TALLINN UNIVERSITY OF TECHNOLOGY
SCHOOL OF ENGINEERING
Department of Materials and Environmental Technology

PERFORMANCE EVALUATION OF FLUE GAS/CO_2 CURED CALCIUM-RICH FLY ASH BASED BUILDING BLOCKS/MATERIALS

KALTSIUMIRIKKA LENDTUHA PÕHISTE SUITSUGAASI/CO_2 ABIL KÕVENDATUD EHITUSMATERJALIDE/-PLOKKIDE TOIMIVUSE HINDAMINE

MASTER THESIS

Student	:	Ademola Michael Adegbile
Student Code	:	194205KAYM
Supervisor	:	Can Rüştü Yörük
Co-supervisor	:	Mustafa Cem Usta

Tallinn, 2021

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Department of Materials and Environmental Technology

THESIS TASK

Student: Ademola Michael Adegbile 194205KAYM

Study programme: KAYM - Materials and Processes for Sustainable Energetics

main speciality: Materials for Sustainable Energetics

Supervisor: Researcher - Can Rüştü Yörük +37258542373

Co-supervisor: PhD Student - Mustafa Cem Usta +37258290725

Thesis topic:

(in English) Performance evaluation of flue gas/CO_2 cured calcium rich fly ash based building blocks/materials

(in Estonian) Kaltsiumirikka lendtuha põhiste suitsugaasi/CO_2 abil kõvendatud ehitusmaterjalide/-plokkide toimivuse hindamine

Thesis main objectives:

1. Feasibility studies on CO_2 sequestration in fly ash through literature review.
2. Laboratory carbonation experiment of fly ash-based compacts.
3. Performance evaluation of experimental results.
4. Conclusion based on the results of the investigation.

Thesis tasks and time schedule:

No	Task description	Deadline
1.	Literature review	19.01.2021
2.	Laboratory mineral carbonation experiments	29.03.2021
3.	Analysis of result	26.04.2021
4.	Finalization of thesis	07.05.2021

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Student: Ademola Michael Adegbile ………… ….2021

/signature/

Supervisor: Can Rüştü Yörük Ph.D ………….. …..2021

/signature/

Head of study programme: Sergei Bereznev Ph.D ………. ……2021

/signature/

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PREFACE

This master’s thesis research was carried out in the Laboratory of Inorganic Materials at Tallinn University of Technology under the tutelage of Researcher Can Rüştü Yörük and PhD Student Mustafa Cem Usta.

I would like to thank Prof. Andres Trikkel for giving me the opportunity to carry out the experiments needed in his laboratory for this thesis work. I especially appreciate the guidance of my supervisors Researcher Can Rüştü Yörük and Early stage researcher Mustafa Cem Usta for their valuable input towards the successful completion of this thesis work. Furthermore, I would like to thank Tiina Hain for her timely and prompt input towards this thesis work. I would like to thank all staff members of the laboratory of Inorganic Materials for creating a conducive research environment and being helpful. I would also like to thank my parents John and Folashade Adegbile as well as my siblings for the support and encouragement throughout this project and my studies. I also acknowledge the inspiration imparted by my grandparents late Engineer Victor and Mrs. Felicia Johnson to tow this path. Finally, I appreciate all my friends and well-wishers who helped throughout the duration of this project.

In this thesis work, carbon capture by valorization of fly ash is explored as well as its perormance in building materials. The evaluation of performance of these fly ash based carbonated compacts was also explored in this master thesis.

Tallinn, May 7th, 2021.

Ademola Michael Adegbile.

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List of Abbreviations and symbols

ASW	Alkaline Solid Waste
C	100% CO_2 Carbonated Sample
CCS	Carbon Capture And Storage
CCUS	Carbon Capture, Utilization And Storage
CFB	Circulating Fluidized Bed
DAC	Direct Air Capture
EU-LTS	European Union Long Term Strategic Vision
FA	Fly Ash
FGC	Flue Gas Carbonated Sample
FT-IR	Fourier-Transform Infrared Spectroscopy
GHG	Greenhouse Gases
IEA	International Energy Agency
OS	Oil Shale
OSA	Oil Shale Ash
OSA/WA	50% Oil Shale Ash/50% Wood Ash
PSD	Particle Size Distribution
RTS	Reference Technology Scenario
SSA	Specific Surface Area
TGA	Thermogravimetric Analysis
UC	Uncarbonated
WA	Wood Ash
XRD	X-Ray Diffraction Spectrocopy
XRF	X-Ray Flourescence Spectroscopy

1. INTRODUCTION

1.1 General outlook on the industrial wastes as raw materials: CO_2 and alkaline solid wastes

Greenhouse gases (GHG) from industrial processes have long been a menace to the human environment with warmer climate and worsening many types of natural disasters since pre-industrial levels. The current major challenge towards climate control is still the same concern due to the continuously raising level of CO_2 emission as one of the major GHG. Among human activities, fossil fuel-based energy production of the world has been identified as major contributor at around 78% and the cement making industry has also been responsible from 8% of total CO_2 emissions worldwide [1]. Besides, the CO_2 emissions from the cement industry are expected to increase by 4% globally according to the International Energy Agency (IEA) Reference Technology Scenario (RTS) by 2050 [2]. The figure 1.1 below shows the trend (historical and projected) of CO_2 emissions from some fuels (coal, liquid fossil fuels and natural gas) between 1990-2050. It can be observed that the emissions from the use of coal in energy production overtook that from liquid around 2005. This run is expected to continue well into 2050 for coal along with an increase in emissions from the other fuels as it is shown in the chart.

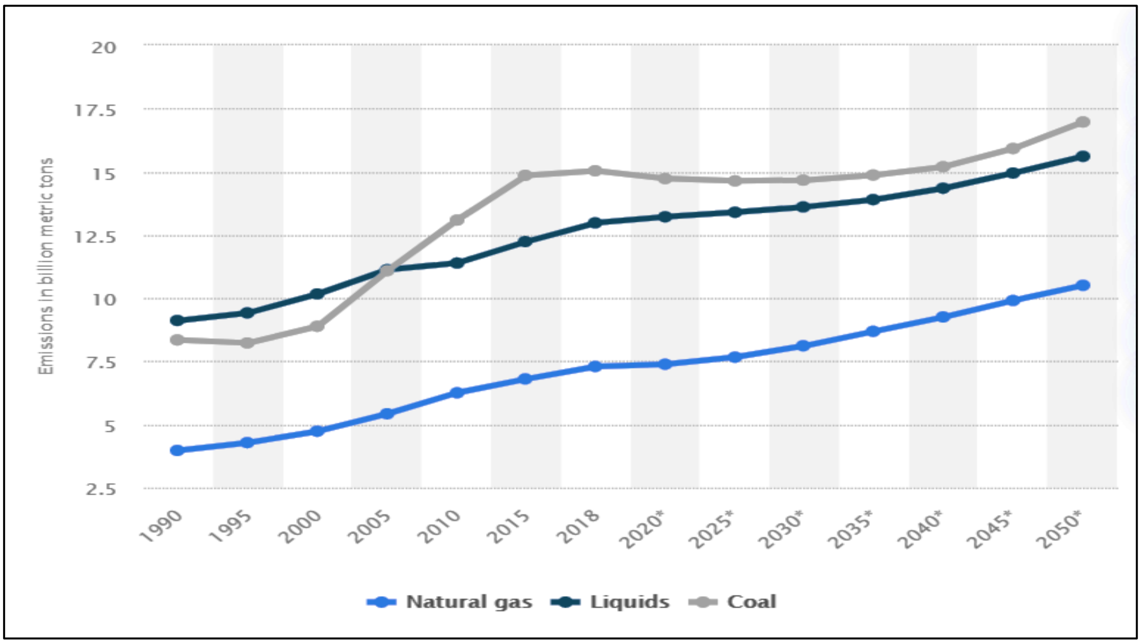


Figure 1.1 Energy related CO_2 emissions worldwide, by fuel in billion metric tonnes (1990-2050) [3].

Ever-increasing need for energy and construction materials have mounted an increased pressure on the energy and cement sectors to find variety of approaches and technologies first, to capture CO_2 and later turn it into products or use it in different applications to decrease carbon footprint of future products. One of the ways currently being explored to remedy CO_2 emissions, although still relatively novel, is the carbon capture and storage (CCS) technologies sometimes called as carbon capture, utilization, and storage (CCUS) if there is a potential to utilize the captured CO_2 in other sectors. Although the concept of CCS has become very popular in recent years, the real-life applications did not hit the estimated targets of current and future CO_2 cuts on a big scale due to the cancelled projects and lack of public awareness [4]. In Figure 1.2, it is expected that new model of CO_2 capture-direct air capture (DAC) of CO_2 appears minimally in 2040 and eventually increases in 2050 to just under 400 Mtonnes CO_2. By these numbers, the amount of CO_2 captured from fossil fuel (biomass, gas and coal) combustion in 2050 is expected to increase significantly by the year 2050 towards achieving carbon neutrality. The captured CO_2 is projected to be reused as a fuel in steady increment over the 20 years period. These projections can be found in more detail from the JRC-EU-TIMES (Joint Research Center) and EU LTS (European Union Long Term Strategic) vision scenarios [5].

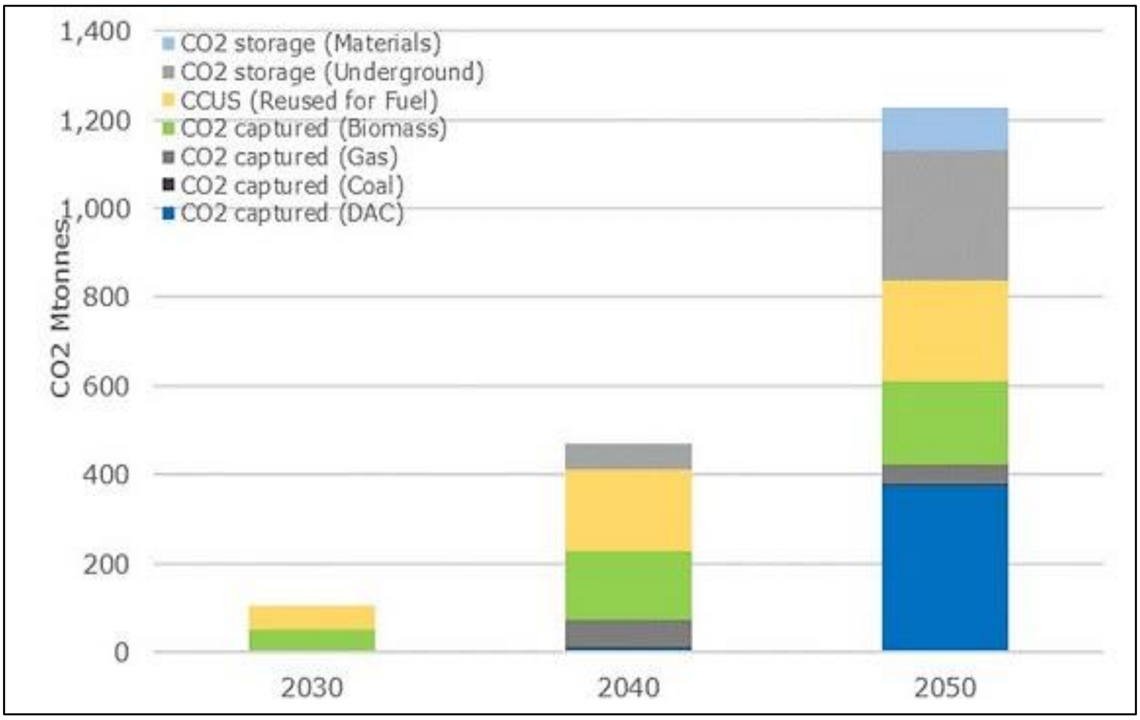


Figure 1.2 Projected CO_2 stored, used and captured toward 2050 carbon neutrality from JRC-EU-TIMES and EU LTS vision scenarios [5].

In addition to problem of CO_2, other cost of industrial activities, especially in energy production, ending up getting disposed as waste in landfills is alkaline solid wastes (ASW) including mainly fly ash (FA) from coal, oil shale (OS), municipal solid waste, and biomass combustion, as well as mining wastes, clinker dusts, construction demolition wastes etc. [6]. Among these wastes, the wastes generated related to energy sector accounts the biggest portion, further solid fuels especially different types of coals, biomass and OS will continue to remain a major player in the generation of power and electricity in today's and near future's world. It is as near as possible that the numbers will grow regarding landfilled wastes since it is also projected that the solid fuel-based power sectors will provide as minimum 44% of world electricity by 2030 which further backs the need for the valorization of combustion products [7].

Countries such as China, India and USA are large consumers of coal at 565 Mt/yr., 197 Mt/yr. and 107,4 Mt/yr., respectively. This reliance on coal as a primary energy source put the total FA generation around the world at 1,2 billion tons in 2016 [8]. Additionally, according to a report by European Coal Combustion Products Association, it is estimated that 40 million tons of coal combustion product was generated in the European Union (EU15) in 2016 and only 40,8% of it was utilized mainly as concrete additive [6]. In the grand scheme this is an alarming figure that has been agreed to be a disturbance to the environment and because of this, ashes from power plants took a public attention and has been a wake-up call to researchers around the world to pursue ways to utilize waste materials generated from these industries. Like other ASWs, FA is considered as valuable binder and filling material which can be used in several ways to make the standard processes of cement, concrete, and ceramic productions more energy-efficient and environmentally friendly. As a result, recently FA is being more pushed to be incorporated in various sectors such as the construction industry including the applications of production of clinker, partial substitution with Portland cement, manufacturing of different types of building blocks and road construction [9]. Additionally, FAs appear to be sources of CaO/MgO and Ca/Mg-silicates which make them potential raw materials for CO_2 sequestration *via* carbonation which is the process that both fixes CO_2 and changes the physical, microstructural, and chemical properties of the raw materials [10]. This form of sequestration is a permanent method since the mineral carbonates are stable over millions of years. In the light of recent developments, both energy and construction industries becoming more and more attracted by means of adopting new technologies with low carbon emissions and reduced environmental concerns regarding to the land filled ASWs [11]. One of these technologies where both waste CO_2 and FA can meet is accelerated carbonation technology which can be employed for both CO_2 sequestration and FA stabilization within the production of low carbon footprint building materials. The idea of using CO_2 from flue gas can improve the practicality and scaling up of the carbonation process units. However, there is a need to do research and compare the usage of flue gas with 100% CO_2 to investigate the rate limiting affects and strength development of compacts in low CO_2 concentration. In this context, the current thesis work addresses these questions and studies the methods of accelerated carbonation technologies for finding most environmentally friendly approaches for the valorization of local alkaline solids wastes of Estonia.

1.2 Estonian perspective on the volarization of CO_2 and alkaline solid wastes

OS is a low-quality fossil fuel, yet very crucial fuel in terms of being fuel independent in OS dominated countries who do not have other abundant natural resources and rapid recovery from renewables. There are challenges of the usage of OS-type fossil fuels which are the large amount of remaining ash and emitting CO_2 emissions. Estonia is one of the visible example that the amount of OS ashes which forms every year is on the level of 7 million tons and has the most carbon intensive economy among OECD countries due to the heavy reliance on OS [12]. Since there are ash/CO_2 utilization and related environmental problems existing together with growing landfill space demand for the OS processing wastes and problems related to finding a safe and permanent storage solution for CO_2. Furthermore, OS mining and use activities will continue to develop according to the planned duties for 2016–2030 which is currently in motion which also indicates that the Estonian government does not plan to replace OS in the short term [13]. Figure 1.3 depicts the carbon intensity of power generation in some IEA countries (including Estonia) over a 17-year period. The Estonian power sector displayed a high carbon intensity which is due to a heavy reliance on OS. Estonia is second only to Australia in terms of CO_2 intensity among IEA countries. In 2017, heat and power generation in Estonia recorded an average emission of 617 gCO_2/kWh which is 66% greater than the IEA average (372 gCO_2/kWh). It is therefore a must to find a solution to mitigate the emissions resulting from the use of OS in energy production to fulfil the EU and national objective of reducing emissions [14].

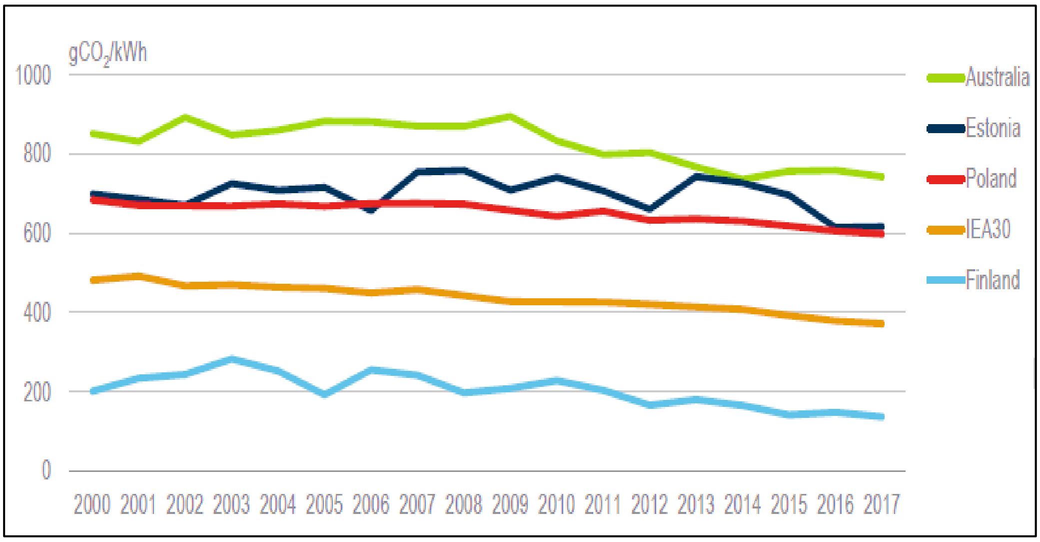


Figure 1.3 CO_2 intensity of heat and power generation in Estonia relative to some IEA member countries between 2000-2017 [14]

Previously in Estonia, OS ash was partially used as second main constituent of portland cement and coarse fractions were used in building materials industry including construction of road sublayers and production of cellular concrete blocks Despite the numerous ways of use, only a very small amount of OS ash is currently utilized (≈2%) as a raw material in the production of construction materials and agricultural purposes [15]. However, above mentioned similar activities do not exist substantially because of changed ash properties and lack of financing. Therefore, the question of utilization of solid wastes and long-term sustainability in OS sector of Estonia remains as a key issue and valorization in more diverse range is required to diminish to ash quantities to landfill and improve the carbon management of the country.

OS ash and its specific chemical composition presents a wide range of opportunities for its utilization. Due to the high content of carbonates (calcite) in OS, the OS ash is highly alkaline and has potential as a source of Ca [16]. Calcium is considered as one of the most dominant and most reactive (with respect to CO_2) alkaline earth metals found in industrial residues [17]. In principle, OS ashes containing high amount of calcium could be useful for both capture and permanent sequestration of CO_2 through the formation of $CaCO_3$. Other ash containing high amounts of calcium is forestry wood ash (WA) which are also intensively used in power and heat production of Estonia. The ash content of typical OS can be much higher than the coals, although the ash content in solid biofuels is much smaller. Nevertheless, the processing of both OS and forestry fuels in power and heat production are well-established in Estonia and the generation of ashes on a large scale are becoming an important environmental problem. Recent studies also show that there is reasonably good links between the FAs which have high content of free

CaO and MgO, even though low in self-cementitious properties to produce alternative carbonate bonded building materials via accelerated carbonation [18]. A country like Estonia that has limited options for geological in-situ mineral carbonation for CO_2 storage and large amount of ash production could consider this twofold solution because of recent progresses made in accelerated carbonation technologies: first, carbon sequestration via CO_2 mineralization using FAs and second, valorization of these FAs to produce alternatively hardened (via carbonation) construction materials (aggregates, building blocks).

The following literature review of this thesis work focuses on the aspects of FA and CO_2 utilization and evaluates the recent scientific developments where the incorporation of ASWs, mainly FA, is achieved with the accelerated carbonation technology for the production alternative building materials.

2. LITERATURE REVIEW

2.1 Mineral carbonation chemistry

The mineral carbonation process is known as the capture of gaseous CO_2 into a more stable compound by its introduction to an inorganic solid material. The formation of insoluble carbonates are products of this reaction between CO_2 and i.e., metal oxides. These products are stable and are suitable to store CO_2 for long periods of time [19]. Alkaline materials when exposed to atmospheric conditions would age and undergo carbonation which would take thousands of years at atmospheric conditions. Prevalent monitoring is available for well-known minerals such as magnesium and calcium silicates and in such case the capacity of carbon storage is found to be quite limited in a short period of time [20].

Mineral carbonation process is exothermic in nature. The general set of chemical reactions for the mineral carbonation are represented below:

Silicates

$$(Ca,Mg)_xSi_yO_{x+2y+z}H_{2z(s)} + xCO_{2(g)} \longleftrightarrow x(Ca,Mg)CO_{3(s)} + y\,SiO_{2(s)} + zH_2O_{(l/g)} \quad (2.1)$$

Serpentine:

$$Mg_3Si_2O_5(OH)_4 + 3CO_2 \longleftrightarrow 3MgCO_3 + 2SiO_2 + 2H_2O \quad (2.2)$$

Olivine:

$$Mg_2SiO_4 + 2CO_2 \longleftrightarrow 2MgCO_3 + SiO_2 \quad (2.3)$$

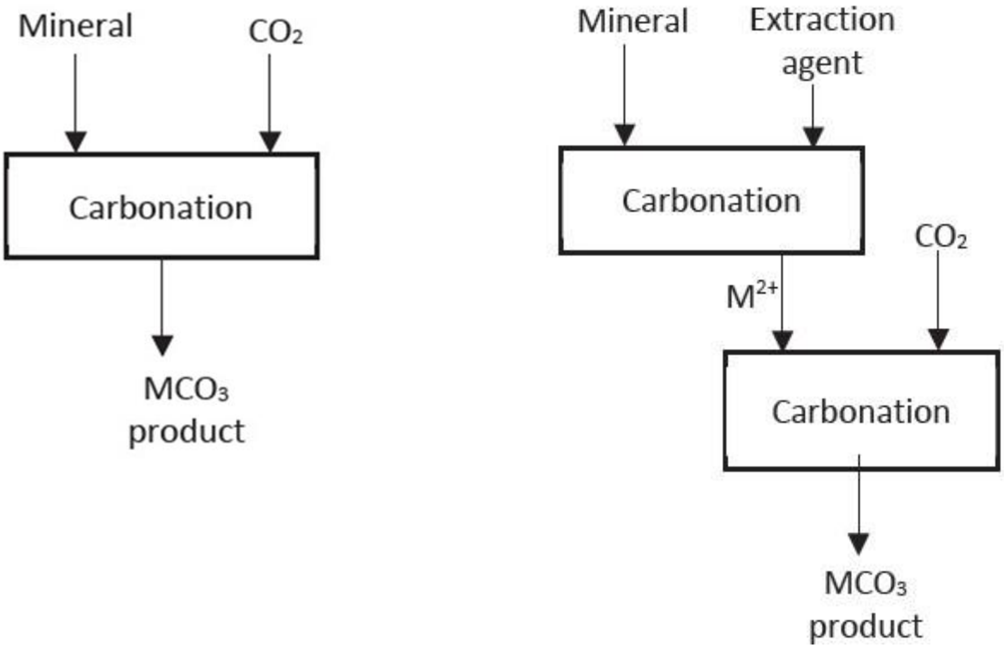
Wollastonite:

$$CaSiO_3 + CO_2 \longleftrightarrow CaCO_3 + SiO_2 \quad (2.4)$$

The carbonate phases are favored at certain conditions (temperature, humidity, partial pressure of CO_2 etc.) to be produced energetically when CO_2 reacts with silicate phases such as olivine, serpentine, enstatite and anorthite [21-24].

2.2 Carbonation processes

Carbonation involves the bringing in contact of reactive minerals with high concentrations of CO_2 to achieve. It is different from its natural counterpart in that it gives the opportunity to complete a process in hours or days which would otherwise have taken years to complete in natural environment [25]. There are two main ways to approach the carbonation according to the relevant literature. These are direct and indirect carbonation methods [26]. The Figure 2.1 below shows the schematic of the direct and indirect carbonation processes .In the current thesis work, focus will be given to the direct carbonation method (Gas-Solid carbonation).



(a) (b)

Figure 2.1 Schematic diagram of (a) direct carbonation process (b) Indirect Carbonation [27]

2.2.1 Direct carbonation

The direct method of carbonation is reported to consist of gas-solid carbonation and aqueous carbonation. It requires a minimal amount of reagent and complex set-up is not necessary [28].

The kinetics of the process of the carbonation can be accelerated by controlling (a) CO_2 pressure (b) Moisture content (c) temperature and CO_2 percent of air. The kinetic of the reaction is affected greatly by the pressure of CO_2 i.e., the solubility of CO_2 gas is directly related to its partial pressure [29]. A brief detail on some factors that affect the carbonation process are listed below:

1. Reaction time: Increment in the time of exposure of reactive mineral to CO_2 significantly increases the probability of storing more CO_2 and yielding calcium carbonate. On the other hand, poorly developed crystals result from short time exposure [30]. The availability of reactive materials however is a major determining factor in this regard.
2. CO_2 pressure: Higher CO_2 pressure enhances the diffusion of CO_2 molecules. This makes CO_2 molecules more available for capture and thus results in a faster rate of reaction [31].

3. Particle size distribution (PSD): The carbonation rate and maximum carbonation efficiency are greatly affected by the PSD of the reactive material. Small particle size could cause an increase in surface area of materials, that would help in removing high concentrations of metal ions from reactive materials [32]. Although, in fine-grained materials, the reaction could be inhibited caused by tighter particle packing restricting CO_2 permeation [33,34].

Gas-Solid Carbonation is a type of carbonation that has been described as the most direct method of carbonation [35] and was first studied by Lackner et.al [36] For example, the gas-solid carbonation of olivine is given as:

$$Mg_2SiO_{4(s)} + 2CO_{2(g)} \longleftrightarrow 2MgCO_{3(s)} + SiO_{2(s)} \qquad (2.5)$$

A direct dry process for the trapping of CO_2 was developed which involved passing flue gas through a bed of silicate rocks (Olivine, Serpentine and Wollastonite) finely ground to around 2,5 – 60 µm [37]. During the carbonation process, the ground silicate rocks were replenished by use of a conveyer. It was observed according to the report that when 5g of olivine was used within a temperature range of 100 – 500°C, 8,3 % H_2O and flue gas containing 10% CO_2, the storage capacity was 0,12 gCO_2 per gram of olivine after 30 minutes [37].

In direct carbonation with mechanical pre-treatment, increment in surface area is achieved by mechanical grinding that disorders the mineral lattice. To liberate certain valuable mineral grain of interest, the particle size reduction is carried out in the sequence of crushing followed by grinding [38].

Due to water-saturation caused by carbonation reaction of portlandite to form calcite and water in monoliths, CO_2 diffusion is slowed down by pores containing water and this makes carbonation process slow [35]. A relative humidity of between 40% - 90% is ideal for the carbonation process. Neutralization of pore water alkalinity and formation of carbonates are some of the known effects of carbonation [39]. Products of thermal processes are alkaline in nature due to the presence of high magnesium and calcium content.

In a study carried out on fly ash carbonation it was revealed that the medium sized particles (5−20 µm) were reduced after carbonation meanwhile the larger (≥20 µm) and smaller (≤5µm) sized particles displayed the opposite of this trend [40]. In another research on carbonation of lime pastes it was observed through the aid of the FTIR and

XRD analysis that calcite is the only crystalline $CaCO_3$ polymorph present along with amorphous $CaCO_3$ [41].

2.3 Fly ash Overview

FA is a major by-product of most of the combustion processes where solid fuel ignites, generating heat and producing a molten mineral residue that is carried off in the flue gas. FA is usually collected from flue gas by means of collection device such as cyclones and electrostatic precipitators [42].

The composition of FA depends on the composition of source solid fuels and co-feed materials, combustion technology and pollution control technology (FA handling technology). In general, FA is a heterogeneous substance composed mostly of amorphous aluminosilicate spheres with small quantities of iron-rich spheres, several crystalline phases, and a small amount of unburned carbon. A summary of the pathways which the disposal of FA can threaten the environment and health is shown in the Figure 2.2 below. The dumping of FA whether dry or wet leaches toxic metals into groundwater, rivers, and lakes. These metals in low concentration pose little to no environmental risk but their accumulation in the biological ecosystem causes a spike in their concentration and so pose risk to human health when aquatic plants and animals are consumed. Dumping of FA in landfills also makes the atmosphere prone to FA dust carried through wind and inhaled by inhabitants of nearby residence [43].

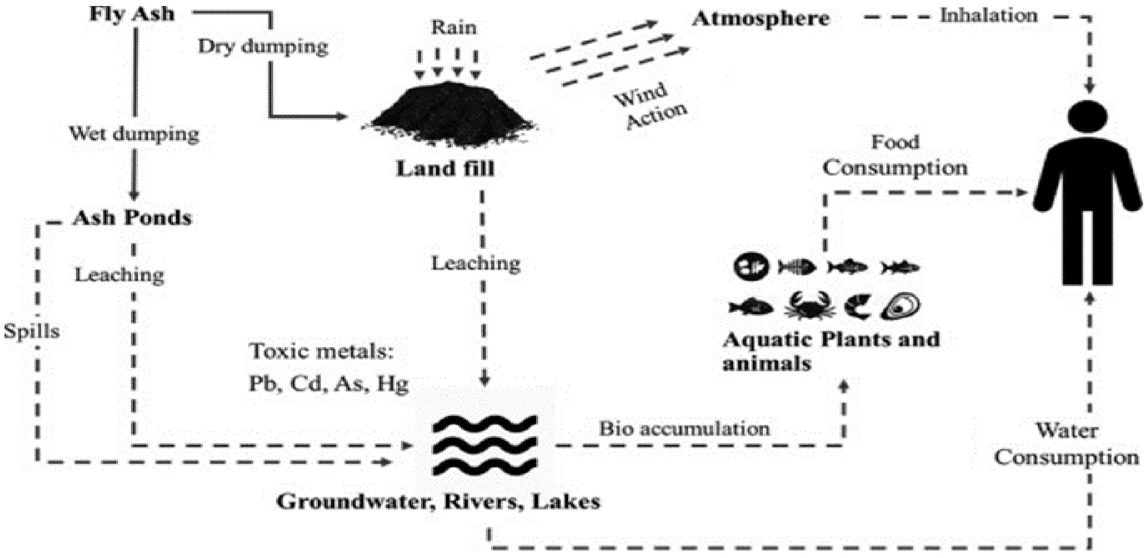


Figure 2.2 Pathways of FA disposal threatening the environment [43]

2.3.1 Physical characteristics of fly ash

Typical FA consists of an intricate mix of organic (1-9 %) and inorganic (90-99 %) substances and of this, 30-80 % can be amorphous in nature while the crystalline part can be 63% [44]. Depending on the amount of unburnt carbon present in the FA, it is color can vary between tan, gray and black. The lighter the color tan observed in a FA sample, the lower the amount of the unburnt carbon content. Also, typically when a light color is observed in a FA sample, it is usually indicative of the presence of a high percentage of lime, i.e., OS ash [42]. Most of the FA released from combustion processes are alkaline in nature (pH 8-13). The alkalinity of FA is dependent on the amount of free lime present in the ash matrix. The American Society of Testing and Materials (ASTM) developed a system for classifying ash into class C or F based on the Ca, Al, Si and Fe content (class C = Ca + Al + Si + Fe > 50 while class F = Ca + Al + Si + Fe > 70). The class C FA is usually characterized by a high content of calcium while class F is typically low in calcium content [45]. The particle size distribution (PSD) of FA has a significance on its reactivity while also helps to determine the utilization potential of the FA that includes the enrichment of trace elements from the FA. Based on the combustion technology and parameters in a power plant, the PSD of FAs can vary [46-49], although the most predominant range of PSD found in FAs can be between 10-100 μm.

2.3.2 Chemical characteristics of FA

FA chemical composition and behavior varies due to some factors such as source of fuel, combustion, and ash collection method [50]. The major constituents contained in coal FAs are oxides of silicon, aluminum, and iron [42]. In OS FA, the main constituents are found to be CaO, Al_2O_3, Fe_2O_3 and SiO_2. As seen from Table 2.1, OS FA had the highest range of value for CaO when compared to coal and biomass FAs [51]. In biomass FA however a high range of value is noted for K_2O with reference to the other FAs in Table 4 and as earlier stated in this section it is difficult to generalize FA characterization of which the same is true for biomass FA (Table 2.1) [52]. As earlier stated in this section however, the chemical composition of each FA is dependent on fuel source and combustion method among other factors. Also present in most FAs are minor amounts of oxide of magnesium, and sulfur along with trace amount of unburnt carbon[51]. FAs also contain some trace elements such as lead, antimony (Sb), strontium (Sr), zirconium (Zr) and to some extent silver (Ag) [42]. The Table 2.1 below shows the chemical composition found in typical coal, OS and biomass FAs [42,51,52].

Table 2.1 Chemical composition of a typical coal, oil shale and biomass FA [42,51,52]

Main constituents	Coal FA (wt %)	Oil shale (wt %) FA	Biomass FA (wt %)
SiO_2	35 - 70	20 - 50	6,12 – 58,09
Al_2O_3	10 - 35	5 - 15	1,44 – 7,89
CaO	0,2 - 20	30 - 60	1,14 – 19,18
Fe_2O_3	2 - 7	2 - 9	0,25 – 6,57
K_2O	0,05 – 0.90	2 - 6	1,71 – 18,07
MgO	0,01 – 4,50	1 - 6	0,52 – 3,94
Na_2O	0,05 – 2,00	0,1 – 0,5	0,20 – 1,71

Figure 2.3 shows the major chemical constituents of FAs based on the fuel combusted to yield the FA. It can be observed from the bar chart that a significant number of FAs contains CaO which is considered a potential CO_2 binding agent. The most CaO content can be found in FAs which are generated from waste-based fuel and thus could potentially bind more CO_2- In contrast, the least constituent of burnt lime was found in peat wood [53].

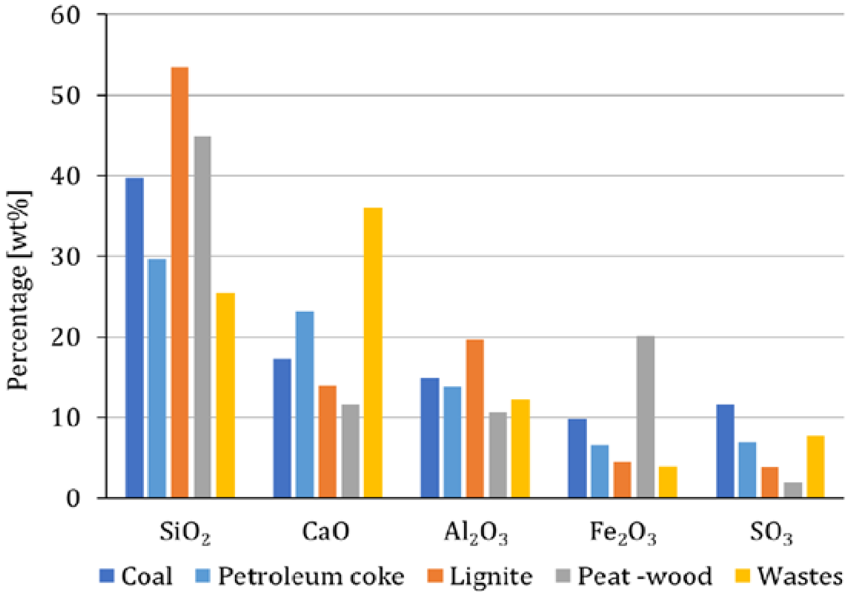
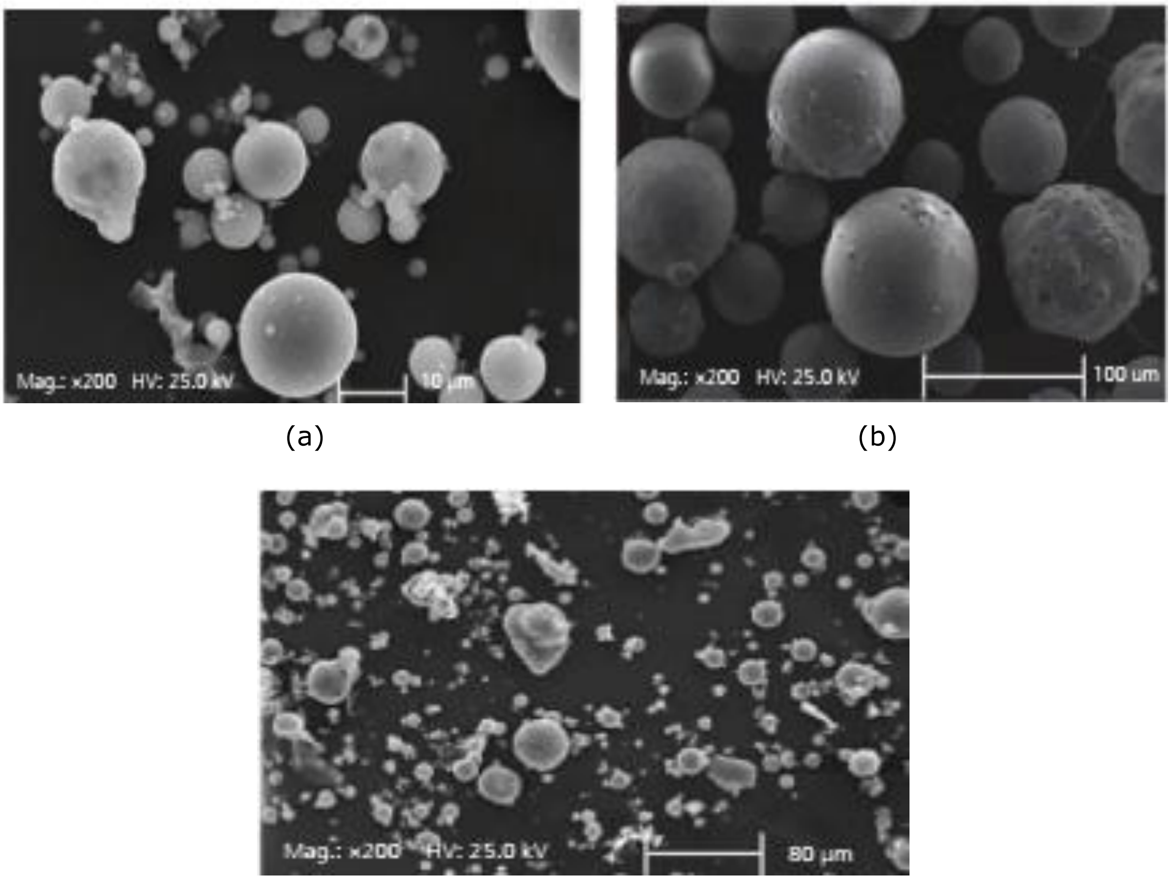


Figure 2.3 Chemical composition of FAs based on combusted fuel [53]

2.3.3 Morphological Properties of FA

Pulverized coal combustion FA possesses a shape which is spherical in nature and glassy while fluidized bed combustion (FBC) generated FA has been observed to be crystalline in nature and the shape is described as random which is attributed to the subjection to lower burning temperatures during firing i.e., 800 – 900 °C [50]. Although both combustion methods have their advantages, the inclination of most modern power plant to employ the FBC system can be attributed to its ability to combust fuels from agriculture, biomass, various type of waste including the traditional coal fuel which is also recommended and currently used for OS combustion in Estonia [50]. The spherical makeup of the FA may either contain voids or be compact. When the spheres are hollow, this is called a cenosphere while if a FA sphere consist of smaller spheres it is known as plerosheres [42] The figure 2.4 shows the morphology of FA from an SEM (scanning electron microscope) image.



(a) (b)

(c)

Figure 2.4 SEM images of fly ash: (a) general view (b) cenospheres (c) plerospheres [42]

2.4 Carbonation of industrial residues

Some of the challenge of employing mineral carbonation on the main earth minerals could be circumvented by using waste generated from large scale industrial operations (coal, biomass or OS power plants, cement plants, steel, cement, and paper making plants) as raw materials [54,55]. The utilization of these industrial residues has a lot of advantages because utilizing these wastes would rid the environment of toxicity [28]. These types of wastes require minimal pre-treatment processes to get optimal carbon storage capacity [35,56] due to the readily available source of magnesium and calcium minerals without the rigors of mining. Besides, the product of the carbonation can be modified for using in construction or road base materials [57]. Metallurgical wastes generated from industrial activities have been considered to have potential in carbon storage technology. Industrial metal waste such as phosphorus slag, ground granulated blast furnace slag, water/air-cooled copper slag and steel slag are being researched as viable materials for the long-term storage of CO_2 due to the presence of magnesium and calcium oxides they possess [57]. An estimated 180 Mt of CO_2 was released in 2017 during the production of steel in the EU which amounted to 4-5 % [58,59]. On the other hand, an estimated 470 – 610 Mt of slag was generated during this period and could mitigate the effect of the CO_2 generated [60]. Owing to the high reactiveness of some slag phases (e.g., Larnite)[61], there is a rapid carbonation process in slags compared to natural silicates. This could in turn lead to low energy consumption and cost in mineral carbonation process [62].

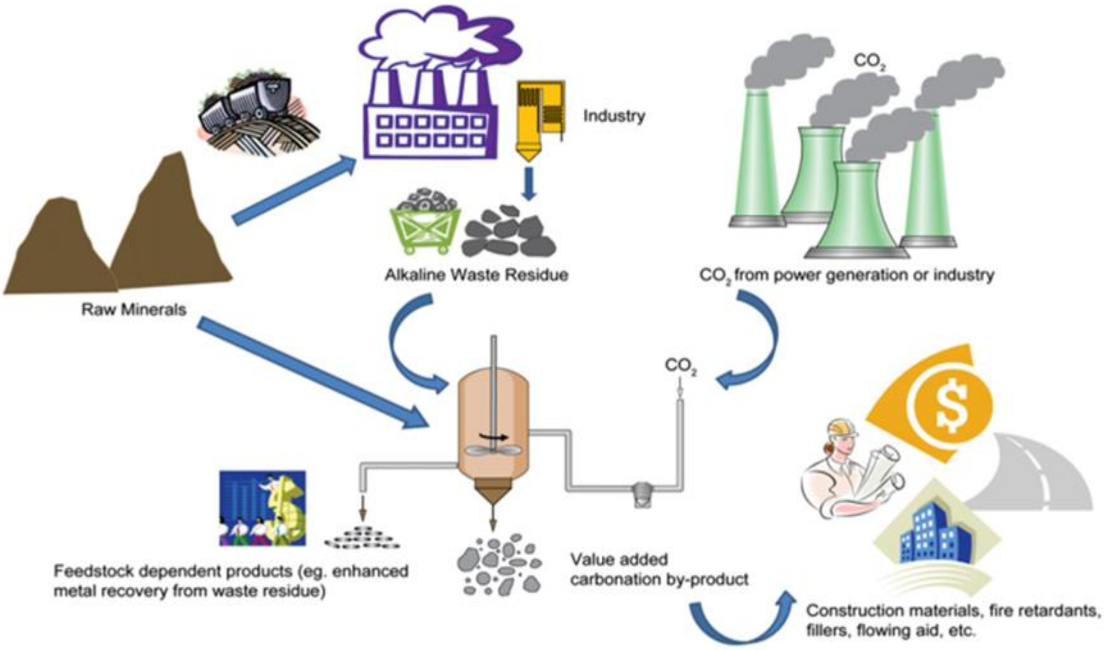


Figure 2.5 Alkaline waste material flux, carbonation and derived products [21]

Figure 2.5 shows the material flow that comprise the carbonation process up to the end of the chain which is the carbonation products are incorporated into sectors such as in construction, fire retardants, among others. The use of construction waste has been an attractive prospect for researchers over the years. Due to the presence of free lime, recycled concrete aggregate (RCA) along with cement kiln dust (CKD) and cement by-pass dust possess a high potential for carbonation [63]. Recycled concrete aggregate (RCA) pH is dependent on the amount of portlandite ($Ca(OH)_2$) present and ranges between 11 and 13 caused by dissolution of portlandite and the production of OH- in water [64]. The Figure 2.6 shows the correlation between CaO content and average CO_2 sequestration capacity of some industrial residues. The average CO_2 uptake for most of the residues can be directly connected to the amount of CaO contained. Thus, knowing the composition of a residue can give a general indication of how reactive it would be when exposed to CO_2 [65].

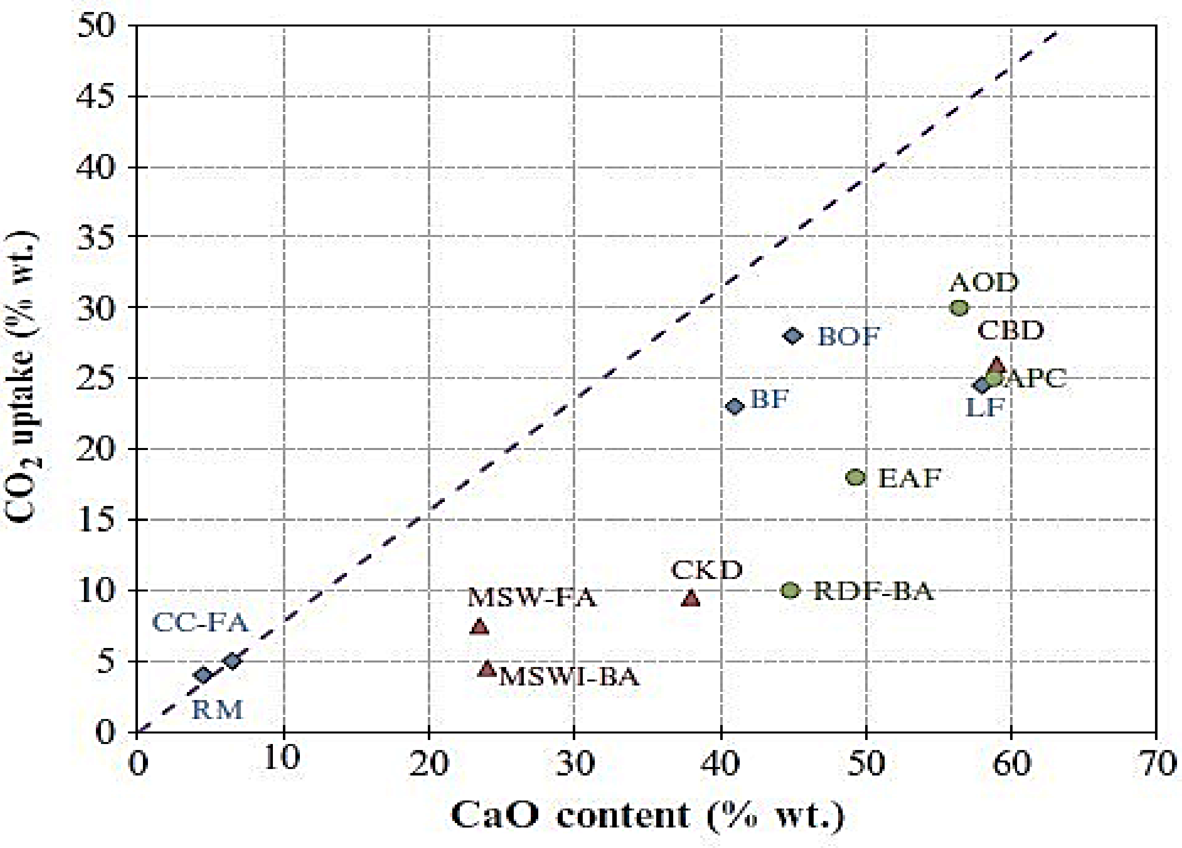


Figure 2.6 Comparing average CO_2 uptake of some industrial residues as a function of CaO content. (CC-FA: coal combustion fly ash, RM: red mud, MSW-FA: municipal solid waste incineration fly ash, MSW-BA: municipal solid waste bottom ash, CKD: cement kiln dust, RDF-BA: refuse-derived fuel bottom ash, EAF: electric arc furnace slag, BF: blast furnace slag, LF: ladle furnace slags, BOF: basic oxygen furnace slag, APC: air pollution control residues, CBD: cement bypass dust, AOD: argon oxygen decarburization slag) [65].

In the context of building materials, there numerous studies carried out with FAs as additives by employing AC curing on concrete applications. The effect of AC on pulverized firing FAs and biomass FAs by humidifying the samples up to 20%, then treated with 100% CO_2 at 3 bar for 120 hours showed that this treatment reduced the pH of the samples from 12,3-12,8 to 8,8-9,7. Calcite precipitation was also recorded as a main product [66]. For 100% CO_2 curing, the CO_2 uptake was about 16% by mass and the compressive strength was greater compared to a concrete cured conventionally for 60 days. For the 25% CO_2 concentration curing, the uptake was estimated to be 9,7% by mass and the strength of concrete was lower than that cured with 100% concentration of CO_2 [67].

Further experimentation was carried out by the carbonation of FBC FA obtained from coal combustion. The study was carried out in a pressurized thermogravimetric analyzer (PTGA) at 1 and 11 bars and 165^oC temperature. It was found that hydrated FA reacted faster with CO_2 in comparison to non-hydrated FA. This translates to a high conversion percentage of 60 % for hydrated FA owing to an increase in surface area caused by the hydration in comparison to 27,4 % for non-hydrated FA [68]. In another research of the carbonation of slurry paste of FA from a coal combustion power plant, it was observed that there was a high reactivity between the lime and CO_2 at atmospheric pressure and a temperature of 30°C depending on the lime content of ash.

Furthermore, the strength development was studied with the evaluation of compressive strength values of carbonated and uncarbonated concrete mixes made with recycled concrete aggregates. The curing condition was 20% CO_2 concentration for 7 days at ambient pressure. It was found that the uncarbonated samples were 8-15 % less than the reference sample in terms of the compressive strength value while the carbonated samples had strength comparable to the reference [69].

2.5 Aim and scope

The aim of this research is to find a way to utilize local alkaline solid wastes of Estonia with accelerated carbonation technology which also enables mitigation of CO_2 emissions in the background. Based on the recent developments achieved on acceleration carbonation technologies, twofold solution can be proposed for Estonia; the first is CO_2 capture and storage from flue gas via CO_2 mineralization with FAs and the second is valorization of these FAs to produce alternative hardened/building materials.

The previous research carried out (including carbonation of alkaline solid wastes) in the past focused on mainly coal ashes and industrial slags as substitute of cement and the most of the developed mix designs prepared with binders (cement, gypsum, lime etc.) and binding agents (polymers, bitumen, etc.) further carbonating with 100%CO_2 yet very few studies were carried out with flue gas. However, the application of carbonation hardening of the 100% FA based building block contrasts from ordinary applications of building materials which uses additional materials for classical hydraulic hardening. As a result of restricted knowledge and lack of studies especially on OSA there are several questions unanswered especially for the applications with direct flue gas curing of FAs with low cementitious properties. Therefore, it is essential to carry out a research to determine the optimal conditions (flue gas/CO_2 pressure, curing time, L/S ratio etc.) necessary to achieve successful operation of this process. In this respect, this preliminary work is important as it enables to make comparative feasibility study by evaluating the physical, chemical, and mechanical properties of the flue gas carbonated FA based building blocks.

The specific objectives set to reach this aim in this thesis work are listed below:

- To characterize the selected FAs in terms of physical and chemical properties,
- To investigate hydration and compaction behavior of FAs for further most effective CO_2 and flue gas curing,
- To test flue gas curing methodology and investigate effects of different gas pressures on carbonation reaction rates and final CO_2 uptake levels in short curing times,
- To compare CO_2 uptake and strength development capacities of FA based compacts in relation to enhanced properties during sample preparation and flue gas curing.

3. MATERIALS AND METHODS

3.1 Materials

Two FA samples were selected; the first FA was obtained from Auvere power plant which is OS derived (OSA) and collected from the electrostatic precipitators of the CFB boiler, the second FA was wood ash (WA), (collected from bag filter) obtained from Utilitas AS district heating plant located in Mustamäe, Tallinn.

3.2 Methods

3.2.1 Characterization of samples

The material characterization was carried out using the methods described in Table 3.1 on the FA samples and the product of the carbonation process.

Table 3.1 Methods used to characterize initial materials and carbonation products

Character	Method
Particle size distribution	Laser Scattering Particle Size Distribution Analyzer LA-950 (HORIBA)
Brunauer-Emmett-Teller (BET) specific surface area (SSA)	The SSA analysis was carried out using the Kelvin 1042 sorptometer.
Phase Composition	The X-ray Diffraction (XRD) was conducted at the University of Tartu, using the Bruker D8 advanced methods, in which a scanning step of 0.02° 2θ from 2° to 75°, and a counting time of 0.5 s. The phase composition of the samples was determined.
Elemental composition	XRF (X-ray Fluorescence) spectroscopy (Rigaku Primus II) at the University of Tartu.
Infrared spectrum	Fourier-transform infrared spectroscopy (FTIR) spectra were obtained for initial and carbonated samples using the Bruker's ALPHA-P FTIR spectrometer. The measurements were recorded in the 400-4000 cm^{-1} range.
Compressive strength	This test was conducted in Building Materials Department of Taltech, on a Toni TechnikD-13355 which works in accordance with EN ISO 7500-1 (2018).
Thermogravimetry	The thermogravimetric analysis (TGA) was carried out using the Setaram Labsys 2000 thermoanalyzer (20K/min, 21%O_2/79%Ar).

3.2.2 Preparation of compacts and experimental setup

The sample preparation and experimental testing were carried out at the Laboratory of Inorganic Materials, TalTech. After making several tests with different liquid to solid ratios, the mix ratio of FA compact was prepared using a liquid to solid ratio of 0,25 w/w. The water and FA were carefully quantified and mixed using a semi batch Eirich mixer at 300rpm for 300 seconds. To ensure proper hydration, the mix is labelled and stored in a sealed bag for 24hrs for the molding process. The compacts for this study were press molded using a cylindrical mold of dimensions 20 mm diameter and 20 mm height. A hydraulic press at a pressure of 150 and 300 kg/cm^2 were used for compaction. A total of over fifty compacts were made to compare the test results and performances. The carbonation tests of FA compacts were performed in a carbonation chamber with special care as the robust system requires a lot of physical effort for its technicality due to the use many gas sensors, sealers and gas transformation lines from model flue gas and CO_2 balloons which all need to be well tightened for zero gas leakage. Some components of the setup are shown in Figure 3.1a, b, and c below. The carbonation of the FA bricks was carried out at pressures of 5, 10, and 15 bar at both 100% CO_2 and model flue gas conditions (16%CO_2/6%O_2/78%N_2). Flue gas carbonation tests were performed by flushing and refilling the carbonation chamber in every 20 min to ensure the stable CO_2 concentration during the curing process.

Table 3.2 Compact code-labelling, content, compaction pressure and gas pressures.

Sample Name and compact label code	Content (%)	Water (%)	Compaction pressure (kg/cm^2)	100% CO_2/ flue gas Pressure (bar)		
Oil shale ash (OSA)	100 + 0	25	150[a]/300[b]	5	10	15
Wood ash (WA)	100 + 0	25	150[a]/300[b]	5	10	15
Oil shale ash + Wood ash(OSA/WA)	50 + 50	25	150[a]/300[b]	5	10	15

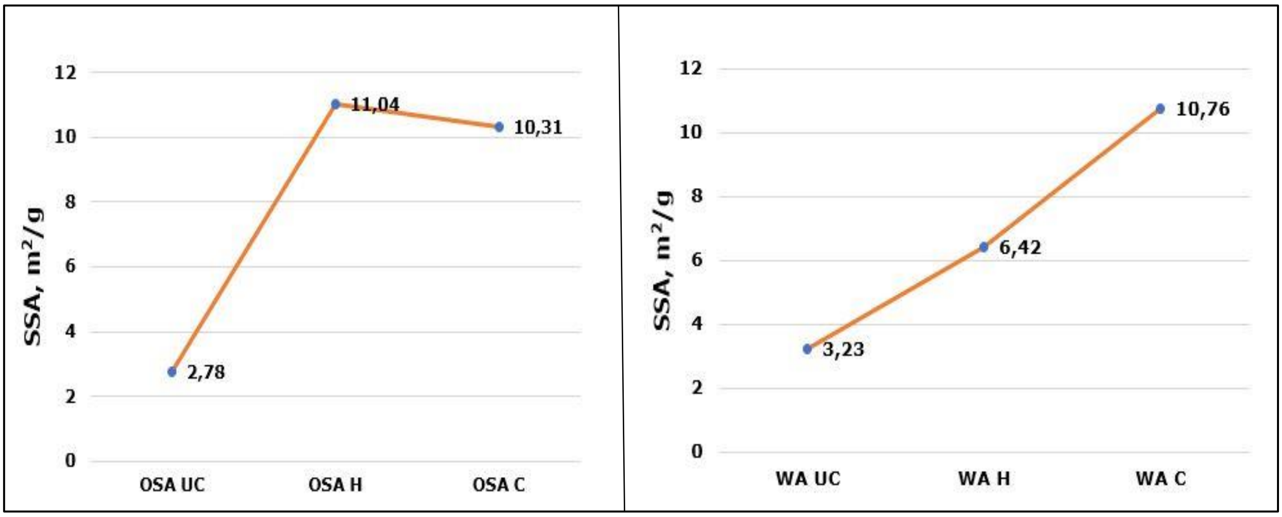
(a: compaction pressure for 15 bar cured samples, b: compaction pressure for 5 and 10 bar cured samples)

(a) (b) (c)

Figure 3.1 Experimental set up (a) Gas flow monitoring unit (b) chamber (c) CO_2 gas cylinder

3.3 Physical Characteristics

The results obtained from the Laser Scattering Particle Size Distribution Analyzer LA-950 (HORIBA) showed that the WA has a greater particle than OSA where median (d_{50}) particle diameter for OSA is approximately two times smaller than WA (see Table 3.3, Figures 3.3 and 3.4 for full PSD). Furthermore, the SSA shown in Figure 3.2a and 3.2b shows the response of the OSA and WA samples to hydration and carbonation compared to the uncured samples. The SSA of both samples increased, with hydrated OSA having about 5 times that of its initial sample. The same trend is noticed in hydrated WA where the SSA doubled to give 6,42 m^2/g. Additionally, there was a slight dip of around 1m^2/g in the SSA of carbonated OSA between the hydrated and carbonated sample while the opposite of this trend was observed for WA, showing the further increase of SSA which could be related to forming finer $CaCO_3$ crystals after carbonation.



(a) (b)

Figure 3.2 BET SSA of (a) OSA and (b) WA for UC, H and C samples (UC: uncarbonated, H: hydrated and C: carbonated)

Table 3.3 Particle size distribution for OSA and WA samples

Sample	D_{10} (μm)	D_{50}(μm)	D_{90}(μm)
OSA	9,84	23,06	60,39
WA	12,94	54,73	231,12

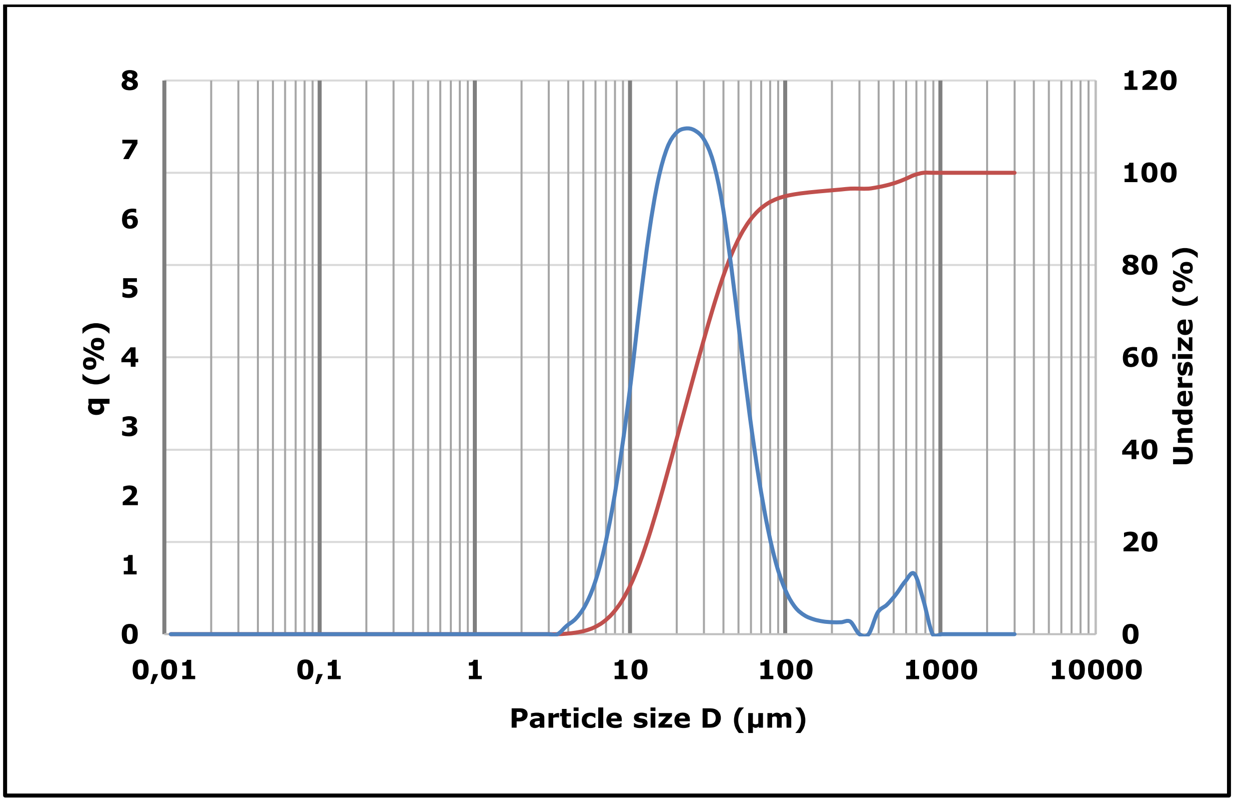


Figure 3.3 PSD for oil shale ash (OSA)

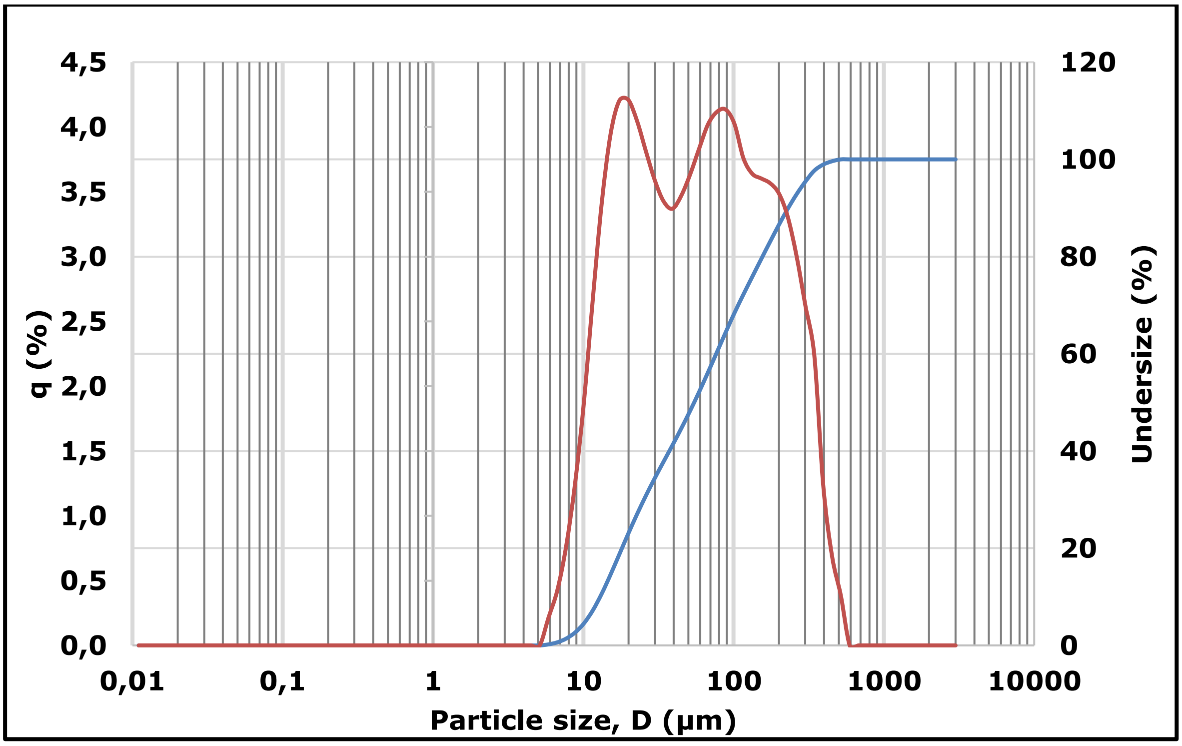


Figure 3.4 PSD for wood ash (WA)

3.4 Chemical and phase composition

According to the XRF results, the amount of Ca- and Si- compounds present in OSA and WA added up to over 60% (Figure 3.5). Furthermore, the XRD analysis indicated that both samples contain an almost equal amount of free lime which WA was 4% greater than OSA. Additionally, considerable number of Ca-silicates was found in both samples which is slightly less in WA compared to OSA (Figure 3.6). These phases along with portlandite found in the samples are considered as potential CO_2 binders.

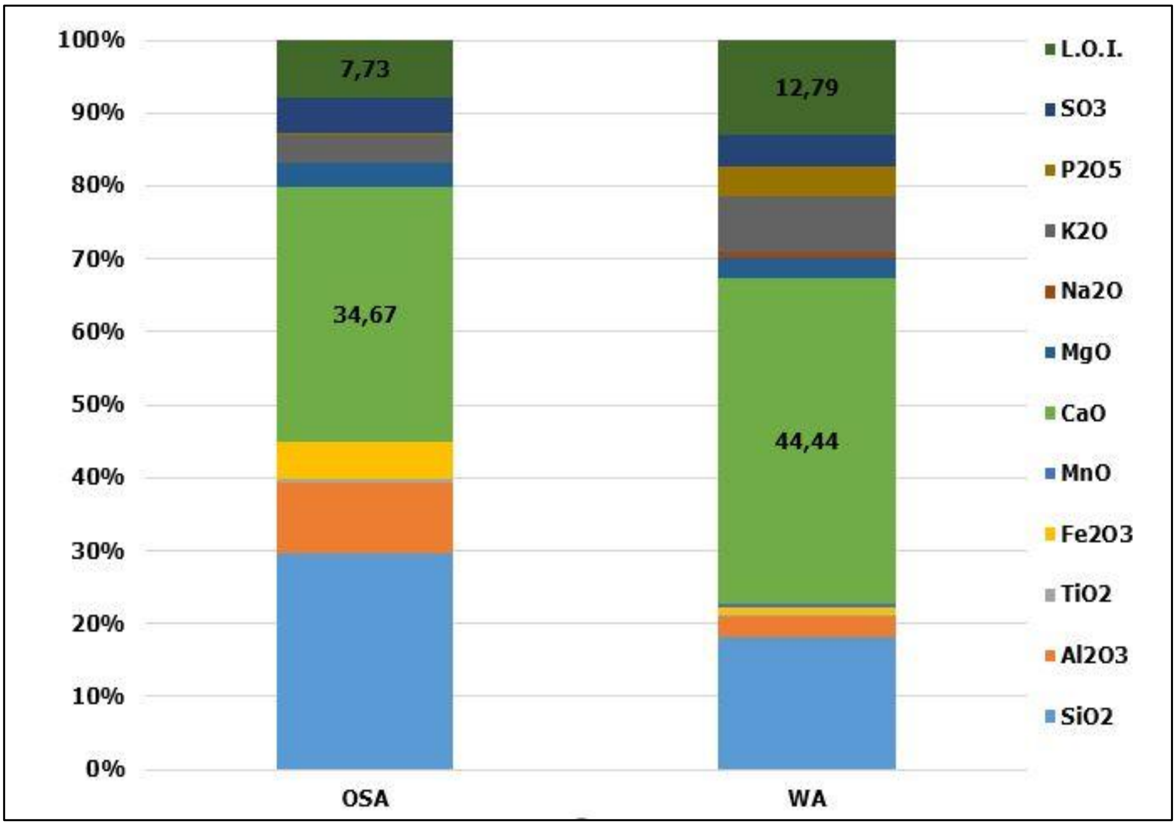


Figure 3.5 Chemical composition in percentile

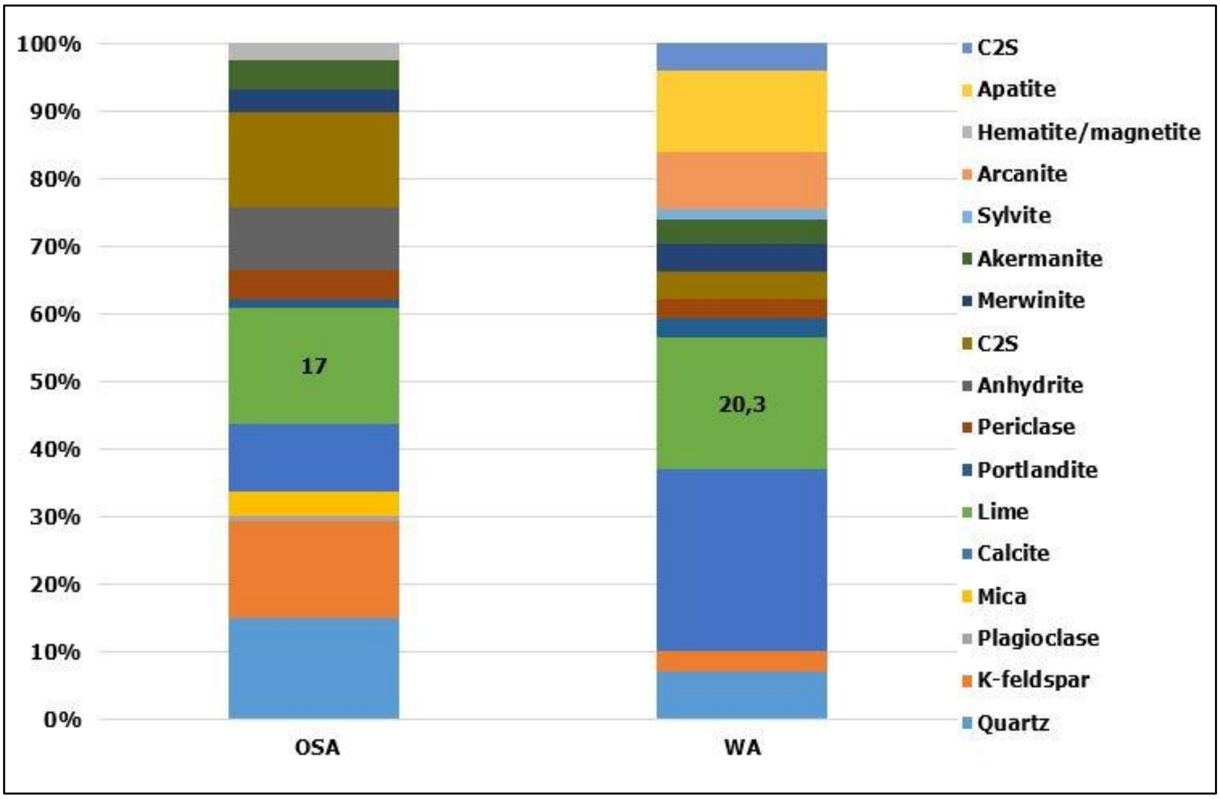


Figure 3.6 Phase composition in percentile

3.5 Theoretical CO_2 storage potential

To calculate the CO_2 binding capacity of the samples CO_{2max}, the CO_2, fCaO, $Ca_2MgSi_2O_7$, Ca_2SiO_4 and $Ca_3Mg(SiO_4)_2$ content of the sample materials as determined by the quantitative XRD analysis were used as the basis for the calculation in Eq.3.1 below.

$$\mathrm{CO_{2max}} = \frac{\frac{\mathrm{fCaO} \times \mathrm{M_{CO_2}}}{\mathrm{M_{CaO}}} + \frac{\mathrm{Ca_2MgSi_2O_7} \times \mathrm{M_{CO_2}}}{\mathrm{M_{Ca_2MgSi_2O_7}}} + \frac{2 \times \mathrm{Ca_2SiO_4} \times \mathrm{M_{CO_2}}}{\mathrm{M_{Ca_2SiO_4}}} + \frac{3 \times \mathrm{Ca_3Mg(SiO_4)_2} \times \mathrm{M_{CO_2}}}{\mathrm{M_{Ca_3Mg(SiO_4)_2}}} + \mathrm{CO_2}}{100 + \frac{\mathrm{fCaO} \times \mathrm{M_{CO_2}}}{\mathrm{M_{CaO}}} + \frac{\mathrm{Ca_2MgSi_2O_7} \times \mathrm{M_{CO_2}}}{\mathrm{M_{Ca_2MgSi_2O_7}}} + \frac{2 \times \mathrm{Ca_2SiO_4} \times \mathrm{M_{CO_2}}}{\mathrm{M_{Ca_2SiO_4}}} + \frac{3 \times \mathrm{Ca_3Mg(SiO_4)_2} \times \mathrm{M_{CO_2}}}{\mathrm{M_{Ca_3Mg(SiO_4)_2}}}} \times 100\% \qquad (3.1)$$

The theoretical CO_2 binding capacity of the OSA sample and the WA samples were estimated from Eq. 3.1 above to be 22,52% for OSA and 26,42% for WA (see Figure 3.7). The free lime contained in the OSA and WA samples are 18,4% and 23,3% respectively as shown in the Figure 3.7 below.

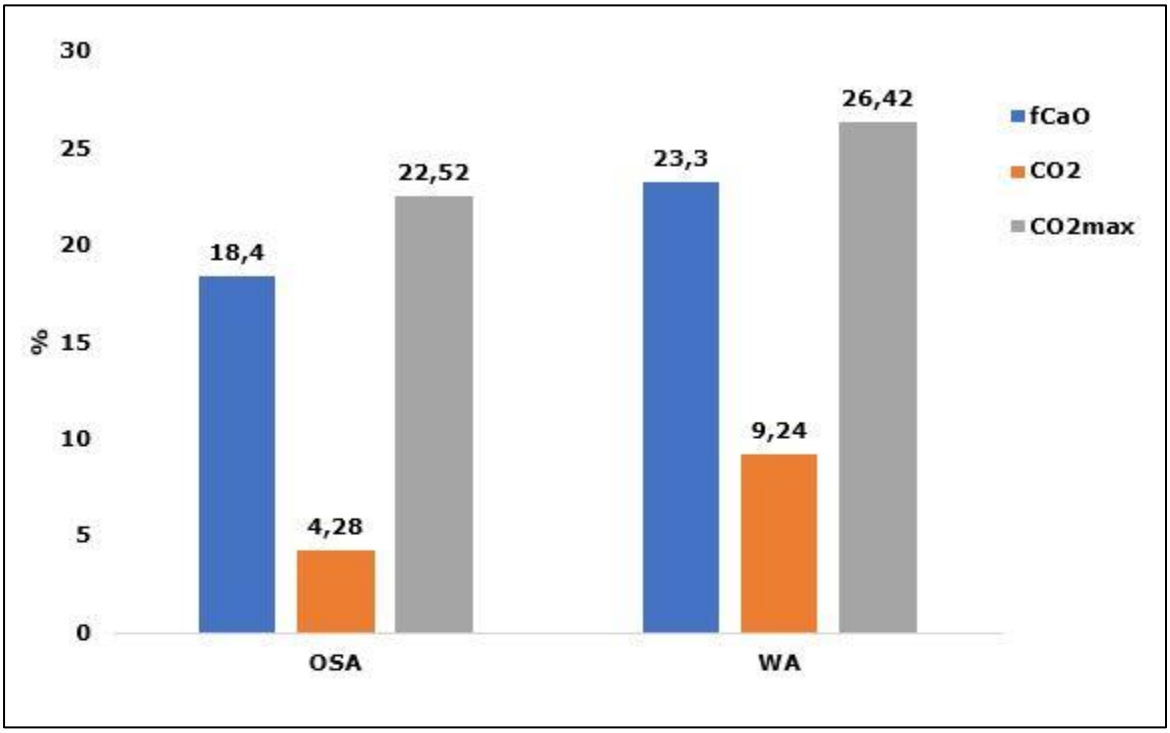


Figure 3.6 Mineral CO_2 and fCaO content of initial samples of oil shale ash (OSA) and wood ash (WA)

4. RESULTS AND DISCUSSION

4.1 Thermogravimetric analysis

The TGA result indicates a drop in mass observed between room temperature to around 150 °C due to the loss of adsorbed water in the samples as shown in Figures 4.1 and 4.2 showing the mass loss for uncarbonated (UC), 100% CO_2 (C) and flue gas carbonated (FGC) OSA, WA and OSA/WA samples. Furthermore, it can be observed that between temperatures of 400-490 °C there is a fall in mass which indicates the decomposition of portlandite ($Ca(OH)_2 \rightleftharpoons CaO + H_2O$). This decline in mass is more notable across all uncarbonated samples with OSA showing the highest portlandite decomposition with a mass loss of about 4% (Figure 4.1) and reduces significantly in the C and FGC samples. Furthermore, at temperatures of around 600-800 °C, the decomposition of mineralized CO_2 in the form of $CaCO_3$ is also observed and it is important to point out that both ashes include $CaCO_3$ already in their initial forms. This decline in mass is used to calculate the CO_2 uptake of each sample represented in Table 4.1. From the table, the value of CO_2 uptake for C samples was greater than FGC samples. All samples experienced an increase in CO_2 uptake with increasing gas pressure (see Table 4.1). Between 5 and 10 bar for all samples, the CO_2 uptake was around +1 gCO_2/100g FA compact in increment for C while for FGC samples it was between +0,3 – 1,3 gCO_2/100g FA compact. Furthermore, when the pressure was increased from 10 bar to 15 bar, the same trend of increment can be observed in all samples (Table 4.1). The difference in CO_2 uptake between C and FGC OSA and WA compact is 1,7% and 2,2% respectively. A 50-50% mix of both FAs (OSA/WA) gave a result that lie between the values obtained for OSA and WA. Therefore, based on these trends we can infer that the low CO_2 concentration in flue gas has negligible adverse effect on the final uptake levels. The same trend can be observed when comparing the OSA compacts to OSA/WA as well. This trend between OSA and WA (despite WA having a slightly high amount of free lime than OSA according to the XRD analysis) can be explained by the effect of particle size on CO_2 storage ability. OSA and WA has been reported through the PSD analysis to have median particle diameter (D_{50}) of 23,06 μm and 54,73 μm.

Table 4.1 CO_2 uptake of cured samples at 100% CO_2 and flue gas

	gCO₂/100g FA compact					
Sample name	5 bar		10 bar		15 bar	
	C	FGC	C	FGC	C	FGC
OSA	9,1	6,4	9,5	7,6	10,6	9,7
OSA/WA	6,9	4,9	7,7	6,2	8,4	7,4
WA	7,6	5,2	8,3	5,5	8,9	7,5

(C: 100% CO_2 cured at 15 bar, FGC: flue gas cured at 5,10 and 15 bar)

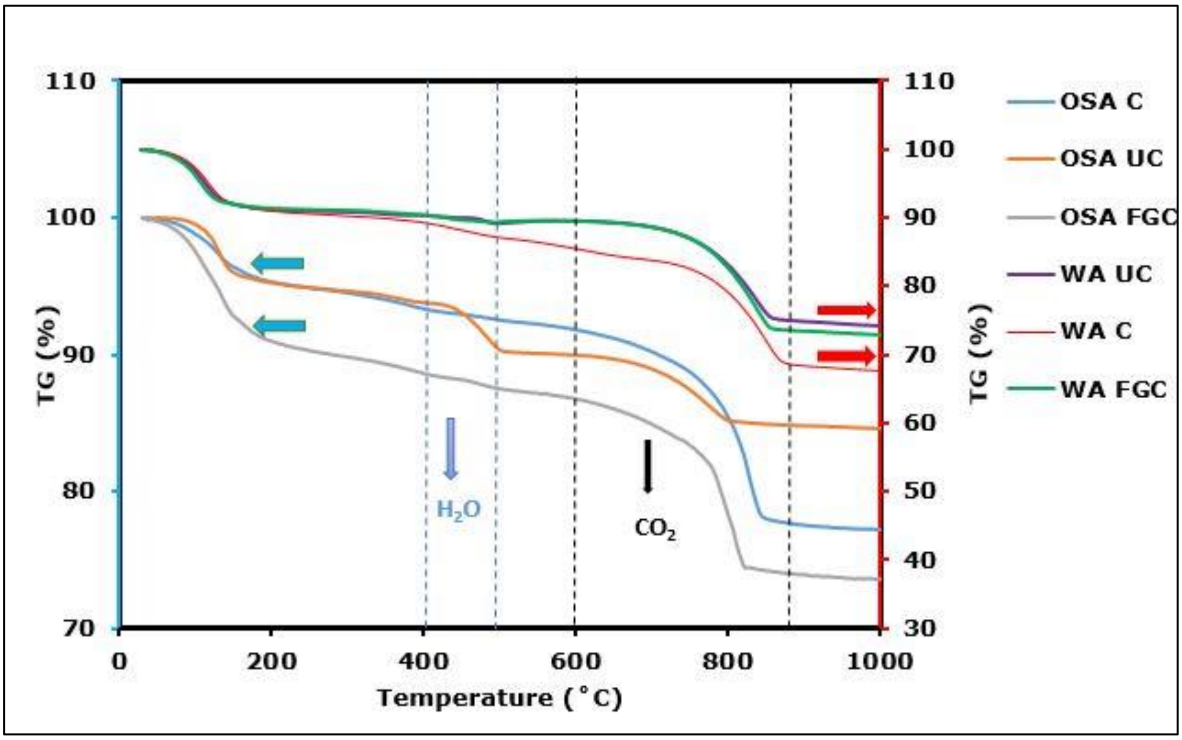


Figure 4. 1 Mass loss curves of OSA and WA

(C: 100% CO_2 cured at 15 bar, UC: uncarbonated, FGC: flue gas cured at 15 bar)

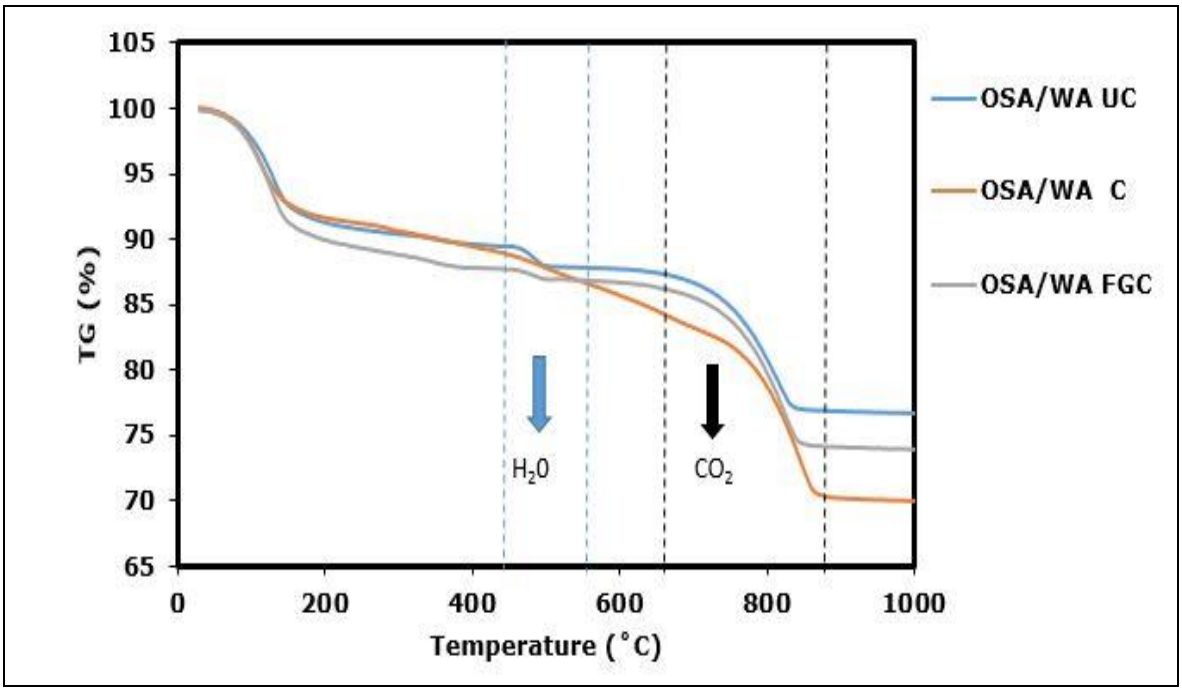


Figure 4. 2 Mass loss curves of OSA/WA

(C: 100% CO_2 cured at 15 bar, UC: uncarbonated, FGC: flue gas cured at 15 bar)

4.2 Gas monitoring results

The experimental results of both OSA and WA carbonation are shown in Figure 4.3, where the CO_2 uptake are plotted versus time. These results were in good agreement with calculated results from experimental TGA data (±1%). It can be seen that the carbonation reaction in OSA is fast at the initial stage, and after this stage, a stage with slower reaction rate takes place due to the diffusion limitation through the product layer. There is no visible positive effect of increasing pressure on carbonation reaction of OSA at the first stage of reaction. However, there is slight improve on the reaction rates in the diffusion controlled stage. The CO_2 uptake trend in terms of carbonation rate is different in WA and vary in different pressures. The positive effect of increasing pressure on the rate growth of WA carbonation is more distinguishable pointing out more kinetic controlled reaction phenomena, especially at the early carbonation stage. The increase of pressure elongates the time of the fast carbonation period, providing the WA react for a longer time, before process reaches to a more diffusion controlled stage. However, in order to clarify and be more concise, there is a necessity to the further study these findings with the well-known gas-solid reaction models developed for rate equation theory as future work.

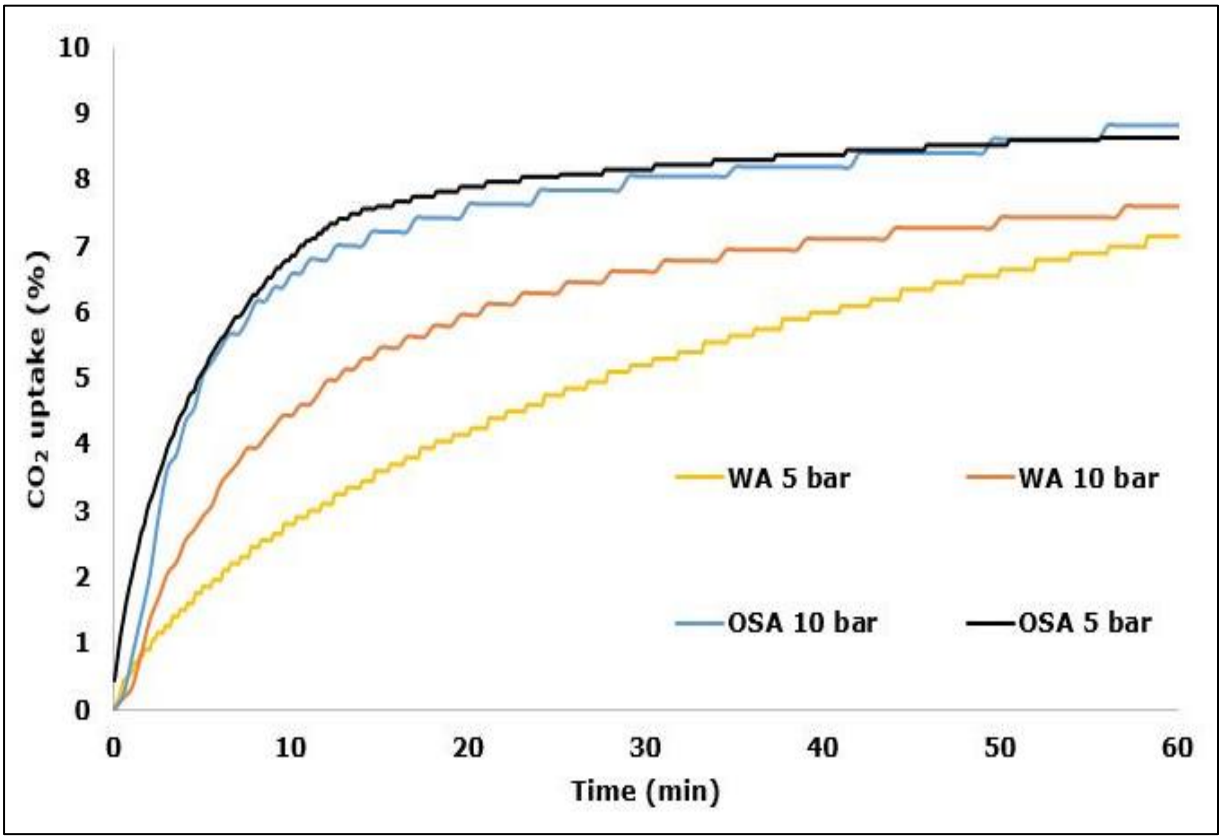


Figure 4. 3 Gas monitoring results for OSA and WA 100% CO_2 gas curing (5 and 10 bar). (Min: Minutes)

4.3 Compressive strength and water absorption results

The impact of compaction pressure was apparent as the compacts prepared with higher compaction pressure reached the highest compressive strength. The strength of samples cured in 100%CO_2 are slightly higher than the FGC samples. This could be somewhat linked to less CO_2 uptake levels as the formation of carbonate phases in compact bodies can lead to increase in solid phase volume by reducing porosity and development of compressive strength. Furthermore, the table depicts a slight uptrend in strength under compression between 5 and 10 bar pressure by an increment of about +1MPa for OSA and OSA/WA samples while WA had an increment of about +2MPa for C. Also, for FGC samples at the same pressure range (5-10 bar) the same trend can be seen in Table 4.2. In the range of 10 and 15 bar pressure, there was a great leap in strength in all the samples with OSA having the greatest spike at about +13MPa increment for C and +12,1 MPa for FGC sample (see Table 4.2 for full result) which can be attribute to compaction pressure (300 kg/cm^2). The highest performing sample in terms of strength can be observed (from Table 4.2) to be OSA at 35,10 MPa. Due to the higher content Ca-Mg silicates (C2S) which participate in hydraulic or pozzolanic reactions in OSA compacts the compressive strength values were higher than WA compacts. Therefore, from the data presented in Table 4.2 it can be deduced that it is possible to achieve sequestration of CO_2 in FA compacts without compromising strength. The water absorption test involves soaking of samples for 24 hours according to the EN771-1:2003. The water absorption test result when compared to the uncarbonated samples as given in Table 4.3 below shows the same trend for all samples. When the samples were CO_2 cured, it can be observed that the there was a significant decrease in the average water absorbing capacity of OSA, WA and OSA/WA at -5,46%, -4,67% and -1,35% respectively (Table 4.3).

Table 4.2 Compressive Strength (MPa)

	Compressive Strength (MPa)					
Sample Name	5 bar		10 bar		15 bar	
	C	FGC	C	FGC	C	FGC
OSA	21,50	15,40	22,20	16,10	35,10	28,20
OSA/WA	15,60	10,90	16,40	12,70	27,50	21,30
WA	7,10	4,80	9,30	8,90	14,70	12,50

Measurements shown in table 4.2 are average number of each set of 4 samples with deviation of 3%. (C-100%CO_2 cured, FGC- flue gas cured).

Table 4.3 Water absorption

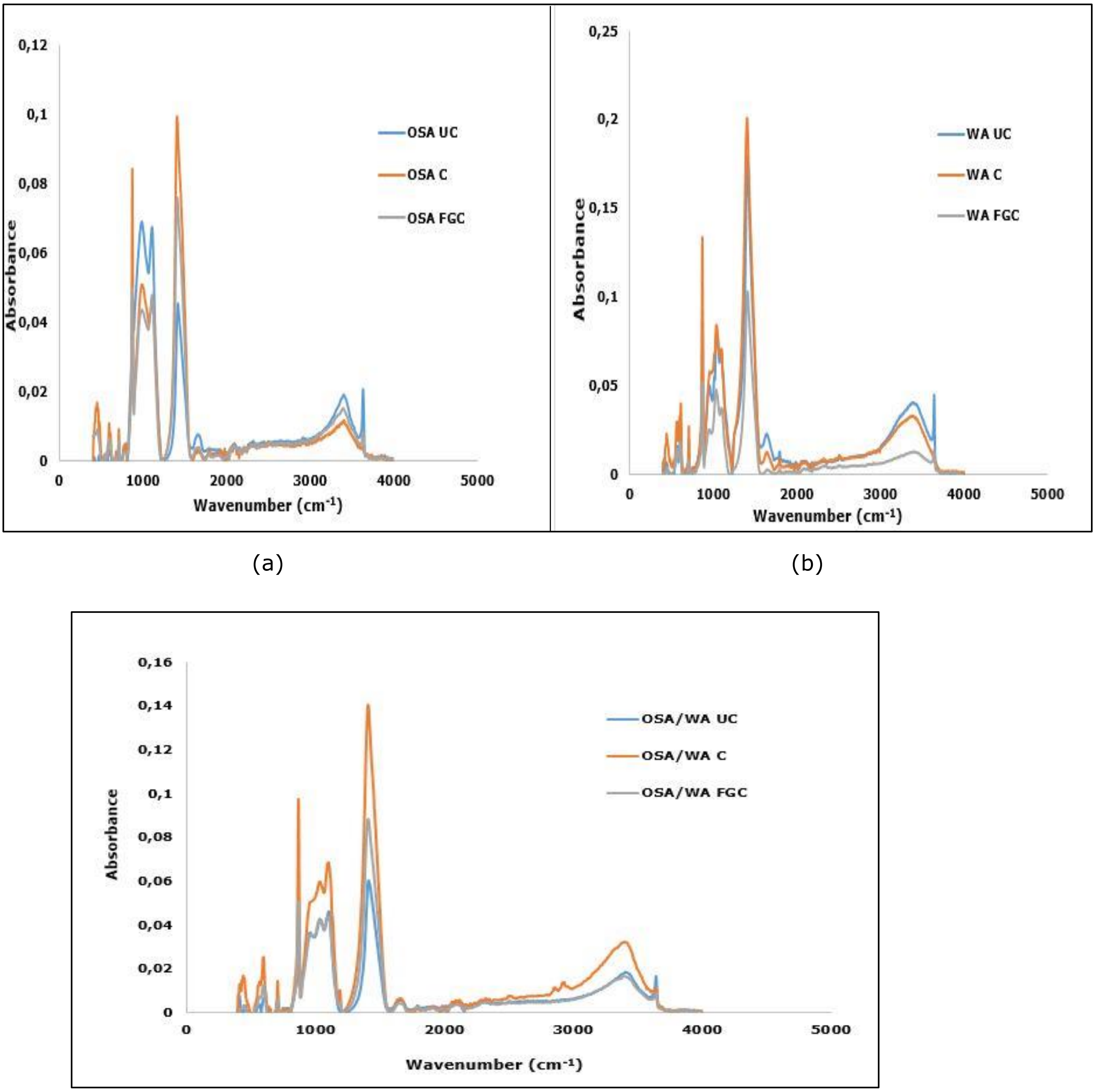
Sample	Water Absorption Average (%) (UC)	Water Absorption Average (%) (C)
OSA	14,24	8,78
WA	5,91	1,24
OSA/WA	3,04	1,69

(C: 100% CO_2 cured, UC: uncarbonated, FGC: flue gas cured at 15 bar)

4.4 FT-IR analysis results

According to the FT-IR analysis of the samples, for OSA, the intensity of the spectral band at 3642 cm^{-1} of $Ca(OH)_2$ reduced after carbonation had taken place. Furthermore, it can be observed that the Ca-silicates (950, 1152 cm^{-1}) were passive in the process of carbonation. The spectral band around 1420 cm^{-1} indicates that there was an increase in CO_2 uptake of the OSA sample Figure 4.4a. Additionally, the intensity of the 100%

CO_2 cured OSA was observed to be greater than the FGC sample which may likely be due to the difference in CO_2 concentration. The same trend can be observed for WA and OSA/WA samples (see Figure 4.4(b,c)). Furthermore, the band around 3750 cm^{-1} is attributed to the vibrational stretch and bend of OH in H_2O which indicates the presence of a small amount of molecular water in the samples. This molecular water reduces in the samples with carbonation intensity between C and FGC curing.



(a)

(b)

(C)

Figure 4. 4 FT-IR analysis of (a) OSA, (b) WA, and (c) OSA/WA samples cured at 15 bar using 100% CO_2 and flue gas

5. CONCLUSIONS

In this study, calcium rich FA (OSA and WA) based compacts were preapared and subjected to accelerated carbonation at different gas pressures of CO_2 and flue gas. The amount of mineralized CO_2 was investigated by evaluating the CO_2 uptake and the compressive strength performance of the compacts.
Based on the results obtained within this thesis work, the following conclusions can be drawn;

- The impact of compaction pressure was apparent as the compacts prepared with higher compaction pressure reached the highest compressive strength,

o The CO_2 uptake was not influenced by the possible low permeability of CO_2 gas. However, this effect could be more critical at lower curing pressures.

- Due to the higher content Ca-Mg silicates which participate in hydraulic or pozzolanic reactions in OSA compacts the compressive strength values were higher than WA compacts.

o Similar phenomenon also exists in mix design (OSA/WA) where there was no peculiar interaction between these two ashes as the results of both CO_2 uptake and compressive strength were proportional with single FA compact performances.

- The potential adverse low reaction rate effect due to the low CO_2 concentration in flue gas was negligible during the short curing process of fly ashes(2h),

- The strength of samples cured in 100% CO_2 are slightly higher than the samples cured in flue gas. This could be somewhat linked to less CO_2 uptake levels as the formation of carbonate phases in compact bodies can lead to increase in solid phase volume by reducing porosity and development of compressive strength,

- The slow rate of reaction at the diffusion-controlled stage can further be improved by applying elevated gas pressures,

- Main reacting phases in OSA and WA during the carbonation reaction are lime and portlandite (forming $CaCO_3$) and both TGA and FTIR results show that there is still some portlandite left uncarbonated in the samples.

o However, it is possible to achieve compressive strength values between 12-28 MPa while binding 75-90 kgCO_2/ton of FA with rather short curing times.

Consequently, the results of this study shows that the production of carbonation hardened building materials can be bright and promising way of valorization of out of furnace wastes where there is necessity of controlling both industrial alkaline solid wastes and CO_2 emissions.

SUMMARY

The need to find use for industrial wastes and the necessity of reducing CO_2 emissions in the environment is the main motivation behind the innovative ways of capturing CO_2. Recently, the mineral capture of CO_2 into stable carbonates has been a promising route to the net zero carbon energy future target. The use of wastes and particularly ashes generated from power plants are a major players in the conservation of the environment through this role in spurring the movement towards a greener economy. Carbonated FAs have a wide variety of use ranging from agricultural purposes and filling to construction.

Similarly, the alkaline nature of OSA and WA is due to the presence of free lime which makes them a candidate in the capturing of CO_2 through mineral carbonation. Building on previous works of research in this field, this master thesis investigates the performance of these calcium-rich FAs when made into compacts and CO_2 is sequestered in them. Furthermore, the feasibility of using flue gas in place of 100% CO_2 gas in curing the compacts is something that was thoroughly explored in this research.

In the first step, OSA and WA were taken into consideration as main local alkaline wastes for the production of building blocks using a press molding method with a given hollow cylindrical monoliths. In the second step, prepared compacts were subjected to accelerated carbonation process in an autoclave at different gas pressures of both flue gas and 100% CO_2 to compare performance of each curing process and relative to uncarbonated compacts as well. The carbonated samples were monitored during curing. Later, all samples were then subjected to a series of test such as compressive strength test, water absorption test, TGA and FT-IR respectively to determine the CO_2 uptake and performance.

The results obtained indicates that carbonation increased the ability of OSA and WA compacts to withstand compressive loads at 14-36Mpa for 100% CO_2 gas cured and 17-29Mpa for flue gas cured compacts. In contrast the uncarbonated samples ranged between 10-19Mpa. The sequestration of CO_2 is a crucial part of this undertaking and we found out that it is possible to sequester 70-100 kgCO_2/ton of FA compact with flue gas curing at 15 bars for a period of 2hours and 90-100kgCO_2/ton of FA compact for 100% CO_2 curing over the same period and pressure conditions. Also, the use of flue gas in the carbonation resulted in an insignificant change in the results of the tests results obtained. This can serve as a precursor to the scaling up of this process to an industrial level where a stationary and constant source of flue gas can be obtained. Hence, further research should be carried out to refine and improve

this carbon capture method to achieve both zero emission energy generation and use of alkaline industrial waste in a meaningful way.

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Appendix 1 Derivative weight loss for OSA, WA and OSA/WA

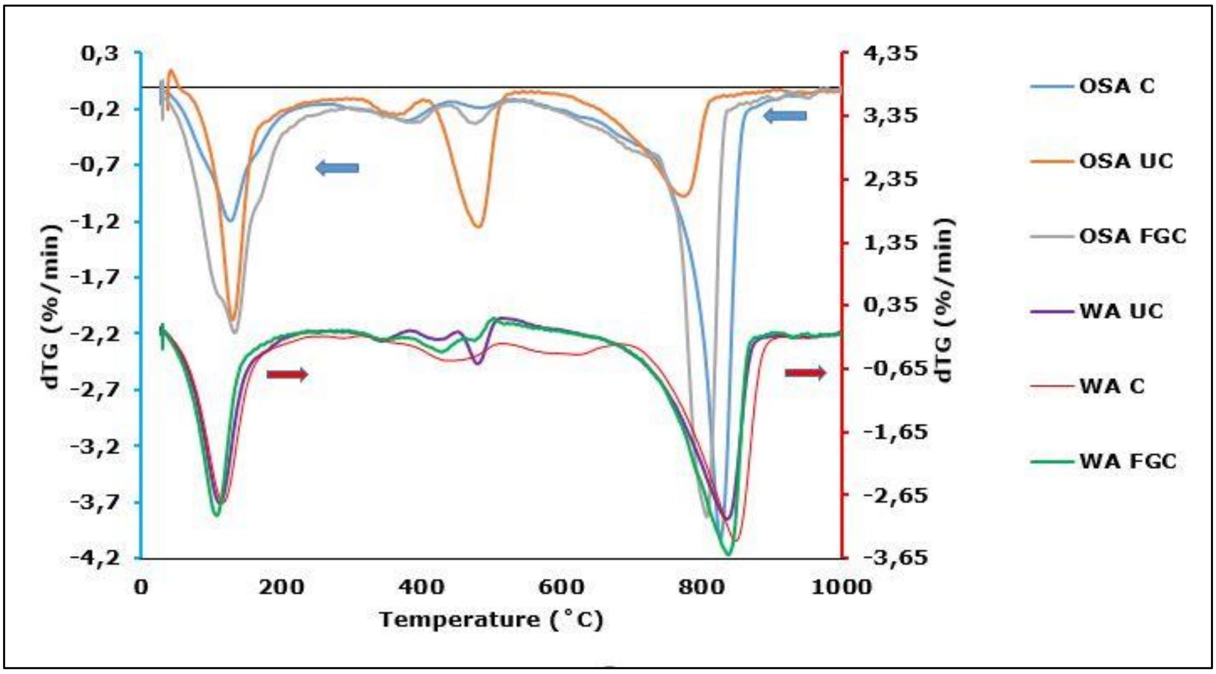

Figure 4. 5 Derivative weight loss for OSA and WA.

(C: 100% CO_2 cured at 15 bar, UC: uncarbonated, FGC: flue gas cured at 15 bar)

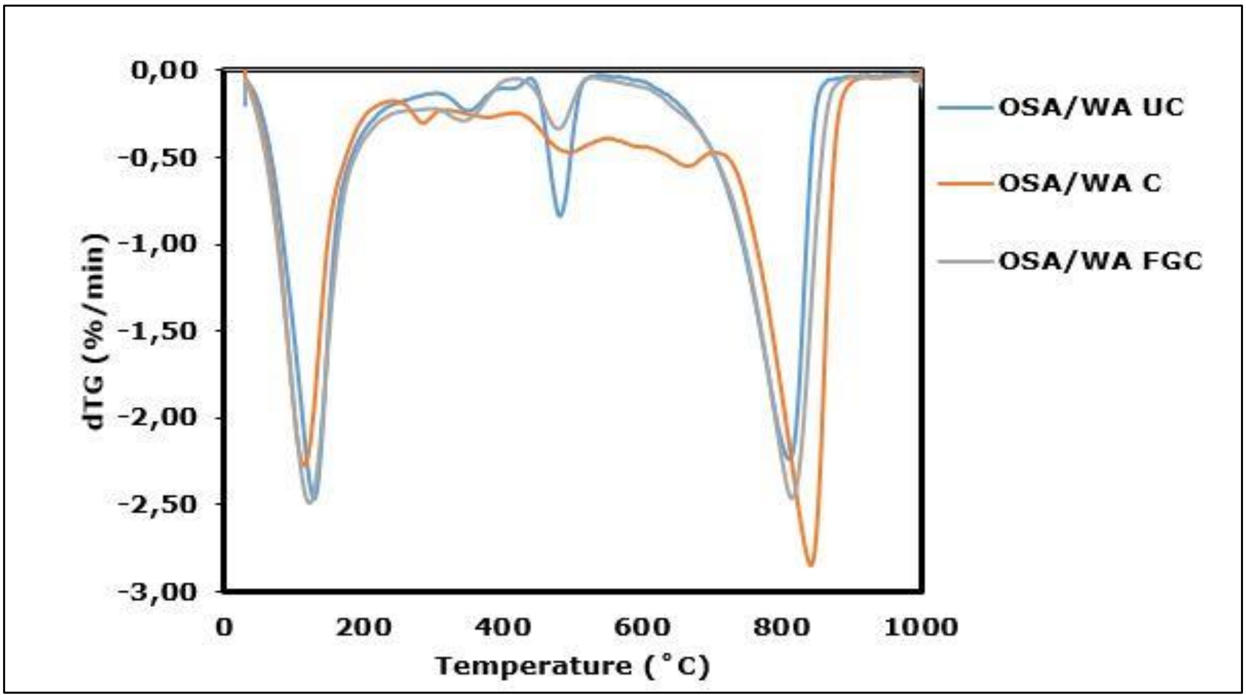

Figure 4. 6 Derivative weight loss for OSA/WA.

(C: 100% CO_2 cured at 15 bar, UC: uncarbonated, FGC: flue gas cured at 15 bar)