carbonate for 28-day cured carbonated sample (autoclave I) is 6.6% and weight loss from decomposition of carbonate in reference sample is 2.1%. The amount of bound CO_2 is the difference in weight between carbonated and reference sample's weight loss, which is (6.6%-2.1%=4.5%).

The TGA and DTA plots among different binder types shows same number of peaks and temperature ranges. The differences that can be observed are that the peaks are higher in some of binder types (for example CEMI Vs GTC3) which implies higher carbonate decomposition amount.

In figure 4-3a, the highest weight loss from carbonate decomposition was obtained for CEMIII_SC samples which were carbonated in supercritical CO₂ environment. The amount obtained was 5.9% just after carbonation (5-days) and 6.6% at 28-days of curing. The lowest values were obtained from sample stabilized with GTC3, 4.4% just after carbonation and 4.7% at 28-days of curing (autoclave I). The bound CO₂ variation regarding method of carbonation being less than 0.5% for UCEMII_SC, CEMII_SC and GTC3_SC. According to TGA analysis for samples stabilized with GTC3, there was no increase bound CO₂ amount with higher duration of curing days.

Duration of curing

Regarding effect of curing duration on carbonation, with increase in curing duration an increase in mass loss, from decomposition of carbonate, was observed for both the reference and carbonated samples. The reference sample at 28 and 90 days have the same peak and temperature range until 600 °C. At the third peak (between 600 °C to 800 °C), higher peak is observed on 90-day reference sample. Similarly on carbonated samples, the difference can be seen clearly as the third peak (between 600 °C to 800 °C) DTA for samples of longer curing duration has risen above shorter curing duration samples (figure 4-1 & 4-4). When these peaks get quantified as weight loss the amount of weight loss was between 0.0% and 1.7%, varying by binder type and method of carbonation. The highest effect was seen on CEMI_SC. The increase amount for 28-day sample from 5-day sample was 0.8% (autoclave I), and 1.4% (autoclave II) and 1.2% (28 day to 90 days curing day).

Carbonation environment

Comparing the effect regarding the carbonation environment, samples placed in supercritical CO₂ environment show higher weight loss (%) from decomposition of carbonate. This comparison is done on sample tested just after carbonation (5 days). In fly ash (UPM+CEMII) stabilized clay, exposing

samples in higher temperature (24 °C to 97 °C) and pressure (4900 kPa to 7200 kPa) showed to more than 1.5% increase in the amount of bound CO₂. For example, a carbonated (autoclave II) CEMIII_SC with binder content 100kg/m³ was able to sequestrate 4.6% by weight CO₂. This was seen to be higher (6.2%) when carbonation is done in autoclave I (SCO₂).

Similar trend was observed on CEMIII stabilized clay where the capacity increase by 0.5%. Whereas, for CEMI and GTC3 stabilized clay samples a fluctuating and reduction in bound CO_2 (lower than 0.5% in amount) were found, respectively. In GTC3 stabilized clay the sample in autoclave II CO_2 environment tend to show 0.2% higher bound CO_2 than the supercritical CO_2 environment. For CEMI stabilized clay samples, the carbonation environment may not have affected the bound CO_2 capacity, as the thermogravimeter result at the end of carbonation (5 day) is 2.8% and 2.9%, for CO_2 and SCO_2 both environments, respectively.

Several studies also have indicated similar finding despite difference the variation in the stabilized material (clay, silt, CFA), the pressure amount (max 1000 kPa) and control parameter (most of them relate pressure to strength gain) in the studies. Revathy et al (2015) indicated that the sequestration capacity of coal fly ash increases with the CO₂ pressure. Most studies investigated the increase in CO₂ pressure with respect to strength development of stabilized soil (Yi, et al., 2013; Mohammed et al., 2021). Yet, it was indicated by Horpibulsuk et al., (2010) that the strength gain in carbonated sample could be related to the formation of carbonate. As such, the finding is consistent with (Yi, et al., 2013; Mohammed et al., 2021; Fasihnikoutalab et al., 2017). While in this study, the pressure (4.9MPa) is significantly higher than what was studied in previous studies (2 kPa- 200 kPa). The study on Malmi clay, especially, indicated the effect at higher pressure amount and varies binder types.

Investigation in longer curing duration (28 days) showed slight increase in carbonate content in fly ash stabilized soil. While higher carbonate formation observed in cement type 1 stabilized samples. In detail, the amount of CO₂ sequestrated in samples exposed higher pressure and temperature (supercritical CO₂) at 28 days of curing was found to be 4.5%, 4.2%, 4.1% and 2.8% for CEMIII_SC, UCEMII_SC, CEMI_SC and UCEMII_SC (figure 4-3a). Whereas, for samples exposed in normal CO₂ environment (Autoclave I) the amount of CO₂ sequestrated in samples was obtained to be 4.1%, 3.5%, 3.0% and 2.8% for CEMI_SC, CEMII_SC, GTC3_SC and UCEMII_SC, respectively (figure 4-3b). At 28-day curing duration for samples under supercritical CO₂ environment the bound CO₂ amount was found to be higher in CEMIII_SC and UCE-MII_SC. T. Except for CEMI stabilized clay, Sample in normal CO₂ environment does not show significant increase in carbonate content with increase in curing duration (from 5 day to 28 day). This could indicate that the carbonation period applied in this study, 5 days (120 hour), might have passed the equilibrium threshold of the carbonation period. Several studies found different carbonation period equilibrium point depending on binder type, the temperature and pressure of CO₂ applied in the vessels. Carbonation happens at early stage and reach peak point in the first 1 hour (Revathy et al., 2015), and 3 hours (Yu et al., 2013) of carbonation. Further study could be required to find the threshold for the equilibrium of carbonation. This finding will play major role in designing efficient method of carbonation where one can avoid excess CO₂ injection and energy waste.

For GTC3_SC, both the carbonation environment and curing duration does not result in significant change in the amount of bound CO₂. The maximum obtained CO₂ sequestration being 3.0% and the minimum is 2.6%.





Figure 4-3 (a) weight loss from decarbonation autoclave I & II, (b) amount of bound CO₂ for autoclave I & II

However, for sample stabilized by CEMI the duration of curing was seen to have significance on the amount of bound CO₂. Bound CO₂ in CEMI_SC under autoclave I increase by 1.5 time from the amount at 5-day to 28-day. On the other hand, under autoclave II the increase is 1.28 times.

Overall, the obtained amount of bound CO_2 in samples carbonated in supercritical CO_2 environment was found to has shown an equal or higher than the amount found in samples under normal CO_2 environment (autoclave II). It can also be concluded that the increase in curing duration found to increase the bound CO_2 amount.

4.1.2 Thermogravimetry test result for experiment in Carbonation chamber with curing duration of 14, 28 and 90 days

In this sub section, the CO₂ absorption capacity of stabilized clay under a single carbonation environment will be studied at three curing durations 14-day, 28-day, and 90-day. The carbonation environment was established in carbonation chamber with CO₂ concentration (10-15%), pressure (atmospheric) and temperature 11°C. TG tests were done at end of carbonation (14-day), at 28-day and 90 days (figure 4-6).



Figure 4-4 Derivative of thermogravimeter (%/ $^{\circ}$ C) results of reference and carbonated specimen of CEMIII for Autoclave I&II, carbonation chamber III to V



Figure 4-5 Comparing thermogravimeter test result of reference and carbonated specimen of CEMIII binder for Autoclave I&II, carbonation chamber III to V:

In figure 4-5, the amount of weight loss from carbonation was highest in CEMI_SC. The same sample show higher carbonation with increase in duration of curing. Initial high carbonation on UPM carbonated sample but the carbonation tends to increase on reference sample as curing duration increase which result in lower bound CO_2 at 90 days. This also indicate that the reference specimen itself higher rate of carbonation than carbonated sample when the curing duration increases. Overall, the carbonation performance of carbonation chamber is lower in terms of the obtained bound CO_2 amount than the autoclave.

The net absorbed CO₂ was seen to decrease in the plot is an indication for to increase in carbonate content in reference samples than it does in carbonated samples. In case of carbonated samples, it was seen that carbonation happen at high rate during early stage of carbonation which then increase in small rate as shown in the figure 4-6a. Cement type I stabilized clay has an increase in carbonate content on both carbonated and uncarbonated stabilized soil with increase in curing duration.





4.1.3 Estimation of net CO₂ emission per cubic meter of carbonated mixture

One of the main goals of implementing carbonation of stabilized clay is to introduce sustainable method of soil stabilization technique with low carbon footprint. In this sub section, estimation of net CO₂ emission from carbonated stabilized samples is presented. The major CO₂ emission source being binders used ins stabilization of soil, the amount of bound CO₂ obtained from carbonated samples will be deducted from the emission from the binder type used for the given binder content. For simplification of calculation an estimation was made for one cubic meter of mixture. The actual density and water content of stabilized clay was used.

Based on TG analysis in subsections 4.1.1 & 4.1.2, autoclave II was found to bring a combined benefit on the obtained amount of bound CO_2 and in its proximity to the field mixing environment. Thus, TG test result from autoclave II used for emission calculations. The information about the CO_2 emission of binders was collected from manufactures. It should also be noted that this emission calculations do not include the mission from transporting binders to the construction site.

The measured CO₂ (%) or weight loss from decarbonation obtained from thermogravimetric analysis correspond to the over dried specimen. Thus, the dry density of stabilized clay is used to compute the released and bound CO₂ mass per cubic meter of mixture. The density (kg/m³) and moisture content of 28 days cured stabilized clay measured in laboratory. The density was found to be 1560, 1540, 1570 and 1520 kg/m³ for GTC3 stabilized clay, UPM+CEMII stabilized clay, CEMIII stabilized clay and CEMI stabilized clay, respectively. The water content was found to be 70.3%, 69.8%, 67.3% and 71.2% for GTC3 stabilized clay, UPM+CEMII stabilized clay, UPM+CEMII stabilized clay, UPM+CEMII stabilized clay, UPM+CEMII stabilized clay, Stabilized clay, UPM+CEMII stabilized clay, CEMIII stabilized clay, St

The results in table 4-1, considering all binder types studied the sequestration capacity of carbonated stabilized clay range between 3% to 4.1% of dry weight. The biggest sequestration capacity is measured in CEMI stabilized clay followed by CEMIII. When it is converted to weight of equivalent CO₂ using dry density, a carbonated stabilized clay of one cubic meter could absorb 25 to 37 kg CO₂ equivalent emission, all binder types in the study considered. This amount was found above the emission value for production of GTC3 which indicates the carbonation of GTC3 stabilized clay will make the use of GTC3 carbon neutral binder.

The measured CO_2 in the reference samples range between 1.8 to 2.3% of dry weight of stabilized clay which is equivalent to 16.9 to 20.1 kg CO_2 equivalent emission factor (table 4-1).

Based on manufactures data, GTC3 has the least CO_2 equivalent emission factor (18.4 kg CO_2 eq. e. /100kg of GTC3) followed by UPM+CEMII (28.2 kg CO_2 eq. e. /100 kg of UPM+CEMII).

Table 4-1 Computation for estimated bound CO₂ per cubic meter of stabilized clay. Based on data from 28 day cured carbonated and reference samples.

Curing duration 28-day cured autoclave II (CO ₂)										
Water		Wet density	Dry den-	Bound CO ₂	Bound CO ₂					
	content	(kg/m ³)	sity	(% dry	(kg/ m³)					
	(%)	-	(kg/m ³)	weight)	-					
GTC3*	70.3	1560	920	3.0%	28.0					
UPM+CEMII	69.8	1540	910	2.8%	25.9					
(7:3)**										
CEMIII*	67.3	1570	940	3.5%	33.8					
CEMI*	71.2	1520	890	4.1%	36.8					
Reference sample_28-day cured										
	Water	Wet density	Dry den-	Weight loss from decar-						
	content		sity	bonation CO ₂						
	(%)	(kg/m³)	(kg/m³)	(%)	(kg)					
GTC3*	71.31	1520	890	1.89%	16.9					
UPM+CEMII	72.37	1490	880	2.23%	19.4					
(7:3)**										
CEMIII*	70.45	1520	890	2.09%	18.7					
CEMI*	74.8	1520	870	2.30%	20.1					
-										

Remark: *Binder content 100kg/m³

**Binder content 150kg/m³

The amount of CO₂ absorbed through carbonation of stabilized clay brought the emission value to a value of below zero in case of GTC3 and closer to carbon neutral when UPM+CEMII is used. In figure 4-8, carbonated GTC3 stabilized clay has a net CO₂ equivalent emission of -9.4 kg/m³ (carbon negative) per one cubic meter of stabilized clay. The net CO₂ equivalent emission factor for UPM+CEMII stabilized clay is 2.3 kg/m³ per one cubic meter stabilized clay. These two binder types have low emission during production when compared with the emission production of CEMI and CEMIII.

Figure 4-7 shows the measured amount of CO₂ in the reference sample and carbonated sample. The measured CO₂ amount on carbonated samples of CEMIII stabilized clay and CEMI stabilized clay is the largest, 52.5 kg and 56.8 kg, respectively. However, the absorbed CO₂ from carbonation did not overtake the production emission from production of CEMI and CEMIII. This is due to the relatively huge (when compared with GTC3) emission factor for during production of these binders. The production emission factor for

CEMIII and CEMI is (47 kg CO_2 eq. e. /100 kg of CEMIII) and (77.6 kg CO_2 eq. e. /100 kg of CEMI), respectively.

There was no significant difference in the measured CO_2 amount between different binder types used in the study, the maximum and minimum value are 16.9 kg/m³ to 20.1 kg/m³, respectively. By deducting the amount of CO_2 absorbed in reference sample from the amount measured in carbonated samples will give the amount of bound CO_2 .



Remark:

A: Measured amount of CO₂ in carbonated sample during decarbonation

B: Measured amount of CO₂ in reference sample during decarbonation

Figure 4-7 Measured amount of CO₂ in carbonated and reference sample for all binder types [kg CO₂ equivalent emission/m³] (Autoclave II curing duration of 28 days)

In figure 4.8, the amount of bound CO_2 is presented with the equivalent emission from production of binder and the net CO_2 emission equivalent for carbonated samples. The net CO_2 emission equivalent factor for carbonated sample is obtained by the amount of CO_2 absorbed by carbonation of samples (bound CO_2) from the CO_2 emission data from production of the binder during production.

The net emission factor from carbonated stabilized soil using CEMIII and CEMI was 13.2 kg/m³ and 40.8 kg/m³, respectively. Thus, the achieved reduction of emission from production by carbonating the stabilized soil was found to be 92%, 72% and 47% for UPM+CEMII (7:3), CEMIII and CEMI, respectively. Whereas GTC3 stabilized soil is in carbon negative side(-9.4kg/m³), that it absorbed 150% of equivalent CO₂ emission during carbonation.



Remark:

C: Amount of bound CO₂ (kg/m³) achieved through carbonation of stabilized clay (A-B) from figure 4-7

D: CO₂emission from production of binders (*100kg Binder CO₂eq. emission (kg)

**150kg binder CO₂ eq (kg)

E: Net CO₂ eq (kg/m³) emission factor for carbonated stabilized clay (D-C)

Figure 4-8 Net CO₂ equivalent emissions (kg/m³) of carbonated-stabilized Malmi clay (under CO₂ environment at curing duration of 28 days)

4.1.4 Comparison of the CO₂ absorption capacity

Figure 4-9 shows a comparison of the measured CO₂ after carbonation of stabilized Malmi clay, stabilized clay types from other studies and concrete. Even though longer carbonation duration and more pressure used in the current study than the other studies, the sequestration capacity measured was found to be comparably closer to the finding of Liu et al., (2017), Yu et al., (2021) and Mohammed et al., (2021).

The measured CO_2 using thermogravimeter analysis from this study were found to have a closer CO_2 content with previous studies done on steel slag stabilized clays. The result from current study, considering binders containing steel slag (GTC3 and CEMIII) the measured CO_2 using thermogravimetry at the end of carbonation (5 days) was 4.7% and 5.5%. Which is a closer result with a previous study by Yu et al. (2021) and Mohammed et al., (2021). The measured CO_2 in the studies were 4.79% and 5.2%, respectively (Figure 4-9).

4.2 Unconfined compression test

Unconfined compressive strength test was performed for both carbonated and reference samples. The UCS test were performed at 14-day, 28-day and 90-day cured duration for samples under carbonation chamber. For samples carbonated in autoclave the strength test was done after 28 days of curing. The compressive strength values discussed below are average value of two parallel specimens for carbonated samples and average value of three parallel specimen for reference samples. The standard deviation is also showed in the figure 4.10.

As described in compression test methodology section, the curing of reference sample followed the same procedure as applied for carbonated samples. Which mean samples were extruded from the plastic tube after one day of curing at room temperature. Thus, there was no confinement around sample during the curing period.



Figure 4-9 Measure CO₂ (based on weight loss from decarbonation) using thermogravimeter instrument of previous studies and carbonated-stabilized Malmi clay

In figure 4-10, the 28-day compressive strength (UCS) result for samples placed in normal CO₂ environment (autoclave II), supercritical CO₂ environment (autoclave I), and reference sample are presented. Comparing the compressive strength of carbonated and non-carbonated sample, the effect of carbonation on compressive strength found to differ with binder types and method of carbonation. In CEMI and GTC3 stabilized clay, the non-carbonated (reference) sample has above 3-fold higher strength than carbonated

sample. While in UPMCEMII stabilized samples, the carbonated samples have greater compressive strength in autoclave II method and equal strength in carbonated under normal CO₂ environment.

Whereas in CEMIII stabilized sample, compressive strength of sample in elevated pressure and temperature (supercritical CO₂) environment has a slightly higher strength than reference sample strength, considering the upper bound strength of both samples. Only observing the average compressive strength value, reference sample has bigger strength than samples in both carbonation environments.

In all binder types the 28-day UCS of carbonated samples, under normal CO₂ environment, were found to have lower compressive strength than the reference specimen. Comparison in UCS between the carbonation environments, samples place in supercritical CO₂ environment (autoclave I) found to have higher 28-day UCS.

Even though several studies compare the carbonation effect at lower pressure (2 kPa to 200 kPa), the result is consistent with the finding by (Yi *et al.*, 2013; Fesihnkoutalab et al., 2017; Mohammed et al., 2021). In the previous studies and this study, it was found that higher pressure and carbonation duration could be related higher UCS than sample under lower CO₂ pressure. The strength gain from raising the temperature and pressure (CO₂) was found to be 150%, 85% and 47% for CEMIII_SC, UPMCEMII_SC and CEMI stabilized clay. In a study by Mohammed et al., (2021) the strength gain of carbonating GGBS stabilized brown kaolin clay due to increased pressure by 100 kPa with 168hr carbonation was found to be 20 and 25%. In addition, the higher carbonate content found in samples carbonated at supercritical CO₂ environment could also be related to the higher strength in these samples than the samples placed in normal CO₂ environment. However, the strength difference was not significant in GTC stabilized samples.

In figure 4-10, for samples under normal CO₂ environment the 28-day UCS range between 51 kPa and 95 kPa. While for samples under supercritical CO₂ environment the UCS is higher which range between 46 kPa and 176 kPa. Plant fly ash stabilized clay (UPM+CEMII), where the sample carbonated in elevated temperature and pressure CO₂ environment (supercritical CO₂) was found to have highest strength than the reference and normal CO₂ environment sample.



Figure 4-10 UCS result at 28 day curing time for samples carbonated autoclave I and II, and reference sample (the UCS result of reference sample is average of 3 parallel specimens, while for carbonated sample it is average for 2 parallel specimen), the error bar indicates standard deviation.

For GTC3 stabilized samples, the 28-day compressive strength of carbonated samples was found to be 51 kPa and 46 kPa under normal CO₂ environment and supercritical CO₂ (SCO₂) environment, respectively. GTC3 stabilized reference sample was found to have a compressive strength of 190 kPa, which is around 3.5-fold bigger than carbonated samples strength.

The compressive strength of CEMIII stabilized clay was found to exhibit better strength than the GTC3 and UPMCEMII stabilized samples. This result is valid for both carbonation environments and reference sample. Carbonated CEMIII stabilized clay was found to have the biggest compressive strength than all carbonated samples of the remaining binders. The carbonated sample strength of CEMIII is 176kPa when carbonated in supercritical CO₂ environment and 95kPa in normal CO₂ environment.

Non-carbonated CEMI stabilized clay has the largest compressive strength, 364kPa. The carbonated sample has showed a compressive strength of 109kPa. The difference in strength between reference and carbonated sample of CEMI stabilized sample is significantly higher which reached the highest 28-day UCS was found on reference sample stabilized by CEMI and CEMIII, 364 kPa and 228 kPa, respectively.

The result of this study indicates a need for further study for understanding the effect of carbonation on strength development and to find out the reason behind lowed strength in carbonated sample. The study of the strength comparison in longer duration than 28 days might play role to allow enough strength development duration.

In figure 4-11, the strength gain with longer curing duration for reference samples (non-carbonated) presented. The 90-day cured sample test result showed that CEMIII, CEMI, GTC3 and UPM+CEMI has a strength of 608 kPa,491 kPa,291 kPa and 66 kPa, respectively. Plant-fly ash stabilized soil with CEMI was found to be mixture with the least strength and low rate of strength development with curing duration. While CEMI and CEMII stabilized binders seem to have comparable strength. With the longer curing duration the strength development was seen to increase gradually for CEMI, CEMIII and GTC3 stabilized soil. It should be noted that the compressive strength result presented in table 4,11 are for samples placed in plastic tube during the time of curing.



Figure 4-11 UCS result for reference sample at 14, 28 and 90 days of curing (binder content of 100kg/m^3), the average UCS for three parallel specimens were presented (n=3).

Table 4-2 presents the selected method of carbonation (autoclave II) for comparison of absorption capacity and estimation of emission factor presented. Based on its ease for implementation (normal CO₂ pressure and room temperature) and the achieved CO₂ absorption capacity was found way closer to supercritical environment, autoclave II was selected for further analysis of result.

Table 4-2 Bound CO_2 , unconfined compressive strength and estimation of emission factor for sample in autoclave II (CO_2) and reference sample at 28-day curing

	Curing duration 28-day autoclave II (CO ₂)									
Binder type	Weight loss from decarbona- tion (TGA result)			UCS (kPa)	Estimation of emission equivalent factor for 1m ³ mixture. *					
	а	b	С	d	е	f	g			
	Car- bonated sample	Reference sample	Bound CO ₂ (a-b)	28-Day (kPa)	kg CO ₂ eq. e. /m ³	kg CO2 eq. e. /m ³	=(e- f)/f			
GTC3	4.9%	1.89%	3.0%	55	16.9	-9.4	151%			
UPM+CE- MII(7:3)**	5.0%	2.23%	2.8%	51	19.4	2.3	92%			
CEMIII	5.6%	2.09%	3.5%	95	18.7	13.2	72%			
CEMI	6.4%	2.30%	4.1%	74	20.1	40.8	47%			

* e: Amount of bound CO₂ (kg/m³) achieved through carbonation of stabilized clay
f: Net CO₂ eq (kg/m³) emission factor for carbonated stabilized clay
g: the reduction in CO₂ (kg/m³) equivalent to CO₂ the emission factor from production of the binder.

**Binder content 150kg/m³

Four binder types were investigated against the absorption capacity and UCS. Cement type I and cement type III were found to be the binder with the highest CO_2 absorption capacity and UCS. However, from emission perspective, the emission during manufacturing of these binders was significantly higher than the remaining two binders studied. Cement type I and cement type III has CO_2 equivalent emission factor from production of 77.6 kg and 47 kg CO_2 eq. e./m³. As such, the carbonation was estimated to reduce its emission factor from production by 47% for Cement type I and by 72% for cement type III. This means the net CO_2 emission factor for aforementioned binders will be 40.8 and 13.2 kg CO_2 eq. e. /m³, respectively (Table 4-1).

The absorption capacity of GTC3 and UPM+CEMII were found to be 3.0% and 2.8%. Both binders have low emission factor from manufacturing which enabled the net emission factor from carbonated stabilized clay to be on carbon negative side for GTC3 (by 9.4kg) and below 5 kg CO₂ equivalent emission per m³ for UPM+CEMII. This is a promising result for achieving carbon neutral or even carbon negative soil stabilization method. One of the drawbacks related to UPM+CEMII is that it requires higher content of the binder to achieve higher UCS. As presented in previous section, the 90-UCS cured reference sample with 150kg/m³ binder content was only 66 kPa. The result presented in Table 4-2 shows that carbonation of soil stabilization made with GTC3, and plant fly ash (UPM Jämsänkoski) reduces the emission factor from production by more than 150% and 90%, respectively.



Figure 4-12 comparison of compressive strength and net emission value between different carbonated stabilized samples at 28day curing (a) compressive strength and net CO_2 equivalent emissions (kg/m³) (b) compressive strength and production emission reduction

4.3 SEM analysis

SEM was conducted for CEMII_SC after 90 days of curing. The sample was placed in autoclave at supercritical CO₂ environment for a period of 48hrs. The morphology of the Malmi clay, carbonated CEMIII and uncarbonated CEMIII_SC studied using SEM are presented I the figure above.





A change in structure of clay particles was observed after stabilization with CEMII and after carbonation. The SEM images of Malmi clay displays (figure 4.11a) a sheet-like flaky particles. The stabilized microstructure of stabilized

sample was observed to be agglomerated around clay particles, less discontinuous than the original clay, spindle like structures seen on uncarbonated stabilized clay.

Spindle-like structures were seen on uncarbonated sample figure 4-11b. These spindle-like structures resemble the struture of enttringite, as identified in prevoisuy studies (Nontananandh *et al.*, 2005; Ahmed, 2014; Ural, 2021). Thus, these formation on figure 4.11b could be ettringites.

Figure 4.11c shows the SEM image of carbonated samples. The formation that could be ettringite which was seen in uncarbonated sample was observed to be less in number but larger in size as it can be seen on 25x magnification image. The figure 4.11c, reveals crystal structures with a shape cubic and hexagonal which could be formed on the surface of the clay structure. These crystal structure could be calcite solids (Revathy *et al.*, 2015).

Based on observational analysis of SEM image, the pore spaces seem bigger in natural clay than the stabilized clay. The pores were observed to look smaller in size in carbonated sample than the uncarbonated. These could be the attributed to the formation of carbonate and bonding in carbonated samples. The similar observation was presented by Liu et al. (2021), where smaller pore and bonding observed on reactive MgO stabilized (on field carbonated) soft soil.

5 Conclusions and future perspectives

A comprehensive investigation into the CO₂ sequestration capacity of carbonated stabilized clays has been conducted in this paper. Four binder types were used for stabilization of the clay which are then placed in carbon dioxide environment. Stabilized clay samples were carbonated under various pressure and temperature conditions. The amount of bound CO₂ in samples was studied using thermogravimeter. The morphology for cement type III stabilized clay was observed via SEM.

The result suggested that carbonation of stabilized soil samples has vital role in establishing a carbon neutral deep mixing method. For the four binder types studied, the sequestration capacity of carbonated-stabilized soil was found to range between 2.8% to 4.1% of dry mass or 25 to 37 kg CO₂ equivalent per cubic meter of mixture. The CO₂ absorption capacity of binders with low emission factor (Nordkalk Terra GTC3 and UPM Jämsänkoski fly ash +CEMII 70%:30%) during production were found to give a promising step toward carbon neutral ground improvement techniques. The equivalent CO₂ emission factor from production of these binders was reduced indirectly by the implementation of carbonation on stabilized soil.

The binder type that has the biggest potential to be carbon negative was Nordkalk Terra GTC3. While the use of plant fly ash (UPM) with Cement type II as an activator has shown to bring an emission value closer to zero. Despite its relatively high sequestration capacity of Cement type III the relatively bigger emissions, than GTC3 and UPM, at production of binder holds the effort to reach zero emission value. Carbonation has shown to reduce 70% of the emission factor during production of cement type III.

The obtained result has revealed that the exposure of samples to CO₂ has led to increase in carbonated content in samples. This increase was demonstrated by higher amount of weight loss from decomposition of carbonates obtained for carbonated samples. This amount was higher in carbonated samples than the uncarbonated samples, for all binder types. The minimum weight loss (in thermogravimeter) due to decarbonation obtained was 4.4% and maximum was 6.6%.

The amount of bound CO₂ varies with the type of binder used for stabilization of the clay. For uncarbonated samples the amount of bound CO₂ does not vary significantly with different binder types. Whereas, for carbonated samples the amount of bound CO₂ varies with the type of binder. The amount of bound CO₂ was found to be 4.1%, 3.5%, 3.0% and 2.8% for CEMI, CEMIII, GTC3, and UPM+CEMII stabilized clay, respectively. The weight loss due to decomposition of carbonates was not significantly different between sample at 14-, 28- and 90-day curing. Which indicate that major portion of carbonation occur during early periods of exposure to CO₂ which then has very low gradual increase after the peak point.

In fly ash (UPM+CEMII) and CEMIII stabilized clay, exposing samples in higher temperature (24°C to 97°C) and pressure (4.9 MPa to 72 MPa) CO₂ environment found to increase the absorbed CO₂ amount by more than 1.5 time. Whereas this effect was not found to be significant in clay stabilized by CEMI and GTC3. Carbonation in autoclave was found to provide CO₂ exposure environment with maintained natural moisture content of sample and higher carbonation capacity than carbonation chamber. Supercritical CO₂ environment. Supercritical CO₂ environment refers to elevated temperature and pressure than normal CO₂ environment at room temperature.

The comparison of 28-day compressive strength of carbonated and non-carbonated samples indicated the existence of difference in strength due carbonation. The compressive strength of carbonated soils was found to range between 50 to 175 kPa, where the carbonated sample strength range between 65 to 364 kPa. The compressive strength obtained from different carbonation method was also found to differ significantly within the same and different binder type. The samples carbonated in normal CO₂ environment (autoclave II) has lower strength than reference sample in all binder types.

Whereas, for sample carbonated in elevated temperature and pressure (autoclave I) the effect differed with binder type. In GTC3 and CEMI stabilized samples the reference sample strength was higher. While in UPM stabilized samples the carbonated sample has bigger strength. In CEMIII stabilized sample, even though the average strength value is higher in reference sample, the maximum compressive strength obtained in both reference and carbonated sample is very close, 270kPa and 255kPa. Overall difference in strength is significant In CEMI and GTC3 stabilized clay, the non-carbonated (reference) sample has above 3-fold higher strength than carbonated sample. While carbonated UPMCEMII stabilized sample has a closer strength with reference sample.

Carbonation in autoclave found to well resembles the field condition (except the temperature). Based on visual observation, the samples taken out of the autoclave has the moisture and texture of sample not changed significantly from the condition before carbonation. While in carbonation chamber the exposure of samples ambient temperature and pressure lead to drying and loss of moisture. Which could have effect on the rate of CO₂ diffusion into the sample and rate carbonate formation on samples. By lowering the

temperature in autoclave to the temperature of ground condition help to obtain CO_2 sequestration capacity of stabilized clay approaching the nature ground environment.

A change in structure of clay particles was observed after stabilization with CEMIII. In microstructure of carbonated CEMIII stabilized clay, spindle-like clusters which could be generated calcites and ettringite were observed. Increased bondage and less pore space were observed in carbonated samples than uncarbonated and the natural clay.

An estimation on net CO₂ emission due to soil stabilization shows that carbonation of stabilized clay may lead to zero to negative CO₂ emission equivalent deep mixing technique. The net CO₂ emission estimate from one cubic meter mixture of UPM+CEMII stabilized clay was 2.3 (kg.CO₂.e/m³) and GTC3 stabilized clay was -9.4 kg CO₂ equivalent per m³ of mixture.

The finding of this study showed that the use of GTC3 and UPM (fly ash+CE-MII) in carbonation of soil stabilization will lead to neutral deep mixing method. A further study on optimum binder content which will give the highest CO₂ sequestration capacity and desirable strength.

Likewise previous studies this study also found the carbonation environment to affect the sequestration capacity of carbonated stabilized clay. It was found that the carbonation in stabilized clay was influenced by the amount of CO_2 pressure applied during carbonation. It is also indicated in the literature portion of this paper that the increase in pressure will also increase the carbonation rate however the optimum pressure from the perspective of the rate of carbonation and practicality needs further study. The finding on the measured CO_2 along with duration of carbonation shows the peak carbonate content were found on 5-day carbonated sample. Further, research should consider studying lower duration of carbonation and obtaining the optimum duration of carbonation and the rate of carbonate formation.

As this thesis delimited in laboratory scale a further study at field scale could be good to incorporate the machinery effect during mixing and diffusion of CO₂ in bigger soil mass. The study can also be expanded through studying the carbonation on different clay type, binder content and wet mixing method. All in all, carbonation of stabilized soil needs more study to have a better understanding of the effect of carbonation and implementation of findings.

In addition to the previous work done in producing low carbon emission binders the implementation of carbonation by injecting CO₂ gas in to stabilized soil will play major role in promoting the deep mixing method to a carbon neutral method of construction.

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List of Annex

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Annex 4: Binder component data from suppliers
Annex 1: Sample testing schdeule a. for samples carbonated using carbonation chamber

		curing	Preparation	Test Date(DD	D/MM/YY)	
	Content	date	date	UCS	Thermogravimeter	Number of sample
	(kg/m³)				(TGA)	
Nordkalk GTC3	100	14 day	8/10/2021	22/10/21	22/10/21	6
		28 days	8/10/2021	5/11/21	5/11/21	6
		90 days	8/10/2021	6/1/22	6/1/22	6
Cement type III	100	14 day	10/11/2021	24/11/21	25/11/22	6
		28 days	10/11/2021	10/12/21	11/12/21	6
		90 days	23/12/2021	22/02/22	23/02/22	6
UPS+CEMII (7:3)	100	14 day	11/11/2021	25/11/21	26/11/21	6
		28 days	11/11/2021	9/12/21	10/12/21	6
		90 days	22/12/2021	22/02/22	23/02/22	6
Cement type I	100	14 day	15/11/2021	29/11/21	30/11/21	6
		28 days	22/11/2021	20/12/21	21/12/21	6
		90 days	22/12/2021	22/02/22	23/02/22	6

	Content	curing	Preparation	Test Date (dd	l/mm/yy)	
	(kg/m³)	date	date	UCS	Thermogravime-	Number of sample
					ter (TGA)	
Nordkalk GTC3	100	14 days	8/10/21	22/10/21	22/10/21	4
		28 days	8/10/21	5/11/21	5/11/21	4
Cement type III	100	14 days	10/11/21	24/11/21	25/11/22	4
		28 days	10/11/21	10/12/21	11/12/21	4
UPS+CEMII	150	14days	11/11/21	25/11/21	26/11/21	4
(7:3)						
		28 days	11/11/21	9/12/21	10/12/21	4
Cement type I	100	14 days	15/11/21	29/11/21	30/11/21	4
		28 days	22/11/21	20/12/21	21/12/21	4
	Reference sa	mples placed	in storage room aft	er being remove	d from plastic tube	·
Nordkalk GTC3	100	28 days	18/06/2022	16/07/2022	n/a	3
Cement type III	100	28 days	18/06/2022	16/07/2022	n/a	3
UPS+CEMII	150	28 days	18/06/2022	16/07/2022	n/a	3
(7:3)						
Cement type I	100	28 days	18/06/2022	16/07/2022	n/a	3

b. Sample testing timesheet for samples carbonated using autoclave

Annex 2: Decarbonation weight loss calculation based on TGA analysis result

		GTC	3			UPM+CEMII						
Autoclave I (Au-	Curing Dura- tion	Temperature*	475	800			Temperature*	475	800			
toclave 5 day SCO2)	5 day	carbonated sample **	97.65	93.21	4.44	5D	carbonated sam- ple **	97.96	91.75	6.21		
	28 day	REF sample	80.27	78.38	1.89	28D	REF sample	96.49	94.26	2.23		
				Net(%)	2.55				Net(%)	3.98		
		GTC	3			UPM+CEMII						
		Temperature	475	800			Temperature*	475	800			
toclave 5 day	5 day	CO2	97.35	92.43	4.92	5D	carbonated sam- ple **	97.06	92.42	4.64		
(02)	28 day	REF	80.27	78.38	1.89	28D	REF sample	96.49	94.26	2.23		
				Net(%)	3.03				Net(%)	2.41		
		GTC	3			UPM	+CEMII					
		Temperature*	475	800			Temperature*	475	800			
toclave 28 day	28 days	carbonated sample **	96.92	92.20	4.72	28D	carbonated sam- ple **	97.11	90.71	6.40		
3002)	28 days	REF sample	80.27	78.38	1.89	28D	REF sample	96.49	94.26	2.23		
				Net(%)	2.83				Net(%)	4.17		
		GTC	3				UPM	+CEMII				
Autoclave II (Au-		Temperature*	475	800			Temperature*	475	800			
toclave 28 day	28 days	Carb.	97.49	92.56	4.93	28D	carb.	97.25	92.44	4.81		
CO2)	28 days	REF	80.27	78.38	1.89	28D	REF sample	96.49	94.26	2.23		
				Net(%)	3.04				Net(%)	2.58		

- Decarbonation weight loss calculation based on TGA result of sample in autoclave

* Temperature in ^oC; **weight loss in (%); REF. sample: reference sample

		CI	EMIII				(CEMI		
		Temperature*	475	800			Temperature*	475	800	
Autoclave I (Auto- clave 5 day SCO2)	5D	carbonated sam- ple **	97.29	91.36	5.93	5D	carbonated sam- ple **	97.28	92.07	5.21
	28D	REF. sample	96.00	93.91	2.09	28D	REF. sample	96.28	93.98	2.30
				Net(%)	3.85				Net	2.91
		CI	EMIII				(CEMI		
		Temperature	475.00	800.00			Temperature	475.00	800.00	
Autoclave II (Auto- clave 5 day CO2)	5D	carbonated sam- ple	95.95	90.41	5.54	5D	carbonated sam- ple	97.12	92.07	5.05
	28D	REF. sample	96.00	93.91	2.09	28D	REF sample	96.28	93.98	2.30
				Net	3.45				Net	2.75
		CI	EMIII				(CEMI		
		Temperature	475.00	800.00			Temperature	475.00	800.00	
Autoclave I (Auto- clave 28 day SCO2)	28D	carbonated sam- ple	97.06	90.47	6.58	28D	carbonated sam- ple	96.83	90.78	6.05
	28D	REF. sample	96.00	93.91	2.09	28D	REF sample	96.28	93.98	2.30
				Net	4.50					3.75
		CI	EMIII				. (CEMI		
		Temperature	475.00	800.00			Temperature	475.00	800.00	
Autoclave II (Auto- clave 28 day CO2)	28D	carbonated sam- ple	97.03	91.47	5.56	28D	carbonated sam- ple	96.99	90.55	6.44
	28D	REF. sample	96.00	93.91	2.09	28D	REF. sample	96.28	93.98	2.30
					3.47					4.14

Decarbonation weight loss calculation based on TGA result of sample in autoclave

* Temperature (°C); **weight loss (%)

Decarbonation weight loss calculation based on TGA result of Carbonation chamber
--

		G	STC3			UPM+CEMI						
		Temperature*	475	800				475	800			
Carbonation cham- ber (III) 14 days	14D	carbonated sample	95.87	91.35	4.52	14D	carbonated sam-	93.46	89.66	3.80		
	28D	REF. sample	80.27	78.38	1.89	14D	REF. sample	96.89	95.23	1.66		
					2.63					2.14		
		G	STC3			UPM+CEMI						
		Temperature	475.00	800.00			Temperature	475.00	800.00			
Carbonation cham- ber (IV) 28 days	28D	carbonated sample	95.00	90.87	4.13	28D	carbonated sam- ple	95.50	91.84	3.66		
	28D	REF. sample	80.27	78.38	1.89	28D	REF. sample	96.49	94.26	2.23		
					2.24					1.43		
		G	STC3				UPN	A+CEMII				
		Temperature	475.00	800.00			Temperature	475.00	800.00			
Carbonation cham- ber(V) 90 days	90D	carbonated sample	94.73	90.54	4.19	90D	carbonated sam- ple	94.48	90.75	3.73		
	90D	REF. sample	95.14	92.56	2.58	90D	REF. sample	96.26	93.81	2.45		
					1.61					1.28		

* Temperature (°C); **weight loss (%)

		С	EMIII				(CEMI				
		Temperature*	475	800			Temperature	475	800			
Carbonation cham- ber(III) 14 days	14D	carbonated sam- ple **	91.83	86.81	5.02	14D	carbonated sam- ple	88.89	85.19	3.70		
	14D	REF sample	96.06	93.99	2.07	14D	REF sample	95.59	93.21	2.38		
					2.95							
		С	EMIII				(CEMI				
		Temperature	475.00	800.00			Temperature	475	800			
Carbonation cham-		carbonated sam-					carbonated sam-					
ber (IV) 28 days	28D	ple	90.38	85.40	4.98	28D	ple	93.18	87.37	5.81		
	14D	REF sample	96.00	93.91	2.09	28D	REF sample	96.28	93.98	2.30		
					2.89					3.51		
		С	EMIII				(CEMI				
		Temperature	475.00	800.00			Temperature	475	800.00			
Carbonation cham- ber(V) 90 day	28D	carbonated sam- ple	97.59	92.76	4.83	90D	carbonated sam- ple	96.95	89.93	7.02		
	28D	REF sample	96.17	93.91	2.26	90D	REF sample	83.35	81.34	2.01		
					2.57					5.01		

Decarbonation weight loss calculation based on TGA result of Carbonation chamber

* Temperature (°C); **weight loss (%)

Annex 3 Unconfined compression test results

					GTC3						
Autoclave I_28 day	Spec- imen	Туре	Measured Specimen Diameter, Average (mm)	Measured Specimen height, Average (mm)	Ratio (H/Ø)	Density (g/cm³)	Moisture content (%)	Failure Ioad (kN)	Failure Strain (%)	UCS (kPa)	Average UCS (kPa)
SCO2	1	Carbonated	46.93	100.57	2.14	1.592	76.92	0.048	2.955	27.1	
	2	Carbonated	46.78	96.77	2.07	1.545	63.73	0.122	7.5	65.5	46.36
	3	Reference	50.02	100.5	2.01	1.454	88.72	0.325	1.711	162.3	
	4	Reference	49.62	100.55	2.03	1.457	86.92	0.375	2.224	186.4	174.37
					GTC3						
Autoclave	1	Carbonated	49.31	99.9	2.03	1.565	70.32	0.094	2.984	47.7	
II_28 day	2	Carbonated	49.55	100.76	2.03	1.55	70.01	0.107	3.922	53.4	50.56
CO ₂	3	Reference	49.75	100.73	2.02	1.516	71.31	0.598	2.435	300.1	
	4	Reference	49.797	99.95	2.01	1.517	70.74	0.581	2.328	291.4	295.80

UCS test result for samples in Autoclave

28 day	5	Reference	49,22	99,25	2,02	1,456	89,99	0,361	0,955	187,82	189,60
(round 2)	6	Reference	49,51	100,35	2,03	1,467	90,05	0,38	0,954	195,54	
	7	Reference	50	100,2	2,00	1,451	89,74	0,368	1,139	185,44	

28 day (round 2): Reference sample without being confined in plastic tube.

					CEMII						
	Speci- men	Туре	Measured Specimen Di- ameter, Aver- age (mm)	Measured Specimen height, Av- erage (mm)	Ratio (H/Ø)	Density (g/cm ³)	Mois- ture con- tent(%)	Failure Ioad(kN)	Failure Strain(%)	UCS (kPa)	Aver- age UCS (kPa)
Autoclave	1	Carbonated	48.14	97.53	2.03	1.405	65.33	0.152	3.076	80.9	175 50
I_28 day	2	Carbonated	46.52	97.53	2.097	1.533	52.31	0.488	5.862	270.2	1/5.59
SCO ₂	4	Reference	49.03	100.82	2.03	1.404	80.64	0.339	2.564	235.3	252.01
					CEMII						
Autoclave	1	Carbonated	49.5	100.22	2.03	1.554	67.43	0.165	1.683	84.403	
II_28 day	2	Carbonated	49.92	97.53	1.95	1.59	67.2	0.211	1.76	105.7	95.06
CO ₂	3	Reference	49.61	99.53	2.01	1.529	70.53	1.139	2.305	575.5	
	4	Reference	49.68	100.28	2.02	1.517	70.45	1.008	2.738	505.9	540.71

28 day	5	Reference	49,73	100,47	2,02	1,451	85,84	0,358	0,494	183,12	228,12
(round 2)	6	Reference	49,7	99,95	2,01	1,465	85,84	0,481	0,881	245,85	
	7	Reference	50,39	100,79	2,00	1,462	85,55	0,515	1,122	255,38	

28 day (round 2): Reference sample without being confined in plastic tube.

r											
					UPM+CE	ALL (70·30)					
	1	Carbonated	47.86	105.6	2.21	1.531	67.91	0.173	3.7	92.5	
Autoclave I	2	Carbonated	46.51	99.79	2.15	1.605	57.61	0.324	3.825	183.5	138.04
28 day SCO ₂	3	Reference	49.49	101.38	2.05	1.459	83.94	0.185	2.687	93.7	
	4	Reference	49.81	100.21	2.01	1.446	83.92	0.149	1.591	75.1	84.42
					UPM+CEN	√II (70:30)					
	1	Carbonated	49.89	100.75	2.019	1.544	69.29	0.113	2.132	56.5	
Autoclave II 28 day CO ₂	2	Carbonated	50.05	101.88	2.035	1.532	70.23	0.109	3.115	53.7	55.10
20 00 002	3	Reference	49.35	100.49	2.036	1.522	72.17	0.208	1.956	106.5	
	4	Reference	49.81	100.21	2.011	1.486	72.37	0.209	2.072	105.1	105.88

28 day	5	Reference	49,59	100,59	2,03	1,457	87,47	0,125	1,949	63,7	64,69
(round 2)	6	Reference	49,84	100,42	2,01	1,465	87,07	0,131	2,386	65,68	

28 day (round 2): Reference sample without being confined in plastic tube.

					CEM						
	1	Carbonated	46.52	100.13	2.15	1.61	58.65	0.199	6.86	109.2	
Autoclave_I _	2	Carbonated	49.46	100.66	2.04	1.516	69.84	0.09	3.0	45.4	109.24
28 day SCO ₂	3	Reference	49.79	100.33	2.02	1.462	83.99	0.609	2.28	305.4	
	4	Reference	49.79	100.26	2.01	1.454	83.57	0.609	2.28	305.5	305.50
	CEMI										
	1	Carbonated	49.6	101.27	2.04	1.51	71.6	0.135	1.91	68.7	
28 day CO ₂	2	Carbonated	50.06	105.07	2.10	1.53	70.75	0.158	1.16	79.4	74.05
20 ddy 002	3	Reference	49.62	100.28	2.02	1.52	74.8	0.793	2.75	398.99	
	4	Reference	49.806	99.83	2.00	1.48	71.03	0.759	3.06	377.6	388.28

28 day (round	5	Reference	49,59	99,83	2,01	1,486	85,44	0,747	0,85	383,32	363,76
2)	6	Reference	49,51	100,15	2,02	1,467	85,62	0,675	1,12	346,9	
	7	Reference	50,1	99,98	2,00	1,453	85,39	0,718	0,85	361,07	

28 day (round 2): Reference sample without being confined in plastic tube.

UCS test result for samples in Carbonation chamber

					GT	C3					
	Speci- men	Туре	Diameter, Average (mm)	Height, Average (mm)	Ratio (Height/Di- ameter)	Density (g/cm³)	Moisture content(%)	Failure load(kN)	Failure Strain(%)	UCS qu(kPa)	Average UCS (kPa)
Carbonation chamber III_14 days	1	Carbonated	43.12	89.51	2.08	1.147		0.485	6.456	310.4	
	2	Carbonated	43.8933	91.01	2.07	1.121		0.451	6.771	277.5	
uays	3	Carbonated	43.97	87.02	1.98	1.077		0.553	6.585	339.9	293.98
	4	Reference	49.81	100.68	2.02	1.416	94.03	0.353	0.813	179.7	
	5	Reference	49.51	100.17	2.02	1.438	92.52	0.377	1.246	193.4	
	6	Reference	49.52	100.17	2.02	1.439	92.67	0.378	0.951	194.4	189.22
					GT	C3					
Carbonation	1	Carbonated	42.81	96.82	2.26	1.187		0.43	4.702	284.9	
	2	Carbonated	43.34	88.90	2.05	1.121		0.504	6.272	319.9	
chamber IV_28	3	Carbonated	43.07	97.77	2.27	1.184		0.467	6.034	304.4	303.13
days	4	Reference	50.03	100.37	2.01	1.401	98.06	0.425	1.726	212.5	
	5	Reference	49.59	100.48	2.03	1.419	96.92	0.458	1.125	234.3	
	6	Reference	49.88	98.37	1.97	1.444	96.3	0.498	1.231	251.7	223.47
					GT	C3					
	1	Carbonated	43.1	99.68	2.31	1.41	86.5	0.594	6.201	381.9	
Carbonation chamber V_90	2	Carbonated	43.11	97.075	2.25			0.63	6.535	403.7	
	3	Carbonated			<2.0						392.85
day CO2	4	Reference	49.82	99.98	2.01	1.47	74	0.584	1.836	293.8	
	5	Reference	49.82	100.25	2.01	1.504	72.23	0.567	1.974	284.9	
	6	Reference	49.74	100.25	2.02	1.488	70.53	0.558	1.837	281.7	286.86

					UPM+CEN	ЛI (70:30)					
	Speci- men	Туре	Diame- ter, Av- erage (mm)	Height, Av- erage (mm)	Ratio (H /Ø)	Density (g/cm³)	Moisture con- tent(%)	Failure load(kN)	Failure Strain(%)	UCS (kPa)	Average UCS (kPa)
Carbonation	1	Carbonated	42.06	86.26	2.05			0.858	1.633	607.772	
days)	2	Carbonated	41.693	87.84	2.11			0.867	4.525	606.396	
-	3	Carbonated	41.81	106.05	2.54			0.592	3.711	415.344	607.084
	4	Reference	49.14	100.08	2.04	1.49	85.91	0.066	3.634	33.373	
	5	Reference	-	-	-	-	-	-	-	low UCS	
	6	Reference	-	-	-	-	-	-	-	low UCS	33.373
					UPM+CEN	ЛІ (70:30)					
	1	Carbonated	40.19	93.7	2.33			0.581	4.5	437.542	
Carbonation	2	Carbonated	40.57	91.94	2.266			0.556	4.942	408.873	
chamber_IV_28	3	Carbonated	40.95	81	1.98			0.601	4.456	436.059	427.49
days	4	Reference	49.1	100.36	2.04	1.471	98.88	0.075	4.01	38.137	
	5	Reference	-	-			-	-	-	-	
	6	Reference	-	-	-	-	-	-		-	38.14
			r		UPM+CEN	ЛІ (70:30)	r	r		-	
	1	Carbonated	42.56	85.32	2.00	1.524	-	0.649	4.925	433.89	
Carbonation	2	Carbonated	42.28	91.94	2.17	1.45	-	0.665	4.386	453.06	
chamber_V 90	3	Carbonated	-	-	<2.0	-	-	-	-	-	443.48
day CO2	4	Reference	47	109.28	2.33	1.685	77.56	0.134	2.36	75.33	
	5	Reference	49.86	100.93	2.02	1.447	81.15	0.112	2.69	55.69	
	6	Reference									65.51

					CEI	MIII					
Carbonation	Spec- imen	Туре	Diame- ter,Aver- age (mm)	height, Aver- age(mm)	Ratio(H/Ø)	Density (g/cm³)	Moisture con- tent(%)	Failure load(kN)	Failure Strain(%)	UCS (kPa)	Average UCS (kPa)
chamber_III 14	1	Carbonated	44.51	97.16	2.18	-	-	1.078	5.318	655.91	
days	2	Carbonated	43.57	95.98	2.20	-	-	0.838	5.205	532.5	
	3	Carbonated	-		<2.0	-	-	-	-	-	594.24
	4	Reference	49.84	100.49	2.02	-	85.96	0.434	1.641	218.7	
	5	Reference	49.95	101.33	2.03	-	85.85	0.466	1.463	234.3	
	6	Reference	49.71	99.89	2.01	-	85.2	0.537	1.51	272.5	241.87
					CE	MIII					
	1	Carbonated	43.74	97.07	2.22	1.24	-	0.447	7.612	274.6	
CArbonation	2	Carbonated	44.39	94.9	2.14	1.18	-	0.273	6.868	164.5	
chamber_IV 28	3	Carbonated	43.71	97.42	2.23	1.21	-	0.403	7.903	247.2	228.84
uays	4	Reference	49.84	100.73	2.02	1.43	94.59	0.558	1.769	286.02	
	5	Reference	49.71	100.04	2.01	1.43	93.84	0.542	2.323	272.7	
	6	Reference	49.57	100.05	2.02	1.44	94.86	0.572	2.247	289.7	282.82
					CE	MIII	1	r			
	1	Carbonated	44.54	101.15	2.27	1.3416	-	0.553	6.833	332.0	
Carbonation	2	Carbonated	44.53	104.04	2.34	1.3629	-	0.605	6.255	363.9	
chamber _V 90	3	Carbonated	-	-	<2.00		-	-	-	-	347.95
uay CO2	4	Reference	49.78	100.22	2.01	1.4876	74.96	0.553	6.896	264.5	
	5	Reference	49.797	100.11	2.01	1.515	74.21	1.219	2.03	613.2	
	6	Reference	49.59	99.96	2.02	1.513	75	1.189	2.159	602.4	607.88

						CEMI					
	Speci- men	Туре	Diameter, Average (mm)	height, Aver- age (mm)	Ratio (H/Ø)	Density (g/cm³)	Moisture content(%)	Failure load(kN)	Failure Strain(%)	UCS (kPa)	Average UCS (kPa)
Carbona-	1	Carbonated	43.49	94.71	2.18	-	-	0.812	8.3	500.9	
ber III (14	2	Carbonated	43.3	90.42	2.09	-	-	0.755	8.6	468.5	
days)	3	Carbonated	43.4	91.5	2.11	-	-	0.676	6.9	425.1	464.89
	4	Reference	49.7	100.32	2.02	1.49	81.32	0.875	2.7	438.6	
	5	Reference	49.95	100.18	2.01	1.47	81.28	0.995	2.2	496.4	
	6	Reference	50.08	100.48	2.01	1.47	81.78	0.731	2.5	361.7	432.29
						CEMI					
	1	Carb.	45.26	102.25	2.26	-	-	0.535	6.3	311.7	
Carbona-	2	Carb.	45.6	107.17	2.35	1.257	-	0.461	58	265.8	
ber IV (28	3	Carb.	45.27	104.38	2.31	1.272		0.577	5.9	337.5	305.02
days)	4	Reference	49.84	100.32	2.01	1.495	75.49	0.756	1.9	380.3	_
	5	Reference	49.4	100.77	2.04	1.507	75.71	0.918	2.6	466.1	_
	6	Reference	49.75	100.08	2.01	1.53	74.14	0.671	2.3	337.1	394.56
		T	1	1	1	CEMI	1	1	T	1	
	1	Carb.	44.98	93.89	2.09	1.2455	-	0.7	7.598	406.8	_
Carbona-	2	Carb.	44.78	99.05	2.21	1.278	-	0.639	5.524	383.6	_
cahmber V	3	Carb.	-	-	-	<2.00	-	-	-	-	395.22
(90 day)	4	Reference	49.57	100.04	2.02	1.511	63.92	1.051	2.572	530.6	_
	5	Reference	50.61	100.15	1.97	1.455	60.69	1.232	2.445	597.6	
	6	Reference	49.83	99.85	2.00	1.505	63.79	0.9	2.204	451.5	491.10

Annex 4: Binder component data from suppliers

Kolmosseme	Kolmossementti					
Korkean 52,5-lujuusluo	Korkean 52,5-lujuusluokan masuunikuonasementti					
Sementin ominaisuuksia	Tulokset	Vaatimukset				
Puristuslujuus 1 vrk	812 MPa	ei vaatimusta				
Puristuslujuus 2 vrk	1923 MPa	≥ 10 MPa				
Puristuslujuus 7 vrk	3641 MPa	ei vaatimusta				
Puristuslujuus 28 vrk	5662 MPa	≥ 52,5 MPa				
Sitoutumisaika	150250 min	≥ 45 min				
Tilavuuden pysyvyys	01,5 mm	≤ 10 mm				
Hienous	450520 m²/kg	ei vaatimusta				
Hehkutushäviö	04 %	≤ 5,0 %				
Liukenematon jäännös	04 %	≤ 5,0 %				
SO3	3,03,5 %	≤ 4,0 %				
Kloridipitoisuus	≤ 0,08 %	≤ 0,10 %				
Cr6+	02 mg/kg	≤ 2 mg/kg				

Sementtien sisältämät seosaineet	en _t	, Vaatimus
Yhteensä	4046 %	≥ 36 % ja ≤ 65 %
Sivuosa-aineet	05 %	05 %
Masuunikuona	4046 %	≥ 36 % ja ≤ 65 %

Klinkkerin tyypillinen kemiallinen koostumus	*	
CaO	6365 %	
SiO ₂	2022 %	
Al ₂ O ₃	4,05,4 %	
Fe ₂ O ₃	2,83,3 %	
MgO	2,53,2 %	



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Oiva-sementti

Sementit Hillmikuu 2020

Normaalisti kovettuva portlandseossementti

CEM II/B-M (S-LL) 42,5 N

iementin ominaisuuksia	Turus des	aedmuliset
Puristusujuus 1 vrk	12-16 MPa	ei vaatimusta
Puristusujaus 2 vrk	23-27 MPa	≥ 10 MPa
Puristusujuus 7 vrk	36-41 MPa	ei vaatimusta
Puristusujuus 28 vrk	47-53 MPa	≥ 42,5 MPa ja ≤ 62,5 MPa
Sitoutumisaika	150-210 min	≥ 60 min
Tilavuuden pysyvyys	0-1,5 mm	≤ 10 mm
Hienous	400-480 m ² /kg	ei vaatimusta
Hehkutushāviö		ei vaatimusta
Liukenematon jäännös		ei vaatimusta
50,	3,0-3,3 %	≤ 3,5 %
Kloridipitoisuus	≤ 0,08 %	≤ 0,10 %
Cr6+	0-2 mg/kg	≤ 2 mg/kg

Sementtien sisältämät seosaineet		Vaedmus
Yhteensä	21-35	≥ 21 % ja ≤ 35 %
Kalkkikivi	6-20	
Masuunikuona	6-25	

Klinkkerin tyypillinen kemiallinen koostumus	-10
CaO	63-65
SiO ₂	20-22
A1,0,	4,0-5,4
Fe ₂ O ₂	2,8-3,3
MgO	2,5-3,2



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Pikasementti

Erittain nopeasti kovettuva portlandsementti

Kesakuu 2019 CEM 152,5 R

Sementit

Sementin ominaisuuksia	Tujokset	Vaatimukset	
Lujuus 1d	2832 MPa	ei vaatimusta	
Lujuus 2d	4146 MPa	≥ 30,0 MPa	
Lujuus 7d	4860 MPa	ei vaatimusta	
Lujuus 28d	5768 MPa	≥ 52,5 MPa	
Sitoutumisajan alku	120180 min	≥ 45 min	
Tilavuuden pysyvyys	02,0 mm	≤ 10 mm	
Hienous (Blaine)	490570 m²/kg	ervaatimusta	
Hehkutushāviõ	1,83,0 %	≤ 5,0 %	
Liukenematon jäännös	0,30,9 %	≤ 5,0 %	
SO4	3,53,9 %	≤ 4,0 %	_
Kloridipitoisuus	≤ 0,08 %	≤ 0,10 %	
Cr6+	02 mg/kg	≤ 2 mg/kg	_

Sementtien sisältämät seosaineet	*	Vaatimus	
Yhteensä	05 %	≤ 5,0 %	_
Kalkkikivi	05 %		
Masuunikuona			

Klinkkerin tyypillinen

emiallinen koostumus	-	
CaO	6365 %	_
SiO ₂	2022 %	
Al ₂ O ₃	4,05,4 %	
Fe ₂ O ₃	2,83,3 %	
MgO	2,53,2 %	



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Nordkalk

Nordkalk Terra-tuotteiden hiilijalanjälki pienenee

Finnsementin tuotevalikoima on laajentunut syksyllä 2021 uudella vähähillisellä sementillä. Käyttöön on otettu Kolmossementii, joka on Korkean 52,5-lujuusluokan masuunikuonasementti. Kolmossementin ehdoton valtti on ympäristöystävällisyys: sen hillijalanjälki on huomattavasti pienempi kuin portlandsementtien. Olva-sementtiin verrattuna hiilijalanjälki on noin 25 prosenttia pienempi.

Nordkalk Terra -seoksissa käytettävä Oiva-sementti korvataan Kolmossementillä toukokuun 2022 alusta lähtien.

Tänä vuonna hillidioksidin päästöölkeuksien hinta on noussut huomattavasti vuoden takaiseen verrattuna ja Ukrainan sota on aiheuttanut erittäin kovan energian hinnan nousun. Tämä on johtanut silhen, että etenkin perinteisten kalkkisementtiseosten hinta on noussut huomattavasti. Samaan aikaan tietoisuus sideaineiden päästöistä on lisännyt kiinnostusta kiertotalouspohjaisiin tuotteisiimme - GTC, GREEN ja POZ.

Nordkalk Terra POZ ja GREEN sisältävät kalkkiuunin reaktiivista sähkösuodinpölyä (LKD) ja sillä saadaan vastaavia ominaisuuksia kuin KC-seoksilla.

Nordkalk Terra tuotteiden hiilijalanjälki



Epävirailisten laskelmien mukaan Nordkalk Terra -tuotteiden hillijalanjälki, kun seoksissa käytetään Kolmossementtiä ja eri sideaineita.

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Myynnissä olevat Nordkalk Terra tuotteet ovat:
Nordkalk Terra GTC
Nordkalk Terra GREEN
Nordkalk Terra POZ
Nordkalk Terra KC30
Nordkalk Terra KC50
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Lisätietoa Nordkalkin nettisivuilta www.nordkalk./li ja allekirjoittaneelta.

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